

# Determination of Biodiesel Content in Diesel Using Distillation Curves and Multivariate Calibration

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**ABSTRACT:** The partial least-squares (PLS) method was applied to predict the content of biodiesel in diesel using distillation curves (ASTM D86). Furthermore, a comparison between the regression coefficients of all algorithms was carried out, subsequently to the selection of the number of latent variables according to each prediction. The low values obtained for RMSEP and high correlation coefficients between real and predicted values indicated that the PLS was efficient in determining the biodiesel content. The model built contains diesel samples of several different compositions, replicating the diversity of fuels of the Brazilian market. In addition, the proposed method is inexpensive and is easy to implement, since it uses the results of a routine assay performed to evaluate the quality of the diesel used in road transport.

## 1. INTRODUCTION

Biodiesel (fuel derived from renewable sources) is obtained through the transesterification of vegetable oils, or other materials that provide a large quantity of triacylglycerides, such as, animal fat or frying oil, with monohydric alcohols in order to generate the corresponding monoalkylester.<sup>1</sup>

In Brazil, there are dozens of vegetable species that can be used, for instance, soy, castor oil, palm oil, sunflower and palm, and several others, as well as animal fat such as tallow and fish oil. Among the aforementioned raw materials, soybeans are the most commonly used in biodiesel production, approximately 70% of the oil production.<sup>2</sup>

The advantages of using this alternative fuel, besides it being renewable, include the low quantities of emission, especially of sulfur, and its biodegradability, and since it comes from the biomass, it does not contribute to the increase of the carbon content in the atmosphere, thus reducing the greenhouse effect. Moreover, biodiesel is quite safe to handle (flash point above 110 °C); it also has higher lubricity than diesel and produces small emission of pollutants with an adequate engine performance.<sup>3</sup>

The insertion of biodiesel into Brazil's energetic matrix occurred in 2005 through legislation number 11.097/05. This act establishes minimum percentages that must be added to diesel, as well as the monitorship of the insertion of this fuel into the market. From 2005 to 2007, the addition of 2% of biodiesel to diesel, termed mixture B2, was optional. From 2008 onward, this mixture became mandatory, and in the same year, the percentage was increased to 3%. In 2009, the percentage of biodiesel in the diesel mix was raised to 4%; finally, in 2010, the ANP determined the addition of 5% of biodiesel to diesel and termed it B5.<sup>2</sup> This slight expansion in the biodiesel content is related to the price of this biofuel, which is still higher than diesel. Moreover, despite the expansion in the production of fuel, the amount generated is not sufficient to achieve the addition of, for example, 10% of biodiesel in diesel fuel.

The production and use of biodiesel in Brazil provide the development of a source of sustainable energy, which has environmental, economic, and social aspects and also

encompasses the perspective of reducing diesel importations producing foreign exchange for the country. In addition to reducing dependence on imported diesel, the production and usage of biodiesel provides several indirect effects by developing local and regional economies, benefitting the agriculture segment and the industry of property and services as well. Thereby, with the expansion of the biodiesel market, thousands of Brazilian families gained, especially farmers from the semiarid region of Brazil, with the increase of income from growing and commercializing oilseeds used in the production of biodiesel.<sup>2</sup>

Brazil is among the largest producers and consumers of biodiesel in the world with an annual production of 2.7 billion liters in 2011, with an overall capacity to produce 5.8 billion liters.<sup>2</sup>

Biodiesel can be considered as an excellent additive for diesel, since it can function similar to sulfur, ensuring the lubricity of diesel. The lubricating properties of diesel are quite significant toward fuel injection systems, such as, the injection pump. Fuels with low lubricity increase engine wear and the life span of its components.

The available reference method for determining the biodiesel content in the B5 mixture is based on the European standard BS EN 14078.<sup>5</sup> In this method, the reference material (biodiesel) is diluted in a fatty acid free solvent (for instance, cyclohexane), and these solutions are insert in infrared spectroscopy equipment. The concentrations of these solutions are compared to the height of the maximum bandwidth relative to the ester carbonyl ( $1745 \pm 5 \text{ cm}^{-1}$ ), in order to build the analytical curve. To determine the biodiesel content of samples, dilutions are performed (when necessary) and the reading relative to the maximum peak (relative to the esters carbonyl) is compared to the analytical curve.<sup>5</sup>

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The EN 14078 method exhibits certain disadvantages; for instance, it necessitates the diluting the samples and it does not distinguish the biodiesel esters from those present in the mono-, di-, and triglycerides of the vegetable oils.<sup>6</sup> Therefore, this assay is inadequate to assert that the mixture diesel/biodiesel in fact contains biodiesel, for example, in cases of adulteration of diesel by the addition of vegetable oil. Thusly, multivariate calibration methods have been reported in the literature as an alternative for the determination of biodiesel content in diesel using infrared spectroscopy.<sup>4,7,8</sup> Further techniques were also carried out with the same purpose, such as proton NMR (nuclear magnetic resonance)<sup>9,10</sup> and gas chromatography.<sup>11</sup> The advantage of multivariate calibration application is the possibility of use a large number of results, for example, a range from 4000 to 600  $\text{cm}^{-1}$ , instead of a tiny interval ( $1745 \pm 5 \text{ cm}^{-1}$ ) as with the reference method EN 14078.

Pimentel et al.<sup>4</sup> developed multivariate calibration models based on MIR (middle infrared spectroscopy) and NIR (near infrared spectroscopy) to determine the content of biodiesel in diesel/biodiesel mixtures, taking into consideration the presence of vegetable oils from different oleaginous seeds. Once applying the F test to the PLS calibration models, they both presented the same efficiency for both the studied regions with RMSEP values (root mean squared error of prediction) of 0.25 and 0.18% (v/v).

The use of infrared spectroscopy (FTIR-ATR (Fourier transform infrared spectroscopy with attenuated total reflectance configuration) and FT-NIR) to develop PLS calibration models to predict the content of biodiesel in diesel/biodiesel mixtures was proposed by Oliveira et al.<sup>7</sup> Two sets of samples were evaluated: the first (G1) was prepared with one type of biodiesel, and the second (G2) was a mixture of biodiesel from soy, palm, and babaçu. G1 provided RMSEP values of 0.20 and 0.06% (w/w), using FTIR-ATR and FT-NIR, respectively. However, the G2 RMSEP values varied in the range from 0.26 to 0.36% (w/w) and 0.33 to 0.57% (w/w), depending on the type of biodiesel and its techniques FTIR-ATR and FT-NIR, respectively.

Ferrão et al.<sup>8</sup> determined the content of biodiesel in diesel samples in the interval of 0.2 to 30.0% (v/v) using spectroscopy in the infrared and PLS. Several variable selections were proposed; however, the lowest RMSEP value 0.16 (%v/v) was obtained when four regions of the infrared spectrum were used, which correspond to the characteristic absorptions of biodiesel and diesel.

The biodiesel content in diesel samples within the interval of 0.5 to 30.0% (v/v), was predicted by Monteiro et al.<sup>9</sup> using proton NMR, PLS, and PCR (principal component regression). Two types of biodiesel (castor beans and soybeans) were employed in a calibration set containing 40 samples. Depending on the used region of the spectrum, three PLS models were obtained, which were built with three to four latent variables, with the percentage of explained variance of 83.4 to 87.6%. The RMSEP values varied in the range from 0.50 to 0.83% (v/v) depending on the chosen region of the spectrum.

Monteiro et al.<sup>10</sup> determined the content of oils and biodiesel in diesel using proton NMR and PLS. For this determination, three latent variables were employed in each model with an explained variance above 68%. Throughout the calibration, high correlation coefficients for the prediction of oil and biodiesel content were obtained (0.9974 and 0.9951, respectively), and RMSEC (root mean squared error of calibration) = 0.46 and

0.55% (v/v), respectively. Whereas, for the validation, the correlation coefficients were in the order of 0.9938 and 0.9882, and RMSEP of 0.68 and 0.82% (v/v), in the determination of oil and biodiesel content in diesel, respectively.

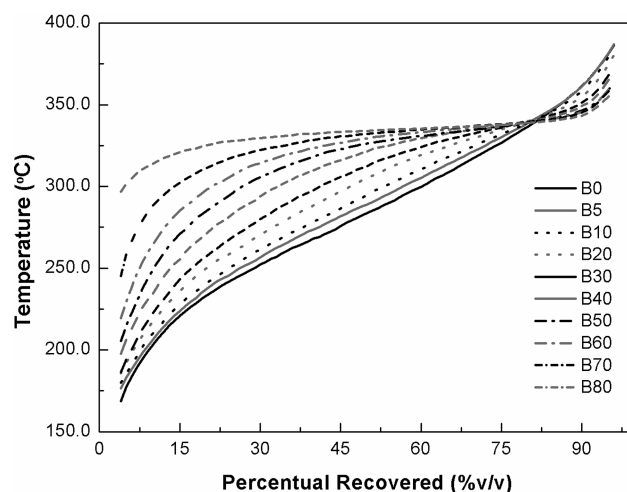
Pierce et al.<sup>11</sup> proposed the use of gas chromatography and PLS regression to predict the content of biodiesel in diesel. This model provided a determination coefficient of 0.99 and RMSECV (root mean squared error of cross-validation) of 0.79% (v/v), with biodiesel samples from different raw materials and diesel from different refineries.

With the aim of simplifying and speeding up the analytical process for diesel throughout inspection procedures, this study proposes the prediction of biodiesel content using distillation curves—routine assay used to evaluate the quality of diesel, allied with multivariate calibration based on partial least-squares regression.

## 2. EXPERIMENTAL SECTION

**2.1. Samples.** **2.1.1. Examining the Addition of Biodiesel to Diesel—Behavior of Distillation Curves.** To evaluate the behavior of the distillation curves with the addition of biodiesel to type A diesel (diesel without biodiesel), S500 (diesel containing 500  $\text{mg}\cdot\text{kg}^{-1}$  of sulfur) was used along with soy biodiesel containing 99.9% (w/w) of esters. This was done in order to keep the system under study as similar as possible to the Brazilian reality, which mainly uses soy to produce biodiesel (approximately 85%).<sup>2</sup>

Mixtures of diesel/biodiesel were prepared (Figure 1), in triplicate, in the range of 0 to 80.0% (v/v). For the interval from 0 to 10.0% (v/v)



**Figure 1.** Diesel distillation curves for different contents of biodiesel, 0–80% (v/v).

v) increments of 1.0% (v/v) were used, whereas in the range from 10.0 to 20.0% (v/v), the mixtures were prepared in intervals of 2.0% (v/v). As for the interval from 20.0 to 80.0% (v/v), increments of 10.0% (v/v) were used. These mixtures were submitted to distillation according to the ASTM D86.<sup>12</sup>

**2.1.2. Building the Chemometric Model.** A total of 220 diesel samples, with biodiesel content in the interval from 0.4 to 7.1% (v/v), were used to carry out the prediction of biodiesel content. These samples were collected in gas stations and represent five distinct refineries and two types (S1800 and S500). The choice of a set with ample variability of samples, origin and type, was aimed to embody, ideally, the real set that reflects the market variability. After assembling, the samples were kept in appropriate polyethylene flasks, which were sealed and kept at room temperature until the assays were carried out. Since the objective of this study was to determine the biodiesel content in diesel within a wider range (0.4 to 20.0% (v/v)), biodiesel

(soy or tallow) was added to 84 (of the 220) samples, with biodiesel content from 4.0 to 6.0% (v/v). The choice of a wider range of biodiesel content is related to future tendency of increase in the biodiesel content. Ultimately, all the 220 samples, with a new biodiesel content interval (0.4 to 20.0% (v/v)) were analyzed following the method based on the EN 14078.<sup>5</sup>

A separation in the set containing 220 samples was required, where it is possible to identify the presence of two line segments in the adjustment graph from the PLS model built from the interval between 0.4 and 20.0% (v/v). Hence, the first regression line contains the interval from 0.4 to 9.6% (v/v), and the second contains the range between 9.8 and 20.0% (v/v). Thus, those 220 samples were split into two sets: the first (S1) showed the range from 0.4 to 9.6% (v/v), a total of 150 samples, and the second (S2) showed the interval between 9.8 and 20.0% (v/v) of biodiesel content, with a total of 70 samples.

Posteriorly, each set was split, employing the Kennard–Stone algorithm<sup>13</sup> to two subsets; S1 was comprised of 100 calibration samples and 50 validation samples, and S2 contained 47 calibration samples and 23 validation samples. These samples were autoscaled in order to attribute equivalent importance to all variables.

## 2.2. Physical Chemical Parameters Analysis. 2.2.1. Distillation.

The samples were distilled with automatic Herzog distillers model HDA 627 according to ASTM-D86. For the distillation procedure, 100 mL of diesel was transferred to a specific distillation flask equipped with a thermocouple sensor and heated, keeping the distillation ratio between 4 and 5 mL min<sup>-1</sup>. The condensate was collected in a cooled test tube (13 to 18 °C), and the recovered volume was measured with a digital volume sensor. Distillation curves (distillation temperature according to the recovered volume) were obtained after adjusting the temperature readings to atmospheric pressure of 101.3 kPa and volume loss after measuring residue volume, according to ASTM-D86.<sup>12</sup>

**2.2.2. Biodiesel Content.** The determination of the biodiesel content in 220 samples of the chemometric models was carried out through a mid infrared spectrometer (ABB Bomem, MB series), according to the BS EN 14078.<sup>5</sup> As the samples were collected at gas stations (and therefore the content of biodiesel is unknown), the reference essay is used to determine the amount of biodiesel present in each sample. In this method, the reference material was diluted with cyclohexane so as to attain five concentrations from the reference material (B100, biodiesel containing 100% esters). After reading these five concentrations with the infrared spectrometer (in the range 4000–400 cm<sup>-1</sup>) the range from 1830 to 1660 cm<sup>-1</sup> was limited, and the correction of the baseline in this interval was made. These spectra (within the interval of 1745 ± 5 cm<sup>-1</sup>) were compared to the values obtained from the concentrations from the reference material through linear regression. The sample, diluted in cyclohexane when required, was introduced into the equipment. Following the spectrum correction by the baseline (in the range 1745 ± 5 cm<sup>-1</sup>), it was compared to the analytical curve and the content of biodiesel of the sample was obtained in % (v/v).

**2.3. Calibration Multivariate Tool.** PLS is a regression method based on simultaneous decomposition of the data matrix (**X**) and the property to be provided (**Y**). Each major component of the model undergoes a minor modification to get the maximum covariance between **X** and **Y** and receive the terminology of the latent variable. This method can be applied to a large number of variables in the presence of interference, since these are included in the calibration model.

In this method, the **X** and **Y** matrices are decomposed into smaller matrices according to the eqs 1 and 2:<sup>14</sup>

$$\mathbf{X} = \mathbf{TP}^t + \mathbf{E} \quad (1)$$

$$\mathbf{Y} = \mathbf{UQ}^t + \mathbf{F} \quad (2)$$

where **X** and **Y** are matrices will be decomposed, **T** and **U** are scores matrices, **P** is the **X** loadings matrix, **E** is the error (residuum) of the **X** matrix, **Q** is the **Y** loading matrix, and **F** is the error (residuum) of the **Y** matrix.

After decomposition of the matrices **X** and **Y**, a linear relationship is established between the scores **T** and **U** according to eq 3:

$$\mathbf{U}_h = \mathbf{B}_h \mathbf{T}_h \quad (3)$$

where **B** is the coefficients regression matrix and *h* is the latent variables number used in the PLS model.

Partial least squares regression was used to determine the biodiesel content, which aims in finding a small number of relevant factors that are predictive for **Y** and uses **X** efficiently.<sup>15</sup> For this purpose, Minitab Software Release Version 14 (Minitab, Lexington, MA, U.S.A.) was used.

## 3. RESULTS AND DISCUSSION

**3.1. Examining the Addition of Biodiesel to Diesel—Behavior of Distillation Curves.** By examining Figure 1, it is possible to evaluate the change in behavior of the distillation curves with the increase of biodiesel content. The addition of biodiesel to the concentration interval between 0 and 5% (v/v) did not produce significant perceivable changes to the profile of the diesels distillation curve. Nevertheless, a comparison through the *t*-test, between biodiesel additions—starting from 1% (v/v), with increments of 1%—and the temperatures used by the National Petroleum Agency (ANP) to examine the quality of diesel (temperatures equal to 10, 50, 85, and 90% of the recovered volume. For point T10, only by adding 7% (v/v) of biodiesel, a significant difference (with 95% of confidence) is perceived in the distillation temperature.

The addition of 1% (v/v) to points T50, T85, and T90 produced a significant difference (with 95% of confidence) in the temperatures corresponding to these points. Therefore, with the application of the *t*-test to four points of the distillation curve, it is possible to conclude that the addition of biodiesel was more evident in the intermediary and final points of the distillation, while the compounds in biodiesel are distilled in larger quantities starting from the range of 40% of recovered volume.<sup>16</sup>

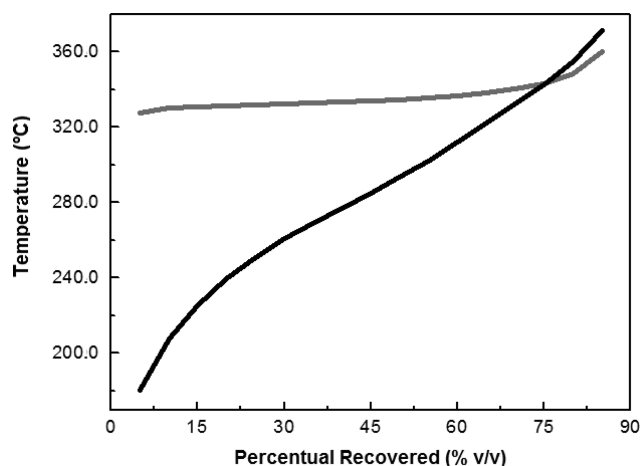
Thus, the use of chemometric techniques (such as PLS regression) becomes necessary in order to predict the content of biodiesel with exceptional accuracy and precision, since performing a visual inspection of the distillation curve will not provide perceivable significant changes produced from the addition of biodiesel.

Figure 1 shows the temperature increase in the initial fractions as the content of biodiesel increases, while in the final fractions of distillation, this process is inverse—the temperature decreases as the biodiesel content increases. Likewise, a coincident inflection point was attained in all biodiesel additions around 80% (v/v). These considerations can be clarified by examining Figure 2.

Figure 2 shows that the initial fractions from the distillation of biodiesel present a higher boiling point than diesel. Usually, the increase in the content of esters in biodiesel causes the elevation of the boiling point temperature. However, in the inflection point around 80% (v/v), the inverse process occurs.<sup>16</sup> In the final fractions of the distillation, a phenomenon follows: the dilution of the heavy fractions of diesel. The dilution of the heavy fractions of diesel, which can reach up to 380 °C, can be carried out by adding methyl esters, which display lower boiling point in this range of the distillation, for instance, methyl stearate and methyl linoleate.

**3.2. Building the Calibration Model.** As seen in section 3.1, the distillation curve varies with the increase of biodiesel content, which is mainly related to the difference in boiling points between the biodiesel and the light and heavy fractions





**Figure 2.** Typical diesel distillation curve (black line) and biodiesel from soy (gray line). Adapted with permission from Windom and Bruno.<sup>14</sup> Copyright Elsevier Publishing, 1998.

of the diesel. Thus, this analytical tool can be associated with a multivariate regression method to predict the biodiesel content.

To build the calibration model, distillation curves (temperature interval related to the percentage of recovered volume in the range from 4 to 91% (v/v)<sup>17</sup>) of 220 samples (S1 and S2) and the reference values of biodiesel content (*Y*) were combined with PLS regression. First, a selection of the number of latent variables for the calibration model was carried out by selecting the number of latent variables related to the lowest PRESS values (predictive residual error sum of squares).<sup>18</sup> The PRESS values were calculated by eq 4:

$$\text{PRESS} = \frac{\sum (Y_{\text{pred}} - Y_{\text{ref}})^2}{n} \quad (4)$$

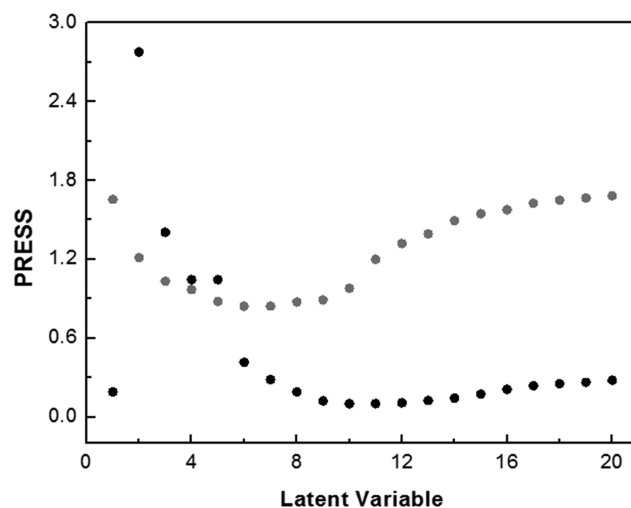
where  $Y_{\text{pred}}$  is the predicted value by model,  $Y_{\text{ref}}$  is the reference value, and  $n$  is the sample number used in the model.

The selection of the adequate latent variables number was carried out in two stages: the first, through the comparison of PRESS values for each latent variable added,<sup>19</sup> and the second, by employing the F test to the PRESS values.<sup>17</sup> Figure 3 shows that the intervals that displayed low PRESS values ranged from 8 to 20 latent variables for S1 and 4 to 10 latent variables for S2 in the prediction of biodiesel content.

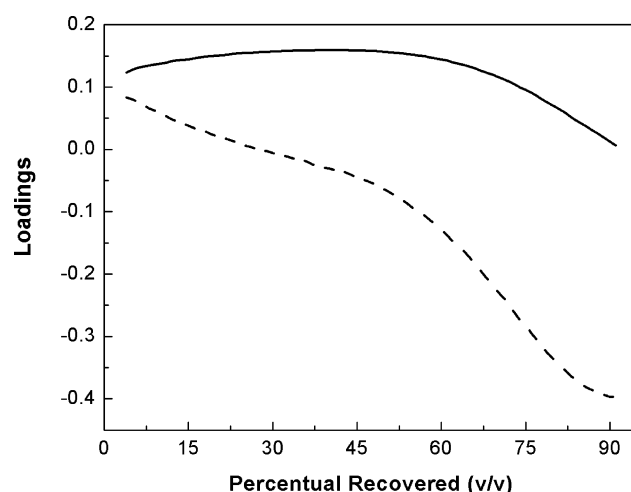
The F test (with 95% of confidence) indicated that S1 only required nine latent variables and S2 required six latent variables in order to build the chemometric models. The nine latent variables used to predict the content of biodiesel of S1 presented 99.9% of explained variance in *X* and 98.6% in *Y*. While the six latent variables used to predict the content of biodiesel in S2 captured 99.7% of explained variance in *X* and 97.1% in *Y*.

After building the calibration model, the loadings graphs were built for the prediction model of biodiesel content for S1 (Figure 4) and S2 (Figure 5).

In the loadings of autoscaled data, the first latent variable presented a percentage of explained variance in *X* of 69.6%, while the second percentage was 18.3%. Figure 4 shows the range from 4 to 60% of recovered volume presented greater loadings; contributing positively to the first latent variable; furthermore, the interval from 61 to 91% of recovered volume presented higher relevance, contributing negatively to the second variable.



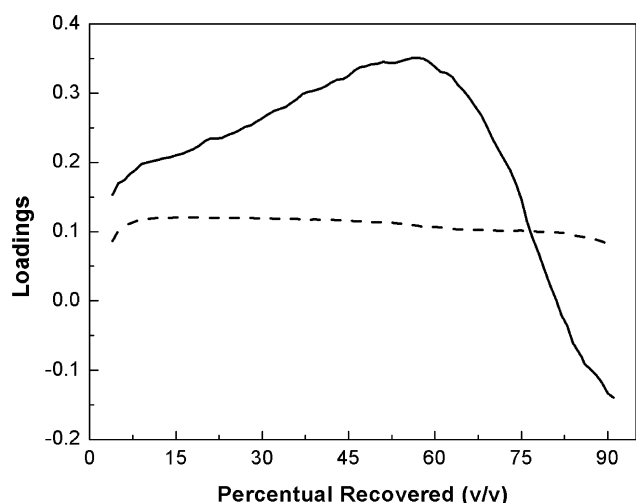
**Figure 3.** PRESS values versus number of latent variables in the prediction of biodiesel content for S1 (black circle) and S2 (gray circle).



**Figure 4.** Loading graph for the first two latent variables, for the determination of biodiesel content in S1, in interval 0.4–9.6% (v/v). (—) LV1 and (---) LV2.

In the range of greater loading for the first latent variable (beginning of distillation), the biodiesel content increases as the temperature increases. This is related to the addition of esters present in biodiesel with higher boiling point temperature as aforementioned. In the interval of greater weight, while building the second latent variable (end of distillation), unlike the beginning of distillation, the content of biodiesel increased as the distillation temperature decreased. This can be related to the dilution of the heavy fractions of diesel (which can reach up to 380 °C), and to the addition of methyl esters that have lower boiling point, such as, methyl stearate and methyl linoleate,<sup>16</sup> as well as to the process of thermal degradation of the compounds present in biodiesel.

The loading graph for the determination of biodiesel content in range of 9.8 to 20.0% (v/v) (Figure 5) presented an outline different from the one obtained for interval from 0.4 to 9.6% (v/v). The first latent variable displayed a percentage of explained variance in *X* of 14.4%, whereas the second presented a percentage of 67.5%. The range from 45 to 65% of recovered volume presented greater importance in LV1, while the interval



**Figure 5.** Loading graph for the first two latent variables, for the determination of biodiesel content in S2, in range 9.8–20.0% (v/v). (—) LV1 and (---) LV2.

from 10 to 45% of recovered volume showed greater relevance to build LV2. Once these results are compared with the distillation curves from the interval from 10 to 20% (v/v) (Figure 1), it is possible to detect the increase of biodiesel content causes the elevation of the boiling temperature. This occurs with the increase of the ester quantity such as methyl palmitate.<sup>16</sup> As for the beginning of the distillation, likewise in set 1, the temperature increases as the concentration of biodiesel increases. A possible explanation for the phenomenon is related to the presence of compounds with lower boiling point temperatures (derived from diesel or from contaminants of an incomplete transesterification reaction), which vaporize before the esters from biodiesel start to boil.<sup>16</sup>

Subsequently to building the calibration model and evaluating the importance of the variables by building this model, it is required to examine the merit figures calculated for each set.

**3.3. Evaluation of the Proposed Method.** The accuracy evaluation of the proposed method was carried out through the calculation of the RMSEP. In Table 1, the RMSEP values were compared to the ones obtained from different analytical techniques and the proposed method.

Table 1 shows (as predicted) that the prediction of the set 1 presented lower RMSEP values when compared to set 2. The RMSEP value of set 1 was lower than the values presented in the literature<sup>4,8–10</sup> using infrared spectroscopy and proton NMR. While the RMSEP obtained with the S2 model presented lower values than the ones obtained by Monteiro et al. using proton NMR.<sup>9,10</sup>

An evaluation test of the presence of systematic errors was carried out using the *t*-test. The *t* calculated values ( $t_{\text{calc}}$ ), for both sets were less (0.60% v/v for S1 and 0.82% v/v for S2) than the *t* tabled values ( $t_{\text{tab } 49\text{DF}} = 2.01$  and  $t_{\text{tab } 22\text{DF}} = 2.08$  for S1 and S2, respectively), with a 95% level of confidence, showing that the systematic error in the models can be considered insignificant.

The accuracy of the proposed method was only calculated for set 1, as the only available distillation curves with samples in the range from 4 to 5% (v/v). Unfortunately, it was not possible to build a set of data that contemplated set 2 due to the lack of equipment to acquire distillation curves. Therefore, the

**Table 1.** RMSEC and RMSEP Values, Among Other Parameters, Obtained in the Prediction of Biodiesel Content using PLS Multivariate Calibration

parameter	S1 (% v/v)	S2 (% v/v)
measured range	0.4–9.6	9.8–20.0
number of latent variables	9	6
correlation coefficient calibration ( $R_{\text{cal}}$ )	0.9949	0.9852
correlation coefficient validation ( $R_{\text{val}}$ )	0.9910	0.9841
X explained variance LV1 (%)	69.6	14.4
X explained variance LV2 (%)	18.3	67.5
RMSEC	0.23	0.47
RMSEP	0.23	0.53
<i>t</i> -test ( $t_{\text{calc}}$ ) validation set	0.60	0.82
<i>t</i> -test ( $t_{\text{tab}}$ ) validation set	2.01	2.08
repeatability (proposed method)	0.37	
reproducibility (proposed method)	0.39	
repeatability (EN 14078 experimental)	0.14	
reproducibility (EN 14078 experimental)	0.20	
max. repeatability (EN 14078)	0.30	
max. reproducibility (EN 14078)	0.90	

accuracy of the proposed method was examined through the repeatability and reproducibility calculation from the S1 data.<sup>19</sup> Table 1 presents the repeatability and reproducibility values for the content of biodiesel assay of the proposed method, also the standard method,<sup>5</sup> as well as the maximum permitted values for this assay.

Table 1 shows that only the reproducibility value of the proposed method was inferior to the maximum permitted value by the EN 14078. However, when the accuracy of the experimental value obtained through the EN 14078 was compared to the accuracy of the proposed method EN 14708, it presented repeatability and reproducibility values inferior to the distillation curve method allied with PLS.

A high coefficient correlation between the reference values and predicted values was obtained for set 1, indicating that the built model presented good adjustment of data (Table 1). Furthermore, this value was inferior to the one obtained by Pimentel et al.<sup>4</sup> through mid-infrared spectroscopy (0.9860). A smaller correlation coefficient was obtained for set 2, indicating a larger dispersion of points along the adjusted line, through the least-squares method in comparison to set 1.

In this study, it was possible to detect that the different distillation curve profiles did not prevent obtaining low RMSEP values compared to models from the literature,<sup>9,10</sup> with high correlation between predicted and reference values.

## 4. CONCLUSION

The addition of biodiesel to diesel caused visual changes to the profile of the distillation curve starting at 5% (v/v). At the beginning of the distillation, the increase in temperature biodiesel because of the addition of biodiesel was detected, while at the end of the distillation the inverse process was identified.

Distillation curves obtained from the ASTM D86 associated with PLS multivariate calibration were efficient in predicting the biodiesel content, which is an important property to examine the quality of diesel in the ranges from 0.4 to 9.6% (v/v) and 9.8 to 20.0% (v/v), regardless of its origin, the type of diesel or raw material used in the production of biodiesel.

In both the obtained models, the RMSEP values were satisfactory, lower than the values presented in the literature,

based on techniques such as proton NMR.<sup>9,10</sup> The accuracy of the method was satisfactory, since the reproducibility of the method was superior to the specified limit by EN 14078. These models displayed an elevated adjustment between the predicted and reference values, the systematic errors were insignificant, and thusly disregarded.

The proposed method for the determination of biodiesel content through distillation curves and multivariate calibration was useful in speeding up the analytical process and reducing the time and costs of analysis, since distillation assays are within the scope of laboratory analysis.

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### Notes

The authors declare no competing financial interest.

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