Journal of Natural Gas Science and Engineering 27 (2015) 1852–1862

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

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

Quantitative study of the macromolecular structures of tectonically deformed coal using high-resolution transmission electron microscopy

Jienan Pan [a, b, *], Sen Wang [a, b], Yiwen Ju [c], Quanlin Hou [c], Qinghe Niu [a, b], Kai Wang [a, b], Meng Li [a, b], Xinghua Shi [a, b]

[a] School of Resources & Environment, Henan Polytechnic University, Jiaozuo 454000, China
[b] Collaborative Innovation Center of Coalbed Methane and Shale Gas for Central Plains Economic Region, Henan Province, Jiaozuo 454000, China
[c] Key Lab of Computational Geodynamics, College of Earth Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 11 July 2015
Received in revised form
4 November 2015
Accepted 6 November 2015
Available online 11 November 2015

Keywords:
Tectonic deformation
High-resolution transmission electron microscopy
Tectonically deformed coal
Macromolecular structures
Quantitative analysis

ABSTRACT

Tectonic deformations damage the macrostructure and impact the macromolecular structures of coal. In this study, high-resolution transmission electron microscopy (HRTEM) was applied to observe the macromolecular structures of six different types of tectonically deformed coal, and quantitative analyses were conducted by using image analysis algorithms to extract the images of lattice fringes to obtain the following three structural parameters: fringe length, fringe tortuosity and fringe separation. The results show that coal rank has an important influence on the macromolecular structures of coal, and this effect varies with different stages of metamorphism. For weak tectonically deformed coal, increases in coal rank indicate an increase in fringe length and decrease in fringe separation and fringe tortuosity. The increments in the fringe separation and fringe length first increase and then decrease, and the maximum values occur during the evolution from mid metamorphic stage to high metamorphic stage. Fringe tortuosity shows a gradually decreasing trend. Tectonic deformation also has an important influence on the macromolecular structure of coal, and this effect varies with different stages of coal rank. With decreases of tectonic deformation, fringe length is increased and fringe separation and tortuosity are decreased; however, the impact of tectonic deformation on the macromolecular parameters of low-rank coal is stronger than that of the mid-rank coal. The impacts of tectonic deformation on the nanoscale pores, coal methane adsorption capacity and coalbed methane contents of low-rank coal are higher than those of the mid-rank coal.

1. Introduction

High-resolution transmission electron microscopy (HRTEM) is an effective method for observing the structure of carbonaceous materials (such as coal, char, soot and carbon) at atomic levels (Sharma et al., 1999, 2000a, 2000b, 2002; Vander Wal et al., 2004; Niekerk and Mathews, 2010; Yehliu et al., 2011a, 2011b; Castro-Marcano et al., 2012a,b; Mathews and Sharma, 2012; Pre et al., 2013; Roberts et al., 2015). In recent years, a number of studies have observed the macromolecular structure of coal using transmission electron microscopy (TEM). Sharma et al. (2000a) reported a clear TEM lattice fringe image of coal for the first time and observed that the molecular structure displayed in the entire image was amorphous except for the edge of the fringe, which showed a degree of orientation, and this finding supports the X-ray diffraction (XRD) analysis by Millward (1979) in which "aromatic layers tend towards parallel stacking with imperfect planarity and orientation." Using the semi-quantitative analysis method, Sharma et al. (1999) calculated the size of the fringe (aromatic layer) and number of layers per stack. The comparison indicated that fringe length increases with increases in coal rank, and the number of layers per stack was also increased. Sharma et al. (2000b) investigated the fringe length and number in a stack of Argonne Premium coal using a semi-quantitative method and found that the average fringe length and number in an aromatic stack with a carbon content of

* Corresponding author. School of Resources & Environment, Henan Polytechnic University, Jiaozuo 454000, China.
E-mail address: panjienan@163.com (J. Pan).

http://dx.doi.org/10.1016/j.jngse.2015.11.012
1875-5100/

70%–85% were similar at 1 nm and 2.2, respectively, and the comparative analysis of the fringe image for the macerals of vitrinite and inertinite in Pocahontas No.3 coal revealed that inertinite had a stronger oriented structure, larger fringe length and larger fringe number in a stack than vitrinite. Niekerk and Mathews (2010) first binarised the HRTEM lattice fringe image from Sharma et al. (2000b) and then manually extracted the fringe. The fringe parameters obtained by the image analysis algorithms showed little difference from the corresponding analysis results of Sharma et al. (2000b) indicating that manual extraction of the fringe is feasible. Therefore, this method was applied in the study of South Africa coal nanostructure to obtain data on its fringe length. A comparison with certain groupings showed that the distributions of fringe in inertinite rich coal and vitrinite rich coal were surprisingly similar. Mathews and Sharma (2012) used the Image Processing Toolkit (Reindeer Graphics, Inc., Asheville, USA) within Adobe Photoshop to analyze the binarised HRTEM image of Argonne Premium raw coal fringes with different coal ranks, and they obtained the momentum angle of orientation of all fringes with their distribution, concluding that low-rank coal has a lower orientation.

In summary, the current application of HRTEM for the quantitative analysis of coal structure is mainly for primary un-deformed coal, and few studies have been performed on tectonically deformed coal. Tectonically deformed coal refers to a class of coal with significant changes in the primary structures, pore structures and macromolecular structures under the effect of tectonic stress (Hou et al., 2012; Pan et al., 2012, 2015a, 2015b, 2015c; Wang et al., 2015). In recent years, the application of HRTEM techniques in the study of tectonically deformed coal structure has begun to attract the interest of scholars. For example, Ju and Li (2009) conducted a qualitative analysis of the macromolecular structures of tectonically deformed coal based on TEM lattice fringe images. However, quantitative studies of the macromolecular structures of different types of tectonically deformed coal using HRTEM analysis have been rarely reported. The effects of macromolecular structures of tectonically deformed coal on nanoscale pore structures and coal methane absorption capacity need further discussion. Therefore, in the present study, the macromolecular structure of tectonically deformed coal in different ranks and structural deformation degrees were directly observed using HRTEM, and the macromolecular structural parameters (fringe length, tortuosity and fringe separation) were quantitatively analysed using the image analysis technique. Subsequently, the impact of metamorphism and deformation degree on the macromolecular structural lattice parameters of coal was investigated in depth. The impacts of coal structures on pore structures, adsorption characteristics, CBM content and production were discussed. The present study aims to investigate the effects of coal rank and tectonic deformation on the macromolecular structures of coal and to obtain a better understanding of the relationship between the macromolecular structures of tectonically deformed coal, its adsorption characteristics, and coalbed methane development.

2. Sample selection and test

2.1. Sample selection

The late Paleozoic coal in Northern China has gone through numerous superpositions of tectonic transformations; therefore, the coal structure was subjected to varying degrees of tectonic deformation and formed different types of tectonically deformed coal. Weak tectonically deformed coal presents a weak tectonic stress on the coal body; thus, the overall structure is relatively intact, and the primary structure of coal can be observed. The coal has high mechanical strength and is difficult to separate by hand. The structure of fractures and joints are common, and cracks may occur along the fracture or joint plane with a flat fracture surface (Fig. 1). Strong tectonically deformed coal presents strong tectonic stress on the coal body; thus, the primary structure of coal has been destroyed, and the coal layers basically disappear. The coal is granular with subangular or subrounded particles, exhibits low intensity and can be molded into fine grains or powder by hand (Fig. 1).

To study the effect of the coal metamorphism and tectonic deformation on the macromolecular structure of coal, two types of tectonically deformed coal were selected with the degree of coal metamorphism in between low rank bituminous and anthracite (vitrinite reflectance was in the range of 0.88%–3.77%). The types of coal deformation included weak tectonic deformation and strong tectonic deformation. The selected coal samples include two bituminous coals with lower coal rank from the Xutuan colliery, two bituminous coal with middle coal rank from Hebi colliery and Chaohua colliery, and two anthracite from the Shihe colliery and Fenghuangshan colliery. Quantitative analyses of coal rank and petrographic characteristics were performed on the polished sections of the samples using a standard polarizing microscope and a microdensitometer (MPV-3). Table 1 shows the basic information on the samples.

2.2. Experimental methods

Observation with the naked eyes, coal is made up of different macroscopic components such as vitrain and charain, vitrain has the highest luster, charain second. The bands of vitrain or clarain in the original coal samples were selected and ground to a powder of 0.074 mm in a mortar after demineralization (Ju et al., 2005; Niekerk et al., 2008). Baking in the drying oven, then a part of coal samples can directly carry out X-ray diffraction (XRD) experiment. Before HRTEM observations, appropriate amounts of ethanol and coal were added to a small beaker and then subjected to ultrasonic vibration for 10–30 min to evenly disperse the coal powder. The droplets of coal powder and ethanol homogeneous mixture were pipetted onto a lacey support film. After leaving for 15 min to completely evaporate the ethanol, the HRTEM test was conducted using a 200 KV high-resolution TEM JEM-2100F (JEOL Corporation), with the magnification factor of $\times$50–1,500,000.

2.3. Macromolecular structural parameters of coal

The macromolecular structures of coal assessed from the HRTEM image demonstrated the pattern of “fringe,” so “fringe” was used to represent the aromatic layer, and this term has been mentioned in the literature (Sharma et al., 2000a, 2000b; Niekerk et al., 2008; Mathews and Sharma, 2012). The aromatic layers in the skeleton of the HRTEM image were interconnected as a network with Y- or T-shapes, and the shape links of these Y or T shapes were accurately removed to separate the aromatic layers (Sharma et al., 2000b). In this study, fringe length, fringe separation and tortuosity were used to quantify the fringe image of the coal lattice. Vander Wal et al. (2004) and Yehliu et al. (2011a) defined these three parameters in detail in their quantitative analysis of carbon structure with HRTEM fringe images.

(1) Fringe length

The length of one fringe in the HRTEM lattice image represents the physical length of the fragment in this aromatic layer as shown in Fig. 1(a). In the literature, the choice of the minimum fringe length varies; Vander Wal et al. (2004) used 0.4 nm as the