

Near Infrared Monitoring of Low Conjugated Diolefins Content in Hydrotreated FCC Gasoline Streams

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Résumé — Prédiction de la teneur en dioléfines conjuguées dans les essences de craquage catalytique par PIR — Les essences issues du craquage catalytique (FCC) contiennent des composés indésirables tels que les dioléfines conjuguées. Ces composés sont très réactifs à la polymérisation, forment des gommes qui bouchent les unités de la chaîne de raffinage et dégradent la stabilité des essences commerciales. Les dioléfines conjuguées peuvent être hydrogénées en oléfines par un procédé d'hydrogénation sélective (Selective Hydrogenation Unit ou SHU). La teneur en dioléfines conjuguées peut être déterminée par l'intermédiaire de l'indice d'anhydride maléique (MAV) ou son équivalent "Diene Value" (DV). Ces méthodes sont basées sur l'addition stœchiométrique entre les dioléfines conjuguées et l'anhydride maléique selon la réaction de Diels-Alder. Ces analyses sont toutefois très longues (5 à 7 heures par analyse) et laborieuses pour être pratiquées en routine afin de déterminer les performances du procédé SHU. La spectroscopie Proche Infrarouge (PIR) qui est une technique à la fois rapide et répétable a été utilisée pour modéliser par PLS (*Partial Least Squares*) la teneur en dioléfines conjuguées selon la méthode MAV. La teneur en dioléfines conjuguées dans ces essences est cependant très faible (< 1 % poids) par rapport aux autres hydrocarbures présents dans l'essence, notamment par rapport aux oléfines (20 à 60 % poids) qui absorbent dans des zones très proches des dioléfines. Au lieu de corrélérer directement la MAV, la modélisation de la variation de la MAV (Delta_MAV) a été testée dans ce travail. La modélisation du Delta_MAV a été possible pour le procédé SHU car, pour une charge donnée, les principales variations de composition en hydrocarbures sont majoritairement dues aux dioléfines conjuguées. Le Delta_MAV a été modélisé à l'aide de soustraction entre spectres. Le modèle PIR développé est en très bon accord avec la méthode par voie chimique : 98 % des échantillons de la base de calibration sont prédits dans l'intervalle de confiance de reproductibilité de la méthode de référence. Des résultats de validation externe du modèle sont aussi présentés avec le suivi d'unités pilote d'hydrogénation sélective des essences FCC.

Abstract — Near Infrared Monitoring of Low Conjugated Diolefins Content in Hydrotreated FCC Gasoline Streams — Fluid catalytic cracking (FCC) gasolines contain some undesirable compounds like the conjugated diolefins which are highly reactive to polymerization and plug the downstream refining processes. These compounds also affect the commercial gasolines stability. The Selective Hydrogenation Units (SHU) transform the conjugated diolefins into olefins. The conjugated diolefins content is indirectly measured as the "Maleic Anhydrid Value" (MAV), or as the "Diene value" (DV). These methods are based on the Diels-Alder reaction between conjugated diolefins and maleic anhydrid. These analyses are very time consuming (5 to 7 hours per sample) when daily analyses are required to survey the performances of the SHU process. Since Near InfraRed spectroscopy (NIR) is a faster and more repeatable

technique this work tested the PLS NIR modeling of the conjugated diolefins content according to the MAV method. The diolefins content in these samples is nevertheless very low (< 1 wt%) compared to the other hydrocarbons present in these gasolines, in particular compared to olefins (20-60 wt%) which may interfere with the NIR diolefins wavenumbers absorption. In the SHU process, for a given feed, the chemical differences between the reactor inlet and outlet are mainly the diolefins content. Hence, instead of directly correlating the MAV content, we modeled the MAV variation (Delta_MAV) as a function of spectra subtraction between effluents. The NIR model successfully fitted the experimental data from the calibration database. External validation results based on monitoring analyses of SHU pilot plant effluents that confirm the predictive ability of the NIR model are also presented.

INTRODUCTION

The valorization of heavy cuts implies their conversion into lighter fractions like gasolines or gasoils. Fluid catalytic cracking process (FCC) upgrades heavy cuts producing gasolines that contain unsaturated hydrocarbons like olefins and diolefins. These gasolines do not meet the current specifications of commercial fuels (particularly the total sulfur content) and must undergo other refining processes before their incorporation into the gasoline pool. The conjugated diolefins present in FCC gasolines generate problems like gums formation and therefore, the downstream refining units plugging. Furthermore, these compounds are also detrimental for the fuels stability. In order to transform the conjugated diolefins contained in the FCC gasolines, these cuts are catalytically treated in Selective Hydrogenation Units (SHU) [1]. The main SHU objective is to selectively hydrogenate the conjugated diolefins and at the same time minimize olefins hydrogenation into paraffins. Other secondary reactions like transformation of mercaptans occur, but these compounds are present in trace level (< 0.05 wt%). Other chemical families like paraffins, aromatics and naphthenes do not react in the SHU process, therefore, the hydrocarbon matrix of the gasoline treated is very similar between the reactor inlet and outlet. The operating conditions of SHU units are determined by the content of conjugated diolefins in the effluents; therefore their analysis is critical to survey the process performances.

The content of conjugated diolefins is commonly indirectly determined as the Maleic Anhydrid Value (MAV) or as the DieneValue (DV) [2]. Both methods are based on the Diels-Alder addition reaction between conjugated diolefins and maleic anhydride but this work refers only to the diolefins content measured by the MAV method. MAV is expressed as mg of maleic anhydride that reacted with 1 g of sample (mg/g). MAV varies between 10 to 30 mg/g in FCC gasoline SHU feedstocks. Commonly, for industrial applications, the target MAV after SHU process is ≤ 2 mg/g. For our work, the MAV of the SHU effluents varies from 0.5 to 15 mg/g since we aim to study the process optimization. These MAV values represent approximately 0.06 to 2 weight percent (wt%) of conjugated diolefins. Since the conjugated diolefins amounts are very low, analyses like density or

refractive index are not sensitive enough to be correlated with the diolefins content, hence, the SHU performances can only be measured by the MAV method.

The methods based on the Diels-Alder reaction have a major inconvenient: they are extremely time-consuming (> 5 hours), they are consequently difficult to carry out for routine analyses. Furthermore, they require special caution since a heated gasoline-solvent reaction step is realized and further significant solvent amounts are required for liquid-liquid extractions. A small number of alternative methods have been reported in literature to determine the diolefins content in gasolines. Techniques such as NMR [3-5] and more recently GC-MS and GC-NCD [6] have been applied for detailed characterization of diolefins in gasolines. These analyses are interesting for comprehensive diolefins analyses but they are not practical for daily quantification and furthermore, the diolefins speciation is not necessary for our application.

The total diolefins content has been carried out by differential pulsed polarography by Polák *et al.* [7] and Swarin and Perry [8]. Polarography is based on the measurement of current as a function of potential, commonly with a dropping mercury electrode. Conjugated diolefins are reduced in presence of a proton donor. The principal advantage of this method is the analysis time, which is reduced to 15 min per sample. Polák *et al.* [7] applied this method on pyrolysis gasolines and effluents of selective hydrogenation units. Swarin and Perry [8] tested the method proposed by Polák. These authors analyzed several gasolines and established a correlation between polarographic results and DV. Model molecules were also tested to determine the selectivity of this method and only conjugated diolefins were quantified (no olefins). However, the 2,5-dimethyl-2,4 hexadiene did not react suggesting that hindered molecules may not be measured.

Another approach has been proposed by Ghazvini *et al.* [9] who applied an HPLC-UV method for the detection at 240 nm of conjugated diolefins in gasolines with boiling points of 30-215°C. Results were compared with gas chromatographic analyses. The comparative contents of diolefins obtained by this method indicate an underestimation of diolefins content (-37% to -94%). Albuquerque [10] worked on the determination of conjugated dienes in gasolines by

supercritical fluid chromatography (SFC) and UV detection. This method is reported as selective to conjugated diolefins. The DV range tested was 0.5 to 6.5 (MAV: 1.9 to 25 mg/g). The authors analyzed some samples issued from hydrotreatment of four different FCC gasolines and results were correlated to DV. The response of SFC-UV is sample dependent so a different correlation has to be established to predict the diolefins content for each type of gasoline. Even if the proposed method is much faster (5 min) the inconvenient is that a calibration is needed for each type of gasoline feed.

The advantages of NIR are mainly: excellent repeatability, fast analysis (about 5 min), possibility of prediction of different properties with one spectrum, no sample preparation, possibility of on line analysis without loss of quality results. The principal limitations are that NIR needs a complex calibration procedure using a diversified database of samples with concentration of analytes (MAV) determined by a reference method. Near Infrared spectroscopy (NIR) has already been studied by Wood to the monitoring of the hydrogenation reaction of the itonic acid ($\text{CH}_2 = \text{C}(\text{COOH})-\text{CH}_2-\text{COOH}$). The determination of dienes content in steam cracking gasolines has also been reported [11-12]. Steam cracking is a thermal process that uses heat from steam to crack petroleum hydrocarbons, therefore, these kind of samples have a very high content of diolefins (MAV > 100). No applications to FCC gasolines or SHU effluents were cited (the hydrotreated gasolines have much lower MAV values: 0.5 to 15 mg/g). The NIR modeling of the conjugated diolefins in hydrotreated FCC gasolines faces a difficult challenge: the determination of a small content of conjugated diolefins (< 1 wt%) within a complex mixture of hydrocarbons containing mainly olefins (≈ 20 to 60 wt%), aromatics (5 to 50 wt%) and saturates (≈ 25 to 60 wt%). Furthermore, conjugated diolefins are a chemical sub-family of olefins and we must quantitatively distinguish both families. This paper reports a novel spectra pre-treatment for the NIR modeling and monitoring of the variation of the conjugated diolefins content in hydrotreated FCC gasoline streams. This method is beyond the classical NIR quantification applications.

1 EXPERIMENTAL SECTION

1.1 Samples

All the gasolines analyzed in this work are effluents of selective hydrogenation of several FCC gasolines obtained in the IFP pilot plants. The database is divided in two sets of samples: calibration and external validation. The calibration database has 58 samples and is intended to be used for the estimation of the NIR model parameters. The external validation database contains 26 samples which are only used to evaluate the quality of NIR model predictions. The samples

were characterized by several analyses: density, hydrocarbon chemical families and MAV. Model molecules analyses were also carried-out. Isoprene and 2,3-dimethyl-1,3-butadiene were purchased from Aldrich (minimum purity of 99% and 98% respectively); 1-decene (purity $\geq 97\%$) was provided by Fluka.

1.2 Maleic Anhydrid Value (MAV)

A weighed sample of gasoline is added to 50 mL of a saturated solution of maleic anhydrid in toluene. The mixture is heated to boiling point and refluxed one hour (Diels-Alder reaction between conjugated diolefins and maleic anhydrid). The non-reacted maleic anhydrid is hydrolyzed to maleic acid and then titrated with a strong base (NaOH 0.5 M). A blank is realized and the diolefins content calculated by difference since the reacted maleic anhydrid is related to the initial content of diolefins. The MAV is reported as the number of milligrams of maleic anhydrid that react with 1 g of sample. The weight percent of conjugated diolefins in the sample is calculated as follows:

$$\text{Diolefin}(\text{wt}\%) = \frac{\text{MAV} \cdot \text{MW}_{\text{diolefin}}}{980} \quad (1)$$

where $\text{MW}_{\text{diolefin}}$ is the molecular weight of the quantified diolefin. Real samples contain a complex mixture of diolefins, so $\text{MW}_{\text{diolefin}}$ is an average estimated to 120 g/mol for our samples. The intra-laboratory MAV reproducibility can be calculated from Equation 2. The quantification limit is 0.5 mg/g.

$$R_L = 0.691 \times \text{MAV}^{0.4} \quad (2)$$

1.3 Spectroscopic Conditions and Instrumental

A BOMEM MB160 FTNIR spectrometer operating in transmission mode with a resolution of 4 cm^{-1} was used for this work. This spectrometer is equipped with a DTGS (deuterated tri glycide sulfide) detector. A QX quality cell ($2 \pm 0.02 \text{ mm}$) was used for the analysis of all samples. The temperature of the sample is stabilized by Peltier effect at $27.5 \pm 0.5^\circ\text{C}$. The laboratory temperature varies only between 20 to 25°C . The spectra were recorded with 100 scans per spectrum in the $4000\text{-}12\,000 \text{ cm}^{-1}$ region. The Bomem GRAMS32 software was used for spectra acquisition after a delay time of 5 min while purging with a dry nitrogen flow of 3 L/min. The reference spectrum was recorded with the empty cell in the holder.

1.4 Other Analyses

The density of all samples was realized according to the ASTM D4052 method [13]. The hydrocarbon chemical families distribution was determined by an in-house capillary gas

chromatography (GC) method derived from the ASTM D6733-01 standard [14]. This method provides information about detailed composition of *n*-paraffins (P), iso-paraffins (I), aromatics (A), naphthenes (N) and olefins (O).

1.5 Chemometrics and Data Preprocessing

Prior to the multivariate analysis, a data preprocessing is generally applied to eliminate for instance spectra baseline shifts. The data preprocessing used in this work consists on a baseline correction and a mean centering applied to all spectra in the NIR region used for multivariate analysis.

Principal component analysis (PCA) is a mathematical method that enables the transformation of a high number of correlated variables into a few number of new uncorrelated variables called principal components (factors). PCA is based on an eigenvector decomposition of the covariance matrix of the data variables. The first principal component accounts for as much of the variability in the data as possible. Each succeeding component is orthogonal and successively takes into account the residual variance of the data [15]. PCA is well adapted to problems having a high number of variables compared to the number of samples. Since each NIR spectrum has more than 4000 variables (wavenumbers) most of them inter-correlated, the principal component analysis is commonly used to represent the variability of the spectra and hence the variability of the samples. Commonly the first 10 new variables describe the most part of the variability of the original data. The visualization of the samples *via* the PCA analysis helps to determine the presence of patterns, differences or similarities of the samples.

The Partial Least Squares (PLS) was used to develop the calibration model. PLS is a multivariate linear regression method that enables to correlate the property to be predicted (observation) and the spectra information using new uncorrelated variables. The PLS algorithm is based on the maximization of the covariance between the X-scores (X: spectral data matrix of samples) and the corresponding Y-scores (Y: vector of samples observations). The PLS algorithm used in this work has been described elsewhere [16]. To avoid data overfitting, the number of PLS factors is chosen with a leave-one-out cross validation method. This procedure consists to leave a calibration sample out of the model, calculate a PLS model with the rest of the calibration database and predict the sample left out with this model. This process is repeated for each sample until all samples have been left out once. An average prediction error is then calculated with Equation 3 for each sample left out. In Equation 3, \hat{y}_i are the predicted values, y_i the experimental observations and n the total number of samples. The number of PLS factors is chosen as the minimum RMSE calculated by cross validation.

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (\hat{y}_i - y_i)^2} \quad (3)$$

2 RESULTS AND DISCUSSION

2.1 NIR Features of Model Compounds and their Mixture with a Gasoline Sample

Since our work aims to quantify the conjugated diolefins in the gasoline samples, we have tried to identify the absorbance bands of these kind of chemical bonds in the NIR region. The conjugated diolefins absorption should occur very close to the olefins ones. Yalvac *et al.* [17] worked with mixtures of pure olefins in the NIR region. The first overtone of the asymmetric =CH₂ stretch was identified in the 6080-6160 cm⁻¹ region. The olefins also absorbed in the 4700-4750 cm⁻¹ region. The authors noticed that the increase of the olefins chain length produces the shift of the first overtone of the asymmetric stretch =CH₂ towards longer wavelengths and the diminution of the band intensity. The NIR analysis of 1-decene, 2,3-dimethyl-1,3-butadiene, isoprene, and the mixture of isoprene with an hydrotreated FCC gasoline were carried out in this work to verify if clear differences are observed in these NIR regions. As observed in Figure 4a, in the 6080-6200 cm⁻¹ the olefin tested and the conjugated diolefins absorb in very close regions. The conjugated diolefins are shifted towards higher wavenumbers if compared to 1-decene. The 4620-4800 cm⁻¹ (Fig. 4b) that corresponds to the NIR combinations zone of the spectra shows a difference between the spectra of the olefin and the conjugated diolefins. For the diolefins two absorption bands are observed while only one is obtained for the 1-decene. Two gasolines with different MAV values were also analyzed: gasoline_m and gasoline_n (MAV: 16.5 and 1.7 mg/g respectively). These gasolines present weak absorption bands in the NIR regions cited before. The gasoline with major MAV was mixed with isoprene and the absorbance increases in both zones thus the rough regions of spectra corresponding to the absorption of unsaturated bonds are confirmed. However the NIR modeling of MAV including only these regions is hazardous for two main reasons:

- diolefins must be distinguished and quantified separately within a sample containing a high olefins content;
- the hydrotreated FCC gasolines are very complex mixtures having more than 400 chemical compounds so the matrix effect must be taken into account to ensure the robustness of the NIR prediction.

2.2 Characteristics of the Calibration Data Set

2.2.1 Global Analyses

As indicated before, the database is constituted exclusively of SHU effluents treating FCC gasolines. The 58 samples are issued from five different gasoline feedstocks that will be referred as G1 to G5. Table 1 indicates the average properties of the G1 to G5 effluents included in the calibration

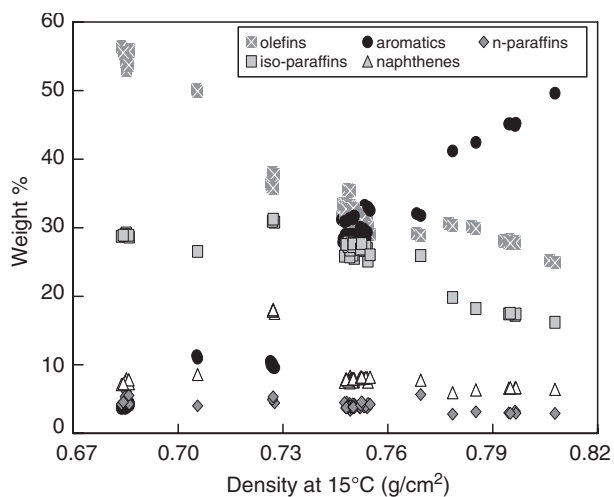


Figure 1

Calibration database major hydrocarbon chemical families as a function of density.

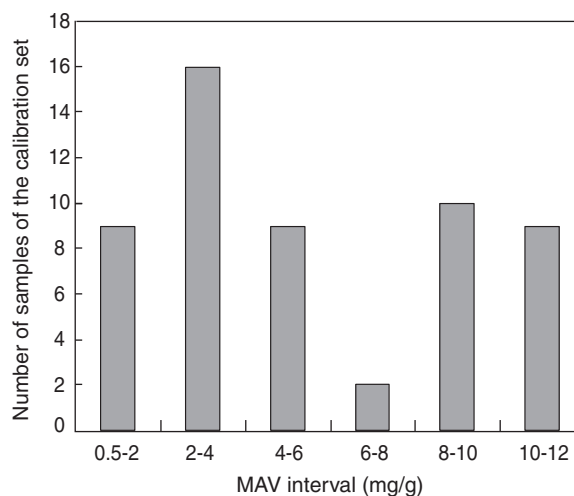


Figure 2

Calibration database MAV distribution.

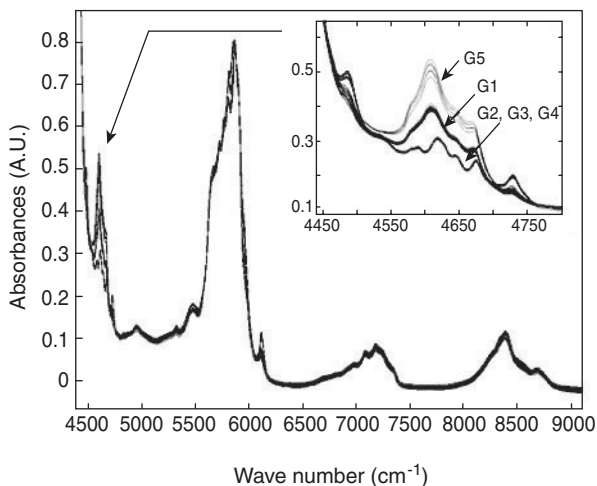


Figure 3

Raw spectra of the calibration database of hydrotreated FCC gasolines. G1: feed 1; G2: feed 2; G3: feed 3; G4: feed 4; G5: feed 5.

database. As indicated by the density, a variety of light to heavy gasoline samples is covered. Figure 1 illustrates the distribution of major chemical families (olefins, aromatics, saturates) as a function of the density. The content of *n*-paraffins and naphthenes is almost constant for all samples which is usual for FCC gasolines. As expected, the aromatics content is higher for heavier samples; the olefins content is higher for the gasolines of low density. Even if the base has a relatively large variety of the samples (regarding chemical composition), almost half of them are concentrated in the 0.75-0.76 g/cm³ density range. Concerning the distribution of MAV in the calibration samples (Fig. 2), 33% of samples are

in the 0.5-3 range; this distribution of MAV is in agreement with the industrial specifications for SHU effluents (MAV < 2 mg/g). The other samples have MAV values from 3 to a maximum of 12.5 mg/g.

2.2.2 NIR Spectra of Hydrotreated FCC Gasolines

The spectra of the calibration database are illustrated in Figure 3. Each spectrum presents four groups of bands with absorbances lower than 0.8 absorbance units (A.U.). The first one in the 4450-4800 cm⁻¹ region, the second with the higher intensity in the 5400-6200 cm⁻¹ region and the two others with similar intensities but approximately 10 times lower than the second one in the 6600-7500 and 8000-8500 cm⁻¹ regions. All the spectra superpose well, this is in accordance with the fact that all the SHU effluents contain the same chemical families (PIONA) but at different concentrations.

2.3 NIR Modeling Results

2.3.1 Principal Component Analysis

The NIR region chosen for PCA representation and PLS modeling is 4450 to 9000 cm⁻¹. The 1st and 2nd PCA scores are presented in Figure 5 and correspond to 99% of the variance of the database (90.6% and 8.5%, respectively). Three groups of samples are observed: G1, G2-G3-G4 and G5 effluents. These clusters are also noticed in the enlargement of 4450-4800 cm⁻¹ region in Figure 3. Since the NIR spectrum is the fingerprint of each gasoline sample, the spectrum reflects the composition of major hydrocarbons present in the sample such as olefins or aromatics. The samples are mainly separated according to their PIONA analysis. G2, G3 and G4 gasoline feedstocks had a very close chemical composition and are grouped between each other; all the G1 effluents

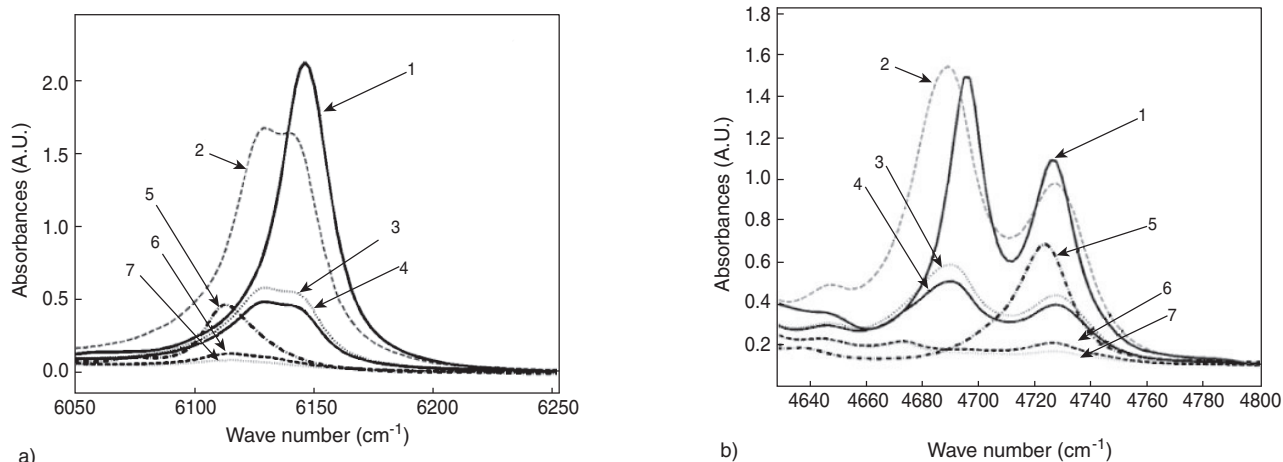


Figure 4

NIR spectra 1: 2,3-dimethyl-1,3-butadiene; 2: isoprene; 3: 30%/70% isoprene-gasoline_m; 4: 24%/76% isoprene-gasoline_m; 5: 1-decene, 6: SHU gasoline_m; 7: SHU gasoline_n.

TABLE 1

Average global properties of the FCC hydrotreated effluents included in the calibration and the external validation databases.

G1: feed 1, G2: feed 2, G3: feed 3, G4: feed 4, G5: feed 5, G6: feed 6, G7: feed 7

Feed reference		G1	G2	G3	G4	G5	G5	G6	G7	
Property	(units)	calibration effluents					external validation effluents			
Average Density at 15°C	(g/cm ³)	0.750	0.700	0.698	0.700	0.796	0.796	0.741	0.775	
Average GC analysis										
<i>n</i> -Paraffins	(wt%)	3.7	4.6	4.5	4.5	3.0	3.1	3.9	3.2	
iso-Paraffins	(wt%)	27.3	27.2	27.1	27.1	17.3	17.7	26.7	18.8	
Naphthenes	(wt%)	7.8	7.6	7.6	7.6	6.5	6.4	8.2	6.4	
Aromatics	(wt%)	28.1	8.4	8.4	8.4	45.4	44.0	27.5	36.7	
Olefins	(wt%)	33.1	52.2	51.8	51.8	27.7	28.8	33.7	34.8	
Average MAV	(mg/g)	3.2	9.4	9.9	10.9	4.0	3.3	3.2	5.9	

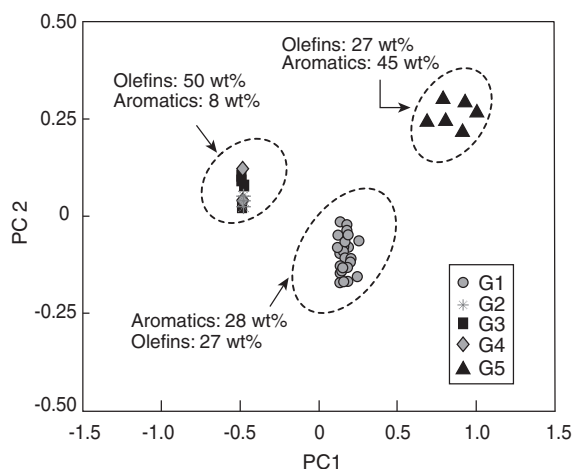


Figure 5

PCA scores plot of the NIR spectra of the hydrotreated FCC gasolines included in the calibration database. G1: feed 1; G2: feed 2; G3: feed 3; G4: feed 4; G5: feed 5.

form also cluster. The G5 effluents that have the most important aromatics content (about 45 wt%) are also clustered in the middle left of the scores plot.

According to these results, two options can be taken into account:

- develop three different MAV models (one per cluster);
- develop one model assuming a linear behavior between the clusters.

The first alternative is very restricting since for the SHU process optimization it is necessary to study a large variety of feeds which can change very frequently; in this case, every new feed can be outlier and the development of a new model is required. This procedure is well known but extremely time-consuming. The second option is dangerous since the accuracy of predictions is not guaranteed. For these reasons, based on the SHU process principle, the NIR MAV modeling has been tackled differently as described in the next paragraph.

2.3.2 Principle of the NIR MAV Model

The Selective Hydrogenation Unit aims to selectively hydrogenate the conjugated diolefins. This means that the olefins hydrogenation is minimized (< 5%) and the major chemical families such as aromatics, paraffins and naphthenes remain almost constant. Therefore, for a given feedstock, the hydrocarbon matrix will be extremely similar between the different effluents. For a set of effluents obtained from the same gasoline feed, if a sample is taken as “reference” and the spectra of the following samples are subtracted from the “reference” sample spectrum, the resulting signal must represent the absorptions produced mainly by the modification in diolefins content between the samples. This difference of diolefins is linked to a variation of MAV. Hence instead of correlating directly NIR with MAV, we tested the modeling of the spectra differences which were correlated with MAV variations (referred in this work as Delta_MAV). Equation 4 defines the Delta_MAV calculation where $MAV_{reference}$ is the MAV of the “reference” sample and MAV_i is the MAV of a subsequent sample i . Equation 5 is applied to calculate the difference between the “reference” sample spectrum and a sample i spectrum at each wavelength (from $k = 1$ to K wavelengths). In Equation 5, A_{refk} is the reference sample absorbance at k wavelength and A_{ik} subsequent sample absorbance at the same wavelength. All the spectra subtractions are realized after baseline correction.

$$\Delta MAV_i = MAV_{reference} - MAV_i \quad (4)$$

$$A_{i_difference\ k} = (A_{refk} - A_{ik}) \quad (5)$$

The principle of the NIR calibration dataset modeling is presented in Table 2. The first set of samples (1 to m) is obtained from the same feedstock A. One sample of this set is taken as the “reference” for this samples series, for example the first. The spectra differences between the “reference” and the other samples from the same set (2 to m) are calculated and with their corresponding Delta_MAV from

Equations 4 and 5, respectively. Even if the operating conditions of the process change, if the feed remains constant (feed A), the samples will still belong to the first set of samples and the reference will remain sample 1. However, if the feed of the process changes (ex. feed B), the effluents will be considered as a new series and another sample must be taken as “reference”, for example sample n . The spectra differences for this set of samples and their Delta_MAV are calculated with this new “reference”. The process is repeated for each set of samples issued from a different feedstock. A particular attention must be taken to this point since the different feeds are composed of different hydrocarbon matrices. If the differences are calculated between samples issued from different feeds, the spectra differences will be mainly produced by the hydrocarbon matrix modifications instead of the MAV variation. For the monitoring purposes, the NIR MAV values are calculated as follows: for a given set of effluents obtained from the same feed, a sample is chosen as “reference” (see Table 2). The spectra subtraction between the “reference” and the current sample is calculated. A Delta_MAV between both samples is predicted by the NIR model. If we determine MAV of the “reference” sample, the MAV from the current sample can be calculated from Equation 4.

The advantage of modeling the Delta_MAV rather than the MAV is that the influence of the major hydrocarbon families is strongly diminished, hence, the correlated NIR absorption is for the most part produced by the diolefins content variation. Indeed, this point is particularly important to quantify the low diolefins contents in the SHU effluents. For NIR modeling purposes for each set of samples of our calibration database, the choice of the “reference” effluent was realized in order to maximize the Delta_MAV.

Some G1 effluents spectra differences are illustrated in Figure 6 as example. For this set of samples, the MAV of the reference sample had a value of 1.4 mg/g and the other effluents had higher MAV values (5.3, 4.2, 3.1, 2.3 and 1.7 mg/g). The sense of arrows indicates the increasing severity of the process operating conditions since the diolefins content

TABLE 2
Principle of Delta_MAV model

	Sample number	Chosen as Reference?	X: spectral differences (responses)	Y: Delta_MAV (modeled property)
Feed A	1	yes	/	/
	2	no	spectrum ₁ - spectrum ₂	Delta_MAV ₁₋₂ = MAV ₁ - MAV ₂
	3	no	spectrum ₁ - spectrum ₃	Delta_MAV ₁₋₃ = MAV ₁ - MAV ₃
	4	no	spectrum ₁ - spectrum ₄	Delta_MAV ₁₋₄ = MAV ₁ - MAV ₄
	...	no
	m	no	spectrum ₁ - spectrum _m	Delta_MAV _{1-m} = MAV ₁ - MAV _m
Feed B	n	yes	/	/
	$n+1$	no	spectrum _n - spectrum _{n+1}	Delta_MAV _{n-(n+1)}} = MAV _n - MAV _{n+1}
	$n+2$	no	spectrum _n - spectrum _{n+2}	Delta_MAV _{n-(n+2)}} = MAV _n - MAV _{n+2}
	...	no

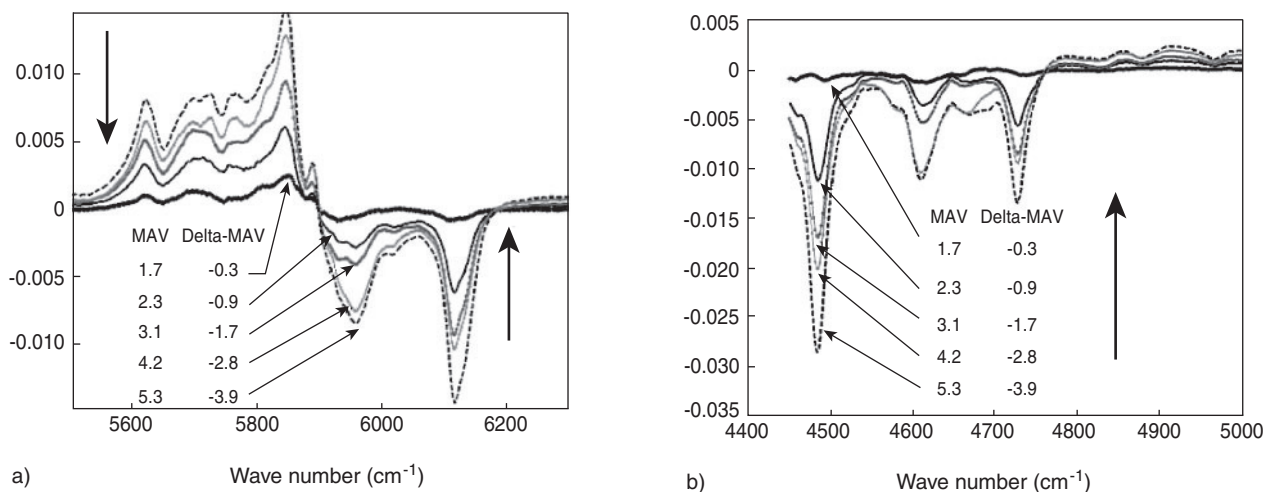


Figure 6

Difference spectra of hydrotreated FCC gasolines issued from feed G1 at different SHU severity conditions.

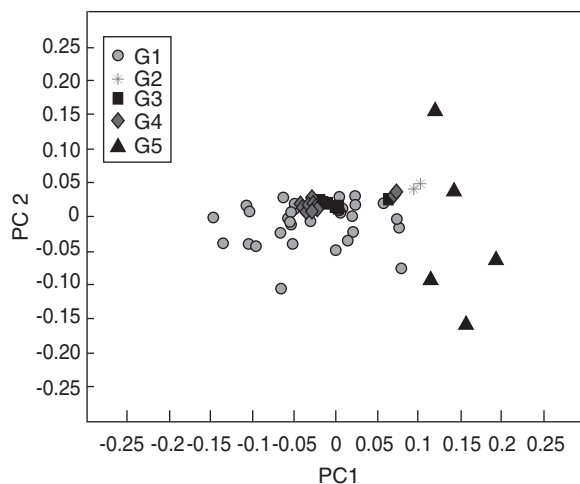


Figure 7

PCA scores plot of the NIR subtraction spectra of the hydrotreated FCC gasolines included in the calibration database. G1: feed 1; G2: feed 2; G3: feed 3; G4: feed 4; G5: feed 5.

(MAV) diminishes in the same sense. As expected, a variation of spectra is observed in the 6080-6160 cm^{-1} region that corresponds to the first overtone of the asymmetric $=\text{CH}_2$ stretch. The unsaturated bond absorption is also clearly enhanced in the 4700-4750 cm^{-1} NIR zone. In the 5500-5900 cm^{-1} region, the decrease of the spectra differences corresponds to the 1st overtone of the CH, CH_2 and CH_3 absorption bands. The same effect in the other sense is observed in the 5900 to 6200 cm^{-1} region. We can conclude that in the 5500-5900 cm^{-1} region we observe the formation of products from double bond hydrogenation and in the 5900-6200 cm^{-1} zone the progressive variation of unsaturated compounds content.

In comparison to the PCA of raw spectra (Fig. 5), the PCA of the spectra differences (Fig. 7) shows that there are no clusters related to the aromatics or the olefins content. The effluents issued from G1 (aromatics $\approx 28\%$, olefins $\approx 27\%$) are placed merged with the G2, G3 and G4 effluents (aromatics 8%, olefins $\approx 50\%$) in the 1st and 2nd scores projections. The G5 effluents are also close to the other samples. With the information provided by the PCA we can expect that the influence of the hydrocarbon matrix is negligible in this spectra database and that the enhancement of the unsaturated absorbance will help to correlate the MAV by NIR.

2.3.3 Partial Least Squares Results

A PLS regression was carried out using the calibration dataset constituted of difference spectra and Delta_MAV values. Six factors were chosen for the PLS model since root mean square error of the calibration calculated by cross validation did not diminish significantly after this number of factors and most of the database variance was accounted at this point: 99.5% and 97.6% of the X and Y variance respectively. The data correlate with a determination coefficient (R^2) of 0.978. The PLS scores of the calibration set are illustrated in Figure 8. As observed, a very similar distribution of the samples between de PCA and the PLS is obtained, therefore, the influence of the hydrocarbon matrix in the PLS model is strongly reduced with the spectra subtraction preprocessing. Since the property modeled by NIR is the Delta_MAV, the predicted NIR MAV for each sample can be calculated from Equation 2 as the difference between the reference sample MAV ($\text{MAV}_{\text{reference}}$) and the Delta_MAV_i . The predicted vs. measured MAV contents are illustrated in Figure 9 where the dotted line represents the reproducibility confidence interval (CI_R) of the reference method (measured

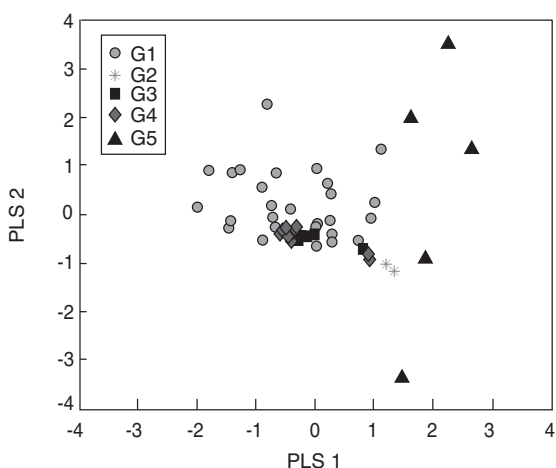


Figure 8

PLS of the Delta_MAV model. G1: feed 1; G2: feed 2; G3: feed 3; G4: feed 4; G5: feed 5.

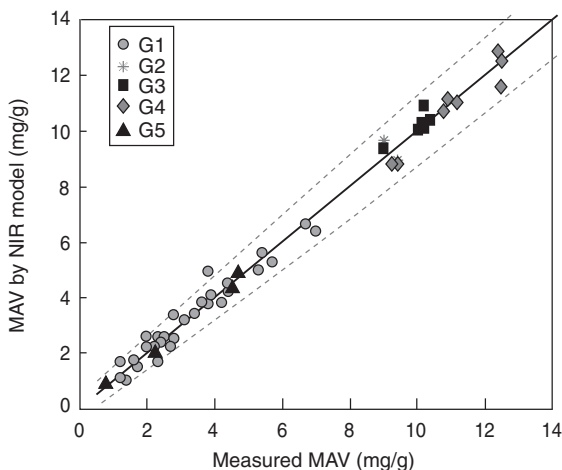


Figure 9

Calibration database: comparison between measured and NIR predicted MAV of FCC hydrotreated gasolines. G1: feed 1; G2: feed 2; G3: feed 3; G4: feed 4; G5: feed 5. Dotted line: confidence interval of intra-laboratory reproducibility.

MAV). As observed, an excellent agreement between experimental and NIR predicted values is obtained; 98% of the calibration dataset samples are predicted within the CI_R . Very good results are observed for all kinds of effluents (G1 to G5), hence there is no bias depending on the feed neither as a function of MAV content.

2.3.4 Application of the NIR Model for Pilot Plant Monitoring

The NIR “Delta_MAV” model was used for the monitoring of SHU pilot plants. The real time monitoring is important to determine if the MAV specification of the effluents is

respected, to verify the catalyst stability or if the process is under steady state for a given set of operating conditions (hydrogen pressure, temperature, liquid hourly space velocity). Moreover, for the process optimization our work must cover a large variety FCC feeds that are treated by the refiners. The predictive ability of the NIR model was checked following two criterions:

- the accuracy of the MAV predicted by NIR compared to the measured MAV;
- the sensitivity of the model to predict the MAV changes if the process operating conditions are modified.

For this reason, the NIR model was tested on three different experimental sets containing samples that were not included in the calibration dataset. These effluents are the external validation dataset. The effluents from each experimental set were obtained from 3 different feeds: G5, G6 and G7. As indicated in Table 1, some G5 effluents were used for calibration but another set of samples obtained from the same feed (G5) were only used for NIR prediction. It should be noticed that any G6 or G7 effluents were included in the calibration data, so we could verify the prediction ability of the model with samples having a different hydrocarbon matrix.

For each experimental set, the SHU operating conditions such as temperature, pressure or hydrogen flowrate were varied to study their effect on the diolefins conversion. For pilot plant monitoring the NIR MAV is determined daily (1 to 2 measures) and the MAV by the reference method (measured MAV) is realized once the unit reaches the steady state for a given set of operating conditions. For this reason, we dispose of more NIR MAV data compared to the measured MAV.

Table 3 presents the comparison between measured MAV and NIR predictions. The results are presented for each series of effluents issued from G5, G6 and G7 feeds. The \pm indicated after the measured MAV corresponds to the confidence interval of reproducibility (CI_R) of the reference method. A very good agreement is obtained for almost all the predicted points since the MAV predicted by the NIR model is within the CI_R of the measured MAV. All the NIR MAV values of G5 effluents are in excellent agreement with the measured MAV. Concerning the G6 and G7 effluents, it must be pointed out that no effluent from these feeds were included in the calibration dataset. For most of the effluents the NIR predictions are within the confidence interval of the reference method. For the samples predicted outside the CI_R , the NIR values are nearly close to the confidence interval. These results prove that the NIR model works well for feeds having a different hydrocarbon matrix (Table 3) compared to the samples included in the calibration data. This point is particularly interesting since the NIR modeling should have been carried out with different clusters depending on the hydrocarbon matrix (Fig. 5). With the subtraction spectra preprocessing, a more general NIR model was developed instead of three local models of very restricting application.

TABLE 3

Monitoring results: comparison between measured and NIR MAV

Series number	Feed reference	Sample reference1	Measured MAV	NIR MAV
1	G5	1	1.8 ± 0.6	1.9
		2	1.5 ± 0.5	1.7
		3	5.8 ± 0.9	6.2
2	G6	4	5.4 ± 0.9	5.4
		5	7.1 ± 1.0	6.9
		6	4.2 ± 0.8	2.8
		7	2.8 ± 0.7	3.2
		8	2.5 ± 0.7	2.6
		9	6.7 ± 1.0	6.6
		10	3.5 ± 0.8	3.7
		11	0.7 ± 0.4	0.6
		12	0.9 ± 0.4	0.9
		13	4.1 ± 0.8	3.6
		3	G7	14
15	6.4 ± 1.0			6.7
16	5.1 ± 0.9			6.0
17	2.8 ± 0.7			3.9
18	7.1 ± 1.0			7.8
19	3.3 ± 0.7			4.4
20	3.5 ± 0.8			4.4
21	8.4 ± 1.1			9.3
22	5.9 ± 0.9			6.4
23	3.7 ± 0.8			3.5
24	7.6 ± 1.0			8.2
25	3.5 ± 0.8			3.2
26	8.6 ± 1.1			8.5

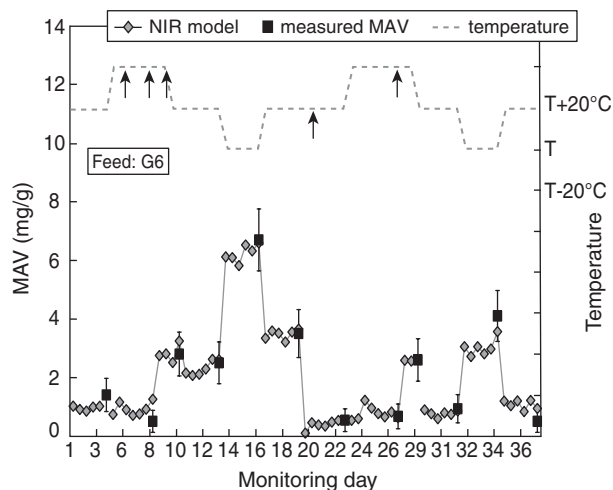


Figure 10

MAV monitoring trends of G6 feed (measured vs. NIR). \uparrow : variation of another operating condition like hydrogen or feed flowrate. Bar line: confidence interval of intra-laboratory reproducibility.

As indicated before, NIR model must be sensitive to predict the MAV changes in the effluents if the SHU operating conditions are modified. Figure 10 shows some monitoring results of the experimental sets obtained from the selective hydrogenation of G6 feed. The x axis represents the monitoring day. The left y axis corresponds to the MAV content (measured and predicted by NIR) and the right y axis illustrates the variations of the reactor temperature. The “ \uparrow ” symbol indicates the variation of another process operating condition like hydrogen or feed flowrate. As illustrated in these figures, the NIR predictions are especially useful to follow the performances of the SHU process, to determine the steady state and to determine the effect of the operating conditions on the diolefins conversion. For example in Figure 10, the 13th monitoring day, the reactor temperature was decreased of 20°C, thus, the diolefins conversion was diminished and the MAV increased as a result of this temperature change. The NIR model predicted in real time the MAV variation. The monitoring values (6.7 mg/g) are coherent with the measured MAV (6.6 mg/g). The temperature change after the 16th monitoring day was immediately reflected on the MAV content calculated by NIR.

Table 4 summarizes the modeling results for the calibration set and the monitoring results. The standard error of deviation of the reference method (σ_{exp}) was calculated as a function of MAV content (Equation 4) for each experimental set (calibration and external validation). The experimental standard deviation is usually compared to the root mean square error (RMSE) since this value is an estimate of the average prediction error of the model. The RMSEC was calculated using the calibration data, the RMSECV using the cross validation results of the calibration set and the RMSEP was obtained from the external validation results.

As indicated in Table 4, for the calibration dataset, the NIR model uncertainty determined by cross validation (RMSECV) is the same as the experimental standard deviation. The prediction error of the external validation dataset (RMSEP) is also comparable to the experimental uncertainty. We can therefore conclude that the NIR results are satisfactory. The average relative errors of the calibration and validation dataset are also very close: 10% and 11%, respectively. It must be pointed out that the diolefins contents are almost at trace level and for all samples the NIR predictions are of the same order of magnitude compared to the measured MAV. Taking into account these remarks, the average relative error between the NIR prediction and the reference method is within the acceptable limits.

CONCLUSIONS

The NIR modeling of the conjugated diolefins content selectively hydrogenated (SHU) FCC gasolines was presented in this work. Commonly, the conjugated diolefins are indirectly

TABLE 4
Global MAV NIR modeling results of calibration and external validation

Calibration set		External validation set	
Number of samples	58	Number of samples*	26
Feed references	G1, G2, G3, G4, G5	Feed references	G5, G6, G7
MAV range (mg/g)	0.7-12.5	MAV range (mg/g)	0.7-8.6
RMSEC	0.36		
RMSECV	0.49	RMSEP	0.59
σ_{exp}	0.49	σ_{exp}	0.45
average relative error	10%	average relative error	11%

* number of samples with measured MAV.

measured as the maleic anhydrid value (MAV). This method is extremely time consuming, therefore we tested the NIR modeling of the MAV analysis. The diolefins content in the SHU effluents is very low (< 1 wt%) and the presence of high contents of olefins that interfere in the NIR region with diolefins makes challenging to model these compounds at these low concentrations by NIR. Furthermore, the strong influence on the NIR spectra of the other major hydrocarbons (aromatics, paraffins, naphthenes, etc.) commonly leads to local NIR models, which are of restricted application and fastidious to update. To circumvent these difficulties, an original spectra preprocessing prior to multivariate modeling has been carried out. This preprocessing consists on the modeling of spectra subtractions between samples having very similar hydrocarbon matrix. The property predicted by NIR is therefore the samples Delta_MAV which is the MAV variation of between two samples. This approach is particularly adapted to the SHU process since the hydrocarbon matrix between the reactor inlet and outlet remains constant with the exception of diolefins and a low olefins fraction. Considering the precision of the reference method, the model could predict accurately the MAV values for both the calibration and the external validation datasets. Hence we can conclude that with the spectra preprocessing proposed in this paper, the hydrocarbon matrix influence has been strongly diminished while enhancing the diolefins NIR signal. As a consequence it was possible to accurately predict very low diolefins contents which are beyond the classical NIR quantification limits. Therefore, the NIR prediction of the conjugated diolefins content in selectively hydrogenated FCC gasolines via the MAV appears as an interesting tool to determine in real time the performances of the selective hydrogenation units.

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