Selection of Shale Preparation Protocol and Outgas Procedures for Applications in Low-Pressure Analysis

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ABSTRACT: The low-pressure gas adsorption (LPGA) method for estimation of pore capacities, pore size distributions, and total surface area using adsorption–desorption isotherms is selected as an effective technique in pore characterization. A recent application of this method is to understand the complex and heterogeneous nature of shales across the globe. The LPGA experiments were conducted on shale samples from Barnett and Eagle Ford formations in the United States using CO₂ for micropores of 0.3–1.5 nm in diameter and N₂ and Ar as the adsorbates to focus on micropores from 1.5 to 2.0 nm and the lower range of mesopores above 2.0–27 nm in diameter. It was hypothesized that a significant error in estimations could occur due to inconsistencies in the shale outgas temperatures. It was observed that lower pore capacities result from lower outgas temperatures, and higher pore capacities result from increasing outgas temperatures. It is hypothesized that lower outgas temperatures fail to completely eliminate adsorbed moisture and adsorbed low-molecular weight hydrocarbon species from shale pores, which leaves the pores partially filled and as such result in lower values of pore capacity. By increasing the outgassing temperature, the adsorbed species in the pores are completely removed, yielding higher pore capacities. The cutoff temperature of 250 °C during outgassing for regeneration of “clean” shale pores was arrived at by analyzing the LPGA results of samples without any outgassing and samples outgassed at 60, 110, and 250 °C. The 250 °C maximum outgas temperature is intended to maximize the results of LPGA while minimizing structural changes to shales. Mass stabilization as shown by thermogravimetric analysis and magnetic suspension balance measurements support the assertion that the shale is not fundamentally altered by processes such as kerogen cracking until a temperature higher than 250 °C is reached. The kerogen had approximately 3.0% weight loss at 110 °C, with an additional 1.3% loss between 110 and 250 °C. Likewise, the desorption experiments carried out on clay at 110 °C were approximately 1.3%, with an additional 0.5% loss between 110 and 250 °C. On the basis of the interpretation of pore size distributions using the LPGA method, it was concluded that accurate shale characterization is achieved when the analysis is limited to results from relative pressures (P/Po) less than or equal to 0.90. At higher relative pressures, the sizes of the adsorbate-occupied pores cannot be distinguished.

1. INTRODUCTION

1.1. Background. While horizontal drilling and hydraulic fracturing have revolutionized shale gas production, problems remain in characterizing the fundamental attributes of shale plays. The issue of shale characterization has also become important in efforts to combat climate change, as shales are considered for geological sequestration of anthropogenic CO₂. Multiple methods are being implemented to assess the dynamics of fluid flow in shales, gas content, system integrity upon injection, and more. An important factor for methane production or CO₂ injection in shale is to have a reasonable estimate of gas storage capacity, whether that be gas-in-place estimates for extraction or capacity available for geologic sequestration of CO₂. While these studies have gathered significant momentum in recent years, some fundamental questions on capacity measurements remain.

Early investigations on shale gas plays have established that the free gas capacity is usually proportionally less in comparison to the adsorbed gas content. The capacity of gas adsorbed is controlled by several geologically constrained factors such as formation temperature, thermal maturity, constituent grain size, moisture content, proportions of organic content and inorganic matter, rock porosity and pore characteristics, etc. The standard International Union of Pure and Applied Chemistry (IUPAC) definition of pore domains will be used throughout this study to include the terms micropores referring to pores less than 2 nm, mesopores from 2 to 50 nm, and nanopores and nanoporosity which the IUPAC defines as pores less than 100 nm in diameter.

It is well known that the pores in the organic content of shale are the primary source of gas, while natural and hydraulically induced fractures allow passage of gas through the reservoir. Although the clay component of shale also contains microporosity and mesoporosity, it remains unclear what its contribution is to both gas storage and transport. Diffusive processes dominate gas transport from the nanoscale storage spaces into the permeable pathways of the shale formation networks. With diffusive transport, it is essential to...
measure pore spaces that are not considered in the multiphase flow regime of conventional petroleum reservoirs because the nanoscale pore capacities of shale are significant contributors to gas storage.

1.2. Low-Pressure Gas Adsorption. An accepted technique is low-pressure gas adsorption (LPGA), which is now being used to measure and identify the micropores and fine mesopores in shale. This characterization technique has the advantage of being widespread, rapid, and easily adapted for a variety of measurements. However, standard protocols must be formally established when using the technique, as varying methods of sample preparation and lack of clearly stated underlying assumptions for models used to compute pore capacity estimates have further compounded the confusion caused by various and often conflicting findings in literature dealing with shale pore characterization.

Saidian et al. concluded that subcritical N₂ adsorption is a “reliable technique for both clay-rich and organic-rich samples” as the gas phase can access a large range of pore sizes in both the organic and the inorganic constituents. Despite the widespread use of low-pressure adsorption to characterize shale, the technique has limitations that are often unacknowledged. The only direct measurement from LPGA is the sorption isotherms, which typically consist of both adsorption and desorption branches. These isotherms show the adsorbate capacity at standard temperature and pressure. Any additional characterization from the experimental data relies on characterization models, which can be used to estimate surface area, pore capacity, and pore size distributions (PSDs). Correct interpretation of the isotherms depends on understanding the assumptions underlying characterization models and choosing the best approximations for each material and isotherm.

Pore size distributions estimated from adsorption data are used to gain information about mesopores and micropores. The standard PSD interpretation for porous materials was proposed by Barrett–Joyner–Halenda (BJH), which is a Kelvin equation-based calculation of pore capacity that uses the desorption isotherm, often with N₂ at 77 K, and assumes a cylindrical pore geometry with typical Langmuir assumptions. The BJH model can be useful for larger mesopores. However, the underlying assumptions of BJH adsorbate layering are not appropriate for micropores and fine mesopores. The simple layering of adsorbates assumed by BJH (and BET) fail to take into account surface chemistry that is essential in micropores and fine mesopores (i.e., from 0.3 to 10 nm) such as surface-to-adsorbate interactions and other molecular behaviors that change in the fine mesopores and micropores. As such, BJH should not be applied to pores filled at relative pressures below 0.35. Application of BJH to pores less than approximately 10 nm for Ar and N₂ adsorption measurements can result in underestimating pore size distributions as much as 20–30%. Detailed information regarding surface area measurements of microporous materials has been reviewed by Thommes and Cychosz.

The traditional method for determining PSDs in micropores relies on CO₂ adsorption isotherms at 273 K. Methods proposed by Dubinin and Radakovitch have been used to determine micropore capacity, based on an assumed CO₂ liquid density, and have been adapted by Dubinin—Astakov (DA) to create micropore size distributions. While potentially insightful, the method proposed by DA relies on a Gaussian distribution, which may enforce an artificial structure on the microporous region.

On the basis of imaging data obtained from the literature, it is known that much of the shale porosity is present in the kerogen, so a model that uses Ar, N₂, or CO₂ on carbon may be used to determine PSDs in this regime using density functional theory (DFT) methods. The actual pore geometries are complex but based on the geological stresses imposed on shale rocks, assuming basic geometries to approximate the pore structures, such as a cylindrical pore geometry for mesopores, and a slit geometry for micropores, can yield valuable insights for approximating shale pore capacities. The current work explores these models and the assumptions behind them in conjunction with experimental data to help direct future efforts associated with achieving accurate gas storage estimates.

2. EXPERIMENTAL SECTION

2.1. Shale Samples. Shale samples for this study have been obtained from the Eagle Ford and Barnett shale formations in the southwestern United States. Composition and depth information, labeled Barnett 1–6 and Eagle Ford 1–6, can be found in Table 1, Figure 5, Figure 6. For the purposes of this work, 12 samples were chosen, with a range of clay and total organic carbon (TOC) contents.

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All of the samples were prepared using a chalcedony mortar and pestle to grind smaller shale chips sourced from well-bore cores. The ground shale samples were then sifted through a 200 mesh sieve, ensuring dimensions of 75 μm or less on at least two sides. The sample was then placed in a scintillation vial and shaken vigorously to ensure the particles were thoroughly mixed. Failure to thoroughly mix the samples results in variation in the samples that reduces the likelihood of having reproducible results. Each analysis was performed with an independent sample from each of the ground and mixed powder source shales with a weight of at least 100 mg.

2.2. Isolated Kerogen and Illite. The isolated kerogen sample was isolated from a Silurian shale by Chevron and provided in a dry powdered form. The illite sample is from the Green River Shale formation obtained from Ward's Natural Science Establishment, Rochester, NY.

2.3. TOC Analysis. Total organic carbon (TOC) of the shale and isolated kerogen was measured using the method described in Psarras et al., which first removes inorganic carbon with repeated application of hydrochloric acid (HCl 1 N) and then combusts the samples in pure oxygen using a Carlo Erba NA 1500 Series 2 analyzer.

2.4. X-ray Diffraction. A Rigaku model CM2029 with a Cu Kr X-ray source was used to collect X-ray diffractograms of the Green River Illite, Barnett, and Eagle Ford shales. The diffractograms were collected over the 2θ range from 5° to 70° that were then analyzed using the JADE diffraction software package’s least-squares “EZ Computation” and National Institute of Standards and Technology peak database as described in Psarras et al.
2.5. Thermogravimetric Analysis. Thermogravimetric analysis was performed using a Netzsch Instruments STA 449 F3 Jupiter Simultaneous Thermal Analyzer (TG-DSC/DTA). Samples were prepared as described in section 2.1, with a sample size ranging from 3.6 mg for the Silurian kerogen to 15–40 mg for the shale samples. Instrument resolution is 1 μg. Each sample was run under a N2 atmosphere, with a temperature increase ramp of 5 °C/min from 20 to 400 °C, followed by a temperature decrease ramp of 5 °C/min to approximately 100 °C. Each run included a blank run on the sample crucible, followed by the sample being run in the same crucible.

2.6. Magnetic-Suspension Balance Analysis. Weight loss over time for the Silurian kerogen and Illite clay was measured on a Rubotherm magnetic-suspension balance. Samples were prepared as described in section 2.1, with a sample size of 21.6 mg for the Silurian kerogen and 1.35 g for the Illite clay sample. Instrument resolution is 1 μg. Each sample was run under continuous vacuum, with a final pressure of 0.06 bar. The temperature increase was ramped at a maximum of 5 °C/min from approximately 20 to 250 °C. The weight was measured continuously every 2 min for approximately 4 days.

2.7. Low-Pressure Gas Adsorption Analysis. The LPGA analysis was performed on all samples using a commercially available Quantachrome Autosorb iQ2. Any adsorption analysis requires two steps, outgassing and isotherm analysis, both of which can be performed using the Autosorb equipment. All samples were outgassed for final analysis at the maximum outgassing temperature of 250 °C. Outgassing on the Autosorb is under vacuum of as low as 10⁻⁷ Torr (0.133 Pa). The 250 °C outgassing protocol was programmed to ramp at 2 °C min⁻¹ from ambient temperature to 110 °C and was held at 110 °C for 3 h followed by a ramp of 5 °C min⁻¹ to 250 °C and held for 6 h. Further discussion of the effects of outgas temperature is in section 3.1. Two samples were selected to be outgassed at progressively higher temperatures to document the increase in pore capacities resulting from higher outgases temperatures. Three different outgas temperatures for the Barnett 1 and Barnett 6 samples were considered in this investigation: 60, 110, and 250 °C. The 60 °C outgassing protocol was programmed to ramp at 2 °C min⁻¹ from ambient room temperature to 60 °C and held at 60 °C for at least 9 h. The 110 °C outgassing protocol was programmed to ramp to 2 °C min⁻¹ from ambient room temperature to 110 °C and held at 110 °C for 3 h. The final outgassing at 250 °C was ramped from ambient temperature at 5 °C min⁻¹ and held for 6 h so as to be comparable to the other 250 °C outgassed samples.

Low-pressure adsorption analysis was performed with 3 different adsorbate gases: CO2 at 273 K, N2 at 77 K, and Ar at 87 K. The N2 and Ar were both research-grade 5.0 gases, and CO2 was research-grade 4.8 gas, obtained from Praxair. The sample temperature was maintained using liquid N2 (for 77 K), liquid Ar (for 87 K), and a Julabo circulating cooler with a 50/50 mixture of ethylene glycol and water (for 273 K). Adsorption and desorption isotherms were obtained when using N2 and Ar as the adsorbate, while only adsorption isotherms were obtained when CO2 was used as the adsorbate.

2.8. Model Selection. The N2 and Ar isotherm measurements were used to calculate pore capacities and pores size distributions with Quantachrome’s quenched solid density functional theory (QSDFT) models, assuming carbon as the adsorbent and cylindrical pores. All PSDs were calculated from the adsorption branch to avoid metastability issues (such as cavitation) present in the desorption branch at a partial pressure of approximately 0.5, as evidenced by the characteristic desorption curve drop as shown in Figure 3 for the Barnett samples and Figure 5 for the Eagle Ford samples. The use of the adsorption curves to interpret these samples has been corroborated and supported by Dr. Matthias Thommes of Quantachrome (Thommes, M. Personal communication, April 17, 2015). The CO2 adsorption isotherms were used with Quantachrome’s nonlocal density functional theory (NLDFT), which assume slit pore geometry on a carbon adsorbent.

3. RESULTS AND DISCUSSION

3.1. Samples. Samples were ground to a powder due to previous experimental experience that attempted to use shale core chips. The experimental attempts with the chips were abandoned because results indicated large chips of shale did not provide consistent and repeatable isotherms. Additionally, analyzing chip samples gives estimates only of interconnected pores and permeable pathways, which leaves a large portion of the unconnected pore capacity unmeasured. It is important to note that it is unclear how available these originally inaccessible pores will become upon stimulation or fracturing, but they are of key significance as technologies improve for gas extraction and geologic CO2 sequestration. Understanding the pore capacities and PSDs are important for understanding potential capacities for CO2 sequestration in depleted gas wells, which will have the required fractures for injection purposes.

While the fractures themselves will not be responsible for significant quantities of CO2 storage in the long term but rather the pores in the geologic formation. While the amount of extractable gas based on fracture networks is useful for estimates of recoverable gas, it does not give estimates of total gas in place because it fails to account for the pore capacities that exist but are not connected. The inability to account for unconnected pore capacity is unsuitable for shales gas reservoirs as it is standard practice to induce connectivity with techniques such as hydraulic fracturing. Thus, the gas-in-place estimates for shale gas reservoirs should be based on both disconnected and connected pore networks. Once a gas-in-place estimate is determined, the portion of the gas that is extractable would decrease to the degree to which the pores can be accessed, which would be dependent on the fracturing techniques and methods employed by the reservoir engineers. As diffusive processes dominate the transport of gas out of the storage space into the permeable pathways of the formation networks, it is essential to measure pore spaces that are not considered in conventional petroleum reservoirs and to include them in gas-in-place estimates. As such, these pore capacities in this case are considered a part of the total porosity, which requires fully removing water and other adsorbed low-molecular-weight hydrocarbon species that are considered irreducible saturations in conventional petroleum reservoirs.

3.2. Outgas Parameters. The impact of the outgas procedure on low-pressure adsorption results must be considered before analysis and interpretation of the adsorption results. This is true for all materials but especially in the case of shale, where there may still be CO2, H2O, and other distilled hydrocarbons adsorbed. Since the interpretation techniques rely on a “clean” surface, meaning free of nonstructural, adsorbed species, and assume physisorption of the adsorbate, any adsorbed species that remain on the surface may prevent further gas adsorption, thereby decreasing the total observed pore capacity. This leads to inconsistency within samples and an inability to compare results across multiple samples, since the initial state of the sample surface should be considered as an unknown. Figure 1 shows the effect the outgas temperature (following methods described in section 2.4) has on the isotherms in the Barnett 6 sample and on the Eagle Ford sample.

There is a clear increase in total adsorbed gas at STP for both the Barnett and the Eagle Ford samples as shown in Figure 1. For the Barnett 6 sample, when the sample is not outgassed (maintained at ambient room temperature prior to analysis)
and Eagle Ford 4 sample is at 60 °C, there is little porosity observed at relative pressures ($P/P_0$) below 0.5. When the maximum outgas temperature is raised to 110 °C for the Barnett 6 sample, a temperature which is expected to desorb water from the pore system, there is a slight increase observed in porosity at relative pressures ($P/P_0$) below 0.25 and approximately a doubling of gas adsorbed from relative pressures ($P/P_0$) 0.25 to 0.75 as compared to when the sample was not outgassed. When the maximum outgas temperature is raised to 250 °C, for both samples, where most adsorbed species are expected to be desorbed, there is an increase in total gas adsorbed not only ($P/P_0$) below 0.25 but also again an approximate doubling of total gas adsorbed from relative pressures ($P/P_0$) 0.25 to 0.75 compared to when the sample was outgassed at 110 °C. This general increase in total gas adsorbed with increasing outgassing temperature is represented in the isotherm plot as a shift of the entire isotherm upward along the y axis. This shift upward is interpreted as a result of desorbing gases, rather than other structural changes in the shale itself. This is an indication that outgassing at 60 and 110 °C is incomplete and unable to fully remove adsorbed species in the smallest mesopore region, even if species in the larger mesopores were effectively desorbed.

The Barnett 6 sample has a high compositional fraction of both clay and TOC, so the effect of the maximum outgas temperature may be outsize compared to samples with lower clay and TOC. Figure 1 shows a similar trend for the Eagle Ford 4 sample outgassed at 60 and 250 °C. It is clear that the presence of higher amounts of TOC affects the increase in the smallest mesopores observed, but both samples show an increase that can be attributed to native gas species desorbed from the smallest mesopores when brought to 250 °C.

There is a concern when working with natural samples that the high outgas temperatures may be fundamentally altering the shale, and previous literature has typically taken the stance that the maximum outgas temperature for shale should be around 100 °C in order to ensure the removal of adsorbed water. The liquid to vapor transition for water at 60 °C is at approximately 20 kPa (150 Torr). Thus, under a 0.01 Torr vacuum typical of the outgas settings for the vacuum on the Autosorb iQ2, water and heavier species will be desorbed from the shale. However, much of the scientific value from low-pressure adsorption relies on the assumption of a clean surface. Any desorbed species that remain after outgassing will alter the final interpretation. As such, desorption of adsorbed species such as water, methane, etc., is required for LPGA, leading to the need for the highest possible temperature that minimizes any fundamental alterations to the structure of the shale, such as loss of kerogen mass from “cracking” that results in evolved hydrocarbons. To contribute to verification that the 250 °C outgassing temperatures result in minimal structural changes, we tested each sample using TGA, as described in section 2.3 with results shown in Figure 2.
The key aspect of focus in the TGA results shown in Figure 2 is the initial decrease in weight starting at around 60 °C and ending at around 110 °C. This weight loss occurs in both the isolated kerogen sample and the Illite sample, both of which can be attributed to the desorption of water. This supports outgassing at temperatures above 110 °C. In the kerogen sample, there is then a relatively stable portion between 110 and 200 °C, with a slight decrease from 200 to 250 °C. This stable region is supported by the literature, which indicates that evolution of hydrocarbons from kerogen does not begin with significance until temperatures greater than 250 °C. The purpose of outgassing at the highest possible temperature is to maximize the LPGA results by gaining access to the cleanest pores possible. Using 250 °C as an approximation for the maximum outgassing temperature is recommended across all shale samples, as it should lie in the vicinity of the “pre-generation trough” minimum located between the S1 and the S2 pyrolysis curves for most samples.  

The second important aspect of these results is the continual decrease in weight of the Illite and shale samples as the temperature of the sample increases above 110 °C. This steady decrease in weight, while minor (the maximum total decrease in weight for any of the shale samples between 110 and 250 °C is 0.39%, equivalent to 6 μg), is important, and the results of this decrease can be seen as the increase in capacity in the smallest mesopores as shown in Figures 4 and 5. While Figure 2 indicates a continuous decrease in weight with increasing temperature, it should not be confused with a continuous weight loss with increased time during outgassing because the actual outgassing maintains the sample at 250 °C for 6 h, whereas the TGA is continuously ramping the temperature up with time, resulting in additional weight loss when the temperature exceeds 250 °C. The Rubotherm magnetic-
suspension balance results illustrate the stability of the mass of the kerogen and clay components of shale over several days at 250 °C. Disregarding the first 12 h while the sample is brought up to temperature allowing the balance suspension arm to mechanically stabilize, the weight of both the kerogen and the Illite remains constant for the next 3.5 consecutive days. The kerogen weight loss in the first 12 h is responsible for a 5.1% decrease from the initial weight. An additional 0.3% of the kerogen’s initial weight is lost in the subsequent 3.5 days. The Illite weight loss in the first 12 h is responsible for a 1.1% decrease from the initial weight. An additional 0.08% of the Illite weight is lost over the subsequent 3.5 days (see Supporting Information). The stabilization of the mass for several days indicates that the length of outgassing time is secondary to (if not inconsequential) the outgassing temperature. Aspects of clay dehydration and dehydroxilation can be found in the literature.38−40,39,41

3.3. Selection of Adsorption Branch. As discussed in section 1, there are a number of options for determining the pore size distribution. On the basis of the limits of the traditional methods (BJH, DR/DA), DFT-based methods have been chosen for the PSD interpretation. However, before the PSD distribution can be considered, both adsorption and desorption isotherms should be evaluated before selecting either branch. Figures 3 and 5 show the adsorption isotherms using N2 as the adsorbate for the Barnett and Eagle Ford shale samples, respectively. Both sets of adsorption isotherms are indicative of materials with complex micro- and mesoporous pore networks, leading into larger macropores. This is observable in the steady increase in the adsorbed capacity over the entire range of $P/P_0$ and the sharp increase in adsorbed capacity around $P/P_0 = 0.9$. The sharp increase is representative of bulk pore filling, where the adsorbate is forming a bulk phase in the macropores but not necessarily...
3.4. Interpretation of PSDs. Using CO₂ as the adsorbate, two samples, Barnett 1 and Barnett 6, were analyzed for changes in micropore (the Quantachrome CO₂ model is limited to pores 0.3−1.5 nm for CO₂) capacities and PSDs resulting from changes in outgassing temperature as shown in Figure 7. The samples were outgassed at 60 and 250 °C, but neither sample showed significant changes in the micropores for pore capacities. Barnett 1 had a CO₂ pore capacity of 0.002 cc/g at 60 °C and a pore capacity of 0.001 cc/g with the 250 °C outgassing. Barnett 6 had a CO₂ pore capacity of 0.005 at 60 °C and a pore capacity of 0.005 with the 250 °C outgassing. The samples showed only slight variations in the PSDs, as shown in Figures 4 and 6. As such, the remaining samples were only analyzed at the 250 °C outgassing temperature for the cumulative pore capacities reported in Table 2. Additional plots of the cumulative pore capacities were created by splicing CO₂ and N₂ results together. The spliced CO₂ and N₂ PSDs and cumulative pore capacities of all 12 samples are shown in the SI. The pore size distributions for N₂ are characteristic of those reported in the literature and are shown in Figure 4 for the Barnett samples and Figure 6 for the Eagle Ford samples. The cumulative pore volumes increase with increasing TOC and clay content, which is consistent with the literature.

4. CONCLUSIONS

Different methods to estimate the pore size distributions and total pore capacities in shales yield different estimates and make a reasonably accurate estimation difficult. The low-pressure gas adsorption method is a viable option to characterize shale due to its adaptability, widespread utility, and coverage over a large range of pore sizes relevant to gas shales. This study reviews the different methodologies and identifies potential deficiencies in the gas-in-place estimates even in the best-fit technique of LPGA. Experimental investigation was conducted on samples of different depths from Eagle Ford and Barnett formations. The TOC content of the Eagle Ford shales varied from 2.4% to 5.3%, while that of the Barnett shales ranged from 1.1% to 6.3%.

An important aspect of this study was to define an appropriate outgas procedure to maximize the adsorbed gas estimates. It was found that while no outgassing yielded low pore capacity estimates, raising the outgas temperature to 250 °C led to maximum desorption of adsorbed species as indicated by maximum uptake of gas during the sorption phase. High temperatures therefore complete the process of outgassing, giving better gas-in-place estimates when the adsorbed gas can gain access to micropores and mesopores in shales. The commonly used 60 and 110 °C for outgassing are not recommended as the release of water and adsorbed distilled hydrocarbons in the smallest nanopores is not complete. On the basis of TGA results, a temperature of 250 °C is recommended as a standard procedure for outgassing as raising the temperatures further may alter the fundamental characteristics or clay and kerogen in shales. Repeatable isotherms for samples outgassed at 250 °C further support this claim. While the 250 °C maximum outgas temperature is intended to maximize the results of LPGA while minimizing structural changes to shales, further spectroscopic techniques should be employed to verify any structural shifts that may occur even without mass loss, as there is the potential for other kerogen deformation or transformation to occur at the 250 °C maximum not accounted for even with a stable mass. As such, 250 °C maximum is intended as a general guideline for LPGA.

Pore size distribution obtained from the LPGA analysis showed the characteristic drop in the desorption isotherm around a relative pressure of 0.4−0.5. This drop may lead to misinterpretation of the PSDs, and as such, the adsorption branch is recommended for use with shales. When the isotherms end in an upward “spike” approaching relative pressure of 0.995, it is suggested that a maximum pore diameter of 15 nm should be taken when using this method to obtain consistent results using both N₂ and Ar. Samples tested on both Ar and N₂ were in agreement, and either could be used for LPGA on shales, although Ar is preferred as recommended by IUPAC, although N₂ may continue to predominate as Ar can be cost prohibitive and harder to obtain.

DOI: 10.1021/acs.energyfuels.7b01297
Energy Fuels 2017, 31, 9041−9051
Magnetic suspension balance results showing kerogen weight stabilizing after the first 12 h at 250 °C; magnetic suspension balance results showing Illite weight stabilizing after the first 12 h at 250 °C; CO₂ and N₂ pore size distributions and cumulative pore capacities through 27 nm for the Barnett shales; CO₂ and N₂ pore size distributions and cumulative pore capacities through 27 nm for the Eagle Ford shales (PDF).

**ACKNOWLEDGMENTS**

We thank Dr. Adam Douglas Jew for help and training on the X-ray diffraction. We thank Dr. Doug McCarty and Chevron, as well as Prof. Mark Zoback and ConocoPhillips, for the sample contributions. Lastly, an extended thank you to Dr. Matthias Thommes and Dr. Katie Cychosz at Quantachrome Instruments for the extra time and effort spent lending their incredible scientific mentorship.

**REFERENCES**


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<th>Table 2. Cumulative Pore Capacities for Samples Outgassed at 250 °C</th>
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**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.7b01297.
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