Determination of specific gravity and kinematic viscosity of diesel using distillation curves and multivariate calibration

Helga G. Aleme, Rosely A. Assunção, Mariana M.O. Carvalho, Paulo J.S. Barbeira *

Laboratório de Ensaios de Combustíveis, Departamento de Química—Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Av. Antônio Carlos 6627, 31270–901, Belo Horizonte, Minas Gerais, Brazil

ABSTRACT

In order to predict specific gravity and kinematic viscosity, distillation curves (used in the quality control of diesel) were associated with the partial least squares method (PLS). The regression coefficients of the algorithms were compared after selecting the appropriate number of latent variables for each prediction. The low values (0.82 kg m^{-3} and $0.095 \text{ mm}^2 \text{ s}^{-1}$) obtained for *RMSEP* (Root Mean Squared Error Prediction) and the high correlation coefficients (0.9973 and 0.9943) between real and predicted values showed that *PLS* associated with distillation curves was efficient to determine specific gravity and kinematic viscosity. Models created with diesel samples of different composition were used for these predictions, thus reflecting the variety of fuel in the Brazilian market. In addition, the proposed method is low cost and easy to carry out, since it resorts to the results of a routine assay performed to assess the quality of highway diesel fuel.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

A diesel engine is an internal combustion motor that burns fuel due to the increase of temperature caused by compression of a flammable mixture. It works in four stages: injection, compression and combustion of fuel, and discharge of gases produced by the process of burning [1]. This engine is primarily used in vehicles in need of high power, such as buses, trucks, tractors and mining, and dredging machines [2].

Despite the high efficiency and durability of diesel engines (approximately ten times more than a gasoline engine) [1] and the low price of diesel, these engines present some disadvantages, as large amounts of toxic emissions (nitrogen and sulfur oxides) and, in some countries, high content of sulfur. Toxic emissions are due to the content of polycyclic aromatic hydrocarbons, and derivates alkyl, sulfonate and nitrogen, as well as aliphatic hydrocarbons with 9–28 carbon atoms, that boil at temperatures ranging from 160 to 410 °C [2].

A fuel obtained from petroleum distillation, diesel is a formulated mixture of several products as gas oil, naphtha, heavy and light diesel, derived from various stages of crude oil processing. The ratio of these components in diesel is made so as to frame the final product within previously defined specifications which enable good performance of the product, minimize wear of engines and components and, yet, maintain toxic emissions caused by fuel burning at acceptable rates [3]. Against this background, the evaluation of parameters such as distillation, viscosity and specific gravity is important, because these tests, which are related to volatility and fluidity of diesel, have great influence on fuel injection and on the preparation of mixture for self-ignition in the engine.

Specific gravity is an important property of diesel, for the injection system, pump and injectors are adjusted to deliver a predetermined volume of fuel, the determining parameter in the combustion chamber being the air–fuel mass ratio. The establishment of a minimum specific gravity is justified by the need to obtain the maximum power for the engine that uses a fuel, with flow control in the injection pump [4]. Therefore, specific gravity variations may cause an increase of toxic emissions (as hydrocarbons, carbon monoxide and particulate matter) when values are above the engine tune-up, or loss of engine power and an increase of fuel consumption when the specific gravity of a mixture is lower than that of the range of adjustment of the engine. Generally, the specific gravity of diesel worldwide varies from 811 to 857 kg m^{-3} [4].

Viscosity is a measure of flow resistance of diesel. This property directly affects the engine's operation and combustion process, whose efficiency depends on the maximum power developed by the engine. The purpose of controlling viscosity is to allow for the good atomization of the oil and for the preservation of its lubricating characteristics. Lower viscosity values may lead to excessive wear of the self-lubricated parts of the injection system, leakage in the fuel pump and an increase of fuel pump operation, which will work under pressure and wear out more. For high values of viscosity, the result is bad atomization of fuel and, therefore, incomplete combustion and increase of fume emissions [4].

The specific gravity test may be carried out using methods ASTM D1298 and D4052. ASTM D1298 [5] describes the specific gravity test using glass hydrometers while ASTM D4052 [6] describes the test using the automatic densimeter, whereby a small volume of liquid sample is

---

* Corresponding author. Tel.: +55 3134095767; fax: +55 3134096650.
  E-mail address: barbeira@ufmg.br (P.J.S. Barbeira).

introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the specific gravity of the sample. In Brazil, the specific gravity value of a suitable diesel sample must present between 820 and 880 kg m^{-3}, depending of the type, according to ANP (National Agency of Petroleum, Natural Gas and Biofuels) [7].

The kinematic viscosity test is performed following ASTM D445 [8], whereby diesel flows under gravity through a glass capillary viscometer at 40 °C. The flow time between the two meniscus marked on the capillary tube is recorded and correlated to the viscosity constant of the tube used. The kinematic viscosity value is stated in mm^2 s^{-1}. The viscosity of an appropriate diesel sample for this assay ranges between 2.0 and 5.0 mm^2 s^{-1} [7].

These standard methods for determining specific gravity and kinematic viscosity have some disadvantages: they are slow (viscosity takes on average 50 min for each sample) and implementation and maintenance of the equipment is expensive. Thus, alternative methods have been proposed in literature associating different analytical techniques, such as infrared spectroscopy [9–13] and FT-Raman (Fourier Transform Raman) [12,14], with chemometric tools as Stepwise Multiple Linear Regression (SMLR) [11] and Genetic Inverse Least Squares (GILS) [15].

Sikora et al. [9] associated near infrared spectroscopy (NIR), between 1695 and 1915 nm, with SMLR to predict different physicochemical properties of diesel. For specific gravity, the authors found a *SEP* value (Standard Error of Prediction) of 4.7 kg m^{-3}, while for viscosity the *SEP* value was 0.187 mm^2 s^{-1}.

The use of infrared spectroscopy together with PLS multivariate calibration allowed the determination of some physicochemical parameters, including specific gravity and viscosity, with *RMSEP* values varying from 0.6 to 6.0 kg m^{-3} and 0.09 to 0.23 mm^2 s^{-1}, respectively [10–13].

As well as PLS, Soyemi et al. [11] associated near infrared spectroscopy with PCR, a chemometric tool for determining different physicochemical parameters, including specific gravity and viscosity. The *RMSEP* values were 2.0 kg m^{-3} and 0.19 mm^2 s^{-1}, respectively.

Santos Jr. et al. [12] defined a few physicochemical parameters used to evaluate the quality of diesel, including specific gravity and a viscosity, using FT-Raman associated with PLS as well as infrared spectroscopy. The *RMSEP* values obtained were 2.1 kg m^{-3} for specific gravity and 0.23 mm^2 s^{-1} for viscosity. Using the same analytical technique, Andrade et al. [14] determined the viscosity of aviation fuel samples, with *RMSEP* value of 0.19 mm^2 s^{-1}.

The determination of some parameters for analysis of diesel, including viscosity, was made by Ozdemir [15] using genetics multivariate calibration associated with near infrared spectroscopy, who obtained *SEP* values of 0.10 mm^2 s^{-1}.

In order to simplify and accelerate the analytical procedure for diesel during inspection or production procedures, this study proposes predicting specific gravity and kinematic viscosity using distillation curves (ASTM D86), a routine test which is performed to assess the quality of diesel, associated with multivariate calibration, based on partial least squares regression.

Distillation is a physicochemical assay used to measure the complexity of liquid mixtures, which is related to the volatility of the sample components [16]. This assay is used to verify the appropriateness of the light and heavy fractions of fuel in order to attain good performance. For diesel, ANP determines maximum temperature values for 50%, 85% and 90% of the recovered volume [7].

The distillation curves created in this assay (ASTM D86) provided a data matrix whose percentage values of recovered volume are in columns and the temperatures of each sample, on lines. This allows the use of multivariate models, an advantageous alternative to determine physicochemical parameters, because analytical techniques associated with multivariate calibration are fast, relatively low-cost and are useful for online inspection and control procedures.

2. Experimental

2.1. Samples

For determining specific gravity and kinematic viscosity, a total of 300 diesel samples were collected and analyzed. These samples were selected from an assortment of approximately 2100, which were collected during one year. At the moment of collecting the samples the name of the refinery of origin of each specimen was registered and five different refineries identified. As well as different origins, these samples presented two types of diesel, according to their sulfur content: 500 and 1800 mg kg^{-1}. Three criteria were followed for the selection of calibration and validation sets: greatest range of values, samples from different refineries and types. The choice of a set with a wide range of samples (origin and type) was made aiming at representing, as much as possible, the set that reflects the diversity of the market. After collecting the samples, they were stored in appropriate polyethylene bottles, sealed and kept at room temperature until their use.

2.2. Analyses of physicochemical parameters

2.2.1. Distillation

Distillation of the samples was performed in Herzog HDA-627 automatic distillers following ASTM D86. For the procedure, 100 mL of diesel were transferred to a specific distillation flask equipped with a thermocouple sensor and heated to keep the distillation ratio between 4 and 5 mL min^{-1}. The distilled and condensed steam 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 correcting temperature readings to atmospheric pressure of 101.3 kPa, and volume loss after measuring residue volume, according to ASTM D86 [16].

2.2.2. Specific gravity

A digital automatic densimeter, Anton Paar DMA, model 4500 was used to carry out the specific gravity assays. Approximately 0.7 mL of diesel, at room temperature, were introduced with a clean and dry syringe in an oscillating sample tube and the change in oscillation frequency caused by the change in the mass of the tube was used, together with the calibration data, to determine the specific gravity of the sample [6]. After stabilizing the temperature of the measure cell at 20 °C, the specific gravity value was measured and the result shown in kg m^{-3}.

2.2.3. Kinematic viscosity

For the determination of kinematic viscosity, approximately 10 mL of diesel were introduced in a clean, dry and previously calibrated capillary, Cannon-Fenske (model J376 or Tam75). This tube was immersed in a thermostatic bath Termo Haake (Phoenix 003–5900 model) in which the temperature did not vary more than 40.00 ± 0.02 °C. After stabilizing the temperature of the system (approximately 30 min) and with the aid of a vacuum pump, the sample was drawn until it reached the upper meniscus in the viscometer tube. The flow time between the upper and lower meniscus was counted using a calibrated chronometer that measured up to hundredths per second. After reaching determinability of the assay for each sample (two readings of time for the interval: average value ± 0.20%), the average value of the readings was multiplied by the viscosity constant in the viscometer tube, and the result shown in mm^2 s^{-1} [8].

2.3. Calibration multivariate tool

To determine specific gravity and kinematic viscosity, partial least squares regression was used, which aims at finding a small number of relevant factors that are predictive for **Y** and uses **X** efficiently [17]. Minitab Release (version 14 for Windows) and Solo software (version 2007–2008 for Windows) were used in this procedure.

2.4. Evaluation of accuracy

In assessing the accuracy of the proposed method, *RMSEP* and residual predictive deviation (*RPD*) [17] values were calculated. In addition, the results of the validation set (in the range of 839 to 873 kg m^{-3} for specific gravity and 2.42 to 4.79 mm^2 s^{-1} for kinematic viscosity) obtained by the proposed method were compared with those of methods ASTM D4052 and D445, using *t* test [18].

T test was also used to compare the results of specific gravity and kinematic viscosity of five samples of interlaboratory programs [19,20] with the results of the proposed method. To this end, the distillation curves of those samples were applied to the calibration set of the proposed method and the predicted values were compared with the values obtained by the interlaboratory programs using *t* test.

2.5. Evaluation of repeatability and reproducibility

The evaluation of repeatability and reproducibility of the methods was carried out according to ISO-5725-2 [21]. Therefore, for the specific gravity and kinematic viscosity, seven samples of diesel were used and, for each sample, assays were done by three different analysts with seven replicates for each one [22], producing a total of 147 results.

3. Results and discussion

3.1. Data organization

For the construction of the models, temperatures ranging from 4 to 91% of the recovered volume were used. According to ASTM D86 [16], the distillation of the sample must occur at 4 to 5 mL min^{-1} and, to reach this rate, initial heating adjustments of the resistance are necessary to produce a vigorous boiling, which causes temperature oscillation from the initial point of distillation until approximately 4%. However, pyrolysis of larger molecules may occur in the final stage of distillation reducing boiling temperature [16]. As the composition of diesel samples differs according to the refineries of origin, some of the curves so not show all the points in the final part of the distillation, that is, in the 92 to 99% range of recovered volume. Taking into consideration these variations, the initial and final points were excluded from the data sets.

The results of the physicochemical tests were arranged in matrixes in which the lines correspond to samples and the columns to results. For the prediction of physicochemical parameters, were built matrixes containing different samples in the 830 to 876 kg m^{-3} range for specific gravity and 2.39 to 4.83 mm^2 s^{-1} for viscosity. These matrixes were auto-scaled to assign equal importance to all the variables.

For the application of PLS regression, the set of samples was subdivided randomly in calibration set (100 samples) and test set, or external validation (50 samples). Cross validation leave-one-out [23] was used as internal validation. In this method, each sample is left out of the model and the parameter of interest is predicted by the new model that is obtained.

3.2. Prediction of specific gravity

For the construction of calibration model, the number of latent variables was selected based on the lowest *PRESS* value (Predictive Residual Error Sum of Squares) [24]. With numerous and correlated X-variables there is a substantial risk of over-fitting, thus creating a well fitting model with little or no predictive power. Hence, a strict test of the predictive significance of each PLS component is necessary, stopping when components start to be non-significant [25]. The selection of an appropriate number of variables was carried out in two stages. In the first stage the *PRESS* values of each added latent variable [26] were compared. F test was used for the following stage [25].

Fig. 1 shows that the range from 10 to 20 variables presented low *PRESS* values. F test applied to these values indicated that the model should be constructed using ten latent variables (with total variance of the system in **X** of 99.99%) to obtain a model with high predictive power, thus avoiding overfitting in the calibration model.

The first two latent variables presented 96% of explained percentage: the first latent variable 75.4% and the second, 20.6%. The first latent variable was used for the construction of the loading graph, which presented a high percentage of explained variance in the model. Fig. 2 shows that the 30 to 60% interval of recovered volume presented higher loadings for the first latent variable. This interval shows aromatic compounds containing both sulfur and nitrogen, as benzothiophene and indol [27] which may present intermolecular interactions and cause high specific gravity values [28].

In addition to the loading graph analyses of the first two latent variables, average distillation curves at different intervals of specific gravity were constructed (Fig. 3A). Analyzing these distillation curves it was observed that specific gravity value increases as distillation temperature rises. As specific gravity is related to the composition of fuel, in the same kind of compounds this physicochemical property increases according to the amount of carbons in the chain, while in compounds with the same amount of carbons, specific gravity grows in the following order: paraffins<cycloparaffins<aromatics [28].

The estimate of *RMSEP* [26] was carried out for a preliminary assessment of the model. Table 1 shows that the proposed method presented an *RMSEP* value (0.82 kg m^{-3}) lower than the values obtained in studies using traditional techniques, such as infrared spectroscopy (0.7 a 2.9 kg m^{-3}) and FT-Raman (2.1 kg m^{-3}) [11,12]. These results demonstrate that the use of samples with different compositions, which reflect the diversity of the market, provided low errors compared to samples of a single origin and/or type.

Aside from *RMSEP*, the residual predictive deviation—*RPD*, defined as the ratio between the standard deviation of the population's reference values (*SD*) and the bias-corrected mean error of prediction of the validation standard error of prediction (*SEP*$_{bias}$), was calculated [17]. To evaluate the quality of validation, the *RPD* estimate is more significant than just considering the prediction error. This is because *RPD* may help in the detection of calibration models which have a small range of reference values and low prediction errors.

Alternatively, when a model is constructed with a wide range of reference values and a homogeneous distribution of these values, there is high variance which causes high *RDP* [17]. As shown in Table 2, the outcome was a high *RPD* value (12.6), which indicates that the calibration model built was accurate and may be used for quality control of diesel [17]. In addition to high *RPD*, high correlation (0.9973) between real and predicted values of that calibration model and high percentage of
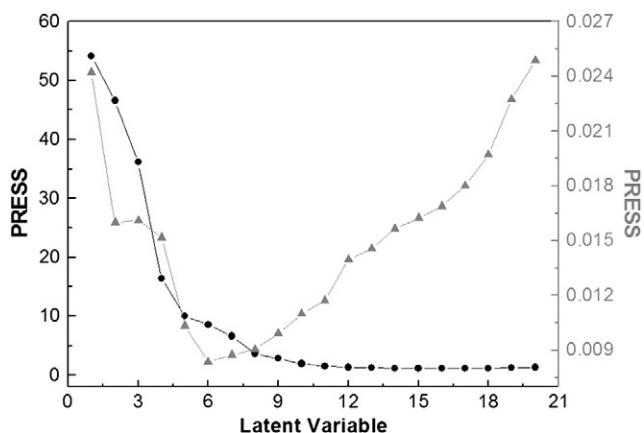

Fig. 1. *PRESS* values versus number of latent variables for the prediction of specific gravity (●) and kinematic viscosity (▲).
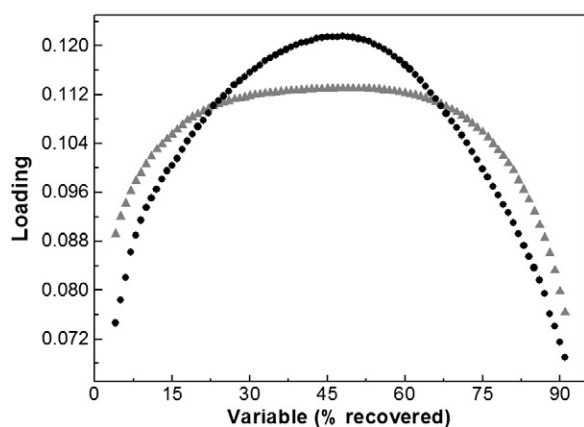
Fig. 2. Loading graphs of variables (distillation curve) for the construction of the first latent variable (VL1) to determine specific gravity (●) and kinematic viscosity (▲).

explained variance in **y**, obtained with only ten latent variables (99.5%) was also observed.

As well as *RMSEP* and *RPD* estimates, the evaluation of accuracy of the proposed method was carried out by comparing the results of specific gravity of the validation set using the proposed method with those obtained by the ASTM D4052 method, using *t* test [18]. Table 2 shows that the t tabulated value (2.01) was higher than the calculated t value (0.60), with 95% confidence. This indicates there is no significant difference between the PLS model based on distillation curves and the ASTM D4052 method.
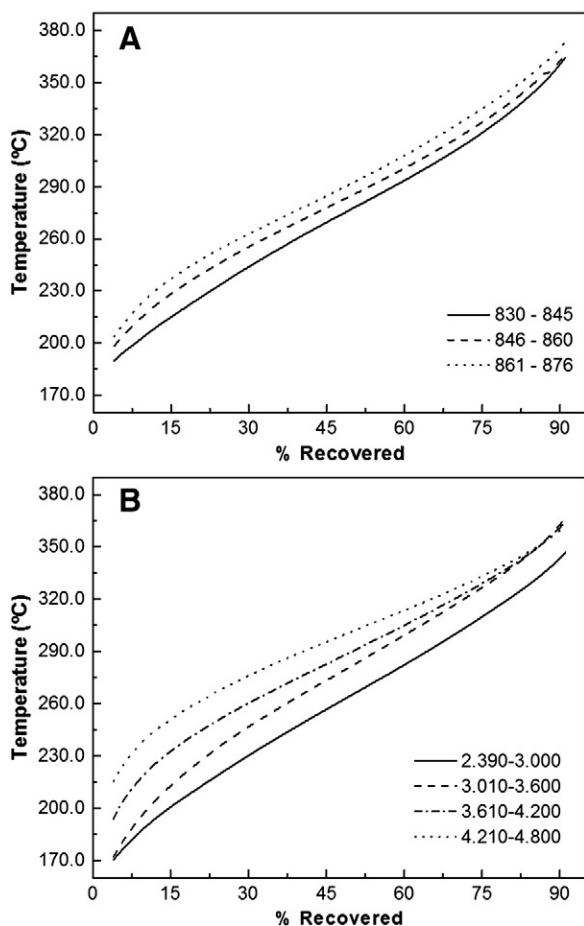

Fig. 3. Average distillation curves of samples used to determine specific gravity (A) and kinematic viscosity (B).

Table 1
Comparison between *RMSEP* values obtained with the model using distillation curves with other analytical techniques (the number in brackets corresponds to the number of the reference).

Parameter/technique	Specific gravity (kg m^{-3})	Viscosity (mm^2 s^{-1})
Distillation curves	0.82	0.095
Raman [11]	2.1	0.23
IR [9]	0.6	0.09
NIR	0.70 [15]	0.14 [11]
	1.3 [11]	0.23 [10]
	6.0 [10]	1.3 [15]

Another way used to evaluate the accuracy of the proposed method was to compare the values obtained when distillation curves of samples from interlaboratory programs were applied to the calibration set of the proposed method and those obtained by different laboratories in interlaboratory programs. Table 2 shows that the t calculated value (1.72) was lower than the t tabulated value (2.78), thus indicating that the proposed method produced similar results, with 95% confidence, to those obtained in interlaboratory programs.

The accuracy of the proposed method was evaluated by the repeatability and reproducibility [21] estimate and these values compared with the manual (ASTM D1298) and automatic (ASTM D4052) specific gravity methods. Table 2 shows that the repeatability and reproducibility values obtained by the proposed method were higher than the maximum values permitted by ASTM D1298 and D4052. Nevertheless, the proposed method showed low repeatability and reproducibility values, below 0.25%, indicating that the proposed methodology is highly accurate.

3.3. Prediction of kinematic viscosity

For the prediction of kinematic viscosity, multivariate calibration was associated with distillation curves of samples of a different calibration set from that used to predict specific gravity. This was necessary due to the fact that the set of samples of item 3.2 presented narrow kinematic viscosity range and a different set was used to obtain the highest possible amplitude.

The number of latent variables was selected in a similar way as for item 3.2. In Fig. 1 it may be observed that the interval with low *PRESS* values was that of 6 to 8 latent variables. The F test applied to *PRESS* values showed that only six latent variables (with 99.99% of total variability of the system in **X**) were necessary to construct the chemometric model.

Table 2
RMSEC, *RMSEP* and *R* values, among other parameters, obtained in the determination of specific gravity and kinematic viscosity using calibration curves and multivariate calibration (PLS).

Parameter	SG (kg m^{-3})	KV (mm^2 s^{-1})
Number of latent variables	10	6
Correlation coefficient (R)	0.9973	0.9943
X-Explained variance LV1 (%)	75.4	88.7
X-Explained variance LV2 (%)	20.6	10.1
X-Explained variance LV3 (%)	2.8	0.8
RMSEC	0.81	0.081
RMSEP	0.82	0.095
RPD	12.6	7.6
t test (t_{calc}) validation set	0.60	1.14
t test (t_{tab}) validation set	2.01	2.01
t test (t_{calc}) interlaboratorial program set	1.72	1.80
t test (t_{tab}) interlaboratorial program set	2.78	2.78
Repeatability	1.59	0.0390
Reproducibility	1.98	0.0425
Maximum repeatability (standard method)	0.10 (D1298)	0.0039 (D445)
Maximum reproducibility (standard method)	0.50 (D1298)	0.0228 (D445)
Maximum repeatability (standard method)	0.50 (D4052)	–
Maximum reproducibility (standard method)	1.20 (D4052)	–

The loading graph obtained for the prediction of kinematic viscosity presented a similar behavior to the obtained for the prediction of specific gravity (Fig. 2). This was an expected result, because samples with high specific gravity present greater resistance to drainage and, therefore, greater kinematic viscosity [28].

The first latent variable presented an explained variance percentage in **X** of 88.7%, while for the second, this percentage was 10.1%. As in the prediction of specific gravity, the loading graph was only built for the first latent variable. Fig. 2 shows that the variables corresponding to the range from 20 to 70% of recovered volume presented more importance in the construction of the first latent variable. In this area of the distillation curve there are aromatic compounds containing both sulfur and nitrogen, as benzothiophene and indol [27] which may present intermolecular interactions causing high viscosity values [29].

Analyzing the average distillation curves (Fig. 3B), it was observed that viscosity increases as distillation temperature rises. Thus, hydrocarbons of greater complexity, as polyaromatic hydrocarbons, present higher molecular weight and have therefore greater resistance to drainage than simple hydrocarbons, as heptanes [29].

As for the prediction of specific gravity, the evaluation of accuracy of the calibration model started by estimating the *RMSEP* value. Table 1 shows that the *RMSEP* (0.095 mm^2 s^{-1}) value was lower than those described in literature, using infrared spectroscopy (0.14 to 1.3 mm^2 s^{-1}) [11–13] and FT-Raman (0.23 mm^2 s^{-1}) [12]. This fact demonstrates that using samples of different types and origins, with different profiles in the distillation curve, provided a predictive model of excellent performance.

Once again, high *RPD* (7.6) was obtained for the calibration model created from distillation curves and PLS, demonstrating that this model is accurate in the prediction of kinematic viscosity and may be used for quality control of diesel [17]. In addition, a high coefficient of correlation between real values and those predicted by the calibration model (0.9943) was obtained and a percentage of explained variance in **y** of 88.4% was observed using only six latent variables.

In a similar manner to item 3.2, the results of ASTM D445 and the proposed methods for the validation set were compared using *t* test. The t estimated values obtained for the proposed method (1.14) were lower than the t tabulated values (2.01). This shows that the method produces similar results to the standard method according to ASTM D445, with 95% confidence.

When the proposed method was submitted to the evaluation of accuracy using samples of interlaboratory programs, it presented similar results, with 95% of confidence, to those described in the interlaboratory programs, with an estimated t value (1.80) lower than the t tabulated value (2.78).

The accuracy of the proposed method was evaluated by the repeatability and reproducibility [8] estimate, as in item 3.2. Table 2 shows that the values obtained by the proposed method are higher than the values obtained by ASTM D445 and than the maximum values allowed for this regulation. Nevertheless, these values were lower than those obtained by Andrade et al. [14] (0.35 and 0.16 mm^2 s^{-1}, respectively) using FT-Raman and PLS multivariate calibration. This indicates that the proposed method is highly precise in the determination of kinematic viscosity.

4. Conclusions

Distillation curves obtained by ASTM D86 together with PLS multivariate calibration were efficient to predict important properties for the operation of diesel engines: specific gravity in the 830 to 876 kg m^{-3} interval and kinematic viscosity in the 2.39 to 4.83 mm^2 s^{-1} range, regardless origin and type of diesel.

The proposed method presented excellent accuracy, *RMSEP* values lower than those mentioned in literature for other models based on spectrometric techniques, and high *RPD* value. Moreover, this method showed similar results to those obtained when performing the referenced methods (ASTM D4052 and D445), with 95% confidence. Likewise, when comparing the results of interlaboratory programs with those of the proposed method, similar results were observed, with 95% confidence, for the two predicted physicochemical parameters. This method also presented satisfactory repeatability and reproducibility values. As for kinematic viscosity, the proposed method showed lower repeatability and reproducibility values than those obtained in literature using FT-Raman and PLS multivariate calibration.

The use of distillation curves to predict two important parameters to assess the quality of diesel proved useful to speed up the analytical process and, thus, reduce time and costs of analyses.

References

[1] M. Behar, Motores diesel, fourth ed. Hemus, São Paulo, 1978.
[2] S. Braun, L.G. Appel, M. Schmal, A poluição gerada por máquinas de combustão interna movidas à diesel—a questão dos particulados. Estratégias atuais para a redução e controle das emissões e tendências futuras, Quimica Nova 27 (2003) 472–482.
[3] J.A. Santos, Informativo PETROBRAS—Produtos PETROBRAS: Óleo Diesel—Refinaria Gabriel Passos, fifth ed. Guanabara Comunicação, Rio de Janeiro, 2000.
[4] E.W. de Menezes, R. da Silva, R. Cataluña, R.J.C. Ortega, Effect of ethers and ether/ethanol additives on the physicochemical properties of diesel fuel and on engine tests, Fuel 85 (2006) 815–822.
[5] ASTM D1298:2005 Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method. Washington, DC: American Society for Testing and Materials.
[6] ASTM D4052:2009 Standard test for density and relative density of liquids by digital density meter. Washington, DC: American Society for Testing and Materials.
[7] Resolução ANP N° 33, de 29.09.2010—DOU 30.09.2010available at, http://www.anp.gov.bracessed in 27.02.2011.
[8] ASTM D445:2010 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity). Washington, DC: American Society for Testing and Materials.
[9] Z. Sikora, W. Salacki, Use of near-infrared (NIR) spectroscopy to predict several physical and operating properties of oil fractions and diesel fuels, Petroleum and Coal 38 (1996) 65–68.
[10] G.E. Fodor, R.A. Mason, S.A. Hutzler, Estimation of middle distillate fuel properties by FT-IR, Applied Spectroscopy 53 (1999) 1292–1298.
[11] O.O. Soyemi, M.A. Busch, K.W. Busch, Multivariate analysis of near-infrared spectra using the G-programming language, Journal of Chemical Information and Computer Sciences 40 (2000) 1093–1100.
[12] V.O. Santos Jr., F.C.C. Oliveira, D.G. Lima, A.C. Petry, E. Garcia, P.A.Z. Suarez, J.C. Rubim, A comparative study of diesel analysis by FTIR, FTNIR and FT-Raman spectroscopy using PLS and artificial neural network analysis, Analytica Chimica Acta 547 (2005) 188–196.
[13] J.A. Cramer, R.E. Morris, B. Giordano, S.L. Rose-Pehrsson, Partial least-squares predictions of nonpetroleum-derived fuel content and resultant properties when blended with petroleum-derived fuels, Energy & Fuels 23 (2009) 894–902.
[14] J.M. Andrade, S. Garrigues, M. de la Guardia, M. Gómez-Carracedo, D. Prada, Nondestructive and clean prediction of aviation fuel characteristics through Fourier transform-Raman spectroscopy and multivariate calibration, Analytica Chimica Acta 482 (2003) 115–128.
[15] D. Ozdemir, Near infrared spectroscopic determination of diesel fuel parameters using genetic multivariate calibration, Petroleum Science and Technology 26 (2008) 101–113.
[16] ASTM D86:2010 Standard Test for Distillation of Petroleum Products at Atmospheric Pressure. Washington, DC: American Society for Testing and Materials.
[17] J.P. Conzen, Multivariate Calibration. A Practical Guide for the Method Development in the Analytical Chemistry, second ed. Bruker Optick GmbH, 2006.
[18] D.C. Harris, Análise Química Quantitativa, quinta ed. LTC Editora, Rio de Janeiro, 2001.
[19] Interlaboratorial Program in Diesel Oil, Associação Rede de Metrologia e Ensaios do Rio Grande do Sul, BrasilAvailable at, http://www.redemetrologica.com.bracessed in 25.10.2010.
[20] Interlaboratorial Program in Automotive Fuels, Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, BrasilAvailable at, http://www.anp.gov.bracessed in 25.10.2010.
[21] ISO/IEC 5725–2:2002 Accuracy (Trueness and precision) of measurement methods and results. Part 2. Basic method for the determination of repeatability and reproducibility of a standard measurement method.
[22] INMETRO DOQ-CGCRE-008, Orientação sobre Validação de Métodos de Ensaios Químicos, 2010.
[23] P. Geladi, B.R. Kowalsky, Partial least-squares regression: a tutorial, Analytica Chimica Acta 185 (1986) 1–17.
[24] S. Wold, M. Sjöström, L. Eriksson, PLS-regression: a basic tool of chemometrics, Chemometrics and Intelligent Laboratory Systems 58 (2001) 109–130.

[25] J.A. Cramer, K.E. Kramer, K.J. Johnson, R.E. Morris, S.L. Rose-Pehrsson, Automated wavelength selection for spectroscopic fuel models by symmetrically contracting repeated unmoving window partial least squares, Chemometrics and Intelligent Laboratory Systems 92 (2008) 13–21.

[26] D.L. Massart, B.G.M. Vandeginste, L.M.C. Buydens, S. Jong, P.J. Lewi, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics Part B, first ed. Elsevier Publ., Amsterdam, Lausanne, New York, Oxford, Shannon, Singapore, Tokyo, 1998.

[27] J.G. Speight, The Chemistry and Technology of Petroleum, fourth ed. CRC Press, Boca Raton London, New York, 2006.

[28] H. Yang, Z. Ring, Y. Briker, N. McLean, W. Friesen, C. Fairbrigde, Neural network prediction of cetane number and density of diesel fuel from its chemical composition determined by LC and GC-MS, Fuel 81 (2002) 65–74.

[29] V.A. Kalichevsky, K.A. Kobe, Petroleum Refining with Chemicals, first ed. Elsevier Publishing Company, Amsterdam, London, New York, 1956.