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Time Domain-NMR Combined with Chemometrics Analysis: An Alternative Tool for Monitoring Diesel Fuel Quality

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ABSTRACT: Time-domain nuclear magnetic resonance (TD-NMR) was explored as a rapid method for simultaneous assessment of the quality parameters in commercial diesel samples (B5 diesel-biodiesel blend). A principal component analysis (PCA) obtained with the relaxation decay curves revealed tight and well-separated clusters, allowing discrimination of the diesel samples according to the sulfur content: 10 (S10), 500 (S500), and 1800 (S1800) mg kg⁻¹. Classification models based on the soft independent modeling of class analogy (SIMCA) showed a good discrimination power with a percentage of correct classification ranging from 90% (for S500 diesel samples) to 100% (for S10 and S1800 diesel samples). Partial least-squares regression (PLSR) was used to estimate the cetane index, density, flash point, and temperature achieved during distillation to obtain 50% of the distilled (T50) physicochemical parameters in the commercial diesel samples. The best PLSR models were obtained with two latent variables, providing a standard error of prediction (RMSEP) of 0.60, 2.37 kg m⁻³, 3.24, and 2.20 °C for the cetane index, density, flash point, and T50, respectively, which represents the accuracy of the models. The results support the application of TD-NMR to evaluate the quality of B5 diesel, providing a simple, rapid, and nondestructive method for the petrofuel industry.

1. INTRODUCTION

In recent decades, the interest in fuel quality, performance, and production has increased due to the environmental impact (i.e., climate changes and air pollution), the magnitude of global energy consumption, and depletion of fossil fuel resources.^{1,2} Among the petrofuels, diesel fuel engines have several advantages over other internal combustion engines, such as high thermal efficiency and high fuel economy.³ However, diesel engine combustion releases large amounts of particulate matter (PM) and gases (CO, CO₂, SO_x, NO_x) to the atmosphere which are directly related to health and environmental issues.^{4,5} Consequently, governmental agencies all over the world have introduced stringent regulations to reduce the diesel engine emissions. Since 2010, the Environmental Protection Agency (EPA) established the upper limit of sulfur content in commercial diesel fuel to 15 mg kg⁻¹,⁶ which is similar 10 mg kg⁻¹ established by the European Union (EU) Euro V.⁷

The quality of commercial diesel has been determined by standard methods. In the United States, the American Society for Testing and Materials (ASTM) has documented a wide range of methods to determine the performance and the physical properties of petroleum fuel products.⁸ In the European Union, the quality of petrofuel products are specified by the European Standards Organization (EN),⁹ whereas in Brazil the National Agency of Petroleum, Natural Gas and Biofuels (ANP) regulate the methods used to check the quality and performance of petrofuel products.¹⁰

Flash point (ASTM D93),¹¹ cetane index (ASTM D976),¹² density (ASTM D4052),¹³ and distillation (ASTM D86)¹⁴ are some of the physicochemical parameters used to monitor diesel quality and performance. Although the standard methods established to determine these properties are widely accepted, each property is determined separately, following different methods and using different instruments, resulting in a high economical cost and time consumption.

Nuclear magnetic resonance (NMR) represents an attractive alternative method for fuel analysis^{15–18} due to the ability to analyze samples with little or no sample preparation, fast data collection, and provide a nondestructive and noninvasive method. These advantages result in reduction in time required for the analysis, cost savings, and an increase in the number of samples that can be analyzed. In particular, the measurements based on time domain-nuclear magnetic resonance (TD-NMR), using benchtop equipment, have been shown to be a powerful tool for fuel quality analysis with potential for in-line measurements. Muhammad and Azeredo have compared the performance of ¹H NMR spectroscopy and low-field relaxometry to predict viscosity and API gravity of Brazilian crude oils.¹⁹ According to their results, partial least-squares regression (PLSR) models obtained with the transversal relaxation time (T₂) curves showed better predictive perform-

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Table 1. Diesel Properties Corresponding to the 60 Commercial Diesel Samples^a

diesel property	ABNT NBR	S10	S500	S1800
cetane index	14759	49.40 ± 1.16	45.60 ± 0.30	44.31 ± 0.14
density (kg m ⁻³)	14065	840.78 ± 2.08	851.63 ± 3.05	854.90 ± 0.62
flash point (°C)	14598	59.40 ± 6.03	43.45 ± 1.81	43.78 ± 1.12
T50 (°C)	9619	271.70 ± 7.83	282.96 ± 3.05	280.82 ± 1.06

^aThe values are expressed as mean ± standard deviation.

ances, when compared with the models developed using ¹H NMR spectra. Ramos et al. have also applied TD-NMR to predict the viscosity of crude oil.²⁰ ¹H transverse relaxation times (T_2) of 68 Brazilian crude oils were measured in the benchtop NMR spectrometer (2 MHz for ¹H), and PLSR models were developed using the T_2 relaxation decays and their respective T_2 relaxation spectra. In both cases, the PLSR models showed good performance, with a standard error of prediction of 0.161 and 0.135 log cP for the T_2 relaxation spectra and relaxation curves, respectively. Honorato et al. have reported the application of TD-NMR to monitor the chemical and physical properties of Brazilian heavy oil submitted to plasma treatment.²¹ The crude oil was treated in a dielectric barrier discharge plasma reactor using natural gas, CO₂, or H₂ as the working gas. The results indicated a large drop in the water content of the plasma-treated samples as compared to the crude oil, allowing the application of low-field NMR to follow the effects of plasma treatments on heavy oils. Although several applications of TD-NMR in fuel analysis could be found in the literature, this technique has not been applied for the determination of diesel fuel quality and its physicochemical parameters. Furthermore, TD-NMR is cheaper, smaller, and easier to operate than a high-field NMR (HF-NMR) instrument. From a user point of view it is therefore of interest to investigate if TD-NMR can give similar (or better) results than HF-NMR.

The aim of this study is to demonstrate the ability to apply TD-NMR combined with chemometric analysis to classify and predict quality parameters of commercial diesel samples simultaneously. Qualitative and quantitative models were developed using pattern recognition techniques including soft independent modeling of class analogy (SIMCA), k nearest neighbors (kNN), partial least-squares discriminant analysis (PLS-DA), and partial least squares regression (PLSR).

2. MATERIALS AND METHODS

2.1. Samples. Commercial diesel samples denominated B5 (diesel-biodiesel blend containing 5% biodiesel v/v) were provided by the Center for Characterization and Development of Materials (CCDM, São Paulo, Brazil). The samples were designated according to the sulfur content (S10, S500, and S1800, which correspond to 10, 500, and 1800 mg kg⁻¹ S maximum content, respectively, giving a total of 60 commercial diesel samples (20 samples of each category).

Cetane index, density, flash point, and temperature achieved during distillation to obtain 50% of the sample distilled (T50) reference values were obtained according to the Brazilian standard methods (ABNT NBR), which are in agreement with the international standard methods. The results are shown in Table 1 (mean ± standard deviation).

2.2. TD-NMR Measurements. TD-NMR experiments were evaluated in the SLK 100 TD-NMR benchtop spectrometer (Spinlock Magnetic Resonance Solution, Cordoba, Argentina) equipped with a 0.23-T permanent magnet (8.9 MHz for ¹H). ¹H transverse relaxation decays, T_2 , were performed using the Carr-Purcell Meiboom-Gill (CPMG) pulse sequence with a $\pi/2$ pulse width of 6.4 μ s, time between echoes of 2 ms, 1000 echoes, and a recycle delay of 1.5 s. The

TD-NMR experiments were recorded at room temperature (approximately 24 °C). A total of 180 decays were collected from the commercial diesel samples: 60 (samples) × 3 (independent replicates per sample).

Different analysis approaches were applied to determine T_2 and population sizes values from the CPMG relaxation curves: (1) by fitting with an exponential function available in the Origin software (version 8.1, OriginLab, Northampton, MA, USA), (2) using the inverse Laplace transformation (ILT), and (3) using slicing.^{22,23} Slicing was performed in Matlab 7.14 (Mathworks, Natwick, USA) with algorithms from www.models.life.ku.dk.

2.3. Data Processing. Multivariate analyses were evaluated in Pirouette software (version 4.0, Infometrix Inc., Woodville, WA). The TD-NMR decays were maximum-normalized, mean-centered and analyzed using unsupervised pattern recognition methods (e.g., principal component analysis, PCA), supervised pattern recognition methods (e.g., soft independent modeling of class analogy, SIMCA, k nearest neighbors, kNN, and partial least-squares discriminant analysis, PLS-DA) and regression methods (e.g., partial least-squares regression, PLSR).

Principal component analysis is often the first step of the data analysis used for exploring data in order to obtain a preliminary assessment of the importance of different variables, clustering, and detection of outliers. This decomposition technique replaces the original (many) variables with a lower number of latent variables or principal components (PC), allowing the transformed data set to be easily visualized as a series of scores and loadings plots. Scores plots contain information about the samples, and loadings plots contain information about the variables.

Soft independent modeling of class analogy (SIMCA), k nearest neighbors (kNN), and partial least-squares discriminant analysis (PLS-DA) supervised pattern recognition methods were applied to developed classifications models. The classification models were evaluated in order to discriminate the commercial diesel samples based on the classification adopted by the Brazilian National Petroleum Agency (ANP): S10, S500, and S1800. Classification model performances were examined in terms of misclassifications (percentage of samples correctly allocated to their real groups).

Partial least-squares regression (PLSR) was used to predict four diesel quality attributes (Y-variables) from the instrumental data (X-variables). The performance of the calibration models were evaluated based on the figures of merit: accuracy, precision, and linearity. The accuracy was expressed by root-mean-square error of calibration (RMSEC), root-mean-square error of cross validation (RMSECV), and root-mean-square error of prediction (RMSEP). Among these parameters, RMSEP is the most robust one because it is estimated from external validation samples. The precision was assessed in terms of repeatability based on the relative standard deviation (RSD) for three replicates of a sample. The linearity of the developed methods was estimated using a linear fit of the predicted versus reference values.

3. RESULTS AND DISCUSSION

3.1. TD-NMR Data. Figure 1 shows the normalized average of T_2 relaxation curves (60 decays of each category) of S10, S500, and S1800 commercial diesel samples (Figure 1a) and their respective T_2 relaxation spectra (Figure 1b). The T_2 relaxation spectra were obtained using ILT, and the results showed the presence of two populations, indicating the

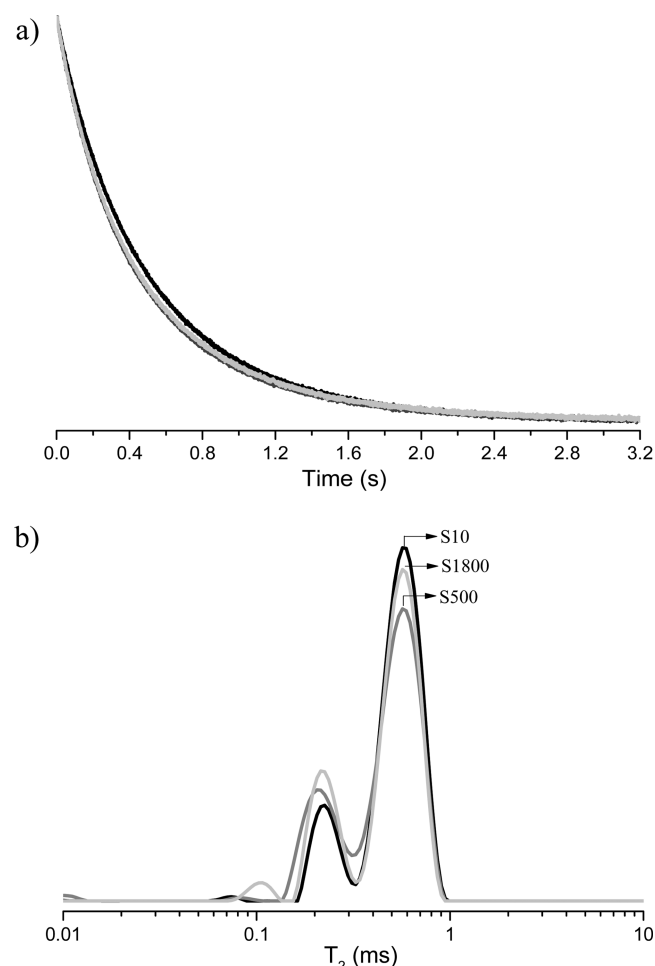


Figure 1. (a) TD-NMR average of all T_2 relaxation curves obtained for S10 (marked by black line), S500 (marked by gray line), and S1800 (marked by light gray line) B5 diesel samples and (b) their respective relaxation spectra obtained by inverse Laplace transformation (ILT).

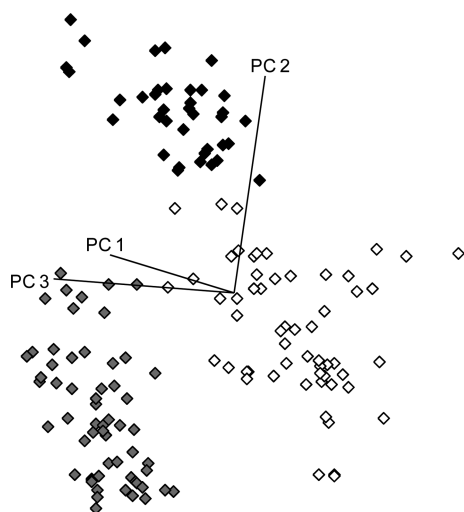


Figure 2. PCA scores plot illustrating the clusters for data sets composed by S10 (black rhombus), S500 (white rhombus), and S1800 (gray rhombus) commercial diesel samples.

existence of two proton components in the commercial diesel samples.

Table 2. Classification Results Obtained for the Validation Set

	S10	S500	S1800	no match
Performance obtained with SIMCA				
S10	17	0	0	0
S500	2	18	0	0
S1800	0	0	10	0
Performance obtained with PLS-DA				
S10	17	0	0	0
S500	0	14	0	6
S1800	0	0	10	0
Performance obtained with kNN				
S10	17	0	0	0
S500	14	6	0	0
S1800	0	0	10	0

Table 3. PLSR Model Performances to Predict Diesel Quality Parameters by TD-NMR

figures of merit	parameter	cetane index	density (kg m^{-3})	flash point ($^{\circ}\text{C}$)	T50 ($^{\circ}\text{C}$)
accuracy	RMSEC	0.74	2.17	3.65	1.97
	RMSECV	0.71	2.13	3.59	1.94
	RMSEP	0.67	2.41	2.78	2.22
precision	RSD	0.31	0.09	2.11	0.41
linearity	slope	0.85 ^a	0.87 ^a	0.76 ^a	0.91 ^a
	intercept	6.75 ^a	104.19 ^a	11.15 ^a	23.71 ^a
	correlation coefficient	0.94 ^a	0.94 ^a	0.92 ^a	0.96 ^a

^aValues for the line fitted to the calibration samples.

The transversal relaxation times $T_{2,1}$ and $T_{2,2}$ from slicing (T_2 calculated from the loadings of PARAFAC, parallel factor analysis)²⁴ for the 60 diesel samples were very similar, with mean values of 0.258 and 0.593 s, respectively. $T_{2,1}$ and $T_{2,2}$ values obtained with ILT and exponential fitting were on the same order of magnitude. The longer T_2 ($T_{2,2} = 0.593$ s) can be assigned to the higher hydrogen mobility (i.e., molecules with low molecular weight) in the sample and represent more than the half of the total protons in the diesel samples ($M_{0,1} = 60.3$). The shorter T_2 ($T_{2,2} = 0.259$ s) can be associated with the hydrogen that is strictly associated with high molecular weight.

In order to obtain an overview of the variation in the multivariate TD-NMR relaxation decays, PCA was performed on the maximum normalized CPMG data. The PCA score plot of the TD-NMR relaxation is shown in Figure 2. The first principal component (PC1) described 67.8% of the variation, whereas the second (PC2) and the third (PC3) principal components explained 21.8% and 0.4% of the remaining variation, respectively. The PCA score plot results showed a formation of three distinct clusters, composed of S10, S500, and S1800 commercial diesel samples. In PCA analysis, samples located in the same cluster present similar characteristics and the ones in different clusters could be considered distinct. This result indicated that the S10, S500, and S1800 commercial diesel had different TD-NMR patterns and could be distinguished into separate classes. Thus, the possibility to apply TD-NMR to discriminate the samples according to the classification adopted by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) was investigated. Supervised pattern recognition methods were applied to develop classifications models and the results are presented in the following Classification section.

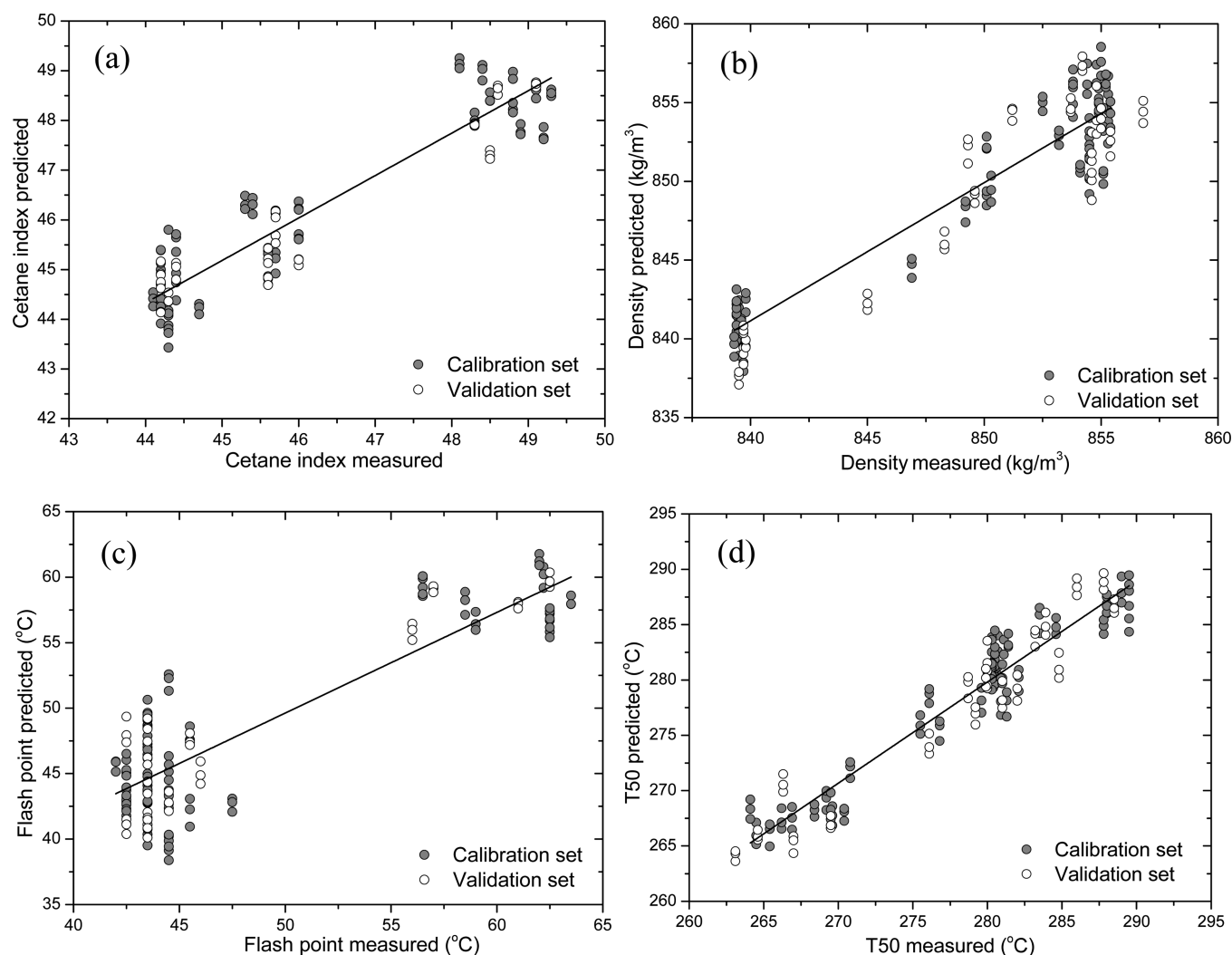


Figure 3. PLSR correlation plot graphics of reference versus predicted values for (a) cetane index, (b) density, (c) flash point, and (d) T50 parameters. Calibration (gray) and validation (white) samples.

3.2. Classification. Table 2 summarizes the classification accuracy of SIMCA, kNN, and PLS-DA models to discriminate the commercial diesel samples according to the sulfur content. SIMCA and PLS-DA models were evaluated using 3 PCs and latent variables (for each class), with a confidence level of 95%. For kNN modeling, the number of neighbors (k) used were 8. Prior to the analysis, the 180 CPMG relaxation curves (60 samples \times 3 independent replicates per sample) were randomly divided into training and validation sets with 126 and 54 decays, respectively.

SIMCA model showed the highest predictability, with 96% of samples correctly classified into their corresponding categories. Only 10% (2 samples) of S500 diesel samples were not allocated into their original group and were classified as S10 diesel samples. According to different international regulations, the concentration of sulfur in commercial diesel must be lower than 10 mg kg⁻¹. Thus, the SIMCA model provided the wrong results classifying samples which do not attend the legislation as samples that attend, false negative results. False negative results should be more rigorously controlled, avoiding the environmental problems and health hazards associated with the high concentration of sulfur compounds in the diesel fuel.

PLS-DA's misclassification showed an average of 88% of correct classification. Although this model showed a lower

predictability than the SIMCA model, no false positive results were obtained. The highest percentage of misclassification were obtained with the S500 diesel samples, with 30% of the samples classified in the none category. The poorest accuracy in discrimination power was presented by the kNN classification model which classified 70% of S500 diesel samples as S10 (false negative).

3.3. Determination of Diesel Quality Parameters by PLSR Calibration Models.

A summary of prediction performance of PLSR models is shown in Table 3. For development of PLSR models, the 180 CPMG relaxation curves were divided into approximately two-thirds (126) for the calibration set and one-third (54) for the validation set. The number of latent variables (LV) was selected based on the smallest RMSECV. The best PLSR models were obtained using 2 LV, which accounts for more than 85% of the total variance of the data. Accuracy values represented by RMSEC and RMSEP (Table 3) showed that the estimated values of all multivariate models presented good agreement with reference methods (ABNT NBR). The precision of the models were evaluated in terms of repeatability and, with RSD values ranging from 0.09% to 2.11%, models were considered precise. The plot of reference versus predicted values shown in Figure 3 indicated

the linearity of the PLSR models with a high coefficient of correlation ($r_{\text{Cal}} > 0.94$).

PLSR correlation graph (calibration and validation models) for cetane index are presented in Figure 3a. The model showed high coefficient of correlation ($r_{\text{Cal}} = 0.94$) and good precision ($\text{RMSECV} = 0.71$ and $\text{RMSEP} = 0.60$), with similar or better performance than those described in the literature. Alves et al. have applied NIR spectroscopy, and data were analyzed by PLSR obtaining a model with RMSEP of 1.14.²⁵ Santos, Jr. et al. have compared the performance of NIR, Raman, and MIR spectroscopy to predict the cetane index in diesel samples.²⁶ The best result was obtained using Raman, with RMSEP of 0.58. MIR and Raman spectroscopy have also been applied to determine the cetane index and RMSECV of 0.42 and 0.56, respectively, were reported.²⁷

The PLSR model was developed to predict the density in the commercial diesel samples and also showed better precision than those described in the literature. The plot of reference versus predicted values (Figure 3b) showed a high coefficient of correlation ($r_{\text{Cal}} > 0.94$). RMSEC , RMSECV , and RMSEP of 1.93, 2.05, and 2.73 kg m^{-3} , respectively, were observed (Table 3). A variety of spectroscopic methods have been used in the density determination. PLSR models developed using NIR, MIR, and Raman spectroscopy showed RMSEP of 0.974, 0.831, and 0.668 kg L^{-1} , respectively.²⁶ Similarly, PLSR models obtained with NIR data showed a RMSEP of 2.20 kg m^{-3} .²⁸

Figure 3c shows the PLSR correlation graph (calibration and validation models) for the flash point parameter. The values of RMSEC , RMSEP , and RMSECV ranged from 2.78 to 3.65 $^{\circ}\text{C}$, showing higher precision than those reported in the literature.²⁸ The value obtained for the coefficient of correlation was higher than 0.90 ($r_{\text{Cal}} = 0.92$), suggesting a good linearity of the model.

PLSR graphic for the T50 predicted against the reference values are shown in Figure 3d. PLSR statistic performance (Table 3) showed a RMSEC of 1.97 $^{\circ}\text{C}$, RMSECV of 1.94 $^{\circ}\text{C}$, RMSEP of 2.22 $^{\circ}\text{C}$, and r_{Cal} of 0.96. NIR, MIR, and Raman spectroscopies have been widely used to predict T50 in diesel samples, and the best prediction ability was obtained with NIR, with a RMSEP of 1.6 $^{\circ}\text{C}$.²⁶

4. CONCLUSION

This study has shown the possibility of the use of TD-NMR for measuring quality parameters in commercial diesel samples providing a powerful tool for the petrofuel industry. Quantitatively, it was demonstrated here that TD-NMR can simultaneously monitor cetane index, flash point, density, and especially T50 in commercial diesel samples. The use of multivariate data analysis and TD-NMR has the advantage to easily perform several parameters analysis, without any sample preparation, and shows the possibility for in situ and online measurements.

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Notes

The authors declare no competing financial interest.

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