Fuel 206 (2017) 555–563

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full length article

FTIR and Raman spectroscopy characterization of functional groups in various rank coals

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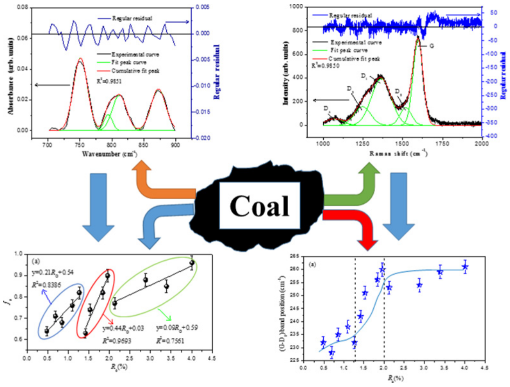
HIGHLIGHTS

- Chemical structure of coals varying in rank from lignite to anthracite were comprehensively characterized.
- The evolutionary process of coal structure is complex with three stage characteristics.
- The rapid defunctionalization of C=O groups is the main characteristic at $R_o = 0.4–1.3\%$.
- Aromatic rings and graphitization degree are significantly enhanced with the strongest aromatization at $R_o = 1.3–2.0\%$
- Microcrystalline structure in coal is gradually perfected at $R_o = 2.0–4.0\%$, closer to graphite structure.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 January 2017
Received in revised form 30 May 2017
Accepted 31 May 2017

Keywords:
FTIR
Raman spectroscopy
Functional groups
Coal
Evolutionary trend

ABSTRACT

Coals varying in rank from lignite to anthracite were comprehensively characterized with regard to chemical structure using FTIR and Raman spectroscopy. Structural parameters were determined from spectrum deconvolution, and correlations were established for these parameters. The evolution of coal structure is complex with three stage characteristics at $R_o = 0.4–1.3\%$, 1.3–2.0% and 2.0–4.0%, respectively. At $R_o = 0.4–1.3\%$, the rapid decline in oxygen-containing functional groups accompanied with the enrichment of aliphatic compounds is the main characteristic. When $R_o = 1.3–2.0\%$, the sharp changes of the band position difference (G-D_1), A_{D1}/A_G and apparent aromaticity (f_a) are caused by the strongest aromatization at this period. The aromatic rings and degree of graphitization are significantly enhanced, with the length of aliphatic chains ($A(CH_2)/A(CH_3)$) decreasing to the lowest level. When $R_o = 2.0–4.0\%$, the slow variation of parameters (f_a, 'C', G-D_1 and A_{D1}/A_G) confirms that most of heterocycle compounds and amorphous carbon structures have been lost. The size of aromatic clusters and graphite crystallite continuously increase, and the microcrystalline structure in coal is gradually perfected, closer to graphite structure. These findings can provide a comprehensive understanding of chemical and physical properties of coals.

1. Introduction

Coal or rock dynamic disaster, such as coal and gas outburst, rock burst etc., has been a major geological hazard to underground

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http://dx.doi.org/10.1016/j.fuel.2017.05.101
0016-2361/

coal mining for over 150 years, and with the increasing depth of coal mines and the rising extraction rates, it continues to cause serious problems in all over the world [1–3]. The precise mechanism of coal and gas outbursts is still unknown, but it is widely believed that the interaction between coalbed methane (CBM) and coal molecules plays an important role in the occurrence of coal and gas outbursts [4–7]. This makes it crucial to improve the knowledge of physical and chemical properties of coal [8,9].

Coal is a typical example of a highly chemically heterogeneous material, containing a complex macromolecular network of organic structural units linked by covalent and noncovalent bonds with different sizes. Large carbon based molecular building blocks in coals are composed of fused aromatic and hydroaromatic ring clusters which may also include some heteroatoms, such as sulfur, oxygen, nitrogen, etc. [10–13]. The resulting heterogeneity makes it difficult to use a single technique to characterize the chemical structure of coal, and thus a wider range of techniques is quite necessary to provide the greatest insight into the coal properties. The recent increase in software advances and technical development has led to the appearance of a large number of new analytical methods. These include: Fourier transform infrared (FTIR) spectroscopy [14–17], Raman spectroscopy [18–23], solid state ^{13}C nuclear magnetic resonance (NMR) [24–26], high resolution transmission electron microscopy (HRTEM) ([27–29], scanning electron microscopy with energy-dispersive X-ray (SEM-EDX) [30,31], X-ray photoelectron spectrometer (XPS) [32–35], X-ray diffraction (XRD) [36–39], X-ray absorption near-edge spectroscopy (XANES) [40], and Atomic Force Microscopy (AFM) [41] etc.

It is generally accepted that the coal structure varies with coal types. In recent years, extensive efforts have been made by a number of researchers [15,18,24,26,37]. The carbon skeletal features of superfine pulverized coal were elucidated by Liu and co-workers through ^{13}C NMR analysis [42]. Okolo et al. [43] analyzed the chemical-structural properties of four South African bituminous coals using various analytical techniques, and good agreement and consistency were found between these different techniques. Besides, they also proved that both the fraction of amorphous carbon and the index of disorder decrease with increasing coal maturity for bituminous coals. Ulyanova et al. [44] studied the fine structure of *G* and *D* bands in Raman spectra of various coal samples, and made comparisons between fat coals (Mine Skochinskogo) from outburst safe, outburst inclined and outburst broken. A linear relationship between the aromaticity and H/C ratio of bituminous coals was verified through various techniques by Maroto-Valer et al. [45] and Li et al. [46]. Marques et al. [47] drew a similar conclusion about coal chemical and structural evolution, combining Raman spectroscopy and X-ray diffraction. Chen et al. [48,49] demonstrated the first study reporting the application of micro-FTIR mapping for *in situ* characterization of coal macerals. Both Han et al. [50] and Li et al. [51] employed multiple techniques to investigate the chemical structures of coal and discussed their changes during pyrolysis. Studies by Supaluknari et al. [52] and Odeh et al. [53] have shown that the carbon molecular skeleton of coals mainly consists of aromatic sheets or layers. These techniques have enabled a better understanding of coal molecular chemical structure with varying degrees of success [54–59]. Despite all these studies, our current knowledge of fine details of coal macromolecular structure during the coalification process is still far from complete, due to its heterogeneity and complexity [46,60].

Among all the chemical characterization techniques, FTIR and Raman spectroscopy are unique, since they are nondestructive and capable of identifying the molecular level chemistry of solid fossil fuels through the identification of the vibrational signatures related to specific types of chemical bonds [61,62]. FTIR provides important information on molecular structure, especially the chemical functional groups of organic compounds, while Raman spectroscopy gives information about microcrystalline carbon structure, such as the degree of ordering and crystallinity [37,63]. These two techniques are complementary to some extent, and the combination of them can provide clearer insights into the complex nature of coal structure.

In this paper, both the distribution of functional groups and the chemical structure evolution of selected coal samples with various ranks during the coalification process was assessed using FTIR and Raman spectroscopy. The structural parameters were determined from curve-fitting analysis. These data will enable us to gain an in-depth and comprehensive understanding of different aspects of chemical and physical properties of coals. This study would provide a theoretical basis for further studies, including the development of coal molecular models, coal utilization, CO_2 geological sequestration and even the prevention of coal and gas outburst in underground coalmines [44].

2. Materials and methods

2.1. Materials preparation

A suite of coal samples varying in rank from lignite to anthracite was collected from working faces of typical coal basins in the northern China mining area, such as Qinshui Coalfield and Pingdingshan Coalfield. All the samples were crushed to pass through a 200-mesh sieve (particle size of <74 μm), followed by the conventional analyses. Proximate and ultimate analyses of the selected samples have been conducted, according the China National Standards GB/T 212-2008, GB/T 476-2008 and GB/T 214-2007. The vitrinite reflectance (R_o) analysis was performed following the standard coal petrographic procedures (GB/T 6948-2008).

2.2. FTIR spectroscopy

2.2.1. FTIR measurements

Samples should be demineralized before FTIR measurements to avoid the influence of the inorganic mineral matter of the coals on the structural analysis. For the demineralization experiments, a typical three step HCl-HF-HCl procedure was adopted [43], following the Chinese standard (GB/T 7560-2001). The crushed coal was initially washed with 20% HCl for 24 h under nitrogen atmosphere, then filtered and washed with distilled water until the pH of the filtrate became neutral. After that, 40% HF was added immediately to the HCl washed coal and stirred for 24 h, and then washed with 20% HCl. Finally, the products were further washed in excess distilled water to ensure the filtrate was neutral.

The present FTIR study uses the traditional KBr pellet method. Prior to analysis, both the samples and KBr were dried in vacuum oven at 353 K for 12 h to minimize the effect of moisture on the spectrum. It is noted that thermal drying of low rank coals can cause irreversible changes to the coal structure, but this relative mild thermal drying conditions in this paper is acceptable for the selected coal samples [16,51]. Subsequently, samples of 1 mg (±0.1 mg) were ground with 300 mg KBr for 2 min and pressed into pellets in an evacuated die under 10 MPa pressure for 2 min. FTIR measurements were carried out using Thermo Scientific Nicolet 380 IR spectrometer. Samples were analyzed at ambient temperature, from a collection of 32 scans per spectrum (interferograms), with the scan range of 450–4000 cm^{-1}, at a resolution of 4 cm^{-1}.

2.2.2. Determination of FTIR parameters

2.2.2.1. Aromatic structural parameters. The apparent aromaticity, f_a, of coal samples was used to characterize the aromatic carbon