



Formation and development of the pore structure in Chang 7 member oil-shale from Ordos Basin during organic matter evolution induced by hydrous pyrolysis



Lina Sun^{a,b}, Jincui Tuo^{a,*}, Mingfeng Zhang^a, Chenjun Wu^a, Zixiang Wang^{a,b}, Youwei Zheng^{a,b}

^a Key Laboratory of Petroleum Resources, Gansu Province/Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences, Lanzhou 730000, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- The pore evolution process of oil-shale was simulated by hydrous pyrolysis.
- The nitrogen quantity adsorbed increased with increasing pyrolysis temperature.
- The development of the pore structure was associated with organic matter evolution.
- The pyrolysis products in different thermal stages may be the basic factor to affect porosity.
- The pore evolution was roughly divided into the stages of reforming, formation and development.

ARTICLE INFO

Article history:

Received 16 December 2014
Received in revised form 19 May 2015
Accepted 26 May 2015
Available online 3 June 2015

Keywords:

Oil-shale
Hydrous pyrolysis
Nitrogen adsorption
Organic matter evolution
Pore structure

ABSTRACT

To obtain information about the pore characterization during the evolution of sedimentary organic matter, the pore structures of residual samples from oil-shale hydrous pyrolysis experiments were analyzed via low-pressure nitrogen adsorption measurements. These seven experiments were conducted at different temperatures, while other experiment factors, such as original samples, the heating time and rate, the lithostatic pressure and the hydrodynamic pressure, were kept same. Nitrogen adsorption measurements were performed on unheated samples and other solid residues after pyrolysis at different simulation temperatures to analyze and characterize the nature of the pore structure. The results showed that Type IV nitrogen adsorption isotherms with Type H3 hysteresis loops are present in these samples, so mesopores may be predominant. With increasing pyrolysis temperature, the quantity of nitrogen adsorbed generally presents an increasing trend at a relative P/P_0 value of approximately 0.996 MPa. The total pore volume and specific surface area were positively correlated with the pyrolysis temperature, and their correlation coefficients (R^2) were 0.91 and 0.83, respectively. The pore volume and surface area of the micropores, mesopores and macropores all increased, as did the quantities of the corresponding pores. By combining the different scales of pore development with the pyrolysis products, a model for the stages of porosity evolution was acquired. With the increasing simulation temperature, the changing of porosity calculated roughly by the decreased amount of TOC present a same tendency with the measured values by N_2 adsorption method. But the relative deviation between them was higher in lower maturity, the opposite occurred in higher maturity. Therefore, the effect of TOC on the evolution of pore structure may be related to the maturity. And the pore connectivity which resulted from the generation and migration of pyrolysis products, can be seen as the important factor on the increased porosity. In further level, shale oil-gas were better preserved in lower maturity, but likely to migrate in higher thermal evolution.

© 2015 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +86 931 4960854; fax: +86 931 8278667.

E-mail address: jctuo@ns.lzb.ac.cn (J. Tuo).

1. Introduction

Kerogen-rich mudstones are important both as a traditional oil shale resource [1–3] and as source rocks for conventional [4] and unconventional oil and gas [5–7]. The Chang 7 member of the Triassic Yanchang Formation in the Ordos Basin has all three attributes, having sourced traditional oil reservoirs [8,9], being considered as a target for production from the mature source rock by hydraulic fracturing [10–12], and occurring near the surface with organic carbon content greater than 10% by weight.

The evolution of the pore structure during kerogen maturation is particularly important for retention of oil and gas in the mature source rock, hence it has a large impact on a formation's potential importance as an unconventional source of oil and gas. The porosity comes from conversion of organic matter to oil and gas, and much of the porosity is in small diameter pores that facilitate adsorption and capillary condensation at reservoir conditions [13].

Scholars have already conducted studies on how the pore structures change with thermal evolution by different measurement techniques [14–24]. For example, small-angle and ultra-small-angle neutron scattering (SANS/USANS) and gas (N_2 and CO_2) adsorption techniques were used by Mastalerz et al. [21] to study the porosity characteristics of two shale samples with similar maturities (the vitrinite reflectance (R_o) was 0.55% and 0.62%) but different total organic carbon (TOC) contents (15.8% and 5.8%). The results showed that the micropore networks were affected by organic matter (OM). Tiwari et al. [19] used three-dimensional X-ray micro-tomography (XMT) to analyze the different pore network structure characteristics before and after pyrolysis and found that a larger (the pores were 500 μm developed after pyrolysis) pore space was produced in sample with higher maturity than that with lower maturity. Analyzing Woodford shale samples with different R_o (from 0.51% to 6.36%) by focused ion beam milling and scanning electron microscopy (FIB–SEM), Curtis et al. [20] found that thermal maturity alone is not enough to predict porosity in OM, but other factors, such as OM composition, are also needed to be considered. Low-pressure gas adsorption (N_2 , CO_2 and CH_4) has also been used to analyze the porosity evolution during thermal maturation [14–18]. Kuila et al. [17] used N_2 adsorption to measure the pore structure before and after removing OM from thermally mature mudrocks. The results of the reduction of the pore volume indicated that the interior of the OM can be a host for pores. Romero-Sarmiento et al. [18] proved that surface areas and mesopores have a positive relationship with maturity by N_2 adsorption. Wei et al. [16] found that thermal maturity plays an important role in controlling the total porosity in organic-rich shales by the pore analysis of N_2 and CO_2 adsorption, but they obtained better predictions when combining other factors (e.g., OM type, TOC and mineralogy). Chen and Xiao [15] analyzed the evolution of the nanoporosity in shales during an anhydrous pyrolysis experiment by N_2 and CO_2 adsorption and concluded that nanoporosity has a positive linear correlation with thermal maturity after the oil window stage, and they divided the evolution into the three stages of formation (R_o from 0.6% to 2.0%), development (R_o from 2.0% to 3.5%) and conversion and destruction ($R_o > 3.5\%$) of OM-hosted nanopores. Hu et al. [14] used N_2 , CO_2 and CH_4 adsorption methods to investigate the methane adsorption of bitumen-free Woodford shales, which were artificially matured by hydrous pyrolysis, and found that the increasing pore surface area and volume were mainly due to the abundant content of mesopores in the OM during thermal treatment. Therefore, although recent research on the development of pores during thermal maturation has been conducted, there is no agreement thus far [14–24]. This may be caused by the different geological factors, such as mineral composition, TOC, OM type and

chemical composition, diagenesis and maturity [17,19,25], or because the measurement techniques and experimental conditions affect the pore evolution.

Therefore, it is necessary to study how porosity develops in oil-shale samples during thermal treatment and how the development is affected by other factors (e.g., TOC, OM, diagenesis, and water). Our current study focused on the characteristics of porosity evolution in artificially matured samples by hydrous pyrolysis. These hydrous pyrolysis experiments were conducted on the same samples and at the same lithostatic pressure, hydrodynamic pressure, heating rate and time but at different temperatures. The pore structures of the solid residual samples at every temperature were analyzed by low pressure nitrogen adsorption. The goals were (1) to understand the effect of thermal maturity on the pore evolution, (2) to analyze the relationship between pore development and pyrolysis products, (3) to investigate the pore size distribution during thermal treatment, and (4) to research the effect of TOC on porosity. These results provide evidence to the characteristics of pore structures during the evolution of OM.

2. Experiment

2.1. Sample

In this research, the oil-shale samples were collected from Chang 7 Yanchang Formation, Triassic, in Tongchuan, Ordos Basin, Shanxi Province, western China. The block samples were collected from an outcrop in a mining pit, and the depth was about 10 m. Before pyrolysis, the block sample were drilled into cylindrical samples with a diameter of 25 mm. The sample was organic-rich, with a TOC of 13.75%, and the Rock–Eval pyrolysis presented a hydrocarbon index (HI) of 483.49 mg/g TOC, an oxygen index (OI) of 0.95 mg/g TOC and a T_{max} of 451 °C. The values of S_1 peak (dissolved hydrocarbon), S_2 peak (pyrolysed hydrocarbons) and S_3 peak (CO_2) were 2.78 mg/g, 66.48 mg/g and 0.13 mg/g respectively. Based on the values of HI and OI, what we concluded that the type of kerogen was Type I–II. Then according to the classification by the ratio of S_2/S_3 (Type I: >20 ; Type II₁: $5 \sim 20$; Type II₂: $2.5 \sim 5$; Type III: <2.5), which was 511, so the kerogen of the sample was Type I. The vitrinite reflectance (R_o) is about 0.7, and the productivity index (PI) equaled to 0.04, which all indicated that the thermal maturity of the OM in this oil-shale sample was immature to early mature.

2.2. Pyrolysis

2.2.1. Experimental apparatus

The pyrolysis experiments were conducted in a WYMN-3 HTHP simulation instrument (Fig. 1), which generally contains a software control system (computer) and a hardware performance system (apparatus). It can be seen as a semi-open high-temperature, high-pressure (HTHP) simulation system. The computer procedure is used to set experimental conditions and collect data. The corresponding performance system includes the following subprime systems: reaction (autoclave), heating, hydraulic control (control of the lithostatic pressure), fluid supplement (adding deionized water and control of the hydrodynamic pressure) and collecting (storing pyrolysis productions) systems. The opening degree of the pyrolysis system can be controlled by a two-position three-way solenoid valve and is achieved by the relationship between the hydrocarbon expulsion pressure limit and the pressure threshold. In these experiments, the hydrodynamic pressure, hydrocarbon expulsion pressure limit and pressure threshold were 50, 55 and 5 MPa, respectively, and were set on the computer. When the hydrodynamic pressure in the sample cell reached the

Download English Version:

<https://daneshyari.com/en/article/6635041>

Download Persian Version:

<https://daneshyari.com/article/6635041>

[Daneshyari.com](https://daneshyari.com)