Prediction of the quality of coke obtained from vacuum residues by using spectroscopy infrared FTIR-ART

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Abstract. According to the trend of the heavy crudes and high demand of fuels, it is projected a considerable increase in the production of vacuum residues. With the purpose of taking advantage of these loads, the refineries have been improving conversion processes for the production of better quality distillates. However, as increasing the severity conditions and the species content of resins and asphaltenes high concentrations of coke are obtained. To provide an insight into the quality and cokes properties, in this study fifty (50) coke samples obtained from vacuum residues processed under conditions of thermal cracking and hydroconversion were selected. Each coke was analysed in detail with properties such as fixed carbon, volatile material, ash, and calorific value. Subsequently, a characterization methodology was developed to predict the properties of cokes, by using partial least squares regression, and infrared spectroscopy (FTIR-ATR) in the spectral range from 4000 to 500cm⁻¹. The models obtained by chemometrics allowed to predict the quality of the coke produced from vacuum residues with reliable responses in short periods of time.

1. Introduction
The increase in the production of heavy oil, the demand for clean fuels and the increase in the production of vacuum residues require the implementation of new studies and tools to improve technology conventional processes. Within the refining processes of vacuum residues, conversion technologies play an important role in the treatment of hydrocarbons 525°C, for obtaining products of low molecular weight and low content of contaminants such as metals and heteroatoms [1, 2]. In the hydroconversion processes and thermal cracking simultaneously large amounts of coke are generated, which contain high metal content, heteroatoms and aromatic structures polycondensates [3]. Reza et al. [3], Martinez at al. [4], and Hauser et al. [5], performed previous research related to the conversion of heavy crudes and vacuum residues under different conditions of severity. The results indicated that yields of liquids, gases and coke are clearly affected by temperature and catalyst. Meanwhile, hydrocarbons of large molecular size are converted to smaller fractions oriented towards light products with boiling points below 525°C, and a high relation hydrogen/carbon, H/C. The solids are mainly formed by the thermal cracking of aromatic polycondensates. Coke is an economic byproduct of refining crude oil with a high calorific value, but its physicochemical properties and its composition depend on the nature of vacuum residue and the process conditions. For this reason, it is important to perform an extensive characterization of the coke to determine its quality. Currently, methodologies have been developed that provide characterization information from the quality of products, in which monitoring and process control is common based on information provided by analytical techniques. Several authors have used the technique of chemometrics from partial least squares regression and spectroscopy techniques to predict physicochemical properties of heavy crude oil fractions and vacuum residues. For example, Falla et al.
[6] and Satya et al. [7] developed methodologies for estimating of distillation curves, SARA composition, CCR Conradson carbon residue, density and molecular weight for crudes and its heavier fractions using infrared spectroscopy technique. On the other hand, Alciaturi et al. [8], developed correlations to predict the properties in mineral coals as the percentages of moisture, fixed carbon, total sulphur, calorific value and C/H, from infrared spectroscopy. In this study, four models were developed to determine the properties as ash, fixed carbon, volatile material and calorific value of coke produced from vacuum residue in conversion conditions, by using partial least squares regression, and infrared spectroscopy (FTIR-ATR).

2. Experimental methodology

For the development of this work 50 coke samples obtained in conversion processes of vacuum residues of crude oil mixtures were selected. The characterization of samples was performed in order to determine its quality from analysis such as volatile matter (D 3175), ash (D 3174) and fixed carbon. The calorific value was determined using the norm ASTM D 5865. The characterization methodology petroleum coke was developed using multivariate analysis with principal components (PCA) and spectroscopy in the region of the middle infrared (FTIR-ATR). The measurements of spectra were performed in a Nicolet FTIR Thermo Scientific, which has a diamond ATR cell with incidence angle of 45°. Measurements were made in the region between 500 and 4000cm⁻¹ with a resolution of 4cm⁻¹ and 32 scans (scans). The air was taken as a reference spectrum. Prediction models of quality properties of coke were performed by principal component analysis (PCA), using the software The Unscrambler X version 10 (CAMO) and information of mid-infrared spectroscopy FTIR-ATR. Principal component analyses allow to determine the discrepant samples in the data set of calibration. For each one of the studied properties different spectral regions included between 650-1650cm⁻¹ and 2850-3000cm⁻¹ were selected. The root-mean-square error of cross-validation (RMSEP) and variance were used to estimate the optimum number of latent variables for each model.

3. Results and discussion

Table 1 shows the range of analysed properties of cokes selected in this study.

| Property             | Min   | Max   |
|----------------------|-------|-------|
| Volatile matter, % wt| 9.21  | 22.68 |
| Fixed carbon, % wt   | 73.94 | 85.64 |
| Ash, %wt             | 0.44  | 1.09  |
| Calorific value, KJ/g| 30.53 | 42.71 |

It is evident from data that the cokes obtained from the vacuum residues differ significantly in their properties. The volatile matter content, fixed carbon and ashes vary in a factor of 2.46, 1.16 and 2.48, respectively. Meanwhile the calorific value has a variation factor of 1.4. Figure 1 shows the FTIR-ATR spectra for five (5) cokes obtained from vacuum residues in the process of thermal cracking and hydroconversion under different operating conditions. The results show that cokes differ in its vibration characteristics across the spectrum, which indicates that these samples have significant variations in chemical composition. In the spectrum are identified vibrations of symmetric stretch and asymmetric for aliphatic bonds CH2 and CH3 between 2920-2850cm⁻¹, and deformation vibrations of the methyl and methylene group δCH3 and δCH3-CH2 near 1375cm⁻¹ and 1460cm⁻¹ were identified, respectively.

The wavelengths of deformation vibration of methyl groups are identified between 720-727cm⁻¹. Also, wavelengths were identified in the spectrum for polyaromatic rings between 870 and 740cm⁻¹ are identified. The assignment of stretching near the wavelength at 1600cm⁻¹ is attributed to double bond C=C aromatic. The displacement of the intensities in the infrared spectra for samples of coke is due to changes caused by the cracking reactions that experience the class compounds of the vacuum residues,
particularly the condensation of aromatic rings in the coking reactions. Therefore, the treatment of principal component models (PCA) was performed with the spectral information obtained in the range of wavelengths from 1700-650 and 3000-2800cm\(^{-1}\). Table 2 shows the principal components required to explain the properties of the petroleum cokes. Root Mean Square Error of Cross Validation (RMSEP) and variance were used to estimate the optimal number of principal components.

**Figure 1.** FTIR-ATR spectrum of cokes obtained from vacuum residues.

**Table 2.** Principal component analysis.

| Property               | PC | RMSEP | R\(^2\) |
|------------------------|----|-------|---------|
| Volatile matter, VM, % wt | 3  | 1.006 | 0.977   |
| Fixed carbon, FC, % wt  | 7  | 0.245 | 0.988   |
| Ash, %wt               | 6  | 0.022 | 0.976   |
| Calorific value, Cv, KJ/g | 6  | 0.209 | 0.985   |

The models show deviations between 0.2-1 and correlation coefficients higher than 97%, indicating high reliability of the developed models. Figure 2 shows that the results of prediction of fixed carbon and calorific value obtained from FTIR-ATR spectroscopy have small differences, with respect to the data obtained with the standard methodologies.

**Figure 2.** Calibration curve for the properties of petroleum coke: (a) volatile matter and (b) calorific value.
To determine the reliability of the models, it was necessary to calculate the overall error ($\%\delta_o$) in the prediction models, using the expression $\%\delta_o = \frac{\text{RMSEP}}{\text{MPE}} \times 100$. Where the $%$ average error (MPE) was determined from all samples. Figure 3 shows the results obtained for the overall error.

![Overall percentage of error ($\%\delta_o$) for the properties of petroleum cokes.](image)

Figure 3. Overall percentage of error ($\%\delta_o$) for the properties of petroleum cokes.

The developed models have overall error below to 5%, so they are favourable and can be used with confidence in predicting properties of petroleum cokes such as volatile, fixed carbon and calorific value.

4. Conclusions
The technique of infrared spectroscopy FTIR-ATR allows to identify regions with greater variance, which are in the ranges of 3000-2600 cm$^{-1}$ and 1700-650 cm$^{-1}$. In these spectral regions were obtained the predictive models of properties such as volatile material, fixed carbon and calorific with satisfactory results, because the chemical structure of samples of petroleum coke are related with the aromatic and aliphatic functional groups.

The proposed methodology for characterizing from information FTIR-ATR spectroscopy and chemometrics technique using PCA can predict properties such as fixed carbon, volatile matter, ash and calorific value of cokes produced from vacuum residues in short periods of time.

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