

Water Adsorption/Desorption Isotherms for Characterization of Micro porosity in Powder River Basin Subbituminous Coal

Z. Huang, M.A. Urynowicz, J.H. Holles, and R.D. Pribyl

Department of Civil and Architectural Engineering, University of Wyoming, USA

Director, Center for Biogenic Natural Gas Research, University of Wyoming, USA

Department of Chemical and Petroleum Engineering, University of Wyoming, USA

Abstract— Pore geometry of coal matrix, including total porosity, pore size distribution, and specific surface area, influences the fate and transport of fluids within coal. A better understanding of the physico-chemical properties of the coal matrix will lead to improved techniques for modeling coal seams for the purpose of enhanced biogenic natural gas production and carbon sequestration. This paper presents the water sorption isotherm data of intact subbituminous coal cores (approximately 4 cm in diameter and 1.5 cm in height) collected from two wells located within the Upper Wyodak Formation of the Powder River basin (PBR). The isotherm data were collected gravimetrically over a period of five years using sealed glass enclosures that were humidity controlled by glycerol/water solutions. The coal contains large amount of Brunauer-Emmett-Teller (BET) surface areas determined by water sorption curves, which ranged from 217.6 to 863.5 m²/g-coal. The samples also had relatively low diffusivities in the range of 1.2×10^{-23} to 1.8×10^{-22} m²/s, as determined using the unipore model. The totally porosity of the coal was determined gravitationally and estimated to be approximately 0.4. The pore size distributions determined by wetting and drying curves varied significantly and data derived from the wetting curves were thought to be more reliable. The sorption isotherms were Type IV for both coals and an IUPAC classification of Type H2 hysteresis was observed. The study extends our knowledge and understanding on coal microstructure and may have implication in the real world application.

Index Terms—Sub bituminous coal, enhanced coal bed natural gas, water sorption isotherms, micro porosity, BET surface area, pore size distribution.

I. INTRODUCTION

Coal seams containing coal bed methane (CBM) usually adsorbs onto the coal surface attributed to the pressure of water in coal beds [1], [2]. Partial dewatering of the target coal seams is required to relieve the hydrological pressure for CBM extraction. Unlike conventional natural gas reservoirs, which store gas in the network of natural fractures, CBM is primarily adsorbed within the coal matrix on the internal surfaces of the coal. Consequently, micro pores generally accounts for the majority of the in-place gas in these reservoirs [2]-[5]. Although most of the gas is contained within the micro pores, the macro pores are largely responsible for coal permeability, which determines the gas flow rate and hence commercial prospects of CBM extraction [2]. According to IUPAC, pores with widths not exceeding 2 nm are defined as micro pores while pores with widths

exceeding 50 nm are categorized as macro pores. All other pores (diameters between 2 and 50 nm) are designated as mesopores [6]. However, in this study we used 2.1 nm and 53 nm which is slightly different from IUPAC for the pore size classification because they correspond to the capillary pressure at 60% and 98% relative humidity, respectively (see Table III). The geometry of the pore space including pore size distribution, total porosity and specific surface area as well as the architecture of the pores profoundly influence the behavior of coal as a reservoir rock [7], among which the micro porosity is particularly important. Micro pores are believed to provide the majority of the storage for methane onto which surface the methane molecules adsorb [2]. Adsorption/desorption isotherms have provided an alternative approach for the determination of micro porosity. Sorption isotherms express the amount of a gas species that can be stored within the coal matrix at a specific temperature and pressure and the results of these studies can be empirically used to estimate the gas storage/holding capacities within coal. Adsorption starts with the formation of a monolayer on the surface followed by multilayer formation and finally capillary condensation, which is capable of filling the micro- and mesopores [8]. Capillary pressure is defined as the pressure difference between two immiscible fluids that are in contact with each other in a capillary tube and form a clear interface attributed to the interfacial tension effect [9], [10]. Capillary pressure is important because it is a major factor controlling the fluid distribution in a reservoir rock. It is widely used to obtain information about pore size and pore size distribution [11]. The small pores in a reservoir rock can be assumed to a capillary tube [9]. A variety of methods have been developed for controlling capillary pressure, including mercury injection and numerous centrifuge techniques [12]. Various types of humidity control agents have also been used (e.g., saturated salt solution or sulfuric acid). There are advantages and disadvantages associated with each method and some methods may not be suitable for different types of materials. For example, the high pressures associated with mercury injection may affect the fragile pore structure of some types of reservoir rock, which may result in an inaccurate determination of the total pore space and the inability to restore the tested sample to its original state [13]. Furthermore, there are also environmental and toxicological concerns that may need to be considered [12]. Glycerol is

non-toxic and non-corrosive and hygroscopic under anhydrous conditions. It is also safe to handle, mixes completely with water at any proportion, and has negligible vapor pressure at ambient conditions [14]. Moreover, sorption isotherm data can be obtained by extending capillary pressures to very high values by using glycerol to regulate humidity. A relative humidity of 60% represents a water/air capillary pressure of 69.36 MPa is the dividing line between micro pores and mesopores, while a relative humidity of 98% corresponds to the dividing line of mesopores and macro pores [13]. Coalbed methane is believed to be stored primarily in micro pores by adsorption onto the pore surface [2]. It is important to learn the pore size distribution and pore surface area as they determine the maximum gas holding capacity. Few publications can be found in the literature using intact cores for pore size characterization of coals. One reason may be the time that it takes to complete a water isotherm using the glycerol approach. As in [13], Fischer and coworkers performed an adsorption study on sandstone and limestone rock cores using a similar approach. However, the physical and chemical properties of these rocks are significantly different than coal. They have much lower surface area and porosity and, unlike coal, are not friable. As a result, the experiments were completed over a much shorter period of time than the nearly five years required for completing this study. The present study aimed at evaluation of pore size distribution and BET surface areas for a subbituminous coal using water sorption data. The data were used for determination of Brunauer-Emmett-Teller (BET) surface area and obtaining the information on pore size distribution. Unipore model was also used for the fitting to calculate the effective diffusion coefficients. To the best of our knowledge, this paper appears to be the first to present water sorption isotherms using intact coal cores collected from the Powder River Basin (PRB), which is more representative to the real situation than the powder or ground coal. Similar isotherm studies have been performed on ground coal, for example in [15], Charriere and Behra had performed the studies on French lignite for evaluating BET surface area and diffusion coefficient. However, the ground samples are thought to be less representative of the coal *in situ*. This study extends our knowledge and understanding on microstructure of coal and may have implication in the real world application.

II. MATERIALS AND METHODS

A. Coal

Coal samples were obtained from Upper Wyodak Formation (Paleocene) at two different sites in the Powder River basin (PRB) located approximately 18 miles and 31 miles, respectively, west of the Powder River on the Montana side of the Montana-Wyoming state line. The first well (SL-3) was located in the Smith Aquifer at coordinates 45.00792° North and 106.53133° West. Smith Coal samples were collected on April 29, 2005 from depths between 349 feet and 358 feet. The second well (SL-5) was located in the Canyon Aquifer at coordinates 45.01189° North and 106.27149°

West. Coal samples were collected on June 10, 2005, from depths between 408 feet and 431 feet. The coal is subbituminous C in rank as indicated in Section 3.1. The boreholes were first drilled to the coal seams and then lined with 5-inch diameter steel casing. Coal samples were then collected from the underlying coal seam using a 3-inch diameter split spoon tube. Once the split spoon was retrieved to the surface, the split spoon was laid on its side and opened. A quick description of the core was made, including length and physical state, and then the samples were carefully placed into rigid PVC tubes roughly 5.5 feet in length, filled with produced water, and sealed. The samples were transported to the University of Wyoming, in Laramie, Wyoming, where they were stored in a cold room at a temperature of 3° C (37° F) prior to use.

B. Methods

The experimental method described in [13] was used in this study. The coal samples were subjected to relative humidities of 20, 40, 60, 70, 80, 85, 90, 93, and 98% and the change in water mass associated with each relative humidity was determined gravimetrically. High-purity glycerol (ACS grade, EMD) and distilled water (ultrapure water system, NAPONpure) solutions were used to control the relative humidity. Two experimental trials were performed; one with dried coal (wetting curve) and the other using water saturated coal (drying curve). Triplicate samples of Canyon (CC1, CC2, CC3) and Smith coal (SC1, SC2, SC3) were used for each trial. Intact coal coupons (cylinder in shape) weighing between 15 to 25 grams (approximately 4 cm in diameter and 1.5 cm in height) were cut from large core samples (3 inch in diameter) under vacuum condition. The coal coupons for establishing the drying curves (designated as initially saturated) were saturated with deionized water under vacuum and the coupons used for establishing the wetting curve (designated as initial dry) were dried in an evaporation oven at 105° C until no significant change in mass was observed. The coal coupons were placed in small glass Petri dishes situated directly above the glycerol-water solution contained within 250 mm glass desiccators (Fisher brand). The desiccators were maintained at 98% relative humidity for the initially saturated samples and 20% relative humidity for initially dry samples, respectively. The samples were weighed weekly until relative equilibrium was established. (The change in weight was less than 0.05%.) This process was repeated at the next lower or higher relative humidity, depending on the sample, until the wetting or drying process was completed. Desiccators were stored in a cooler with a thermometer to monitor the experiment temperature. The study was performed at an ambient room temperature of $20 \pm 1^\circ$ C. Prior to beginning the study the glassware was treated with Lysol™ Mold and Mildew Killer to prevent microorganisms from growing on the samples. To ensure and maintain accurate relative humidities within the desiccators, the density of the water-glycerol solutions were checked periodically using a density meter (DMA 48, PAAR) and additional water or glycerol was added as necessary. The time required to reach the equilibrium moisture content at each relative humidity varied from several weeks to several

months, depending on the size of the sample and the relative vapor pressure. Samples generally took longer to reach a constant mass as the relative humidity increased [13]. Proximate and ultimate analyses were performed on the Canyon and Smith coal (as-mined basis) by Wyoming Analytical Laboratories in Laramie, Wyoming. The samples were the splits that were also used for coal coupons preparation. The analyses were conducted in accordance with ASTM standards D-5142, D-5373 and D-5865. BET analysis was done using a Micromeritics ASAP 2020. 5-point BET nitrogen analysis was completed at 77.35 K (liquid nitrogen temperature) for each sample which completes adsorption analysis at a series of five different nitrogen pressures ranging 6 to 60 mmHg. Coal samples were lightly crushed using a mortar and pestle and ~1 g was added to the BET sample tube. A glass filler rod was added and the tube was capped with a vacuum seal cap. Each sample was loaded to a degas port for degassing overnight at 110°C under vacuum. The sample was then backfilled with nitrogen to atmospheric pressure and moved to the analysis port.

III. RESULTS AND DISCUSSIONS

A. Coal Characterization

The results of the proximate analysis are shown in Table I, and the results of the ultimate analysis are shown in Table II.

Table I: Proximate Analysis and heating value of Sampled Coals (as received) in wt.%.

	Canyon Coal	Smith Coal
Moisture	31.3	30.3
Ash	2.7	4.8
Volatile Matter	28.8	27.6
Fixed Carbon	37.5	37.3
Heating Value (Btu/lb)	8277	8782

Table 2: Ultimate Analysis of Sampled Coals (as received) in wt.%.

	Canyon Coal	Smith Coal
Moisture	31.1	30.3
Hydrogen	2.7	2.5
Carbon	48.2	50.4
Nitrogen	3.8	1.4
Sulfur	0.2	1.0
Oxygen	11.4	9.6
Ash	2.7	4.8

Canyon coal: $C_{100}H_{67.2}O_{17.7}N_{6.8}S_{0.2}$; Smith Coal: $C_{100}H_{59.5}O_{14.3}N_{2.4}S_{0.7}$ Coal properties including the caloric value, volatile matter and agglomerating character were used to determine the coal rank while fixed carbon and gross calorific value were used to classify the coal [16]. Lower-rank coals (i.e., gross calorific value less than 14000 Btu/lb) are classified based on their gross calorific value as determined on a moist, mineral-matter-free basis. As shown in Table I, the caloric heating values of both coals samples as determined on a moist, mineral-matter-free basis falls within the range of

rank C subbituminous coal (8.3-9.55 x1 0³ Btu/lb) which agrees with published data [17].

B. Water Sorption Isotherms

Sorption isotherms were calculated using the Kelvin equation (1), where R is the universal gas constant (8.3144 cm³-MPa/(mol·K)), T is the temperature (K), P/P₀ (=Hr) is the relative vapor pressure, P_c is the capillary pressure (MPa), and α is the molar volume of H₂O (18.05 cm³/mol). The equation relates the mass of water adsorbed at each relative humidity to the capillary pressure as described in [13] and [18]. The shape of the sorption isotherms are related to physical sorption on coal surface at low relative humidity and capillary condensation and evaporation in pore space at high Hr [13]. The capillary pressure, in turn, can be expressed as a pore size radius as shown in (2), where σ is the surface tension (0.072 N/m), and r_m is the mean radius of curvature (m). This makes it possible to determine the size of the pores and the pore volume composed of those pore sizes. The equations are assumed to be valid for cylindrical pore geometry [19]. Reference [20] used the captive-bubble technique for measurement of coal hydrophobicity and found that the low rank coal (below HVA bituminous) had hydrophobicity close to 0% while high rank coal had higher percentage of hydrophobicity. Therefore, for simplicity, we assumed that the contact angle is zero and thus the simplified form of (2).

$$RT \ln(P / P_0) = -P_c \alpha \tag{1}$$

$$P_c = 2\sigma / r_m \tag{2}$$

By comparing the change in mass of the sample at each relative humidity to the change in mass between completely saturated and completely dry values (i.e., total porosity), an accurate pore size distribution is determined. Pore sizes were related to the corresponding capillary pressure that was imposed for condensation (see Table III). Of special interest are the pore sizes related to relative humidities of 60 and 98% as they coincide with the transition between micro porosity and mesoporosity, and mesoporosity and macro porosity, respectively [13]. The relative humidity of 60% corresponds to water/air capillary pressure that represents the transition of condensation between micro pores and mesopores while 98% is for the transition between mesopores and macro pores. The relative vapor pressures and corresponding capillary pressures are shown in Table III.

Table III: Capillary Pressure and Pore Size at corresponding Relative Humidities (Fischer et al., 2007). The capillary pressures were determined by Equation (1) and pore sizes were determined by Equation (2), assuming at temperature 293 K.

Relative Humidity (%)	Pc (MPa)	Pore Size (nm)
0		< 0.7
20	217.2	0.7
40	123.7	1.2
60	68.9	2.1
70	48.1	3.0
80	30.1	4.8
85	21.9	6.6
90	14.2	10

93	9.8	15
96	5.5	26
98	2.7	53
100	0	> 53

Fig. 1 and 2 show the water sorption curves for Canyon Coal and Smith Coal, respectively. Fig. 3 was manipulated by shifting the desorption curve to the left to omit the gas at the high relative humidity region of Canyon Coal. One may turn the figures 90° counter-clockwise to view the sorption isotherms. It is noted that the shape of the isotherms are Type IV for both the Canyon and Smith coal, according to IUPAC classification [19].

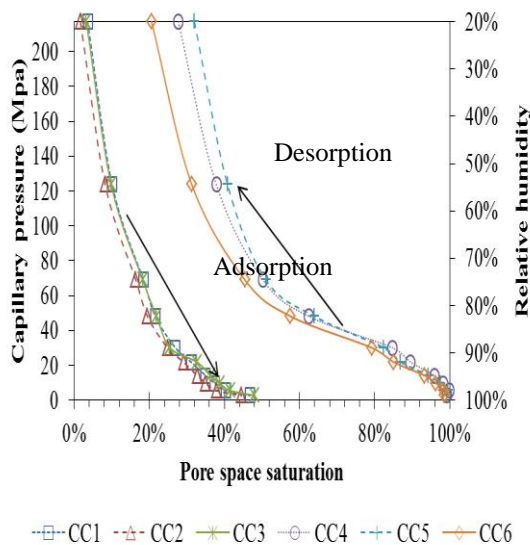


Fig.1. Adsorption (wetting) and desorption (drying) curves for Canyon Coal. CC1, CC2 and CC3 are the adsorption curves while CC4, CC5 and CC6 are the desorption curves. One may turn the figure 90° counter-clockwise to obtain water sorption isotherms.

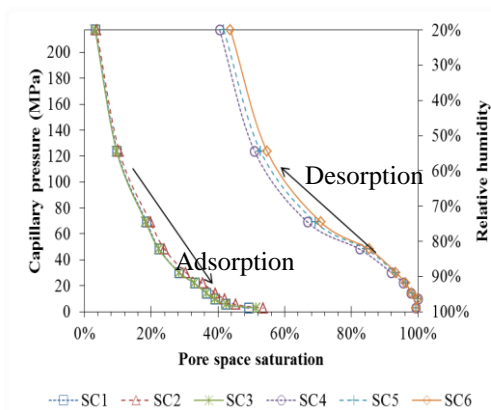


Fig.2. Adsorption (wetting) and desorption (drying) curves for Smith Coal. SC1, SC2 and SC3 are the adsorption curves while SC4, SC5 and SC6 are the desorption curves. One may turn the figure 90° counter-clockwise to obtain water sorption isotherms.

Type IV isotherm with the hysteresis loop as its characteristic features implies the phenomenon of capillary

condensation in mesopores. It also shows the limiting uptake of adsorbate over the high relative humidity range. In Fig. 3, a classification of IUPAC Type H2 hysteresis was observed [19]. The hysteresis can be attributed to structural heterogeneity, the chemical interactions between water the coal surface, the network effects of the adsorbent and structural changes of the coal as demonstrated by other studies [19], [21], [22]. At 20% humidity the drying and wetting curves also showed gaps of approximately 27.4% (Fig. 3) and 40.6% (data not shown in the figure) for the Canyon and Smith coals, respectively. Reference [23] also reported non-convergence for coal adsorption isotherms in the lower capillary region.

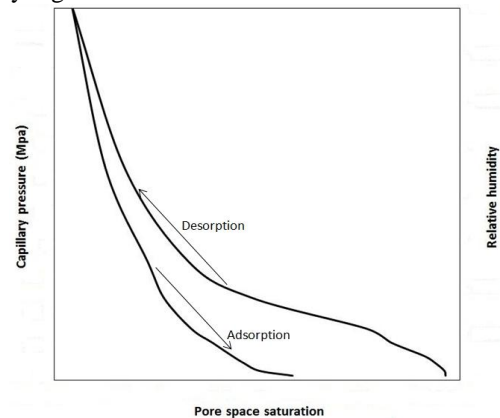


Fig.3. Hysteresis of adsorption/desorption isotherms of Canyon coal.

The phenomena can be explained by the adsorption and capillary condensation theory [21], [24]. Single and then multilayer adsorption occurs within the pore space and followed by capillary condensation until the available pore space is filled with water at the pore size under its corresponding capillary pressure. Capillary condensation does not occur in the macro pores. Therefore, the water contained in the macro pores of the initially wet coal samples is irreversibly lost during the drying process (i.e. cannot be replaced during re-adsorption). Non-convergence in the lower capillary region may also be explained by changes in the wetting properties of the pore surface as a result of drying which may result in pore spaces that were once occupied by water being irreversibly replaced by gas [25]. Subbituminous coal contains hydroxide (-OH) and carboxyl (-COOH) functional groups and that are capable of interacting with water molecules through hydrogen bonding [22], [23]. It is likely that the initially saturated coal contained water molecules that were chemically bound to functional groups on the coal surface. These chemically bound water molecules may only be removed at higher temperatures and/or lower pressures. For example, in [23] it has found that higher temperature drying yielded higher apparent coal moisture contents. Others found that only 35 and 60% of the water removed from Arkansas lignite and Wyoming subbituminous coal dried at temperatures ranging from 24 °C to 100 °C could

be replaced by re-exposing the samples to water vapor [26], [27].

C. Porosity and Pore Size Distribution

The percent micro pores, mesopores and macro pores as determined by the drying and wetting curves for each coal type are presented in Fig. 4. As shown, the values as determined by the drying and wetting curves vary significantly for both the Canyon and Smith coals. The micro porosity was shown to be approximately 48.9% of the total porosity for the Canyon coal and 69.0% of the total porosity for the Smith coal as determined using the drying curves. However, the micro porosity values were much smaller for the coal samples as determined using the wetting curves for Canyon coal 17.7% and Smith coal 18.9%, respectively, with most of the total porosity consisting of macro pores. In [28], Clarkson and Bustin reported micro pore volume of several bituminous coal using CO₂ sorption isotherms. The micro pore volumes varied from 0.028 cm³/g coal to 0.055 cm³/g coal. The average micropore volumes of this study are 0.235 cm³/g coal and 0.073 cm³/g coal obtained from drying and wetting curves, respectively. To be noted, the same authors found that the values of the total pore volume of the coal determine by helium and mercury porosimetry were actually smaller than the micro pore volumes attributed to the swelling caused by the preferential adsorption of CO₂. The difference of the values of micro porosity is huge determined by wetting and drying curves. The question becomes which values are representative of the “true porosity”. In an IUPAC guideline of reporting physisorption data for gas/solid systems, it concluded that the desorption (drying) branch of a Type H2 loop should not be used for calculation of pore size distribution because of its unreliability [19]. The results are consistent with other studies that macro pores account for the majority of the porosity in lower rank coals [7], [29], [30]. Therefore, the authors feel that the porosity data derived from the wetting curves are more reliable and more representative of the actual matrix porosity of the coal.

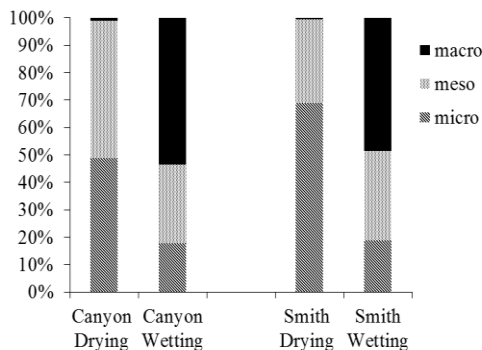


Fig.4. Porosity for micro pores (Hr<60%), mesopores (60%<Hr<98%) and macro pores (Hr<98%) for Canyon Coal and Smith Coal as determined by the drying (desorption) and wetting (adsorption) curves.

D. BET Surface Area

The BET model, which is based on Langmuir’s theory, is suitable for unimolecular layers and provides a good

description of sorption for micro porous sorbents such as coal [15], [31]-[33]. Assuming a fixed number of sites on the coal surface, the monolayer adsorption capacity and specific surface area of the coal solids were determined using the inflection point corresponding to the beginning of the formation of second layer. The relation of the amount of adsorbed gas and saturation pressure is shown in (3) where *v* is the volume of water adsorbed at pressure *P*, *v_m* is the volume of water adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer, *c* is the appropriate constant, and *P₀* is the saturation pressure.

$$v = (v_m c P) / \{ (P_0 - P) [1 + (c - 1)(P / P_0)] \} \tag{3}$$

In [34], Dannenberg and Opie have suggested that the condensation of water in capillaries likely occurs before a monomolecular layer is completely formed with water adsorbing to either high binding energy (primary) or low binding energy (secondary) sites. Equation (3) can only be used to fit data for *P/P₀* values < 0.35. The authors of [15] developed the modified BET model shown below (Equation (4)) to fit the higher *P/P₀* data and (5) and (6) to determine volume of water adsorbed by the primary and secondary sites. It was assumed that water was adsorbed on two types of surface sites, i.e., directly on high binding energy sites of the surface and on lower binding energy sites.

$$v = (v_m c_1 \frac{P}{P_0}) / [(1 - c_2 \frac{P}{P_0})(1 - c_2 \frac{P}{P_0} + c_1 \frac{P}{P_0})] \tag{4}$$

$$v_1 = (v_m c_1 \frac{P}{P_0}) / (1 - c_2 \frac{P}{P_0} + c_1 \frac{P}{P_0}) \tag{5}$$

$$v_2 = [c_1 c_2 (\frac{P}{P_0})^2] / (1 - c_2 \frac{P}{P_0} + c_1 \frac{P}{P_0}) \tag{6}$$

The constants *c₁*, *c₂*, and *v_m* can be obtained empirically from the adsorption isotherm data using (7) [35] where *Hr* = *P/P₀*, *A* = 1 / (*v_mc₁*) , *B* = (*c₁ - c₂*) / (*v_mc₁*) , and *C* = (*c₁c₂ - c₂²*) / (*v_mc₁*) .

$$\frac{Hr}{v} = A + BHr - CHr^2 \tag{7}$$

And thus, the specific surface area (*S_{BET}*, m²/g) can be determined using (8) where *N_A* is Avogadro’s constant (6.022x10²³ mol⁻¹), *A* is the cross sectional area of the adsorbed gas molecule (0.106 nm² for water), *V* is the molar volume of adsorbed gas (18.05 cm³/mol for water) and *M* is the mass (g) of the coal samples.

$$S_{BET} = (v_m N_A A) / (VM) \tag{8}$$

The calculated BET surface areas from water desorption are compared with the direct measurements of BET using nitrogen (N₂) gas in Table IV for the Canyon and Smith Coals. The calculated surface areas are significantly higher than those determined in [13] for sandstone and carbonates rock (0.2-1.6 m²/g). The BET surface areas calculated from water adsorption are in similar ranges with those reported in [36] for high rank bituminous coal using CO₂ gas adsorption. Our reported values (for subbituminous coal) range from 217 to 864 m²/g while Linge reports 165 to 311 m²/g [36]. In [29] the

authors also reported a BET surface area of 308 m²/g for a Wyodak subbituminous coal using carbon dioxide adsorption isotherms. The authors of [37] measured BET surface areas on a high volatile bituminous coal (N₂ sorption method) and reported values ranging from 1.8 to 22.9 m²/g. Linge also measured the surface areas for the bituminous coals using single point BET nitrogen gas adsorption. Using N₂ BET Linge [36] reports surface area values of 2 to 7 m²/g which are again consistent with the values of 0.1 to 3.8 in Table IV. The approximately two orders of magnitude difference that we observe between water sorption BET and N₂ BET is consistent with literature reports. Furthermore, the study in [38] compared surface area determination using N₂ adsorption at liquid nitrogen temperature with CO₂ adsorption at room temperature for the characterizations of porous carbons. They conclude that samples with narrow micro porosity cannot be properly characterized by N₂ at 77K due to the existence of diffusional problems (i.e., the N₂ molecules cannot reach the narrowest micro pores). In [29], it also reported that the surface areas were consistently higher calculated from carbon dioxide adsorption at 298 K than those calculated from nitrogen at 77 K. They concluded that this was attributed to the molecular sieve character of the coals. Since Fig. 4 shows that our coals (wetting) have significant micro porosity, it also appears that N₂ adsorption at 77K is inappropriate for the characterization of these coals.

Table IV: BET surface area for water and nitrogen gas of Canyon Coal and Smith Coal.

Coals	S _{BET} (m ² /g) wetting (293 K)	S _{BET} (m ² /g) N ₂ (77 K)
CC1	344.4	0.4
CC2	390.8	1.7
CC3	244.3	3.8
SC1	229.4	0.3
SC2	268.8	0.3
SC3	217.6	0.4
CC4	496.2	0.5
CC5	460.3	0.2
CC6	497.8	0.1
SC4	776.5	0.5
SC5	847.8	0.4
SC6	863.5	0.2

Table V: Effective diffusion coefficients of Canyon Coal and Smith Coal.

Coals	D (m ² /s) Wetting	Coals	D (m ² /s) Drying
CC1	8.5E-23	CC4	4.2E-23
CC2	7.1E-23	CC5	4.2E-23
CC3	1.8E-22	CC6	4.8E-23
SC1	1.7E-22	SC4	1.7E-23
SC2	1.2E-22	SC5	1.3E-23
SC3	1.8E-22	SC6	1.2E-23

E. Effective Diffusion Coefficient

Diffusion parameters can be estimated from kinetic data by various models. Unipore model was used in this study because it allows an approximation of the diffusion parameter

for gas in coal [15]. The unipore model can be used to estimate the water diffusion coefficient in coal using (9) [34], [39], [40], where: M_t (g) is the water uptake at time t (s), M_∞ (g) is the total water uptake, D (m²/s) is the effective diffusion coefficient, S (m²/g) is the specific surface area, and V_p (m³/g) is the specific pore volume.

$$\frac{M_t}{M_\infty} = \frac{2S}{V_p} \sqrt{\frac{Dt}{\pi}} \tag{9}$$

Plotting M_t/M_∞ vs. t^{1/2} results in a slope equal to (2S/V_p)(D/π)^{1/2}. Fig. 5 is an example of a plot of the fitted diffusion model. Table V shows the effective diffusion coefficient of Canyon Coal and Smith Coal. In [39], it was estimated that the effective diffusion coefficient of coal ranges from 10⁻¹⁶ m²/s to 10⁻²⁴ m²/s. All the values of our estimates are within that range although they are close to the lower end of the estimated values. It is likely that this is the first paper to report effective diffusion coefficient values of a subbituminous coal from PRB using the unipore model.

IV. CONCLUSION

The present study aimed at evaluation of pore size distribution and BET surface areas for a subbituminous coal using water sorption isotherms. This specific characterization is a difficult task and time consuming attributed to the innate characteristics in that coal is highly complex in structure, and highly heterogeneous. However, it is an important subject because methane is believed to be store in the micro pores by adsorption onto the surface. The pore surface area also determines the maximum gas holding potential of a coal reservoir [2]. The studied coal contained large amount of BET surface area that was determined by waster sorption isotherms (up to 863.5 m²/g-coal). That explains the different gas storage behaviors between the conventional rock and coalbed. The data were also used for extrapolation of pore size distribution. The drying curves and wetting curves gave rise to significantly different results and difficult to be explained. The water sorption methodology has the advantage over CO₂ in that sorption of CO₂ causes swelling within coal structures resulting in increased errors [41], [42]. The study extends our knowledge and understanding on coal microstructure and may have implication in the real world application.

V. ACKNOWLEDGMENT

Funding for this project is provided by DOE-NETL, Solicitation No.: DE-PS26-04NT15460-02 “Produced Water Management and Beneficial Use” and RPSEA through the “Ultra-Deepwater and Unconventional Natural Gas and Other Petroleum Resources” program authorized by the U.S. Energy Policy Act of 2005. RPSEA (www.rpsea.org) is a nonprofit corporation whose mission is to provide a stewardship role in ensuring the focused research, development and deployment of safe and environmentally responsible technology that can effectively deliver hydrocarbons from domestic resources to the citizens of the

United States. RPSEA, operating as a consortium of premier U.S. energy research universities, industry, and independent research organizations, manages the program under a contract with the U.S. Department of Energy's National Energy Technology Laboratory.

REFERENCES

- [1] White, C.M., Smith, D.H., Jones, K.L., Goodman, A.L., Jikich, S.A., LaCount, R.B., DuBose, S.B., Ozdemir, E., Morsi, B.I., Schroeder, K.T., 2005. Sequestration of carbon dioxide in coal with enhanced coalbed methane recovery – A review. *Energy Fuels* 19(3), 659-724.
- [2] Moore, T.A., 2012. Coalbed methane: A review. *International Journal of Coal Geology* 101, 36-81.
- [3] Ohen, H.A., Amaefule, J.O., Hyman, L.A., Daneshjou, D., 1991. A systems response model for simultaneous determination of capillary pressure and relative permeability characteristics of coalbed methane. *SPE Annual Technical Conference and Exhibition* 22912, 247-261.
- [4] Roadifer, R.D., Moore, T.R., Raterman, K.T., Farnan, R.A., Crabtree, B.J., 2003. Coalbed methane parametric study: what's really important to production and when? *SPE Annual Technical Conference and Exhibition* 84425, 1-11.
- [5] Saites, F., 2005. Laboratory evaluation of coals for coalbed methane. Master Thesis, University of Calgary, Canada.
- [6] Rodrigues, C.F., Lemos de Sousa, M.J., 2002. The measurement of coal porosity with different gases. *International Journal of Coal Geology* 48(3), 245-251.
- [7] Radlinski, A.P., Mastalerz, M., Hinde, A.L., Hainbuchner, M., Rauch, H., Baron, M., Lin, J.S., Fan, L., Thiyagarajan, P., 2004. Application of SAXS and SANS in evaluation of porosity, pore size distribution and surface area of coal. *International Journal of Coal Geology* 59(3), 245-271.
- [8] Tompsett, G.A., Krogh, L., Griffin, D.W., Conner, W.C., 2005. Hysteresis and scanning behavior of meso porous molecular sieves. *Langmuir* 21, 8214-8225.
- [9] Amyx, J.W., Bass, D.M., Whiting, R.L., 1960. *Petroleum Reservoir Engineering*. McGraw Hill, New York, NY.
- [10] Dandekar, A.Y., 2013. *Petroleum Reservoir Rock and Fluid Properties*. 2nd Ed. CRC Press, Boca Raton, FL.
- [11] Ward J.S., Morrow, N.R., 1987. Capillary pressures and gas relative permeability's of low-permeability sandstone. *SPE Formation Evaluation* 2(3), 345-356.
- [12] Tiab, D., Donaldson. E., 2004. *Theory and practice of measuring reservoir rock and fluid transport properties*. 2nd Edition, Elsevier, Amsterdam.
- [13] Fischer, H., Morrow, N.R., Mason, G., 2007. Water adsorption/desorption isotherms for characterization of micro porosity in sandstone and carbonate rocks. In *Characterization of Porous Solids VII - Proceedings of the 7th International Symposium on the Characterization of Porous Solids (COPS-VII)*, Aix-en-Provence, France, 26-28 May 2005, (160) 295-302.
- [14] Root, L.J., Berne, B.J., 1997. Effect of pressure on hydrogen bonding in glycerol: A molecular dynamics investigation. *The Journal of Chemical Physics* 107(11), 4350-4357.
- [15] Charriere, D., Behra, P., 2010. Water sorption on coals. *Journal of Colloid and Interface Science* 344(2), 460-467.
- [16] ASTM D 388-99 2005. Standard classification of coals by rank. ASTM International.
- [17] Kloubek, J., 1994. Investigation of porous structures using mercury reintrusion and retention. *Journal of Colloid and Interface Science* 163(1), 10-18.
- [18] Melrose, J.C., 1998. Use of water-vapor desorption data in the determination of capillary pressures at low water saturations. *SPE Reservoir Engineering* 3(3), 913-918.
- [19] Sing, K.S.W., 1982. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry* 54(11), 2201-2218.
- [20] Gutierrez-Rodriguez, J.A., Purcell, R.J. Jr, Aplan, F.F., 1984. Estimating the hydrophobicity of coal. *Colloids and Surface* 12, 1-25.
- [21] Shang, S., Horne, R.D., Ramey, H.Jr., 1995. Water vapor adsorption on geothermal reservoir rocks. *Geothermics* 24(4), 523-540.
- [22] McCutcheon, A.L., Barton, W.A., Wilson, M.A., 2003. Characterization of water adsorbed on bituminous coals. *Energy and Fuel* 17(1), 107-112.
- [23] Deevi, S.C., Suuberg, E.M., 1987. Physical changes accompanying drying of western US lignites. *Fuel* 66(4), 454-460.
- [24] Brunauer, S., Deming, L.S., Edwards, W., 1940. On a theory of the van der Waals adsorption of gases. *Journal of the American Chemical Society* 62(7), 1723-1732.
- [25] Gorbaty, M.L., 1978. Effect of drying on the adsorptive properties of subbituminous coal. *Fuel* 57(12), 796-797.
- [26] Levine, D.G., Schlosberg, R.H., Silbernagel, B.G., 1982. Understanding the chemistry and physics of coal structure (a review). *Proceedings of the National Academy of Sciences* 79(10), 3365-3370.
- [27] Suuberg, E.M., Otake, Y., Yun, Y., Deevi, S.C., 1993. Role of moisture in coal structure and the effects of drying upon the accessibility of the coal structure. *Energy Fuels* 7(3), 384-392.
- [28] Clarkson, C.R., Bustin, R.M., 1999. The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modeling study. 1. Isotherms and pore volume distributions. *Fuel* 78(11), 1333-1344.
- [29] Gan, H., Nandi, S.P., Walker, P.L. Jr., 1972. Nature of the porosity in American coals. *Fuel* 51(4), 272-277.
- [30] Laubach, S.E., Marrett, R.A., Olson, J.E., Scott, A.R., 1998. Characteristics and origins of coal cleat: a review. *International Journal of Coal Geology* 35, 175-207.
- [31] Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* 60(2), 309-319.
- [32] Burwell, R.L., 1975. *Manual of Symbols and Terminology for Physicochemical Quantities and Units—Appendix II Part II: Heterogeneous Catalysis*. *Pure and Applied Chemistry* 46, 71-90.

- [33] Sing, K.S.W., 2001. The use of nitrogen adsorption for the characterization of porous materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 187-188, 3-9.
- [34] Dannenberg, E.M., Opie, W.H., 1958. A study of the moisture adsorption properties of carbon blacks. *Rubber World* 136(6), 849-855.
- [35] Rawat, S.P.S., Khali, D.P., 1999. Studies on adsorption behavior of water vapor in lignin using the Brunauer-Emmett-Teller theory. *European Journal of Wood and Wood Products* 57(3), 203-204.
- [36] Linge, H.G., 1989. The surface area of coal particles. *Fuel*, 68, 111-113.
- [37] Mastalerz, M., Drobnik, A., Strapoć, D., Solano Acosta, W., Rupp, J., 2008. Variations in pore characteristics in high volatile bituminous coals: Implications for coal bed gas content. *International Journal of Coal Geology* 76, 205–216.
- [38] Lozano-Castillo, D, Carzola-Amoros, D., and Linares-Solano, A., 2004. Usefulness of CO₂ adsorption at 273K for the characterization of porous carbons. *Carbon*, 42, 1231-1236.
- [39] Zwietering, P., Overeem, J., Van Krevelen, D.W., 1956. Chemical structure and properties of coal XIII--activated diffusion of gases in coal. *Fuel* 35, 66-70.
- [40] Debelak, K.A., Schrodt, J.T., 1979. Comparison of pore structure in Kentucky coals by mercury penetration and carbon dioxide adsorption. *Fuel* 58(10), 732-736.
- [41] Larsen, J.W., 2004. The effects of dissolved CO₂ on coal structure and properties. *International Journal of Coal Geology* 57, 63-70.
- [42] Romanov, V.N., Goofman, A.L., Larsen, J.W., 2006. Errors in CO₂ adsorption measurements caused by coal swelling. *Energy and Fuel* 20(1), 415-416.

and President of Wyoming-based ENWYO, a technology start-up company at the University of Wyoming. Dr. Urynowicz received his Bachelor of Science in Chemical Engineering from Michigan State University, his Master of Science in Civil & Environmental Engineering from the University of Wisconsin, and his Ph.D. in Environmental Science & Engineering from the Colorado School of Mines. Prior to joining the faculty at the University of Wyoming, he worked in the manufacturing industry and as an environmental consultant. He was also the Founder, Managing Director and Principal Engineer at Envirox LLC, an environmental company specializing in the remediation of complex hazardous waste sites. During his career, Dr. Urynowicz has been involved in a wide range of research related to secondary biogenic coalbed natural gas, in situ chemical oxidation and the remediation of contaminated sites. He has published numerous technical papers and reports and has given invited lectures across the United States and abroad.



Joseph H. Holles Joseph Holles is an associate professor of Chemical Engineering within the Department of Chemical & Petroleum Engineering at the University of Wyoming. Dr. Holles received his Bachelor of Science in Iowa State University, both his Master of Engineering and Ph.D from University of Virginia. All degrees are in Chemical Engineering. Dr. Holles specialized in several area of research including heterogeneous catalysis, material characterization, renewable fuels, etc. His particular research interest focuses on nanoscale materials design and synthesis for catalytic applications. The design and synthesis is then complemented with reactivity studies and in-situ characterization of the catalytic material. In particular, X-ray absorption spectroscopy (XAS) experiments are periodically conducted at the Advanced Photon Source at Argonne National Laboratory. The combination of design, synthesis, and characterization allows for the direct translation of variations in the material at the atomic/molecular scale to expressed macroscopic properties such as improved reactivity. The main area of current research involving nanoscale design and synthesis of catalytic materials is pseudo orphic over layer bimetallic catalysts. He has published numerous technical papers and reports and is the holder of several patents.

AUTHOR'S PROFILE



Zaixing Huang Zaixing Huang is a research scientist of Environmental Engineering within the Center for Biogenic Natural Gas Research at the University of Wyoming. His major task is to develop new technologies for enhancing the in situ production of biogenic natural gas from coal and other hydrocarbon reservoirs. The realization that many of the world's fossil fuel reserves contain

secondary biogenic natural gas (i.e., methane produced by indigenous microorganisms living within these reservoirs) promises to transform the way we view and manage these important energy resources. Through the development of technologies that enhance the production of biogenic natural gas we now have the opportunity to extend the lifetime of these resources indefinitely. In places like Wyoming's Powder River Basin this could mean putting coal bed methane related infrastructure back into long-term economic production. To date, research performed through the Center has resulted in the filling of several technology patents. Dr. Huang received his Bachelor of Science in biotechnology from Harbin Institute of Technology in Harbin, China. He earned a Master of Science in environmental science from Chalmers University of Technology in Gothenburg, Sweden. He received his Doctoral degree in Civil Engineering from University of Wyoming in Laramie, USA. As a junior researcher, he has published several technical papers, a book in biogenic CBM and a patent.



Michael A. Urynowicz Michael Urynowicz is an Associate Professor of Environmental Engineering within the Department of Civil & Architectural Engineering at the University of Wyoming, Director of the Coal Bed Natural Gas Center of Excellence and a Licensed Professional Engineer. He is also Co-founder