Adsorption of Methane, Nitrogen, Carbon Dioxide and Their Mixtures on Wet Tiffany Coal

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Abstract

Gas adsorption was measured for methane, nitrogen, CO_2 and their binary and ternary mixtures on a wet Tiffany coal sample. The measurements were conducted at 327.6 K (130.0°F) at pressures to 13.8 MPa (2000 psia). The expected uncertainties in the amounts adsorbed vary with pressure and composition. In general, average uncertainties are about 5% (0.01-0.08 mmol/g) for the total adsorption; however, the expected percentage uncertainties in the amount of individual-component adsorption are significantly higher for the lesser-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO_2 system).

The Langmuir/loading ratio correlation (LRC) and the Zhou-Gasem-Robinson (ZGR) two-dimensional equation of state (EOS) are capable of representing the *total* adsorption for the pure, binary and ternary systems within their expected experimental uncertainties. However, the quality of fit for the individual–component adsorption varies significantly, ranging from 3% (0.01 mmol/g) for the more-adsorbed methane or CO_2 to 32% (0.01 mmol/g) for the lesser-adsorbed nitrogen. Further, the LRC and ZGR EOS predict binary adsorption isotherms, based solely on pure-fluid adsorption parameters, within twice their experimental uncertainties.

Key Words: Adsorption, Coal, Mixtures, 2-D EOS

1. Introduction

Our long-range objective is to develop reliable models to predict the adsorption behavior of supercritical gases on coals, with specific applications to (a) coalbed methane production and (b) the use of coalbeds to sequester the greenhouse gas carbon dioxide. In pursuit of that objective, we have performed both experimental and modeling studies [1-8].

Our recent studies indicate that adsorption equilibrium models originating from three different frameworks, i.e., two-dimensional (2-D) equations of state (EOS), the simplified local density / Peng-Robinson model (SLD-PR), and the Ono-Kondo (OK) lattice model, are effective in modeling near-critical and supercritical adsorption systems of the type encountered in CBM recovery and CO_2 sequestration [4-8]. The model evaluations were conducted using our recent measurements for the adsorption of pure CO_2, methane and nitrogen and their binary mixtures on various coals and activated carbons at 318-328K and pressures to 13.7 MPa [1-3].

Modeling success notwithstanding, the physics of CO_2 interactions with coal continues to be an active subject of discussion among researchers. In fact, ten different hypotheses were outlined recently to delineate such interactions [9]. Our experiments and modeling efforts for the past 15 years lead us to believe that, although some secondary effects may exist, equilibrium physical adsorption is the main phenomenon. Further, we have shown that the use of adsorbent-calibrated models can yield *a priori* predictions for gas adsorption on various coals [3]. This provides some evidence for the adequacy of our assumptions regarding the physics of the phenomenon and the models developed.

The major objectives of the present study were to (a) measure the adsorption behavior of methane, nitrogen, CO_2 and their binary and ternary mixtures on wet Tiffany coal at 327.6 K (130.0°F) and pressures to 13.8 MPa (2000 psia); and (b) correlate the equilibrium adsorption data using the Langmuir model, the extended Langmuir model, the loading ratio correlation and the Zhou-Gasem-Robinson EOS.

The specific tasks of the adsorption measurements and correlations for Tiffany coal were to:

- Prepare representative coal samples from Injection Well #1 and Injection Well #10.
- Determine (a) equilibrium moisture content, (b) particle size distribution, (c) compositional analyses, and (d) vitrinite reflectance analysis for each coal sample.
- Measure the adsorption behavior of methane, nitrogen, CO_2 and their binary and ternary mixtures on a Tiffany equal-mass, mixed-coal sample from Injector Wells #1 and #10 at 327.6 K and pressures to 13.8 MPa. The nominal molar feed compositions for the methane/nitrogen, methane/CO_2, and nitrogen/CO_2 binary mixtures were specified at 50/50, 40/60, and 20/80, respectively. The nominal molar feed composition for the methane/nitrogen/CO_2 ternary mixture was 10/40/50.
- Correlate the equilibrium adsorption isotherm data using the Langmuir model, the extended Langmuir model, the loading ratio correlation and the Zhou-Gasem-Robinson EOS.

2. Experimental Methods and Procedures

2.1 Adsorption Measurements

Our experimental technique employs a mass balance method, utilizing volumetric accounting principles. The experimental apparatus, shown schematically in Figure 1, has been used successfully in previous measurements [1, 2]. Brief descriptions of the experimental apparatus and procedures follow.

The entire apparatus (both Pump and Cell sections) is maintained in a constant temperature air bath. The equilibrium cellis filled with the coal to be studied, and the cell is placed under vacuum prior to gas injection. The void (gas) volume, V_{void}, in the equilibrium cell is then determined by injecting a known quantity of helium from a calibrated injection pump. Since helium is not adsorbed, the void volume can be determined from measured values of the temperature, pressure and amount of helium injected into the cell. The void volume equations are

$$V_{void} = n_{He}(Z_{He}RT/P)_{cell} \quad (1)$$

$$n_{He} = (PV/(Z_{He}RT))_{pump} \quad (2)$$

In these equations, n_{He} is the number of moles of helium injected into the cell, V is the volume of gas injected from the pump, Z_{He} is the compressibility factor of helium, R is the universal gas constant, T is the temperature, P is the pressure, and the subscripts "cell" and "pump" refer to conditions in the cell and pump sections of the apparatus, respectively.

The amount of gas (methane, for example) adsorbed at a given pressure can be calculated based on the preliminary calibrations described above. First, a given quantity of methane, n_{inj}, is injected into the cell. This amount is determined by an

equation analogous to Equation 2, above. A magnetic recirculating pump is used to circulate methane over the adsorbent until equilibrium is reached, where no further methane is adsorbed. The amount of unadsorbed methane, n_{unads}, is then determined based on the fact that any unadsorbed methane will remain in the void volume (determined from the helium calibration). The expression for this quantity is

$$n_{unads} = (PV_{void}/Z_{methane}RT)_{cell} \quad (3)$$

where the pressure P is measured after equilibrium is reached in the cell. In addition, we estimate the amount of gas dissolved in water, n_{dis}, using correlations for gas solubility [10]. The amount of adsorbed methane, n_{ads}, is then calculated by difference as

$$n_{ads} = n_{inj} - n_{unads} - n_{dis} \quad (4)$$

These steps are repeated at sequentially higher pressures to yield a complete adsorption isotherm.

The gas is presumed to dissolve in all the water present in the coal sample, whether the water is adsorbed or not. The amount of gas dissolved in the water is significant only for CO_2. Literature data [11, 12] were used to construct an empirical relationship for CO_2-water solubility at temperatures from 40°C to 75°C.

In mixture studies, a gas mixture of known composition is injected, so the total amount of each component fed into the cell is known. The amount of unadsorbed gas at each pressure is calculated by Equation 3 with $Z_{methane}$ replaced by Z_{mix}, the gas mixture compressibility factor. The composition of the gas mixture in the void volume is determined by chromatographic analysis of a microliter-size sample captured in a sampling valve. This permits the total amount of unadsorbed gas to be

apportioned among the various components according to their mole fractions in the gas. Equation 4 can be then applied to each component in the gas mixture. For methane/nitrogen/CO_2 mixtures, the mixture Z factors (Z_{mix}) were determined from the Benedict-Webb-Rubin (BWR) EOS, as described below.

The estimated experimental uncertainties in each measured quantity is as follows: temperature 0.1°C, pressure 6.9 kPa, injected gas volumes 0.02 cm^3, bulk gas-phase composition 0.001 mole fraction. The expected uncertainties in the amounts adsorbed are estimated using error propagation in all the measured variables and are confirmed by replicate runs.

2.2 Compressibility Factors

As indicated by Equations 1-3, accurate gas-phase compressibility (*Z*) factors are required for methane, nitrogen and carbon dioxide and their mixtures to analyze the experimental data properly. The compressibility factors for pure methane, nitrogen, and CO_2 were determined from highly accurate equations of state [13-15]. For void volume determination, the helium compressibility factor is given by [10]:

$$Z_{He} = 1 + \left(1.471\text{x}10^{-3} - 4.779\text{x}10^{-6}\,T + 4.92\text{x}10^{-9}\,T^2\right)/P \qquad (5)$$

where T is in Kelvin and P is in atmosphere. This expression is based on experimental data from the National Bureau of Standards Technical Note 631 for helium [16].

A careful evaluation of the current literature led us to conclude that an adequate predictive capability for the *mixture Z* factors did not exist. Therefore, we elected to use available pure-fluid and binary mixture data to refit the BWR EOS and improve its accuracy significantly. In general, the new BWR parameters yield

deviations in *Z* factors of less than 0.5%. This allowed us to address our compressibility factor needs for the binary and ternary adsorption mixtures. Details of the BWR expressions are given elsewhere [17].

2.3 Relationship between Gibbs and Absolute Adsorption

The calculations described above yield the so-called *Gibbs* adsorption. The data may also be reported in terms of *absolute* adsorption. Calculations for the Gibbs and absolute adsorption differ in the manner by which n_{unads} is calculated. The Gibbs adsorption calculation, described above, neglects the volume occupied by the adsorbed phase in calculating the amount of unadsorbed gas (i.e., in Equation 3, the entire void volume, V_{void}, is viewed as being available to the unadsorbed gas).

In a previous article [2], we have presented a discussion to clarify the relationships between the Gibbs and absolute adsorption and to highlight the approximate nature of the calculated absolute adsorption. In addition, expressions were presented which facilitate calculation of the absolute component adsorption, $n_{ads(i)}^{Abs}$, and the adsorbed-phase mole fraction, x_i^{Abs}, in terms of the Gibbs adsorption.

2.4 Materials

Two wet coal samples were received from BP Amoco [18]. The samples originated from Injection Wells #1 and #10 of the San Juan Basin. Proximate analysis conducted by Huffman Laboratories indicate that the two coal samples are similar in composition of fixed carbon and volatile matter, respectively 35% and 15% on a dry basis. The particle size distributions for the two coals were similar: for both

coals, about 41-46% of the particles were between 0.85 and 1.70 mm, and 23-25% were between 0.43 and 0.85 mm.

Table 1 presents the compositional analyses for coal samples from Wells #1 and #10. The dry basis sums are not 100% because of poor replication of the carbon analysis. The coal appeared oily when ground for analysis and this may be, in part, the reason why poor replication was obtained. Another reason is that carbonates in the ash content contributed both to the analyses of the carbon and the ash content. The carbon analysis was repeated three times and the values were averaged. Measurements other than carbon were replicated and their values are shown. The oxygen analysis was obtained by the direct method.

The density of the compact solid coal is called the coal helium density, in reference to the helium displacement measurements used to determine the adsorbent density [19]. We have measured the coal helium densities for Well #1, Well #10, and the mixed sample. They are 1.73, 1.57, and 1.67±0.07 g/cm^3, respectively.

Vitrinite reflectance analyses conducted by National Petrographic Services indicate that the present Tiffany coal samples are medium volatility bituminous coal. As summarized in Table 2, Wells #1 and 10 have average oil-based vitrinite reflectance values of 1.31 and 1.35, respectively.

The pure gases used in this work were obtained from Airgas-Pennsylvania with reported purities of 99.99% or higher and were used as received.

2.5 Determination of Coal Moisture Content

A pre-weighed, as-received wet coal sample was placed in a pre-weighed container. The container was subjected to a continuous vacuum in a 102-104°C oven. Vacuum was applied overnight to remove moisture. After the moisture was removed, the container was re-weighed, and the difference was attributed to the moisture loss.

Another wet sample was placed on a flat pan in a 35.0°C air atmosphere at 97-99% relative humidity. The sample weight was determined periodically to gauge the constancy of weight, which indicates the approach of the sample to equilibrium moisture content. Once a constant sample weight was achieved, the sample was assumed to be at its "equilibrium moisture content" or EMC.

The equilibrium sample was then placed in a continuous vacuum at 102-104°C. The moisture loss determined by weight difference was used to calculate the EMC. For the Tiffany samples considered in this study, the moisture content of the as-received samples was found to be higher than the EMC. The equilibrium moisture content of Well #1 coal sample is 3.8±0.2% and the equilibrium moisture content of Well #10 coal sample is 3.7±0.2%.

As previously reported [1], water content values above the equilibrium water content have no significant effect on the adsorption behavior.

3. Experimental Results

Complete tabular data for all pure-component, binary, and ternary systems studied are presented in supplementary materials [20], which are available from the publisher.

3.1 Comparison of Tiffany Coal Samples

Initially, methane adsorption was measured for separate coal samples from Wells #1 and #10. Results are presented for both Gibbs and absolute adsorption in (on a moisture-free basis) in Figures 2-3. They indicate that the adsorption capacities of samples from the two wells are comparable with a maximum variation of 5% in the amount adsorbed at 13.8 MPa.

Based on the similarity in the methane adsorption behavior for Tiffany Well #1 and Well #10 coal samples, and upon agreement with BP Amoco personnel, coal samples from the two wells were mixed on an equal-mass basis. Large chunks of coal (dime-size) were broken up and the coal mixture was gently shaken to ensure a final homogenous mixture. The coal samples were placed into a tightly-capped jar. Helium was injected into the jar to prevent oxidation of the coal.

3.2 Adsorption Isotherms

Pure Gas Adsorption: Gas adsorption measurements for pure methane, nitrogen and CO_2 were conducted on wet Tiffany coal samples at 327.6 K and pressures to 13.8 MPa. Our error analysis indicates that the average uncertainties for the methane, nitrogen, and CO_2 adsorption measurements are approximately 3% (0.01 mmol/g), 6% (0.01 mmol/g) and 7% (0.08 mmol/g), respectively. These estimates, which are depicted as error bars in some of the figures, were generated by error propagation of uncertainties in all measured quantities. The repeated isotherms confirm the estimated precision of the measurements.

Figure 2 presents the Gibbs adsorption isotherms for methane, nitrogen, and CO_2, respectively. The absolute adsorption data for these gases are presented in

Figure 3. In this study, unless otherwise noted, we use the adsorbed-phase density approximation suggested by Arri and Yee [21]. For nitrogen, methane, and CO_2, densities of 0.808, 0.421, and 1.18 g/cm^3, respectively, were used to convert the Gibbs to absolute adsorption.

Figure 2 presents isotherms for methane on Well #1 and Well #10 coal samples, respectively. Replicate runs were conducted to confirm our measurements. These measurements show good agreement between the replicate runs, which yield an expected uncertainty of about 5%. A four-point adsorption isotherm was measured on the Tiffany mixed coal sample, as presented in Figure 2. As expected, the mixed coal sample produced an intermediate adsorption capacity; i.e., it shows less adsorption than the Well #1 coal sample and more than the Well #10 sample.

The replicate runs for methane show good agreement. The average expected uncertainty for these measurements is approximately 3% (0.01 mmol/g), as depicted by the error bars in Figures 2 and 3. (Notice that error bars are included only for one run).

The adsorption isotherm for pure nitrogen on the mixed Tiffany coal sample is presented in Figures 2 and 3. No significant differences exist between the replicate runs. The average expected uncertainty for these measurements is approximately 6% (0.01 mmol/g). Similarly, adsorption isotherm measurements for pure CO_2 on wet Tiffany mixed coal sample are given in Figures 2 and 3. The replicate runs show reasonable agreement with an average expected uncertainty of about 7% (0.08 mmol/g).

Both methane and nitrogen adsorption measurements on Tiffany coal indicate lower adsorption capacity than the adsorption on the Fruitland coal we reported previously [1]. The absolute adsorption on Tiffany coal at 327.6 K is about one half that on Fruitland coal at 319.3K. This difference might be due to variations in coal composition. Ash content in Tiffany coal is about twice that of the Fruitland coal. In contrast, the carbon content in Tiffany coal is about two thirds that in Fruitland coal. Nevertheless, the new measurements agree with the previous ones in the *relative* amounts of nitrogen, methane and CO_2 adsorbed, which are in the approximate ratio of 1 : 2.7 : 5 at 6.9 MPa.

As previously reported [1], a slightly different moisture content in each measurement set indicates that water content values beyond the equilibrium water content have no significant effect on the adsorption behavior. The adsorbed-phase density estimates do, however, affect the calculated absolute adsorption isotherm, as we have discussed previously [2, 5]. Figure 4 illustrates the effect of variation in the adsorbed-phase density on the CO_2 absolute adsorption. Here, three estimates are used: (1) the triple point liquid density (1.18 g/cm^3), (2) the ZGR model estimate (1.25 g/cm^3), and (3) a graphical estimate based on the Gibbs adsorption isotherm (1.40 g/cm^3). Differences in the calculated adsorption increase with pressure, rising to as much as 15% at 13.8 MPa.

Binary Mixture Adsorption: Adsorption isotherms were measured for methane/nitrogen, methane/CO_2 and nitrogen/CO_2 on wet, mixed Tiffany coal at 327.6 K and pressures to 13.8 MPa. The measurements were conducted at one feed composition for each mixture. The expected uncertainties in the amount

adsorbed for these binary mixtures vary with pressure and composition. In general, percentage average uncertainties are below 5% (0.03 mmol/g) for total adsorption; however, the expected percentage uncertainties in the amount of individual-component adsorption are significantly higher for the lesser-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO_2 system).

Mixture absolute adsorption estimates were calculated assuming ideal-solution additive volumes in the adsorbed phase (i.e., the mixture volume is the mole-fraction-weighted average of the pure component volumes). The values of 0.808 g/cm^3, 0.421 g/cm^3, and 1.18 g/cm^3, were used to estimate the adsorbed-phase density of methane, nitrogen, and CO_2, respectively.

Figure 5 presents the experimental Gibbs adsorption data for methane/nitrogen adsorption at the nominal molar feed composition of 50% methane. In general, the average expected uncertainties in the amount of individual-component Gibbs adsorption are 7% (0.02 mmol/g) for methane, and 17% (0.01 mmol/g) for nitrogen. The total adsorption has estimated uncertainties of 7% (0.02 mmol/g). Figure 6 presents the absolute adsorption for this binary system, including predictions from the LRC and ZGR models. As shown in Figures 5 and 6, methane is more strongly adsorbed than nitrogen.

Figure 7 presents the experimental data of methane/CO_2 absolute adsorption at a nominal molar feed composition of 40% methane. The average expected uncertainties in the amount of individual-component adsorption are 7% (0.01 mmol/g) for methane, and 6% (0.02 mmol/g) for CO_2. The total adsorption has

estimated uncertainties of 4% (0.03 mmol/g). Figure 7 indicates that the amount of CO_2 adsorbed is almost three times that observed for methane.

Figure 8 presents the experimental data of nitrogen/CO_2 absolute adsorption at the nominal molar feed composition of 20% nitrogen. A small amount of nitrogen is adsorbed at this feed composition. This results in higher *percentage* uncertainties for the nitrogen component adsorption, which is approximately 29% (0.01 mmol/g). In comparison, the CO_2 component adsorption has estimated uncertainties of 6% (0.03 mmol/g), and the total adsorption has estimated uncertainties of 5% (0.03 mmol/g). Figure 8 indicates that the amount of CO_2 adsorbed is almost 20 times that observed for nitrogen.

Ternary Mixture Adsorption: The ternary adsorption of methane/nitrogen/CO_2 on wet, mixed Tiffany coal at 327.6 K and pressures to 13.8 MPa was conducted at 10/40/50 mole % feed composition.

Figure 12 presents the absolute adsorption data for this mixture. The average expected uncertainty for the Gibbs total adsorption and CO_2 adsorption is about 5% (0.02 mmol/g). However, the low adsorption of nitrogen and methane in this ternary mixture yielded experimental uncertainties of 14% (0.01 mmol/g) and 27% (0.01 mmol/g), respectively. The absolute adsorption data for this ternary mixture were generated using the same procedure as for the binary mixtures.

4. Data Correlation and Model Evaluation

The newly-acquired adsorption data on the Tiffany coal samples were correlated using (a) the extended Langmuir model [e.g., 21], (b) the loading ratio correlation, and (c) the Zhou-Gasem-Robinson (ZGR) two-dimensional equation of

state [4]. Following is a brief description of the models used. An assessment for the quality of their representation and prediction of the present pure and mixture Tiffany coal data is presented in Section 4.3.

4.1 Langmuir/Loading Ratio Correlation

Historically, simple models have been used to represent the behavior of pure and mixed gas adsorption on coal. The extended Langmuir model is used almost exclusively in literature studies [e.g., 21], although the Ideal Adsorbed Solution (IAS) model has also been employed [22, 23]. Both of these models work well for essentially ideal adsorbed solutions, but neither is capable of handling nonidealities in the adsorbed phase with any accuracy. The extended Langmuir model is shown below as an illustration of the simple modeling approach used in most previous studies. For mixtures, it is

$$\theta_i = \frac{\omega_i}{L_i} = \frac{B_i P y_i}{1 + \sum_j B_j P y_j} \tag{6}$$

where ω_i is the amount of component "i" adsorbed (mmole of "i" adsorbed per gram of coal), L_i and B_i are Langmuir constants for "i", P is pressure, and y_i is the mole fraction of "i" in the gas phase. This relation allows mixture adsorption to be predicted solely from pure-component data, since values of L_i and B_i may be determined from the pure-component form of Equation 6. For pure-fluid adsorption, Equation 6 reduces to the Langmuir model:

$$\theta = \frac{\omega}{L} = \frac{BP}{1 + BP} \tag{7}$$

The combined Langmuir-Freundlick adsorption isotherm, expressed in terms of ω_i, yields the loading ratio correlation (LRC) for mixtures:

$$\theta_i = \frac{\omega_i}{L_i} = \frac{(B_i P y_i)^{\eta_i}}{1 + \sum_j (B_j P y_j)^{\eta_j}} \tag{8}$$

The additional parameter (η_i) in the LRC lends more flexibility to the Langmuir model. Although the simplicity of these Langmuir models is attractive, our data show that they are inadequate to represent the behavior of mixtures of the gases CO_2, methane, and nitrogen.

4.2 ZGR Equation of State

Simulations of coalbed gas recovery and CO_2 sequestering require reliable, yet simple, analytic models beyond Langmuir-type correlations. Equation-of-state (EOS) frameworks offer an attractive potential for satisfying such requirements. A general two-dimensional EOS can be written as follows [4]:

$$\left[A\pi + \frac{\alpha\omega^2}{1 + U\beta\omega + W(\beta\omega)^2} \right] \left[1 - (\beta\omega)^m \right] = \omega RT \tag{9}$$

where A is the specific surface area, π is the spreading pressure, ω is the specific amount adsorbed, and α, β and m are model parameters. The model coefficients, U, W, and m must be specified to obtain a specific form of the 2-D EOS for application. For example, an analog of the van der Waals (VDW) EOS is obtained by setting m = 1 and U = W = 0; similarly for the Soave-Redlich-Kwong (SRK) (m =1, U = 1 and, W = 0); the Peng-Robinson (PR) (m = 1, U = 2, and W = -1); and the Eyring (m = 1/2 and U = W = 0) EOS.

This general 2-D EOS can be used to investigate EOS behaviors by specifying various combinations of model coefficients. Selection of the model coefficient m is the most important among the EOS model coefficients, because it has a significant effect on the shape of the pure adsorption isotherm. If U and W are equal to zero, then by setting m to values of 1, and 1/2, we obtain the 2-D VDW EOS, and the Eyring EOS, respectively. Actually, the pure gas isotherms vary considerably in shape and we have found that it is sometimes desirable to select an m value even smaller than 1/2 to describe pure isotherms. We have determined that an equation with m = 1/3 and U = W = 0 (the ZGR EOS) is promising [4]. The 2-D EOS can be applied to adsorbed phases containing mixtures by utilizing the traditional mixing rules (where x is the mole fraction in the adsorbed phase):

$$\alpha = \sum_i \sum_j x_i x_j \alpha_{ij} \tag{10}$$

$$\beta = \sum_i \sum_j x_i x_j \beta_{ij} \tag{11}$$

along with the non-traditional combination rules [4],

$$\begin{aligned} \alpha_{ij} &= (1 - C_{ij})(\alpha_i + \alpha_j)/2 \\ \beta_{ij} &= (1 + D_{ij})\sqrt{\beta_i \beta_j} \end{aligned} \tag{12}$$

where C_{ij} and D_{ij} are the EOS binary interaction parameters.

4.3 *Modeling Results*

The data correlation and model evaluation efforts undertaken here address two important issues: (a) the ability of the LRC and ZGR EOS to correlate or represent the acquired adsorption data, and (b) the ability of the two models to predict the binary and ternary mixture adsorptions. Thus, beyond establishing the

model precision in summarizing existing data, we are also interested in evaluating the efficacy of such models when using pure and/or binary measurements to provide accurate predictions for ternary and other multicomponent mixtures.

In the following discussion two case studies are considered. First, we evaluate model **representations** of the Tiffany adsorption data, where the model parameters (L, B, and η for the LRC; α, β, C_{ij}, D_{ij} for ZGR EOS) are regressed to correlate the data considered and to establish the quality of precision attainable for the present models. Next, we examine binary model **predictions** based on pure-fluid parameters, and ternary predictions based on pure or a combination of pure and binary parameters.

The following weighted-error objective function was used to regress the model parameters:

$$SS = \sum_i \sum_j \left(\frac{\omega_{ij}^{calc} - \omega_{ij}^{exp\,t}}{\sigma_{ij}^{exp\,t}} \right)^2 \quad \text{i=1, NPTS; j=1, NC} \tag{13}$$

Here, i and j are data point component indices, respectively, NC the total number of components in the mixture, NPTS the total number of data points, and $\sigma_{ij}^{exp\,t}$ is the expected experimental uncertainty for the individual data point. The root-mean-square error (RMSE) and the %AAD for the individual isotherms, calculated as

$$RMSE = \sqrt{\frac{\sum_i^{NPTS} (\omega_i^{calc} - \omega_i^{exp\,t})^2}{NPTS}} \tag{14}$$

$$\%AAD = 100 \sum_i^{NPTS} \left| \frac{\omega_i^{calc} - \omega_i^{exp\,t}}{\omega_i^{exp\,t}} \right| \tag{15}$$

were used to express the quality of fit in our model evaluations. Similar expressions were used for the overall fit.

Pure-Gas Adsorption: Tables 3-6 present a summary of our model evaluation results for the three models used to correlate our adsorption data for methane, nitrogen, and CO_2. The model parameters were determined by minimizing the sum of squares of weighted errors, SS, in the calculated adsorption, ω, for the pure gas of interest.

Table 3 presents the results for the Langmuir model. AADs of 2 to 4% (0.005-0.02 mmol/g) were obtained for the systems considered. Table 4 presents the results for the LRC using system-specific pressure exponents (η_i). The results indicate that the LRC produces better fit than the Langmuir correlation for the three gases studied. This in part reflects the added flexibility gained by the additional parameter η_i in the regressions. AADs of 1 to 2% (0.003-0.02 mmol/g) were observed for the systems considered. When a common pressure exponent (η) was forced on the model, a value of 0.90 was obtained. Table 8 presents the results of this LRC using the common exponent, which yielded an AAD of about 2% (0.003-0.016 mmol/g).

Table 6 presents a summary of our model evaluation results for ZGR EOS. These results reveal the ability of the ZGR EOS to represent the adsorption of CO_2, methane and nitrogen on Tiffany coals within their expected experimental uncertainties. Similar to the LRC results, fits with 2 to 3% AAD (0.004-0.02 mmol/g) were obtained.

Figure 3 illustrates the abilities of the LRC and ZGR models to describe the present pure-fluid adsorption data.

***Binary Mixture Adsorption**:* Figures 6 - 8 present the LRC **representations** of the binary absolute adsorption data. The LRC parameters generated from the model representations of binary mixture absolute adsorption data for these mixtures and the model statistics are given in Table 7. In general, AADs of 3-32% (0.004-0.05 mmol/g) are observed for the individual-component adsorption. The AAD of 32% (0.02 mmol/g) was obtained for the nitrogen adsorption in the nitrogen/CO_2 mixture adsorption. As indicated, the %AAD may be high while the RMSE is low for component adsorption due to the low values of absolute adsorption for the least-adsorbed component.

Table 8 summarizes the results for the **LRC predictions** based on pure-gas adsorption data. As shown in this table, the LRC model predicts the methane/nitrogen and methane/CO_2 individual-component adsorptions within the experimental uncertainties (8-21%, 0.005-0.06 mmol/g) using pure-fluid adsorption parameters; however, the model predictions for the nitrogen/CO_2 binary are less accurate (AAD of 39% or 0.02 mmol/g for the nitrogen adsorption). Moreover, variation of the pressure exponent η does not significantly change the results. Figures 9-11 illustrate the quality of the LRC predictions for the binary mixtures.

Table 9 presents a summary of the evaluation results for ZGR EOS, where various binary parameter regressions have been considered. The results indicate that using two interaction parameters (C_{12} and D_{12}) leads to the best overall fit for the Tiffany coal adsorption data. **Representations** within the expected experimental

uncertainty (AAD of 4-16%, 0.004-0.05 mmol/g) are obtained for the three binaries for the individual-component adsorptions. Figures 6-8 illustrate the abilities of the ZGR EOS to describe the present binary mixture adsorption data. In most cases, the ZGR and LRC give comparable results, with slightly better statistics for the LRC.

In addition, Table 9 summarizes the results for the ZGR **predictions** based on pure-gas adsorption data. As shown in this table and Figures 9-11, the ZGR EOS predicts the individual-component binary adsorption isotherms of methane/nitrogen and methane/CO_2 within twice the experimental uncertainty (about 10-27%, 0.009-0.05 mmol/g). Significantly higher deviations, however, are observed for the lesser-adsorbed nitrogen (up to 49% AAD, 0.02 mmol/g) in the nitrogen/CO_2 binary.

Ternary Mixture Adsorption: The LRC parameters generated for the model **representation** of the ternary adsorption data and the model statistics are given in Table 10. AAD of 3-12% (0.005-0.02 mmol/g) are observed for the individual adsorption, and 0.5% (0.002 mmol/g) for the total adsorption. The results suggest that the quality of fit is directly related to the amount adsorbed.

The **predictive capability** of the LRC is examined in Table 11 and Figure 12. In this case, the LRC model parameters obtained from the pure adsorption were used to predict the ternary mixture adsorption on wet Tiffany coal. Poor model predictions were obtained for this ternary when only pure-adsorption data are utilized in model optimization. AADs of 5-48% (0.003-0.08 mmol/g) were observed for the individual-component isotherms. This translates roughly to prediction errors within

one to four times the expected experimental uncertainty. Variation in the pressure exponent η did not alter the results significantly.

Table 9 includes a summary of ternary prediction results for the ZGR EOS, which indicates the ability of the ZGR EOS to predict the methane/nitrogen/CO_2 individidual-component adsorption isotherms within three times their expected experimental uncertainties (18-56% AAD, 0.006-0.007 mmol/g). The ZGR **predictions** using binary interaction parameters (C_{ij}, D_{ij}) are comparable to those obtained by the LRC using the same amount of input data.

The **predictive capability** of the ZGR EOS is examined in Table 9. The ZGR predictions based on pure (α_i, β_i, k_i) and binary parameters (C_{ij}, D_{ij}) are within three times the experimental uncertainty (10-32% AAD, 0.006-0.07 mmol/g). The results also indicate that (for the present mixtures) little improvement is realized by using binary adsorption data to predict the ternary isotherms of the individual components. Further, the quality of the model predictions indicates that, although the LRC and ZGR EOS are capable of predicting total adsorption isotherms adequately, they predict the individual-component isotherms poorly, especially when dealing with the lesser-adsorbed component of the mixture. In fact, diminishing the influence of the lesser-adsorbed components on the parameter regressions, by using a least-square (un-weighted) objective function, improves the ternary model predictions based on pure and binary data.

These results suggest significant model improvements are required to realize the expected benefit of improving multicomponent predictions using binary adsorption measurements.

5. Summary

- Characterizations of BP Amoco Tiffany coal samples from Injection Wells #1 and #10 were done. Results for (a) particle size distribution, (b) composition, (c) equilibrium moisture content, and (d) vitrinite reflectance indicate similarity of the two samples. Further, adsorption isotherms for pure methane on the two wet Tiffany coal samples (Wells #1 and #10) at 327.6 K and pressures to 13.8 MPa confirm the similarity of the two medium volatility bituminous coal samples.
- Adsorption isotherms were measured for **pure** methane, nitrogen and CO_2 on a mixed Tiffany coal sample at 327.6 K and pressures to 13.8 MPa. The adsorption capacity of the mixed sample is intermediate to that observed for Well #1 and Well #10 samples. The pure adsorption data have average expected experimental uncertainties of 3% (0.01 mmol/g), 6% (0.01 mmol/g) and 7% (0.08 mmol/g) for methane, nitrogen, and CO_2, respectively.
- **Binary** and **ternary** adsorption of methane, nitrogen, and CO_2 mixtures on a wet Tiffany mixed coal at 327.6 K and pressures to 13.8 MPa were measured at one feed composition for each mixture. The expected uncertainties in the amount adsorbed for these binary and ternary mixtures vary with pressure and composition. In general, percent average uncertainties are about 6% (0.02 mmol/g) for total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher, especially at lower feed gas mole fractions of the lesser-adsorbed component (i.e., nitrogen in the nitrogen/CO_2 system at 20/80 mole % feed composition).

- The pure and total adsorption data can be **correlated** within their experimental uncertainties by the loading ratio correlation (LRC) and the 2-D Zhou-Gasem-Robinson (ZGR) equation of state (EOS). However, the quality of fit for the individual–component adsorption from mixtures varies significantly, ranging from 3% for the more-adsorbed methane or CO_2 to 32% for the lesser-adsorbed nitrogen.
- The present results suggest that both the LRC and ZGR EOS are capable of **predicting** binary adsorption isotherms based on pure-fluid adsorption parameters within twice their experimental uncertainties. In comparison, the ternary predictions based on pure-fluid parameters yield three times the experimental uncertainties. Further, for the present system, little improvement is realized by predicting the individual-component ternary isotherms based on parameters generated using both pure and binary adsorption data.

Acknowledgment

The financial support of the U.S. Department of Energy is gratefully acknowledged. This work was supported by DOE under Contract No. DE-FC26-98FT40426.

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Table 1. Compositional Analyses of Tiffany Coal Samples*

Analysis	Well #1	Well #10	Well #1 Dry Basis	Well #10 Dry Basis
Dry Loss %	6.9	18.3		
Carbon %	44.5	46.4	47.8	56.8
Hydrogen %	3.2	4.3	2.6	2.8
Oxygen %	11.9	20.5	6.2	5.2
Nitrogen %	0.86	0.83	0.92	1.0
Sulfur %	0.53	0.42	0.57	0.52
Ash %	46.3	39.0	49.7	47.7
Proximate				
Volatile Matter %	14.4	12.5	15.5	15.4
Fixed Carbon %	32.4	30.1	34.8	36.9

***Analysis was conducted on a mass basis by Huffman Laboratories, Inc., 4630 Indiana Street, Golden, CO 80405.

Table 2. Vitrinite Reflectance Analysis*

	Well #1	**Well #10**
Average VRO	1.31	1.35
Range	1.19-1.43	1.21-1.50
Grain Count	50	50
Rank	Medium Volatility Bituminous Coal	Medium Volatility Bituminous Coal

***Analysis was conducted by National Petrographic Service, Inc., 5933 Bellaire Blvd. Suite 108, Houston, TX 77081.

Table 3. Langmuir Model Representation of Adsorption on Wet Tiffany Coals at 327.6 K

Pure Gas	L_i (mmol/g)	B_i (MPa^{-1})	η_i	RMSE (mmol/g)	%AAD
CH_4 (Well #1)	0.569	0.234	1.0	0.0055	1.9
CH_4 (Well #10)	0.550	0.227	1.0	0.0034	1.1
CH_4 (Mixed Coal)	0.573	0.219	1.0	0.0095	2.6
N_2 (Mixed Coal)	0.352	0.091	1.0	0.0051	3.5
CO_2 (Mixed Coal)	0.779	0.654	1.0	0.0219	2.0

Table 4. LRC Model Representation of Adsorption on Wet Tiffany Coals at 327.6 K

Pure Gas	L_i (mmol/g)	B_i (MPa^{-1})	η_i	RMSE (mmol/g)	%AAD
CH_4 (Well #1)	0.671	0.161	0.89	0.0038	0.8
CH_4 (Well #10)	0.581	0.202	0.96	0.0037	0.9
CH_4 (Mixed Coal)	0.648	0.161	0.91	0.0098	2.3
N_2 (Mixed Coal)	0.549	0.039	0.87	0.0029	2.1
CO_2 (Mixed Coal)	0.832	0.570	0.91	0.0163	1.8

Table 5. LRC Model Representation of Adsorption on Wet, Mixed Tiffany Coals at 327.6 K (common η_i)

Pure Gas	L_i (mmol/g)	B_i (MPa^{-1})	η_i	RMSE (mmol/g)	%AAD
CH_4	0.665	0.157	0.90	0.010	2.3
N_2	0.480	0.051	0.90	0.003	2.3
CO_2	0.836	0.551	0.90	0.016	1.8

Table 6. ZGR Equation-of-State Representation of Adsorption on Wet, Mixed Tiffany Coals at 327.6 K

Pure Gas	α_i (MPa·m^3·g/mol^2)	β_i (mmol/g)$^{-1}$	k_i (mol·MPa/g)	RMSE (mmol/g)	%AAD
CH_4	14.477	1.0140	5.843	0.011	3.0
N_2	19.316	1.3926	1.370	0.002	2.3
CO_2	7.443	0.6069	28.365	0.020	2.1

Table 7. LRC Model Representation of Binary Adsorption on Wet Tiffany Coals at 327.6 K

Mixture	L_i (mmol/g)	B_i (MPa^{-1})	η_i	RMSE (mmol/g)	%AAD
CH_4 / N_2:					
CH_4	0.574	0.221	0.96	0.022	9.7
N_2	0.483	0.049	0.89	0.008	9.0
Total				0.028	8.2
CH_4 / CO_2:					
CH_4	0.574	0.221	0.96	0.016	7.3
CO_2	0.926	0.416	0.80	0.022	4.2
Total				0.007	1.2
N_2 / CO_2:					
N_2	0.483	0049	0.89	0.015	31.6
CO_2	0.926	0.416	0.80	0.048	6.7
Total				0.035	4.7
Pure:					
CH_4	0.574	0.221	0.96	0.011	3.3
N_2	0.483	0.049	0.89	0.004	2.7
CO_2	0.926	0.416	0.80	0.017	2.1

Table 8. LRC Model Predictions of Binary Adsorption on Wet Tiffany Coals at 327.6 K

Mixture	$\eta = 1$ (Langmuir)		Regressed η		$\eta = 0.90$	
	RMSE (mmol/g)	%AAD	RMSE (mmol/g)	%AAD	RMSE (mmol/g)	%AAD
CH_4 / N_2:						
CH_4	0.039	15.8	0.020	9.0	0.031	12.0
N_2	0.005	6.2	0.005	8.3	0.005	9.3
Total	0.040	12.2	0.021	6.4	0.029	8.2
CH_4 / CO_2:						
CH_4	0.048	25.9	0.041	21.1	0.041	21.0
CO_2	0.052	9.0	0.056	10.1	0.058	10.5
Total	0.006	1.2	0.015	1.9	0.017	2.2
N_2 / CO_2:						
N_2	0.020	44.9	0.019	38.9	0.018	37.3
CO_2	0.036	5.2	0.047	5.9	0.044	5.7
Total	0.021	3.5	0.030	3.8	0.028	3.8

Table 9. ZGR EOS Representation of Mixtures on Tiffany Mixed Coal at 327.6 K

Mixture			%AAD			RMSE (mmol/g coal)		
EOS Predictions, C_{12} = D_{12} =0								
	C_{12}	D_{12}	ω_1	ω_2	Total	ω_1	ω_2	Total
CH_4 / N_2	0.000	0.000	11.9	10.0	11.5	0.027	0.009	0.035
CH_4 / CO_2	0.000	0.000	27.0	10.4	1.4	0.040	0.046	0.007
N_2 / CO_2	0.000	0.000	48.7	4.9	3.5	0.017	0.033	0.021
Regressed C_{12} (D_{12}=0)								
	C_{12}	D_{12}	ω_1	ω_2	Total	ω_1	ω_2	Total
CH_4 / N_2	-0.090	0.000	10.6	7.3	7.6	0.025	0.005	0.023
CH_4 / CO_2	-0.125	0.000	8.4	10.6	6.1	0.015	0.043	0.033
N_2 / CO_2	-0.140	0.000	16.0	4.1	3.2	0.005	0.028	0.023
Regressed D_{12} (C_{12}=0)								
	C_{12}	D_{12}	ω_1	ω_2	Total	ω_1	ω_2	Total
CH_4 / N_2	0.000	-0.068	10.6	7.1	7.5	0.024	0.005	0.022
CH_4 / CO_2	0.000	-0.090	7.7	11.0	6.6	0.013	0.046	0.038
N_2 / CO_2	0.000	-0.108	14.5	4.3	3.5	0.004	0.029	0.025
Regressed C_{12} and D_{12}								
	C_{12}	D_{12}	ω_1	ω_2	Total	ω_1	ω_2	Total
CH_4 / N_2	-0.060	-0.023	10.6	7.2	7.5	0.025	0.005	0.023
CH_4 / CO_2	-0.098	-0.019	8.2	10.7	6.2	0.014	0.044	0.034
N_2 / CO_2	-0.011	-0.100	14.6	4.3	3.4	0.004	0.029	0.025

Predicted Ternary								
Mixture	**%AAD**				**RMSE (mmol/g coal)**			
From pure data C_{12} = D_{12} =0								
	ω_1	ω_2	ω_3	Total	ω_1	ω_2	ω_3	Total
CH_4 / N_2 / CO_2	21.6	55.9	17.6	4.3	0.006	0.038	0.068	0.024
C_{12} from Binary (D_{12} =0)								
	ω_1	ω_2	ω_3	Total	ω_1	ω_2	ω_3	Total
CH_4 / N_2 / CO_2	18.0	32.8	17.4	9.3	0.006	0.023	0.063	0.046
D_{12} from Binary (C_{12} =0)								
	ω_1	ω_2	ω_3	Total	ω_1	ω_2	ω_3	Total
CH_4 / N_2 / CO_2	18.3	31.6	17.7	9.7	0.006	0.021	0.065	0.050
C_{12} and D_{12} from Binary								
	ω_1	ω_2	ω_3	Total	ω_1	ω_2	ω_3	Total
CH_4 / N_2 / CO_2	18.6	31.9	17.6	9.6	0.006	0.022	0.065	0.049

Table 10. LRC Model Representation of Ternary Adsorption on Wet Tiffany Coals at 327.6 K

Individual Adsorption	L_i (mmol/g)	B_i (MPa^{-1})	η_i	RMSE (mmol/g)	%AAD
CH_4	0.630	0.264	0.97	0.005	9.0
N_2	0.280	0.297	1.30	0.011	11.7
CO_2	0.832	0.641	1.05	0.017	3.3
Total				0.002	0.5

Table 11. LRC Model Predictions of Ternary Adsorption on Wet Tiffany Coals at 327.6 K

Individual Adsorption	L_i (mmol/g)	B_i (MPa^{-1})	η_i	RMSE (mmol/g)	% AAD
Parameters based on pure data					
η= 1 (Langmuir)					
CH_4	0.573	0.219	1.0	0.008	20.7
N_2	0.352	0.091	1.0	0.039	47.8
CO_2	0.779	0.654	1.0	0.065	13.2
Total				0.020	2.9
η Regressed					
CH_4	0.648	0.161	0.91	0.003	5.3
N_2	0.549	0.039	0.87	0.039	46.1
CO_2	0.832	0.570	0.91	0.081	17.7
Total				0.040	6.7
η= 0.90					
CH_4	0.665	0.157	0.90	0.003	5.2
N_2	0.480	0.051	0.90	0.037	44.5
CO_2	0.836	0.551	0.90	0.072	15.8
Total				0.033	5.4
Parameters based on pure and binary data					
CH_4	0.574	0.221	0.96	0.006	16.6
N_2	0.483	0.049	0.89	0.033	45.8
CO_2	0.926	0.416	0.80	0.058	12.0
Total				0.034	6.0

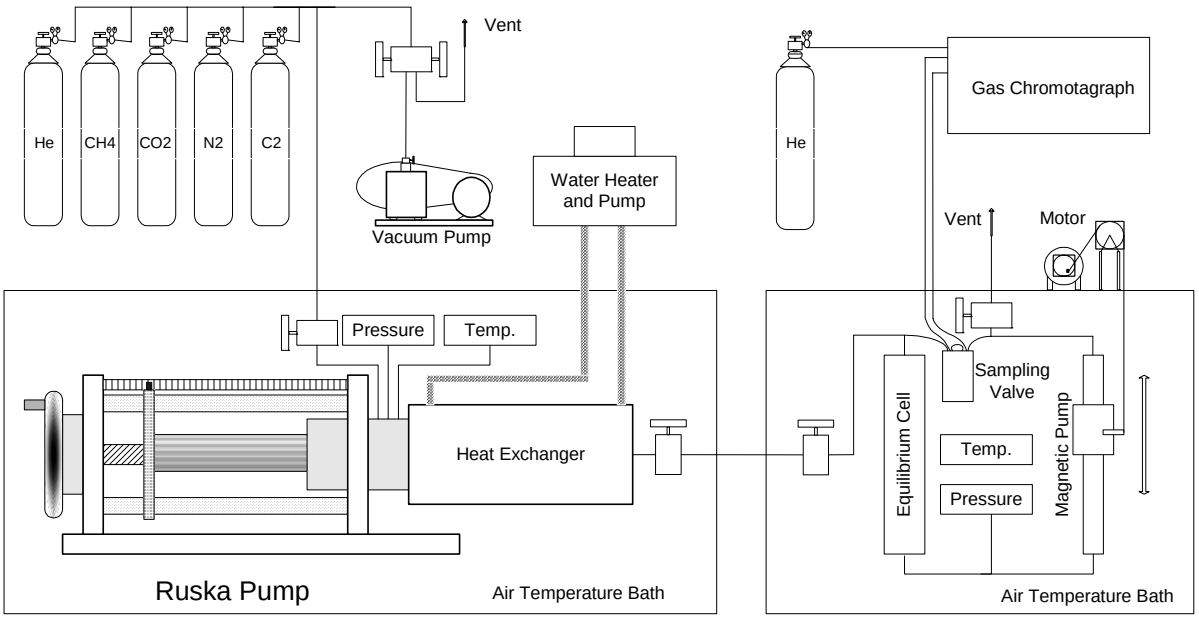

Figure 1. Schematic Diagram of Adsorption Apparatus

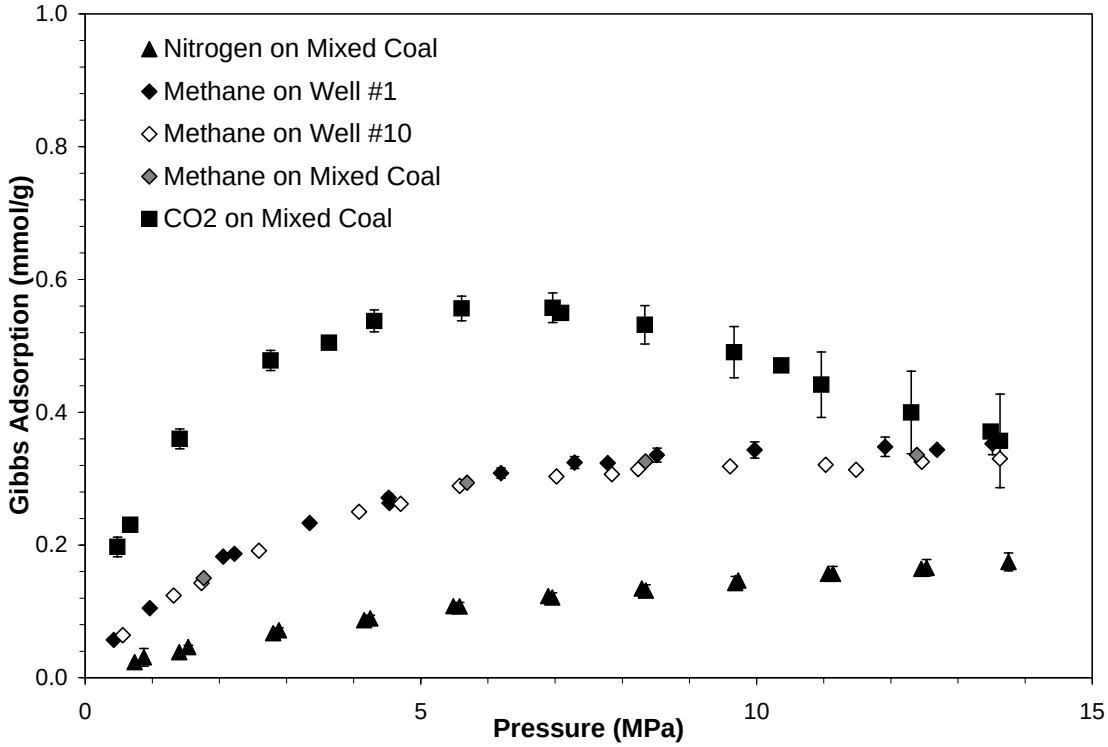

Figure 2. Pure-Gas Gibbs Adsorption on Wet Tiffany Coals at 327.6 K

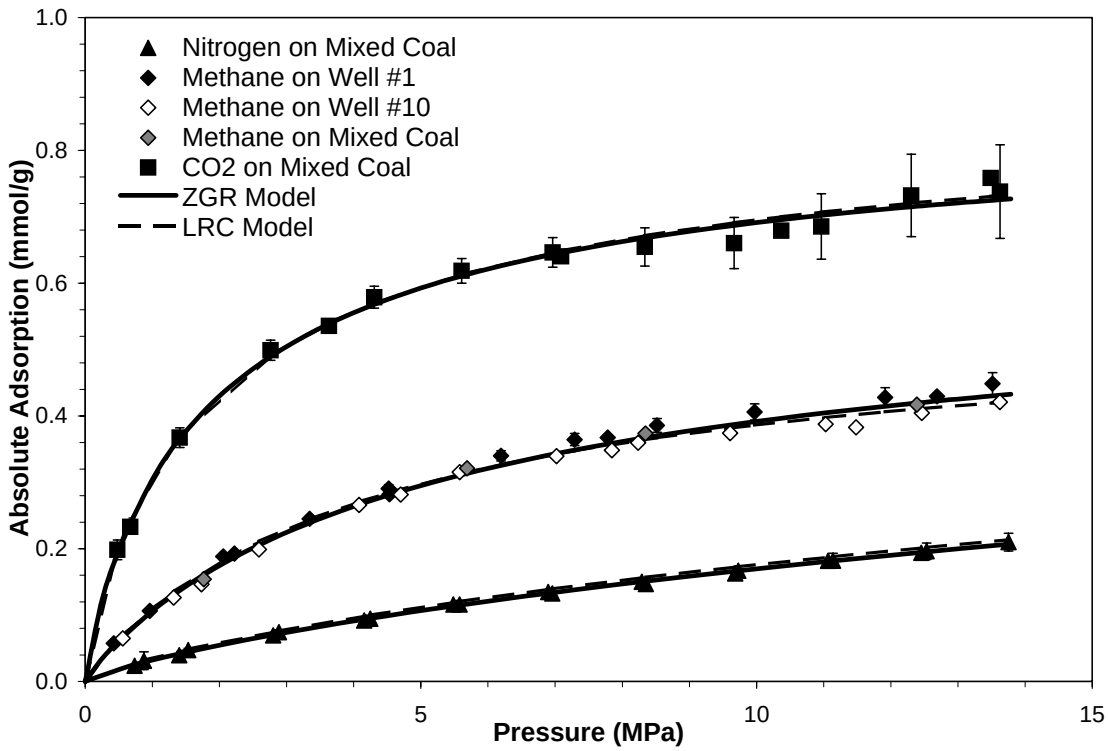

Figure 3. Pure-Gas Absolute Adsorption on Wet Tiffany Coals at 327.6 K

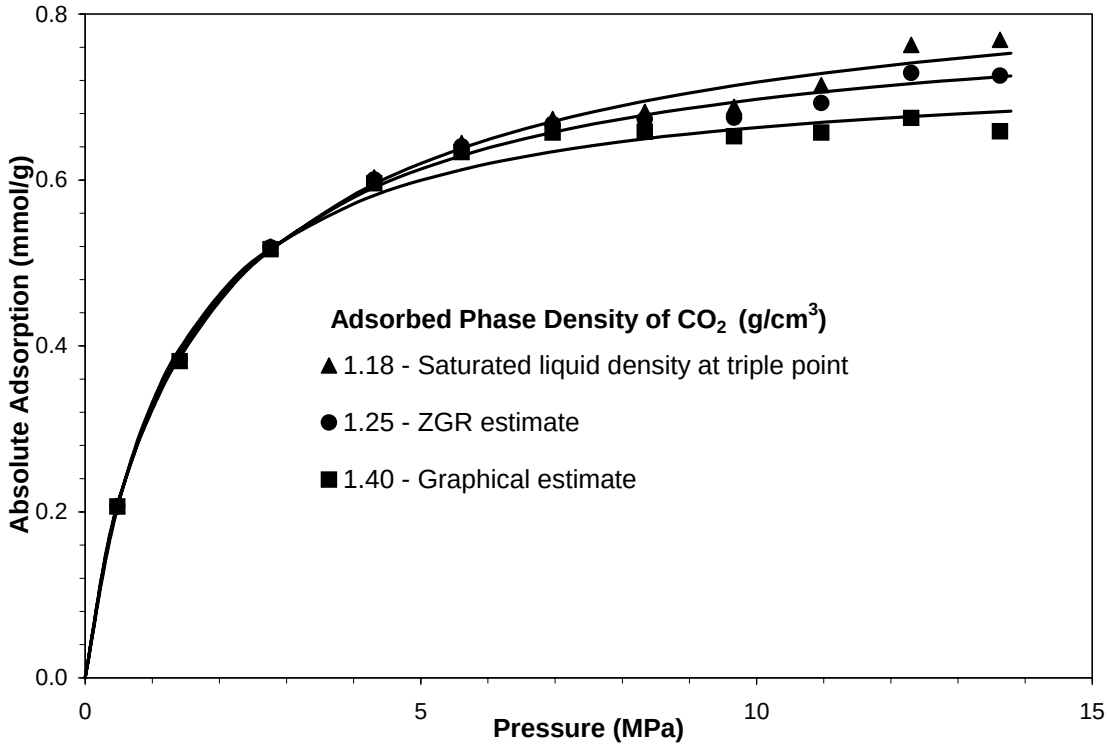

Figure 4. CO_2 Absolute Adsorption on a Wet Tiffany Mixed-Coal Sample at 327.6 K Using Different Adsorbed Phase Densities

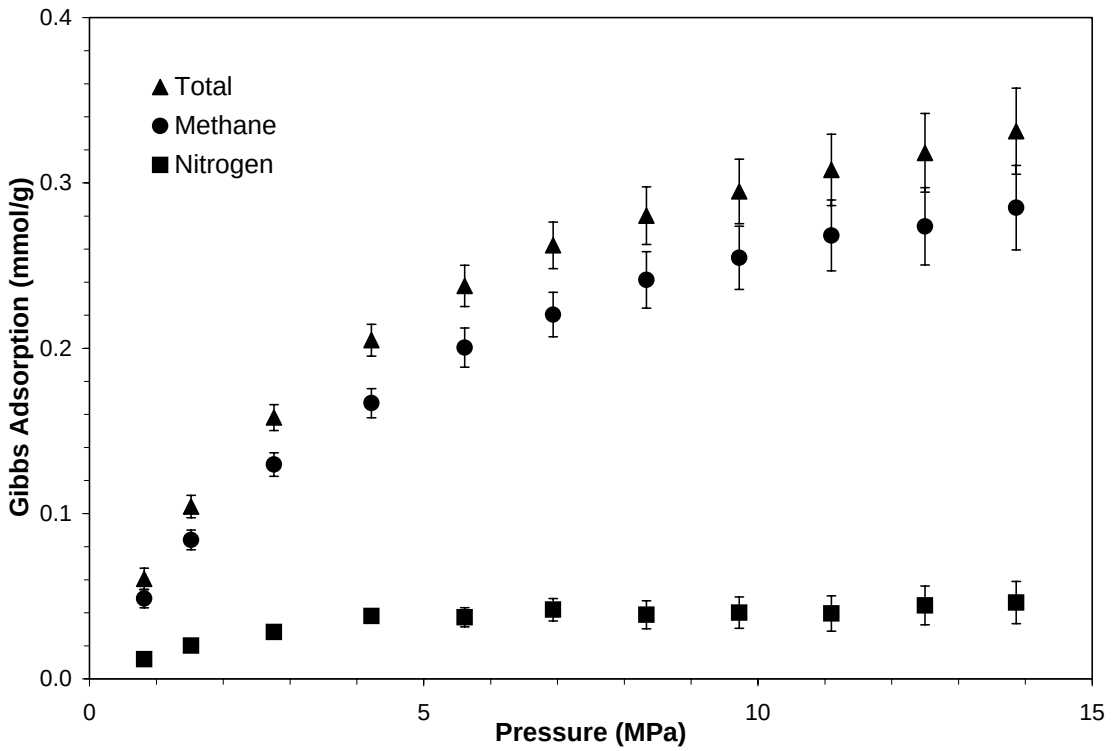

Figure 5. Gibbs Adsorption of 50/50 Mole % Mixture: Methane/Nitrogen Feed Mixture on a Wet Tiffany Mixed-Coal Sample at 327.6 K

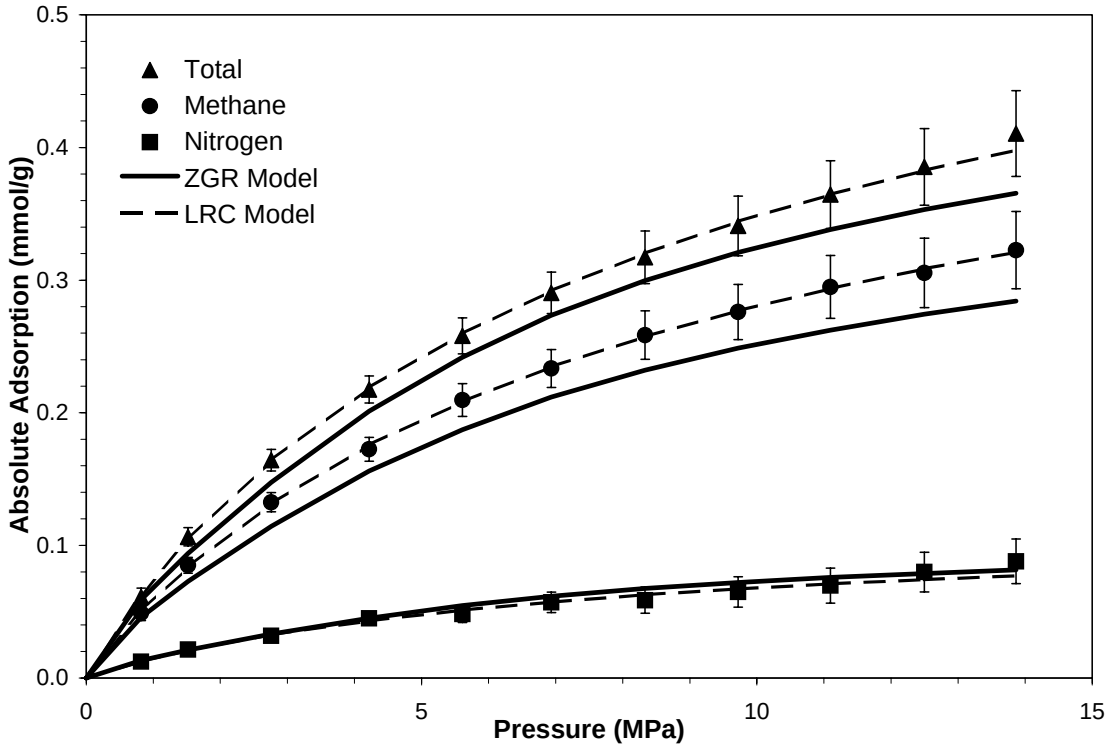

Figure 6. Absolute Adsorption of 50/50 Mole % Mixture: Methane/Nitrogen Feed Mixture on a Wet Tiffany Mixed-Coal Sample at 327.6 K

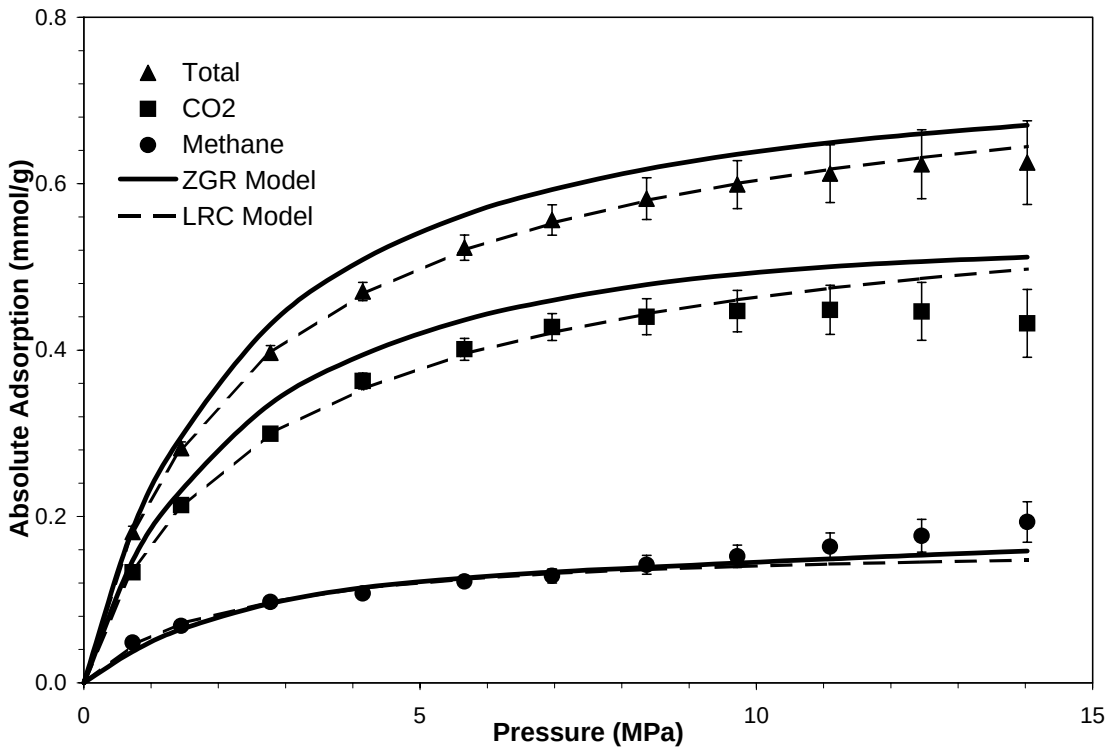

Figure 7. Absolute Adsorption of 40/60 Mole % Mixture: Methane/CO_2 Feed Mixture on a Wet Tiffany Mixed-Coal Sample at 327.6 K

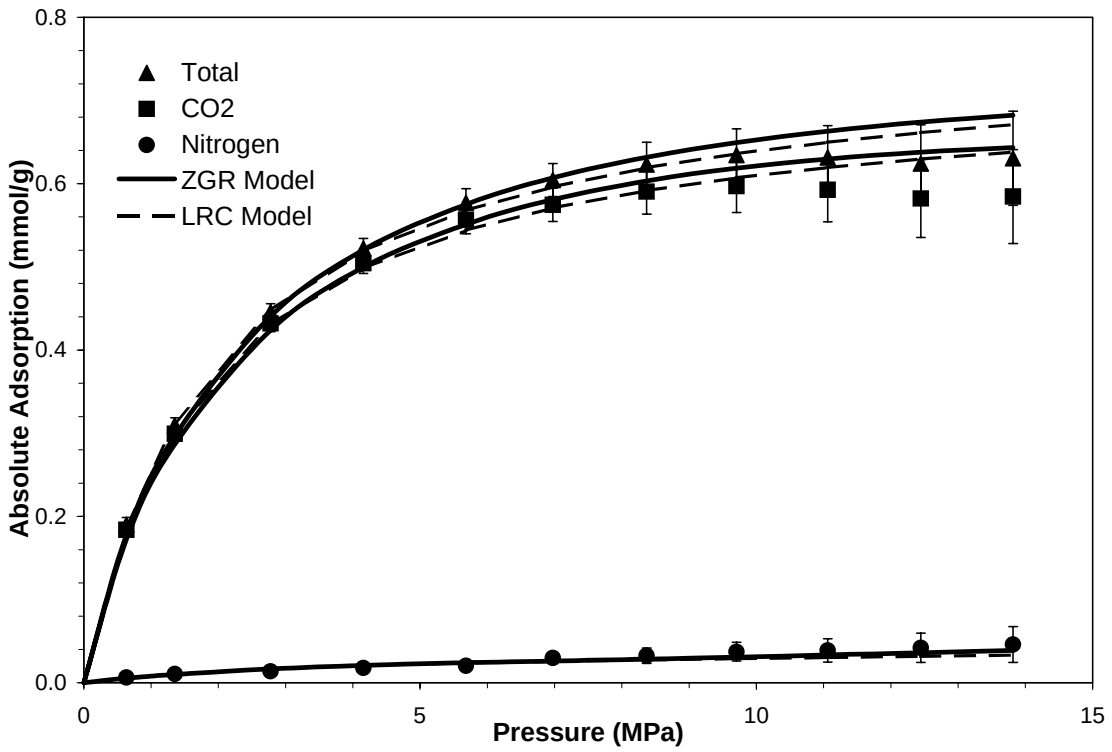

Figure 8. Absolute Adsorption of 20/80 Mole % Mixture: Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed-Coal Sample at 327.6 K

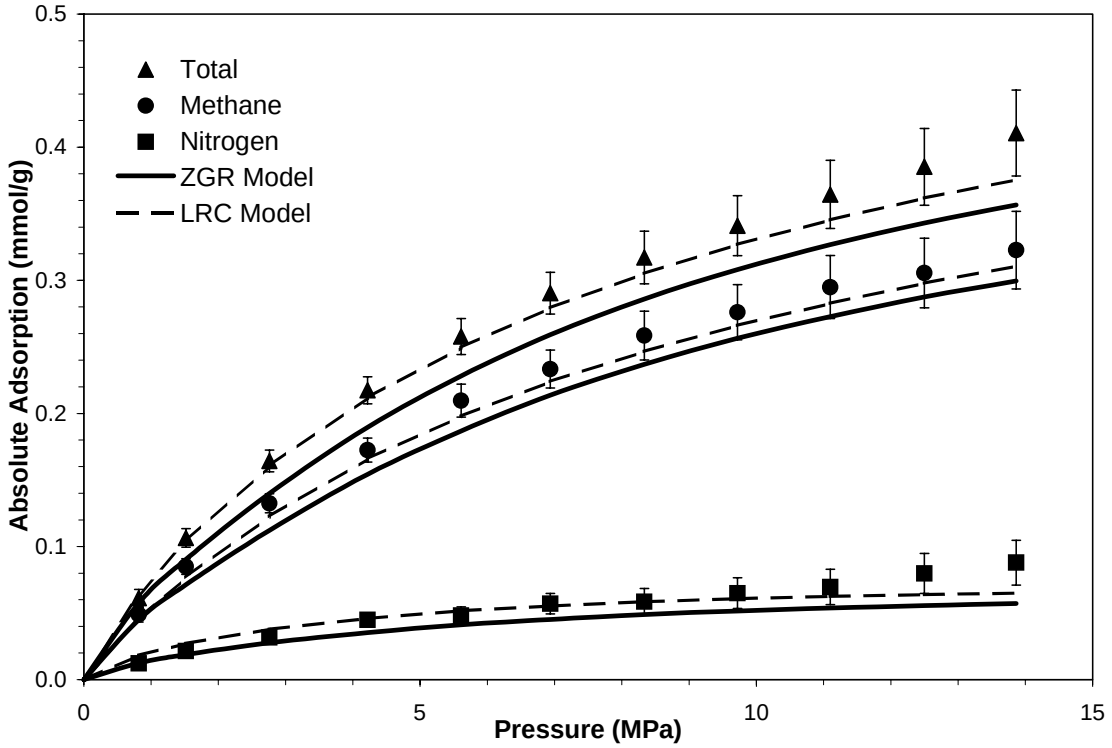

Figure 9. Model Predictions of Absolute Adsorption of 50/50 Mole % Mixture: Methane/Nitrogen Feed Mixture on a Wet Tiffany Mixed-Coal Sample at 327.6 K

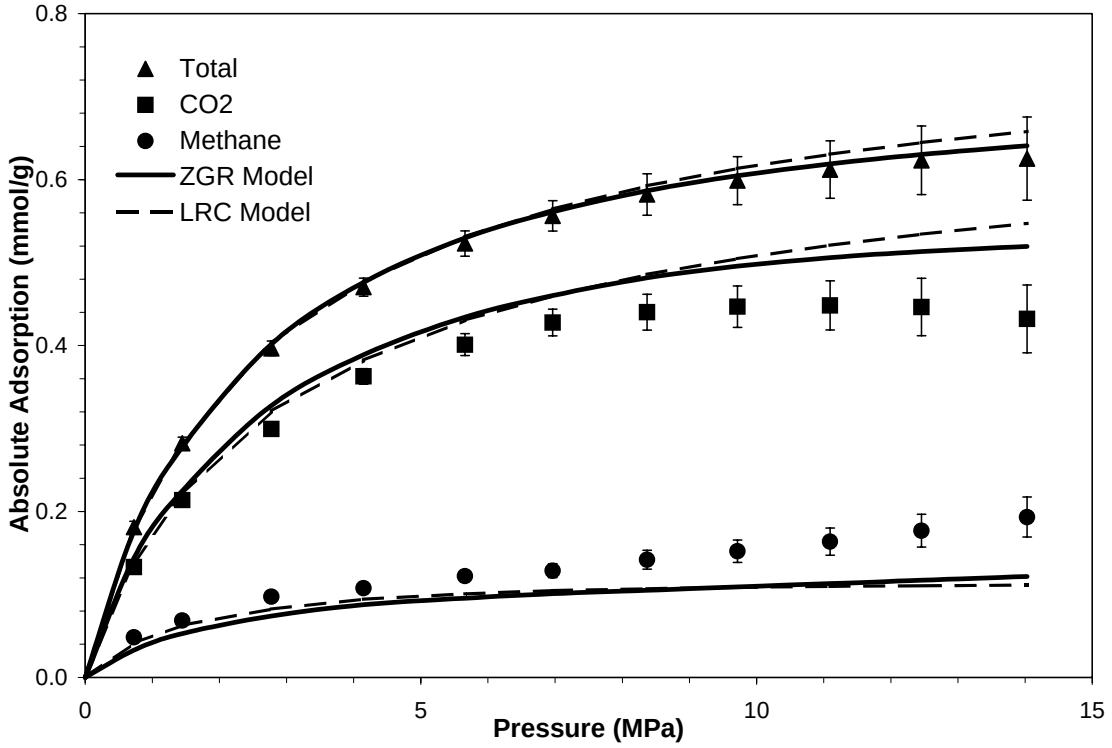

Figure 10. Model Predictions of Absolute Adsorption of 40/60 Mole % Mixture: Methane/CO_2 Feed Mixture on a Wet Tiffany Mixed-Coal Sample at 327.6 K

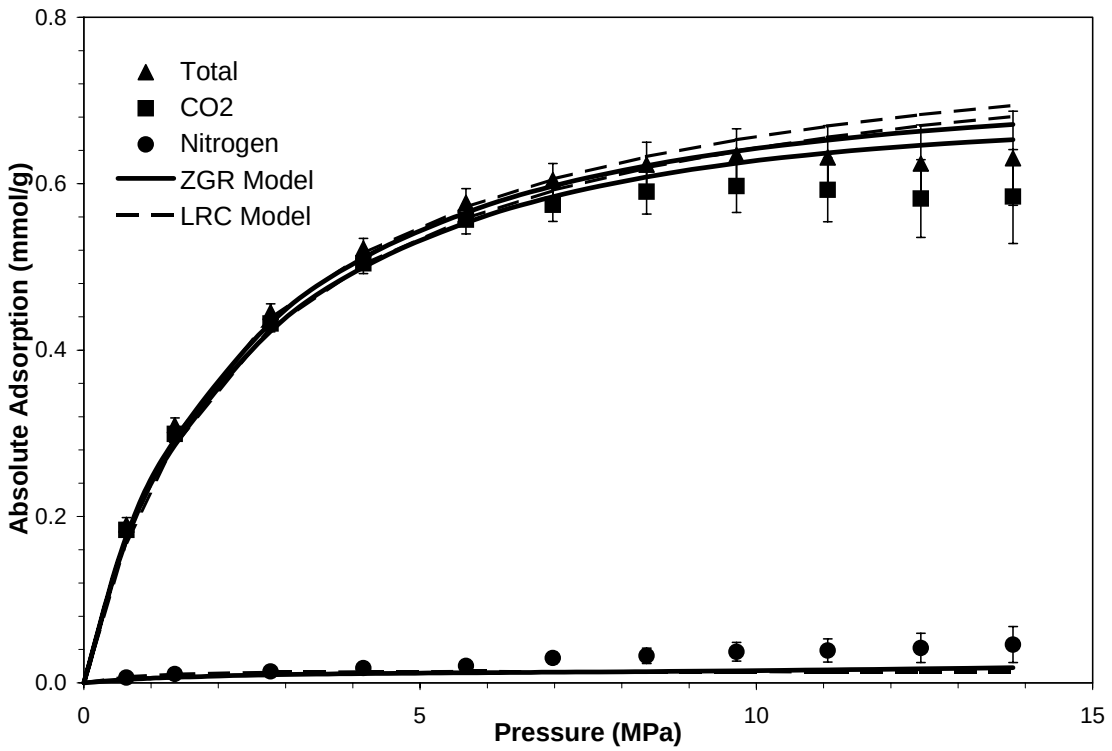

Figure 11. Model Predictions of Absolute Adsorption of 20/80 Mole % Mixture: Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed-Coal Sample at 327.6 K

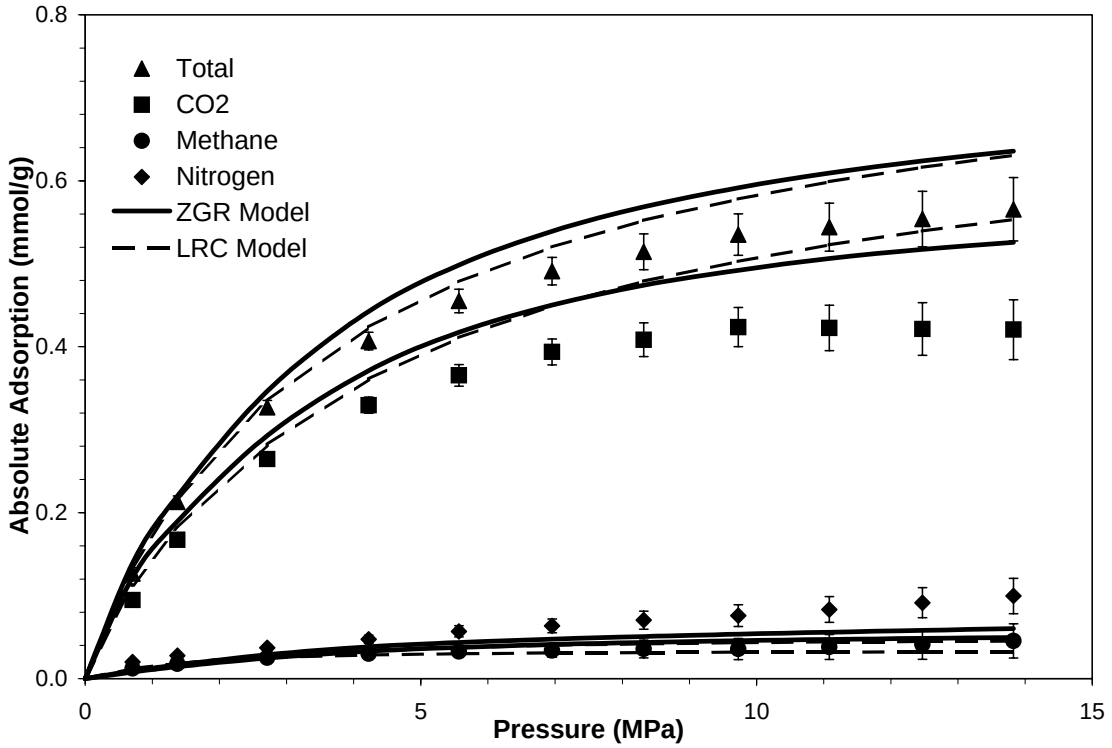

Figure 12. Model Predictions of Absolute Adsorption of 10/40/50 Mole % Mixture: Methane/Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed-Coal Sample at 327.6 K