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A study of the relationships between coal structures and combustion characteristics: The insights from micro-Raman spectroscopy based on 32 kinds of Chinese coals

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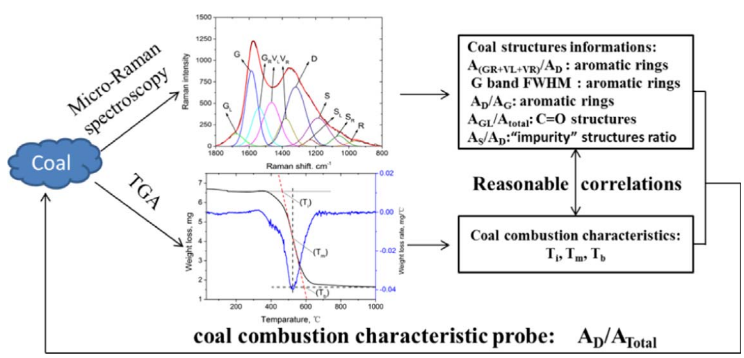
HIGHLIGHTS

- 32 kinds of Chinese coals are studied by Raman spectroscopy and TGA.
- Relations between coal combustion characteristics and Raman parameters are set up.
- Raman parameters can act as probes for coal rank and combustion characteristics.

GRAPHICAL ABSTRACT



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ABSTRACT

Structures and combustion characteristics of 32 kinds of Chinese coals were studied by Micro-Raman spectroscopy and thermal gravimetric analyzer. Changes in coal structures with coalification were investigated by detailed curve-fitting the Raman spectrum with ten Gaussian bands. The relationships between the Raman spectral parameters and coal combustion characteristics were set up and evaluated. The results indicate that the loss of aromatic substituents or aliphatic structures can be responsible for the decrease of V^{daf} for low rank coals (volatiles content in dry ash-free basis (V^{daf}) > 25%), while the rapid growth of aromatic rings along with the increase of cross-linking density of coals mainly occurs under coalification for relative high rank coal (V^{daf} > 25%). Besides, C = O structures in coal increase monotonously with the increase of V^{daf}. The condensation of aromatic rings, loss of C = O structures and reduction of "impurity" structures among large aromatic rings all can increase the coal combustion characteristic temperatures. Reasonable correlations between the coal combustion characteristic temperatures: T_i, T_m, T_b and Raman spectral parameters: $A_{(GR+VL+VR)}/A_D$, A_{GL}/A_{Total}, A_S/A_D, A_D/A_{Total} have been found respectively, and the relationships are all better than that between T_i, T_m, T_b and V^{daf}. Particularly, the Raman spectral parameter A_D/A_{Total} is a combination of above key parameters and related to the coal ignition temperature best with the R-square higher than 0.9. A_D/A_{Total} can act as a good indicator for coal combustion characteristics. This study directly demonstrates that Raman spectroscopy

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can play a probe not only for coal ranks/structures but also coal combustion characteristics and it can provide a new approach to rapidly predict the coal properties.

1. Introduction

Worldwide, coal as expected will remain to be the main energy resource in foreseeable future, especially in developing countries such as China, India and South Africa [1–8]. Combustion for energy production in power plant is the major utilization way of coal [3,4]. The efficiency and pollutant emission of coal-fired power generation are critical for the economy and environment, and it can be significantly influenced by the coal combustion characteristics in boiler [4,9]. It is well known that coal chemical structure is one of the key factors that determine coal combustion characteristics [4,5,9,10]. In the past decades, characterization of coal chemical structure and clarifying the relationships between coal chemical structure and combustion characteristics have attracted a wide spread attention. Many effective characterization technologies such as Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), petrographic analyses and Raman spectroscopy have been developed [2,9–15]. Raman spectroscopy, among these technologies, is being more and more widely used to study the microstructures of coal due to its high-efficiency, non-destructive and high-precision [2,13,16–24]. In addition, it may provide a potential analytical tool for online coal analysis since no complicated sample preparation is needed and one test can be finished in seconds [16,22,23]. Therefore, systematically investigating the coal structures by Raman spectroscopy and setting up the relationships between Raman spectral parameters and coal combustion characteristics are of great importance before its real application.

In the first-order Raman spectrum of highly ordered carbon materials, two characteristic bands mainly exist: D band at about 1340 cm^{-1} and G band at about 1580 cm^{-1} [17–19,24–26]. The G band is found to be attributed to the E_{2g}^{2} mode of graphite and D band is generally assigned to the A_{1g} symmetry mode of the graphite [16–19,24,25]. In some of the studies that used Raman spectroscopy to investigate the raw coals, these two bands were used to curve-fit the Raman spectra and the correlations between the spectral parameters of D or G band and coal maturity/rank were discussed [21,27–30]. Hinrichs et al. [21] found that the G band would shift to larger wavenumber and D band would shift to lower wavenumber with the increase of coal rank (vitrinite reflectance (R_f)). Kwiecinska et al. [27] found that the full width at half maximum (FWHM) of G band generally increased with the increase of H/C atom ratio. Kelemen et al. [28], Marques et al. [29] and Quirico et al. [30] found that the FWHM of G and D bands would decrease with the increase of R_f. These studies indicate that Raman spectrum is sensitive to the coal rank (actually the change of coal microstructures). But limited structure information has been revealed by the simple curve-fitting for the spectrum with just two bands as more bands representing typical structure information in coal are covered by the broad G and D bands [20,21,30,31].

Actually, some efforts have been done to further resolve the Raman spectrum of coals with more bands [18–20]. One method widely used is according to the method proposed by Sadezky et al. [19] for Raman spectra of highly ordered carbon materials. In this method, the Raman spectrum of coals is curve-fitted by five bands at about 1620 cm^{-1} (D_2),

Table 1
Properties of the coal samples.

Sample	Age	Moisture (ad*, %)	Volatiles (ad, %)	Fixed Carbon (ad, %)	Ash (ad, %)	Volatiles (daf*, %)	d_{002}* (nm)	Lc* (nm)
Leiyang	Upper Permian	1.28	4.85	62.02	31.85	7.25	0.3498	2.08
Jingping	Lower Permian	4.48	5.99	68.55	20.98	8.04		
Nanchenpu	Lower Permian	4.32	6.72	62.66	26.31	9.69		
Xinqiao	Lower Permian	1.83	7.53	67.49	23.15	10.04	0.3512	1.92
Jingmei	Lower Permian	1.75	9.72	68.13	20.4	12.49		
Zhicheng	Lower Permian	1.61	10.07	57.94	30.38	14.8		
Sichuan	Upper Permian	1.39	11.81	67.78	19.02	14.84	0.3537	1.85
Maanshan	Upper Permian	2.59	12.70	66.59	18.12	16.02		
Meiku2	Uncertain	3.29	18.88	65.28	12.55	22.44	0.3533	1.95
Xiwujiang	Lower Permian	2.84	10.91	32.18	54.07	25.32		
Xiangmei	Upper Permian	1.62	19.05	48.88	30.45	28.05	0.3535	1.97
Bingxin	Middle Jurassic	3.17	25.04	57.06	14.73	30.50		
Wucaiwan	Middle Jurassic	12.47	25.78	57.11	4.64	31.10	0.3572	1.41
Liupanshui	Upper Permian	4.12	21.69	47.97	26.22	31.14		
Hongshaquan	Middle Jurassic	14.34	24.91	53.91	6.84	31.60	0.3523	1.68
Meiku5	Uncertain	1.90	23.66	49.68	24.76	32.26		
Shanxi1	Carboniferous-Permian	1.64	22.86	47.85	27.65	32.33		
Pingdingshan	Carboniferous-Permian	1.50	22.74	47.40	28.36	32.42	0.3571	1.54
Jiangjunmiao	Middle Jurassic	4.98	29.59	61.69	3.74	32.42		
Shanxi2	Carboniferous - Triassic	2.06	17.80	33.95	46.19	34.40	0.3568	1.77
Meiku1	Uncertain	12.76	22.94	42.36	21.94	35.13		
Huangling	Middle Jurassic	3.07	28.92	51.39	16.62	36.01	0.3587	1.53
Xinggaoshan	Lower Jurassic	13.50	24.24	41.52	20.74	36.86		
Shenfu	Upper Jurassic	8.77	32.25	54.38	4.60	37.23		
Honghe	Carboniferous-Permian	3.97	28.61	46.10	21.32	38.29		
Cangzou	Triassic-Jurassic	7.02	30.37	46.87	15.74	39.32	0.3585	1.76
Nantun	Carboniferous-Permian	3.01	28.27	43.08	25.64	39.62		
Meiku4	Uncertain	15.83	24.87	35.92	23.38	40.91		
Jimei	Carboniferous-Permian	2.68	30.02	41.43	25.87	42.02		
Meiku3	Uncertain	9.61	27.71	33.73	28.95	45.10		
Huolinghe	Jurassic- Cretaceous	26.46	27.28	29.03	17.23	48.45		
Xiaolongtan	Neogene period	22.10	34.93	35.47	7.50	49.62	0.3781	1.22
Graphite				100			0.3377	59.23

*ad: air-dry basis, *daf: dry-ash free basis, *d_{002}: interlayer spacing of crystalline structure, *L_c: stacking height of crystallite. The age of coal samples are from the Geological survey of China.