Fuel 234 (2018) 1123–1131

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

The evolution of nanopores and surface roughness in naturally matured coals in South China: An atomic force microscopy and image processing study

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ARTICLE INFO

Keywords:
Coal pores
Pore morphology
Surface characteristics
Thermal maturity

ABSTRACT

The coals in South China has not been well investigated because the coal mines are small in volume compared with the well-known large-scale coal accumulations in North China, thus the nature of such coals is of significance to study. The nanopore characteristics and surface roughness of 14 coal samples that have experienced low degrees of tectonic deformation as a naturally matured coal series in South China were addressed. Atomic force microscopy (AFM) and image processing were applied in a study of relationships between nanopore development, surface roughness, and thermal maturity (indicated by vitrinite reflectance; R_o = 0.65%–4.43%) in the naturally matured coal series. The results show that areal porosities of the coal samples are 0.78%–9.33%, with mean pore sizes of 7.9–27.9 nm. There were three main stages of pore evolution related to thermal maturity, with R_o values of < 1.3%, 1.3%–3.7%, and > 3.7%. Pore number, areal porosity, and mean pore size follow a cyclical downward/upward trend across the three stages. Arithmetical mean (R_a) and root-mean-square (R_q) surface roughness values are 1.69–17.74 nm and 2.24–28.81 nm, respectively. R_a and R_q values of coal samples with relatively low thermal maturity (R_o < 1.3%) are controlled mainly by coal maceral and mineral composition, whereas values for coals with relatively high thermal maturity (R_o > 1.3%) are controlled by nanopore development. Thermal maturity is an important factor that influences the nanopore and surface roughness characteristics of naturally matured coals in South China.

1. Introduction

Characteristics of coal pores (especially nanopores) including pore size, pore shape, pore number and pore connectivity can greatly influence the adsorption and desorption processes of methane and CO_2 [1]. Characteristics of coal pores are an important consideration because of the additional needs for Coalbed methane (CBM) exploration and exploitation, CO_2 sequestration, as well as coal char combustion [2–11]. Many studies have focused on the pore characteristics of coals in North China because coal resources there are more concentrated and easier to exploit than in South China [12–15]. The pore characteristics of coals are influenced by many factors, including metamorphism degree of coal, degree of deformation, macerals and minerals [16–20]. Methane and CO_2 are adsorbed mainly in nanopores in the coal matrix [6,16,21,22], therefore the characteristics of nanopores are important for the study of the adsorption and desorption behavior of methane and CO_2, as well as the mechanism of CBM accumulation and CO_2 sequestration. Surface roughness of coal can be used as a measure of structural evolution of coal macerals [23,24]. Many methods have been applied in characterizing nanopores in coal, including image analysis, and intrusive and non-intrusive methods [25]. Atomic force microscopy (AFM) is included in image analysis method. Among these methods, AFM has the advantage of characterizing both open and closed pores in coal [26–28], which influence the overall extraction efficiency of CBM [29], as well as pore size distribution and pore shapes in the micropore–macropore range [6,30] (using the pore classification of International Union of Pure and Applied Chemistry [31]). AFM has also been used in studies of the surface characteristics of coal particles [23,24]. However, AFM is not widely used because of the heterogeneity of coals, requirement for large data sets, and complexity of sample preparation and data processing [6].

Previous studies have utilized AFM to obtain the pore characteristics of coals such as areal porosity, pore size and pore area [6,26,28,30,32,33]. Few studies were focused on the quantitative study

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https://doi.org/10.1016/j.fuel.2018.07.102
Received 25 April 2018; Received in revised form 30 June 2018; Accepted 23 July 2018

of pore shape and surface roughness of coals or macerals in coal [23]. This paper focuses on nanopore characteristics and surface roughness of coals that have experienced low degrees of tectonic deformation in South China, particularly those from small coal mines, proposed a method of calculating the form factors (a parameter quantitatively characterize the pore shape) of pores in AFM images, in order to improve our understanding of the nature of these coals and provide support for the further research of accumulation and release of CBM and CO_2 sequestration.

2. Materials and methods

2.1. Samples and procedures

The study involved a set of 14 naturally matured coal samples with vitrinite reflectance (R_o) values of 0.65%–4.43%, collected mainly from South China (Table 1). AFM was applied to 28 subsamples prepared as follows at the National Laboratory of Microstructures, Nanjing University, Nanjing, China. For each coal sample, two subsamples of length 10 mm and thickness 5 mm were cut perpendicular to and parallel to bedding. For grinding and polishing (with a Buehler Ecomet 3000 Variable Speed Grinder–Polisher), subsamples were glued to a sample holder of a platen system, which ensured that the sample surface contacted an aluminum oxide polishing layer or polishing cloth at a certain angle. The subsamples were wet polished sequentially with aluminum oxide of 30, 15, 9, 6, 3, 1, and 0.1 μm particle size, after which a fibrous cloth was used to remove layers of surface deformation and expose the surface structure for AFM analysis [34]. Prepared subsamples measured about 10 mm × 10 mm × 1 mm, and were all checked by ×20 optical microscopy to ensure surface conditions were suitable for AFM analysis (no visible artificial scratch was found), before being detached from the sample holder, dried at 90 °C for 24 h, and glued to the AFM sample holder.

A Nanoscope III AFM system (Digital Instrument Inc.) at the MOE Key Laboratory of Surficial Geochemistry (Nanjing University) was used in this study. The maximum scanning range was 90 × 90 × 5 μm, with horizontal and vertical resolutions of 0.2 nm and 0.03 nm, respectively. Micro-cantilever tips were used in contact mode. To reduce vibration-induced errors, the AFM system was operated on a gas vibration isolation platform. Scanning ranges used in AFM study were 10 × 10, 5 × 5, and 1 × 1 μm^2. The AFM images with 10 × 10, 5 × 5 μm^2 scanning ranges were used to detect artificial scratches which are mainly continuous curves from large scales. At least thirty 1 × 1 μm^2 areas focused on vitrinite were scanned on each subsample for quantitative nanopore characterization. Any scratches caused during polishing were avoided during AFM scanning. AFM data were processed using open-source Gwyddion software [35] and Nanoscope III software (version 5.30). An FEI Helios Nanolab 600 field emission scanning microscope–focused ion beam (FESEM–FIB) dual-beam system housed at the Nanjing National Laboratory of Microstructures, Nanjing, China was used to prepare planar cross-sections and to acquire secondary electrons (SE) images of nanopores in coal samples. The planar cross-sections were prepared perpendicularly to the surface of AFM subsamples.

2.2. Image processing

In the contact mode used in this study, the few scan lines appearing in AFM images may result in substantial errors in quantitative analyses and, as such, they were removed during image processing by Gwyddion [35–37]. The 95% confidence intervals of raw height data were applied to reject anomalously low or high points possibly caused by vibration. The “Grain analysis” and “Invert height” functions of the Gwyddion program were used to identify and quantitatively analyze nanopores in each subsample, and to determine the number of nanopores and their height (z-axis), minimum and maximum bounding sizes (Feret diameters), projected area, and projected boundary length. The form factor of each pore was calculated from pore area and perimeter. The horizontal resolution set the scanning area and scanning frequency of AFM images to 1 × 1 μm^2 and 512 × 512, respectively, yielding a practical pore resolution of 1.9 nm.

2.3. Data processing

Pore width, length, perimeter (grain boundary), area, and number were acquired using Gwyddion. Pore width and length are expressed as maximum and minimum Feret diameters, respectively, and pore size is based on width. Feret diameter (*dF*) is the orthogonal distance between a pair of parallel tangents at a specified angle [38]. Pore perimeter (grain boundary length) was estimated by summing contributions of four-pixel configurations on the boundary (Fig. 1), where gray pixels represent those occupied by the pore, white pixels are not occupied, and lines represent pore perimeters (grain boundary length).

Pixel diagonal length (h) is expressed in terms of h_x and h_y (dimensions along corresponding axes) as:

Table 1
Characteristics of the naturally matured coal series.

Sample	Location	Coal rank	Geological age	R_o %	Mineral content %	Maceral content %		
						Vitrinite	Liptinite	Inertinite
WLTP	Wulong Coal Mine	Medium rank C	K_1s	0.65	19.1	93.2	0.3	6.5
LP-09	Mingshan Coal Mine	Medium rank B	P_3l	0.70	5.6	30.2	65.5	4.3
LT-07	Litang Coal Mine	Medium rank B	P_3l	0.73	25.5	95.0	0.5	4.5
AY-01	Anyuan Coal Mine	Medium rank B	T_3a	0.81	8.3	87.4	5.7	6.9
YZ-02	Yangzishan Coal Mine	Medium rank B	P_3l	0.89	22.9	96.1	0.6	3.3
FC-03	Jianxin Coal mine	Medium rank A	P_3l	1.32	11.1	89.3	3.5	7.2
WC-01	Wuci Coal Mine	Medium rank A	P_2t	1.84	13.6	98.5	0.2	1.3
WL-F	Wulong Coal Mine	High rank C	K_1s	2.16	27.9	97.7	0.3	2.0
WB-01	Wuci Coal Mine	High rank C	P_2t	2.20	16.4	98.7	0.3	1.0
SZ-04	Shangzhuang Coal Mine	High rank C	P_3l	2.41	14.2	95.6	2.3	2.1
SMH-01	Shimenhuang Coal Mine	High rank B	P_3l	3.00	15.3	94.8	0.5	4.7
SW-02	Shaowu Coal Mine	High rank B	P_2t	3.11	12.8	98.3	0.3	1.4
P-47	Jianglelin Coal Mine	High rank B	P_2t	3.52	10.3	98.5	0.4	1.1
LY-166	Renpan Coal Mine	High rank A	P_2t	4.43	40.7	96.1	0.1	3.8

Coal rank is based on the classification scheme of ISO 11760: 2005.
Maceral content is expressed as percent by volume in mineral-free basis.