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Evaluation of the porous structure of Huadian oil shale during pyrolysis using multiple approaches

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ABSTRACT

The porous structure of oil shale plays a vital role in heat transfer and mass transport of its pyrolysis, particularly for the flow behavior of shale oil and gas during in-situ conversion. It is essential to clarify the pore evolution and give a mathematical description of the complex pyrolysis. In this study, the effect of temperature (100–800 °C) on Huadian oil shale pyrolysis, and the creation and evolution of the pore structure during thermal treatment were investigated. The oil shale and residues were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, ultimate analysis, scanning electron microscopy, gas permeability measurement, nitrogen isothermal adsorption/desorption, and mercury intrusion porosimetry method. Furthermore, the fractal theory was employed to understand the complex pore characteristics of the samples. The results demonstrated that heating temperature obviously affect the chemical composition and pore evolution of the residues. The removal of volatile matter resulted in pores with enhanced rough and irregular surface; the permeability of the residues is significantly increased, particularly at 350–450 °C. In addition, the fractal dimension and average pore size demonstrated a good linear relationship.

1. Introduction

Oil shale is an organic macromolecular solid material that is distributed in an inorganic matrix [1,2]; it is structurally heterogeneous, porous, and amorphous. The porous structure and surface morphology of oil shale exhibits capillaries, cracks, and open and closed pores; they are therefore very complex and irregular. During oil shale pyrolysis, the microscopic pore structures and physicochemical properties of oil shale change significantly when volatile matter is generated. The complex microscopic porous structure of oil shale not only affects its physical properties (i.e., mechanical, transport and adsorption properties) but also controls the reactant input and product output during oil shale pyrolysis: (1) the internal microstructural changes of the residues determine the mass transport of volatile matter; (2) the surface area and pore structure developed within the residues significantly influence its reactivity with the gas during pyrolysis [3–5]; (3) the ultimate structure of the residue has a significant impact on both ash formation and the emission of pollutants [6]; (4) the characteristics of the residues, particularly the ash structure, determine its secondary uses, which include building materials, chemical filling materials, and adsorbents [7,8]; and (5) the pore structure evolution during oil shale pyrolysis is essential for heat transfer and the flow of oil/gas, particularly during the in-situ conversion of the oil shale [9–11]. Therefore, it is important to determine the pore structure evolution to elucidate the pyrolysis process and to provide a mathematical description for it.

Previous studies focused on the effect of the pyrolysis conditions (temperature, heating rate, and atmosphere) on the pore structure and the reactivity of oil shale. Burnham [12] investigated the reaction kinetics between CO_2 and residual carbon from Colorado oil shale using Hg porosimetry and BET measurements and estimates a surface area of a few hundred $m^2\,g^{-1}$ in the context of understanding gasification rates, the result that oil shale residual carbon is approximately an order of magnitude more reactive than subbituminous-coal char although the surface areas are similar. Schrodt and Ocampo [13] reported that a high pyrolysis temperature and a rapid heating rate were favorable for the evolution of the pore structure. However, Bai et al. [14] reported that a rapid

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heating rate may inhibit the development of the pores. Han et al. [7,15] characterized the pore structure of combustion ash, and explored the pore-structure-evolution mechanism during oil shale combustion. They also analyzed the effect of the pore structure on the combustion mechanism. Wang et al. [16] investigated the variation in the pore structure of oil shale during microwave pyrolysis and reported that the final temperature significantly influenced the development of mesopores. However, the majority of these studies used powdered oil shale without exploring the pore connections. They provided little information on the pore space evolution of oil shale during pyrolysis. Recently, Kang et al. [9] studied the thermal cracking and the corresponding permeability coefficient which is parallel to the shale bedding plane [abbreviated as permeability (PABP)] of oil shale during pyrolysis using a micro-CT system and a high-temperature rock-permeability testing machine. Zhao et al. [17] analyzed the pore evolution of Funshun and Yan'an oil shales during pyrolysis with the use of micro-CT. Tiwari et al. [10] explored the pore structure and permeability (PABP) of the oil shale before and after pyrolysis using X-ray micro-CT and a lattice Bolzmann simulation; they reported that the patchy porosity was dependent on the distribution of kerogen, and this resulted in incompletely connected flow channels. It is well-known that the apparent anisotropy of oil shale produces different properties. Limited data is available on the permeability that is perpendicular to the shale bedding plane [abbreviated as permeability (PEBP)] during pyrolysis. Therefore, the evolution characteristics of the space structure during oil shale pyrolysis remains a topic of interest to be explored.

The microgeometry of the pore-rock interface is an important parameter to understand how the irregularity can affect the transport and adsorption phenomena in shale. The surface or volume morphologies can be described quantitatively as the fractal geometry, which is defined as a self-similarity on surface (or volume) roughness. The value of the fractal dimension that characterizes a surface can be related with the degree of complexity of this surface. In addition, the fractal dimension is an intrinsic property of a surface and, theoretically, does not depend on its size. This is an important fact that makes fractal dimension a useful parameter for characterizing the surface of porous solids, despite pore width or pore distribution.

This study aims to provide comprehensive information on the evolution of the pore structure of oil shale during pyrolysis. The influence of the structural evolution and the morphological changes of the residues on the pyrolysis reactivity of the oil shale were investigated by multiple techniques. The pyrolysis was performed at temperatures of 100–800 °C. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultimate analysis, scanning electron microscopy (SEM), gas permeability measurement, nitrogen isothermal adsorption/desorption, and the mercury intrusion porosimetry (MIP) method. Each technique may lead to different experimental values because they employ different measurement mechanisms. To provide additional information on the texture, the fractal theory was employed to describe the complexities of the pore characteristics. Further understanding on this subject is vital to develop advanced oil shale utilization technologies, particularly for in-situ conversion.

2. Materials and experiments

2.1. Materials

The Gonglangtou mine in Huadian, China supplied the oil shale. The proximate, ultimate, and Fischer assay analysis conformed to ASTM standards; Table 1 shows the results.

Table 1
Physical properties of Huadian oil shale.

Proximate analysis (wt.%, ad)	
Volatiles	41.65
Fixed carbon	1.43
Ash	56.92
Moisture (as received)	3.25
Calorific value (MJ kg^{-1})	13.07
Ultimate analysis (wt.%, ad)	
C	32.86
H	4.47
N	0.84
S	4.92
Fischer assay analysis (wt.%, ad)	
Shale oil	22.41
Gas	6.14
Water	7.16
Residue	64.29

2.2. Pyrolysis experiments

The pyrolysis experiments utilized standard cylindrical samples with a diameter ∼25 mm, length ∼25 mm. They were drilled and processed perpendicular to the bedding plane.

Solid residues were obtained using a tube furnace, which was electrically heated with nitrogen sweeping. Standard cylindrical samples (19–20 g) were packed at the center of the tube furnace. They were uniformly heated at a rate of 5 °C min^{-1} to a specific temperature between 100 and 800 °C (at 50/100 °C intervals), where the sample was maintained for 120 min. Subsequently, the reactor naturally cooled to room temperature and the solid residues were collected.

The raw oil shale was labeled as Sraw. The solid residues from the pyrolysis experiments were labeled as S100, S200, S300, S350, S400, S450, S500, S550, S600, S650, S700, and S800. The number represents the pyrolysis temperature, e.g. S100 denotes the solid residue collected following pyrolyzation at 100 °C.

2.3. Characterization of the oil shale and residues

The samples for the following analytical tests were prepared to ASTM standards. Duplicate experiments were performed to ensure reproducibility.

2.3.1. Thermal characterization

The thermogravimetric (TG) analysis of the oil shale was conducted using a STA 449C thermal analyzer system (Netzsch, Germany). The finely ground sample (<75 μm) was heated from ambient temperature to 800 °C, with a heating rate of 5 °C min^{-1}. The flow rate of high-purity nitrogen (>99.99%) was maintained at 60 mL min^{-1}.

2.3.2. Chemical characterization

The XRD pattern of the finely ground sample (<75 μm) was recorded on a Rigaku D/MAX 2550 diffractometer (Japan) with Cu Kα radiation. The FTIR spectrum (KBr) of the finely ground sample (<75 μm) was obtained using the IFS 66V/S FTIR spectrometer (Bruker, Germany) in the mid-IR region of 400–4000 cm^{-1}. The ultimate analysis of the powdered sample (<75 μm) was performed by vario MICRO (Elementer, Germany). The carbon, hydrogen, nitrogen, and sulfur contents were directly determined.

2.3.3. Physical characterization

The surface morphology analysis of the lamellose sample was performed using an S-4800 field emission SEM (Hitachi, Japan), with an acceleration voltage of 1.5 kV. The nitrogen adsorption/desorption experiment for the grained sample (0.2–0.3 mm) was