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Application of small angle X-ray scattering in evaluation of pore structure of superfine pulverized coal/char

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HIGHLIGHTS

- A comprehensive study on the pore structures of superfine pulverized coal was conducted.
- Synchrotron radiation-induced small angle X-ray scattering was adopted and results were analyzed quantitatively through fractal dimensions.
- The effect of particle size on the pore network was concerned.
- The influence of different pyrolysis conditions on the changing process of pore structure was investigated.

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ABSTRACT

Superfine pulverized coal as a new energy utilization method plays a significant role in alleviating pollutant emissions. It is of great interest to study the physicochemical properties of superfine pulverized coal. Pore structures acting as the channel of heat and mass transfer change with temperatures, coal ranks and pyrolysis atmospheres, etc. The investigation of the pore structure evolution during coal pyrolysis is beneficial for understanding the pyrolysis mechanisms, and guiding the practical application of superfine pulverized coal. Synchrotron radiation small angle X-ray scattering (SAXS) is a nondestructive test method with high accuracy, which can detect the open and closed pores simultaneously. Furthermore, the fractal dimensions were adopted here to characterize the coal pore structures quantitatively. The final results indicated that the fractal dimensions of pore surfaces decreased with the increase of coal ranks. Moreover, as elevating the pyrolysis temperatures, the fractal dimensions increased initially up to about 550 °C, and decreased afterwards in the lower temperature region (<800 °C). When the temperature is higher than 800 °C, there was a monotonically increasing trend of the fractal dimensions. In addition, the influence of different pyrolysis atmospheres on the pore networks was also discussed in the work. The results provide new insights into the influence of particle sizes on the evolution of pore structures during coal pyrolysis, and are helpful for developing representative molecular models of superfine pulverized coal.

1. Introduction

Coal, as a main fossil fuel, plays an important role in the development of national economy. Thermal power from the combustion of coal makes life more convenient but leads to several serious environmental problems. Superfine pulverized coal [1] that is a new energy utilization method has noticeable advantages in reducing the pollutant emissions as compared to the conventional pulverized coal and it has a great industrial application prospect. As is known to all, coal reburning technology can reduce the NO_x emissions. It achieves good environment benefits and economic benefits in commercial operation [2]. Meanwhile, due to the short dwell time for pulverized coal in furnace, low combustion temperature in initial burning and the lack of oxygen, these lead to high incomplete combustion loss. The reactivity of pulverized coal can be improved by reducing particle size. Because of the improvement of the reactivity, superfine pulverized coal is easier to form reducing atmosphere in initial burning, which is beneficial to prolong the dwell time in reducing atmosphere for flue gas. At the same time, it is favorable to the reduction of NO_x with the increase of the specific surface area of superfine pulverized coal tar. The superfine pulverized coal technology makes it possible that lean coal and soft coal can be used as reburning fuel, which brings great convenience for the application of pulverized coal reburning system.

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Meanwhile, compared with combustion in air, the flame is unstable and the burnout rate is lower in oxygen-enrich atmosphere for conventional pulverized coal combustion [3]. Because of the high specific heat capacity of CO_2, the velocity of flame propagation is lower in oxygen-enrich atmosphere than in air [4]. So the ignition is retarded. Due to the superiority on flaming stability, higher combustion efficiency and lower unburnt combustibles of superfine pulverized coal, superfine pulverized coal technology perfectly matched oxygen-enrich combustion.

Though the power consumption of coal mills for superfine pulverized coal is higher than conventional pulverized coal, the costs of pollutant treatment are less. From the merits of superfine pulverized coal properties, it indicates that the technology of superfine pulverized coal combustion can lower the expenses of the abrasions of metallic materials, desulfurization and denitrification, the oil consumptions for ignition and ash deposition and so on [5]. Based on the test at 700 MW pulverized coal firing boiler, Nakamura et al. [6] found that the running costs could be saved by 1.7$/kW per annum when micro-pulverized coal combustion was applied. The optimum pulverized coal fineness varies with different coal ranks. Considering energy, environment and safety factors, it is reasonable to speculate that the optimum pulverized coal fineness is less than conventional pulverized coal size and it commonly ranges from 10 μm to 40 μm.

Further clarifying the physicochemical properties has important guidance for superfine pulverized coal combustion. Extrusion deformation emerges due to the intense mechanical force, which leads to the breakage of pore structures. Within a certain range, smaller particle sizes are obtained with larger mechanical force. Molecular structures, pore structures and the releasing of volatiles are influenced not only by particle size but also by the pyrolysis temperature. Therefore, it is important to study the effect of temperature and mechanical force on pore structures, which will be propitious to reveal the physicochemical properties of superfine pulverized coal. Some workers have done vast work to explore the evolution of pore structures in the pyrolysis process. The pores of three chars from different Chinese coals are fractal-like, and can be classified as micro-pores, transition-pores and macro-pores based on their fractal dimensions [7]. The change trend of D_s is similar as that of S_{BET}, which is mean that D_s really reflects the character of the inner pores [8]. Han et al. [9] have confirmed that the roughness of pore structures can be evaluated using fractal dimension obtained by the N_2 adsorption isotherm method. Several test methods have been used to study pore network, such as adsorption method, mercury intrusion method, high resolution transmission electron microscopy (TEM) and scanning electron microscopy (SEM). However, these measuring methods have their own limitations. For example, transmission electron microscopy and scanning electron microscopy can present the size of pore morphology directly, however they stress on qualitative information. The quantitative results of open pores can be provided by adsorption method and mercury intrusion method which need pretreatment for samples, while the information of closed ones can't be surveyed. Small angle X-ray scattering (SAXS) is used as an important means for pore structure investigation of porous materials [10,11]. Due to the penetration of X-rays, all the information of open pores and closed ones can be reflected [12]. As an advanced measuring technique, SAXS possess vast number of advantages, such as non-destructive, high accuracy, good collimation and non-pretreatment for samples, that leads to its wide application. The complicated pore structures in coal and char can be denoted accurately by SAXS, which profits to study the variation of pore structures with various parameters, such as temperature and particle size. Bale and Schmidt [13] have investigated the surface fractal dimension of lignite, which is regarded as the first application of fractal geometry on the micro porous structure of coal. Benedetti and Ciccariello [14] have discovered that the scattering intensity of coals with different ranks has different forms. The study of Radlinski et al. has shown that there is great applicability and superiority to detect pore structures of coal by SAXS and SANS [12]. Furthermore, the surface roughness and irregularities of porous solids were also discussed [15]. The application of fractal theory can be characterized for the geometrical shape of pores [7], which is too complex to describe with classical geometry. Fractal theory, as one of the non-linear mathematics methods, is widely applied due to its unique advantage in characterizing intricate phenomena [8]. Fractal dimension of the surface of a porous solid does not depend, theoretically, on the size of the pores or the amount of surface and is an intrinsic characteristic of the surface itself [16]. Surface fractal dimension has been put to work by researchers in many fields [17–19]. Meanwhile, it has also been attested the existence of fractal characteristic in inner pore network of coal [15,20,21]. Pore structures show a relationship with the fractal dimension (D_s) [22–24]. The research findings of Nakagawa et al. give evidence that D_s of Witbank coal changes with heating, which is closely related to the softening and melting of coal [21].

However, further investigation of pore structures of coal is inhibited by the lack of high precision SAXS line station and the difficulty in data processing. To the best of our knowledge, little is known for pore structures evolution during the pyrolysis of superfine pulverized coal characterized by fractal dimension. The small angle X-ray scattering station at shanghai synchrotron radiation facility (SSRF), has been applied to study the pore structures evolution during the pyrolysis of superfine pulverized coal. The aim of the present paper is to explore the influence of several parameters on pore structures, such as coal ranks, particle sizes, pyrolysis temperatures and pyrolysis atmospheres. So far no wholly satisfactory nor complete description of pore structure in different pyrolysis parameters is available.

2. Experimental

2.1. Materials

Five typical coals with different ranks, ShanXi (SX), HeNan (HN), Neimongol (MM), ShenHua (SH) and TieLing (TL) were chosen for this experiment. Coal samples were pulverized into different sizes by super-micro mill machinery. The specific equivalent mean particle sizes of all samples are listed in Table 1. The ultimate and proximate analysis of tested samples are summarized in Table 2, from which it can be attained that SX and HN coal are anthracite, while MM and SH coal are bituminous coal and TL coal is brown coal. The ultimate analysis of samples is checked by Elemental Analysis (Germany). The proximate analysis of samples is measured according to Chinese national standard GB/T 212-2001. Particle size is so small that the influence of temperature distribution in the sample particles can be ignored.

2.2. Apparatus and procedure

The sketch map of fixed bed pyrolysis experiment device can be found in our previous work [25]. The reactor is a high temperature

Table 1
Specific equivalent mean particle sizes of tested coal samples.

Coal samples	Mean diameter (μm)				
SX	9.8	12.0	19.2	27.2	39.4
HN	8.4	12.7	19.9	27.6	36.8
MM	9.6	13.0	21.1	30.5	39.0
SH	8.9	12	18.8	28.2	38.1
TL	8.9	12.2	21.2	32.8	43.3