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Qualitative and quantitative ATR-FTIR analysis and its application to coal char of different ranks

Andrew O. Odeh

(Coal Research Group, Unit of Energy Systems, School of Chemical and Minerals Engineering, North-West University, Potchefstroom Campus, Potchefstroom 2520, South Africa)

Abstract: This paper analyzes the coal to char stages of char formation of six coals of different ranks by using Fourier transform infrared coupled with attenuated total reflectance (ATR-FTIR). The chars were obtained by coal pyrolysis carried out at temperature range of 450 ~ 700 °C. The data obtained shows the pragmatic disappearance of the aliphatic hydrogen content with increasing char formation temperature. Numerical evaluation of the spectra enabled the determination of aromaticity, f_a . The aromaticity was found to be between 0.66 ~ 0.79 for lignite, 0.75 ~ 0.90 for sub-bituminous, 0.84 ~ 1.00 for low volatile bituminous, 0.83 ~ 1.00 for high volatile bituminous, 0.94 ~ 1.00 for semi-anthracite, and 0.97 ~ 1.00 for anthracite respectively. With increasing rank of coal samples, spectra exhibit rising aromaticity and enhanced condensation of aromatic rings, whereas the aliphatic chain lengths decrease.

Keywords: qualitative; quantitative; FT-IR; coal char

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The complex and heterogeneous nature of coal and coal char makes investigations on understanding its molecular structure an on-going exercise among researchers globally. The understanding of the structural properties of coal would aid in the prediction of the behavior of coal during combustion, gasification and liquefaction processes. Several conventional (proximate, ultimate and calorific value analyses) and advanced analytical techniques such as scanning electron microscopy (SEM)^[1], solid-state nuclear magnetic resonance microscopy (SSNMR)^[2], high resolution transmission electron microscopy (HRTEM)^[3], X-ray diffraction spectroscopy (XRD)^[4], small angle X-ray scattering (SAXS)^[5], X-ray photoelectron spectroscopy (XPS)^[6], X-ray absorption near edge spectroscopy (XANES)^[7], Raman spectroscopy^[8] and Fourier transform-infrared spectroscopy (FT-IR)^[9] has been widely and extensively used in characterizing the chemical structural properties of coal. The characterization of the resultant chars from coal conversion processes has equally been extensively researched employing both the basic conventional and advanced analytical techniques^[10~16]. However, each of the analytical techniques has its own limitations and thus cannot completely explain the structural properties of coal and its coal char independently^[11,13,17]. FT-IR has been extensively

used for the characterization of coal and its subsequent chars as it provides important information on molecular structure, especially the functionalities of organic compounds. However, the potentials of the FT-IR has previously been restricted to only its qualitative use as some difficulties has been identified in obtaining quantitative information in FT-IR spectra. For example, in KBr pellet method, 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^[17], the diffuse reflectance Fourier transform spectroscopy (DRIFT) has its limitation attached to the requirement of optically thin and highly scattered sample^[18], while photoacoustic-FTIR (PA-FTIR)^[19] and attenuated total reflectance-FTIR (ATR-FTIR) spectroscopy disadvantage is based on the lack of mathematical description, which would make it possible to perform a quantitative interpretation of the spectra^[17,20].

Although many studies have been carried out to understand the structural variations in coal and its subsequent char, the importance of a systematic investigation of the transformation of coal to char using improved analytical technique such as Fourier transform-infrared spectroscopy (FT-IR) has not been adequately explored quantitatively to be best of our knowledge, to explain the structural transitions in coal to char.

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Corresponding author: Tel: +27 18 299 1991, Fax: + 27 86 654 5434, E-mail: odehandy@yahoo.com.

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This study uses ATR-FTIR for integrally probing the functional groups and structural changes in coal char during its slow pyrolysis done at various temperature intervals from 450 to 700 °C for 1 h at atmospheric pressure on six coals of different ranks. To achieve this, the selected coals were acid-treated in order to study the effect of the organic part only.

1 Experimental

1.1 Sample preparation

Six coals of varying rank were used; a lignite coal from Germany (LIG); a sub-bituminous coal from Nigeria (SUB); two South African bituminous coals (one is low volatile bituminous (BIT-LV) and the other, high volatile bituminous coal (BIT-HV); South African semi-anthracite (SA); and anthracite from South Africa (ANT). The coal samples were pulverized to coal particle size of $\leq 75 \mu\text{m}$ by employing a mechanical size reduction jaw crusher (Samuel Osborne (SA) LTD, model: 66YROLL) and a Fritsch P-14 rotary mill containing ceramic balls (Model number: 46-126). The required particle size of $-75 \mu\text{m}$ was finally obtained from screening the particles from the rotary mill using a $75 \mu\text{m}$ screen. All the samples were stored under argon in sealed bags.

The prepared coal samples were acid washed by sequential leaching with hydrofluoric acid (HF) and hydrochloric acid (HCl) as detailed in Strydom et al.^[21]. The HF (48%) and HCl (32%) were obtained from Associated Chemical Enterprise (ACE), South Africa.

1.2 Apparatus and procedure

The coal samples (40 g) were placed in a ceramic boat in a horizontal tube furnace at atmospheric conditions initially. The samples were flushed with nitrogen (AFROX, ultra high purity grade) at atmospheric conditions, to remove oxygen from the oven for 15 min at a flow rate of 1 L/min. The furnace was then heated at 20 °C/min to the target temperature, and held isothermally for 60 min. The target temperature ranged from 450 to 700 °C, while keeping the samples under a nitrogen atmosphere. The char samples were stored in sealed bags.

The conventional chemical analyses (proximate and ultimate analyses) of the raw coal, and acid-washed samples were performed according to the ISO 1928, ASTM 3172 and ASTM 3176 standards respectively at Advanced Coal Technology (ACT), Pretoria, South Africa.

The spectra used in obtaining the structural properties of both the coal and char were obtained

from the Fourier-transform infrared spectrometer equipped with an attenuated total reflectance (ATR-FTIR), model Perkin-Elmer Spectrum 400. The procedure of ATR-FTIR as detailed by Li et al.^[22] was used. In the ATR-FTIR method, the sample to be analyzed is placed directly into the sample cell, where a good and reproducible contact between the sample and the crystal of reflection is obtained non-destructively, and producing good quality infrared spectra.

The FT-IR spectra of the raw and thermal treated (chars) were recorded in the range of 4 000 ~ 650 cm^{-1} . The peak separation and quantitative calculation were performed using a curve fitting program of Origin 8.0 software. Selected regions of the FT-IR spectra were linearized for baseline correction by connecting the left and right points of the band area of the interval with a straight line. The band area of the regions 900 ~ 700 cm^{-1} and 3 000 ~ 2 815 cm^{-1} was integrated separately using the Origin software to obtain definite values. Aromaticity (f_a) was obtained from the ratio of aromatic band area in the 900 ~ 700 cm^{-1} region to the aliphatic and aromatic bands in the 3 000 ~ 2 815 cm^{-1} region following the method detailed in^[23]. The degree of aromatic ring condensation ($\frac{R}{c}$)_u was determined from the relationship^[17]:

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

Where f_a is aromaticity and H/C is the atomic hydrogen to carbon ratio expressed on dry ash free basis.

The degree of aromatic ring condensation accounts for the number of rings of atomic carbon by monomer, since coal is considered as a polymeric carbonaceous material with monomers of several sizes^[17]. The degree of aromatic ring condensation, like the aromaticity, is considered as a rank measurement parameter. These structural parameters provide evidence of the loss of aliphatic structures and oxygen-containing functional groups when coals are subjected to heat treatment processes such as pyrolysis, gasification and combustion. Also, the aromatic hydrogen tends to increase with increasing heat treatment temperature as a result of the different cross-linking behaviors.

2 Results and discussion

2.1 Qualitative analysis of spectra

Figure 1 and Figure 2 are used as examples to illustrate the spectra obtained from this study and to give a quantitative analysis of the coal to char

transition. The raw and the acid cleaned coal spectra for all the coal samples used in this investigation demonstrated a broad similar trend with a minimum shift of the band position of the acid cleaned sample to the left (Figure 1).

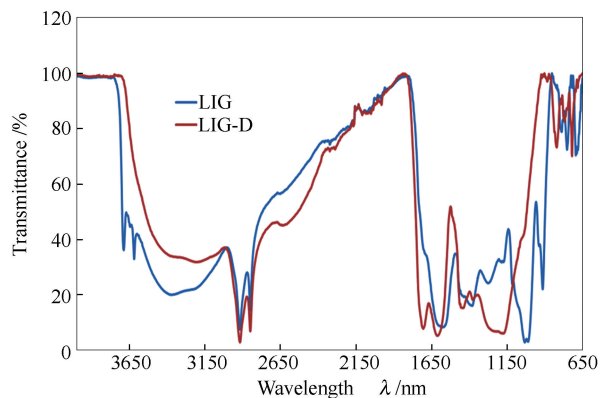


Figure 1 Spectral comparison between raw lignite (LIG) and acid cleaned lignite (LIG-D)

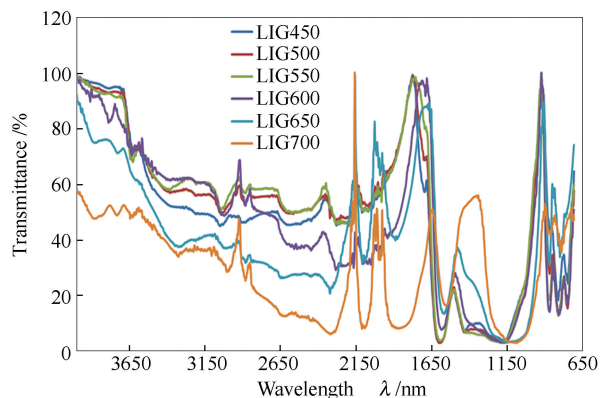


Figure 2 Spectral change with char formation temperature for lignite

The same story could be relayed concerning the heat treated coal samples (i. e. the coal chars) (Figure 2). The interpretation of the spectra was done using the detailed findings of many previous workers^[17,23-26]. It is known that the broad absorption band with maximum near 3300 cm^{-1} correspond to the hydroxyl ($-\text{OH}$) groups in the organic component of coal which consists mainly of phenolic OH or alkyl hydroxyls (peroxidic)^[17,23]. The broad absorption band at 3300 cm^{-1} overlay a weak broad band in the region of 3000 to 2700 cm^{-1} which is generally attributed to hydrogen bonded NH groups^[23]. The low rank coals (LIG and SUB) have the highest intensity band at this region probably because they contain the largest percentage of oxygen functional groups. Of interest also in this region is the intensity difference between the raw coal and acid cleaned coal, with the acid cleaned coal having a

higher intensity compared to the raw coal. This observation can be attributed to the impact of the acid cleaning of the coal (Figure 1). The small absorption band at $3030 \sim 3050\text{ cm}^{-1}$ is attributed to aromatic CH stretch, due to the fact that CH_3 content in this region is small and weak, while the aliphatic CH stretch is attributed to the region of $2920 \sim 2850\text{ cm}^{-1}$, with the CH_2 group being the dominant contributor to the region^[23]. As can be seen in Figure 1, the intensity of the aliphatic CH stretching absorption is significantly greater than that of the aromatic CH stretching for all the coal samples investigated in this study. The band region between 1900 to 1650 cm^{-1} corresponds to residual water vapor^[25], of which a small concentration of $\text{C}=\text{O}$ groups in the organic matrix of coal in this region is assigned the absorption band at 1700 cm^{-1} ^[25]. As can be seen in Figure 1, this band is more pronounced for the acid cleaned coal than the raw coal. Though some uncertainties still surround the assignment of the 1600 cm^{-1} band to only aromatic $\text{C}=\text{C}$ groups due to the fact that previous workers has reported the tendency of oxygen containing functional groups accentuating the intensity of this band, in this study, the band is assigned to poly aromatic systems and benzene rings due to the observed consistency exhibited in all the coal samples^[28]. The broad spectrum band at 1500 cm^{-1} is generally attributed $\text{C}=\text{C}$ bonds in benzene rings which is more visibly noticed in the acid cleaned coal compared to the raw coal sample (Figure 1)^[25]. Generally, the $1450 \sim 1440\text{ cm}^{-1}$ and $1380 \sim 1375\text{ cm}^{-1}$ bands corresponds to aliphatic bending modes, and $1261 \sim 1251\text{ cm}^{-1}$ band is attributed to $\text{C}=\text{O}$ stretching, due to the predominant presence of ethers and etheric oxygen^[29,30]. The absorption bands at 1091 , 1031 , 1010 cm^{-1} corresponds to ash in the coal, and as can be seen in Figure 1, this is more pronounced in the raw coal and did not appear in the acid cleaned coal^[26,27]. The bands between 900 and 700 cm^{-1} correspond to aromatic bending modes and are mainly due to aromatic HCC (hydrogen-carbon-carbon) rocking vibrations in aromatic and condensed aromatic ring systems^[17,31]. The assignments of every band of the coal and char spectra are shown in Table 1^[23]. Table 2 and Table 3 gives the conventional analyses of the raw and acid cleaned coal respectively, where the coals are listed in increasing rank.

Similar interpretation of the spectra as illustrated for the raw and acid cleaned coal can be given for the acid cleaned heat-treated coals (chars). In most of the spectra for the chars (obtained at temperature range of

450 ~ 700 °C), for instance, the 3 300, 2 950 ~ 2 850 and 1 450 ~ 1 440 cm^{-1} band did not appear (Figure 2). This may be explained by the facts that, increased substitution of the benzene ring is known generally to

weaken the band, and, as the degree of condensation increases, the band is displaced to smaller wave numbers and finally disappears in the strong absorption bands due to the impact of the heat treatment.

Table 1 Bands assignment observed on ATR-FTIR for organic component of coal and chars^[23]

Band position σ / cm^{-1}	Functional groups
3 300	stretching -OH, -NH, -OH (phenolic), -OH (peroxidic)
3 030 ~ 3 050	stretching C-H aromatic, aromatic H ₂
2 950 ~ 2 850	stretching C-H aliphatic, R-CH ₃ asymmetric stretching, R ₂ CH ₂ - asymmetric stretching, RCH ₂ - symmetric stretching
1 900 ~ 1 650	residual water vapor
1 700	conjugate C=O
1 600 ~ 1 590	(C-H) _{ar} poly aromatic system, benzene rings
1 500	stretching C-C aromatic
1 450 ~ 1 440	bending C-H aliphatic
1 380 ~ 1 375	symmetric deformation -CH ₂ - (bending)
1 261 ~ 1 251	weak band of C=O stretching
1 091, 1 031, 1 010	ash in coal
900 ~ 700	aromatic bands mainly due to aromatic-carbon-carbon (HCC) rocking vibrations
872 ~ 870	substituted benzene ring with isolated hydrogen
805 ~ 800	substituted benzene ring with two neighbouring hydrogen/ or angular condensation ring systems
758 ~ 750	benzene ring orto-substituted and meta-substituted and condensed ring systems

Table 2 Proximate and ultimate analyses of raw coal

Raw coal	Proximate analysis $w_{ad}/\%$				Ultimate analysis $w_d/\%$				
	M	A	V	FC	C	H	N	O	S
LIG	15.4	12.4	45.7	26.4	70.5	6.6	0.6	18.5	3.7
SUB	9.6	9	37.6	43.8	75.6	5.2	1.7	16.9	0.7
BIT-LV	4.2	29.1	21.4	45.3	77.5	4.5	2.2	15.4	0.4
BIT-HV	2.1	16.2	26.7	55	81.6	4.6	2	10.7	1.2
SA	1	17.3	7.6	74.1	90.4	3.5	2	3.3	0.9
ANT	1.5	11.2	5.3	82	90.2	2.7	2.2	2.7	2.3

Table 3 Proximate and ultimate analyses of acid-washed coal

Acid-washer coal	Proximate analysis $w_{ad}/\%$				Ultimate analysis $w_d/\%$				
	M	A	V	FC	C	H	N	O	S
LIG	1.7	0.8	60.3	37.3	69.2	6.2	0.6	20.3	2.7
SUB	1.9	2	43.2	53	75.1	5.2	1.8	17.4	0.1
BIT-LV	1.3	3.3	25	70.4	80.9	4.2	2.3	12.3	0.3
BIT-HV	2.7	1.2	27.2	68.9	83.4	4.6	2	9.1	1
SA	2.3	1.8	9.6	86.3	89	3.3	1.8	5	0.7
ANT	2.5	1.5	6.8	89.2	85.6	2.4	2.0	7.7	2.1

2.2 Quantitative analysis of spectra

Table 4 gives a comprehensive summary of some of the determined fundamental properties of the coal and chars used in this study, where coals are listed by increasing rank (lignite to anthracite) as determined

by petrographic analysis. As a result of certain peaks in coal and char spectra overlapping, extreme care was taken in assigning the peaks and in the determination of the fundamental properties.

Table 4 Determined fundamental properties of coal and chars

Sample	Intensity of spectra				Aromaticity	Degree of condensation
	CH ₃	C=O	C=C	CH ₂		
LIG						
Parent coal	22.82	0	8.71	0	0.38	0.25
Demin coal	10.40	8.25	5.87	17.78	0.40	0.26
450 °C	46.27	57.38	3.19	9.58	0.66	0.44
500 °C	47.87	3.35	6.85	3.63	0.69	0.45
550 °C	57.24	0	3.91	0	0.73	0.49
600 °C	53.06	92.07	8.36	0	0.74	0.49
650 °C	32.12	0	15.04	0	0.76	0.51
700 °C	25.48	0	16.66	0	0.79	0.54
SUB						
Parent coal	34.47	0	3.65	14.57	0.57	0.30
Demin coal	36.77	19.05	3.19	11.72	0.58	0.30
450 °C	38.94	0	3.24	8.96	0.75	0.40
500 °C	83.48	0	4.39	0	0.78	0.42
550 °C	54.71	0	5.61	0	0.81	0.43
600 °C	50.65	0	8.46	0	0.84	0.45
650 °C	53.28	0	13.85	0	0.87	0.49
700 °C	81.00	0	12.30	0	0.90	0.49
BIT-LV						
Parent coal	52.37	67.26	21.85	31.87	0.70	0.30
Demin coal	62.56	0	3.45	14.14	0.74	0.32
450 °C	37.46	58.28	3.56	0	0.84	0.37
500 °C	49.55	91.63	7.60	0	0.88	0.38
550 °C	36.90	72.73	5.19	0	0.90	0.39
600 °C	27.31	0	11.67	0	0.93	0.40
650 °C	54.24	0	12.94	0	0.97	0.42
700 °C	71.74	0	15.74	0	1.00	0.46
BIT-HV						
Parent coal	31.89	0	11.33	12.58	0.71	0.31
Demin coal	22.86	0	3.41	11.51	0.72	0.31
450 °C	30.48	87.38	5.93	0	0.83	0.36
500 °C	41.53	91.71	4.96	0	0.86	0.38
550 °C	38.52	0	8.58	0	0.89	0.38
600 °C	42.43	0	11.54	0	0.92	0.40
650 °C	36.74	0	14.97	0	0.95	0.42
700 °C	29.57	0	10.49	0	1.00	0.43
SA						
Parent coal	63.96	0	45.81	56.64	0.91	0.32
Demin coal	24.35	0	5.16	10.22	0.84	0.36
450 °C	0	0	5.52	0	0.94	0.33
500 °C	35.45	0	10.63	10.49	0.95	0.33
550 °C	33.50	53.68	11.41	0	0.98	0.34
600 °C	46.83	55.00	14.44	0	1.00	0.36
650 °C	37.61	0	13.79	0	1.00	0.40
700 °C	26.97	0	10.67	0	1.00	0.44
ANT						
Parent coal	68.34	0	34.48	62.45	0.97	0.34
Demin coal	84.13	0	7.18	0	0.98	0.34
450 °C	49.90	0	10.15	19.04	0.97	0.36
500 °C	69.82	91.51	38.98	82.52	0.98	0.37
550 °C	72.81	98.71	50.08	93.44	1.00	0.36
600 °C	45.92	97.16	8.09	0	1.00	0.38
650 °C	56.95	74.43	7.15	35.84	1.00	0.39
700 °C	21.11	0	21.40	0	1.00	0.44

Where values of 0 are written against in Table 4 implies that the band did not appear in the spectra. No consistent trend was observed for the CH_3 , $\text{C}=\text{O}$, $\text{C}=\text{C}$, CH_2 determined from the intensities of the spectra as revealed in Table 4 and Figure 3 and Figure 4 respectively as expected because of the complicated and complex nature of coal and coal char. However, for the aromaticity and the degree of aromatic

condensation, it was observed that coal increases in both aromaticity and degree of aromatic condensation with increasing char formation temperature. This could be attributed to the removal of aliphatic side chains from the coal carbon matrix as a result of increase in the heat treatment temperature which results in the shift of most of the bands in Figure 2 to lower wavenumbers.

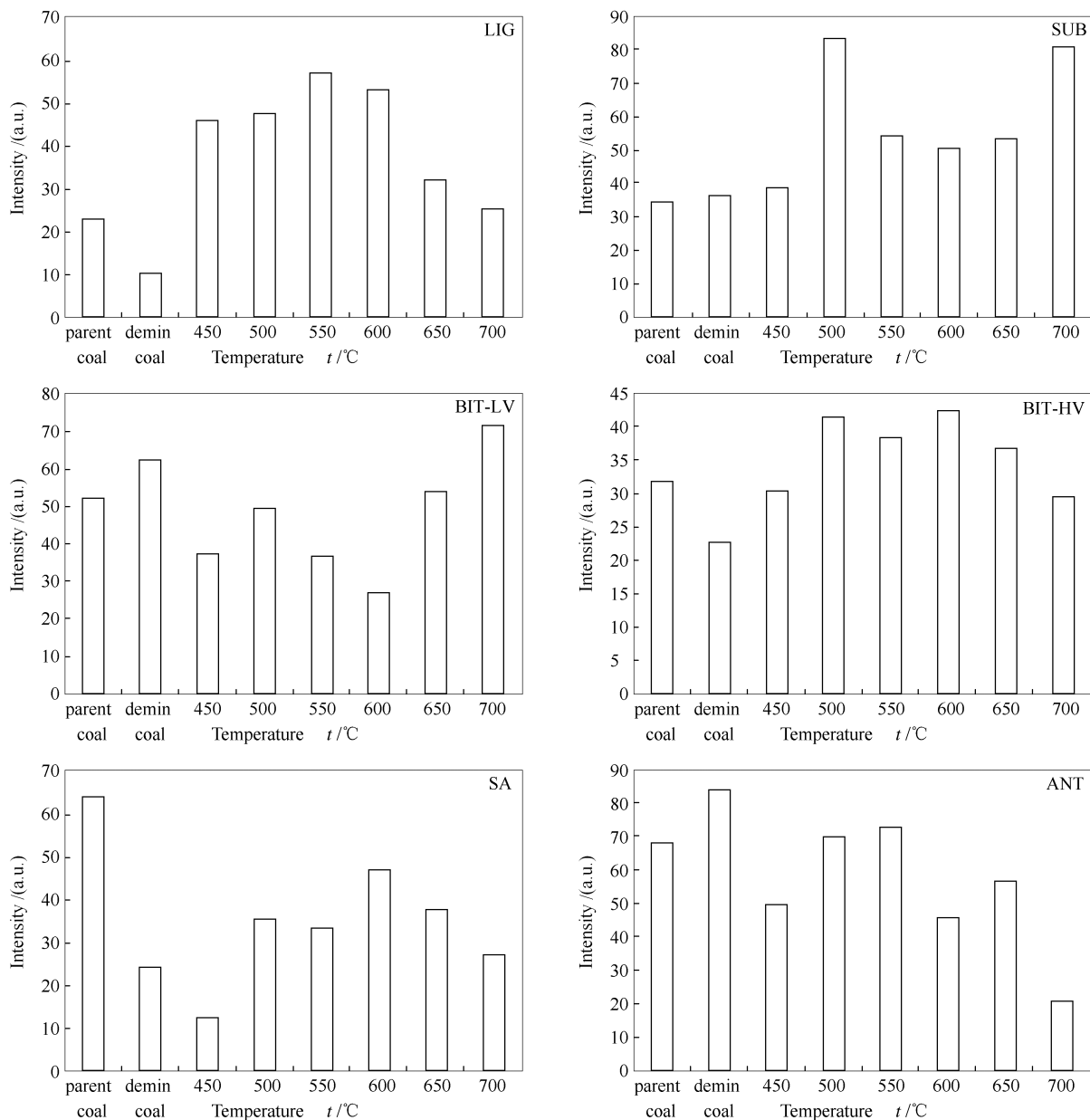


Figure 3 Transitional changes of the CH_3 with char formation temperature

The aromaticities obtained in this study are given in Table 4 and Figure 5, which shows an increasing trend with increasing char formation temperature, which implies that more structurally ordered and oriented carbon crystallites are obtained as the char formation process proceed to higher temperatures. A

convergence of the aromaticity to a value of 1.00 was obtained for the medium and high rank coals at the final char formation temperature of 700 °C, while the low rank coals increased maximally with increasing char formation temperature of 700 °C with values of 0.79 and 0.90 for lignite (LIG) and sub-bituminous

(SUB) coals respectively.

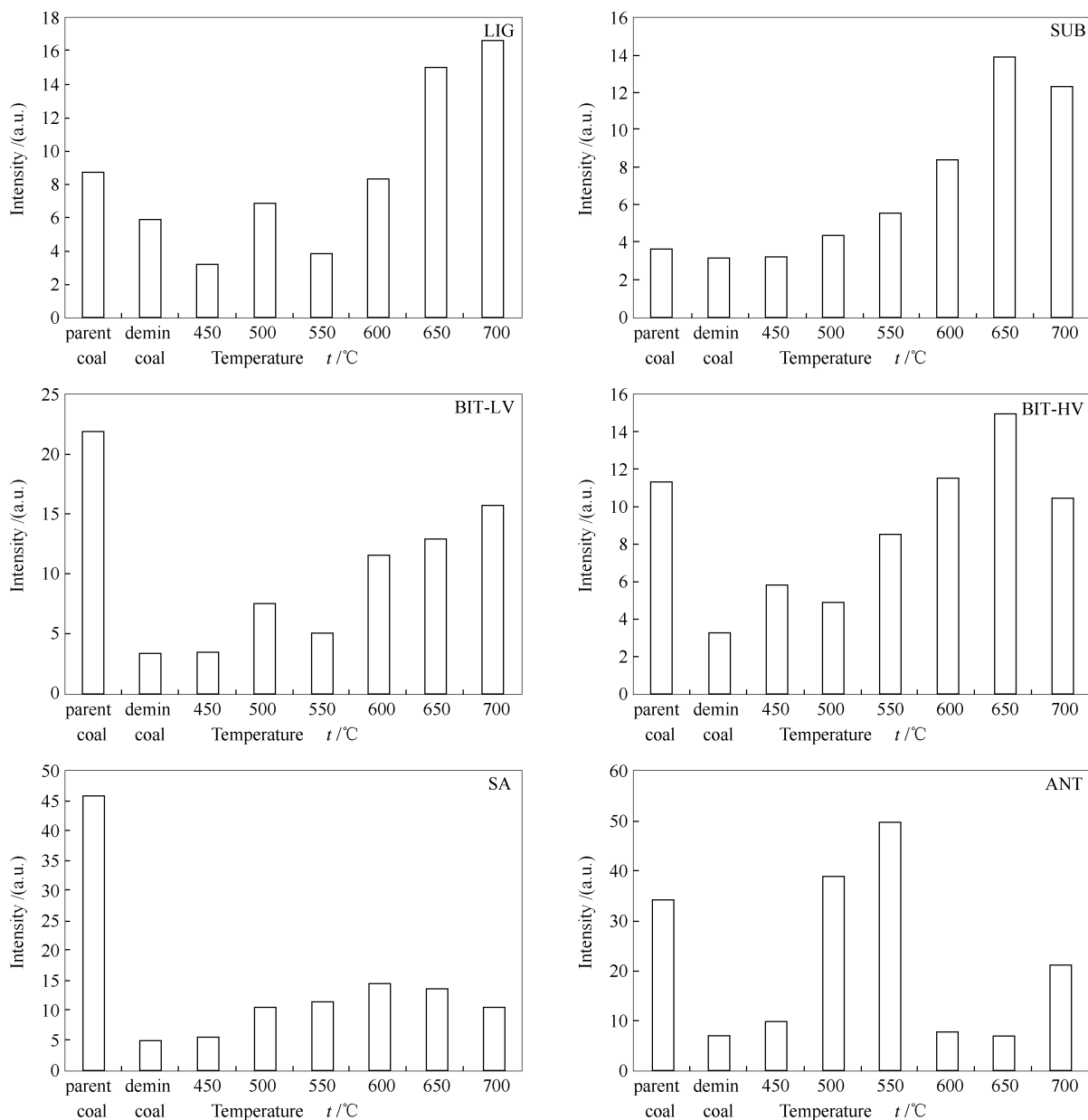


Figure 4 Transitional changes of C=C with char formation temperature

The degree of aromatic condensation of the lignite sample have the least value of 0.25, while the anthracite coal have the highest value of 0.34, giving an indication of increasing trend of degree of aromatic condensation with increasing coal rank, as can be seen in Table 4 and Figure 6. However, with the heat treated coal samples, the low rank coals (LIG and SUB) exhibited the highest degree of aromatic condensation with a value of 0.54 and 0.49 respectively at 700 °C, while the medium rank and high rank coals have a value of ≈ 0.44 . This observed trend could be attributed to the fact that the low rank coals do contain high oxygen content when

compared to the medium and high rank coals.

A similar increasing trend was obtained for the aromaticity and degree of condensation and compares well with those of Ibarra et al^[26] that employed both ¹³C-NMR and FT-IR in the determination of aromaticity and degree of aromatic condensation respectively. The values obtained in this study compare well with those of Orrego-Ruiz et al^[17] that employed PA-FTIR, who reported values ranging from 0.235 for low rank Columbian sub-bituminous coal to 0.339 for Columbian anthracite for the degree of aromatic condensation against 0.25 and 0.34 for lignite and anthracite.

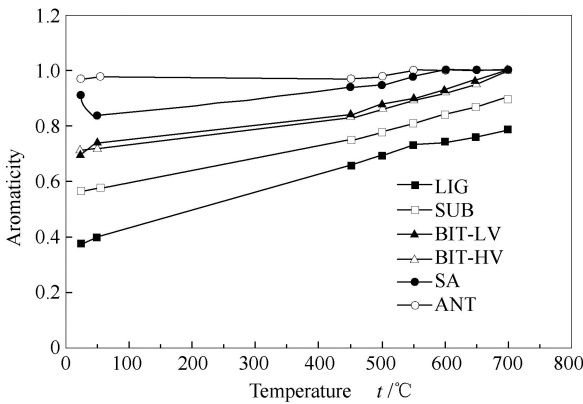


Figure 5 Transitional changes of the aromaticity with char formation temperature

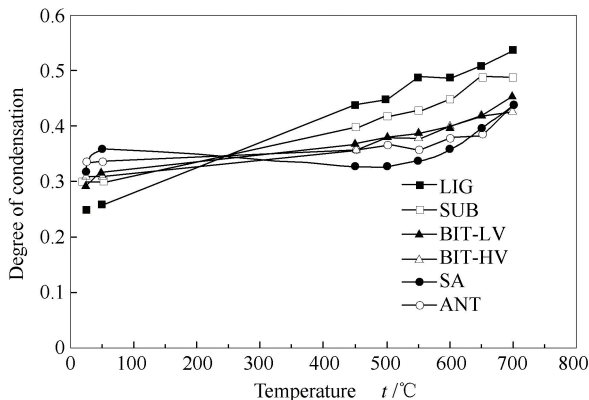


Figure 6 Transitional changes of the degree of condensation with char formation temperature

The aromaticity reported by Orrego-Ruiz equally demonstrated similar trend of increasing aromaticity with rank, with the sub-bituminous having a value of

0.662 and the anthracite a value of 0.984. The value obtained in this study for sub-bituminous coal is 0.57, while the value for anthracite is 0.97. Comparing the values obtained from these three different studies revealed that the aromaticity obtained using the PA-FTIR was over estimated. This implies that ATR-FTIR technique whose value aligns with the value obtained using the ^{13}C -NMR method is feasible and reliable.

3 Conclusions

The ATR-FTIR spectroscopy method was used successfully in this study to investigate the coal to char transition of six coals of different ranks employing both qualitative and quantitative approaches. This method appears to be reliable and easy to use in comparison with other FT-IR spectroscopy techniques. Regardless of the rank of the parent raw coals, all the acid cleaned coals apart from the low rank coals behave like a highly carbonized coal such that they similarly exhibited the same aromaticity at 700 °C. The same trend was revealed in the degree of aromatic condensation for the medium to high rank coals converging to the same value at temperature of 700 °C, while the two low rank coals exhibited the highest order of degree of aromatic condensation at the final temperature of 700 °C. As far as the authors could assess, this is a novel finding, which could provide researchers with new questions that need to be answered to better understand the complex and heterogeneous nature of coal during coal conversion processes such as combustion, gasification and liquefaction.

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