Characterization of petroleum using near-infrared spectroscopy: Quantitative modeling for the true boiling point curve and specific gravity

Celio Pasquini [a,*], Aerenton Ferreira Bueno [b]

[a] *Instituto de Química, Universidade Estadual de Campinas, Caixa Postal: 6154, CEP: 13084-971 Campinas, SP, Brazil*
[b] *Petrobras – Refinaria Henrique Lage, REVAP, São José dos Campos, CEP: 12223-900 São José dos Campos, SP, Brazil*

Abstract

This work describes a new approach to predict the true boiling point (TBP) curve and to estimate the API gravity in order to characterize the petroleum processed in refineries by using the information present in its absorbance spectrum obtained in the near-infrared region (NIR). The absorbance spectra were obtained in the range from 3700 to 10000 cm^{-1} employing a CaF_2 transmittance cell with a 0.5 mm light path. Three spectral regions were evaluated for modeling purpose: 5000–3900 cm^{-1}, 6000–3700 cm^{-1}, and 9000–700 cm^{-1}. The spectral region corresponding to the combination of C–H vibrations produces absorption spectra with very good quality while the region above 6500 cm^{-1} is dominated by scattering of the radiation. The absorbance spectra of a total of 122 samples of petroleum and petroleum blends coming from various producing regions in Brazil and abroad were obtained and pre-processed to correct for base line shift and for the integrated area. Two approaches were employed to obtain the models: one using artificial neural networks (ANN) and the other using partial least squares (PLS). The results showed that PLS gives better predictions than ANN for the API gravity and the TBP curve. The best results were obtained using the 5000–3900 cm^{-1} spectral range. In an external validation, the average RMSEP for the volume of distillate along the TBP curve employing PLS model was 1.13V% while that for API gravity was 0.24. A comparison between the results obtained by a simulator used by the refinery and the PLS model revealed a better performance for the model based on NIR spectrometry.

1. Introduction

Petroleum or crude oil is a complex mixture of hydrocarbons, mainly normal alkanes, isoalkanes, cycloalkanes and aromatics. Compounds containing nitrogen, sulphur and oxygen, such as the resins and asphaltenes, and traces of metallic species, such as vanadium, nickel, and copper are also present. Due to its heterogeneity, petroleum obtained from different production fields shows distinct and widely variable characteristics. Furthermore, the petroleum processed in a refinery usually is a mixture of crude oils of different origin, presenting intermediate characteristics determined by the diverse fractions present in the raw material.

Crude petroleum is characterised by its physico-chemical properties such as its specific gravity (API gravity) and its true boiling point (TBP) curve. These parameters are accessed by well established standard procedures. The API (American Petroleum Industry) gravity is determined as described by the ASTM D 287 and D 1298 standard methods [1,2]. The procedure is fast and employs low cost instrumentation.

In contrast, the TBP curve is determined as described by ASTM D 2892 [3] or by simulated distillation (SimDis), obtained by gas chromatography as recommended by

---

* Corresponding author. Tel.: +55 19 35213136; fax: +55 19 35213023.
E-mail address: pasquini@iqm.unicamp.br (C. Pasquini).

ASTM D 2887 [4]. The first procedure is based in a real distillation and closely approaches the situation in the distillation tower of a petroleum refinery. Therefore, it is employed to predict relevant parameters for controlling the processing of the crude oil. The ASTM D 2892 method requires very expensive equipment and takes about two days to determine the TBP curve of a crude oil. This fact practically forbids the use of the standard method for on-line monitoring of the raw material entering the process plant.

Both the API gravity and the TBP curve have great importance in the characterization of the raw material processed in a distillation plant. The products derived after crude oil fractionation in the plant, such as fuel gas, light or heavy naphtha, kerosene, aviation fuel, light or heavy gasoil and the amount of residuals, are all strongly dependent on the quality of the petroleum characterised by these two properties.

Near-infrared (NIR) spectroscopy has been employed for characterization of products derived from petroleum, such as gasoline and diesel fuel, with considerable success. The intrinsic capacity of the NIR spectrum to obtain information on the different types of C–H bonds as well as other chemical bonds of interest (such as S–H and N–H) has been proved to be valuable in the prediction of quality parameters such as octane number, ethanol content, MTBE (methyl *tert*-butyl ether) content, distillation points, Reid vapour pressure and aromatic and saturated contents in gasoline [5–10]. The information present in the NIR spectrum can be successfully applied to the prediction of quality parameters for diesel fuel such as cetane number, distillation points, density, viscosity [11] and sulphur content [12]. Aviation fuel also had properties and composition, such as freezing point and aromatic and saturated contents, predicted by NIR spectroscopy [13]. Even for heavy products, such as bitumen, NIR spectroscopy, with the aid of non-linear calibration, has achieved success in predicting the product penetration, an important quality property [14].

In contrast, there are few papers in the literature dealing with the use of NIR spectroscopy for assessment of the properties of petroleum, if compared with those dealing with its derived products. One paper predicted the contents of saturated and aromatic hydrocarbons as well as resins and asphaltenes in petroleum [15]. The results showed that both NIR and MIR (mid-infrared spectroscopy) can be used to predict these parameters in crude petroleum. Petroleum emulsions have been characterised by using NIR spectroscopy through the prediction of water content and Exssol D-80 in the emulsion samples [16]. Petroleum quality has been investigated using NIR spectroscopy through the prediction of the density and the fractions of LPG (liquefied petroleum gas), kerosene, diesel fuel and residue [17]. Some of the achievements regarding the use of NIR spectroscopy in petroleum characterization are subjected to international patents [18,19]. In those patents the usefulness of NIR spectroscopy has been demonstrated to characterise petroleum according to its distillation parameters and composition both in the laboratory [18] and directly in the production field [19].

This work aimed at investigating the use of NIR absorption spectroscopy to predict two relevant properties of petroleum: API gravity and true boiling point (TBP) curve. The effectiveness of the NIR method in predicting the variables necessary for process control in a refinery is demonstrated by external validation and by comparison with a simulator used at the refinery.

2. Experimental

2.1. Samples

Two sample groups were employed in this work. The first was constituted of 79 samples of mixtures of crude petroleum used as raw material for the Henrique Lage (REVAP) refinery located in São José dos Campos, SP, Brazil and collected between January of 2002 and August of 2003. The range of the API gravity of this group was 23.7–30.4°, with 26.8° as average and a standard deviation of 1.63°. The second group was made up of 43 petroleum samples obtained from different exploration fields (non-mixed). Thirty three samples came from Brazilians fields and 10 from international fields around the world. The API gravity of this last group extended from 13.2° to 49.6°.

2.2. Determination of the TBP curves and the API gravity

The TBP curves for the samples described above were obtained in the Petrobras Research and Development Center (CENPES), in Rio de Janeiro, Brazil. The procedures described by ASTM D 2892 [3] and ASTM D 5236 [20] were followed. The TBP curves were represented by 29 pairs of points of accumulated distilled volume *versus* temperature (in °C), in the range of 28–750 °C. The precision established by the reference method (reproducibility) for the accumulated distilled volume (V%) at each temperature, is 1.2% for atmospheric distillation and 1.5% for vacuum distillation.

The API gravity was determined following the procedure described in ASTM D 1298 [2].

2.3. NIR instrumentation and NIR spectra

The instrument employed for acquisition of the NIR absorption spectra of the petroleum samples was a Bomem, model MB-160, supplied with a DTGS detector and CaF_2 optics. An absorbance cell, with CaF_2 windows having a 0.5 mm light path, was employed (International Crystals Labs., model SL-4). The cell was filled with the aid of a syringe and washed and dried after each spectrum acquisition employing toluene, pentane and air, successively. The use of a transflectance probe (with different light paths) was also investigated.

The absorption spectra were obtained in the range 10000–3700 cm^{-1} as the average of 128 scans with a resolu-

tion of 8 cm^{-1} using ambient air as reference (empty cell). The ambient temperature was kept between 22 and 24 °C.

2.4. Treatment of the spectral data and model development

Three spectral intervals were investigated to construct the models for prediction of the TBP curve and API gravity. Interval 1: 5000–3900 cm^{-1}; interval 2: 6000–3700 cm^{-1} and interval 3: 9000–3700 cm^{-1}. The TBP curves were represented by 21 (of the 29 points obtained) in the range from 50 to 750 °C. Extreme points were eliminated because they are determined with lower accuracy by the reference method and because they are only correlated with gaseous products and with the distillation residue. Therefore, extreme points in the TBP curve do not carry much relevant information for petroleum processing.

The spectral data were treated to correct for the base line by taking the absorbance at 4780 cm^{-1} as reference for all points of each spectra. The absorbance values were subtracted from that at 4780 cm^{-1}. The spectra set was also normalised after correction, in order to compensate for temperature and path length variations, following the procedure established by the spectrometer manufacturer [21]. For the purpose of normalisation, every spectrum was corrected using the following equation:

$$\overline{S}_c = \frac{\overline{S}}{\sum\limits_{i=a}^{z} S'_i} \qquad (1)$$

where $\overline{S}_c$ is the corrected spectrum, $\overline{S}$ is the original spectrum and S'_i is the absorbance value at the ith point of the original (base line corrected) spectrum. The spectrum range used as a reference for the correction is defined by a and z (a was set to 4000 cm^{-1} and z to 4800 cm^{-1}).

The partial least square (PLS) models were developed by using the software Pirouette (Infometrix Inc.). The spectral data were mean centred before processing. Full cross validation was always employed for internal validation. The number of factors for each model was selected as the minimum producing the lowest standard error of internal validation (SEV). An independent model to predict the accumulated distilled volume for each of the 21 temperature points of the TBP curve was developed. The temperatures selected were: 50, 75, 95, 125, 149, 175, 200, 225, 250, 275, 300, 325, 350, 400, 425, 450, 500, 550, 600, 700, and 750 °C.

Outlier samples were detected by looking at influence graphics (residuals *versus* leverage) after a principal components analysis (PCA).

Models based on artificial neural networks (ANN) were also developed. In this case, the original absorbance variables were replaced by the scores of the most relevant principal components, obtained after a PCA of the spectral data set, as described elsewhere [22]. The PCA was performed in the Pirouette software. The calibration samples for ANN were grouped in the proportion 2:1 for training and monitoring the network performance, respectively.

The groups were balanced in order to incorporate a similar distribution of sample types, as identified by the score distribution in the first two principal components.

After the initial investigation made as described above, a PCA model made only by using the training set was employed to estimate the scores for the monitoring and validation sample sets. The spectral variables were, afterward, represented by the scores of the three sample sets in the first 15 principal components. The scores values were scaled between −1 and +1 which is a suitable range for the sigmoid transfer function employed. This data and the points of the TBP curves were inserted in the Trajan neural networks program for development of the ANN models.

The network configuration and selection of the input parameters were automatically made by the software. A three layer (input, intermediate and output) neural network was employed and trained through back-propagation.

It was found that the TBP curves determined by the reference method adequately fit the general third order polynomial equation

$$V\% = aT^3 + bT^2 + cT + d \qquad (2)$$

where V% is the accumulated volume of distillate at temperature T, in °C. The coefficients a, b and c showed the magnitude of 10^{-7}, 10^{-4} and 10^{-2}, respectively. The observed correlation coefficients were better than 0.99. This fact was exploited to fit a third order polynomial equation to the points predicted by a multivariate model and the new accumulated volumes produced by the equation were taken for comparison with the values obtained by the reference method.

Twenty two samples from the raw material employed in the REVAP refinery were employed for external validation of the models.

3. Results and discussion

The first experiments attempted to find the best conditions for spectrum acquisition of the crude petroleum samples. These samples are viscous and dark due the presence of heavy components known as asphaltenes. The characteristics of the samples require the use of a short light path. Initially a transflectance probe was tried and it did not produce a useful spectrum even for the shortest effective path possible of 1 mm [5]. This can be explained by the fact that the radiation is strongly scattered, preventing light collection by the optical fibre bundle after striking the mirror upon passing through the sample.

In consequence, the efforts were directed to the use of a short light path CaF$_2$ cell. A cell with a 0.5 mm light path supplied good spectra for a wider range of the NIR spectral window investigated. The petroleum samples can be adequately transferred to the cell (even those with low API gravity) by the use of a syringe.

Fig. 1a shows some raw spectra obtained for 27 samples in the wide spectral interval (3700–9000 cm^{-1}). The sample set reflects the variability of types of petroleum employed
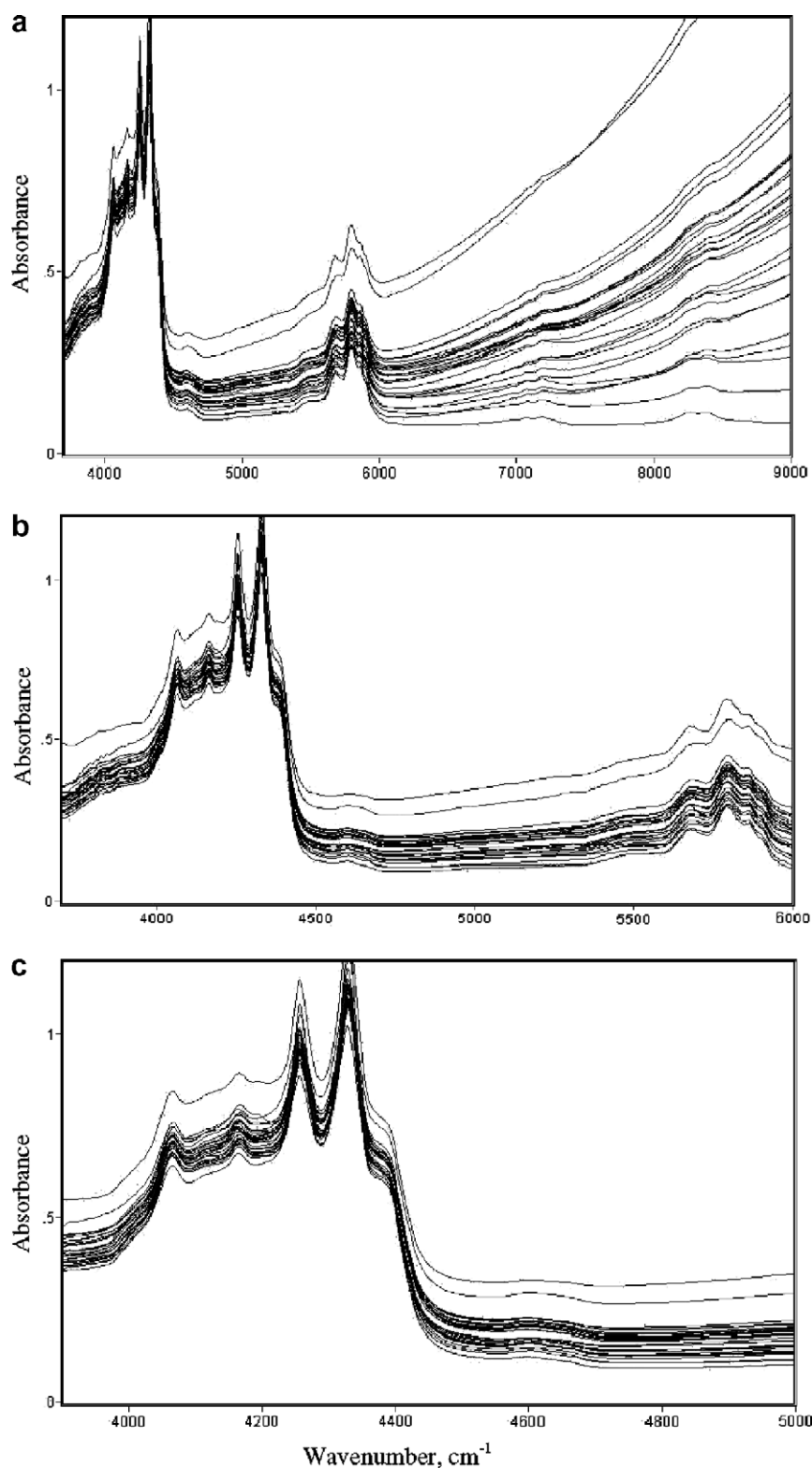
Fig. 1. Raw NIR absorbance spectra for 27 representative samples of crude petroleum: (a) spectral interval 1, showing the severe scattering effect of the NIR radiation for wavenumbers above 6500 cm^{-1}, (b) spectral interval including the combination and first overtone regions, and (c) The best spectral interval which includes only the combination region.

in this study. The spectra are dominated by intense scattering of the radiation above about 6500 cm^{-1}. The effect is more pronounceable for the samples of low API gravity, richer in high molar mass components belonging to the asphaltenes class. On the other hand, the spectral interval from 3700 to 6500 cm^{-1} shows well behaved spectral features presenting absorptions bands that can be attributed largely to the combinations of vibrational modes for the

C–H bonds (4500–4000 cm^{-1}) and to the first overtones of C–H bonds (5500–6250 cm^{-1}). Figs. 1b and c detail the spectra of petroleum in the two spectral intervals selected to be evaluated for constructing the multivariate models to predict the TBP curves and API gravity from the NIR absorption data.

Fig. 2a and b confirm that the information present in the NIR absorption spectra of the petroleum samples is relevant to predict the TBP curve. Fig. 2a shows three TBP curves for samples having the same API gravity value of 26.2. The raw NIR spectra shown in Fig. 2b, however, reflect the composition of the petroleum samples and are quite different. The two closest spectra (I and II) are of the samples presenting similar TBP curves (Fig. 2a).

After processing the spectral data, as described in the experimental part, six sets of 22 models were produced (21 to predict the V% for each temperature and another one for prediction of the API gravity). The models sets are labeled and defined in Table 1 where it is also possible to evaluate and compare their average performance.

Table 1
Description of the models developed for determination of the API gravity and TBP curve using NIR spectral data and their mean RMSEP

Spectral region label	Spectral region (cm^{-1})	Multivariate method	Mean RMSEP for TBP (V%)	RMSEP for API gravity (°API)
P1	5000–3900	Partial least	1.13	0.24
P2	6000–3700	squares	1.32	0.43
P3	9000–3700		1.17	0.37
N1	5000–3900	Artificial neural	1.52	0.95
N2	6000–3700	network	1.28	0.44
N3	9000–3700		1.61	1.08

The results for the RMSEP [23] obtained after external validation made by using 22 petroleum samples (not employed during the construction of the models) were used to compare the models for prediction of the TBP curves and API gravity. Table 1 shows the average results of the RMSEP for prediction of the 21 points of the TBP curves and of the RMSEP for the API gravity prediction. Fig. 3 compares the RMSEP obtained for the external validation of the TBP curves models. The improved performance of the P1 and P2 models over the other models may be noted. P1 models employ only the spectral interval referring to the combination bands of C–H bonds (5000–3900 cm^{-1}) while P2 includes the first overtone for C–H strengths. However, the information added by these last spectral features is apparently not necessary for a good modeling of the NIR data aiming at the prediction of the TBP curves and the API gravity. Models P3 and N3 employed a spectral region that includes the severe effect of radiation scattering. The intention was to include more information on the content of heavy hydrocarbon species in the petroleum samples and to better the prediction of the distilled accumulated volume for the high temperature points in the TBP curve. However, the inclusion of that region resulted in no improvement of the models.

Fig. 2. (a) Experimental true boiling point curves for different types of petroleum presenting the same value of API gravity (26.3° API) obtained by the reference ASTM method. (b) Raw spectra obtained for the same samples as in (a) demonstrating the ability of NIR spectroscopy to differentiate among those samples; I and II are the samples that show similar TBP curves in (a) while III presented the separate curve.
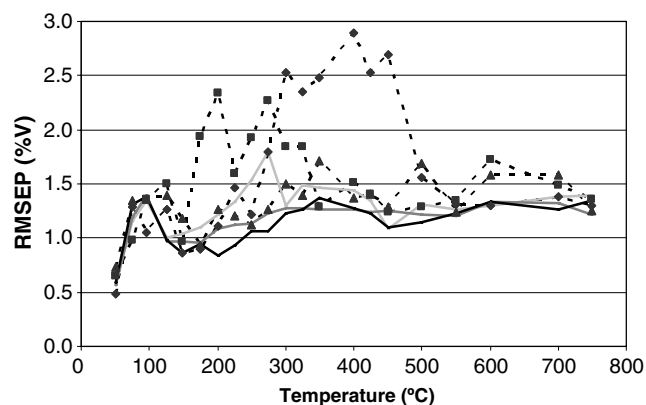

Fig. 3. RMSEP values for the external validation of the PLS and ANN models evaluated for prediction of the TBP curves of petroleum samples: P1 models (black line), P2 models (grey line), P3 models (lighter grey), N1 models (▲), N2 models ANN (■) and N3 models (♦).

Analysis of the results reveals that the P1 models, obtained by PLS, presents better overall performance. With the exception of P2 models, all the other models produce results that are statistically different from model P1 at the 95% confidence level after applying a *t* test. Table 2 shows the number of latent variables employed for each of the 21 P1 models, the root mean square error of prediction (RMSEP) and the coefficient of determination (r^2) that resulted from external validation. The results shown in Table 2 indicate that the extreme points of the TBP curve are predicted with low accuracy. The P1 spectral range shows a very good performance for API gravity prediction requiring 7 latent variables and achieving $r^2 = 0.923$ for the external validation of the PLS model.

The better overall performance of the models constructed by using PLS instead of ANN is also shown in Fig. 3. Although the calibration performance (as shown by internal validation) was similar for PLS and ANN, the external validation shows that the PLS models are more robust and perform better in predicting new samples while any model constructed with ANN is fragile and always appears to better fit the calibration than the validation data. Because it is well known that ANN models perform better for data sets presenting non-linearity, it is possible to conclude that the NIR spectral data correlates linearly with the parameters of the TBP curve and API gravity or, if some slight non-linearity is present, it can be overcome by the inclusion of more latent variables in the structure of the PLS models.

The adjustment of the polynomial curve to the accumulated distilled volume values predicted by the P1 model

shows good results. Fig. 4 shows an example illustrating the values for V% predicted after curve fitting, which present residuals in relation to the experimental values that are smoothed in relation to the original values found only by comparing the predicted V% values using the P1 model. Therefore, polynomial fitting before defining the definitive TBP curve is recommended as a procedure to avoid abrupt differences among the V% finally predicted for each distilling temperature.

The precision of the P1 model was evaluated for three samples with distinct TBP curves and API gravity. The repeatability has been estimated as

$$R = 1.96\sqrt{2}S \tag{3}$$

where R is the repeatability and S is the standard deviation of the predicted values. Each sample was measured ten times in a procedure that simulated in full the measurement operation, including empting and filling the cell between measurements. The repeatability for the API gravity was determined as 0.18°, 0.18°, and 0.19° API for the three samples. Fig. 5 shows the results for the TBP curves of

Table 2
Number of latent variables necessary for the models based on the P1 spectral range, root mean square error of prediction (RMSEP) and coefficient of determination (r^2) obtained after the external validation of the PLS models

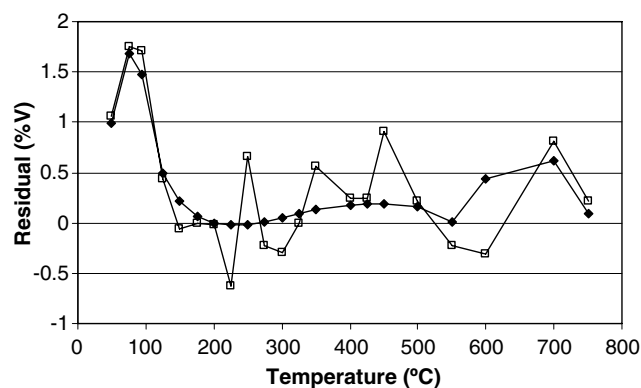| Temperature (°C)	Latent variables	RMSEP (V%)	r^2 (external validation)
50	7	0.59	0.1495
75	6	1.31	0.1762
95	7	1.38	0.2331
125	7	0.98	0.4700
149	7	0.86	0.6075
175	6	0.95	0.6758
200	7	0.83	0.7667
225	7	0.93	0.7854
250	7	1.07	0.6764
275	8	1.07	0.7708
300	7	1.23	0.7422
325	7	1.26	0.7112
350	7	1.37	0.6486
400	7	1.27	0.7384
425	7	1.22	0.7646
450	7	1.09	0.6559
500	8	1.14	0.5962
550	7	1.22	0.5912
600	7	1.34	0.5860
700	6	1.26	0.2700
750	8	1.35	0.2916

Fig. 4. Residuals (predicted V% – reference V%) obtained before (□) and after (▲) smoothing through polynomial fitting using the predicted distillate volume by P1 PLS models (see text for details).
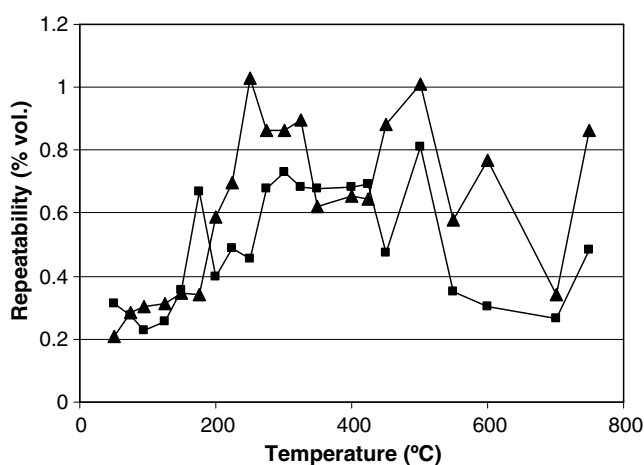

Fig. 5. Repeatability of the NIR method tested using three petroleum samples.
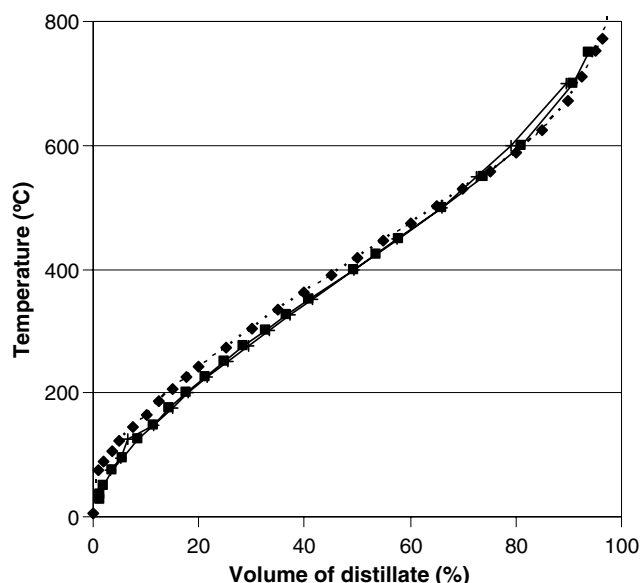
Fig. 6. Comparison between the simulator and the NIR method for the prediction of the TBP curve for a typical petroleum sample. ♦, TBP curve predicted by the simulator. The other two nearly superimposed curves were obtained by the reference (■) and by the NIR method (+).

the three samples. These results allow concluding that the NIR technique presents a repeatability similar to that obtained by the reference methods, both for prediction of the TBP curve and API gravity.

The performance of the P1 model has been evaluated against a process simulator (Hysys, Hyprotech – USA) usually employed in the REVAP refinery in São José dos Campos, SP, Brazil. This simulator predicts the TBP curve using the weighted average of the TBP curves of the petroleum brands that make up the raw material entering the refinery plant. Fig. 6 shows an example of the superior agreement of the TBP curve predicted by the NIR model with that obtained by the reference method while that predicted by the process simulator shows larger residuals. The process simulator is subjected to uncertainty in the raw material composition while the NIR model employs the spectral information of the raw material after the mixture has been made.

4. Conclusion

This work has demonstrated that the NIR absorbance spectrum of crude petroleum contains enough information to be successfully employed to characterise the raw material entering a refinery plant in terms of two relevant parameters: its API gravity and its TBP curve.

The models constructed by using the PLS algorithm showed superior performance over those constructed using ANN, which gave good results during the calibration but failed in the external validation.

Fitting of the function to the points of the TBP curve predicted by the PLS model proved that this procedure can be used to smooth the residuals between the predicted and measured accumulated volume of distillate.

The PLS model can reproduce the TBP curve obtained by the reference method in approximately five minutes, predicting V% for each of the 21 temperatures from the absorbance spectrum of the petroleum. The mean values of the RMSEP for the external validation are within the expected reproducibility of the reference method. The short time interval necessary to predict the API gravity and the TBP curve can be used to advantage to incorporate the NIR method for petroleum characterization in real time process monitoring.

Acknowledgements

References

[1] American Society for Testing Materials, ASTM D 287: standard test method for API gravity of crude petroleum and petroleum products (Hydrometer method). West Conshohoken, (PA), 1992. [Reapproved 2000 E^1].

[2] American Society for Testing Materials, ASTM D 1298 E^2; standard test method for density, relative density or API gravity of crude petroleum and liquid petroleum products by hydrometer method. West Conshohoken, PA, 1999.

[3] American Society for Testing Materials, ASTM D 2892 Rev. A: Standard test method for distillation of crude petroleum (15-theoretical plate column). West Conshohoken, (PA), 2003.

[4] American society for testing materials, ASTM D 2887 Rev. A: Standard test method for boiling range distribution of petroleum fractions by gas chromatography. West Conshohoken, PA, 2004.

[5] Pasquini C. Near infrared spectroscopy: fundamentals, practical aspects and analytical applications. J Braz Chem Soc 2003;14:198–219.

[6] McClure WF. 204 years of near infrared technology: 1800–2003. J Near Infrared Spectrosc 2003;11:487–518.

[7] Guchardi R, Filho PAC, Poppi RJ, Pasquini C. Determination of ethanol and methyl tert-butyl ether (MTBE) in gasoline by NIR-AOTF-based spectroscopy and multiple linear regression with variables selected by genetic algorithm. J Near Infrared Spectrosc 1998;6:333–9.

[8] Zhaohui C, Xinlu F. Use of NIR spectroscopy for in-line gasoline analysis hydrocarbon processing. Houston, vol. 71. 1992. p. 94–6.

[9] Fodor G, Kohl K, Mason R. Analysis of gasoline by FT-IR spectroscopy. Anal Chem 1996;68:23–30.

[10] Valleur M. Spectroscopic methods in refining and petrochemicals. Petrol Technol 1999;4:81–5.

[11] Foulk S, Desimas B. Near-infrared (NIR) determination of key parameters for diesel fuels. Proc Control Qual 1992;2:69–72.

[12] Braitkreitz MC, Raimundo Jr IM, Rohwedder JJR, Pasquini C, Dantas Filho HA, José GE, et al. Determination of total sulphur in diesel fuel employing NIR spectroscopy and multivariate calibration. Analyst 2003;128:1204–7.

[13] Lysaght M, Kelly J, Callis J. Rapid spectroscopic determination of per cent aromatics, per cent saturates and freezing point of JP-4 aviation fuel. Fuel 1993;72:623–31.

[14] Blanco M, Maspoch S, Villarroya I, Peralta X, González JM, Torres J. Determination of physical properties of bitumens by use of near-infrared spectroscopy with neural networks. Joint modelling of linear and non-linear parameters. Analyst 2001;125:378–82.

[15] Aske N, Kallevik H, Sjoblom J. Determination of saturate, aromatic, resin and asphaltenic (SARA) components in crude oils by means of infrared and near-infrared spectroscopy. Energ Fuels 2001;15:1304–12.

[16] Kallevik H, Hansen S, Saether O, Kvalheim OM, Sjoblom J. Crude oil model emulsion characterized by means of near infrared spectroscopy and multivariate techniques. J Dispersion Sci Technol 2000;21:245–62.

[17] Hidajad K, Chong S. Quality characterization of crude oils by partial least square calibration of NIR spectral profiles. J Near Infrared Spectrosc 2000;8:53–9.

[18] Cho In-Ho, Choi Jin-Kyu, Chung Hoe-Il. Automatic analysis method of crude petroleum oils using spectroscopy. United States Patent, Patent Cooperation Treaty, PCT Int Appl WO 00 39,561 (CL GO1N21/25); 2000.

[19] European Patent. BP Chemicals S.N.C. Determination of crude oil properties, EP 659.236 (CI GO1N33/28) Appl. 97/430.007, 1997.

[20] American Society for Testing Materials. ASTM D 5236: Standard test method for distillation of heavy hydrocarbon mixtures (vaccum potstill method). West Conshohoken, (PA), 2003.

[21] AIRS QA and AIRS Professional User's Guide. Quebec. ABB Bomem, 2001. p. 275 (rev. 2.1).

[22] Despagne F, Massart D. Neural networks in multivariate calibration. Analyst 1998;123:157R–78R.

[23] Esbensen K. Multivariate data analysis – in practice. 5th ed., Oslo: Camo Process AS; 2002.