Physico-chemical characterization of products from vacuum oil under delayed coking process by infrared spectroscopy and chemometrics methods

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Abstract. Eight vacuum residues and their delayed coking liquids products from Colombian crude were studied by infrared spectroscopy with attenuated total reflectance (FTIR-ATR) and principal component analysis (PCA). For the samples the structural parameters of aromaticity factor (fa), alifaticity (A2500-3100 cm⁻¹), aromatic condensation degree (GCA), length of aliphatic chains (LCA) and aliphatic chain length associated with aromatic (LACAR) were determined through the development of a methodology, which includes the previous processing of spectroscopy data, identifying the regions in the IR spectra of greatest variance using PCA and molecules patterns. The parameters were compared with the results obtained from proton magnetic resonance (¹H-NMR) and ¹³C-NMR. The results showed the influence and correlation of structural parameters with some physicochemical properties such as API gravity, weight percent sulphur (% S) and Conradson carbon content (% CCR).

1. Introduction
The delayed coking is a chemical conversion process for exposure of samples at high temperatures. This is normally applied to heavy crudes and vacuum residues (VR) for light products such as gasoline and gas oils, also is obtained as residue carbon materials concentrated called coke with impurities presents in the initial charge as sulphur, nitrogen, vanadium, among others [1]. Vacuum residues (VR) are a heavy fraction of the process of vacuum distillation of oil, which until recently, was consider as a by-product of low commercial value because it concentrates the most complex molecules and many of the impurities present in the crude. these impurities include up to 6% w of sulphur, 0.1-2% nitrogen, 0.005-1.5% oxygen, forming functional groups such as carboxylic acids, aldehydes, ketones, thiophenes, pyrrole rings nitrogen bases such as pyridine, trace metals such as nickel, copper and vanadium, present as oxides, salts or also occupying the centre of organometallic porphyrin type structures [2]. Nevertheless, because oil is a nonrenewable energy resource and demand is growing, has generated the need to modify and implement new refining processes and characterization of this material.

Therefore many qualitative and quantitative researches approach have been conducted in order to characterize VR, in which; the nuclear magnetic resonance spectroscopy (NMR) of ¹H and ¹³C is a technique that has been widely used since 1958 [3]. This technique can provide information at the molecular level, as a percentage of aromatic carbons, n-paraffinic naphthenic, average length of the side alkyl chains, the degree of substitutions and condensations, in addition to providing the
percentage of compounds aromatic, aliphatic and naphthenic, etc. [4]. However, in recent studies have found that through spectroscopic data from infrared spectroscopy and chemometrics methods as principal components analysis (PCA) can calculated structural parameters related to physicochemical properties of samples. The aim of this paper is to demonstrate the capability of FTIR-ATR for use as a complementary technique or as an alternative method to the characterization of complex samples.

2. Experimental description
The properties (API gravity, percentage S and percentage CCR) of the VR and liquid products from the delayed coking process (10-20 psi and 490-510°C) were obtained according to standard tests [5-7]. FTIR-ATR analysis was carried out in a Nicolet iS 50 equipped with an ATR diamond cell with a simple reflexion. The angle of incidence of the IR beam was 45°. Each spectrum was acquired with 32 scans, 4cm⁻¹ resolution and wave number from 4000 to 400cm⁻¹.

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III NMR spectrometer equipped with a 5mm and 10mm probe resonating at the frequency of 400.16 and 100.62 MHz, for ¹H and ¹³C respectively. The conventional ¹H spectra were carried out using 4% w/v sample solutions in CDCl₃ (99.8% Merck) with zg30 pulse sequence, eight number of scans, 10s relaxation delay. The ¹³C NMR spectra of the sample were recorded using 20% (w/v) in CDCl₃ solutions, with Cr (acac)₃ 0.05M as paramagnetic relaxant. Total 1024 numbers of scans were collected using a 20s relaxation delay. All the ¹³C spectra were obtained with zgig30 bruker pulse sequence. Before analysis, the spectra obtained were corrected for phase and baseline and then each of them were separated into different regions which correspond to different types of protons and carbons according to their position in the molecule. Later, each spectrum was integrated thrice and averaged within the indicated regions.

The patterns molecules to find the most important signals in the infrared spectra are shower in Figure 1. This was selected according with the typical molecules structures present in VR [8].

3. Results and discussion
3.1. Data processing
The processing and chemometric analysis were performed with the software Unscrambler 10.3. The best methods were determined calculating the relative standard deviation (RSD) for signals representative signals of the spectra (see Figure 2).

Figure 1. Patterns molecules. (B) Anthracene, (K) dibenzothiophene, (C) cyclohexane, (D) benzoate ethyl, (J) naphthalene, (H) tetrahydronaphthalene, (I) pyrene, (E) phenanthrene, (F) fluorine, (G) methyl naphthalene and (A) hexadecylamine.

Figure 2. (a) Original spectra. (b) Area normalization spectra. (c) Identification of signals with patterns molecules (aliphatic chains and mono and polyaromatics rings)
3.2. FTIR-ATR spectrum analysis

In general for crudes and fractions, the most intense bands in the spectra appear near 3000 cm\(^{-1}\): C–H stretch in CH\(_2\) at 2918 cm\(^{-1}\) and 2853 cm\(^{-1}\). There are also intense bands at 1495 cm\(^{-1}\) and 1377 cm\(^{-1}\), corresponding to twisting scissors (symmetric and asymmetric) of the CH\(_2\) group. Other bands are found at low frequencies although of more complex assignment such as the deformation bands of aromatic C–H in the plane and outside of it.

3.3. Principal component analysis

Principal component analysis (PCA) is a well-known chemometric technique in multivariate data analysis for size reduction, displaying most of the original variability of data in a small space. PCA is commonly used for making a new dimension of data set by reducing the total number of variables into a small number, which are linear combinations of the original variables, orthogonal and contain the maximum variance within them [9]. As shown in Figure 3(a) the graph of scores allows correlation between neighbouring patches in the PC1-PC2 plane, in the Figure 3(b) loadings plot shows the X-variables in the PC1 that best describe each group, for distillates around 720 cm\(^{-1}\) ((CH\(_2\))\(_n\), n>4), finally the explained variance chart shows that the first three PCs contain 100% of the variance of the data (see Figure 3(c)).

![Image](a)

![Image](b)

![Image](c)

**Figure 3.** PCA plots (a) Scores. (b) Loadings in spectra. (c) Explained variance.

3.4. Structural parameters

The variables used to determine the structural parameters were found from the PCA analysis of the IR data and the signals identified with patterns molecules for deconvolution; taking into account a previous work done in our research group [8].

\[
LCA = \frac{\Sigma A_{2913-2929} + \Sigma A_{2850-2857}}{\Sigma A_{2860-2873} + \Sigma A_{2943-2960}}
\]

(1)

\[
GCA = \frac{A_{835-899 cm^{-1}}}{A_{733-775 cm^{-1}}}
\]

(2)

\[
f_a = \frac{A_{900-700 cm^{-1}}}{A_{3000-2800 cm^{-1}}}
\]

(3)

\[
LACAR = \frac{A_{704-730 cm^{-1}}}{A_{732-920 cm^{-1}}}
\]

(4)

\[
Alifaticity = \frac{A_{2800-3000 cm^{-1}}}{A_{2800-3000 cm^{-1}}}
\]

(5)

For all samples were calculated the found structural parameters (see Table 1). The results show that the structural parameters (1), (2) and (4) are higher for VRs than products. This is because the delayed
Coking process produces the bond breaking and therefore a shortening of aliphatic chains occurs, and also the accumulation of the polycondensates rings in the residual coke decreases GCA in distillates products. For the same reasons the alifaticity is higher for products (light content is greater). LCA, fa and LACAR parameters are commonly calculated by NMR, so the comparison of these was realized by IR and NMR spectroscopy. In the Figure 4 the black line represents the parameters calculated by NMR spectroscopy and the red bars the parameters calculated by FTIR-ATR. Since the data obtained by both techniques are different, trend of parameters is evaluated, not its numerical value. In general the trend is the same for both techniques.

**Table 1.** Structural parameters of VRs and products.

|                 | Vacuum Residues |          |          |          |          | Products |          |          |          |
|-----------------|-----------------|----------|----------|----------|----------|----------|----------|----------|----------|
|                 | LCA             | LACAR    | GCA      | Alifaticity | fa       | LCA      | LACAR    | GCA      | Alifaticity | fa       |
| Minimum         | 1.994           | 0.123    | 0.588    | 77.241    | 0.184    | 1.668    | 0.109    | 0.474    | 74.808    | 0.214    |
| Maximum         | 30.729          | 0.227    | 12.246   | 853.487   | 0.319    | 21.177   | 0.190    | 0.734    | 818.553   | 0.407    |
| Average         | 23.265          | 0.183    | 2.216    | 701.386   | 0.238    | 16.058   | 0.148    | 0.559    | 755.222   | 0.269    |

**Figure 4.** Structural parameters calculated by NMR and IR-ATR data.

3.5. **Correlation between structural parameters and properties**

To correlate the physicochemical properties of the samples with the calculated parameters, a multiple lineal regression (MLR) was performed (see Table 2).

The F ratio, $\frac{MS_{model}}{MS_{error}}$, was positive and greater than 66.6 for all models indicating that much of the total variance is being described by the fitted model. This is confirmed by the $R^2$ value which was close to 1.

**Table 2.** Results of MLR models.

| Properties | F ratio | Residual Average | $R^2$ |
|------------|---------|------------------|-------|
| PI         | 139.8   | $\pm$ 1.3        | 0.99  |
| %w S       | 156.5   | $\pm$ 0.2        | 0.98  |
| %w CC      | 66.6    | $\pm$ 0.6        | 0.98  |

4. **Conclusions**

This work demonstrates through determining structural parameters is possible to identify and correlate the molecular changes of VRs when they are submitted to the Delayed Coking process with physicochemical properties.

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