

INFRARED SPECTROPHOTOMETRY, A RAPID AND EFFECTIVE TOOL FOR CHARACTERIZATION OF DIRECT DISTILLATION NAPHTHAS

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(Received 15 June 2005; Accepted 1 December 2005)

The characterization of naphtha obtained by direct distillation of medium and heavy crude oils is often limited by the low yield of these fractions. Gas chromatography is a technique that allows a complete determination of the chemical composition of these fraction. However, the prediction of properties such as octane rating and RVP from chromatographic data is a difficult task because there are not adequate models to predict the interaction of the different components, and particularly in the case of heavier fractions, there are some problems for the complete separation of components under the gas chromatographic conditions. The IR technology constitutes a rapid and effective tool to predict several properties of naphtha from the correlation of the spectrum in the infrared area and the properties. In this study, prediction models were developed in a Petrospec Cetane 2000 analyzer, in order to predict in a fast and simple way, the density, the antiknock index and the aromatic content of straight run naphtha obtained in a standard crude oil distillation unit. The equipment used was designed in the factory for the exclusive characterization of medium distillation and not for lighter fractions therefore this work constitutes an innovation given the extensive applications of this type of analyzers.

Keywords: chemometrics, infrared spectrophotometry, infrared analyzer, petroleum naphthas, octane rating of naphthas.

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La caracterización de naftas obtenidas por destilación directa de crudos medios y pesados a menudo se ve limitada por el bajo rendimiento de dichas fracciones. La cromatografía de gases es una técnica que permite determinar la composición química detallada de estas fracciones pero la predicción de propiedades como el octanaje y el RVP a partir de los datos cromatográficos es una tarea difícil pues no se cuenta con modelos adecuados para predecir las interacciones de los diversos componentes y, especialmente en el caso de las fracciones más pesadas, se presentan dificultades en la separación completa de componentes en las condiciones cromatográficas. La tecnología IR constituye una herramienta rápida y efectiva para predecir varias propiedades de una nafta a partir de la correlación del espectro en la región del infrarojo y las propiedades. En el presente estudio se desarrollaron modelos predictivos en un analizador Petrospec Cetane 2000 para predecir en forma rápida y sencilla la densidad, el índice antidetonante y el contenido de aromáticos de naftas de destilación directa de crudos. El equipo utilizado es diseñado en fábrica para caracterizar exclusivamente destilados medios y no fracciones más livianas por lo cual, este trabajo constituye una innovación dado que amplía las aplicaciones de este tipo de analizadores.

Palabras claves: *quimiometría, espectrofotometría infraroja, analizador infrarojo, naftas del petróleo, octanaje de naftas.*

INTRODUCTION

For the complete characterization of a crude oil it is necessary to measure several physical-chemical properties of the whole crude oil and every cut obtained by direct distillation of it under standard conditions.

Light crude oils (API > 28) typically present a high yield of naphtha which allows the complete chemical characterization of these fractions. Medium and heavy crude oils have a lower yield in their lighter cuts, which constitutes an important limitation for the chemical characterization of those fractions.

The chemical composition of naphtha is typically determined by gas chromatography with capillary column or multi-columns equipment with valves (Beens *et al.*, 2003). The chemical composition of naphtha makes it possible to obtain approximate values of the RON and MON octane rating of it, using statistical methods developed for that purpose (Anderson *et al.*, 1972; Crawford and Hellmuth, 1990). However, the accuracy of this prediction depends on the detailed knowledge of the interactions of the different compounds present in the naphtha. Even though, many of the gas chromatographs dedicated to the analysis of gasoline include in their software the facility to calculate the antiknock index from the chemical composition. The accuracy of the predicted values in some cases is far from ideal, and therefore it is necessary to find other technologies in order to make a better estimate of this property.

In addition to the above, it is worth mentioning, that the heavier the cut of naphtha the lesser the accuracy of the analysis of the chemical composition obtained by gas chromatography, due to superposition of peaks because of limitations in the resolution of the separation columns.

The NIR technology has been used lately as an effective tool to predict the properties of fuels and some companies have developed methods for simultaneous prediction of several properties of gasoline, including among others, chemical composition, octane rating, RVP and distillation curve (Bohács *et al.*, 1998). Likewise, works has been performed for predicting the properties of fractions that are the feedstock for catalytic reforming process, which are normally developed in NIR equipments with Fourier Transform. On this

subject there are powerful applications reported, that allow the prediction of the results of PIANO analysis in this type of matrixes (Chung *et al.*, 1999).

The near infrared area which covers a range of 12800 to 4000 cm^{-1} shows absorption bands which correspond to overtones and combinations of fundamental C – H, O – H and N – H vibrations because of the large anharmonicity of those vibrations involving the light hydrogen atoms. Consequently a spectrum is expected to be much simpler than a conventional mid IR region (4000–400 cm^{-1}) spectrum. Given that the overtones and the combination bands are much weaker than the fundamental bands (usually by a factor of 10 to 100), the near infrared spectroscopy (NIR) allows the analysis of samples up to several millimeters thick (Bokobza, 1998). The great development of the NIR technology is associated to the current developments of optical fiber which enables the transmission of optical data information efficiently, and therefore has been associated with the development of on-line process analyzers.

Notwithstanding the above, the spectroscopy in the medium infrared contains more analytical information based on which it is possible to develop stronger predictive models. The Cetane 2000 was developed based on this; it is an equipment that operates by using filters, most of which operate in the middle infrared region. This allows the equipment to work with small optic path (200 micrometers) and volume samples as low as 20 ml (Croudace, 2001).

The machine uses the Petrospec R software that allows to develop all the calibration models. The calibration models used by the PetroSpec Cetane 2000 instrument are calculated using the mathematical procedure called multi-linear regression (MLR) analysis. The models have the form:

$$P_x = M_0 + M_1 * F_1 + M_2 * F_2 + \dots + M_z * F_z \quad (1)$$

Where:

P_x is the component concentration or value for property x

F_z is the absorbance value obtained from filter z

M_z is the parameter estimate for filter z calculated using MLR analysis.

M_0 is the intercept for the model.

The M_z and M_0 values constitute the calibration model used for predicting the parameter P_x for a sample using the absorbance data F_z . To calculate the calibration model, an equation is written for each sample in the calibration set by substituting the component concentration or property value for P_x (the dependent variable) and the absorbance values for F_x (the independent variables). The MLR analysis is used to calculate the values for M_z and M_0 that represent the best solution for the set of calibration equations. The best solution is obtained by minimizing the difference between the P_x values obtained using standard methods (observed value) and the P_x values obtained by substituting the M_z , M_0 , and F_z values into *Equation 1* and solving for P_x (estimated value).

The M_z and M_0 values are substituted into an equation of the form described in *Equation 1*. An estimate of the property value is calculated by substituting the absorbance data, F_z , from a sample into the equation for the chemical concentration or property value. There is one equation for each chemical concentration or property value linked to a trigger.

A calibration model is used to transform spectroscopic data acquired from a sample into a prediction of a physical property value or component concentration for the sample. In the application of the calibration model, the instrument acquires the infrared absorption spectrum of the sample, and the mathematical model stored in the computer memory is used to convert the spectral data into a property value. A unique model is used to predict each physical property value and chemical concentration.

This study evaluates the applicability of this analyzer in the characterization of straight run naphthas.

EXPERIMENTAL PART

For this study it was used a Cetane 2000 analyzer with Petrospec R software. The optical system of this equipment consists of 14 filters and the pathlength is 200 micrometers.

All the samples referenced in Table 1 were selected as the calibration set and were read as standards in

the Cetane 2000 using a pumping time of 60 seconds. Most of these samples were obtained by direct distillation of crudes in one atmospheric distillation unit operated according the ASTM D2882 standard. The chemical composition of the naphtha samples were determined in an Agilent 6890 chromatograph provided with a capillary column of fused silica, 100 m long and 0,5 μm wide. The compositional analysis software used was Hydrocarbon Expert of Separation Systems. The density of the samples was determined by the ASTM D 4052 method. The octane rating of the reference samples was determined by the following methods: ASTM D2699 (RON) and ASTM D2700 (MON).

With the objective of assembling a robust model, the samples comprising the calibration set were selected with the idea of having sufficient variability in the concentration of the chemical components to cover the range expected to be present in the samples to be analyzed.

RESULTS

Table 1 summarizes the type and properties of the samples used to develop the predictive models. Most of the naphtha samples used for the calibration of the equipment were medium and heavy naphtha obtained in the distillation lab from Colombian crude oils. Very few samples of light naphtha could be used in the training set. To have more light samples in the calibration set there were included some light naphthas obtained directly in the refinery distillation units.

As expected, for any given naphtha the RON and MON octane ratings are very close to each other. Generally speaking, as the naphtha becomes heavier the octane rating becomes lower and the aromatic content becomes higher.

Figure 1, shows how some of the infrared spectra of naphthas used for the calibration, look like on the detector of the Cetane 2000 equipment. All the observed differences in these spectra were used to develop the models that correlate a defined property with the spectra using the petrospec R software incorporated in the equipment.

Table 1. Properties of the samples used for calibration

Identification	RON	MON	Aromatics GC (%p)	Density kg/L
Medium Naphtha Rio Ceibas	70,4	69,7	19,9	0,7759
Heavy Naphtha Rio Ceibas	65,8	65,2	39,0	0,80950
Medium Naphtha Guando	66,9	68,0	9,4	0,7662
Heavy Naphtha Chichimene	40,0	43,4	29,2	0,7899
Medium Naphtha Trinidad	33,5	40,0	1,7	0,7337
Heavy Naphtha Trinidad	15,0	15,0	18,3	0,7648
Light Naphtha 1 Rancho Hermoso	65,2	65,0	3,4	0,6349
Medium Naphtha 2 Rancho Hermoso	N. A.	65,0	3,4	0,7174
Medium Naphtha Rancho Hermoso	54,4	53,9	15,3	0,7589
Heavy Naphtha Rancho Hermoso	45,1	45,3	38,0	0,7938
Light Naphtha 2 Suria	65,3	65,0	4,4	0,717
Medium Naphtha Suria	55,6	54,4	17,4	0,7622
Heavy Naphtha Suria	44,7	43,0	36,3	0,7929
Light Naphtha 2 Balcon	N. A.	66,4	4,7	0,7186
Heavy Naphtha Balcon	44,8	46,4	36,4	0,795
Light Naphtha 2 San Francisco	76,0	76,0	6,1	0,7356
Medium Naphtha San Francisco	70,4	71,8	17,2	0,7784
Heavy Naphtha San Francisco	64,0	65,7	34,4	0,8115
Light Naphtha 2 Gavan	62,4	58,9	18,8	0,7068
Medium Naphtha Gavan	43,2	44,0	3,1	0,7382
Heavy Naphtha Gavan	25,0	30,0	25,0	0,772
Light Naphtha 2 Tello	68,0	67,4	2,6	0,7208
Medium Naphtha Tello	56,0	55,1	8,9	0,7602
Heavy Naphtha Tello	48,4	48,0	33,2	0,7982
Light Naphtha 2 Dina	69,5	69,5	3,0	0,7256
Medium Naphtha Dina	60,5	61,2	9,4	0,764
Heavy Naphtha Dina	49,1	50,0	33,0	0,7974
Light Naphtha 2 Yaguara	69,4	69,1	2,9	0,7245
Medium Naphtha Yaguara	59,2	60,0	7,8	0,7591
Heavy Naphtha Yagyara	48,0	50,0	27,9	0,7942
Heavy Naphtha Apiay	40,0	39,5	33,6	0,7888
Light Naphtha 2 Chiguiro	63,0	63,5	0,4	0,714
Medium Naphtha Chiguiros	48,0	48,0	3,9	0,7479
Heavy Naphtha Chiguiros	30,9	34,0	28,9	0,7853
Ligth Naphta from refinery (Tower 152)	72,2	70,9	3,9	0,6903
Ligth Naphta from refinery (Tower 205)	73,4	71,0	4,2	0,6895
Ligth Naphta from refinery (Tower 1301)	75,3	73,6	1,4	0,6490

N. A. : Not analized

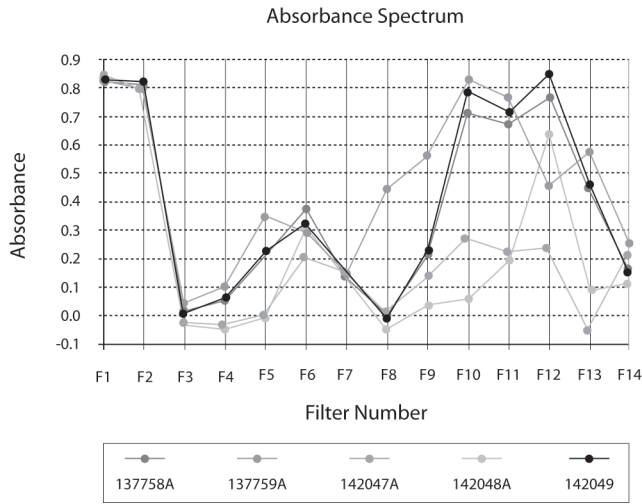


Figure 1. Infrared spectra of some naphthas obtained in the cetane 2000

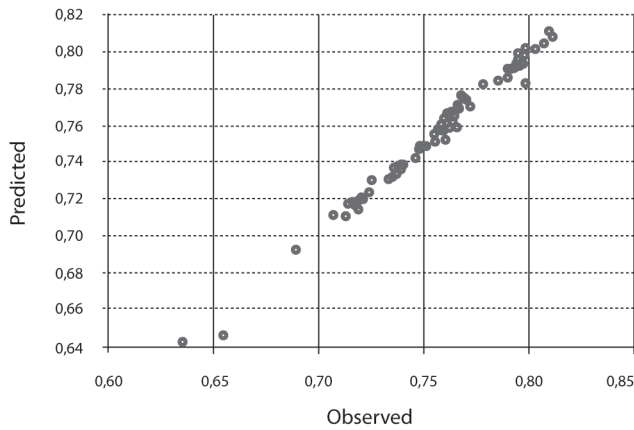


Figure 2. Correlation between experimental density and value predicted by the IR model that was developed

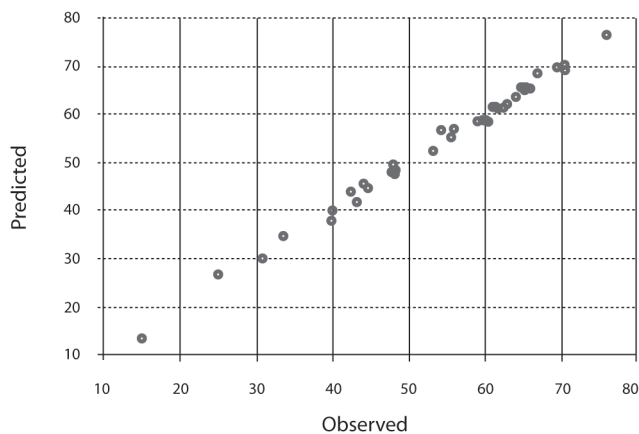


Figure 3. Correlation between experimental ron octane rating and value predicted by the IR model that was developed

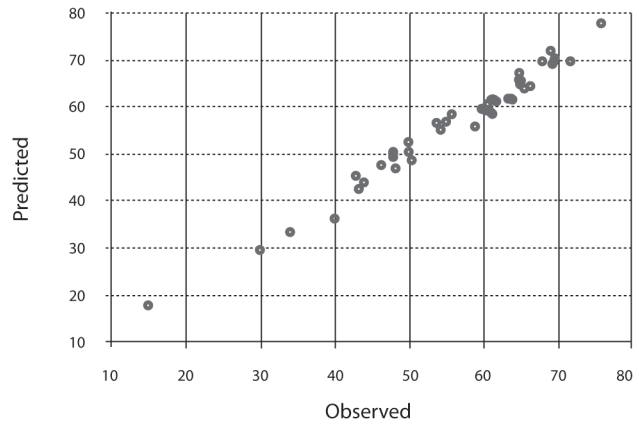


Figure 4. Correlation between experimental mon octane rating and value predicted by the IR model that was developed

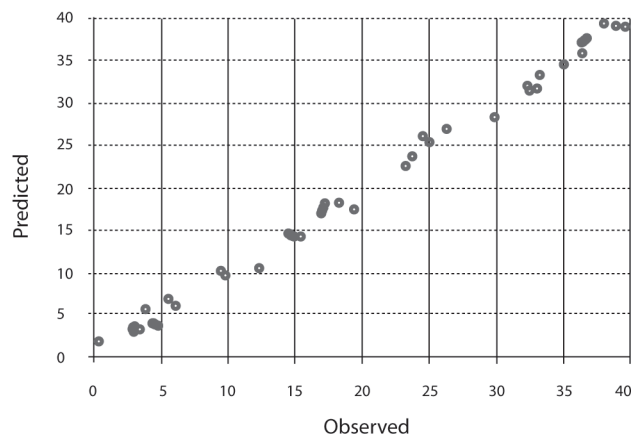


Figure 5. Correlation between the experimental aromatic content and the predicted value by the developed IR model

Figures 2, 3, 4 and 5, show the good linearity found between the measured property and the value predicted from the respective IR spectrum of the sample. These results indicate that the quality of the predictive models is good in all the cases.

Table 2 summarizes the parameters obtained with the calibration data set that define the statistical performance of each of the predictive models developed herein.

All the results show the quality of the values that may be obtained with the predictive models that were developed.

Table 3 resumes some of the data obtained with samples selected for the model validation step. The samples considered in this set cover the whole range

Table 2. Statistical data of the predictive models that were developed

Property	Statistical Parameter	Value
Density (15,6 °C)	RMSEC	0,00335
	R Square	0,99075
	Adjusted R Square	0,98814
	Coefficient Variation	0,4414
	Sum Of Residuals	0
	Sum Of Square Of Residuals	0,0004
RON octane Rating	RMSEC	2,08795
	R Square	0,97894
	Adjusted R Square	0,97320
	Coefficient Variation	3,63136
	Sum Of Residuals	-2,1e-0,07
	Sum Of Square Of Residuals	139,505
MON octane Rating	RMSEC	1,91115
	R Square	0,97931
	Adjusted R Square	0,97290
	Coefficient Variation	3,3088
	Sum Of Residuals	-1,e-0,08
	Sum Of Square Of Residuals	102,2706
Aromatic Content (Piano Analysis) (%w)	RMSEC	1,80105
	R Square	0,98383
	Adjusted R Square	0,97958
	Coefficient Variation	9,6478
	Sum Of Residuals	4e-0,07
	Sum Of Square Of Residuals	120,0203

from light to heavy naphthas and also there were included samples of straight run naphthas coming directly from the refinery distillation units. The table summarizes the experimental and the predicted value for the evaluated properties.

The performance of the models are usually measured by the root mean square error of prediction (RMSEP), calculated as (Celio, 2003):

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{Np} (\hat{y}_i - y_i)^2}{Np}} \quad (2)$$

Where \hat{y}_i and y_i are, respectively, the predicted and reference values of the concentration/property for

the validation set of Np number of samples. Table 4 summarizes the RMSEP of all the properties predicted. As expected, the prediction errors are a little higher than the calibration errors but considering the speed of the analysis and the limited number of samples included in the calibration set, the predicted data could be considered good.

CONCLUSIONS

- The evaluated technology could be applied for predicting in a fast and simple way the proximate values of octane rating (RON and MON), density, and aromatic content for straight run naphthas.

Table 3. Validation of the predictive models

Sample	RON		MON		Density 15,6°C (kg/l)		Aromatics GC (%W)	
	Exp.	Predicted	Exp.	Predicted	Exp.	Predicted	Exp.	Predicted
Ligth Naphtha	71,1	72,0	70,1	68,5	0,6959	0,7048	3,5	7,8
Load Naphtha	68,3	71,7	68,6	68,7	0,7118	0,7138	12,2	9,4
Naphtha	57,9	57,7	57,5	58,6	0,7601	0,7752	25,2	29,4
Naphtha	59,7	55,9	58,7	57,0	0,7487	0,7721	19,0	24,8
Ligth Naphtha	68,4	69,3	67,6	67,3	0,7017	0,7094	12,7	10,1
Naphtha 4 U200	N. A.	N. A.	N. A.	N. A.	0,7877	0,8108	25,2	27,2
Naphtha 5 U200	N. A.	N. A.	N. A.	N. A.	0,8098	0,7933	40,0	44,2
Naphtha 2 U200	N. A.	N. A.	N. A.	N. A.	0,7248	0,7359	3,1	4,7
Naphtha 1 U200	N. A.	N. A.	N. A.	N. A.	0,6460	0,6286	0,4	0,0

N. A. : Not analyzed.

Table 4. Prediction errors

PREDICTED Property	RMSEP
Research octane number	2,3498
Motor octane number	1,1646
Density at 15,6 C	0,0207
Aromatic content by GC	4,6644

- The method developed constitutes an important contribution to the characterization of naphthas from crudes with low volumetric yield of light fractions.
- Compared to the standard test methods, the proposed methodology reduces substantially not only the analysis costs, but the required sample volume and the analysis time.
- The developed method constitutes and innovative extension of the applications of the Cetane 2000 analyzer, an equipment dedicated to diesel fuel analysis.

ACKNOWLEDGMENTS

The authors would like to thank to the Laboratory and Pilot Plant Coordination Area of the Instituto Co-

lombiano del Petróleo (ICP) for the supply and characterization and of all the samples used for this work and also for the reading of all these samples in the analyzer. Also we want to thank to the Maintenance Department people for the optimization of the pumping system of the analyzer.

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