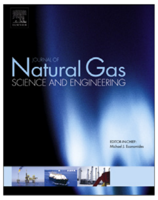
Journal of Natural Gas Science and Engineering 33 (2016) 1078–1086

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

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



A microscopic characterization of wettability in shale kerogen with varying maturity levels

Yinan Hu [a, *], Deepak Devegowda [b], Richard Sigal [c]

[a] Shell Exploration and Production Company, Houston, TX, 77079, USA
[b] Mewbourne School of Petroleum and Geological Engineering, The University of Oklahoma, Norman, OK 73019, USA
[c] Consultant on Shale Reservoir Characterization, Las Vegas, Nevada, 89131, USA

ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form
26 May 2016
Accepted 2 June 2016
Available online 8 June 2016

Keywords:
Kerogen wettability
Kerogen maturity
Organic-rich shale
Molecular simulation

ABSTRACT

Kerogen is defined as the insoluble macromolecular organic matter in sedimentary rocks and is a complex mixture of organic chemical compounds. Typically, a single chemical formula is inadequate to represent kerogen whose composition depends on a long history of geologic events and thermal maturity of the shale. The process of kerogen maturation is accompanied by the loss of functionalized molecules, leading to a decreased H/C and O/C ratios, as well as a reduction in molecular weight. The degree of maturation is well reflected in the van Krevelen diagram with H/C and O/C ratios as indicators. Even though the widely held view for kerogen pores is generally hydrocarbon-wetting, some recent experimental work indicates the existence of water content in kerogen. The key questions arising from this observation are whether kerogen may have mixed-wet characteristics and if so, is this likely to depend on kerogen maturity.

Addressing these concerns is very essential because wettability is directly related to the dynamics of fluids, and is likely to be extremely relevant to developing models for reserves estimates and multiphase flow. Additionally it may provide some answers to the common observation of low recovery of hydraulic fracture water.

In this paper, pore-scale molecular dynamics simulations are used to understand the relationships between kerogen maturity and its wettability. The traditional graphene model is chosen as a proxy for organic pores, and the varying degrees of maturity is approximated by grafting varying amounts of functionalized groups onto the pore surfaces. We study a mixture of water and alkanes in organic pores with effective width of 5 nm. We find that water molecules aggregate together to form clusters due to the polarity of water, and the shapes and the locations of the water clusters are strongly linked to the density of the functionalized groups. By determining the contact angles, we are able to quantify the relationship of kerogen wettability with the maturity level.

The results demonstrate that kerogen maturity governs wettability of organic kerogen pores, due to the influence of surface heterogeneity and the distribution of polar molecules on kerogen. The wettability in kerogen is very likely to be heterogeneous. Depending on the maturity level, kerogen may be hydrocarbon wetting at high maturity, neutral wetting at intermediate maturities or even hydrophilic for organic surfaces of very low maturities. Additionally, our results indicate that in kerogen there may be a critical local density of surface functionalized sites that may create optimal conditions for hydrophilic kerogen surfaces.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Domestic energy security is rapidly becoming a reality because of increasing oil and gas production from shale plays within the United States. This has been made possible by technology development in the areas of horizontal well drilling and hydraulic fracturing, thereby enhancing well deliverability and promoting the tremendous growth in shale development activity. There are, however, several issues related to fluid flow and storage in shales that are not fully understood. For instance, following hydraulic fracturing, field observations indicate poor recovery of hydraulic fracture water during well flowback. The presence of water

---

* Corresponding author.
E-mail address: yinan.hu.us@gmail.com (Y. Hu).

http://dx.doi.org/10.1016/j.jngse.2016.06.014
1875-5100/© 2016 Elsevier B.V. All rights reserved.

adsorption on clay minerals (Makhanov et al., 2014), heterogeneous wettability characteristics of shales (Odusina et al., 2011) and capillary non-equilibrium effects (Michel et al., 2012) have been shown to influence trapping of frac-water. However, there is no dominant theory that can fully explain the low recovery of injecting fluid. Another issue of significant importance is the role of organic and inorganic pore networks in governing fluid distributions, both for hydrocarbons and formation brine. The general consensus is that organic pores are hydrophobic while the inorganic matrix is composed of water-wetting surfaces. These and several other issues become important when quantifying hydrocarbon fluids-in-place, modeling multiphase flow and estimating recovery factors and well drainage areas.

As the organic material within shales, kerogen has been known to be finely dispersed within the inorganic matrix, and molecular phenomena such as adsorption of hydrocarbons occurs within the kerogen (Akkutlu and Fathi, 2012) forming one of the primary mechanisms for storage of hydrocarbons. The kerogen in shales are also typically characterized by pore sizes on the order of a few nanometers (Passey et al., 2010). Additionally, the significant surface area to pore volume ratios of kerogen pores creates conditions where adsorption contributes substantially to total hydrocarbon fluids-in-place estimates (Xiong et al., 2012; Fathi et al., 2012); and the effect of pore confinement on the adsorption (Diaz-Campos, 2010) and the phase behavior (Sapmanee, 2011; Devegowda et al., 2012; Didar, 2012; Firincioglu, 2013; Travalloni et al., 2014) is significant.

Our understanding of the microstructure in shales has been greatly enhanced due to some improved imaging techniques employing focused ion beam-Scanning Electron Microscopy (SEM) methods (Curtis et al., 2011; Chalmers et al., 2012). Heterogeneity (Curtis et al., 2010) and nano-scale pores (Sondergeld et al., 2010) are typically reported in shale samples. For kerogen, the study from Curtis et al. (2011) revealed the presence of complex pore networks, sponge-like internal structure, and the existence of large surface areas for adsorptive storage.

In addition to the heterogeneous and complex microstructure, the wettability of shales is also likely to play a critical role in governing hydrocarbon recovery, oil/gas-in-place estimation, transportation and storage modeling and may possibly address the issue of poor hydraulic fracture water recovery. Heterogeneity in wettability is observed in tight and shale reservoirs. In Lan et al. (2015), rock samples from the Montney and the Horn River in the Western Canadian Sedimentary Basin showed very different wetting behavior and pore connectivity was concluded to play a significant role in governing their wettability. Regarding the wettability in inorganic matter and kerogen within shale, the widely held view is that shale has mixed-wettability with the inorganic matter mainly water wetting and the organic material hydrocarbon-wetting (Elijah, 2011). However, the idea of kerogen being hydrophobic has been recently challenged by some experimental studies that provide evidence of water content in kerogen (Chalmers and Bustin, 2010; Ruppert et al., 2013). Chalmers and Bustin (2010) detected moisture contents from Devonian, Jurassic and Cretaceous shales with maturity from immature to over-mature and pointed out the effect of hydrophobic and hydrophilic sorption sites throughout the pore network on the water moisture content and the methane storage capacity. In Ruppert et al. (2013), pores in Barnett shale samples were reported to have the access to both water and methane, and water was seen to access smaller pores than methane. Quantifying kerogen wettability, and the petrophysical and geological factors controlling wettability therefore become very important.

As a source rock generating hydrocarbons, kerogen forms primarily from dead organisms under sufficient geothermal pressures and evolves with prolonged geologic time (Vandenbroucke and Largeau, 2007). During this continuous evolution, the chemical composition of kerogen changes and the rock progressively becomes mature. This maturation process is responsible for the diverse chemical compositions associated with kerogen (Facelli et al., 2011). As kerogen evolves during maturation, hydrocarbons and functionalized molecules are lost. As a result, the H/C and O/C atomic ratios are reduced and molecular weight is decreased. This process is reflected in the van Krevelen diagram that is used to classify kerogen type based on the maturation (Vandenbroucke et al., 1993; Tissot and Welte, 1978). An example for this is the Type II kerogen from Paris Basin Toarcian. For this sample, at the initiation of diagenesis, the atomic H/C and O/C ratios in the organic material were 1.34 and 0.196 respectively. However, at the end of catagenesis, these values were reduced to an H/C ratio of 0.73 and an O/C ratio of 0.026 (Behar and Vandenbroucke, 1987).

The maturation level of kerogen may possibly impact the wetting property of the organic matter and further play a significant role in dictating the storage and behavior of hydrocarbon and water in organic pores. The purpose of this study is to reveal the impact of kerogen maturity on wettability of organic pore systems, using molecular dynamics simulation. At the scale of nanometers, it is challenging to probe the shale matrix to identify fluid behavior and migration. Molecular dynamics simulations creates a virtual experiment where the behavior of fluid molecules is explored when confined in pores of different shapes and varying surface chemistry. In this work, oxygenated functionalized groups are grafted onto graphite surfaces to obtain different O/C atomic ratios that indicate varying kerogen maturity levels. We then study the behavior of mixtures of hydrocarbon and water confined in pores of a given size. We study cases of both uniformly- and randomly-distributed oxygenated surface functional sites. Our experiments indicate that water molecules tend to form clusters in these pore systems because of their polar nature. The shapes of the water droplets and their positions, however, vary with the densities of the oxygenated functionalized groups. Determination of contact angles of these droplets confirms the dependency of kerogen wettability on atomic O/C ratios and thereby organic maturity levels. When the surface oxygenated groups are randomly placed on the carbon surfaces, the localization effect of surface activation leads to a water sheeting observation adjacent to the pore wall where the surface may be considered to be largely water-wet at low maturity levels. As maturity levels are progressively changed to higher maturities with an accompanying decrease in O/C ratios on the graphite surfaces, our results indicate that the pore surface wettability changes from moderately water-wet to mixed-wet to hydrophobic. These results indicate that careful consideration needs to be given to kerogen maturity when modeling shale hydrocarbon storage, estimating hydrocarbon-in-place, quantifying hydrocarbon recovery and predicting the placement of fracture water. As such, it is the first such study demonstrating a strong link between shale maturity and kerogen wettability.

2. Modeling of kerogen with varying degrees of maturity

The reliability of any molecular simulation study of thermodynamic properties of fluids in porous carbon materials relies on adopting an appropriate model for kerogen pores. While it is desirable to build a realistic model fully representative of the system of interest, the model design should also be simplistic enough to allow ease of interpretation and computational efficiency. The most common model for organic pore surfaces is the graphene model. Striolo et al. (2003) utilized this model to analyze the phenomenon of water adsorption, while Severson and Snurr (2007) studied alkane adsorption with different lengths of the alkane

Download English Version:

https://daneshyari.com/en/article/1757137

Download Persian Version:

https://daneshyari.com/article/1757137

Daneshyari.com