



Changes in gas storage and transport properties of coal as a result of enhanced microbial methane generation



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ARTICLE INFO

Article history:

Received 18 January 2016

Received in revised form 15 March 2016

Accepted 16 March 2016

Available online 26 March 2016

Keywords:

Bioconversion

Methane

Sorption

Diffusion

Pore surface area

Reservoir characterization

ABSTRACT

This study was aimed at identifying the changes in coal storage and transport properties affecting gas production from coal-gas reservoirs, when treated with microbial consortia to generate/enhance production of methane. The work expanded on the technology of bio-conversion, first proposed in order to imitate the natural/microbial process of biogenic gasification leading to recharging coalbed methane reservoirs or, setting up natural gas reservoirs in non-producing coalbeds or, to coal waste, typically in the form of fines/ultra-fines. The pressure parameter was considered critical since, with continued production of methane, the produced gas would first diffuse into the coal matrix and get adsorbed with increasing pressure. During production, the pressure would decrease and the process would be reversed, gas diffusing out of the coal matrix and arriving at the cleat system.

The experimental work tested the variation in the sorption and diffusion properties of treated coal, post continued bio-conversion since these are the first two physical phenomena in CBM production. During the first phase, single component sorption–diffusion experiments were carried out using methane and CO₂ on virgin coals retrieved from the Illinois basin. Coals were then treated with nutrient amended microbial consortia for different periods. Gas production was monitored over thirty and sixty day periods of treatment after which, sorption–diffusion experiments were repeated on treated coals, thus establishing a trend over the sixty-day period. The sorption data was characterized using the Langmuir model. The variation trend in the value of diffusion coefficient, *D*, was also established as a function of pore pressure.

The results indicated an increase in the sorption capacity of coal as a result of continued bioconversion. This was attributed to increased pore surface area due to microbial actions resulting in changes in the pore size or, creation of new pores. It was further shown that the rate of diffusion increased, especially for methane, which exhibited rates higher than that for CO₂. These findings clearly support improved gas storage capacity with continued bio-conversion as well as significantly enhanced diffusion rates. As a continuation of this effort, change in permeability, the second gas transport phenomenon in coal-gas production, is currently being evaluated.

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1. Introduction and background

The origin of methane in coal seams can be distinctly related to two processes: thermogenic and biogenic. Thermo-catalytic conversion of coal is initiated at a temperature greater than 70 °C. At such temperatures, when coal attains a rank of approximately 0.5–0.6% vitrinite reflectance (high volatile, bituminous), continued application of heat and overlying pressure over time results in devolatilization of thermogenic gases, like CO₂, H₂O, CH₄, C₂H₆, H₂S and other higher hydrocarbon gases [1,2]. Biogenic methane,

as the name suggests, has its origin in the biosphere of the subsurface, consisting of various forms of microbes, known as methanogens. Primary biogenic methane and CO₂ are formed microbially during the initial stages of peat formation at shallow depths. Biogenic action from microbes is believed to generate in excess of 6% CO₂ in the northwest San Juan Basin [3]. Due to high porosity and lower burial rates, primary biogenic methane is volatilized over time or dissolved in water and expelled during compaction [4]. Late stage biogenic methane, also known as secondary biogenic methane, is formed post-compaction in all ranks of coal due to combination of active groundwater flow recharging underground systems with suitable microbes, along with uplift of the basin helping in meteoric recharge [1,4].

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Taking cue from the widespread application of microbes in the oil industry as a means to increase overall recovery, and the impact that naturally occurring microbes have had in producing methane in coal, Scott in 1995 introduced the concept of microbially enhanced coalbed methane (MECBM) [5]. It aimed at replicating the natural process of secondary biogenic gasification by treating coal with methanogens along with suitable nutrient amendments and trace elements. Studies conducted by Strapoć [6] and Opara [7] further provided substantial evidence of the potential of generating methane by treating coal fines with bacterial inoculations.

Research in the area of MECBM and bio-conversion has accelerated in the last few years for several reasons. First, natural gas is considered a cleaner and, therefore, preferred source of energy. Second, this technology is applicable to unmineable coals and abandoned coal mines with large amounts of coal left behind. Third, the technology is applicable to coal waste in the form of fines or poor quality material. Fourth, several regions with significant coalbed methane (CBM) activity are maturing, thus providing spread out wells along with other supporting infrastructure required for injection of microbes/nutrients as well as gas recovery and utilization. Finally, the technology is applicable to CBM wells that are abandoned due to poor production rates and recovery, like in the Illinois Basin.

The general advance of research has been toward characterizing and improving the microbial solutions, primarily aimed to economically increase methane production. It has been recognized that the process of bio-conversion, in general, is a relatively slow process. Significant production of methane has been observed over a period of thirty to sixty days, or even higher in some instances [7,8]. These studies have been conducted on powdered coal, providing additional surface areas for the microbes. Production rates for in-situ deposits are expected to be even lower. Under such time dependent production characteristics, it is important to identify the properties of the reservoir affecting flow, and also document the changes in these properties. Identifying, and if needed, improving flow characteristics of produced gas, along with engineering optimum nutrient solutions for the microbial population to thrive in would help decide the viability of the process in terms of techno-economic feasibility. The work reported in this paper provides a starting point to identify such changes, specifically in the sorption–diffusion properties of coal as a result of bio-conversion.

Coal is generally characterized as having a micro- and macroporosity structure. Micropores occur as part of the coal matrix and serve as a storehouse for over 95% of the gas in adsorbed form [9]. The macropore system consists of a network of closely spaced natural fractures surrounding matrix blocks, which is called the cleat system [10]. Flow of methane in the cleat system is permeability-controlled and is dependent on cleat parameters, like the aperture, continuity and spacing. The movement of gas in the coal matrix, on the other hand, is diffusion-controlled and is dependent on pore size, distribution and connectivity. For under-sized waste coal, microporous characteristics are often intact while the macropore system is non-existent.

Gas is stored in coal primarily by adsorption on organic surfaces. For storage of produced gas, it would first diffuse into the micropores onto the sorption sites, where it would get adsorbed. Since coal has a very large internal surface area and methane is tightly packed in a monomolecular layer, large quantities of gas can be adsorbed in the coal matrix. For a given pressure, the amount of gas sorbed is best described by an isotherm, a plot of the volume of sorbed gas as a function of pressure. The most commonly used adsorption model for coal is the Langmuir isotherm. It is simple to use and works well for coal-methane system. The diffusive movement of methane/CO₂ in coal is best described by Fick's second law of diffusion. Diffusion is characterized by the diffusion coefficient (*D*). Given that bio-conversion of coal is expected to

change the physical structure of coal, two properties that would be potentially impacted are the sorption capacity of coal, that is, the ability of coal to store gases, and diffusion in the microstructure of coal. This study, is therefore aimed at evaluating changes in these two properties with continued bio-conversion.

2. Experimental setup and procedure

2.1. Sample procurement and preparation

Blocks of coal for the experimental work were obtained from the central Illinois basin. Details of geographical location has been previously reported by Zhang et al. [8]. The coal was then ground and sieved to obtain a sample size of 40–100 mesh (0.0425–0.0149 cm). This size has been shown to remove the cracks and macropores present in coal completely and yet preserves the microstructure of coal, ensuring that the movement of gas is purely diffusive in nature [11].

The coal sample was then divided into three parts, ~60 g each. Sorption–diffusion experiments were carried out for all three sets. The first set was untreated, virgin coal. The results from this provided a measure of the baseline characteristics. The other two samples were then treated in microcosms with an adapted microbial consortium initially developed from the formation water retrieved from a CBM well [8]. Briefly, each microcosm contained 10 g coal and 45 ml of sterilized medium [12]. Once 5 ml of the adapted consortium was added, each serum bottle was closed with a butyl rubber stopper and sealed by an aluminum crimp. All bottles were stored at 28 °C in a dark environment. The amounts of methane and CO₂ in the headspace were measured at the end of thirty days for the second sample and sixty days for the third sample using gas chromatography. Replicates of the microcosms were discarded at each time point for analyzing sorption–diffusion behavior of the residual coal. A total of twelve reactors were used, of which six was treated for thirty days and the remaining six for sixty days. Detailed information about the reactor setup can be found in Zhang et al. [8].

Prior to conducting the sorption and diffusion experiment, six grams of sample was used for moisture and ash analysis following the ASTM procedures (ASTM D3173-87, 1987; ASTM D3174-04, 2004). Five grams of the sample was used for the ultimate analysis tests following the ASTM standards (D3176-74) to obtain the mass fractions of C, H, N, S and O.

2.2. Gas chromatograph

The gas chromatograph, with a flame ionizing detector (FID), was used to measure the methane and CO₂ content in the headspace of serum bottles. Briefly, a 50 µl aseptic syringe connected to a sterile 25 gauge needle was used to withdraw the gas sample and inject it in the GC column. The carrier gas (Argon) flow rate was set at 10.1 mL/min with a velocity of 55 cm/s. The isothermal zone temperatures for the injector and detector was set at 75 °C and 310 °C respectively. The retention time for methane was 4.73 min and that for CO₂ was 6.71 min. Calibration curves for methane and CO₂ were established using gas standards.

2.3. Sorption–diffusion

The primary component of the experimental setup was a high pressure vessel assembly, consisting of a sample cylinder and a reference volume connected by a two-way valve and a micro-filter to prevent movement of coal particles with changes of pressure. The setup was placed in a constant temperature bath, set at 88°F and capable of maintaining the temperature to within 0.2 °F of the desired temperature. This is important since the processes of sorp-

tion/diffusion in coal are extremely sensitive to changes in temperature. Monitoring of pressure data, which is critical to the experiment, was carried out using high sensitivity pressure transducers connected to the sample and reference vessels and hooked to a data acquisition system (DAS), capable of recording pressure at time intervals of as low as 0.01 s. Fig. 1 represents a schematic of the experimental setup.

The void space volume in the sample container was determined using helium, a non-sorbing gas. Sorption isotherm was then established by increasing pressure steps for methane, followed by CO₂ using the mass balance technique where a known quantity of gas is injected into the sample container. The difference between the quantity injected and that showing up as free gas provides the amount sorbed. By repeating this for increasing pressure steps, the adsorption isotherm is established to a final pressure of ~8.3 MPa (1200 psi) for methane and ~6.2 MPa (900 psi) for CO₂. The desorption part of the experiment was carried out by reversing the process, starting with the highest pressure attained for the adsorption cycle and reducing the pressure in a step-wise manner down to atmospheric. With very high ad/de-sorption rates during the initial period for each step, the DAS was programmed to record two pressure readings every second for one hour. This was followed by changing the time interval to one every 30 min for approximately 23 h, after which, the sample was believed to have attained equilibrium.

Since sorption of CO₂ is believed to induce permanent changes in the coal microstructure and the objective of the study was to evaluate the changes in coal microstructure due to bio-conversion, desorption characteristics of CO₂ were not established to ensure that the sample microstructure was preserved.

3. Measurement technique

3.1. Ad/de-sorption isotherm

The pressure data recorded during each pressure step over an interval of twenty-three hours was used to establish the

adsorption isotherm. Measurement techniques used in the experiment is identical to that used by Pillalamarri et al. [13]. Ultimately, the following form of Langmuir's equation was used to model the sorption characteristics:

$$V = \frac{PV_L}{P + P_L} \quad (1)$$

where V is the volume of gas adsorbed, P is the equilibrium gas pressure, V_L is the Langmuir volume which estimates the maximum volume that can be sorbed at infinite pressure, P_L is the Langmuir pressure at which the sorbed volume is half of the Langmuir volume. V_L and P_L are termed as Langmuir constants.

Given that methanogenesis of coal results in the formation of multiple gases, primarily methane and CO₂, it is important to consider multi-component sorption to characterize gas storage and release. The Extended Langmuir (EL) equation is the simplest and most commonly used model for the prediction of mixed gas adsorption on coal [14]. In order to predict the binary adsorption equilibria, EL requires pure component isotherm data only. The EL equation is given as:

$$V_i = \frac{(V_L)_i b_i P_i}{1 + \sum_j b_j P_j} \quad (2)$$

where V_L and $b (= \frac{1}{P_L})$ are the pure gas isotherm Langmuir constants, and P_i and P_j are the partial pressures of individual gas in free phase. The partial pressure is related to the total pressure by the relation:

$$P_i = P y_i \quad (3)$$

where y_i is the gas phase mole fraction of component i , and P is the total pressure.

3.2. Estimation of diffusion coefficient

Estimation of diffusion coefficient (D) requires continuous monitoring of pressure changes over time in the sample cylinder.

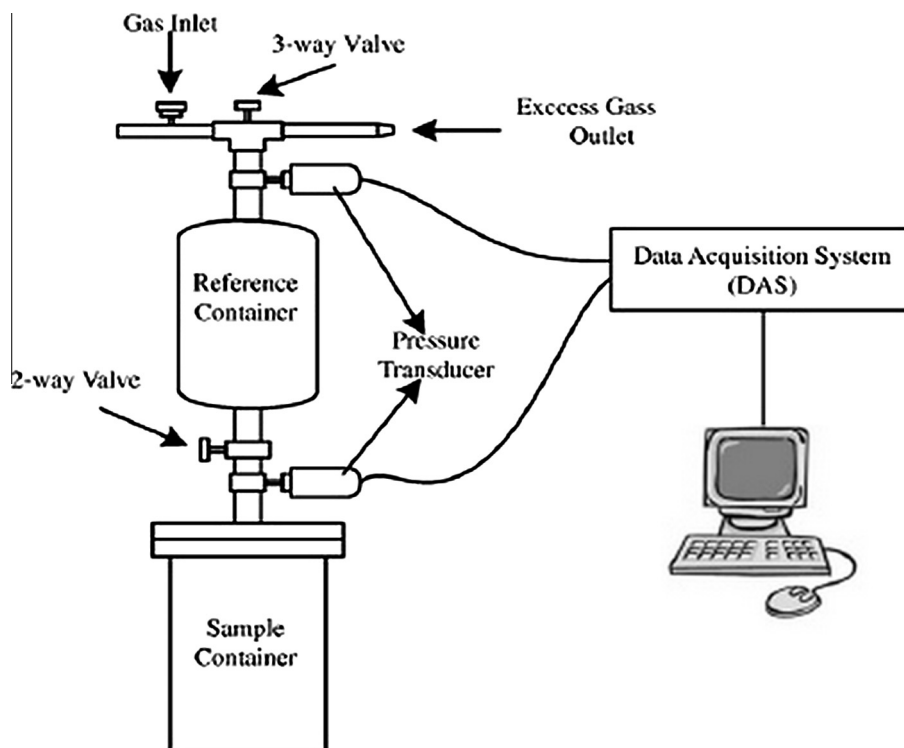


Fig. 1. Experimental setup for sorption/diffusion experiments.

Following the procedure described in the previous section, this was conducted for every pressure step for ad/de-sorption step for pressure changes in the sample cylinder. The uni-pore model, based on the Fick's second law of diffusion for spherically symmetric flow, was used to estimate the diffusion characteristics. Details of the measurement techniques can be found in the works of Pillalamarry et al. [13], where D , for short time durations ($t < 600$ s) was eventually characterized by the following equation:

$$\frac{V_t}{V_\infty} = 6\sqrt{\frac{Dt}{\pi r_p^2}} = 6\sqrt{\frac{D_e t}{\pi}} \quad (4)$$

where V_t is the total volume of gas ad/de-sorbed in time t , V_∞ is the total gas ad/de-sorbed after infinite time, and r_p is the diffusion path length, $D_e = D/r_p^2$, and is known as the effective diffusivity. This study estimated the value of D , similar to the study reported by Mavor et al. [15], where the value of r_p was assumed to be the average particle radius.

4. Results and discussion

4.1. Production of gases

The average volumes of methane and CO₂ produced over thirty and sixty days, normalized to normal cu. m. per ton are presented in Table 1. Since the reactors were purged with nitrogen, the undetected gas can either be nitrogen, or a mixture of nitrogen with other (undetected) gases produced during methanogenesis.

4.2. Adsorption isotherms

The results of the sorption experiments are illustrated in the form of isotherms for the three samples of coal tested. Table 2 presents the ultimate and proximate analysis results of the three coal samples and Table 3 presents the Langmuir parameters obtained for the samples. The maximum equilibrium pressure was ~7.6 MPa (1100 psia) for methane and 5.5 MPa (800 psia) for CO₂. The isotherms for methane and CO₂ for the three tests are illustrated in Figs. 2 and 3 respectively. The plots are based on Langmuir fits. It is apparent that all isotherms are of Type 1, as per Brunauer's classification. The relative errors of deviation of Langmuir-predicted values were found to be acceptable at 0.2% [16].

For sorption of methane, the results indicate increased sorption capacity for treated coal. However, at pressures below ~2.8 MPa (400 psia) for CO₂ and ~6.2 MPa (900 psia) for methane, the volume of methane adsorbed was less for coal treated for thirty days than the untreated sample. For coal treated for sixty days, the sorption capacity steadily increased for all values of pore pressures beyond 2.8 MPa (400 psia). For coal treated for thirty days, the sorption capacity is higher than the untreated coal beyond 8.3 MPa (1200 psia).

Sorption of CO₂ presented a fairly uniform trend. Since CO₂ is adsorbed strongly by coal at lower pressures, there was no noticeable change in the sorption capacity. Beyond 1.7 MPa (250 psi), however, Fig. 3 suggests that additional amount of CO₂ was sorbing on treated coal. The increase in sorption capacity was more noticeable for coal treated for the longer period of time. The trend is well

reflected in the values of the Langmuir constants where the baseline coal sample had a maximum sorption capacity of 21.63 Nm³/t (normal cubic meter per ton); for coal treated for thirty days, it increased to 30.59 Nm³/t; and coal treated for sixty days had a maximum sorption volume of 47.86 Nm³/t.

Isotherms for methane adsorption and desorption for untreated coal are shown in Fig. 4. Ideally, the two isotherms should not deviate from each other for methane. The two, although similar, do exhibit some hysteresis effects. This is not uncommon and has been reported by several researchers in the past [17–20]. Desorption hysteresis may occur due to two reasons. First, changes in the adsorbent properties/structures or, capillary condensation in the adsorbent micropores [21], may result in some difference between the sorbed volumes for increasing and decreasing pressures. Busch et al. [18] attributed hysteresis to a metastable sorbent–sorbate system that prevents release of gas to the extent corresponding to the thermodynamically equilibrium value with decreasing pressure steps. Loss of moisture during desorption is also attributed to hysteresis because the capacity of coal to adsorb gas increases with reduction in moisture content [20]. Finally, the equilibrium during desorption is a slow process and slight deviation from the perfect equilibrium may result in some hysteresis.

Compared to desorption hysteresis observed for untreated coal, that for coal treated for thirty and sixty days, shown in Figs. 5 and 6, is staggering, with such trends being un-reported anywhere in the existing literature. The Langmuir pressure and volume constants for adsorption of methane on coal treated for thirty days were ~7.8 and ~2.7 times the corresponding desorption values respectively. Coal treated for sixty days presented the pressure and volume constants for adsorption to be ~8.5 and 8.2 times the desorption values respectively. For comparison, the corresponding adsorption values for untreated coal were ~0.98 and 1.03 times.

It is well accepted that the presence of moisture has a significant impact on sorption characteristics of coal. Proximate analysis of the coal samples, as shown in Table 2, indicates an increase in moisture content, post bio-conversion. This increase can be attributed to the environment that the coal was subjected to during bio-conversion. To accurately determine the effect of moisture on sorption properties, the gas used for the experiments must be humid (saturated), as was done by Pan et al. [22]. The results obtained for this study were accomplished by using dry helium, methane and CO₂. Over time, the moisture content of the sample is believed to decrease, and effect of moisture can be attributed to the initial stages of methane adsorption. The low volumes of gases sorbed at lower pressures might be a result of the increased moisture content post bio-conversion. For baseline coal, low initial moisture content attributed to higher volumes of methane being sorbed at lower pressures. Desorption characteristics for treated coal might thus be affected by a relatively drier sample. Between the coals treated for thirty and sixty days, there was a slight drop in moisture content, which can be related to the relatively high volumes of gases sorbed at lower pressures for the coal treated for sixty days. However, even with higher moisture content, the amounts of hysteresis in the treated coals, has not been reported previously, even under similar experimental conditions. Additional reasons for such behavior have been discussed in Section 4.7.

4.3. Extended Langmuir isotherm

The results for coal treated for thirty days had ~27% undetected gases in addition to methane and CO₂. Normalizing such a large fraction of undetected gases into methane and CO₂ percentages would be erroneous. The data for coal treated for sixty days had ~2% of undetected gases and it was possible to achieve acceptable results for multi-component sorption with such a small fraction of

Table 1
Produced gases during methanogenesis.

Sample	CH ₄ (Nm ³ /t)	CO ₂ (Nm ³ /t)	Undetected (Nm ³ /t)
Day 30	2.44	1.72	1.60
Day 60	3.73	1.90	0.12

Table 2

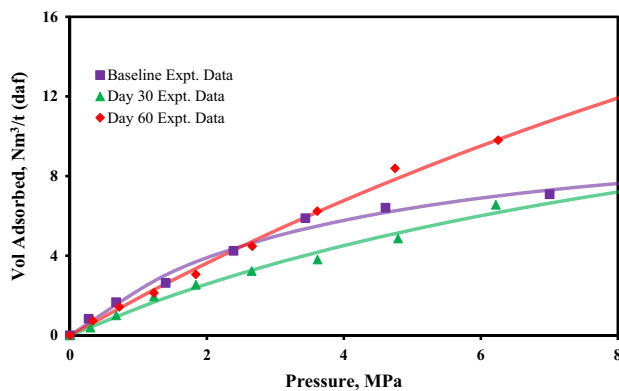
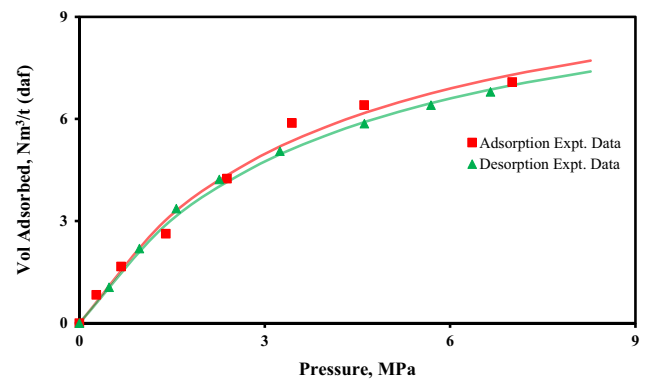
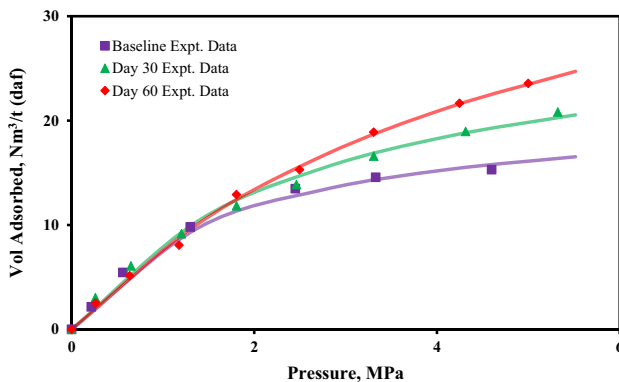
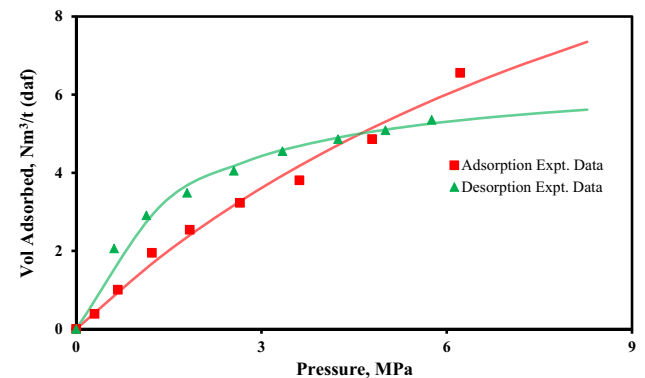
Proximate and ultimate analysis of coal.

Sample	Carbon (%)	Nitrogen (%)	Hydrogen (%)	Oxygen (%)	Sulfur (%)	Ash (%)	Moisture (%)
Baseline	70.1	1.4	5.2	15.4	0.6	6.1	11.5
Day 30	59.5	1.2	4.3	16.8	0.7	8.1	17.4
Day 60	57.3	1.2	4.2	16.6	0.7	7.6	16

Table 3

Results obtained from Langmuir isotherms.

		Baseline coal		Thirty-day treated coal		Sixty-day treated coal	
		Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption
CH ₄	P_L (MPa)	3.80	3.85	11.92	1.51	25.61	3.01
	V_L (Nm ³ /t)	11.25	10.83	17.95	6.65	50.12	6.10
CO ₂	P_L (MPa)	1.70	–	2.70	–	5.16	–
	V_L (Nm ³ /t)	21.63	–	30.59	–	47.86	–

**Fig. 2.** Absolute adsorption isotherms for methane.**Fig. 4.** Absolute ad/de-sorption isotherms for methane: baseline coal.**Fig. 3.** Absolute adsorption isotherms for CO₂.**Fig. 5.** Absolute ad/de-sorption isotherms for methane: thirty day treated coal.

undetected gases. The fractions of methane and CO₂ were then normalized to a cumulative of 100% in order to establish the Extended Langmuir isotherm for the coal treated for sixty days.

Fig. 7 shows the extended Langmuir isotherm, where the normalized free gas composition is 66.2% methane and 33.8% CO₂, both representative of the gases produced after methanogenesis. For CBM production, if CO₂ is detected during the initial production period, its concentration in the produced gas increases with continued production. This has two consequences. First, CO₂ reduces the calorific value of produced gas. Hence, when dealing with high concentration of CO₂, it is necessary to apply separation techniques to bring the gas to pipeline quality. The EL isotherm provides an

estimate of the variation in gas composition over long-term production and can be used to set up suitable separation techniques over the life of a producing reservoir.

4.4. Surface area for sorption

The specific surface area, S_{MB} , in $10^{-3} \text{ km}^2 \text{ kg}^{-1}$, can be estimated by the following equation:

$$S_{MB} = (q_m \times a_{MB} \times N_A \times 10^{-20}) / M \quad (5)$$

where q_m , is derived from the Langmuir constant and provides an estimate of the number of molecules of the sorbate adsorbed at

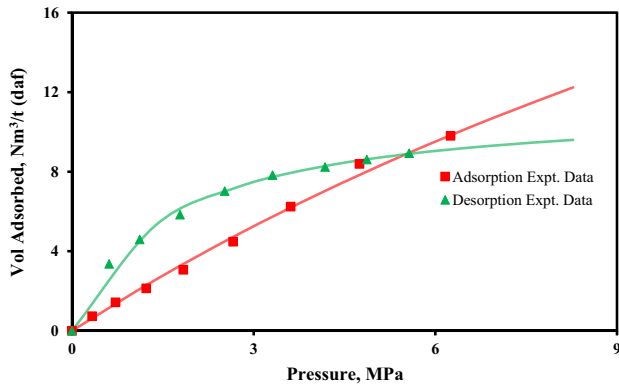


Fig. 6. Absolute ad/de-sorption isotherms for methane: sixty day treated coal.

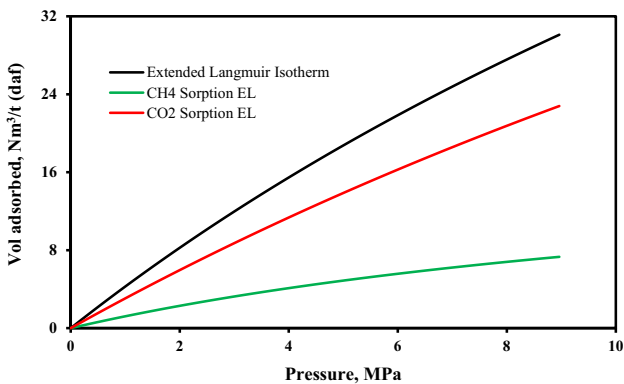


Fig. 7. Extended Langmuir isotherm for coal treated for sixty days.

the mono-layer of coal in milligrams/gram (mg/g); a_{MB} is the surface area occupied by one molecule of sorbate in \AA^2 ; N_A is Avogadro's number with units of mol^{-1} ; and M is the molecular weight of the sorbate in g mol^{-1} . Eq. (5) was used to calculate the ratio of the surface areas available for sorption before and after methanogenesis. The ratio for sorption of same gas on different coals requires calculation of q_m for each coal sample. The ratio of different q_m s can be indicated by the ratio of the Langmuir volumes. Table 4 illustrates the results of the estimated changes in specific surface area. Given that the sorption of coal, for isothermal conditions, is a function of number of sorption sites available, increase in the sorption capacity suggests increase in the number of sites available for sorption. The microbial action is believed to have created new pore spaces, or enlarge the existing pore space. However, it should be borne in mind that Eq. (5) calculates the surface area that is directly estimated by the Langmuir's constants which, in turn, is obtained from curve-fitting exercises. An accurate estimation of surface areas requires low temperature-low pressure nitrogen adsorption techniques. Thus, the changes in specific surface areas should be viewed more as a qualitative assessment, primarily for a comparative analysis.

Since methanogens need carbon to produce methane, ultimate analysis of the baseline and treated coals was performed. The

Table 4
Estimated changes in surface areas.

Treatment period	Change in specific surface area	
	CH ₄ × baseline	CO ₂ × baseline
30 days	1.6	1.4
60 days	4.5	2.2

results suggest that there is a steady decrease in the carbon content of coal treated. The untreated coal contains ~70% carbon and, with gradual methanogenesis, it reduced by ~15% for coal treated for thirty and 18% for coal treated for sixty days. Decrease of carbon content along with increased sorption capacity is indicative of the increase in pore space of coal due to methanogenesis as represented by the increase in surface areas.

4.5. Estimation of diffusion coefficient

Sorption isotherms require measurement of only the final equilibrium pressure for each pressure step. Measurement of diffusion coefficient, on the other hand, requires precise and continuous change in pressure in the sample container over time, especially during the initial period of sorption, for every pressure step. A decrease in the gas pressure in the sample container was converted to the amount of gas adsorbed. The time-step for data collection was decreased as equilibrium approached. Also, for calculation of the diffusion coefficient, only the initial sorption period, where $V_t/V_\infty \sim 0.5$, was considered since the gas sorbs at a relatively fast pace. Eq. (6) was used to calculate the diffusion coefficient for each step.

Figs. 8 and 9 show the variation in estimated diffusion coefficients as a function of methane and CO₂ pressures. First, the general trend of the variation is as expected, with values being higher at lower pressures and progressively declining at higher pressures. Second, the value of D was higher for treated coals. For methane at 0.3 MPa (50 psi), the value of D was ~18 times higher for coal treated for thirty days and ~25 times for that treated for sixty days. For pressures up to 2.8 MPa (400 psi), the diffusion coefficient for both treated coal samples was ~15 to 20 times higher than the baseline values. The estimated value of D for CO₂ was also higher for treated coals than for baseline values. The change in values of D was twice that for coal treated for thirty days as well as sixty days compared to baseline values, the difference between the two being very small.

The diffusion rate for methane was higher than that for CO₂ for treated coal. Most prior studies have reported results that contradict this trend [23,20]. However, such anomalous behavior has been observed by other researchers in the past. Bhowmik and Dutta [24] addressed such aberration primarily to experimental error. However, consistent observation of such behavior cannot be discounted as being experimental inaccuracies. This behavior has been explained in Section 4.7. As seen in Fig. 10, the highest diffusion rate for CO₂ was approximately five times higher than that for methane for baseline coal. With continued bio-conversion, the diffusion coefficient at low pressures for methane was ~2.2 times larger than that for CO₂ for coal treated for thirty days. For the sample treated for

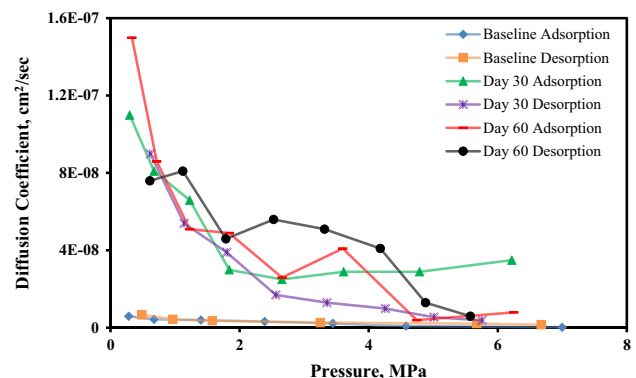


Fig. 8. Variation of diffusion coefficient for sorption of methane for three coal samples.

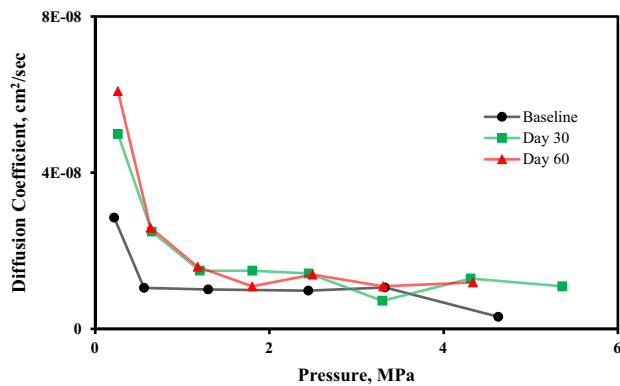


Fig. 9. Variation of diffusion coefficient for adsorption of CO₂ for three coal samples.

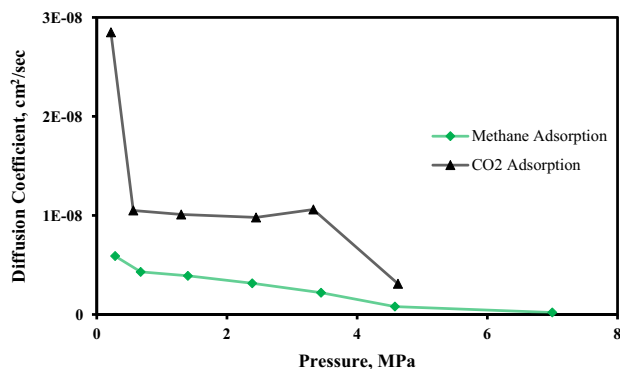


Fig. 10. Comparison between diffusion coefficients of methane and CO₂ for baseline coal samples.

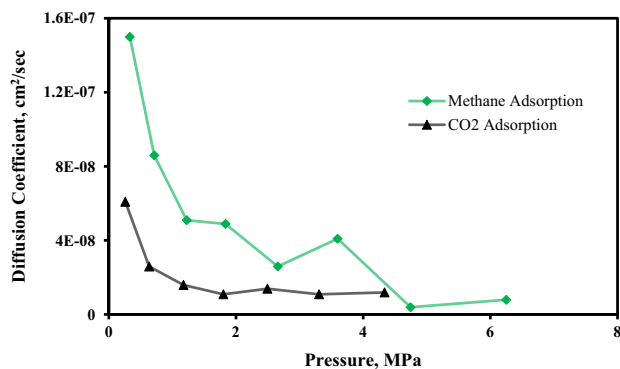


Fig. 11. Comparison between diffusion coefficients of methane and CO₂ for coal treated for sixty days.

sixty days, the difference was ~ 2.5 times (see Fig. 11). These trends suggest that the movement of gas molecules by diffusion faced lower resistance after bio-conversion. An attempt to explain such behavior is made in the following sections.

The work reported by Pan et al. [22] established the deterring role of moisture to the diffusion characteristics of coal. This is to be expected since, for increasing moisture content, the value of D at similar pore pressures decreases. However, for bio-converted coals, the values of D was found to increase even with higher moisture content. This is attributed to the competing effects of increased moisture content having a negative effect; and increase in the pore surface areas providing lower resistance to the flow of gas molecules, having a positive effect. Between bio-converted

coals, the slight decrease in moisture content can explain the slightly higher values of D reported for coal treated for sixty days.

4.6. Klinkenberg effect in diffusion characteristics

The results indicate a negative correlation between pressure and coefficient of diffusion for both methane and CO₂. Kumar [25] successfully linked such trends to be similar to the Klinkenberg effect. It was concluded that, at high pressures, there is a large number of gas molecules that tend to diffuse in/out of the matrix, resulting in increased intermolecular resistance and low diffusivity. As the gas continues to desorb from the matrix, there is a reduction in pressure, thus resulting in lower resistance to movement and hence, increased diffusivity. It was also pointed out that there is shrinkage of coal matrix with continued desorption, which has been found to be universally true for all coal types [26]. For diffusion at the micropore level, as gas pressure decreases, shrinkage of coal matrix results in an increased pore size. As this occurs, movement of methane in the pores is eased, thus resulting in an increase in diffusivity. The relationship between pore size distribution and diffusion, reported in the past [27] supports this argument, since an increase in pore size results in an increase in the value of D . This conclusion has an important implication in our study, as discussed below.

In Kumar's model, variation in the value of D was assumed to be dual in nature, remaining constant at high pressures, and increasing with continued desorption of gas. Mathematically, it was represented as:

$$D = D_D \quad \text{for } P > P_D, \quad (6)$$

where the gas pressure (P) is above the pressure when gas desorption is significant (P_D), and

$$D = D_D + b/P_m \quad \text{for } P < P_D, \quad (7)$$

when gas desorption becomes significant. The value of b is expected to be constant for a particular coal type and gas. To illustrate this phenomenon, the measured values of D were plotted as a reciprocal of gas pressures, as shown in Figs. 12 and 13 for methane and CO₂ respectively.

The diffusion coefficients for CO₂ were found to agree well with the Klinkenberg diffusion hypothesis. Methane diffusion rates, on the other hand, although related positively with the reciprocal pressure, the regression fit was relatively poor. The best fit for both methane and CO₂ cycles were observed for coal treated for sixty days and the fit got progressively poorer for coal samples treated for thirty days and untreated respectively.

Expanding on the assumption of the role of matrix shrinkage on diffusion, there was an increase in the values of D between the baseline and treated coals, more so for methane than for CO₂ post bio-conversion. The differential change in the methane and CO₂ diffusion rates has been explained in Section 4.7. However, the overall increase in the diffusion values, discounting the shrinkage effects, implies a reduction of inter-molecular resistance to flow of gas in the micropores brought about by an increase in the pore volume. The increased pore volume supplements the indication of increase in specific surface areas post bio-conversion.

4.7. Non-monotonic size dependence of effective diffusion constant

The microstructure of coal, illustrating pore and diffusing molecules, is shown in Fig. 14. For spherical molecules of radius r , the Einstein–Stokes equation relating the effective diffusion coefficient is as follows:

$$D_e = \frac{kT}{6\pi\eta r} \quad (8)$$

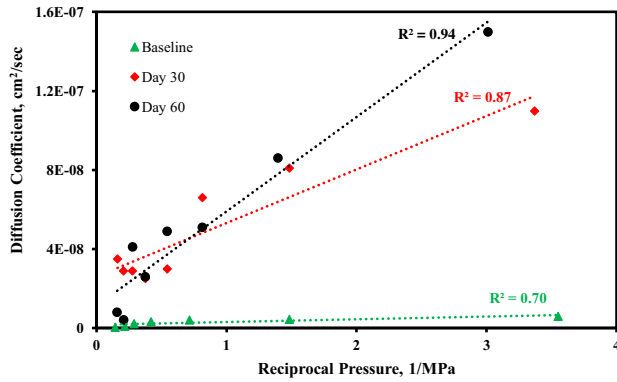


Fig. 12. Klinkenberg plot showing D as a function of methane pressure for the three coal samples tested.

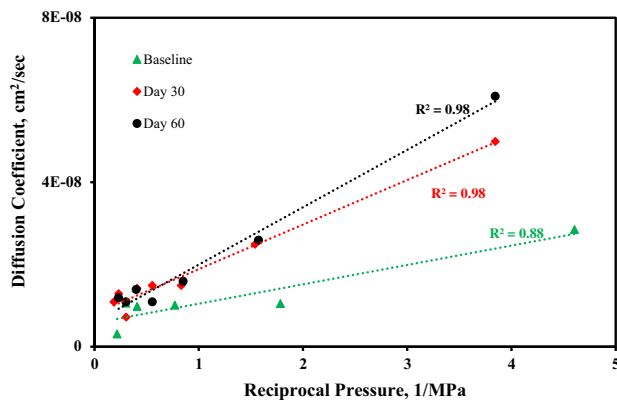


Fig. 13. Klinkenberg plot showing D as a function of CO_2 pressure for the three samples tested.

where D_e is the effective diffusivity, k is the Boltzmann constant, T is the temperature, and η is the viscosity of the fluid. At constant temperature, the term $\frac{kT}{6\pi\eta}$ is constant. The Einstein–Stokes equation thus becomes:

$$D_e \propto \frac{1}{r} \quad (9)$$

The above relation suggests that the diffusing particle with a larger diameter will have a slower rate of diffusion. Although Stokes law was initially developed to characterize particle diffusion, its application has been tested for various conditions and pore geometries. In the study done by Aramov [28], it was concluded that the Stokes law was valid for diffusing particle diameters greater than the size of the building structure of glass forming



Fig. 14. A tube with identical periodic dead ends with entry radius of ' a ' and a diffusing particle of radius ' r '. (Adapted from Dagdug et al., 2008) [32].

melt. Pye et al. [29] characterized the size at $\sim 2.56 \text{ \AA}$. All diameters of methane and CO_2 reported previously are larger than the size of the building structures of glass forming melts, thus validating the use of Stokes law to characterize the diffusion rates. In a coal environment, the molecular diameters of CO_2 and methane are represented by different models. The Lennard-Jones theory estimates methane and CO_2 diameters to be 3.751 and 3.615 \AA respectively [30]. The kinetic diameter is defined as the geometry optimized diameter of a continually moving set of gas molecules. It is tracked using computational geometry models of kinetic structure of gases, and is a reflection of the smallest effective dimension of a given molecule. The kinetic diameter for methane is 3.8 \AA and that of CO_2 is 3.3 \AA [31]. Given that the methane molecule is larger than CO_2 , the diffusion characteristics of baseline coal, which is in agreement with the trends of the past studies, is found to comply with the Einstein–Stokes equation.

Dagdug et al. [32] conducted experiments to determine the diffusion characteristics of spherical particles in a tube with periodic dead ends. The microporous structure of coal can be considered as a tube, from which constricted periodic tubes branch out and terminate as the pore. Fig. 14 depicts such a model representing the pore structure in coals. In the series of experiments performed, it was concluded that the effective diffusion coefficient was inversely related to the size of the diffusing particles, as indicated by the Einstein–Stokes equation. This was found to be true for cases when the radius (size) of the constricted entries/tubes, ' a ', was either much larger or smaller than the radius (size) of the diffusing particles. In essence,

$$D_e \propto \frac{1}{r} \quad \text{for } r \ll a \text{ and } r > a$$

For tube and pore entry diameters of size comparable to the size of the diffusing particles, it was found that values of D_e noticeably deviate from the Einstein–Stokes relation. The deviation is a non-monotonic function of r , where particles of larger radii were found to have a higher value of diffusion coefficient. Such deviating behavior was also observed to be a function of the dead-end geometry. When the dead ends have no cavities, that is, they are purely cylindrical with long ends, diffusion coefficient was found to comply with Eq. (9). When cavities are present, the dependence of $D_e(r)$ was found to be non-monotonic for arbitrary lengths of the connected channels.

Scientifically, this study establishes that, for certain cases, it is possible for larger particles to diffuse faster compared to smaller particles. This is because a larger particle, methane molecule in this study, cannot enter the dead ends and spends all the time diffusing along the tube axis. The smaller particles, on the other hand, waste time traveling in the dead ends and diffuse along the constricted entries for a fraction of the total observation time. Micropores in coals are classified to be $< 20 \text{ \AA}$, with a modal value of 10 \AA . With such distribution of pore sizes, it is expected that the pore entries, which are generally even more constricted than the pore ends, can be smaller or much larger than the size of gas molecules, and might also be of the same size. Some of the end cavities of the pores might be well developed and some similar to the ends of a long cylindrical tubes. With reference to the results obtained from the diffusion experiments in this study, it can be concluded that, during the process of bio-conversion, the pore structure of coal changed in such a way that the diffusion paths facilitated longer diffusion times for CO_2 molecules. Fig. 11, which compares the values of D of methane and CO_2 of coal treated for sixty days provides an indication of such a change. The non-monotonic behavior, therefore, presents a plausible explanation for the trends in the sorption behavior of treated coal.

As previously discussed, and observed in Figs. 2 and 3, the Langmuir constants for sorption were found to increase, reflecting the

availability of larger area for sorption. In spite of the increasing trend exhibited for the experimental pressure range, the amount of methane adsorbed by the coal treated for thirty days was considerably lower than that sorbed by untreated coal. The coal treated for sixty days presented similar trends for pressure lower than 400 psi. Similar trends were not noticeable for sorption of CO₂, which is attributed to the fact that coal has a higher affinity toward CO₂ than for methane. The rate of CO₂ adsorption at lower pressures is much higher than methane, and thus CO₂ covers the monolayer of the sorption sites rather earlier and at a faster pace. This is in agreement with the work completed by previous researchers [33]. Given that methane and CO₂ are adsorbed on the surface of coal, as suggested by the non-monotonic behavior of diffusing particles, it is inferred that methane molecules during early stages of sorption start adsorbing onto the surface of the pore entries and not the pore itself. Given that the porous structure of coal is what provides the enormous surface areas for sorption, the amount of gas sorbed during the initial period of sorption is limited to the entries and, therefore, lower than the amount that would sorb if the methane molecules had unrestricted access to the entire pore geometry. The diffusion characteristics of the untreated coal is indicative of such unrestricted entries.

The theory above is supported by the hypothesis that methanogens, while consuming coal, will have more access to the wider entries that have periodic constricted entries branching from them. It is believed that consumption of coal, resulting in increased surface area is predominantly from these entries, making sorption on these surfaces easier compared to the surface present in virgin coal. Constricted entries make it difficult for the methanogens to avail the pore cavities with large surface areas. The unavailability of such areas is also indicated by the reduced rates of gas generation over time in spite of the substantial amount of carbon remaining in the sample, as indicated by the ultimate analysis results.

Given that sorption of gases on coal is considered to have monolayer coverage, sorption would continue as long as there are sufficient sorption sites available. Thus, it is expected that, with increasing pressure, once the surface of the entries are filled with sorbed molecules, gas molecules will eventually diffuse into the pores due to an increase of Brownian collisions. The amount adsorbed would, therefore, continue to increase with pressure even if the pore entries are filled. The experimental results obtained to date support this hypothesis. For coal treated for sixty days, such behavior was observed at pore pressures >2.8 MPa (400 psi), below which, only the entries were being filled up, resulting in a smaller volume adsorbed compared to the baseline value. Coal treated for thirty days was just starting to exhibit similar behavior at the highest experimental pressure.

While hysteresis during desorption has traditionally been related to capillary condensation and change in moisture content of the sample under laboratory conditions, the levels of desorption hysteresis for methane in this study has not been reported in the literature. While the Langmuir sorption theory assumes that each of the sorption site has an equal probability of being occupied by ad/de-sorbing gas, the non-monotonic dependence of $D_e(r)$ observed adds another factor to the desorption behavior in the experimental results. Given the shape of pore entries, it is possible that the amount of Brownian collisions among desorbing molecules within the pore cavities restricts them from traveling from the pores into the connecting flow path during desorption. This may result in preferential desorption of gas molecules sorbed on the walls of the pore entries since this would have a smaller path to travel in order to reach the free state, where the density of the gas is that of the bulk phase density. This would result in smaller amounts to desorb at high pressures and the isotherm would continue to be asymptotic even as

it approaches lower pressures. With decreasing number of molecules at lower pressures, the Brownian collisions would decline and the desorbing amount would increase. This argument holds for the desorption patterns observed for coal treated for thirty and sixty days.

5. Summary and conclusions

Volumetric method was used to establish adsorption and diffusion characteristics for methane and CO₂ of Illinois basin coal before and after microbial conversion. The Langmuir approach was used to model the sorption data, and the uni-pore model estimated the behavior of diffusion coefficient. Based on work completed, the following conclusions are made:

- Sorption capacity of the coal tested was found to increase with continued bio-conversion. Hence, new surface area is created as a result of bio-conversion. However, in the lower pressure regime, the volume sorbed did not change significantly. This may be attributed to the fact that, at lower pressures, sorption of methane was limited to the surface of the pore entries and not the cavities, thus filling up slowly. Gradual increase of sorption capacities with increasing pressures for treated coal is indicative of the filling of the pore cavities, which offer larger surface areas for sorption. It is hypothesized that methanogens consume more carbon from the entries, thus increasing the surface area along the sides of these entries. A gradual increase in the sorption capacity with increasing pressures for treated coals is indicative of the filling of the pore cavities, offering large surface areas for sorption.
- Desorption of methane from coal surface exhibited significant hysteresis. The hysteresis effect resulted in an asymptotic isotherm at higher pore pressures and significant desorption at lower pressures. It is believed that, at high pressures, increased Brownian collisions within the pore cavities prevent the molecules to diffuse from the pore cavities, allowing them to exist in the free state. This results in preferential desorption from the pore entries, where only a small volume of gas is sorbed. At lower pressures, the gas eventually desorbs from the pore cavities, where large volume of gas is stored.
- Diffusion coefficients for baseline coal exhibited behavioral trends similar to studies completed by prior researchers. But, for treated coal, the nature of data contradicted the expected trend, where diffusion rates of methane for a coal type was found to be higher than CO₂. Such behavior is explained by the non-monotonic size dependence of effective diffusion coefficients.
- The study suggests that CBM wells, which are depleted or nearing depletion, can be recharged by microbial action. Over time, the gases produced can be stored, potentially in excess of the existing storage capacities, which is a function of the ability of the microbial consortia to convert coal to methane and/or CO₂. From a CBM perspective, wells that are depleted or nearing depletion, can be treated with suitable microbial consortia. Given sufficient time and amendments for the production of biogenic gas, the increased sorption capacities of treated coals are encouraging for the potential of long-term production of coalbed gases.
- CBM production in the Illinois basin is traditionally plagued by very low diffusion rates. Extrapolating the trends observed in laboratory conditions, the increase in the diffusion rates of methane due to bioconversion can improve the production rates from producing wells. Also, areas traditionally thought to be un-economical for CBM production, can be recharged although establishing this would need a further study.

- For surface treatment of coal fines, the results might not have any direct significance since the initial treatment silos might not have very high pressure capacities. For pressures greater than ~6.9 MPa (1000 psi), sorption capacity of coal increases substantially, which would enable continuous production over long periods, post treatment. Results of the extended Langmuir isotherms can then be used to predict methane and CO₂ generation rates, thereby making appropriate arrangements for gas separation system.

Acknowledgments

This study was carried out with support, in part by grants made possible by the Department of Energy under Award Number DE-FE0024126 and the Illinois Department of Commerce and Economic Opportunity (DCEO) through the Office of Coal Development and the Illinois Clean Coal Institute (ICCI). The authors wish to thank these organizations for the financial support.

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