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Structures and fractal characteristics of pores in low volatile bituminous deformed coals by low-temperature N_2 adsorption after different solvents treatments

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ABSTRACT

Coal is a porous medium with fractal characteristics. With the removal of soluble fractions under solvent treatment, the structures and fractal characteristics of pores are bound to produce changes. Exampled by low volatile bituminous coals with different degrees of deformation from Huoerxinhe and Changcun coal mines in Qinshui basin, North China, the paper investigated on the changes of pore structure parameters and minerals compositions of coals before and after different solvents treatments, including tetrahydrofuran (THF), hydrochloric acid (HCl) and chlorine dioxide (ClO_2). And Insight into the relationships between fractal dimensions and pore structure parameters and coal compositions were provided. Results show that: The shapes of N_2 adsorption/desorption isotherms rarely change but their adsorption quantities differ sharply after different solvents treatments for coal with same deformation, indicating no change in pore type but a change in the number of pore in the same pore size. Compared to raw coals, with the removal of soluble fractions in coals pore volume (PV) and specific surface area (SSA) tend to ascend after THF extraction; changes in PV and SSA depend jointly on the dissolution of carbonate minerals and the swelling of clay minerals after HCl treatment; and the varieties of PV and SSA, to a great extent, are closely related to the swelling of clay minerals after ClO_2 treatment. Pore structure fractal dimension (D_A) and surface fractal dimension (D_B) are obtained based on Frenkel-Halsey-Hill model. D_A is mainly affected by the proportion of transitional pores and mesopores on PV; therefore, D_A can be used to describe pore volumetric roughness of these transitional pores and mesopores. Meanwhile, D_B is mainly influenced by the proportion of micropores on SSA; therefore, D_B can be utilized to represent pore surface roughness of these micropores. As coal deformation increases, D_A grows for raw coals and coals after extraction with THF; therefore, PV has a significant migration to the pores of small apertures causing the growing contribution of micropores to PV. However, D_A declines for coals treated by HCl and ClO_2, potentially because the welling of clay minerals blocks the pores of small apertures and increase the proportion of the pores of large apertures on PV. D_B shows no clear trends with increasing coal deformation. A “reversed U-shaped” curve relationship is observed between moisture in coal and two fractal dimensions, which is due to the effect of water molecule interfacial tension. Ash correlates negatively with D_A and positively with D_B because of the various influences of minerals on pore homogeneity in pores of different apertures.

1. Introduction

With increasing demands for clean energy and the enhanced difficulty of exploiting conventional reservoirs, unconventional reservoirs for gas production, such as coalbed, shale, and tight sandstone are attracting the growing interest and are highly valued by both many countries and petroleum companies [1–5]. So far, the development of coalbed methane (CBM) has shown huge potentialities in China [6,7]. Compared to conventional oil reservoirs, gases mainly exist in the adsorbed state because coal itself is a carbon-based organic solid material with abundant and complicated pore structure [8–10]. In addition, the complex and amorphous pore system in coal plays a significant impact on gas adsorption/desorption, diffusion, and seepage characteristics [11–13]. As a result, a clear knowledge of pores in coal not only can contribute to understand the gas storage and flow mechanisms, but also provide guidance for CBM exploration and development.

Pores in coal usually are distributed in a three-dimensional space, and conventional geometric methods fail to precisely reflect their heterogeneity owing to theoretical limitations [10,14,15]. Fractal geometry was initially put forward by B.B. Mandelbort in 1975 to describe

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Table 1
Features of coal samples with different degrees of deformation.

Coal type	Features of hand specimens
(I) Intact coal	Macroscopic lithotype is visible clearly. Cut by a set fracture and no displacements between blocks. Cleat or exogenesis fractures can be identified. Coal can be crumbled hardly by hand.
(II) Cataclastic coal	Macroscopic lithotype is visible. Cut by several groups of oblique intersecting fractures. Presented as large-scale block structure without displacements between blocks. Coal can be crumbled into centimeter-sized or millimeter-sized fragments by hand.
(III) Granulated coal	Macroscopic lithotype is not easy to identify. Presented as large-scale block structure with obvious displacements between blocks. Coal can be crumbled into millimeter- and millimeter-sized fragments by hand.
(IV) Mylonitized coal	Macroscopic lithotype is not able to identify. Presented as small-scale angular blocks and different sized granular. Coal can be easily crumbled into powdered by hand.

the surface morphology and pore structure irregularity of porous materials [16,17]. Because the surface morphology and pore structure of coal have the property of self-similarity at different scales, describing its irregularity is reasonable using fractal geometry [18,19]. Over the past several decades, many methods for the calculating fractal dimension of coal have included small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM), nuclear magnetic resonance (NMR), field emission scanning electron microscopy (FESEM), and gas adsorption [1,10,12,20–24]. Among these, gas adsorption has been proven to be a usefully non-linear mathematics method that quantitatively describes and qualifies the pore structure heterogeneity of irregular porous materials and is used extensively to assess the coal fractal characteristics based on its simplicity and convenience [25,26].

Coals with varying degrees of deformation are formed because of geological tectonic movements with the superposition of one or multi phase and different scales [27–29]. The physical and chemical properties, nano-scale pore structure and fractal dimensions produce obvious changes. Song et al. [30] discovered that the pore diameter of deformed coals concentrate upon less than 10 nm according to micro-computer tomography (micro-CT). Based on the results of low-field NMR and X-ray computer tomography (X-CT), Li et al. [31] found that cataclastic coal is rich in well-developed mesopores and macropores but the connectivity of mesopores and macropores in mylonitic coal is poor. Pan et al. [32] revealed that the PV and SSA sharply increase based on the results from the Xutong coal mine in Huaibei mining area, China, using low-temperature N_2 adsorption method. Song et al. [12] investigated the structure and fractal characteristics of micropores and mesopores in low-, middle-rank deformed coals using combined CO_2 and N_2 adsorption and their results demonstrated that tectonic deformation has a more obvious transformation effect for surface heterogeneity than volumetric heterogeneity. Peng et al. [33] compared calculated results from several fractal models and their results confirm that the pore surface and structure fractal dimensions of adsorption pores (< 100 nm in diameter) can be obtained using Frenkel-Halsey-Hill (FHH) model. Zhang et al. [34] manifest that the fractal dimension should be calculated with N_2 adsorption data using 58 coal samples from 14 mining areas according to FHH model. Zhu et al. [10] revealed that the SSA of mesopores and macropores with a mean pore diameter range of 10 nm–220 nm has a significant impact on pore structure fractal dimension and pore surface fractal dimension is mainly affected by the fine mesopores with an mean pore diameter range of 2 nm–10 nm on the total PV. In conclusion, these prior research projects indicate that nano-scale pore characteristics are closely related to pore structure parameters and fractal features.

The permeability of most of coal beds in China is less than 0.1 mD. Therefore, coal reservoirs stimulation measures are applied to enhance seepage property and flow conductivity aiming to effective exploitation of these low-permeability reservoirs [35,36]. Hydraulic fracturing, one of most widely used coal reservoir simulation techniques, has been used to better reservoir penetration through generating a number of new fractures and increasing the width of inherent fractures, and the gas production of most of coalbed methane wells have exhibited obvious growth [37]. The prevalent fracturing fluids include active water, guar gum, and clean fracturing fluids [38]. Concerning fractures in coal bed filled partly or completely with minerals [39,40], some scholars have tried to pump fracturing fluids containing acid solutions into coal reservoirs to dissolve minerals resulting in improved reservoir permeability to varying degrees. The overall change depends on both the distributed condition of inherent fractures and the types of minerals and their respective content [38,41,42]. In recent years, chlorine dioxide of strong oxidizer is pumped into reservoir as a gel breaker to react to fracturing fluid added thickener, getting great feedback and economic performance [43,44]. From the perspective of coal structure, after organic solvent extraction small molecule compounds in the free form and combining with coal macromolecular structure through Van der Waals' force or π-π bond can be dissolved, the removal of extracted fraction can modify the pore structure. Furmann et al. [45] extracted two high-volatile coals with different petrographic compositions from the Illinois basic and the results demonstrate that the overall pore-size distribution shifts towards larger pores due to the enlargement and opening of previously closed micropores. The same conclusion was drawn by Zhang et al. [46]. Ji et al. [47] extracted the anthracite and bituminous coals with tetrahydrofuran and the results showed that the methane sorption properties of the coal are jointly dependent on the modification of the pore structure and the reduction of extractable organic components. Pore fractal characteristics are close correlated with adsorption and seepage properties of coal reservoir, which are very important for CBM storage and development. A larger pore structure fractal dimension is and smaller pore surface fractal dimension is, the stronger the methane adsorption will be [48,49]. Additionally, the compositions have an important effect on fractal dimensions [50]. Pore structures with varying apertures can be modified and the change tendency of pore structure parameters is discussed in detail after different solvents treatments, the pore fractal characteristics are bound to change because of the removal of soluble substances and trapping of foreign matters. Consequently, it is meaningful and necessary that pore fractal features are well worth inquiring.

The Qinshui basin is a significant region for CBM development of high-rank coal in China [33,51]. In this work, before and after different solvents treatments, the structures and fractal characteristics of pores in low volatile bituminous coals with different degrees of deformation from the Huoerxinhe and Changcun coal mines in Qinshui basin, North China, are discussed by combining low-temperature N_2 adsorption and fractal theory. Furthermore, the coal minerals compositions before and after HCl treatment are determined by the EMITECH K1050X Low-temperature (oxygen plasma) Ashing and Rigaku D/max-2500/PC X-ray diffractometer (XRD) after HCl treatment to explore the effect of minerals in coals on pore structure. Finally, insight into the relationships between fractal dimensions and pore structure parameter and compositions and are provided and the influencing mechanism is discussed.