PREDICTION OF PHYSICOCHEMICAL PROPERTIES OF FCC FEEDSTOCK BY CHEMOMETRIC ANALYSIS OF THEIR ULTRAVIOLET SPECTRUM

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Chemometric analysis by Partial Least Squares (PLS) has been applied in this work to correlate the ultraviolet spectrum of combined Fluid Catalytic Cracking (FCC) feedstocks with their physicochemical properties. The prediction errors obtained in the validation process using refinery samples demonstrate the accuracy of the predicted properties. This new analytical methodology allows obtaining in one analysis detailed information about the most important physicochemical properties of FCC feedstocks and could be used as a valuable tool for operational analysis.

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Se presentan resultados de la predicción de las propiedades fisicoquímicas de cargas a procesos de ruptura catalítica en lecho fluidizado (FCC) a partir del análisis quimiométrico del espectro ultravioleta visible de este tipo de fracciones del petróleo. Los errores de predicción observados en el proceso de validación, demuestran la confiabilidad de la metodología desarrollada. Esta nueva herramienta analítica permite obtener en un solo análisis, una información muy completa sobre las propiedades fisicoquímicas más importantes de las cargas a FCC y puede ser aplicada como método de rutina para el análisis operacional.

INTRODUCTION

The Fluid Catalytic Cracking (FCC) process is the most important refinery process in the North America context. The reason for this lies in the ability of the FCC process to convert more of the crude barrel into fuel than any other process. The chemical composition of the feedstock to the FCC unit is the most important variable in determining the basic yield structure from the unit. (Fisher, 1990)

Each type of hydrocarbon reacts under catalytic cracking conditions in certain definite ways. The major difference among hydrocarbons types is in their crackability or extent of conversion for a given set of operating conditions. In all cases, for each type of molecule, increasing the molecular weight or carbon number increases the crackability. A variety of primary and secondary reactions take place during catalytic cracking. These include chain rupture, isomerization, cyclization, dehydrogenation, polymerization, hydrogen transfer, and condensation. Hence, the result of cracking even a simple molecule such as normal paraffin is complex, (Bollas, Vasalos, Lappas, Latridis, & Tsioni, 2004).

Normal paraffins

Crack mostly to olefins and paraffins and give fair yields of very light gasoline (mostly C_5 and C_6 hydrocarbons). The normal paraffins are more difficult to crack than isoparaffins and naphthenes. The reaction rates and products of paraffin cracking are determined by the molecular size and structure.

Naphthenes and Isoparaffins

Tend to crack at about the same rate, but the product distributions are much different. Naphthenes produce relatively little gas and give excellent yields of gasoline. The gasoline is of better quality than that from paraffin cracking and contains appreciable quantities of aromatics, resulting from dehydrogenation of the naphthene rings.

Aromatics

Crack in several ways. The benzene ring is practically impossible to crack. Condensed-ring aromatics without side chains are converted to a limited extent, but almost entirely to coke. Alkyl aromatics with side chains containing at least three carbon atoms crack by the carbon located in the beta position to the aromatic ring (beta fission) leaving one or more methyl radicals linked to the ring. Monoaromatics dealkylate to give a high octane naphtha. With long side chains, secondary reactions will occur, resulting in products similar to those from the cracking of olefins and paraffins. Generally, more aromatic feeds give poorer FCC yields. A contributing factor to this general trend is that, as the number of ring structures in the feed increases, the likelihood increases that dehydrogenation from contaminant metals will cause multi-ring aromatics to form, leading to condensation and coking of the catalyst. The molecular structure of the aromatic hydrocarbons is another important issue regarding their crackability. The distribution of aromatics according to the degree of condensation clearly affects the rate of cracking. As the number of rings in a poly nuclear aromatic molecule increases, the rate of cracking decreases, although the aromatic content appears to remain the same. The net result of the catalytic cracking of aromatic hydrocarbons is moderate yields of gas, very little gasoline, large quantities of very aromatic cycle stock, and high coke yields. (Bollas, *et al.,* 2004).

Olefins

Seldom appear in catalytic cracking feeds, but their reactions are of interest because they are the primary products of other cracking reactions. Olefins heavier than about C_6 are extremely reactive. The products of olefin cracking are primarily propylene and butenes, along with butanes from secondary reactions. Some polymerization and cyclization takes place in olefin cracking to produce a small amount of cycle stock and fairly high coke yields (Bollas, *et al.,* 2004).

Non-hydrocarbon contaminants

Such as nitrogen, iron, nickel, vanadium, and copper compounds, act as poisons to cracking catalysts. Basic nitrogen, reacts with the acid centers on the catalyst and reduces the catalyst activity. However, the basicity of nitrogen compounds at cracking conditions can vary widely. The total nitrogen content is considered as a sound indicator for cracking inhibition by basic nitrogen compounds. The metals deposit on the catalyst

and cause a reduction in throughput by increasing coke formation. Finally, the sulfur content of an FCC feed has no major effect on the crackability of the feed, but it strongly affects the product distribution and quality (Bollas, *et al.,* 2004).

All the above chemical information is obtained by different analytical techniques. Mass spectrometry is maybe the most powerful one used to characterize a FCC feedstock. Sample analysis could be done over the complete sample by high resolution mass spectrometry (Fisher, & Fisher, 1974; Teeter, 1985) or by low resolution mass spectrometry using the Robinson method or over the saturates and the aromatic fractions of the sample using ASTM standard analytical methods (ASTM D2786 and ASTM D3239). By NMR (1H and 13C) it is possible to obtain a detailed information about carbon type analysis and the length of paraffinic chains and lateral paraffinic chains linked to aromatic rings (Bansal, Krishna, Chopra, & Sarpal, 2007). These two techniques allow for the differentiation of hydrocarbon families or carbon types. There are other methods like saturates, aromatics and resins analysis (SAR) that allow the separation of saturates (paraffins and cyclo paraffins), aromatics and resins, by a column chromatographic separation using different solvents (Harding, Zhao, Qian, Rajagopalan, & Cheng, 1996) and HPLC methods that allow a limited discrimination between different types that are present in these type of petroleum fractions (Qiang & Lu, 1999).

Because of the high costs and complexity of mass spectrometry and nuclear magnetic resonance methodologies used to obtain hydrocarbon type information and the required time to perform the standard test methods for determining the concentration of non hydrocarbon contaminants, getting all the above information on a daily bases in a refinery is far from practical. However, the process engineer requires fast and comprehensive information about the feedstock composition and properties in order to be able to define the optimal commercial operations of the unit.

Chemometrics emerges as a possible alternative for the process engineer because it allows predicting most of these properties from spectroscopic data of the feedstock to be processed. This information can be obtained quite quickly.

In the present chemometric models based on near infrared (NIR) and H-NMR are used for FCC feedstock characterization, and there are commercially available on-line analyzers based on these principles. (Gilbert, Gusmão de Lima F., & Bueno., 2004). Both of these options involved the use of samples of the place where the models are going to be applied and require also expensive analyzers and sampling conditioning systems.

Having this in mind this work was developed with the intent of giving cheaper and trustable tools to the process engineer in their daily work. This paper presents analytical methodology that allows obtaining most of the important information about the feedstock in a very short time and at a very low cost through the chemometric analysis of their ultraviolet spectrum. This work complements a previous paper performed to obtain hydrocarbon type analyses data from ultraviolet visible (UVVIS) spectral data analysis of middle petroleum fractions (Baldrich & Novoa, 2007) by generating information about the physical properties that are important for the FCC process and some additional chemical information like saturates and resins content and aromatic carbon type data that is used as feed for FCC optimization programs such as SHARC which was developed by Shell (Mo W., Hadjigeorge, Khouw, Van der Werf R., & Muller, 2002) and also could be applied to heavier samples that contain streams like demetallized oil (DMO) and hydrotreated demetallized oil (DMOH).

EXPERIMENTAL WORK

A total number of 104 samples were used in this work for the calibration set. All the samples were obtained from Ecopetrol S.A. refinery located at Barrancabermeja - Colombia that has four FCC units that process different type of feedstocks. Model IV FCC unit processes vacuum gas oil and Cusiana reduced crude oil; Orthoflow FCC unit processes mainly vaccum gas oil, demetallized oil (DMO) and recycle of cracked products; UOP1 FCC unit processes Cusiana reduced crude oil, hydrotreated demetallized oil (DMOH), vacuum gas oil and visbreaking naphtha and the UOP2 FCC unit which processes Cusiana reduced crude oil, DMOH and vacuum gas oil.

The physicochemical characterization of the different samples was performed following standard procedures. Table 1 includes the analysis methods used to characterize the samples. Table 2 presents the range of physicochemical properties of the calibration sample set.

Table 1. Reference methods used for fcc feedstocks characterization

Property	Reference Method	Measurement Units	Repeatability	Reproducibility
Density	ASTM D5002	Kg.L^{-1}	0,00105*X	0,004112*X
Microcarbon Resid (MCR)	ASTM D4530	%wt	3,161E-02*(X + 3)	4,681E-02*(X + 3)
Basic Nitrogen	UOP 269	%wt	0,0023	NS
Sulphur Content	ASTM D4294	%wt	0,02894(X+0,1691)	0,1215 (X+ 0,0555)
Aromatic Carbon Type			(1)	
Monoaromatic		%wt	0,09	NS
Diaromatic		%wt	0,04	NS
Triaromatic	SMS 2783-95	%wt	0,08	NS
Tetra Aromatic		%wt	0,22	NS
Penta Aromatic		%wt	0,19	NS
Hexa Aromatic		%wt	0,16	NS
Hepta+Aromatic		%wt	0,09	NS
Nickel	ASTM D 5863	ppm(wt)	0,2*X^0,65 (2)	1,3*X^0,53 (2)
Vanadium		ppm(wt)	1,1*X^0,5 (3)	0,33*X^0,9 (3)
SAR Analysis				
Saturates		%wt	2,1	4,0
Aromatics	ASTM D2007	%wt	3,3	3,3
Resins		%wt	1,2	1,8

MCR: Mmicro Carbon Residue   X: Value of the property   NS: Non Established

(1) Expected repeatability according the information published on the web page of Shell. For details about this method it could be contacted Shell Research people in AnalyticalServices@opc.shell.com
(2) 10 mg/kg -100 mg/kg
(3) 50 mg/kg - 500 mg/kg

UVVIS spectra were obtained in an Ultraviolet Visible Sectrophotometer HP 8453 with a diode arrangement detector. Near 40 mg of each sample are placed in a volumetric flask of 10 mL previously weighted in an analytical balance with a 0,1 mg sensibility and then are weighted and diluted to the mark with cyclohexane of analytical grade. After that, an aliquot of this solution varying between 0,2 mL to 0,4 mL is placed in a 10 mL volumetric flask and diluted to the mark with cyclohexane. A sample of this solution is placed in a measuring cell of 1 mm of path length and the UVVIS spectra of the sample is recorded between 190 nm and 400 nm. Sample spectra is normalized taking into account the weight of the sample, the initial dilution volume and the aliquot volume of this sample that is diluted to 10 mL.

Normalized spectra was introduced into unscrambler software V 9,7 of CAMO for making the principal components analysis of the spectral signals and for developing the PLS models used to predict the feedstock properties from the spectral data. 10 samples were used to make a validation of the predictive models. These samples were different to those used for developing the predictive models.

Table 2. Physicochemical properties range of the calibration sample set

Analysis	MINIMUM	MAXIMUM	AVERAGE
Sulphur (%wt)	0,687	1,213	0,8773
Density (15.6°C) (Kg.L^{-1})	0,9169	0,9403	0,9298
API Gravity	18,9	25,2	20,7
Basic Nitrogen (%wt)	0,045	0,077	0,0623
Micro Carbon Resid (%wt)	0,33	5,35	1,69
Nickel (ppm)	0,59	6,74	3,22
Vanadium (ppm)	1,11	9,13	4,54
Saturates (%wt)	43,4	60,9	49,17
Aromatics (%wt)	33,3	50,4	44,73
Polars (%wt)	2,8	9,6	6,11
AROMATIC CARBON TYPE			
Monoaromatic Carbon(%wt)	4,17	5,65	4,78
Diaromatic Carbon (%wt)	3	4,19	3,55
Triaromatic Carbon (%wt)	3,04	4,39	3,66
Tetra Aromatic Carbon (%wt)	1,59	2,51	1,92
Penta Aromatic Carbon (%wt)	0,48	0,89	0,68
Hexa Aromatic Carbon (%wt)	0,17	0,34	0,25
Hepta+ Aromatic Carbon(%wt)	0,14	0,71	0,35

RESULTS

The UVVIS spectra of all the samples used on this research are shown in Figure 1. The wavelength range of all the spectrums shown is 190 nm to 400 nm.
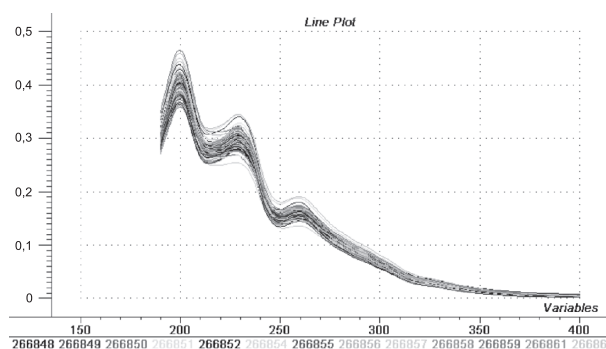

Figure 1. UVVIS spectral data of reference samples

The score plot obtained in the principal components analysis of spectral data shown in Figure 2, distinguishes between three clusters of different samples: one that corresponds to Model IV FCC feedstocks, the other to the Orthoflow FCC unit feedstocks, and the last one corresponds to UOP2 FCC feedstocks. UOP1 FCC feedstocks appear in two of the clusters (Orthoflow and UOP2 clusters). It should be mentioned that the Model IV FCC unit process gas oils and reduced crude oils, meanwhile Orthoflow unit process gas oils and demetallized oil (DMO). UOP1 and UOP2 proccess DMO, DMOH (hydrotreated demetallized oil) and gas oils. So, the principal components analysis gives results that agree with the nature of the samples.

The correlation of these spectrums with the physicochemical properties of the samples by a mathematical approach (PLS) allows the development of the different models for predicting feedstock properties. The equations that represent each model are not included because of their complexity. The internal cross validation routine was used to validate the consistency of the data.
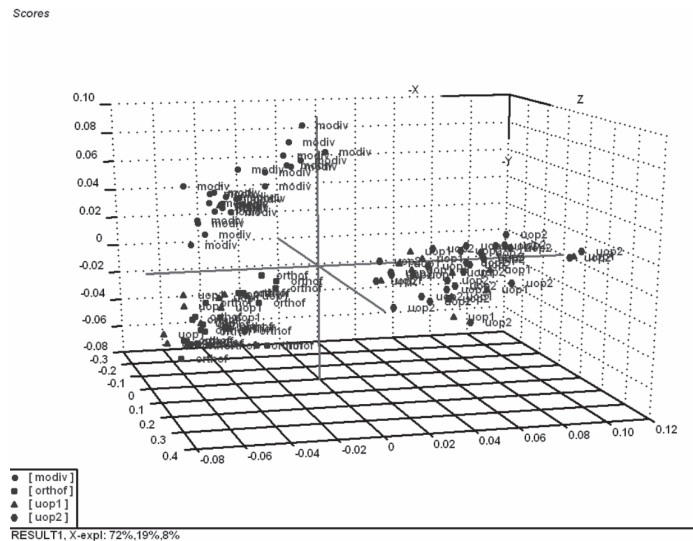
Figure 2. Principal components analysis (PCA) of UVVIS spectrums of Barrancabermeja FCC feedstocks

Table 3 includes information about the number of required components, explained variance in X (physicochemical properties) and Y (spectral data), the square root of the calibration and prediction coefficients by cross validation method and the square root of the calibration and prediction errors.

Table 3. Statistical data that shows the performance of the predictive models

PROPERTY	REMOVED SAMPLES NUMBER	COMPONENTS NUMBER	EXPLAINED Y VARIANCE (%)	EXPLAINED Y VARIANCE (%)	SQUARE ROOT CALIBRATION	SQUARE ROOT VALIDATION	RMSEC	RMSEP
Micro Carbon Residue	7	5	95,94	99,51	0,9658	0,9594	0,12189	0,134
Basic Nitrogen	8	3	94,40	99,00	0,9473	0,9440	0,0021	0,0022
Sulphur	8	7	96,50	99,87	0,9722	0,9650	0,0213	0,0242
Nickel	7	3	88,63	99,05	0,8929	0,8863	0,5177	0,639
Vanadium	11	5	86,65	99,76	0,8822	0,8665	0,6099	0,656
Saturates	14	3	75,35	98,73	0,7798	0,7535	1,9890	2,139
Resins	18	3	79,50	98,72	0,8113	0,7951	0,6467	0,686
Monoaromatic Carbon	0	3	99,71	98,99	0,9973	0,9971	0,0148	0,016
Diaromatic Carbon	0	3	98,54	98,99	0,9866	0,9854	0,0277	0,029
Triaromatic Carbon	0	4	98,65	99,46	0,9883	0,9865	0,0271	0,029
Tetra Aromatic Carbon	4	2	95,49	78,61	0,9586	0,9549	0,0328	0,035
Penta Aromatic Carbon	1	4	98,95	99,44	0,9907	0,9895	0,0103	0,011
Hexa Aromatic Carbon	3	4	97,62	99,42	0,9792	0,9762	0,0059	0,0063
Hepta+Aromatic Carbon	1	6	99,14	99,66	0,9933	0,9914	0,0095	0,0109

Table 4. Evaluation of performance of the developed predictive models

PROPERTY	REFERENCED METHOD	AVERAGE VALUE	REPEATABILITY	REPRODUCIBILITY	RMSEP
Microcarbon Resid (Mcr)	ASTM D4530	1,69	0,1483	0,2195	0,134
Basic Nitrogen	UOP 269	0,0623	0,023	NA	0,0022
Sulphur Content	ASTM D4294	0,8773	0,0303	0,1133	0,0242
Aromatic Carbon Type	SMS 2783-95				
Monoaromatic		4,78	0,09	NA	0,016
Diaromatic		3,55	0,04	NA	0,029
Triaromatic		3,66	0,08	NA	0,029
Tetra Aromatic		1,92	0,22	NA	0,035
Penta Aromatic		0,68	0,19	NA	0,011
Hexa Aromatic		0,25	0,16	NA	0,0063
Hepta+Aromatic		0,35	0,09	NA	0,0109
Nickel	ASTM D 5863	3,22	0.43	2,42	0,64
Vanadium		4,54	1,288	2,34	0,66
SAR Analysis	ASTM D2007				
Saturates		49,17	2,1	4,0	2,1
Aromatics		44,74	3,3	3,3	2,9
Resins		6,11	1,2	1,8	0,7

Good predictive models correspond to those with high values for the square root of the calibration and prediction coefficients, low number of samples that must be removed for developing the model, low square roots of calibration and prediction errors and high values for the explained variances in X and Y data.

As a general rule all the models related to aromatics carbon type composition are good since they have the high values for the square root of calibration and prediction coefficients. Also, for the development of these models the number of samples removed to get a good correlationship is low.

In order to obtain the predictive models for other properties such as micro carbon residue, basic nitrogen, nickel, vanadium, saturates, resins and sulphur it was necessary to remove more samples than those that were removed for aromatic carbon type models developments. Samples that were removed presented data that were considered strange in the calibration data set, for example some samples show a micro carbon residue value of 5,6%wt that is not logic for theses types of samples. Other criteria used to remove some samples from the calibration data set come directly from the PLS regression analysis performed with the Unscrambler software. The score plots obtained in this analysis allow to observe the similarity between the different samples in terms of their spectra and the property values (Baldrich and Novoa, 2007).

According to the tabulated data, the models for predicting saturates and resins require a high number of samples removed and show the lowest explained variance in Y axis and the lowest values for the square root of calibration and validation coefficients. This indicates that these models are the least consistent of all.

The models for predicting the content of metals (Ni and V) require the remotion of less samples than those developed for saturates and resins contents prediction. It is remarkable to get good models for metals content

prediction taking into account the low concentration of these metals in the samples. This fact could be due to the high absorbance in the ultraviolet region of the electromagnetic spectrum of the organometallic compounds in which the metals are contained (Anderson and Klein, 2008).

Models for predicting micro carbon residue, sulphur and basic nitrogen show high values of explained variance in X and Y axes. So the performance of these models is expected to be good.

Table 4 makes a comparison between the repeatability and reproducibility expected for the evaluated properties (according the information of the referenced methods) and the square root of the standard prediction error (RMSEP) obtained by the cross correlation method used for the validation step. For sulphur and micro carbon residue these values were calculated according the tabulated equations using for X the average values of these properties observed in the calibration data set. All the tabulated RMSEP values are lower than the expected reproducibility so in principle, the methodology here developed is reasonable good for use as a process analysis method.

Models validation.

Tables 5A, 5B, 6A, 6B and 7 show the correlation between predictive and laboratory results for the validation sample set. The tabulated data demonstrate that the relative differences between predictive and measured values are small for most of the properties. The bigger differences are obtained for metals and resins contents but it could be said that the absolute values of the predicted properties are near the laboratory values and this fact allow to use the method as a good tool for following the properties of these type of petroleum blends for operational analysis. The standard deviation for almost all properties in the sample set used to validate the method are lower than the calculated reproducibility of the method obtained for the average value of the property using the equations given in the standard method. In all the cases but saturates aromatics and resins (SAR) analysis results it could be said that there is a linear relationship between the predicted and the measured value as could be observed on Figuras. 3 to 10.

All the above mentioned results demonstrate that the predicted results are very consistent with respect to experimental values.

Table 5A. Validation of the models for predicting density, microcarbon residue, sulphur and basic nitrogen in FCC feedstocks

Sample	DENSITY 15,6°C (kg.L⁻¹)			MCR(%wt)			SULPHUR (%wt)			BASIC NITROGEN (%wt)		
	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(% Rel)	Predicted	Lab	DIF(% Rel)
1	0,9320	0,933	0,13	1,80	1,96	8,25	1,0704	1,0640	-0,60	0,0662	0,066	-0,37
2	0,9322	2	0,18	1,89	2,07	8,66	0,7364	0,7190	-2,42	0,0707	0,072	1,87
3	0,9296	0,933	0,26	1,53	1,64	6,93	0,8294	0,8000	-3,67	0,0676	0,066	-2,40
4	0,9297	9	0,16	1,72	1,61	-7,05	0,7795	0,7330	-6,34	0,0684	0,068	-0,55
5	0,9326	0,932	0,18	2,01	1,79	-12,39	0,7261	0,7040	-3,14	0,0710	0,073	2,76
6	0,9234	0	0,33	0,52	0,46	-12,75	0,9865	0,9670	-2,02	0,0548	0,05	-9,69
7	0,9330	0,931	0,19	2,05	2,05	-0,14	0,7567	0,6960	-8,72	0,0733	0,073	-0,46
8	0,9300	2	0,16	1,54	1,78	13,37	0,8677	0,8530	-1,72	0,0666	0,066	-0,97
9	0,9237	0,934	0,32	0,46	0,46	-0,14	0,9885	0,9740	-1,49	0,0550	0,05	-10,07
10	0,9232	3	0,32	0,58	0,60	3,79	1,0292	0,9960	-3,33	0,0565	0,051	-10,76

Table 5B. Validation of the models for predicting metal content and SAR analysis of FCC feedstocks

Sample	NICKEL (ppm)			VANADIUM (ppm)			SATURATES SAR (%wt)			SATURATES SAR (%wt)			RESINS (%wt)		
	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)
1	4,99	6,27	20,42	7,03	8,07	12,78	47,74	43,70	-9,25	45,06	49,10	8,22	7,19	7,20	0,10
2	2,47	1,83	-35,26	3,58	3,44	-4,20	46,86	44,80	-4,61	46,03	49,50	7,00	7,10	5,70	-24,58
3	2,29	2,48	7,56	3,46	3,94	11,95	48,80	46,00	-6,09	44,70	48,10	7,06	6,49	5,90	-10,07
4	2,38	3,09	22,85	4,32	4,50	3,98	48,63	53,10	8,41	44,80	41,00	-9,28	6,56	5,90	-11,22
5	2,66	2,79	4,58	3,90	4,07	4,15	46,38	48,50	4,36	46,69	44,60	-4,68	6,93	6,90	-0,43
6	1,47	1,37	-7,00	2,11	2,59	18,42	53,46	53,90	0,82	41,53	41,70	0,40	5,01	4,40	-13,82
7	2,85	2,81	-1,28	3,92	3,96	0,86	46,39	46,80	0,88	46,29	48,40	4,37	7,33	4,80	-52,64
8	2,75	2,50	-9,99	4,35	4,37	0,40	48,99	46,30	-5,80	44,62	46,50	4,04	6,39	7,20	11,22
9	1,40	1,56	10,55	2,02	2,81	28,24	53,58	53,60	0,04	41,27	42,40	2,66	5,15	4,00	-28,66
10	1,58	1,67	5,43	2,20	2,96	25,83	53,36	53,10	-0,50	41,13	42,10	2,30	5,51	4,80	-14,70

Table 6A. Validation of the models for predicting aromatic carbon type (mono, di, tri and tetraromatic) in FCC feedstocks

Samples	C MONOAROMATIC (%wt)			C DIAROMATIC (%wt)			C TRIAROMATIC (%wt)			C TETRAROMATIC (%wt)		
	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)
1	4,58	4,57	-0,16	3,65	3,67	0,54	3,81	3,72	-2,47	2,05	2,04	-0,55
2	5,16	5,18	0,36	3,37	3,38	0,29	3,42	3,47	1,51	1,99	1,99	-0,03
3	5,01	5,02	0,10	3,44	3,44	0,06	3,48	3,51	0,86	1,90	1,81	-5,14
4	5,20	5,20	-0,05	3,44	3,51	1,86	3,45	3,46	0,38	1,96	1,94	-1,07
5	5,03	5,02	-0,10	3,22	3,23	0,37	3,31	3,31	0,01	1,94	1,94	0,13
6	4,58	4,60	0,36	3,62	3,59	-0,81	3,67	3,71	1,18	1,70	1,71	0,62
7	5,29	5,30	0,27	3,42	3,44	0,64	3,45	3,51	1,83	2,06	2,06	0,05
8	5,08	5,08	-0,06	3,59	3,61	0,65	3,61	3,64	0,80	1,99	1,97	-0,86
9	4,76	4,79	0,68	3,76	3,73	-0,71	3,76	3,86	2,60	1,77	1,78	0,50
10	4,66	4,69	0,57	3,64	3,63	-0,38	3,67	3,69	0,59	1,69	1,71	0,97

Table 6B. Validation of the models for predicting aromatic carbon type (penta, hexa and hepta+ aromatic) in FCC feedstocks

Samples	C PENTAROMATIC (%wt)			C HEXAROMATI (%wt)			C HEPTA+AROMATIC (%wt)		
	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)	Predicted	Lab	DIF(%Rel)
1	0,77	0,77	-0,15	0,29	0,28	-2,53	0,42	0,44	3,53
2	0,73	0,73	-0,13	0,27	0,27	0,51	0,39	0,39	0,79
3	0,68	0,69	2,03	0,25	0,32	22,44	0,34	0,34	-1,35
4	0,73	0,71	-2,18	0,27	0,27	1,51	0,37	0,36	-1,82
5	0,72	0,72	0,01	0,27	0,27	0,88	0,40	0,39	-1,32
6	0,50	0,51	1,09	0,18	0,18	-2,51	0,17	0,17	-0,68
7	0,76	0,76	-0,51	0,28	0,29	3,64	0,41	0,40	-1,85
8	0,73	0,72	-0,82	0,27	0,27	1,77	0,38	0,39	3,63
9	0,53	0,56	5,79	0,19	0,19	-0,79	0,18	0,18	-0,76
10	0,51	0,53	3,89	0,18	0,19	2,70	0,20	0,19	-3,27

Table 7. Validation test with samples not included in the calibration set

PROPERTY	REFERENCED STANDARD TEST	AVERAGE VALUE	REPRODUCIBILITY	OBSERVED DEVIATION		
				MAX	MIN	SAMPLE STANDARD DEVIATION
Density (kg.L^{-1})	ASTM D5002	0,9310	0,0038	0,0031	0,0012	0,0007
CCR (%wt)	ASTM D4530	1,4420	2,0793	0,2380	-0,2218	0,1429
Sulphur (%wt)	ASTM D4294	0,85	0,1101	-0,01	-0,06	0,02
Basic Nitrogen (%wt)	UOP 269	0,0635	NA	0,00	-0,01	0,0027
C Monoaromatic (%wt)	SMS 2783-95	4,95	NA	0,03	-0,01	0,01
C Diaromatic (%wt)		3,52	NA	0,07	-0,03	0,03
CTrairomatic (%wt)		3,59	NA	0,10	-0,09	0,05
CTETRAROMATIC (%wt)		1,90	NA	0,02	-0,09	0,03
CPENTAROMATIC (%wt)		0,67	NA	0,03	-0,02	0,01
CHEXAROMATIC (%wt)		0,25	NA	0,07	-0,01	0,02
CHEPTA+AROMATIC (%wt)		0,33	NA	0,02	-0,01	0,01
NICKEL (ppm)	ASTM D 5863	2,64	2,56	1,28	-0,64	0,52
VANADIUM (ppm)		4,07	2,97	1,03	-0,14	0,39
SATURATES (%wt)	ASTM D2007	48,98	4,00	4,47	-4,04	2,55
AROMATICS (%wt)		45,34	3,30	4,04	-3,80	2,50
RESINS (%wt)		5,68	1,80	0,81	-2,53	0,90
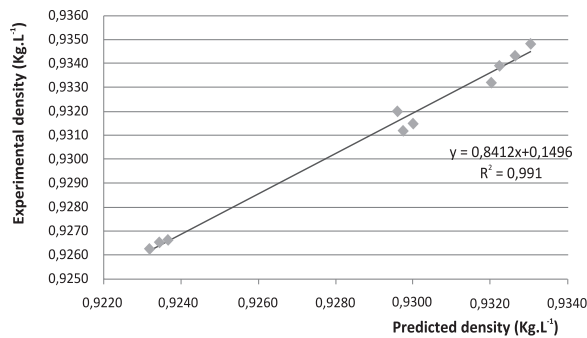
Figure 3. Correlation between experimental and predicted density
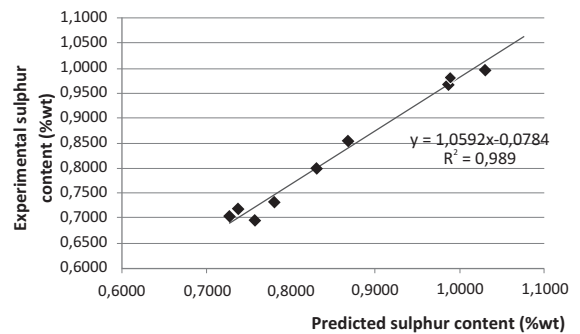
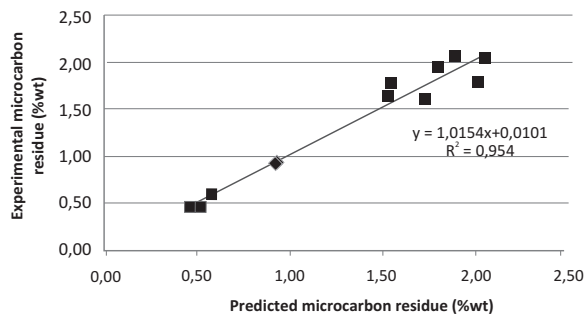Figure 5. Correlation between experimental and predicted sulphur content

Figure 4. Correlation between experimental and predicted microcarbon residue
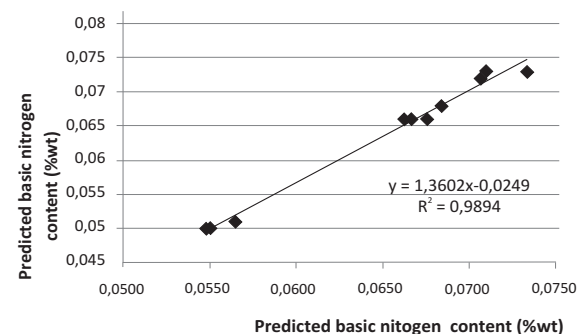

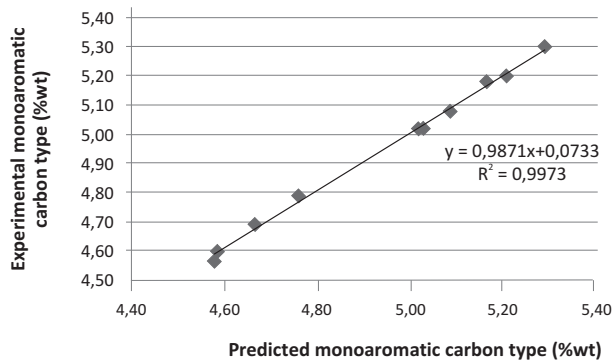Figure 6. Correlation between experimental and predicted basic nitrogen content

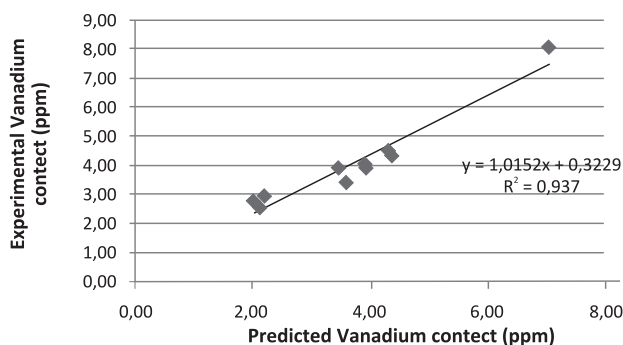Figure 7. Correlation between experimental and predicted monoaromatic carbon type

Figure 10. Correlation between experimental and predicted vanadium content
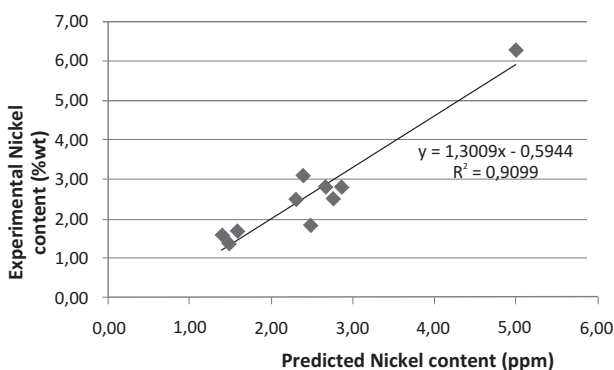

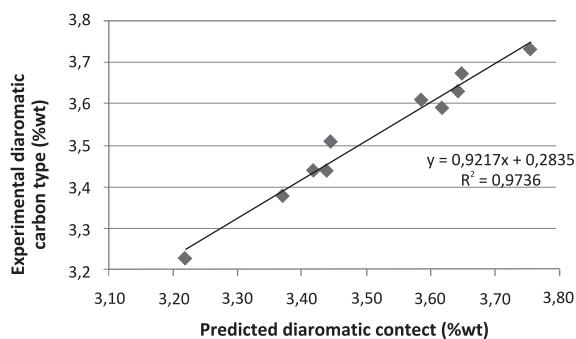Figure 8. Correlation between experimental and predicted nickel content

Feedstock crackability.

Using the same equations developed by Fisher 1990, the information of aromatic carbon type could be used as a way to predict the conversion and the yields to different products in the FCC process under the conditions of maximum conversion in Micro Activity Test (MAT) as follows:

$$\text{Carbon Precursors} = C_{Monoar}+100-\text{sum (total aromatic carbon)} \tag{1}$$

$$\text{MAT conversion} = 1,06*(\text{carbon precursors}) -10 \tag{2}$$

$$\text{Yield of } C_5+ \text{ gasoline} = 0,97*(\text{conversion}) -19,9 \tag{3}$$

$$\text{Yield of LCO} = 56 - 0,5*(\text{conversion}) \tag{4}$$

$$\text{Yield of DO} = 100 - \text{LCO} - (\text{conversion}) \tag{5}$$

$$\text{Yield of } C_3C_4 = 0,2*(\text{conversion}) \tag{6}$$

Where:

C_{Monoar} is the monoaromatic carbon (%wt) in the sample, C_{5+} gasolines is the debutanized gasoline obtained in the cracking process,

LCO is light cycle oil that corresponds to a diaromatic product, and

DO is decant oil that corresponds to a product with condensed aromatic compounds.

Figure 9. Correlation between experimental and predicted diaromaticcarbon type

The main difference between the data that could be obtained by this procedure and the one proposed

by Fisher (1990) is that the aromatic species here considered do not have any aliphatic chain linked to the aromatic ring. In spite of that, the information here considered could be used as a way for following the quality of FCC feedstocks.

Table 8 shows the theoretical results of prediction of maximum conversion and product yields applying the equations developed by Fisher (1990) to the validation data sample set from the aromatic carbon type data obtained in the lab by the Shell method and predicted using the here proposed methodology. Because the results are very similar, it could be said that the developed methodology allows obtaining similar results to the laboratory measurement of aromatic carbon type using the Shell methodology. In spite of that there were not included any experimental result of microactivity test with the samples used in this research, Fisher 1990, mentioned that using carbon type data yields of C_{5+} gasoline are overestimated and so is the calculated conversion value. He recommends the use of a combination of carbon precursors and hydrocarbon precursors to make a better estimation of conversion and yields in microactivity tests at maximum gasoline yield conditions. Hydrocarbon type data could be calculated from aromatic carbon type knowing the saturated compounds content of any sample in a simple way but this will be a matter of a new publication.

CONCLUSIONS

There is a strong correlation between the ultraviolet spectra of FCC feedstocks with some of their physicochemical properties like microcarbon residue, density, aromatic carbon type, basic nitrogen, saturates and aromatics.

Chemometric analysis of the UVVIS spectra of FCC feedstocks could be used as a tool for predicting most of the important physicochemical properties of the FCC feedstocks (microcarbon residue, sulphur, basic nitrogen, aromatic carbon type, saturates and aromatics contents and density) with average errors lower than 10% and may be used as a fast analytical method to monitor the quality of these types of petroleum streams. The developed methodology allows predicting the metal content (Ni and V) with good accuracy.

The linear correlation observed between the experimental and the predicted values of most of the evaluated properties indicates that the method is very sensitive to the variation of properties so it could be used as a trustable method for following the quality of FCC feedstocks in a fast way.

Table 8. Prediction of conversion and product yields at Micro Activity Test Unit (MAT) maximum conversion conditions from carbon precursor for the calibration sample set

Sample	Carbon precursors		MAT maximum conversion		C_{5+} Gasoline yield (%wt)		LCO yield (%wt)		DO yield (%wt)		Coke yield (%wt)		C_3-C_4 yield (%wt)	
	Pred	Lab	Pred	Lab	Pred	Lab	Pred	Lab	Pred	Lab	Pred	Lab	Pred	Lab
1	89,0	89,1	84,4	84,4	61,9	62,0	13,8	13,8	1,8	1,8	3,3	3,3	16,9	16,9
2	89,8	89,8	85,2	85,2	62,8	62,7	13,4	13,4	1,4	1,4	3,2	3,2	17,0	17,0
3	89,9	89,9	85,3	85,3	62,8	62,8	13,3	13,4	1,3	1,4	3,2	3,2	17,1	17,1
4	89,8	89,8	85,2	85,1	62,7	62,7	13,4	13,4	1,4	1,4	3,2	3,2	17,0	17,0
5	90,1	90,1	85,5	85,5	63,1	63,1	13,2	13,2	1,2	1,2	3,1	3,1	17,1	17,1
6	90,2	90,1	85,6	85,5	63,1	63,1	13,2	13,2	1,2	1,2	3,1	3,1	17,1	17,1
7	89,6	89,5	85,0	84,9	62,5	62,5	13,5	13,5	1,5	1,5	3,2	3,2	17,0	17,0
8	89,4	89,4	84,8	84,8	62,4	62,3	13,6	13,6	1,6	1,6	3,2	3,3	17,0	17,0
9	89,8	89,7	85,2	85,1	62,7	62,6	13,4	13,5	1,4	1,5	3,2	3,2	17,0	17,0
10	90,1	90,1	85,5	85,5	63,1	63,0	13,2	13,3	1,2	1,3	3,1	3,1	17,1	17,1

Pred: Obtained from aromatic carbon content predicted by the UVVIS methodology
Lab: Obtained from aromatic carbon measured by Shell methodology

All the above mentioned things make of this method a valuable tool for the operational analysis.

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