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Evolution of Pores in Organic-rich Shales During Thermal Maturation

Tian Hua, Zhang Shuichang, Liu Shaobo, Chen Jianping
RIPED, Beijing, China

1. INTRODUCTION

Shale gas has become an increasingly important source of natural gas in the United States over the past decade, and interest has spread to potential gas-rich shales in Canada, Europe, Asia, and Australia. Shale gas is believed to have stored as free compressed gas in open pores and cracks, as adsorbed gas on the surfaces of kerogen and clay and as diffuse gas stored within the solid organic matters (Sondergeld et al, 2010).

A higher concentration of organic matter can provide excellent original organic richness and high generation potential, resulting in higher gas-in-place volumes (Bowker, 2007). The nanopores in the organic matters are the predominant pore type in the Barnett mudstones and are believed to relate to thermal maturation (Loucks et al, 2009). Most nanopores are found in grains of organic matters as intraparticle pores; many of these grains contain hundreds of pores that range between 5 and 750 nm with the median nanopore size for all grains being approximately 100 nm. Internal porosities of up to 20.2% have been measured for whole grains of organic matters. (Loucks et al, 2009). Some gas is also believed to be partly stored in shale source rocks as gas adsorbed to or within the organic matrix (Jarvie et al, 2007).

Therefore, it is important to understand the evolution of pores in organic matters during the process of thermal maturation in order to qualtitatively predict shale porosity in shale gas exploration. This study aims to document the changes of size, morphology, and abundance of pores in an initial low maturity organic-rich shale during thermal maturation, so as to evaluate the storage ability of shale at different maturities.

2. SAMPLE AND METHOD

In this study, an immature (Ro~0.6%) shale outcrop sample from Fushun mine, Northeast China was selected for pyrolysis. A set of mature samples were also selected for comparison. Thesolid residual samples of pyrolysis at different temperatures were used to compare with the shale at different maturities. The initial sample is relatively immature, with a vitrinite reflectance value of 0.6%, TOC of 7.35%, Hydrogen Index (HI) of 440. The mature outcrop samples are with vitrinite reflectance values of 1.3%-2.8%, TOC values of 5.0-11.2%, HI values of 440-680.

An alloy reactor pyrolysis experimental setup (Figure 1) was set up to performpyrolysis experiments on the immature shale under elevated pressure and heating rate conditions (0.1-10MPa, 0-600^{o}C, 1^{o}C/h). This setup includes the use of a back-pressure valve, with which the user can set a specific pressure value. If the gas pressure in the alloy reactor grows over the given pressure, gases are released. This advantage is more like the geological condition under which the episodic hydrocarbon expulsion under specific pressure.

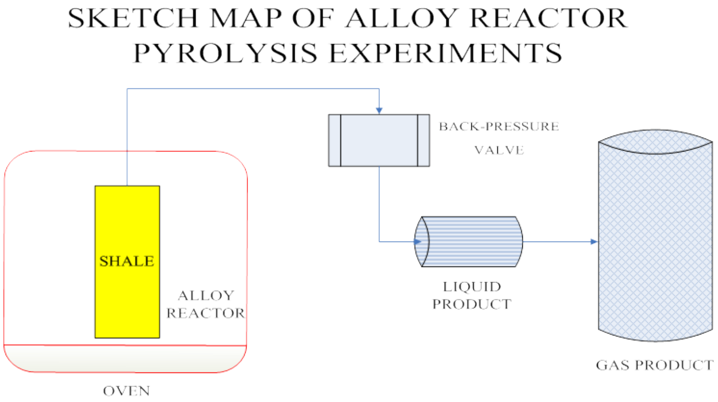

Figure1. Alloy Reactor Pyrolysis Experimental setup

Pyrolysis products were analyzed for gas yields, molecular compositions, and residual vitrinite reflectance (Ro). Solid residual and mature samples were analyzed for thin section, FESEM, NMR analysis, CO_2 low pressure isotherm analysis (D-R method), N_2 low pressure isotherm analysis (BET theory), Hg porosimetry. Pore size, morphology, and abundance in shale gas reservoir were carefully observed.

3. RESULTS AND DISCUSSION

With the increase of thermal maturity, pore abundance becomes higher. Pores in the low-thermal-maturity samples are much fewer than that at high maturity. Two SEM examples are presented here (Figure 2). Sample B (right) have VRo values less than 0.7%, which are at the low end of the hydrocarbon generating window. There are little pores in the organic matters; the surface of the organic matters is relatively flat. Pore networks in sample B contrast greatly with that in sample A (left) of higher-maturity (VRo values > 1.0%). The primary difference is that grains of organic matter in these less mature samples have few or no pore. Also, during thermal maturation, the surface area of shale increase, the percentage of micropores[1] increase.

[1] Using the International Union of Applied and Pure Chemistry(IUAPC)pore classification, micropores are pores<2 nm in diameter, mesopores are in the range of 2-50 nm and macropores are >50nm

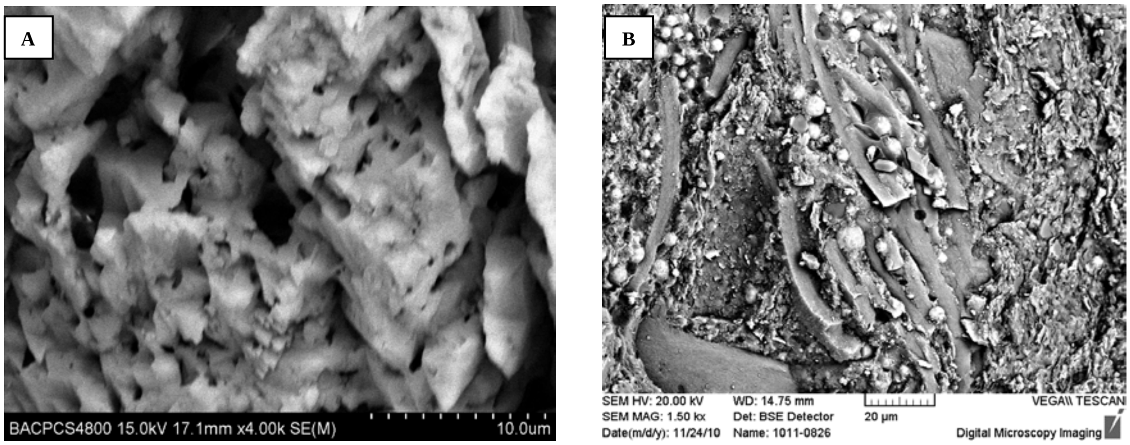

Figure 2. SEM images of organic matters in shale of different maturities. A) shale with VRo values> 1.0% showing well developed pores presented in the organic matters. B) shale with VRo values< 0.7% showing striped organic matters in the matrix with few pores in the organic matters.

Pore size grow greater during thermal maturation, the percentage of micropores and mesopores increase in SEM imagines, CO_2 low pressure isotherm analysis (D-R method), N_2 low pressure isotherm analysis (BET theory), and Hg porosimetry analysis. Pore morphology changed much during thermal maturation. Most pores in immature shale are bubble like and isolated. By contrast, stripe, elliptical and connected pores are much common in mature shale.

During thermal maturation, Pores are formed as kerogen is converted to hydrocarbons, resulting in the formation of liquids and gases (Loucks et al, 2009). Pore body and pore throat size distributions are typically smaller ranging, well below the micro porosity classification (<0.1μm) into the nanometer (nm) territory. (Sondergeld et al, 2010). The thermal conversion of kerogen to petroleum results in the formation of a carbon-rich residue (CR) and increased porosity in the rock matrix, which impacts gas storage capacity. For an average TOC of 6.41 wt.% (mass), When thermal maturation is in the dry-gas window (e.g., >1.4% Ro), approximately 4.3 vol.% porosity is created by organic matter decomposition (Jarvie et al, 2007) .

4. CONCLUSIONS

New alloy reactor pyrolysis experiments with a back-pressure valve were developed to control the outlet pressure of pyrolysis products. This advantage is much like the condition under which the episodic hydrocarbon expulsion under specified pressure.

During thermal maturation, with a series of analysis, pyrolysis solid residual products present higher pore abundance, bigger pore size, and the pore morphology changed from being bubble-like and isolated to striped, elliptical and connected pores, due to the results of hydrocarbon generation.

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