Oil expulsion in marine shale and its influence on the evolution of nanopores during semi-closed pyrolysis

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ABSTRACT

Oil expulsion is an important process for the evolution of shale, especially in the oil-generative window. Low oil expulsion efficiency will cause the retention of oil and gas in mature source rock. This study used semi-closed pyrolysis to simulate the hydrocarbon generation and expulsion process of the Xiamaling Formation marine shale at various conditions. Low-pressure nitrogen (N_2) and carbon dioxide (CO_2) gas adsorption isotherms were obtained for the original shale sample and its thermally evolved solid residues. The results showed that the amount of residual bitumen first increased with increasing expulsion efficiency (EE < 13.43%) and then remained constant with a further increase in EE. This finding implied that the saturation threshold for the source rock must be reached before oil expulsion can proceed. Meanwhile, the evolution of pore volumes with EE can be divided into two stages. The pore volumes decreased sharply in the first stage (EE < 13.43%), whereas they decreased slowly in the second stage (EE > 13.43%). The evolution of volume for micropores and fine mesopores with EE is very similar to that of expelled hydrocarbons. This similar evolution trend was further confirmed by the abovementioned oil expulsion model. This study enhanced understanding of the generation and evolution of shale gas in the oil-generative window.

1. Introduction

Conventional oil and gas are the most important energy sources in the world. Currently, however, unconventional gas is attracting much attention due to the growing energy demand and the great success of the North America shale gas revolution in recent decades (Curtis, 2002; Montgomery et al., 2005; Jarvie et al., 2007; Pollastro, 2007; Dai et al., 2017). Significant breakthroughs have also been obtained in recent evaluations and explorations of shale gas in China (Chen et al., 2011; Sun et al., 2012; Wang et al., 2013; Tan et al., 2014; Zou et al., 2015). Compared to traditional natural gas reservoirs, shale is generally characterized by low porosity and permeability. Additionally, shale gas production depends on the ability of pore systems to store and release hydrocarbon gas (Ross and Bustin, 2007, 2008; Wu et al., 2012; Cao et al., 2015). Thus, pore characterization is very important for the evaluation of shale gas.

The evolution of shale pore structure is very complicated, with a great number of geological factors controlling such processes, such as total organic carbon (TOC), thermal maturity, burial depth and mineralogy (Mastalerz et al., 2008; Loucks et al., 2009; Modica and Lapierre, 2012; Valenza et al., 2013; Suárez-Ruiz et al., 2016). Thermal

maturity is considered the main factor, at least to a large extent, that controls the porosity in organic matter (Loucks et al., 2009; Modica and Lapierre, 2012; Valenza et al., 2013). Many previous studies have focused on the thermal maturity of shale based on the results from both natural maturity sequences (Mastalerz et al., 2013; Wei et al., 2014; Mathia et al., 2016) and artificial thermal simulation experiments (Chen and Xiao, 2014; Tang et al., 2015; Sun et al., 2015; Liu et al., 2017). However, there is no agreement on the evolution of nanopores in shale during thermal maturation. It is probably because of source rock heterogeneity for many factors, such as mineral composition, TOC, the type of organic matter, diagenesis and maturity (Sun et al., 2015). Recently, Mathia et al. (2016) suggested that the evolution of nanoporosity in natural shale is a comprehensive function of multiple factors including (1) the primary shale composition; (2) carbonate diagenesis; (3) compaction (pressure); and (4) the maturation (temperature), micro-migration, local trapping and gasification of heterogeneous organic phases. Therefore, studies of the comprehensive effects of multiple factors may provide more reasonable explanations for the evolution of nanoporosity in natural shale.

Oil expulsion is considered the initial step in the release of generated petroleum compounds from kerogen into the adjacent reservoir or

migration layer through capillaries and narrow pores of a fine-grain source rock (Tissot and Welte, 1984). It is an important process for the evolution of shale, especially in the oil-generative window in which the endured temperature and pressure are not very high. The process of oil expulsion is closely related to pore structure evolution during kerogen maturation (Sun et al., 2015). Namely, high porosity occurring in the mature source rock will promote oil expulsion, whereas low porosity will prohibit oil expulsion. For most commercial shale gas plays, their oil expulsion efficiency is very low due to the low porosity and permeability (Jarvie, 2012). The most pronounced changes in the physical and chemical conditions during natural oil generation and expulsion are the increase in temperature and pressure (Tissot and Welte, 1984). This implies that the oil expulsion efficiency of shale is a comprehensive result of the changes in temperature and pressure. Meanwhile, compaction (pressure) and maturation (temperature) are two important factors for the evolution of nanoporosity in natural shale (Mathia et al., 2016). Thus, studying the oil expulsion influence on nanopore evolution will enhance our understanding of the combined influences of maturity and pressure on the evolution of nanoporosity in natural shale.

This study chose semi-open pyrolysis at temperatures of 300 °C to 370 °C for 72 h (Easy %Ro: 0.7%–1.3%) to investigate the oil expulsion process and evolution of nanopores during the oil-generative window. Most of the shale gas strata in the Sichuan Basin experienced a deep burial of 3–5 km (Liu et al., 2009; Ma et al., 2008; Zhang et al., 2008; Xiao et al., 2013), with a high pressure coefficient of 1.3–2.1 (Zou et al., 2015). Given a normal hydrostatic pressure increase of 10 MPa/km, most of the shale gas strata in the Sichuan Basin experienced a hydrostatic pressure of approximately 40–100 MPa. Thus, a pressure of 50–100 MPa was used in this study, because this range covered most of the conditions of the evolution of shale in Sichuan Basin. Subsequently, the evolution of nanopores in the simulated sequence was analyzed through gas adsorption methods, which have the advantages of convenient operation, maintaining the natural pore characteristics, and the ability to assess the complete nanopore size range (Zhang et al., 2017). The aim of this study is to reveal the oil expulsion process of shale and its influence on the evolution of nanopore systems.

2. Samples and methods

2.1. Samples

The investigated oil shale was sampled from the outcrop of the Xiamaling Formation in the Xiahuanyuan area of Jixian in Tianjing, China. The sample is immature, with a Ro value of 0.6%. The basic petrological and geochemical parameters are presented in Table 1. The sample is organic-rich, with a total organic carbon (TOC) content of 5.39%. Rock-Eval analysis revealed this oil shale to have a Tmax of 434 °C and a HI value of 564 mg/g TOC. The kerogen is type II (Liu et al., 1990; Xie et al., 2013). Minerals in the oil shale include quartz (51.4%), illite (26.4%), albite (10.3%), magnesian calcite (2.6%), and amorphous stuff (9.3%).

2.2. Pyrolysis experiment

This study used semi-closed pyrolysis, which was used to study oil generation (Lu, 1990), to artificially simulate the hydrocarbon generation and expulsion process. A schematic diagram of a high pressure, semi-closed pyrolysis system was shown by Liu et al. (2017). First, the oil shale sample was crushed into ≤80 mesh (180 μm) powder. Then,

the crushed oil shale powder was loaded into a stainless steel cylinder (5 cm o.d. (outer diameter) 3 cm i.d. (inner diameter)) and sealed on both sides. The sealed cylinders were then compacted by a jack under vertical pressures of 50, 75, and 100 MPa, respectively. The cylinders were heated in an oven to 300 °C, 343 °C, and 370 °C and then held for 72 h, respectively. The calculated vitrinite reflectances from the Easy % Ro method (Sweeney and Burnham, 1990) for the kerogen heated to 300 °C, 343 °C, and 370 °C for 72 h were 0.7%, 1.0%, and 1.3%, respectively (in the oil-generative window). After cooling, the sealed cylinders were removed to collect the pyrolyzed products (expelled liquid oil and gas). The expelled oil and gas during the pyrolysis experiment were collected and analyzed. Finally, the pyrolyzed sample was Soxhlet extracted with dichloromethane: methanol (93,7 v:v) for 72 h to obtain the retained hydrocarbon (residual bitumen).

2.3. Methods

2.3.1. Gas composition analysis

The generated hydrocarbon gas was directly injected by a gas-tight syringe from the collecting tube into a customized vacuum line connected to an Agilent 6890 N capillary gas chromatograph modified by Wasson ECE Instrumentation for determination of molecular composition. A Poraplot Q capillary column (30 m × 0.25 mm × 0.25 μm) was used with helium as a carrier gas. The GC oven was held isothermally at 70 °C for 6 mins, programmed to increase to 180 °C at a rate of 15 °C/min and held for 4 min. Gaseous hydrocarbons (C_{1-5}) were quantified by using an external standard. The sum of the expelled hydrocarbon gases for each pyrolysis is shown in Table 2. The relative error is < 0.5% for this method (Pan et al., 2012; Jin et al., 2013).

2.3.2. Pore structure distributions (PSD)

Low-pressure nitrogen (N_2) and carbon dioxide (CO_2) gas adsorption isotherms were conducted on a Micromeritics ASAP-2460 Accelerated Surface Area and Porosimetry System. The pyrolyzed samples were all analyzed before and after Soxhlet extraction using dichloroform (DCM) for 72 h. The samples were crushed to 60–120 mesh size (250–125 μm) and degassed at 110 °C for 12 h in a vacuum chamber prior to analysis to remove the residual volatile material and free water. Nitrogen isotherms at 77 K were collected within a relative pressure (p/p^0) range of 0.005–0.998 (p is the balance pressure, and p^0 is the saturation pressure). Carbon dioxide isotherms were collected at 273.15 K at relative pressures of 0.00006–0.03.

The pore size distributions (PSDs) of the investigated samples were obtained using the composited N_2 and CO_2 non-local-density functional theory (NLDFT) method based on adsorption isotherms (Wei et al., 2016). This method enables the most suitable detection range (0.33–100 nm) and has high reliability and accuracy. As the maximum pore diameter calculated by NLDFT is 100 nm, the NLDFT analysis based on N_2 and CO_2 composited adsorption isotherms is used here to investigate the characteristics of pores with diameters (D) up to 100 nm. To better understand their evolution, the nanopores were subdivided into micropores (D < 2 nm), fine mesopores (2 < D < 10 nm), medium mesopores (10 < D < 25 nm), coarse mesopores (25 < D < 50 nm), and macropores (D > 50 nm), according to the IUPAC classification (Thommes et al., 2015) and previous work (Chalmers et al., 2012).

Table 1
The basic geochemical parameters of the investigated sample.

Sample	Lithology	Kerogen	TOC (%)	S1 (mg/g source rock)	S2 (mg/g source rock)	Tmax (°C)	HI	Ro (%)	$\delta^{13}C$ (‰)
XML	Calcareous shale	II_1 sapropelic	5.39	1.84	42.56	434	564	0.6	−30.97