Thermal diesel-like analysis

Quality control by thermal and chemometric analysis

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Abstract Biofuel has been obtained by cracking of soybean (*Glycine* sp.) oil, which is characterized by acidity index, density, cetane index, copper corrosion, carbon residue, fulgor point, and heat of combustion. In order to evaluate the quality of biofuel as well as detect its adulteration with vegetable oil, partial least squares regression calibration models based on thermogravimetric (TG) analysis were used as a precise and an accurate method. Thirty mixtures of biofuel/diesel/vegetable oil standards were prepared. Twenty of them were used for calibration, and ten for validation. The results have shown that the thermogravimetric analysis, PLS/TG, presented the best performance for the detection of vegetable oil contamination with a root mean square error of prediction (RMSEC% w/w) of 0.23, with a relative error of prediction of 3.6%, corroborating with the success of TG analysis application to determine the quality of biofuels and diesel/biofuel blends, showing that the TG analysis is an excellent tool to control quality of biofuels.

Keywords Diesel-like · Quality control · Thermal analysis · PLS

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Introduction

The conventional fossil fuels are essential to maintain the mankind development and lifestyle [1, 2]. Thus, burgeoning demand of fuels has been increasing day-by-day. On the other hand, the burning of fossil fuels generates high amounts of greenhouse gases, mainly CO_2, producing toxic acid rain gases (NO_x, SO_x). Therefore, the use of environmentally friendly alternative fuels is necessary to reduce the CO_2 and SO_x emissions and maintain the quality of life on Earth [3–5].

Hence, the application of renewable natural sources in the biofuels production has significantly grown over the past decade. Technologies to produce these environmentally friendly fuels based on the conversion of vegetable oils have been highlighted in the last years [5]. One of the methods to obtain green fuels is the production of diesel-like by the pyrolysis of vegetable oils. The pyrolysis methodology to obtain hydrocarbons has been applied since Second World War in China by thermo-cracking of Tung oil [6]. A myriad of studies about thermo-cracking and catalytic cracking have been developed since Second World War [7–11].

On the other hand, the most popular route to produce green fuel is alcoholysis of triacylglycerides, well known as transesterification [4]. However, alcoholysis needs special conditions to obtain biofuel because this reaction requires a large amount of alcohol, acid or basic catalysts, dry reactants, and dry conditions [12]. In other words, at least 3 mol of alcohol is necessary to convert each mol of triacylglyceride into biofuel. The presence of water in this reaction can cause the hydrolysis of distinct esters, and the application of base catalysts results in the formation of soap [12]. Thus, the pyrolysis of vegetable oil is an elegant alternative to produce biofuels. This pyrolyzed or cracked

biofuel presents physical and chemical properties very similar to traditional fossil diesel, and this biofuel production does not show the typical setback of transesterification methodology for producing biofuel.

Nowadays, concerns about global warming and the amount of petroleum sources have generated some governmental actions. One example is the encouragement of the US government to use biofuels offering tax incentives [4]. European Commission adopted Directive 2003/30/EC, and this program indicates the addition of 2% of biodiesel or diesel-like in fossil diesel in 2005 and 5.75% up to 2010 [2].

The Brazilian government has also created a biofuel program, which aims the addition of 2% of biofuel in fossil diesel in 2008 and 5% up to 2013. These programs have been stimulating the biofuels production [13]. Moreover, the Brazilian biofuel program stimulates the biofuel production from vegetable oils by small farms, which could mean an additional profit to simple agricultural breadwinners, improving the Brazilian agricultural workers' lives [13].

One of the preoccupations of these programs is the biofuel purity obtained from vegetable oils. The presence of oils in biofuel is a remarkable problem and should be controlled. Consequently, the development of assays capable of determining the biofuel purity has become necessary. The presence of soybean oil as a contaminant of biofuel is because the majority of the biofuel produced in Brazil comes from soybean oil. This contamination can occur due to a non-effective transformation of vegetable oil into biofuel or even a criminal adulteration of the biofuel.

Chemometric methods provide an effective way to extract quantitative information from many kinds of data, such as UV–VIS [14, 15], IR [16], NMR [17], and fluorescence spectroscopy [18]. Multiple linear regression (MLR), principal components regression (PCR), and partial least squares regression (PLSR) are the most applied multivariate calibration methods relating instrumental responses and the property of interest [19]. Several of these applications have demonstrated that multivariate calibration is able to determine properties of interest in relatively complex systems where no selective signals and significant interferences are observed [14–18]. The application of chemometric methods for analyzing thermal data is less common than in spectroscopy. Examples of works in this research field can be found by applying exploratory and pattern recognition methods such as principal component analysis (PCA) to study the effects of chemicals on cellulose pyrolysis by thermogravimetry–mass spectrometry (TG–MS) [20], the analysis of cellulosic and regenerated fabrics by PCA and Soft Independent Modeling of Class Analogy (SIMCA) [21] and the classification of polyethylenes groups by linear discriminant analysis (LDA) [22].

For quantitative purposes, PLSR has been applied for TG analysis [23–25] and differential TG data [26]. Despite the above cited references, there is a lack of applications of chemometric methods with thermal techniques with several research areas or kinds of samples. Therefore, the research and development of new applications are still necessary to join chemometric and thermal methods to verify the benefits that can be achieved in a wide range of situations. In this way, the proposal of this study is the development of an analytical method for the determination of the presence of vegetable oil in diesel-like through thermogravimetric analysis using chemometric methods.

Theory

Multivariate calibration—PLSR

The PLSR model has been discussed in detail in the literature [17, 19]. Thus, only a brief description of the main information for the model development is presented. The data matrix X is formed by the thermograms of the biodiesel/oil mixtures and the vector y contains the reference values for percentage (w/w) of oil in the sample. In this application, all models were built with the instrumental responses and reference values mean centered. The number of latent variables (LVs) used in the PLSR models was chosen based on the RMSECV values obtained for a trial number of LVs, where the lowest value indicates the correct choice for the number of LVs [27].

Interval partial least square regression (iPLSR) is an interactive extension of PLSR that develops local PLSR models based on equidistant subintervals of the full-thermogram region. Its main use is to provide an overall picture of the relevant information in different subdivisions. Thereby, it focuses on important regions, removes interferences from other ones, and selects the regions that provide the lowest prediction errors. Therefore, IPLSR was applied in this study to select the thermogram region that presented the lowest prediction errors for the model development. The choice of the best iPLSR model was done by comparing the prediction performance of these local models with the global model built with the full thermogram. The comparison is mainly based on the root mean squared error of cross validation (RMSECV) [17, 28].

Analytical figures of merit

Mean prediction error

Reports, in other words, the closeness of agreement between the reference percentages of oil and the value found by the

calibration model. In chemometrics, this is generally expressed as the root mean square error of prediction (RMSEP), which is an approximation of the standard error of the validation samples, obtained as [29]:

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^{I_{\text{val}}} (y_i - \hat{y}_i)^2}{I_{\text{val}}}} \qquad (1)$$

where I_{val} is the number of validation samples. When the calibration samples are used instead of the validation set, the RMSECV is analogously obtained by replacing I_{val} by I_{cal}, where I_{cal} is the number of calibration samples.

According to the definition of the RMSEP, a relative error of prediction (REP) can be obtained as [30]:

$$\text{REP} = \sqrt{\sum_{n=1}^{I} \frac{(y_i - \hat{y}_i)^2}{I_{\text{cal}} y_i^2}} 100 \qquad (2)$$

Confidence intervals

This parameter can be defined as a range within which we may assume, with a given degree of confidence, i.e., a certain probability, that the real value for that concentration of the analyte of interest is included. It can be determined from the application of statistics and the estimated standard error of prediction ($s(\hat{y} - y)$), expressed as [17, 29, 31]:

$$\text{CI}(y_i) = \hat{y}_i \pm t_{v,1-\alpha/2} \times s(\hat{y} - y) \qquad (3)$$

$$\text{CI}(y_i) = \hat{y}_i \pm t_{v,1-\alpha/2} \times \sqrt{\text{MSEC}(1 + h_i + 1/I_{\text{cal}})} \qquad (4)$$

where α is the significance level required for the prediction interval, $t_{v,1-\alpha/2}$ is the corresponding critical level for Student's t distribution with v degrees of freedom, determined as proposed by Van der Voet [32], I_{cal} is the number of calibration samples, MSEC is mean square error estimated in the calibration samples with v degrees of freedom and h_i is the leverage of the sample, estimated as [27]:

$$h_i = t_i^{\text{T}} (T^{\text{T}} T)^{-1} t_i \qquad (5)$$

where t_i and T are the scores for the sample i and for all the calibration samples, respectively.

Capability of detection (CCβ)

According to ISO 11843-2 [33] definitions, the CCβ can be defined as the minimum detectable net quantity with a pre-set of probabilities of false-negative (α) and false-positive (β) errors (usually $\alpha = \beta = 0.05$). Ortiz et al. [34] have extended the CCβ application for multivariate calibration methods such as PLSR. Following this approach, the CCβ can be determined as [34]:

$$CC\beta = \delta_{\alpha,\beta} \frac{s}{b} \sqrt{\frac{1}{m} + \frac{1}{I_{\text{cal}}} + \frac{\bar{y}^2}{\sum_{i=1}^{I_{\text{cal}}} (y_i - \bar{y})^2}} \qquad (6)$$

where s is the standard deviation of the residuals of the regression of the estimated concentrations ($\hat{y}$) against the reference concentration of calibration samples (y) with the intercept "a" and slope "b", m is the number of replicate measurements performed on each sample, $\bar{y}$ is the mean concentration of the standards, and $\delta_{\alpha,\beta,v}$ is the noncentrality parameter from the noncentral t-distribution with I_{cal}-2 degrees of freedom.

Experimental

Chemicals

Vegetable oil (Soya) and diesel (ANP) were used without any purification.

Diesel-like production

Diesel-like was obtained by pyrolysis of soybean oil. Pyrolysis experiments were carried out at temperatures ranging from 350 to 400 °C with a 5 L stainless steel batch unit, as described in detail before [13, 35]. The vegetable oil (2 L) was introduced into the pyrolysis reactor and then heated by an external electric resistance. The temperature was measured at two sites with calibrated thermocouples. When the temperature inside the reactor achieved 350 °C, the vegetable oil was pyrolyzed, vaporized, and a vapor feed left the reaction, by the upper side at temperatures ranging from 200 to 250 °C. Then, the vaporous feed enters into a water cooled heat exchanger. Two liquid fractions were obtained in the collector: an aqueous fraction and an organic one. These fractions were separated by decantation, and the organic phase was distilled by standard oil laboratory techniques [36]. The diesel-like distillates were separated into four fractions with distillation temperature ranges: (a) $T < 80$ °C; (b) $80 \text{ °C} \leq T < 140 \text{ °C}$; (c) $140 \text{ °C} \leq T < 200 \text{ °C}$; (d) $200 \text{ °C} \leq T$ (heavy fraction). The different fractions were weighed and the heaviest one was analyzed according to ASTM standard methods for petroleum fuels.

Diesel-like characterization

Acidity index was determined using 1.0 g of diesel-like solubilized in 10.0 g of 1:1 toluene:isopropanol solution with three drops of ethanolic solution of phenolphthalein 1.0%, as according to AOCS Cd3d63 standard method.

Fig. 1 Common structure of triglyceride of soybean oil
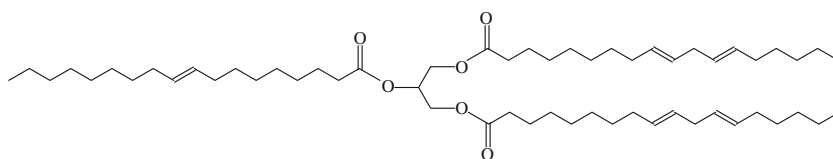
The density of diesel-like was determined in triplicate using an electronic densimeter Anton Paar Model DMA 35N at two distinct temperatures. Samples were maintained at 15 and 20 °C in a thermostatic bath. Density measures were carried out after temperature equilibrium, as stated by ASTM D4052 standard method.

Viscosity was carried out in a Herzog viscosimeter model HVB-438 in triplicate, as according to ASTM D 445 standard method.

Cetane index was obtained using 100 mL of diesel-like were distilled in an automatic distillator Herzog model HDA 627, as according to ASTM D86 standard method.

Cooper corrosion was determined using 30 mL of die-sel-like and copper blade were added in the test tube. The tube was equilibrated at 50.0 ± 1.0 °C for 3 h ± 5 min. Copper blade was separated, and the corrosion degree was determined by the comparison with reference blade as stated by ASTM D130 standard method.

Carbon residue was obtained using 10.0 g of diesel-like were added in a porcelain crucible. The crucible was heated up to smoke formation. Then, the smoke was ignited by a Bunsen flame, as stated by ASTM D189.

Fulgor point of diesel-like was determined by Pensky-Martens apparatus, as according to ASTM D93 standard method.

Thermogravimetry of diesel-like and adulterated diesel-like

Thermal analysis of diesel- and adulterated diesel-like samples were carried out in a thermogravimetric analyzer TA model SDT 2960 with an air flux at 100 mL min^{-1} and a heating rate of 10 °C min^{-1}. In these experiments, 20 samples were used to prepare the calibration method and 9 to obtain the validation. All analyses were carried out in the same week.

Results and discussion

Characterization

The soybean oil is basically composed of triglycerides, which are formed by ±30% of oleic acid framework and ±60% of linoleic acid framework (Fig. 1).
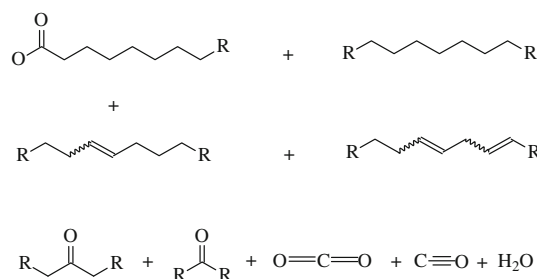

Fig. 2 Proposed structures of biofuels obtained from pyrolysis of soybean oil. Biofuel mixtures present a slightly varied composition depending on feedstock and processing conditions

Table 1 Results for the characterization of the diesel-like and standard values of diesel required by ANP (Brazilian Oil Agency)

Parameter	Diesel-like	Diesel
Density 20 °C/Kg/m^{-3}	872.5	820–880
Viscosity 40 °C/mm^{2}s^{-1}	4.93	2.0–5.0
Acidity index/mg KOH g^{-1} de óleo	90.15	–
Automatic distillation/°C		
10%	147.2	To observe
50%	293.1	245–310
85%	318.8	370 (max)
90%	345.2	370 (max)
Fulgor point/°C	64	38 (min)
Cetane index	36.7	51–54
Copper corrosion	1	1
Carbon residue/%	0.51	0.25

The composition of the pyrolysis mixture from soybean oil is based on various organic and inorganic products such as: C_{11}–C_{24} alkyls, C_7–C_{11} carboxylates, acrolein, CO_2, CO, and water (Fig. 2) [37]. The data of characterization (density, viscosity, acidity index, automatic, fulgor point, cetane index, copper corrosion, and carbon residue) of the biofuel obtained from the pyrolysis of soybean oil are shown in Table 1.

Thermogravimetric analysis

TG curves of the diesel and biofuel obtained from the pyrolysis of soybean oil and diesel/biofuel (50:50, w:w) blend are presented in Fig. 3, which showed only one step of mass loss, which was attributed to the volatilization and/
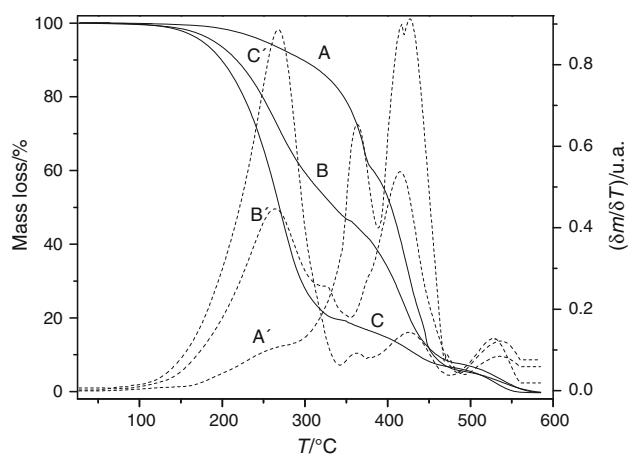
Fig. 3 TG curves of biofuel (*A*), biofuel–diesel blend (50:50,w:w) (*B*), and diesel (*C*)

or combustion of methyl esters from biodiesel and alkyl compounds from diesel.

The TG curves of the biofuel obtained from the pyrolysis of soybean oil, biofuel spiked with soybean oil, and soybean oil were recorded in air (Fig. 3). These curves presented four mass loss steps. The first one (from 25 to 300 °C) was assigned to the volatilization of hydrocarbons. The second step (between 300–350, 350–380, and 300–390 °C for biofuel, biofuel spiked with soybean, and soybean oil, respectively) was attributed to the oxidation of the unsaturated fatty. The third step started at 350, 380, and 390 °C for soybean oil, biofuel spiked with soybean, and biofuel, respectively, and finished at 480 °C for all samples. This mass loss is related to the oxidation of the saturated fatty. The last event (between 480–600 °C) is assigned to the decomposition of the polymers formed during the thermal oxidation process [38–40]. TG curves clearly showed that the volatilization is much more evident

in biofuel than in soybean oil, and the oxidation steps were more evident for soybean oil than biofuel. This fact can be explained by the presence of hydrocarbons and the low weight organic compounds in biofuel, which showed a volatilization temperature lower than the compounds present in vegetable oil. Moreover, vegetable oil is rich in triglycerides, which presents high intermolecular interactions. These interactions make the volatilization difficult, and consequently, cause the degradation by the oxidation of fatty in high temperatures.

### PLSR modeling and validation of the TG data

In order to obtain the PLS calibration model, TG curves were obtained for all blends. All calculations were carried out using the Matlab version 6.5 (MathWorks) and the IPLSR routines available on the web [40].

The optimal number of LVs needed in the calibration model was obtained by cross-validation (CV) choosing the one that provided the lowest RMSECV. The performance of the calibration models was analyzed by calculating the root mean squares errors of CV, RMSECV, and of external validation (Fig. 4).

Figure 4 showed that the best temperature range for model development was between 283 and 309 °C, presenting a RMSECV lower than 0.33% and with 4 LVs.

All TG curves from 25 to 309 °C were shown in Fig. 5. This figure clearly shows the difference among the curves with distinct amounts of soybean oil present in biofuel. It is important to observe that only the best temperature range obtained with IPLSR (between 283 and 309 °C) was used for calibration. The calibration data set was initially composed by 20 samples. However, the samples presenting 4 and 8% soybean oil were excluded from the calibration samples due to the presence of a large error in the

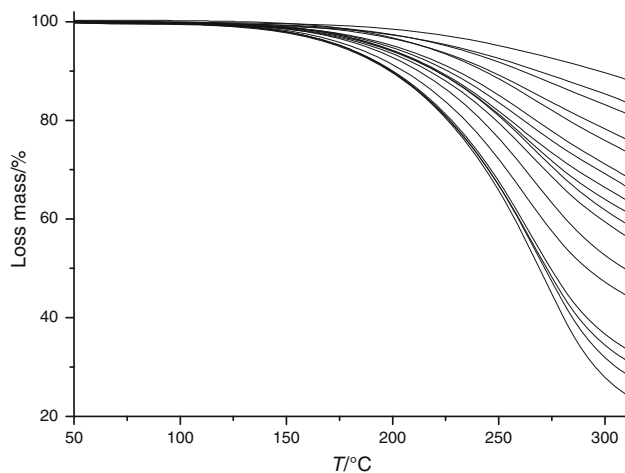**Fig. 4** *Dotted line* is RMSECV (2 LV's) for global model/*Italic numbers* are optimal LVs in interval model
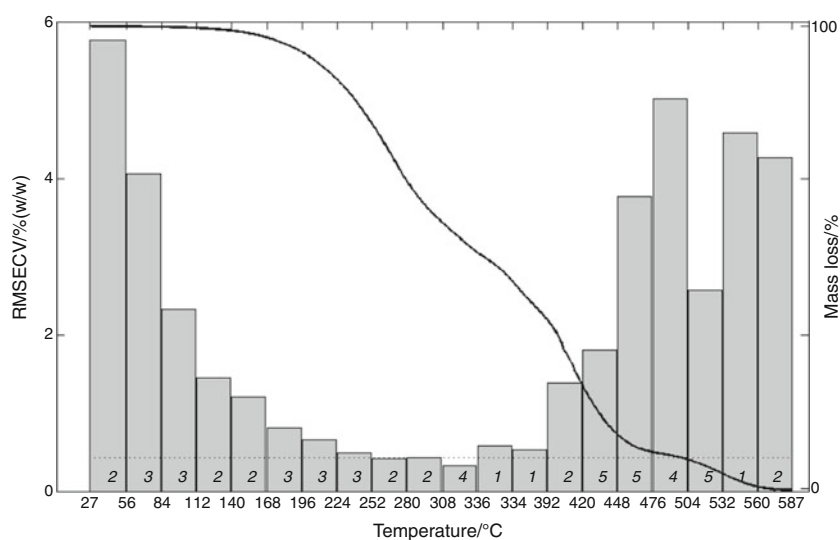
Fig. 5 Thermogravimetric curves of diesel- and diesel-like adulterated with soybean oil from 27 to 310 °C

Table 2 Figures of merit for the PLS model with the interval of 282–309 °C

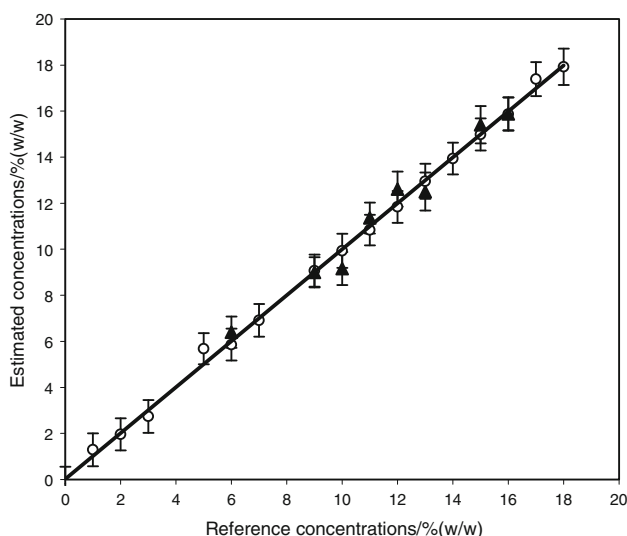| Parameter	
RMSEC[a]	0.23
RMSECV[a]	0.33
RMSEP[a]	0.47
Relative error of prediction[b]	3.6
Capability of detection (CCβ)[a]	1.11
Goodness of fit	
Intercept	0.991 ± 0.024
Slope	0.140 ± 0.267

[a] Expressed as percentage (w/w), [b]Percentage

Fig. 6 PLS regression and external validation for the soybean oil content in biofuel in the temperature range between 283 and 309 °C, (*unfilled circle*) Calibration set, (*filled triangle*) validation set, and (*error bars*) uncertainty of the estimated values with 96% of confidence

prediction values when compared with the reference values. The comparison between the reference and predicted values with their confidence intervals is presented in Fig. 6, where a good agreement and low uncertainty can be observed.

Results for the figures of merit are displayed in Table 2. It can be observed that the mean prediction errors represented by RMSEC (root mean square error of calibration), RMSECV and RMSEP were all lower than 0.50%, whereas the relative error was 3.6%. The mean uncertainty obtained with 95% of confidence (presented graphically in Fig. 6)

was 0.88%. These results indicate the good prediction ability of the model.

The goodness of fit presents the slope and intercepts values for the regression line between the reference and predicted values. Since the confidence intervals for these parameters include the unit (1.0) and zero (0.0), it can be concluded that the IPLSR model does not present any constant or proportional systematic errors, confirming the accuracy of the multivariate model.

The CCβ estimated as proposed by Ortiz et al. [34] includes not only the variation of the noise in the data, but also the error of the regression model. Therefore, it represents a realistic value for this important figure of merit. The estimated value for CCβ was 1.1%, which indicates that the TG method is appropriate to determine the adulterations of biofuel in routine analysis.

Conclusions

The addition of soybean oil increases the heat of combustion of biofuel, which is caused by the presence of organic chains which are bigger than the biofuel ones. TG curves showed that the biofuel presented a volatilization in a temperature lower than soybean oil. The biofuel showed a high mass loss in the volatilization step and a low mass loss in oxidation steps, whereas the soybean oil showed the opposite behavior.

PLSR calibration model developed with the TG data showed a high correlation between the real and predicted concentrations. The method is simple and does not require any additional pretreatments of the fuel samples. The results for accuracy, uncertainty, and CCβ were promising, indicating that the developed model by thermogravimetric analysis is one alternative to be used in the quality control of biofuels.

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