Structural study of colombian coal by fourier transform infrared spectroscopy coupled to attenuated total reflectance (FTIR-ATR)

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The most important Colombian coals were studied using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy. The ATR-FTIR spectra were used to obtain structural parameters of coal and correlating these structural parameters with the rank of the coal. The structural parameters, methylene-methyl ratio (CH_2/CH_3), aromaticity factor (f_a), aliphatic-aromatic ratio (H_{al}/H_{ar}) were determined directly from the ATR-FTIR spectra and f_a was evaluated from spectra data and an elemental analysis in coals studied here. The aliphatic and aromatic regions were considered between 3000 - 2800 cm^{-1} and 912 - 670 cm^{-1}, respectively.

Keywords: Coal; FTIR-ATR; coal rank; colombian coal.

Carbones de las zonas de mayor explotación carbonífera de Colombia fueron estudiados por ATR en el infrarrojo medio. Se presentan el análisis próximo y último de los carbones. Para cada muestra se obtuvieron parámetros estructurales como relación metileno/metilo (CH_2/CH_3), factor de aromaticidad (f_a), Relación hidrógeno alifático/hidrógeno aromático (H_{al}/H_{ar}). Estos parámetros fueron determinados utilizando datos espectrales y el análisis elemental de los carbones estudiados aquí. Además se pudo establecer que la Reflectancia Total Atenuada es una técnica que permite estudiar los carbones de manera rápida y económica respecto a la FTIR convencional. Este estudio se centró en el análisis de tres zonas del infrarrojo medio: 3000 a 2800 cm^{-1} y 912 a 670 cm^{-1} donde se aprecian cambios estructurales que permiten diferenciar un carbón de otro.

Descriptores: Espectroscopia FTIR-ATR; carbón; carbones colombianos.

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1. Introduction

Coal is the most abundant hydrocarbon resource on earth; therefore coal structure should be well understood for its effective utilization. Coal is a heterogeneous aggregate formed of cross-linked molecular network organic components. Coal is also considered as an organic polymeric material, with some inorganic impurities [1]. The study of coal structure presents numerous problems due to heterogeneity, non-crystalline and insolubility. Fourier transform infrared (FTIR) spectroscopy has been used extensively for the study of coal structure and for the characterization of solid and liquid products of coal processing. The infrared spectrum provides important information on molecular structure, especially the functionalities of organic compounds. Early works, on coal characterization using FTIR, were carried out by Painter *et al.*, Solomon and Carangelo, *et al.* [2-10]. Due to the structural complexity of coal, some studies on FTIR [8-12] have done assignments of particular bands to various functional groups.

Most quantitative infrared studies of coal have employed the KBr pellet methodology. There are several disadvantages to this procedure, the most important being that samples must be ground to a fine enough size that maximum absorption is

reached and that only 1-3 mg of coal is used in each pellet [13]. In order to minimize sample preparation, the diffuse reflectance (DRIFT), attenuated total reflectance (ATR) and photoacoustic (PAS) methods developed in the late 1970s have also been used to obtain infrared spectra of coals. Diffuse reflectance Fourier transform spectroscopy (DRIFT) is a much simpler technique than conventional FTIR. The first in applying DRIFT on coal were Fuller and Griffith [14], who attempt to relate the intensities of several bands to the coal ranks. DRIFT has been used to determine the degree of coalificationv and carbonization in coal samples [15-16]. Mean-

TABLE I. Samples of coal studied.

Sample	Bed	Location	Rank♣
COL 1	Cucunubá	Cundinamarca	ND
COL 2	Cerrejón	Guajira	ND
COL 3	Jagua	Cesar	ND
COL 4	Guachetá	Cundinamarca	ND
COL 5	Santagueda	Caldas	Anthracitic
SC*	–	–	Bituminous

*Standard Coal NIST1632b, ♣ND: Not Determined

TABLE II. Proximate analysis of studied coals

Sample	Bed	Location	Rank	%FC	%VM	%Ash
COL 1	Cucunubá	Cundinamarca	ND	49.42	37.04	10.3
COL 2	Cerrejón	Guajira	ND	54.73	36.80	0.98
COL 3	Jagua	Cesar	ND	55.67	38.03	0.40
COL 4	Guachetá	Cundinamarca	ND	65.30	28.53	4.54
COL 5	Santagueda	Caldas	Anthracitic	75.34	8.37	12.49
SC*	–	–	Bituminous			

* Standard Coal NIST1632b; FC: Fixed Coal; VM: Volatil Material

TABLE III. Ultimate analysis of the studied coals (wt% daf).

Sample	C	H	N	O_{diff}	S
COL 1	78.96	5,70	2.89	10.73	1,71
COL 2	79.57	5.60	1.33	12,44	1.05
COL 3	81.53	5.72	1.71	10.70	0.34
COL 4	86.80	5.16	3.24	3.86	0.95
COL 5	90.54	2,56	1.21	5.70	-
SC	82.47	5.30	1.67	8.53	2.03

daf: Dry ash free

while, Painter *et al.* and Golver *et al.* studied, with DRIFT, the pyrolisis coal and heat-treated coal products, respectively [17-18]. Although DRIFT is a very simple technique, it has been displaced by other methods, because it presents problems when attempting quantitative measurements due requires an optically thin, highly scattering sample [17].

On the other hand, application of ATR spectroscopy reduces the sample preparation procedure. The only necessary condition is the optical contact of the sample and the reflection element. Therefore, the influence of fine grinding and matrix material (KBr, nujol) may be avoided. The fact that there is no scattering of radiation interacting with the sample is another advantage. Therefore, a multi-reflection element can be applied, producing good-quality spectra. Moreover, besides very finely dispersed particles (about 1 μm) it is possible to record spectra for samples of coal with larger particles of several dozens of micrometers, *e.g.*, 50-60 μm, which is practically impossible with the transmission method [19]. The basic disadvantage of the ATR method is the lack of mathematical description which would make it possible to perform a quantitative interpretation of the spectra. The quantitative analysis of solid samples may not be precise due to the fact that the intensity of the bands depends on the size of the grains. For quantitative studies to be performed, the samples have to be of the same grain size. In addition, ATR is very dependent upon good, reproducible contact between the sample and the reflection element [20].

In this work, FTIR-ATR spectroscopy has been applied to the characterization and quantitative structural study of Colombian coals using structural parameters as CH_2/CH_3, f_a, and H_{al}/H_{ar}. These parameters such make it possible to obtain some observations in order to know the maturity grade of Colombian coals.

2. Experimental

A group of five coal samples collected from different Colombian regions (Table I) were ground to <56 μm size. To avoid spectral perturbations at 3400 and 1630 cm^{-1}, the adsorbed water was removed maintaining coal samples in a vacuum at 353 K overnight before using it.

The FTIR-ATR spectra were recorded on Shimadzu IR-Prestidge 21 equipment by the accumulation of 64 scans with a spectral resolution of 4 cm^{-1} over the range of 4000-650 cm^{-1}. The spectrometer was equipped with deuterated triglycine sulfate (DTGS) detectors and a Pike Miracle attenuated total reflectance (ATR) diamante cell with simple reflection and incidence angle of 45 °. To assure that sample bellows remained in close contact with the ATR crystal during spectral measurement, an adjustable pressure system was used. After the measurement of the spectra, the remaining sample in the crystal was removed with a soft paper rinsed using with small quantities of petroleum ether. The time taken to acquire 64 scans was approximately 30 seconds. Background spectra of air were collected for every sample immediately before the collection of the sample single-beam spectrum.

3. Results and discussion

3.1. Qualitative analysis of spectra

Tables II and III present the proximate and ultimate analysis of samples studied here, while FTIR-ATR spectra are shown in Fig. 1. The spectrum feature is very similar with the exception of the COL5 sample. The spectrum of the COL sample5 shows a high content of aromatic structure (intense band in the region from 900 to 700 cm^{-1}). In the spectra of the COL1, COL2, COL3, COL4 and SC samples, it is possible to observe characteristic bands of aliphatic

groups (3000-2800 cm^{-1} and 1450-1380 cm^{-1}) and aromatic groups (3060, 1600 and 900-700 cm^{-1}).

The relative intensities of bands in the spectra are in agreement with the ultimate analysis of the samples. The COL1 spectrum presents intense bands around 1000 and 500 cm^{-1} corresponding to mineral material. In addition, the high content of oxygen in COL1 is evidenced with the presence of the band between 3600 and 3000 cm^{-1} assigned to OH groups.

Around 2750 and 3200 cm^{-1} one can observe a group of overlap bands, corresponding to aliphatic and aromatic functional groups. In order to determine the aromaticity factor it is necessary to perform de-convolution in this spectral region (Fig. 2). Deconvolution makes it possible to know the precise position, width, height and areas of each band. From 2750 to 3000 cm^{-1} the bands are attributed to CH$_3$ and CH$_2$ (aliphatic), and after 3000 cm^{-1} the bands are attributed to CH aromatics.
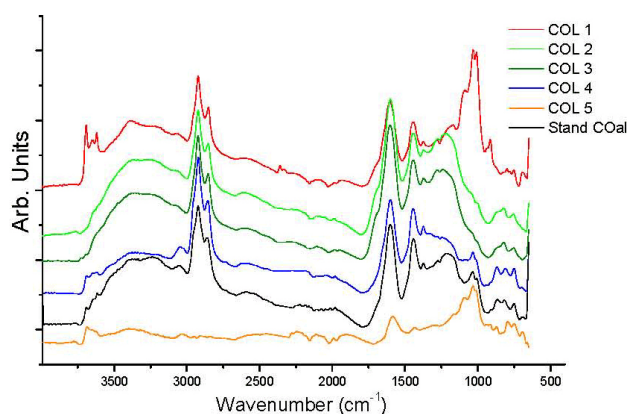

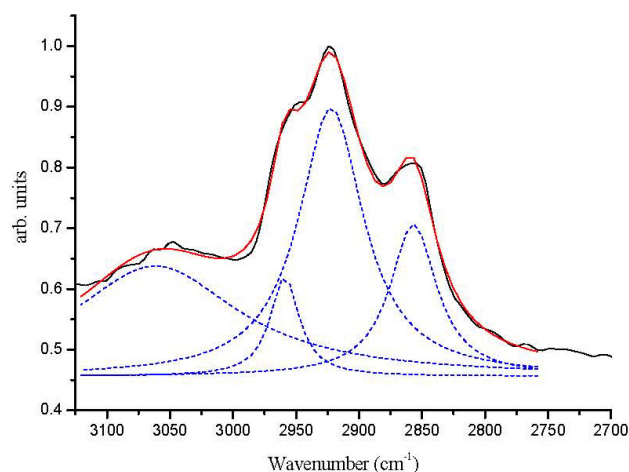
FIGURE 1. FTIR-ATR Normalized spectra of coals.

FIGURE 2. De-convolution of region from 3200 to 2750 cm^{-1}. Black line: original spectra; dotted blue line: de-convolution bands and red line: re-constructed spectra.

3.2. Structural parameters

The aliphatic (H_{al}) and aromatic (H_{ar}) hydrogen contents were determined from the integrated absorbance areas of the bands at 2800-3100 and 700-900 cm^{-1}, respectively. We have used the extinction coefficients determined by Solomon and Carangelo [11] to convert integrated absorbance areas to concentration units, which were 684 and 744 abs cm^{-1} mg cm^{-2}, respectively.

Apparent aromaticity, f_a, of the samples was calculated by using the method of Brown and Ladner [21]:

$$f_a = 1 - \left(\frac{C_{al}}{H_{al}} \right) \left(\frac{H_{al}}{H} \right) \left(\frac{H}{C} \right) \qquad (1)$$

where H/C is the hydrogen-carbon atomic ratio calculated from elemental analysis, H_{al}/H is the fraction of total hydrogen present as aliphatic hydrogen, and C_{al}/H_{al} is the hydrogen-carbon atomic ratio for aliphatic groups, which is generally taken to be 1.8 for coals [22]. The ratio H_{al}/H is usually obtained from ^{1}H NMR analysis, but this technique is not available to all research laboratories by its high costs of operation. FTIR spectroscopy offers, due to its ease and low costs of operation, an alternative way to obtain it as well as other structural parameters.

Coal can be considered a polymeric material with monomers of several sizes. According to this conception of coal structure, van Krevelen [22] proposed the structural parameter $(R/C)_u$, which represents the number of rings by atomic carbon by monomer. Therefore, this structural parameter makes it possible to know the degree of aromatic ring condensation:

$$\left(\frac{R}{C} \right)_u = 1 - \frac{f_a}{2} - \frac{H/C}{2} \qquad (2)$$

The parameter CH_2/CH_3, which is related with length aliphatic chains, was obtained according Eq. (3) by de-convolution of the region from 2750 to 3200 cm^{-1} (Fig. 2) containing 2922 and 2854 cm^{-1} bands attributed to stretching asymmetric of CH$_3$ and CH$_2$ groups, respectively. If this parameter is higher, it is possible to infer that aliphatic chains bounding aromatics rings are longer, since a coal with a high concentration of CH$_3$ has a compact structure with less space between aromatic clusters:

$$\frac{CH_2}{CH_3} = \frac{A_{2922cm^{-1}}}{A_{2952cm^{-1}}}. \qquad (3)$$

Another parameter that is related to the aromatic factor and with a grade of maturity of coals is A_{ar}/A_{al} according to Eq. (4) [23]:

$$\frac{A_{ar}}{A_{al}} = \frac{A_{900-700cm^{-1}}}{A_{3000-2815cm^{-1}}}. \qquad (4)$$

The structural parameters calculated for the FTIR-ATR spectra are presented in Table IV. The results show that COL1 and COL 5 are the coals with the lowest and the highest rank, respectively, according to the ratio A_{ar}/A_{al} and the aromaticity factor f_a. The maturity grade (rank) of coal samples studied here increases from COL 1, COL 3, COL 2,

TABLE IV. Structural parameters deduced of PA-FTIR measurements.

Sample	A_{ar}/A_{al}	CH_2/CH_3	f_a(stan-desvt)		$(R/C)_u$	$H_{al}/(H\text{-}H_{OH})$	C_{ar}/A_{al}
COL1	0,147	2.51	0.65	0.0085	0.243	0,862	1.36
COL 2	0,273	2.89	0.65	0.0064	0.231	0,771	1.77
COL 3	0,222	2.60	0.68	0.0091	0.240	0,806	1.93
COL 4	0,318	1.27	0.71	0.0071	0.289	0,743	0.772
COL 5	2,26	1.33	0.95	0.0096	0.354	0,289	4,80
SC*	0,284	1.05	0.70	0.0072	0.263	0,764	1,18

* Standard Coal NIST1632b

COL 4 to COL 5. Generally, the content of fixed carbon is used to evaluate the rank of coal; this paper shows that it is possible to determine the rank of coal with greater accuracy using structural parameters extracted from FTIR spectra, especially, when the content of fixed coal in two types of coal is very close (COL 2 and COL 3).

4. Conclusions

The FTIR-ATR spectroscopy method has been used successfully to determine the structural parameters of Colombian coals. The method appears to be reliable and easy to use in comparison with other techniques such as Nuclear Magnetic Resonance (RMN) and conventional FTIR. In addition, it is possible to determine the rank of coal studied here, using the structural parameters f_a and $(R/C)_u$.

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