International Journal of Coal Geology 132 (2014) 38–50

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Influence of Soxhlet-extractable bitumen and oil on porosity in thermally maturing organic-rich shales

Lin Wei [a,*], Maria Mastalerz [b], Arndt Schimmelmann [a], Yanyan Chen [a]

[a] Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1405, USA
[b] Indiana Geological Survey, Indiana University, Bloomington, IN 47405-2208, USA

ARTICLE INFO

Article history:
Received 10 July 2014
Received in revised form 5 August 2014
Accepted 5 August 2014
Available online 14 August 2014

Keywords:
Shale
Porosity
Maturity
Adsorption
Extraction
KBr-FTIR

ABSTRACT

Porosity in shales is important for storage of shale gas in reservoirs. As organic-rich shale thermally matures and enters the oil window, generated bitumen and oil can fill pore spaces, block pore connectivity, and reduce porosity. Low-pressure N_2 and CO_2 adsorption techniques were used to quantify mesoporosity (pore size 2–50 nm, accessible to N_2 and CO_2) and microporosity (pore size <2 nm, accessible to CO_2 only) in New Albany Shale samples of Devonian and Mississippian age from Indiana and Illinois ranging from marginally mature (vitrinite reflectance $R_o = 0.55\%$) to post-mature ($R_o = 1.41\%$). After measuring their original porosity, the shale samples were Soxhlet-extracted in refluxing dichloromethane (DCM, boiling temperature 39.6 °C) to remove soluble oil/bitumen, vacuum-dried, and then re-measured for meso and microporosities. Subsequently, the same samples were Soxhlet-extracted in toluene (boiling temperature 111 °C, with enhanced solubility of oil/bitumen), vacuum-dried, and again characterized porosimetrically.

The maturation sequence of the original, non-extracted shales expresses a higher mesoporosity in lower maturity samples (vitrinite reflectance R_o 0.55%, and 0.65%), and an intermittent decrease in mesoporosity in samples of post-mature stage (R_o 1.15%) in two size fractions (4-mesh and 60-mesh). The intermittent decrease in mesoporosity is consistent with partial filling of pore spaces with bitumen and oil until secondary cracking reclaims some of the lost open pore space from liquid hydrocarbon phases. Organic matter (OM) transformation is thus a pivotal cause for the observed evolution of mesoporosity in original, non-extracted shales. Micropore volumes display a varying trend throughout thermal maturation, and are significantly controlled by total organic carbon content. Compared to 4-mesh sample fractions, a reduction in grain size of 60-mesh fractions for gas adsorption porosimetry prominently enhances mesopore volumes, whereas the effects on micropore volumes are variable. These findings may be associated with the fact that for smaller particles it is easier to attain equilibrium during gas adsorption porosimetry.

Solvent extraction of soluble bitumen and oil from the shale samples generally opens additional pore space for N_2 and CO_2 adsorption, although the specific effects on mesoporosity and microporosity depend on maturity, total organic carbon (TOC) content, type of solvent, and grain size of the Soxhlet-extracted shales. The mesopore volume increases more in extracted samples with higher maturity, whereas the strongest gain in micropore volume is observed at elevated TOC content and highest maturity.

Comparative porosities of original and Soxhlet-extracted shale samples constrain the evolution of porosity along maturation, as well as the effect of partial oil/bitumen filling and blocking of pores. This study also employs FTIR analyses of DCM and toluene Soxhlet extracts to differentiate low-temperature DCM-extractable, mostly aliphatic OM from higher-temperature toluene-soluble OM containing condensed cross-linked polyaromatic structures.

1. Introduction

Porosity plays a significant role in evaluating the shale reservoir quality and the hydrocarbon potential (Curtis et al., 2012; Ertas et al., 2006; Hunt, 1995; Jarvie, 2012; Loucks et al., 2009; Romero-Sarmiento et al., 2013). Gas adsorption capacity in shales hinges on the volume of pores (Bustin et al., 2008; Chalmers and Bustin, 2007; Curtis et al., 2011a; Ross and Bustin, 2009), whereas pore size distribution and pore connectivity influence shale permeability (Bustin et al., 2008; Clarkson et al., 2013; Ross and Bustin, 2009). Knowledge of porosity characteristics, gas adsorption volumes, and shale heterogeneity aids in the prediction of shale gas contents of reservoirs, reduces the shale gas exploration risk, and mitigates production uncertainties (Bustin et al., 2008; Pollastro et al., 2007; Ross and Bustin, 2009).

In contrast to conventional reservoirs, shales have complex porosity systems featuring interparticle and intraparticle pore components (Loucks et al., 2009, 2012). Significant contributions of intraparticle

---

* Corresponding author.
E-mail address: linwei@indiana.edu (L. Wei).

http://dx.doi.org/10.1016/j.coal.2014.08.003
0166-5162/

Table 1
Vitrinite reflectance (R_o), total organic carbon (TOC) content, maturity, bitumen content, and total porosity by helium porosimetry of shale samples. The bitumen content was determined by maceral analysis (volume %, on mineral matter free basis, mmf) (modified from Mastalerz et al., 2013).

Sample	R_o (%)	TOC (wt.%)	Depth (m)	Maturity stage	Bitumen content (vol. %, mmf)	Helium porosimetry (total pore volume cm^3/g)
MM4	0.55	13.0	764	Marginally mature	2	0.0186
NA2	0.65	5.3	853	Early mature	10	0.0210
IL-5	1.15	4.3	1607	Late mature	45	0.0059
IL-1	1.41	6.4	78	Post mature	75	0.0141

porosity derive from macerals in organic-rich shales (Chalmers and Bustin, 2008; Jarvie et al., 2011). The existence of abundant nanopores in organic-rich shales has been suggested by various techniques, including low-pressure gas adsorption (e.g., Clarkson et al., 2013; Mastalerz et al., 2013; Ross and Bustin, 2009) and low-angle scattering (e.g., Clarkson et al., 2013; Mastalerz et al., 2012; Melnichenko et al., 2009). Argon ion-milling and subsequent scanning electron microscopy (SEM) of Barnett Shale imaged the presence of nanopores in close association with organic matter (OM) (Loucks et al., 2009; Slatt and O'Brien, 2011). Nanopores are generated during burial and maturation of OM (Bernard et al., 2012; Jarvie et al., 2007) and are generally isolated in organic flakes (Jarvie et al., 2007). Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) image analysis were able to provide an appreciation of the complexity of pore networks in Marcellus Shale (Chalmers et al., 2012) and confirmed that macropores and mesopores are interconnected (Curtis et al., 2011a). Furthermore, the recent petrologic evidence suggests that the thermochemical conversion of kerogen to oil, bitumen, and gas creates an OM-hosted nanopore network (Loucks et al., 2009; Modica and Lapierre, 2012). It is now generally accepted that the pore network in the organic component of OM-rich shales plays an important role for the storage of hydrocarbons (Curtis et al., 2011b; Loucks et al., 2009; Mastalerz et al., 2013; Passey et al., 2010; Wang and Reed, 2009).

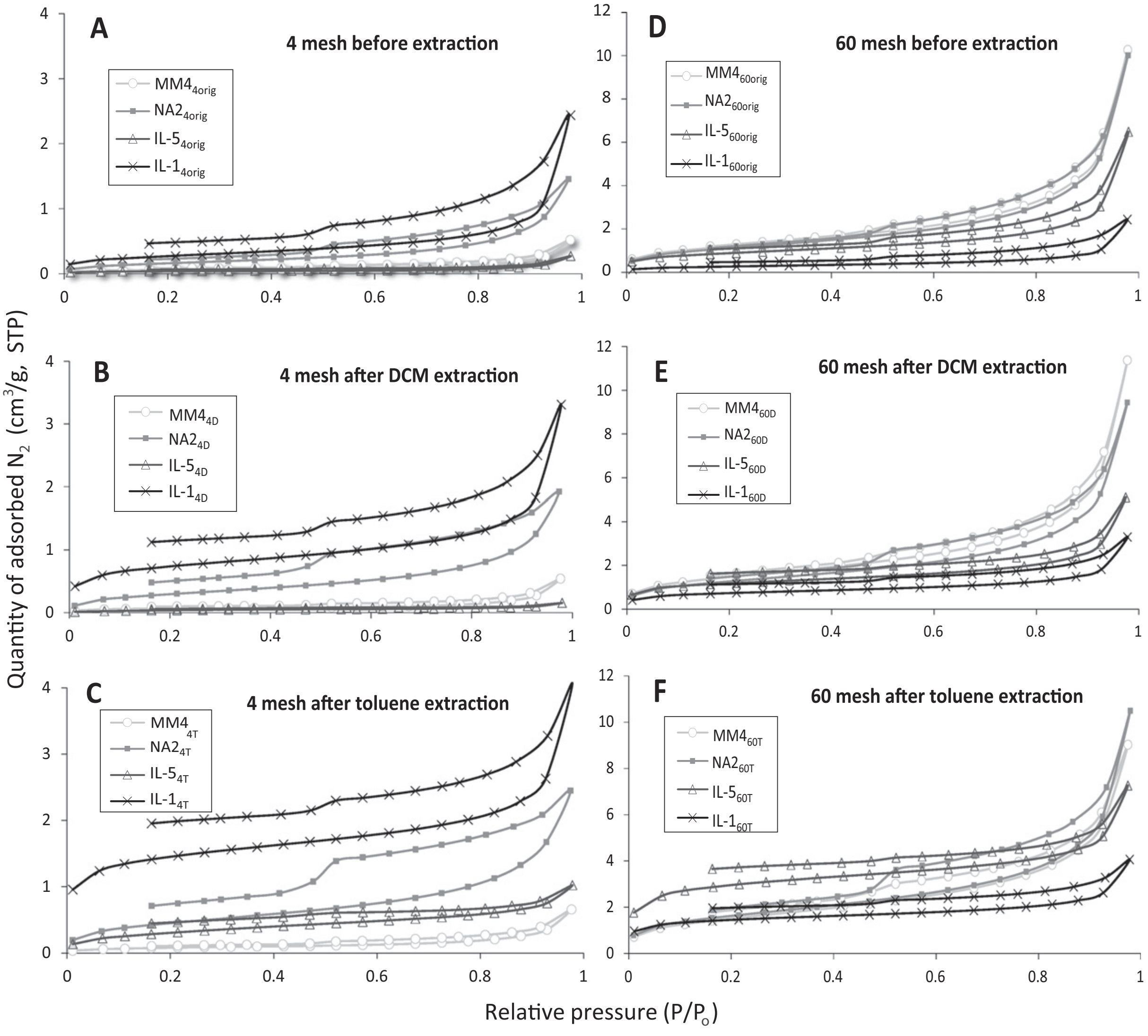

Fig. 1. Low-pressure N_2 adsorption isotherms of shale samples. P = actual gas pressure; P_o = vapor pressure of the adsorbing gas. STP: standard ambient temperature and pressure (25 °C and 100 kPa). We use subscript numbers after sample acronyms to distinguish between 4 and 60-mesh fractions and additionally mark original samples before extraction (e.g., $MM4_{4orig}$ and $MM4_{60orig}$). Solvent-extracted samples are characterized by additional subscript letters D for dichloromethane and T for toluene (e.g., $MM4_{4D}$ and $MM4_{60T}$).