Fuel 187 (2017) 51–57

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Investigation of coal components of Late Permian different ranks bark coal using AFM and Micro-FTIR

Shaoqing Wang [a,*], Shimin Liu [b], Yibo Sun [a], Di Jiang [a], Xiaomei Zhang [a]

[a] College of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), D11, Xueyuan Road, Beijing 100083, PR China
[b] Department of Energy and Mineral Engineering, G³ Center and Energy Institute, The Pennsylvania State University, University Park, PA 16802, USA

HIGHLIGHTS

- Structure characteristics of barkinite were coal rank dependent.
- Barkinite ranges from fibrous to irregular network structure with rank increase.
- Barkinite has similar AFM image feature to vitrinite at a coal rank of 1.12%.
- Surface roughness degree of barkinite decrease with coal rank increase.

ARTICLE INFO

Article history:
Received 7 July 2016
Received in revised form 9 September 2016
Accepted 14 September 2016
Available online 20 September 2016

Keywords:
Coal
Barkinite
Chemical
Micro-FTIR
AFM

ABSTRACT

The structural characteristics of barkinite for different coal ranks were studied by both atomic force microscopy (AFM) and Fourier transform infrared spectroscopy with microscopy (Micro-FTIR). The surface morphological texture differences between barkinite and other macerals (sporinite and vitrinite) were characterized using AFM images. We found that both chemical structure and physical texture were rank-dependent parameters. With increase of vitrinite reflectance (R_o), the morphological structure of barkinite evolves from fibrous to irregular network structure, and the orientation arrangement seems enhanced. Based on our experimental data, the AFM image feature of barkinite is similar to that of vitrinite when R_o is with a minimum value of 1.12% or beyond. In chemical structure, the contents of aliphatic functional group of barkinite decrease whereas that of aromatic group increase. The values of CH_2/CH_3 ratios also decrease with increase in coal rank. The different morphological textures between barkinite and others macerals were characterized with AFM examination. The surface roughness degree of these three samples was found to be in sequence of vitrinite < barkinite < sporinite.

1. Introduction

Atomic force microscopy (AFM), as an alternative probe technique, has been employed to characterize surface properties of coal [1–4], macerals [5–7], and polymers [8–10] at the nanometer scale. A variety of physical properties of coal sample surfaces can be probed by AFM. Lawrie et al. [5] investigated the characteristic surface textures of Bowen Basin coal macerals by AFM and observed that fusinite has higher surface roughness than vitrinite. Bruening and Cohen [7] made an analysis on some surface properties (e.g., topography, roughness, hardness, etc.) of coal macerals using AFM. Morga [6] discussed the changes of surface roughness of semifusinite and fusinite under heat treatments by AFM, the average surface roughness could serve as a parameter to determine structural alteration of inertinite group with heat treatments was showed. Liu et al. [3] measured the topographies of the micron-scale pulverized coal particles with mean particle sizes of 14.705, 17.439, 21.300, and 44.264 μm and found that the surfaces seem to be rougher with larger particles. In addition, AFM was also applied to study the supermolecular structure of natural solid bitumens of different groups from *asphaltites* to *anthraxolites* [11].

Fourier transform infrared spectroscopy (FTIR) has been used extensively to characterize the chemical structure of both coals and individual macerals. The functional groups and carbon skeleton of the coals can be studied by infrared spectroscopy [12–24]. It has been shown that coal consists primarily of aromatic nuclei, aliphatic side chains, and some oxygen-containing groups [13].

* Corresponding author.
E-mail address: wangzq@cumtb.edu.cn (S. Wang).

http://dx.doi.org/10.1016/j.fuel.2016.09.049
0016-2361/

Meanwhile, the chemical structure characteristics of coal macerals can also be studied using transmission and reflectance Micro-FTIR [17,18,21–24]. Mastalerz and Bustin [18] discussed the applicability of the reflectance Micro-FTIR technique to study the functional groups in coal. The results of spectra obtained by reflectance Micro-FTIR, transmission Micro-FTIR, and KBr pellet techniques were compared and showed that reflectance spectra obtained by reflectance Micro-FTIR can be utilized, under most conditions, to characterize functional groups in coal. In the reflectance mode, some absorbance bands are much weaker than those in the transmission mode except the 700–900 cm^{-1} region, but the quantitative aspects of reflectance Micro-FTIR have not been deeply discussed [18]. Mastalerz and Bustin [19] used reflectance Micro-FTIR technique to characterize aliphatic chains of vitrinite and liptinite macerals for a high volatile bituminous coal. Chen et al. [24] studied the evolution of some parameters derived from spectra obtained by Micro-FTIR technique for a series of coals with different ranks from peat to anthracite. Variations in functional group abundances among different maceral groups (vitrinite, liptinite, and inertinite) from iso-rank coals were discussed, thereafter, the coal maceral functional group assessment using Micro-FTIR mapping was initiated.

Barkinite was termed as one of liptinite macerals according to Chinese bituminous maceral classification [25], but it has not yet been recognized as a maceral classification by the International Committee for Coal and Organic Petrology (ICCP). Hower et al. [26] suggested that barkinite should so far be termed as "component" instead of "maceral". Barkinite derives from the periderm or bark of higher order plants in which the cell wall and filling material apparently have become impregnated with suberin substances [25]. The reason why barkinite has not be classified in ICCP is that the chemical structure of barkinite still remains vague to some extent, which is also pointed out in the work of Hower et al. [26]. General chemical structural features of barkinite were studied using some modern analysis methods, such as Fourier transform infrared spectroscopy (FTIR) [27], transmitted-light/Micro-FTIR microspectroscopy [22,28–30], time-of-flight secondary ion mass spectrometry (TOF-SIMS) [31], carbon-13 nuclear magnetic resonance (^{13}C-NMR) [32], and atomic force microscopy [33]. A detailed review on the characterization of chemical structure of barkinite was presented in our previous work [34]. Some differences of chemical characteristics between barkinite and vitrinite by using FTIR/Micro-FTIR were studied [28,35,36], for example, the content of aliphatic group, especially in CH_2 content. However, the changes of chemical structure characteristics of barkinite with the increase of maturity are still unclear. Jiao et al. [33] used an AFM to analyze the morphological features of barkinite and vitrinite and observed the changes of surface microstructures of barkinite, but the differences between barkinite and others liptinitic macerals have not been detailed discussed. To deeply discuss the chemical structure of barkinite, two aspects in barkinite chemical structure should be further studied in detail: (1) the differences of chemical structural characteristics between barkinite and other liptinitic macerals; (2) the evolution of chemical structure of barkinite in different coal ranks. These results can provide a solid geochemical and petrological database for properly positioning the barkinite in international coal macerals classification. Potentially, these results will also be valuable information for paleo-geology interpretation to speculate the paleoclimate evolutions indirectly.

In this study, we will combine Micro-FTIR and AMF to characterize the barkinite and the two primary objectives are: (1) to identify characteristic surface textures of barkinite and other macerals (vitrinite, sporinite) and (2) to discuss the changes of structural characteristics (physical and chemical aspects) of barkinite across different coal ranks.

2. Experimental work

2.1. Sample preparation

A series of natural different rank coals with barkinite was selected from the Mingshan (LP5-1), Dahebian (D407-13), Yueliangtian (Y19-1), and Wangjiazhai coalmines (WJZ3-3). Proximate analysis and ultimate analysis of these samples were conducted. All the samples were crushed to 1 mm to make pellets for determining maceral compositions and vitrinite reflectances (R_o) according to Chinese National Testing Standard GB/T 16773-2008 [37]. A Zeiss Universal reflected-light microscope fitted with a 40X-oil-immersion objective and 10X ocular lenses was used to determine R_o according to GB/T 6948-2008 [38]. The vitrinite reflectance was conducted on 25-mm × 25-mm polished pellets. Reflectance reported was the mean value of 100 measurements. The detailed information of some typical parameters of the samples is listed in Table 1. For these coal samples, the vitrinite reflectances ranges from 0.67% to 1.12% and they have high hydrogen contents (5.41–6.70 (daf, %)). The volatile matter of the samples used are from 39.21 to 55.71% (daf, %). To make Micro-FTIR analysis and AFM analysis, bright bands (vitrain) and dull bands (durain) were separated by hand picking. Petrographic analysis results showed that bright bands were 90% vitrinite and the dull bands were 85% barkinite. The polished block samples were prepared according to the requirement and procedure of GB/T 16773-2008 [37].

2.2. Micro-FTIR analysis

Measurements were made with a Nicolet model 6700 Fourier-transform infrared spectrometer equipped with the microscopy Nicolet Continuμm as well as the OMNIC 8 software. Spectra were recorded by co-adding 300 scans at a resolution of 4 cm^{-1}. For each test, each maceral was chosen and spectra were Kramers-Kronig transformed to obtain an absorbance spectrum. The infrared spectra of individual macerals were measured with cross sectional areas of 60 × 60 μm. In order to observe the reproducibility of barkinite Micro-FTIR spectra, the FTIR spectra in various fields in the same samples were measured. Micro-FTIR spectra show good reproducible with regard to peak locations and intensities of individual bands. A detailed information on Micro-FTIR measurement of coal macerals was introduced by previous works [18,19,24].

To obtain the quantitative data for further analysis, peak separation and semiquantitative calculation of Micro-FTIR were performed using the curve-fitting program of PeakFit software. For each Micro-FTIR, the selected regions were baseline-linearized and an area normalization before curve-fitting. To have a good initial estimate of the frequency and intensity of peaks, it is necessary to determine the number of peaks in a given region. The detailed process for curve-fitting can maybe be found elsewhere [36].

2.3. Atomic force microscopy examination

AFM examination was carried out for each polished sample in the tapping mode with a NanoScope V AFM (Digital Instruments, Veeco). All measurements were performed in air, at room temperature and atmospheric pressure using silicon cantilevers (HQ: NSC15/ALBS, 125 μm in length). Typical scan rate during recording was 1.99 Hz using scan heads with a maximum range of 100 μm × 100 μm. The image analysis has been performed with the 7.20 Version NanoScope V software. To clearly of identify macerals and locate possible AFM scan sites, polished samples were examined first under reflected light microscopy. Macerals were found and marked with a maximum range of 1 mm × 1 mm. Under