

CHARACTERIZATION OF MICRO-PORES IN ORGANIC-RICH UNCONVENTIONAL RESERVOIR ROCKS

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ABSTRACT

Physical measurements of pore-size distributions in many unconventional reservoir rocks are hampered by a combination of very small features that push the limits of many measurement techniques and the challenges associated with removing residual liquids from the pores. Organic-rich reservoir rocks that act both as source and producer are especially difficult to analyze because of the residual liquids, hydrocarbons and formation water that are trapped in the smallest pores. A combination of low-pressure gas adsorption and differential thermal analysis measurements are used to quantify the proportion and distribution of pores in the micro-scale (less than 5 nm). Pore-size estimation with conventional low-pressure gas adsorption using N₂ has a lower limit of several nanometers, but is severely affected by the presence of organic carbon. The use of CO₂ as the absorbent gas improves the size range down to 0.5 nm. Solvent extraction on small chips of sample was successful in removing small amounts of residual water and hydrocarbon that increased the total pore volume by approximately 10-20% compared to as-received samples. That volume increase was dominated by the very smallest pores, less than 5 nm, as measured with CO₂ adsorption. Thermal analysis measurements verified the loss of water and light hydrocarbons from the extracted samples, while the more complex kerogen that decomposed at higher temperatures was less affected by the extraction. The solvent extraction step removed oil from the solid organic matter and opened very small pores in the sample. The combination of results indicated that a majority of pores in these organic-rich samples fell in the 100-500 nm range and that only a small proportion were true micropores. While extraction of residual hydrocarbons opened up a number of very small pores, their contribution to the overall pore volume was small.

INTRODUCTION

Porosity in fine-grain organic-rich shale occurs as a variety of types and sizes, including intergranular pores associated with the mineral matrix and intraparticle pores found in the solid organic matter [1]. The nature of these pores is important not only for understanding storage capacity of the reservoir, but the connectivity amongst the different types of pores affects fluid flow properties. Porosity in shale and kerogen is widely observed with Scanning Electron Microscopy (SEM) with high-resolution detailed images that are used to classify and characterize pore types (Figure 1). These images are the standard for assessing pores in unconventional, very low-permeability reservoir rocks. As

unconventional reservoirs become increasingly vital for oil production, a more quantitative approach becomes necessary to develop viable models.

The analysis of low-pressure gas adsorption measurements allows quantitative insight into pores ranging from 1 to 500 nm [2-7]. Analysis of standard adsorption curves yields a specific surface area, average pore diameter, pore volume and a pore-size distribution (PSD). Nitrogen gas adsorption is a standard analytical tool for porous materials, especially ones with simple networks of sub-micron sized pores [5]. Recent studies have extended the use of low-pressure gas adsorption measurements on more complex fine-grain geological materials to investigate pore size distributions [3]. Based on the type of isotherms and the gas adsorption, a clearer picture of the pore networks within shale was created [3]. Other studies focused on small improvements in technique to minimize and avoid errors related to low pressure gas adsorption analysis in order to address the evaluation of pores in complex geological materials [8,9]. Oversampling data points at very low relative pressures generated a more detailed view of the micropore and mesoporous regions.

Standard core preparation involves extracting a sample with toluene and/or chloroform to remove fluids, especially residual water and oil, prior to testing. Measurements on the “as received” samples versus the post-extraction samples illustrated changes in the pore structures [2]. This study analyzed porosity evolution through the use of sequential solvents of chloroform and two combined solvents with higher polarities. This enhanced evolution showed a recovery of pore systems with each cleaning. The highest recovery of pore space resulted from extracted high maturity samples. Combining N₂ and CO₂ gas adsorption data allows a complete picture of the PSD from 0.5-500 nm [3]. The adsorption of CO₂ has advantages over N₂ when probing nanometer sized pores in organic matter due to the nature of interactions with the carbon surface [10]. These earlier studies often reported Type II isotherms, in large part because only the adsorption curve was acquired. The hysteresis from the desorption often distinguishes Types II and IV and is a necessary component for a complete interpretation (Figure 2).

Many of the previous studies on shale used samples that were size-separated to include all material less than a given maximum size [2-7]. This study focused on shale samples that were sieved to a diameter between 90 and 32 μm. By having a lower limit on the particle size, it ensured that we were looking at pore systems within the shale and not individual particles.

A combination of low pressure gas adsorption and differential scanning calorimetry/thermal gravimetric analysis (DSC/TGA) present the combined tools capable of yielding quantitative data. Thermal analysis generally does not reveal much information about pores and pore volume, but it is useful to characterize different components of a sample. A properly executed thermal gravimetric analysis of an organic-rich shale sample can provide quantitative information on the amounts of residual water and oil in the pore system, kerogen and other organic matter, and even mineral types and abundances. [13]

Quantitative results on the porosity in shale require a combination of techniques to solve the challenge these fine-grained rocks present. These challenges include a highly variable mineralogy that presents surfaces of wildly different adsorption properties along with the difficulties in removing residual liquids from these surfaces prior to testing.

METHODOLOGY

The samples used in the study came from a carbonate-rich unconventional reservoir characterized by variable amounts of clay minerals and organic matter. The samples were first crushed and sieved to a range of 90 to 32 μm before separating into two aliquots. The first aliquot was treated as in the “as-received” state with residual liquids present. The second aliquot was subjected to toluene extraction to remove residual water and oil. The range in crushed-rock particle size was large enough to capture the small pore systems present in the shale while also reducing the enhanced surface area effect associated with very small, sub-micron, particles. Samples from both aliquots were dried overnight at 150 °C. Several grams of the dried samples were degassed under vacuum at 70 °C for ~12 hours in the measurement tube. Samples were then analyzed by nitrogen adsorption at -196 °C and/or by carbon dioxide adsorption at 0 °C (ASAP 2020, Micromeritics). The data acquisition parameter file oversampled the very low relative pressure regions to ensure high resolution in the micropore and mesopore regions. Surface areas were calculated from the slope of the adsorption curve between 0.1-0.3 relative pressure with the Brunauer-Emmet-Teller (B.E.T) model. Pore-size distributions were calculated from the N₂ adsorption data with the Barrett-Joyner-Halenda (BJH) method and a Density Functional Theory (DFT) model for both N₂ and CO₂ data [11,12.]

A much smaller sample, 30-50 mg, of ground and dried shale from both the as-received and extracted workflow was used for thermal analysis (SenSys Evo, Setaram). The instrument monitored simultaneously weight loss as a function of temperature (Thermal Gravimetric Analysis, TGA) and heat flux (Differential Scanning Calorimetry, DSC). The thermal program for these samples started with an initial increase from room temperature by 3 °C/min to 300 °C where temperature was held for 2 hours, before a second ramping up to 820 °C by 3 °C/min. The samples were then cooled and discarded.

RESULTS

The N₂ adsorption and desorption curves for “as-received” samples are characterized by low initial adsorbed volumes followed by a significant volume increase at higher partial pressures (Figure 3). The presence of hysteresis associated with the desorption stage indicates a Type IV adsorption model, in contrast to the Type II adsorption described for shale in the literature [3].

In contrast, the solvent extracted samples have N₂ adsorption curves that suggest quasi-Type I behavior with rapid volume increases at the lowest partial pressures (Figure 4). This observation of a shift in the adsorption curve was seen in other porosity evolution experiments that used different solvents [2]. The desorption curves of the extracted samples do show hysteresis, thereby these samples are not true Type I materials. The CO₂

adsorption covers a limited range of partial pressures up to 0.03 because it was measured at 0°C and not colder temperatures (Figure 3). Even with the limited total pore volume the CO₂ sensed more surface area than the N₂ adsorption.

The carbonate and clay mineral-rich shale used in this study showed a positive correlation between surface area and pore volume (Figure 5). This correlation is not seen in other conventional rock types such as sandstones and carbonates. Despite the small particle size of these shale samples, the actual pore systems are several orders of magnitude smaller and can be filled with condensing gas during adsorption. In contrast, the sandstone pore networks are seldom preserved during sample preparation, where particle size greatly affects the measured surface areas. In the case of fine-grain shale samples the gas adsorption senses both internal and external surface areas, with emphasis on the internal surface area associated with the pores. The CO₂ adsorption curve senses an equivalent surface area at a fraction of the pore volume as it probes the smaller, organic-rich pores in these samples.

The total pore volume measured by N₂ gas adsorption reflects the percentage of pores that fall within the range of size sensed by the gas condensation or pore filling. This set of samples was defined by two lithofacies, one whose N₂ gas pore volume matched the pore volume measured by standard He porosimetry on an extracted sample and a second facies whose He-based pore volume was greater than the N₂-volume (Figure 6). Facies 1 has a narrower range of pore sizes that is captured entirely by the N₂ adsorption curve while Facies 2 has pores larger than the maximum size captured in the N₂ data. A comparison of these two measurements provides a quick estimate of the proportion of meso- and macropores found in fine-grain unconventional reservoir rocks.

Pore size distributions generated from gas adsorption and desorption curves were limited in the range they covered. Nitrogen adsorption yields a pore size distribution that starts at several nanometers up to 300-400 nanometers. The pore-size distribution calculated from the DFT model with the N₂ adsorption data indicates a broad range of pores in the 30 to 100 nm range with a small contribution around 2 nm (Figure 5). In the lower range, 1-10 nm, the error in the calculated PSD is much higher than in the mesopore region [8,9]. The addition of CO₂ adsorption on the same sample allowed for an extension of the pore size distribution down to 0.5 nm [3,10] (Figure 7). Combining nitrogen and carbon dioxide allows for a complete view of the sample from micropores to mesopores. The conversion of the adsorption curves to pore-size distributions enhances the interpretation of additional micropores being developed by solvent extraction (Figure 8). While the extraction process increased the total pore volume by 20%, those new pores were dominated by less than 5 nm pores associated with organic matter in these samples.

The DSC/TGA measurements confirmed the absence of water and light hydrocarbons in the post extraction samples compared to the “as received” (Figure 9). The as received sample shows more water and light hydrocarbons coming off the sample in the 200-500°C range (Figure 10). Post Extraction removed much of the water and light hydrocarbons

shown by smaller weight loss in the sample in the 200-500° C range. These curves overlapped between 600-800°C as similar amount of carbonate minerals decomposed from both samples equally.

CONCLUSIONS

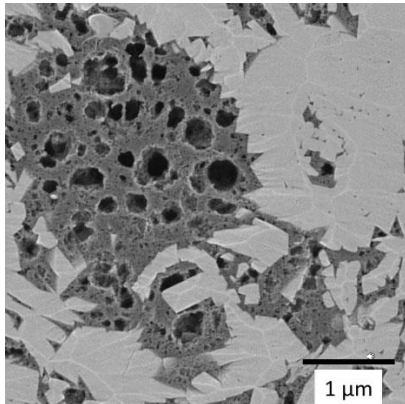
The majority of the pores sensed by the N₂ adsorption fell into a broad distribution of sizes that ranged between 100-500 nm. For many of these samples there was not a distinct pore size that might be used to distinguish lithofacies. Different lithofacies did not exhibit significant differences in pore size distributions nor average pore size, though they did have different total pore volumes. The limitation of the adsorption method for pore size distribution measurement was highlighted by Toluene extraction created a new population of micropores (< 5nm) with a very narrow range of sizes, most likely associated with the organic matter. The solvent extraction increased the porosity of the sample by 10-20%, either through removal of residual liquids or creation of new porosity in the solid organic matter. The DSC/TGA data confirmed water and light hydrocarbons were lost through the extraction process.

REFERENCES

1. Loucks, R., Reed, R., Ruppel, S., and Jarvie, D., "Morphology, genesis and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett shale", *J. Sed. Research*, (2009), 79, 848-861.
2. Zargari S., K. Canter, M. Prasad, "Porosity evolution in oil-prone source rocks," *Fuel*, (2015) **153**, 110-117.
3. Clarkson C., N. Solano, R. Bustin, A. Bustin, G. Chalmers, L. He, Y. Melnichenko, A. Radlinski, T. Blach. "Pore structure characterization of North American shale gas reservoirs using USANS/SANS, gas adsorption and mercury intrusion," *Fuel*, (2013), **103**, 606-616.
4. Labani M., R. Rezaee, A. Saeedi, A. Hinai. "Evaluation of pore size spectrum of gas shale reservoirs using low pressure nitrogen adsorption, gas expansion and mercury porosimetry: A case study from the Perth and Canning Basins, Western Australia," *Journal of Petroleum Science and Engineering*, (2013), **112**, 7-16.
5. Sing, K. "The use of nitrogen adsorption for the characterisation of porous materials," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, (2001), 187-188.
6. Chalmers G.R., R.M. Bustin, I.M. Power, "Characterization of gas shale pore systems by porosimetry, pycnometry, surface area, and field emission scanning electron microscopy/transmission electron microscopy image analyses: Examples from the Barnett, Woodford, Haynesville, Marcellus, and Doig units," *AAPG Bulletin*, (2012), **96**, 1099-1119.
7. Mastalerz M., A. Schimmelmann, A. Drobniak, Y. Chen. "Porosity of Devonian and Mississippian New Albany Shale across a maturation gradient: Insights from organic petrology, gas adsorption, and mercury intrusion," *AAPG Bulletin*, (2013), **97**, 10, 1621-1643.

8. De Lange M., T. Vlugt, J. Gascon, F. Kapteijn, “Adsorptive characterization of porous solids: Error analysis guides the way,” *Microporous and Mesoporous Materials*, (2014), **200**, 199-215.
9. Groen J., L. Peffer, J. Perez-Ramirez, “Pore size determination in modified micro- and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis,” *Microporous and Mesoporous Materials*, (2003), **60**, 1-17. Marsh, H., and Reinoso, F., *Activated Carbon*, (2006) Elsevier Scientific, 554pp.
10. Landers J., G. Gor, A. Neimark, “Density functional theory methods for characterization of porous materials,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2013), **437**, 3-32.
11. Webb, P. and Orr, C., *Analytical Methods in Fine Particle Technology*, (1997), Micromeritics Instrument Corp., 325 pp.
12. Kok, M., “Thermal investigation of Seyitomer oil shale,” *Thermochimica Acta* (2001), **369**, 149-155.

FIGURES



<https://www.fei.com/products/dualbeam/helios-nanolab-660-for-oil-and-gas/>
Figure 1. SEM image from FEI showing differences in porosity in organic matter versus matrix material.

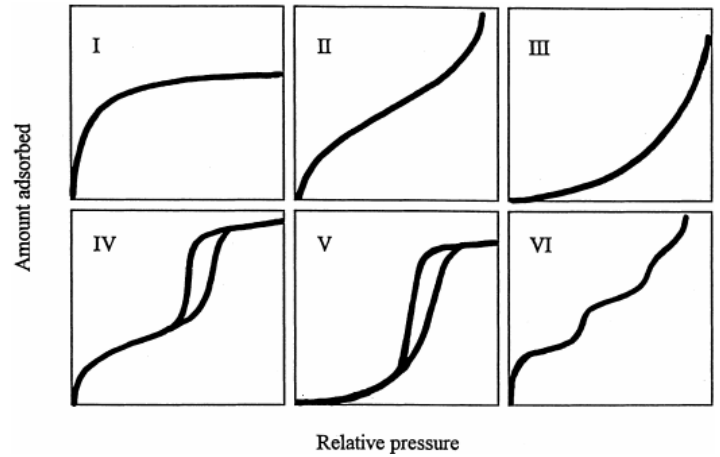


Figure 2. IUPAC Classification of gas adsorption / desorption isotherms.

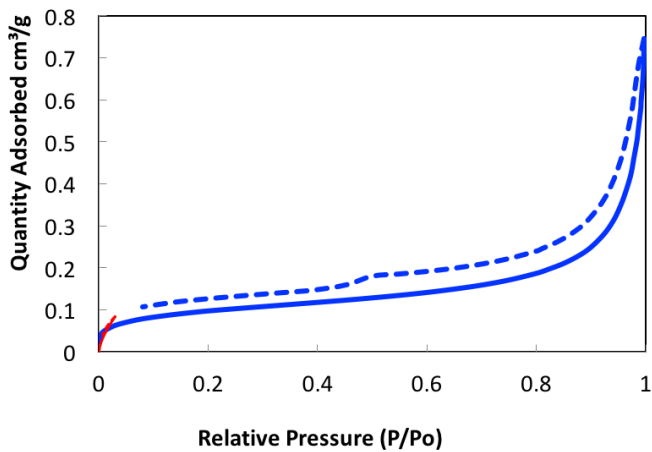


Figure 3. Adsorption-Desorption curves for N₂ (Blue) and CO₂ (red) for single sample in "as-received" state. Solid blue curve is N₂ adsorption and dashed-blue line is N₂ desorption. Note the limited range of partial pressures measured with the CO₂ adsorption test.

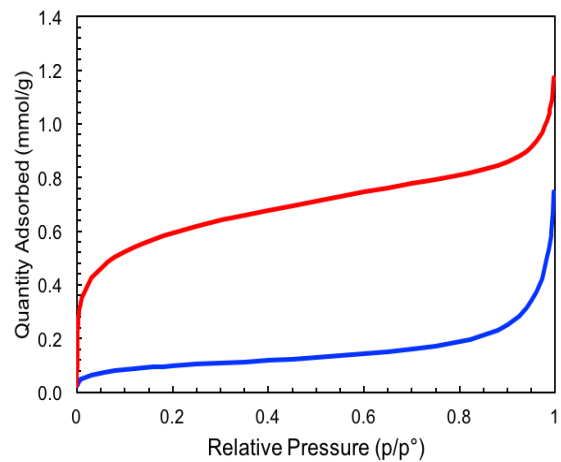


Figure 4. N₂ adsorption curve for sample in "as-received" state (blue) and after solvent extraction with toluene (red). The significant increase in the volume of smallest pores (lowest partial pressures) is reflected in the increase in total pore volume (P/P₀=0.99).

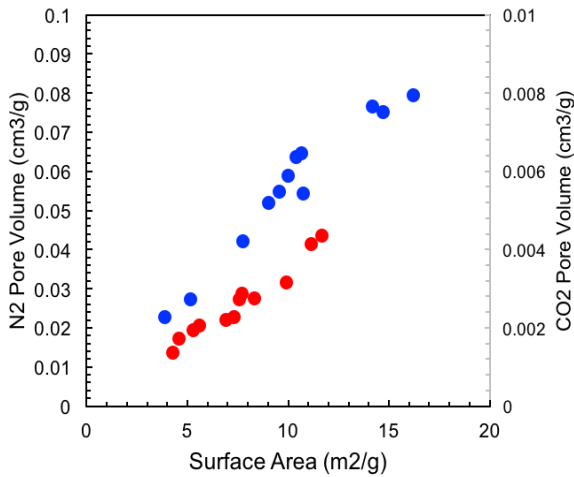


Figure 5. Pore volume correlation with Surface Area for N₂ and CO₂ adsorption measurements. Note the order of magnitude difference in pore volume scale for the different gases. This positive correlation is not observed for other coarser-grain rock samples..

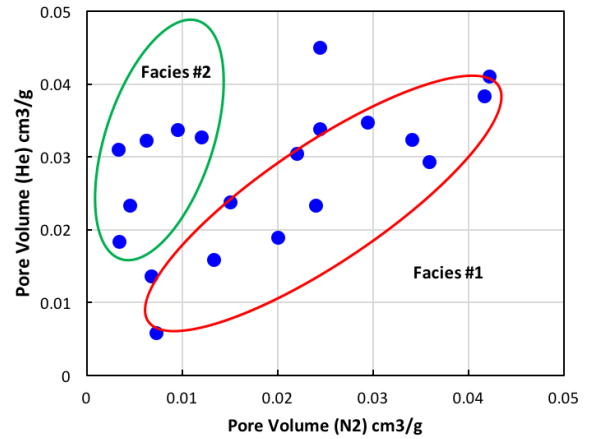


Figure 6. Comparison of pore volume measured by N₂ gas adsorption and standard He-porosimeter on cleaned crushed rock samples. Facies #1 has a 1:1 correspondence that indicates all of the pores in the sample are filled at maximum partial pressure for N₂, and therefore less than 400 nm. Facies #2 has a larger pore volume measured with He that indicates some of the pores in these samples are larger than the maximum pore diameter sensed by N₂ adsorption.

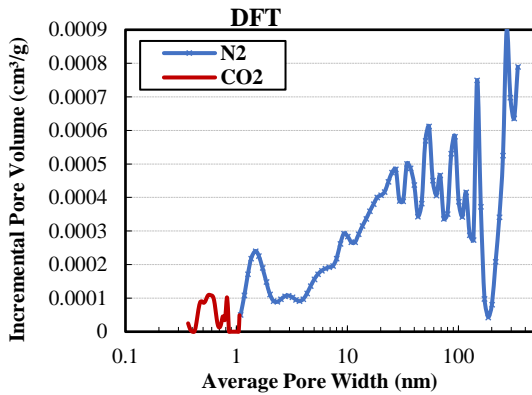


Figure 7. Combined Pore Size Distribution of CO₂ and N₂. CO₂ shows pores sizes down to 0.5 nm and combined with N₂ we can see from micropore to mesopore range.

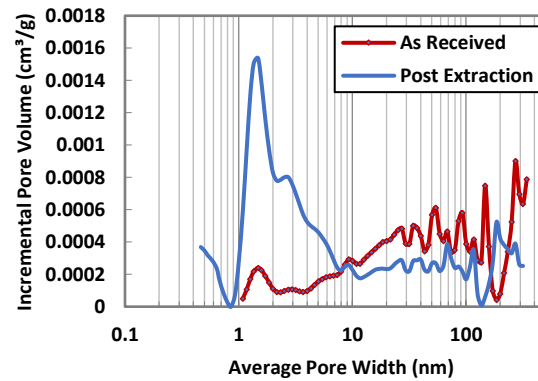


Figure 8. Pore Width plotted versus Pore Volume shows the difference between a sample before and after cleaning as seen in Figure 4. Post cleaning with toluene shows a dramatic increase in microporosity, but little change in mesopore and macropore volumes.

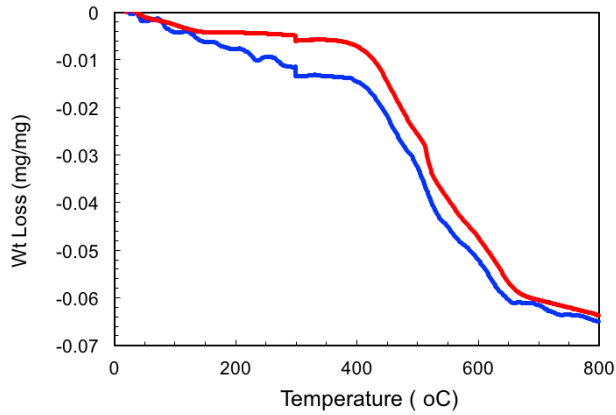


Figure 9. TGA curves for organic and clay-mineral rich "as-received shale (blue) and solvent extracted (red). The larger weight loss between 100 and 425°C for the as-received sample indicates the presence of water and light hydrocarbons that were mostly removed by the extraction process. Carbonates decompose at temperatures above 550°C and are not affected by extraction.

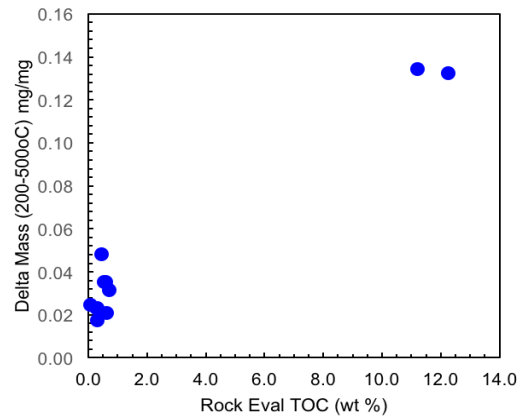


Figure 10. TGA weight loss between 200 and 500°C compared to TOC weight percent from RockEval. Two organic-rich samples obscure the trend between the two properties at lower TOC values.