Modeling the Temperature Dependence of Supercritical Gas Adsorption on Activated Carbons, Coals and Shales

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Abstract

The recovery of natural gas from unconventional gas reservoirs such as shales and coal beds has increased significantly over the past few years. Since a majority of gas in these reservoirs is in an adsorbed state, knowledge of adsorption behavior of gases is essential for reliable gas-in-place estimates of these reservoirs. Further, some of these reservoirs also offer the potential for carbon dioxide sequestration. The existence of geothermal gradients in such reservoirs can affect the amount of gas. Since the temperatures in a reservoir are generally in the near-critical or supercritical region of the adsorbed gases, an adsorption model should be capable of reliable predictions of temperature dependence of adsorption in this region. To date, limited studies exist in the literature for modeling of temperature dependence of *supercritical* gas adsorption. In this work, we present a modification of the simplified local density (SLD) model to improve predictions of the temperature dependence of supercritical gas adsorption.

Activated carbons were chosen as the reference adsorbents in the development of the modifications to the model since adsorption data on activated carbons are much more plentiful than data on coals and shales, for which data at multiple temperatures are extremely limited. Since activated carbons are simpler structural analogs of other carbonaceous adsorbents such as coals and shales, a model for activated carbons should serve as a basis for extension to the more complex coals and shales.

To undertake this study, a database was compiled that includes adsorption data at several temperatures for 11 gases on 18 activated carbons containing about 2600 data points. The database also included adsorption isotherms measured on six coals and six shales at multiple temperatures with a total of 670 data points.

The SLD model was modified by introducing a new temperature-dependence expression in the model. The modified SLD model was tested for its efficacy in describing the temperature dependence of near-critical and supercritical gas adsorption on the adsorbents contained in the above database. Results indicate that the modified SLD model is effective in modeling supercritical and near-critical gas adsorption. Further, the model was generalized to predict the temperature dependence of adsorption as a function of adsorbate and adsorbent properties. The generalized model was tested with an extended dataset and was found capable of predicting the temperature dependence with an average absolute deviation of 5%, in general.

The modified SLD model was tested with adsorption data on coals and shales at multiple temperatures. The model appears capable of describing the temperature dependence of adsorption on coals and shales with reasonable accuracy. We note, however, that the development of a completely generalized model requires additional experimental data on coals and shales and further model testing.

Keywords: Temperature dependence, gas adsorption isotherms, local-density model, generalization, thermal expansion coefficient, CO₂ sequestration, shale gas, coalbed methane, unconventional gas reservoirs.

1. Introduction

Shale and coalbed methane reservoirs have become an important source of natural gas, and a significant portion of the gas in these reservoirs exists in an adsorbed state. Thus, knowledge of gas adsorption behavior over a range of pressures and temperatures is required to estimate the gas-in-place for these reservoirs. Further, some of these reservoirs can offer potential sites for CO₂ sequestration. Gases commonly encountered in these reservoirs are the natural gas components including carbon dioxide and nitrogen with the latter two being especially important in enhanced gas recovery and carbon dioxide sequestration. Since gas adsorption is temperature dependent, the presence of geothermal gradients in a reservoir affects the adsorption capacity of these gases. For example, in the Black Warrior basin the coal bed reservoir temperature varies from about 300 K to 325 K within the 0.3-1.8 km depth-range (Pashin and McIntyre (2003)). Thus, an accurate accounting for temperature dependence of gas adsorption is important for reliable gas-in-place estimates as well as CO₂ sequestration capacity of such reservoirs.

To date, few studies in the literature have focused on modeling the temperature dependence of supercritical gas adsorption. Among previous studies, the Dubinin micropore filling theory (Dubinin, 1960) was used by Clarkson et al., (1997) and Ruppel et al., (1974). The theory offered a convenient method for predicting adsorption capacities over a range of temperatures based on the linear and temperature-independent characteristic curves. Clarkson et al., (1997) and Ruppel et al., (1974) tested the validity of such characteristic curves. In their work, the characteristic curves appeared to be non-linear, especially at large temperature and pressure ranges, indicating that the temperature invariance of the characteristic curve may not be valid over a wide temperature range. Czerny et al. (2005) observed that the temperature-

independent characteristic energy of adsorption, ε in Dubinin's theory, varies linearly with temperature. Richard et al. (2009) modified the Dubinin-Ashtakov (D-A) model by expressing ε as a linear function of temperature. They concluded that better model representations for adsorption were obtained after the modification of ε was introduced. Dundar et al. (2012) utilized the multicomponent potential theory of adsorption (MPTA) model, which can be extended to describe adsorption of gas mixtures. Similar to the modification in Richard et al. (2009), Dundar and co-workers replaced the constant adsorbed-phase volume, Z_0 in the Dubinin-Radushkevish-Astakov (DRA) potential, with the variable Z_0 expressed as a linear function of temperature. The modified DRA potential (MDP) was then used to account for the solid-gas interaction in MPTA model. The results obtained in Dundar's work indicated that the MPTA-MDP model improved the representations of adsorption on several activated carbons when compared to the results obtained from the MPTA-DRA model.

Although some success has been attained in modeling of supercritical gas adsorption, the adsorption models listed above have not been generalized to provide *a priori* predictions for a wide range of adsorbent/adsorbate pairs. In this work, we present a generalized model that is found capable of predicting temperature dependence of near-critical and supercritical gas adsorption for diverse adsorbate/adsorbent pairs over larger temperature ranges.

The simplified local density (SLD) model has been used successfully in our previous studies. In a recent work, the SLD model was extended to represent adsorption behavior on shales (Chareonsuppanimit et al., 2012). Further, the SLD model was integrated with the Pan and Connell (Pan and Connell, 2007) (PC) swelling model to account for adsorption-induced swelling of coals (Chareonsuppanimit et al., 2014). The swelling results obtained from the integrated SLD-PC model provided useful predictions of linear strain and gas permeability

changes in coals due to gas adsorption. Thus, the SLD model offers distinct advantages in providing predictions for a spectrum of adsorption-related phenomena from adsorption to permeability on coals and shales, which are crucial for more realistic reservoir simulations.

Notwithstanding the progress in modeling these systems, our analysis indicated that the inherent temperature dependence in the original SLD model was inadequate over wider temperature ranges. To remedy this problem, a new temperature-dependence expression is incorporated in the SLD model in this work based on the volume-expansivity approach proposed by Do (Do, 1998).

In this work, the SLD model was modified by introducing a new temperature dependence for the adsorbed-phase volume. The modified SLD model was tested initially using adsorption data on several activated carbons. Results indicate that inclusion of this new temperature dependence in the SLD model provided marked improvements for representations over larger temperature ranges compared to representations from the original SLD model. These initial evaluations utilized activated carbons since the adsorption data covering wide temperature ranges are extremely limited for both coals and shales. Further, since activated carbons are simpler structural analogs of other carbon-based adsorbents such as coals and shales, a model should be applicable to activated carbons as a precursor to extending it to coals and shales.

Some of the noteworthy aspects of this work include: (1) A large database for adsorption on activated carbons was compiled that contains adsorption data for 11 adsorbates on 18 adsorbents with a total of about 2600 data points (2) A generalized adsorption model was developed to predict the supercritical gas adsorption over significant temperature ranges (3) The generalized model was validated with an external dataset and (4) the modified model was tested to describe adsorption on coals and shales (additional 670 data points) at multiple temperatures.

The remainder of this paper is organized as follows: Section 2 describes the SLD model and the modifications undertaken to account for the temperature dependence of gas adsorption, Section 3 presents the literature database employed and Section 4 presents the results obtained in this work.

2.1 Simplified Local Density Adsorption Model

The SLD model envisions the adsorbent to be composed of rectangular-shaped slits and the adsorbate molecules reside within these two-surface slits. A molecule within a slit has interactions with both walls of the adsorbent slit. The SLD model accounts for both fluid-fluid and fluid-solid interactions in the slit-shaped pore. The model was first developed by Rangarajan et al. (1995), who used the van der Waals equation of state (EOS) to account for the fluid-fluid interactions. Following our earlier work (Fitzgerald et al., 2006; Mohammad et al., 2009), the Peng-Robinson EOS is used in this work. The following paragraphs provide the essential details of the SLD model as used in this work.

At equilibrium, the chemical potential of the fluid, μ , is expressed as the sum of the fluid-fluid and fluid-solid potentials at a position, “ z ”, between the slit surfaces, as follows:

$$\mu(z) = \mu_{ff}(z) + \mu_{fs}(z) = \mu_{bulk} \quad (1)$$

where subscript “bulk” refers to the bulk fluid and “ff” and “fs” refer to the fluid-fluid and fluid-solid interactions, respectively. The equation shows how the chemical potential of the adsorbed fluid reflects the proximity of the fluid to the molecular wall of the adsorbent. Thus, the SLD model considers the inhomogeneity of the adsorbed phase in describing the molecular interactions of the adsorbed fluid with the adsorbent. The chemical potential of the bulk fluid can be expressed in terms of fugacity as

$$\mu_{bulk} = \mu_0(T) + RT \ln \frac{f_{bulk}}{f_0} \quad (2)$$

where subscript “0” designates an arbitrary reference state and “f” refers to fugacity. Similarly, the chemical potential from fluid-fluid interactions is given as

$$\mu_{ff}(z) = \mu_0(T) + RT \ln \frac{f_{ff}(z)}{f_0} \quad (3)$$

where “ $f_{ff}(z)$ ” is fluid fugacity at position z and “ f_0 ” refers to the same arbitrary reference state as in Equation (2).

The fluid-solid interactions in the model are accounted for through a potential energy function. In particular, the fluid-solid potential is given as

$$\mu_{fs}(z) = N_A [\Psi^{fs}(z) + \Psi^{fs}(L - z)] \quad (4)$$

where “ N_A ” is Avogadro’s number, “ $\Psi(z)$ ” and “ $\Psi(L-z)$ ” are the fluid-solid interactions for the two surfaces of a slit of length L .

Substituting Equations (2), (3) and (4) into Equation (1) provides the equilibrium relationship for adsorption within the slit:

$$f_{ff}(z) = f_{bulk} \exp\left(-\frac{\Psi^{fs}(z) + \Psi^{fs}(L - z)}{kT}\right) \quad (5)$$

where k is the Boltzmann’s constant.

Applying the SLD model, the excess adsorption (n^{Ex}) is given as

$$n^{Ex} = \frac{SA}{2} \int_{\text{Left Side of Slit}}^{\text{Right Side of Slit}} (\rho(z) - \rho_{bulk}) dz \quad (6)$$

where n^{Ex} is the excess adsorption of adsorbate in number of moles per unit mass of adsorbent, and “ SA ” is the surface area of the adsorbate on a particular solid. The lower limit in Equation (6) is $3/8 \sigma_{ff}$, which is $3/8$ of the diameter of an adsorbed molecule touching the left plane surface. The upper limit is $L - 3/8 \sigma_{ff}$, the location of an adsorbed molecule touching the right plane surface. The local density is assumed to be zero for the distances less than $3/8 \sigma_{ff}$ away

from the wall. The left and right sides of the slit each comprise half of the total surface area. The selection of the lower and upper integration limits has been discussed in one of our previous works (Fitzgerald et al., 2006).

The fluid-solid interaction, $\Psi^{fs}(z)$, was represented by Lee's partially-integrated 10-4 potential (Lee, 1988), which is a truncated form of Steele's 10-4-3 potential (Steele, 1974)

$$\Psi^{fs}(z) = 4\pi\rho_{\text{atoms}}\varepsilon_{fs}\sigma_{fs}^2\left(\frac{\sigma_{fs}^{10}}{5(z')^{10}} - \frac{1}{2}\sum_{i=1}^4\frac{\sigma_{fs}^4}{(z'+(i-1)-\sigma_{ss})^4}\right) \quad (7)$$

$$\varepsilon_{fs} = \sqrt{\varepsilon_{ff} \times \varepsilon_{ss}} \quad (8)$$

where ε_{fs} and ε_{ss} are the fluid-solid and solid-solid interaction energy parameters, respectively, and $\rho_{\text{atoms}} = 0.382 \text{ atoms/\AA}^2$. The parameters σ_{ff} and σ_{ss} signify, respectively, the molecular diameter of the adsorbate and the carbon interplanar distances. The carbon interplanar distance was taken to be the value for graphite, 0.335 nm (Subramanian et al., 1995) and values of σ_{ff} and ε_{ff} were taken from Reid et al. (1987). The fluid-solid molecular diameter, σ_{fs} and dummy coordinate z' used in numerical integration of Equation (6) are defined as:

$$\sigma_{fs} = \frac{\sigma_{ff} + \sigma_{ss}}{2} \quad (9)$$

$$z' = z + \frac{\sigma_{ss}}{2} \quad (10)$$

Absolute adsorption ($n_{\text{ads}}^{\text{Abs}}$) can also be determined readily from the adsorbent geometry envisioned in the SLD slit-pore model (Fitzgerald et al., 2003). Specifically, the absolute adsorption calculated in the SLD model is given as

$$n_{\text{ads}}^{\text{Abs}} = V_{\text{ads}}\rho_{\text{ads}} \quad (11)$$

where V_{ads} is adsorbed-phase volume per gram of adsorbent, ρ_{Ads} is adsorbed-phase density estimated by averaging the local adsorbed density across the slit. The adsorbed-phase volume appearing in Equation (11) is given as

$$V_{\text{ads}} = \frac{SA}{2} \left[L - \frac{3}{4} \sigma_{\text{ff}} \right] \quad (12)$$

In this manner, the original SLD model contains three regressed parameters: surface area, SA, slit length, L and solid-solid interaction energy, ϵ_{ss}/k . As explained below, the modification of the SLD model includes an initial regression of one more parameter, δ , the thermal expansion coefficient for the adsorbate.

2.2 Modifying the SLD Model for Improved Temperature Dependence of Adsorption

In this work, an additional modification was implemented in the SLD model to improve the modeling of gas adsorption over larger temperature ranges. The increase in temperature can lead to the expansion of the adsorbed phase. This gives rise to less dense packing of the adsorbed molecules within the adsorbent pore volume, thus decreasing the amount of gas adsorbed. Do (Do, 1998) presented an approach for estimating the changes in adsorbed-phase volume as a function of temperature. In this work, we have implemented a similar approach within the SLD model and incorporated a temperature-dependent adsorbed-phase volume in the SLD model. Specifically, the changes in the adsorbed-phase volume can be related to temperature with the following expression:

$$\int_{V_{\text{ads},0}}^{V_{\text{ads}}} \frac{dV}{V} = - \int_{T_0}^T \delta dT \quad (13)$$

Integrating Equation (13) yields

$$V_{\text{ads}} = V_{\text{ads},0} \exp(-\delta(T - T_0)) \quad (14)$$

where V_{ads} is adsorbed-phase volume, $V_{\text{ads},0}$ is adsorbed-phase volume at a reference temperature T_0 and δ is the thermal expansion coefficient. In this manner, Equation (14) was used to account for the changes in adsorbed-phase volume in the SLD model.

3.1 Database Employed for Adsorption Modeling over Larger Temperature Ranges

To extend the temperature-dependence in SLD model, pure-gas adsorption data on activated carbons were used initially for several reasons, including:

- (a) Adsorption data on coals and shales over wide temperature ranges are extremely limited.
- (b) Adsorption data at multiple temperatures on several activated carbons are readily available in literature.
- (c) Activated carbons possess simpler chemical composition and structure relative to coals and shales while exhibiting similar qualitative adsorption behavior.

A large database was compiled for pure-gas adsorption of 17 adsorbates on 18 activated carbons over significant temperature ranges. Several of the systems were obtained from a database compiled recently by Talu (Talu, 2013), and additional systems were added to enlarge the database for adsorption of natural gas components on several activated carbons. An important criteria used in the database was the presence of adsorbates in the near-critical and supercritical region as well as availability of data for at least three temperatures. Table 1 provides details of the database on activated carbons used in this work. Overall, a total of 2650 adsorption data points were included in the database. About 2100 data points were used for model development and the remaining 500 data points were used as an external set for validation of the generalized model. Further, the available data in the literature on coals and shales at multiple temperatures was also included in the expanded database. These data included

seven coals and six shale samples. The details of these data are listed in Table 1. Thus, the complete database included adsorption measurements on activated carbons, coals and shales.

3.2 Modeling Methodology

The following methodology was used to develop the generalized model presented in this work:

1. The modified SLD model parameters (namely, surface area, SA, slit length (L), solid-solid interaction energy, ϵ_{ss}/k and thermal expansion coefficient, δ) were first regressed to obtain precise representations of the adsorption data. For a given adsorbate/adsorbent pair, data at all temperatures were regressed simultaneously to obtain the parameters.
2. The regressed values of δ were then used to develop a generalized model in terms of available adsorbent and adsorbate molecular properties.
3. The generalized values of δ from the above step were then used in the modified SLD model to obtain *predictions* for the systems in the database as well as systems not used in the model development.

Since the experimental uncertainties in gas adsorption data were generally not provided with the original data in the literature, the objective function (OF) used in the model regressions was the average absolute percentage deviation (%AAD). The regressions were performed by minimizing %AAD in excess adsorption as given below.

$$OF = \frac{1}{N} \sum_{i=1}^N \left(\frac{n_{Cal}^{Ex} - n_{Exp}^{Ex}}{n_{Exp}^{Ex}} \right)_i \times 100 \quad (15)$$

where N is the number of data points, n_{Cal}^{Ex} and n_{Exp}^{Ex} are the calculated and experimental excess adsorption, respectively.

3.3 Generalized Model Development

The regressed values for the thermal expansion coefficient, δ , were used to develop a generalized model in terms of adsorbate and adsorbent properties. The generalized expression for δ was developed by using techniques outlined in some of our earlier work (Golla et al., 2009a). Specifically, a sequential regression algorithm was used to identify properties that best correlate with δ . To prevent over-fitting and retain the predictive capability of the generalized model, the number of properties used in the model was restricted to five.

Results and Discussion

4.1 Modified SLD Model Representations for Gas Adsorption on Activated Carbons

The modified SLD model was used to represent gas adsorption data on several activated carbons from the literature. (In the following discussion, “representations” refer to results obtained with model parameter regressions and “predictions” refers to the results obtained with the generalized model.) Table 2 presents the model parameters for each of the datasets used in this work. The regression results yielded parameters that characterize adsorbent surface properties such as the surface area (in the range of 600-1200 m²/g), effective pore width (in the range of 0.7-1.3 nm) and solid-solid interaction energy (in the range of 20-30 K). These regressed parameters were within the range expected for activated carbons. The thermal expansion coefficient, δ , had an average value of 1.8E-03 [1/R], which was comparable to the average value of 1.7E-03 [1/R] reported by (Do, 1998). Further, the values of δ were similar for closely-related adsorbates such as ethane-ethylene and propane-propylene. However, the values of δ were different for a specific gas adsorbed on different adsorbents. Thus, the thermal expansion coefficient varies as a function of *both* adsorbent and adsorbate properties.

Table 3 presents the overall percentage average absolute deviation (%AAD) obtained in representing gas adsorption on these activated carbons. Three distinct cases were considered in these model regressions. Case 1 utilized a constant adsorbed-phase volume (original SLD model), Case 2 included a temperature-dependent adsorbed-phase volume (modified SLD model) and model regressions were undertaken, whereas Case 3 was based on the generalized model. As evident from Table 3, the overall %AADs for Cases 2 and 3 were about one-half those for Case 1, indicating significant improvement of model representations obtained with the modified SLD model.

Figures 1(a)-(c) depict deviations in excess adsorption from Cases 1 and 2 for selected datasets and clearly show improvement in model representations. As evident in Figure 1, the improved representations were attributed to the datasets that have wider temperature range. Thus, the major advantage of the modification in the work would be the improved descriptions of the temperature dependence of adsorption over larger temperature ranges. Figures 2(a)-(e) illustrate typical examples of model representations obtained from the modified SLD model. These figures also provide comparisons between the original and the modified SLD models and show significantly better fits obtained from the modified SLD model (Case 2). Thus, the adsorbed-phase volume expression utilized in the modified SLD model appears to be effective in improving the temperature-dependence in the model.

The adsorbed-phase volumes from Equation 14 were compared with the volumes obtained from the original SLD model. This was performed on datasets that have adsorption data over wider temperature ranges. In Figure 3, the straight line represents adsorbed-phase volumes determined from Equation 14, whereas each data point represents the adsorbed phase volume obtained from the original SLD model through regressions at each temperature conducted

separately. As evident from Figure 3, the new expression for temperature-dependence of adsorbed-phase volume allows us to predict the variation of adsorbed-phase volume with reasonable accuracy.

4.2 Generalized Model for Predicting Temperature-Dependence of Adsorption

The regressed values for thermal expansion coefficient, δ in Table 2 were used to develop a generalized model in terms of adsorbate and adsorbent properties. A sequential search algorithm outlined elsewhere (Golla et al., 2009b) was used to identify the most significant properties and correlate these properties to describe thermal expansion coefficient, δ . Table 4 lists the properties of adsorbates and adsorbents that were found to be significant in predicting the thermal expansion coefficient. Thus, the thermal expansion coefficient, δ , was generalized with the following expression determined from the approach discussed above.

$$\delta = 6.03\text{E} - 08 M_1^2 - \frac{6.37\text{E} - 03}{M_2} + 4.62\text{E} - 02 M_3^2 - \frac{5.85\text{E} - 01}{M_4} - 3.73\text{E} - 01 \log(M_5) + 8.95\text{E} - 03 \quad (15)$$

where the M_1 to M_5 denote the properties of adsorbates and adsorbents listed in Table 4.

In this manner, Equation (15) was used to obtain generalized values of δ for the systems considered. These values were used in the modified SLD model to obtain the generalized predictions. The statistics for the modified SLD model predictions are listed in Table 3. The overall %AAD for predictions was about 4.9%, which is close to the overall %AAD of 4.3% from direct regressions. Thus, using the generalized expression for δ was useful in obtaining improved accuracy in predictions on these activated carbons, as illustrated in Figures 4(a)-(c).

4.3 Validation of the Generalized Model

The generalized model was validated by testing the model on four additional datasets that were not included in the model development. Thus, these systems were ideally suited to test the model for more realistic predictive capability. Table 5 presents the predictions obtained for each

of these datasets. As shown in the table, the overall %AAD for the generalized predictions on these systems was about 6.4%. This compares with %AAD of 5.1% when direct parameter regressions were performed. Note that the generalized predictions on these systems were obtained by using the δ values from Equation (15). Thus, the comparable level of errors observed for the systems in Table 5 illustrates the promise of the generalized model. An example of this generalized prediction is shown in Figures 5(a)-(b) for adsorbents used for validation. Other systems produced similar predictions, but are not shown here for brevity.

4.4 Comparisons between the Modified SLD Model and Adsorption Models in the Literature

The representations from the modified SLD model were also compared with two adsorption models from the literature, the MPTA-MDP and the modified D-A models (Dundar et al., 2012; Richard et al., 2009). Note that for each adsorbent/adsorbate pair, the MPTA-MDP model contains four parameters of which three are specific to the adsorbate and one is specific for the adsorbent, whereas the modified D-A model has five parameters and all five are specific to the adsorbate. The modified SLD model contains four parameters and two of them are specific to particular gas adsorbed. Thus, for an example of one adsorbent with three adsorbates, the MPTA-MDP, the modified DA and the modified SLD models will require 10, 15 and 8 parameters, respectively.

Adsorption data for methane and nitrogen on activated carbons (Dundar et al., 2012 and Richard et al., 2009) were represented by the SLD model for comparative purposes. The statistics for the SLD, modified D-A, and MPTA-MDP models are provided in Table 6. The RMSEs for the SLD model representation are comparable for nitrogen, but slightly higher for methane compared the modified D-A and MPTA-MDP models. Note that the number of regressed parameters used in the modified SLD model is lowest among these adsorption models.

Further, the SLD model has been generalized in terms of molecular properties, which has not been performed with the literature models. Figures 6(a) and (b) present a comparison of deviations obtained from these models for the above systems. As evident from these figures, the modified SLD model provides a uniform distribution of deviations throughout the pressure and temperature range of measurements for these systems.

Each of the models can provide estimates of the adsorbed-phase density; results are compared in Table 6. The adsorbed phase density is generally needed for estimating absolute adsorption values, which are required for reservoir simulation. Since gas in the adsorbed state is liquid-like, commonly used estimates for the adsorbed-phase densities of methane and nitrogen are the liquid densities at their normal boiling points (Arri and Yee, 1992). As evident from Table 6, among these adsorption models the adsorbed-phase densities predicted by the modified SLD model are closest to the densities of methane and nitrogen at normal boiling points, which are reported to be 0.42 g/cc (Daniel G. Friend, 1988) and 0.8 g/cc (Jacobsen and Stewart, 1973), respectively. Thus, the modified SLD model provides consistent predictions of the adsorbed-phase density based on the experimentally measured excess adsorption.

4.5 Modified SLD Model Predictions at Multiple Temperatures based on Data at a Single Temperature

As part of this work, we tested the efficacy of the modified SLD model to *predict* adsorption data at multiple temperatures based on adsorption data available at a *single* temperature. The activated carbon data were obtained from Berlier and Frère (1997), Frère and De Weireld (2002), Payne et al. (1968) and Zhou et al. (2000). The values of δ were predicted from the generalized correlation developed in this work (Equation 15). The steps contained in this prediction case include: (1) the parameters in the original SLD model, i.e. SA , $\epsilon_{ss/k}$ and L were regressed based on a single adsorption isotherm and (2) the modified SLD model with the

generalized δ values obtained from Equation (15) was then used to *predict* the adsorption at other temperatures.

The overall %AAD for these datasets was about 3.7%, as shown in Table 7. Figures 7(a)-(c) illustrate modified SLD model predictions for adsorption obtained with this approach. The modified SLD model appears capable of providing reliable predictions at several temperatures based on available measurements at only a *single* temperature.

4.6 Modified SLD Model Results for Gas Adsorption at Multiple temperatures on Coals

Based on the promising results of our study of adsorption on activated carbons, we investigated the capability of the modified SLD model to describe gas adsorption at multiple temperatures on coals. The adsorption data on coals were obtained from Sakurovs et al. (2008) and Li et al. (2010). Two specific case studies were conducted depending on the type of available adsorption data. If the adsorption measurements were available at only two temperatures for a gas, the modified SLD model parameters were regressed to obtain model representations. If the adsorption measurements were available at more than two temperatures, then the model parameters were obtained based on two temperature levels and the remaining isotherms were then predicted.

The adsorption data from Sakurovs et al. (2008) were available at 308 and 328 K and therefore, the modified SLD model parameters were regressed from these data. Table 8 lists the regressed SLD model parameters on these coals. The regressed parameters SA , $\epsilon_{ss/k}$ and L were within the range observed in our previous study on coals (Mohammad et al., 2009). Further, the regressed values of δ were comparable to those obtained for activated carbons in this study.

Table 9 presents the statistics for model regressions on these coals. The %AADs for adsorption of CO_2 at temperatures of 308 and 328 K were relatively higher than those of other

gases, which can be attributed to errors in gas density predictions from the equation of state at conditions very close to critical state of CO₂. Overall, the modified SLD model appeared capable of providing precise representations of gas adsorption on coals at different temperatures, as evident from the overall %AAD of about 3%. For illustration purposes, Figure 8 depicts the SLD model representations on Pocahontas coal. Other systems listed in Table 9 produced similar representations, but are not shown here for brevity.

The adsorption data from Li et al. (2010) were available at 308, 318 and 328 K and therefore, the SLD parameters were obtained by using the data at 308 and 318 K. Then, using these parameters, the adsorption isotherms for 328 K were *predicted*. Table 10 presents the SLD model parameters obtained from the isotherms at 308 and 318 K. Using the parameters listed in Table 10, the adsorption at 328 K was predicted. The model statistics for these predictions are listed in Table 11, along with results for 308 and 318 K. For illustration purposes, Figure 9 presents the model predictions obtained at 328 K. Overall, the %AAD for adsorption of methane and CO₂ at 328 K was about 2%, based on the model parameters obtained from other temperatures. Thus, the modified SLD model appears capable of useful predictions of adsorption on these coals. Notwithstanding this result, the approach presented in this study requires additional testing with adsorption data on more coals at wider ranges of temperature.

4.7 Modified SLD Model Representations of Gas Adsorption at Multiple Temperatures on Shales

The modified SLD model was also used to describe adsorption data on shales. The adsorption data on shales were obtained from Rexer et al. (2014). Table 12 presents the SLD model parameters for representations on shale samples. The regressed SLD model parameters such as SA, $\epsilon_{ss/k}$ and L were within ranges observed in our previous work on shale gas adsorption

(Chareonsuppanimit et al., 2012) and the regressed thermal expansion coefficients were also comparable to the values obtained for activated carbons and coals.

Table 13 presents the statistics for model representations on shale samples. The %AAD for each sample varied from about 3 to 6% and the overall %AAD was about 4%. Figures 10(a)-(c) illustrate typical model representations obtained, which indicate useful representations provided by the modified SLD model. Thus, the modified SLD model appears capable of describing the supercritical gas adsorption at multiple temperatures on these shale samples.

5. Conclusions

A modeling study was conducted to extend the SLD model's predictive capability for the temperature dependence of supercritical gas adsorption. The SLD model was modified by including a temperature-dependent expression for the adsorbed-phase volume. The expression accounts for the changes in adsorbed-phase volume with temperature. The thermal expansion coefficient, δ , used to extend the temperature dependence was developed based on data for activated carbons. The modified SLD model thus obtained provided improved representations of gas adsorption on activated carbons over wider ranges of temperature.

The model for thermal expansion coefficient was generalized in terms of molecular properties of adsorbates and adsorbents. Results obtained from the generalized model were comparable to the results obtained from direct regressions. A validation of the generalized model was performed by testing with data on systems that were not utilized in the model development. The generalized model was also used to obtain predictions at multiple temperatures based on available adsorption isotherm at only a single temperature. The modified model was utilized to describe supercritical gas adsorption on coals and shales at multiple temperatures. The model was found capable of providing accurate description of adsorption at multiple temperatures on

these adsorbents. The modeling results on coals and shales indicated that the model is capable of describing gas adsorption at several temperatures. The generalized model presented in this work can be further tested once additional data on coals and shales at wider ranges of temperatures becomes available.

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Table 1. Database for Pure-Gas Adsorption on Activated Carbons, Coals and Shales

Adsorbent	Adsorbate	Pressure Range (MPa)	Temperature Range (K)	BET Surface Area (m ² /g)	NDP*	Reference
Data Set for Activated Carbons						
PCB	CH ₄	0.1-3.7	296-480	1150	65	(Ritter and Yang, 1987)
	CO ₂	0.2-5.8				
	CO	0.1-1.3				
	H ₂ S	0.3-6.7				
Norit-RB1	CH ₄	0.1-0.8	294-350	1100	128	(Van Der Vaart et al., 2000)
	CO ₂					
Nuxit-Al	CH ₄	0.01-0.6	293-363	1200	447	(Szepeszy, 1963)
	C ₂ H ₂	0.001-0.1				
	C ₂ H ₆	0.01-0.7				
	C ₂ H ₄	0.01-0.6				
	C ₃ H ₈	0.01-0.7				
	C ₃ H ₆	0.01-0.8				
	nC ₄ H ₁₀	0.001-0.1				
Columbia Grade L	CH ₄	0.02-1.5	311-478	1152	272	(Ray and Box, 1950)
	N ₂	0.03-1.5				
	C ₂ H ₂	0.01-0.1				
	C ₂ H ₆	0.01-1.5				
	C ₂ H ₄	0.01-1.5				
	C ₃ H ₈	0.01-0.7				
	C ₃ H ₆	0.01-0.1				
BPL	CH ₄	0.01-3.8	213-301	988	233	(Reich, 1980)
	CO ₂	0.003-3.84				
	C ₂ H ₆	0.001-1.71				
	C ₂ H ₄	0.001-1.70				
F30/470	CH ₄	0.44-6.0	303-383	993	154	(Berlier and Frère, 1997)
	N ₂	0.39-6.0				
F30/470	CO ₂	0.05-2.5	288-328	993	113	(Frère and De Weireld, 2002)

**Table 1. Database for Pure-Gas Adsorption on Activated Carbons, Coals and Shales –
Cont'd**

Adsorbent	Adsorbate	Pressure Range (MPa)	Temperature Range (K)	BET Surface Area (m2/g)	NDP*	Reference
LAC	C ₃ H ₈	0.001-0.1	273-343	1011	102	(Mofarahi et al., 2003)
	C ₃ H ₆					
Carbotech	CH ₄	0.006-3.4	300-318	885	32	(Martin et al., 2011)
KT	CH ₄	0.6-3.4	300-318	668	31	
Maxsorb II	CH ₄	0.1-1.2	281-343	2768	126	(Wang et al., 2010)
Templated Carbon	CH ₄	0.05-4.6	263-303	1500	71	(Chen et al., 2011)
	C ₂ H ₆	0.02-2.0				
Maxsorb III	CH ₄	0.06-2.4	263-303	3140	128	(Loh et al., 2010)
Columbia Grade G	CH ₄	0.1-13.8	283-343	1157	141	(Payne et al., 1968)
	nC ₄ H ₁₀	0.003-0.8				
	C ₃ H ₈	0.001-1.4				
JX101	CH ₄	0.01-1.0	283-313	1500	107	(Qin Wu, 2005)
External Data Set For Activated Carbons Used for Validation						
Coconut shell-derived carbon	CH ₄	0.1-9.3	235-333	3106	122	(Zhou et al., 2000)
	N ₂	0.5-9.0	198-298		61	
F-400	CO ₂	0.14-9.4	303-318	850	116	(Humayun and Tomasko, 2000)
CNS-201	CH ₄	0.01-6.8	243-333	2000	62	(Dundar et al., 2012)
CO-64	N ₂	0.01-6.6	153-298	1150	135	
Data Set for Coals						
Pocahontas	CH ₄	1.4-13.8	308-328	N/A*	20	(Sakurovs et al., 2008)
	N ₂		298-328		20	
	CO ₂		308-328		20	
Illinois-6	CH ₄	14-13.8	308-328	N/A	20	
	N ₂		298-328		20	
	CO ₂		308-328		20	

**Table 1. Database for Pure-Gas Adsorption on Activated Carbons, Coals and Shales –
Cont'd**

Adsorbent	Adsorbate	Pressure Range (MPa)	Temperature Range (K)	BET Surface Area (m2/g)	NDP*	Reference
Data Set for Coals (Cont'd)						
Beulah Zap	CH ₄	14-13.8	308-328	N/A	20	(Sakurovs et al., 2008)
	N ₂		298-328		20	
	CO ₂		308-328		20	
Hulun Buir	CH ₄	2.5-19.1	308-328	N/A	41	(Li et al., 2010)
	CO ₂	3.8-24.2			80	
Pingdingshan	CH ₄	3.0-19.7	308-328	N/A	43	
	CO ₂	5.2-24.6			71	
Jingcheng	CH ₄	1.2-19.0	308-328	N/A	48	
	CO ₂	3.6-24.6			67	
Data Set for Shales						
WIC7145	CH ₄	0.07-12.5	318-358	6.7	26	(Rexer et al., 2014)
WIC7155		0.05-13.0		4.3	28	
HAR7038		0.02-12.0		N/A	25	
HAR7060		0.06-13.5		N/A	14	
HAD7090		0.05-12.8		25.1	23	
HAD7119		0.07-13.8		21.0	29	
Total					3321	

*NDP is number of data points and N/A denotes not available.

**Table 2. Modified SLD Model Parameters for Gas Adsorption
on Activated Carbons**

Adsorbent	Adsorbate	Model Parameters			
		SA (m ² /g)	δ (1/R)	L (nm)	$\epsilon_{ss/k}$ (K)
PCB	CH ₄	708.1	1.42E-03	0.94	29.0
	CO ₂	849.3	1.82E-03		
	CO	755.8	6.66E-04		
	H ₂ S	971.5	9.23E-04		
Norit-RB1	CH ₄	639.2	1.26E-03	1.04	35.3
	CO ₂	647.0	3.16E-03		
Nuxit-Al	CH ₄	512.7	2.40E-03	1.09	34.2
	C ₂ H ₂	664.2	2.56E-03		
	C ₂ H ₆	685.5	2.39E-03		
	C ₂ H ₄	699.9	2.42E-03		
	C ₃ H ₈	827.1	1.74E-03		
	C ₃ H ₆	798.4	1.80E-03		
	nC ₄ H ₁₀	825.3	1.11E-03		
Columbia Grade L	CH ₄	694.6	1.59E-03	1.16	36.6
	N ₂	636.7	9.39E-04		
	C ₂ H ₂	709.7	3.98E-03		
	C ₂ H ₆	826.9	1.41E-03		
	C ₂ H ₄	795.6	1.05E-03		
	C ₃ H ₈	844.4	1.10E-03		
	C ₃ H ₆	956.1	1.93E-03		
BPL	CH ₄	524.4	1.89E-03	1.00	30.5
	CO ₂	627.9	2.71E-03		
	C ₂ H ₆	710.9	1.90E-03		
	C ₂ H ₄	686.8	1.97E-03		
F30/470	CH ₄	580.2	1.76E-03	1.07	36.2
	N ₂	477.4	1.63E-03		
F30/470	CO ₂	667.4	2.49E-03	1.07	36.2
LAC	C ₃ H ₈	924.8	2.61E-03	1.00	33.9
	C ₃ H ₆	1006.9	1.80E-03		
Carbotech	CH ₄	449.5	1.38E-03	1.27	37.2
KT	CH ₄	407.3	5.36E-04	0.86	41.2
Maxsorb II	CH ₄	1813.8	1.76E-03	0.71	14.7

**Table 2. Modified SLD Model Parameters for Gas Adsorption
on Activated Carbons - Cont'd**

Adsorbent	Adsorbate	Parameters			
		SA (m ² /g)	δ (1/R)	L (nm)	$\epsilon_{ss/k}$ (K)
Templated Carbon	CH ₄	973.6	4.71E-04	1.39	21.7
	C ₂ H ₆	1076.6	2.16E-03		
Maxsorb III	CH ₄	1088.6	1.64E-03	1.85	23.7
Columbia Grade G	CH ₄	770.2	1.68E-03	1.11	29.6
	nC ₄ H ₁₀	984.6	6.95E-04		
	C ₃ H ₈	1127.6	1.10E-03		
JX101	CH ₄	665.3	2.57E-03	0.76	26.7
	N ₂	634.3	2.13E-03		

**Table 3. SLD Results for Modeling Temperature Dependence of Adsorption
on Activated Carbons**

Adsorbent	Adsorbate	NDP	%AAD in Excess Adsorption		
			Original SLD Model (Case 1)	Modified SLD Model	
				Regressed δ (Case 2)	Generalized δ (Case 3)
PCB	CH ₄	22	14.9	3.3	3.9
	CO ₂	12	19.0	5.2	11.5
	CO	15	10.3	5.7	5.8
	H ₂ S	16	9.9	4.3	5.8
Norit RB-1	CH ₄	64	7.3	4.5	4.3
	CO ₂	64	9.5	5.1	5.4
Nuxit Al	CH ₄	29	6.3	3.4	3.5
	C ₂ H ₂	99	10.7	5.5	5.6
	C ₂ H ₆	92	10.7	4.1	4.5
	C ₂ H ₄	72	3.2	3.2	3.2
	C ₃ H ₈	67	4.8	4.8	4.8
	C ₃ H ₆	54	5.1	2.8	2.9
	nC ₄ H ₁₀	34	10.9	4.4	5.0
Columbia Grade L	CH ₄	43	11.4	5.2	5.1
	N ₂	32	9.5	4.7	4.6
	C ₂ H ₂	11	12.7	6.1	8.4
	C ₂ H ₆	57	10.9	4.9	12.4
	C ₂ H ₄	62	9.9	6.3	9.7
	C ₃ H ₈	46	15.8	6.2	6.4
	C ₃ H ₆	21	7.2	5.7	9.0
BPL	CH ₄	60	16.2	6.2	6.9
	CO ₂	49	11.6	4.9	4.9
	C ₂ H ₆	52	11.4	3.9	3.7
	C ₂ H ₄	72	10.5	2.7	4.7
F30/470	CH ₄	82	9.0	4.5	4.2
	N ₂	72	7.1	1.9	1.7
F30/470	CO ₂	113	5.0	2.6	2.6
LAC	C ₃ H ₈	51	12.2	7.9	7.9
	C ₃ H ₆	51	12.6	6.9	9.2
Carbotech	CH ₄	32	3.0	2.5	2.5
KT	CH ₄	31	1.1	1.0	1.3
Maxsorb II	CH ₄	126	5.9	2.3	2.3
Templated Carbon	CH ₄	41	7.7	6.3	8.1
	C ₂ H ₆	30	7.6	4.3	4.4
Maxsorb III	CH ₄	128	6.2	3.3	3.5

Table 3. SLD Results for Modeling Temperature Dependence of Adsorption on Activated Carbons – Cont'd

Adsorbent	Adsorbate	NDP	%AAD in Excess Adsorption		
			Original SLD Model (Case 1)	Modified SLD Model	
				Regressed δ (Case 2)	Generalized δ (Case 3)
Columbia Grade G	CH ₄	39	4.8	4.8	4.8
	nC ₄ H ₁₀	55	4.8	3.5	3.5
	C ₃ H ₈	47	4.7	3.8	3.9
JX101	CH ₄	52	5.8	4.9	4.7
	N ₂	55	5.5	3.5	3.8
Overall		2150	8.2	4.3	4.9

Table 4. Molecular Properties of Adsorbates and Adsorbents Used in Generalized Expression for Thermal Expansion Coefficient, δ

Notation from Equation (15)	Molecular Property	Description	Type of Molecular Property
M ₁	%C	% of carbon atoms	constitutional index
M ₂	Mor13m	signal 13 weighted by mass	3-D geometrical index
M ₃	Mor06v	signal 06 weighted by van der Waals volume	3-D geometrical index
M ₄	BET	BET surface area of adsorbent	adsorbent surface property
M ₅	Di	D total accessibility index / weighted by ionization potential	whim descriptor

Table 5. Validation Results for the Modified SLD Model on Datasets Not Used in the Model Development

Adsorbent	Adsorbate	NDP	%AAD in Excess Adsorption		Reference
			Regressed δ	Generalized δ	
Coconut shell-derived carbon	CH ₄ , N ₂	183	2.7	4.0	(Zhou et al., 2000)
F-400	CO ₂	116	9.1	9.3	(Humayun and Tomasko, 2000)
CNS-201	CH ₄	62	3.9	5.4	(Dundar et al., 2012)
CO-64	N ₂	135	4.6	7.0	
Overall		496	5.1	6.4	

**Table 6. Pure-Gas Adsorption on CNS-201 and CO-64 Activated Carbons:
Comparison with Literature Models**

Model	Number of Regressed Parameters	Overall RMSE* (mmol/g)		Adsorbed Phase Density Prediction (g/cc)		Liquid Density at Normal Boiling Point (g/cc)		Reference
		CH ₄ on CNS-201	N ₂ on CO-64	CH ₄ on CNS-201	N ₂ on CO-64	CH ₄	N ₂	
MPTA-MDP	10	0.10	0.35	0.49	0.96	0.42	0.81	(Dundar et al., 2012)
Modified DA	15	0.11	0.58	0.58	1.01			(Dundar et al., 2012)
Modified SLD	8	0.19	0.35	0.36	0.73			This work

*RMSE is the root mean squared error in excess adsorption.

Table 7. Modified SLD Model Results for Predicting Adsorption Based on Data at a Single Temperature

Adsorbent	Adsorbate	Temperature (K)	NDP	%AAD in Excess Adsorption*
F30/470	CH ₄	303	16	1.6
		323	16	2.0
		343	17	2.0
	N ₂	303	16	3.4
		323	12	2.4
		343	15	3.3
	CO ₂	303	16	3.1
		308	32	3.1
		318	16	4.1
		328	17	4.0
Columbia Grade G	C ₃ H ₈	303	10	3.4
		313	11	6.1
		323	10	7.5
		333	10	5.7
	CH ₄	303	12	1.6
		313	10	2.1
		323	13	2.7
Coconut shell-derived carbon	CH ₄	313	20	1.2
		333	19	2.9
Overall				3.7

*%AADs in the highlighted rows are percentage average absolute deviation for SLD model representations with respect to experimental data at 303 or 313 K. Overall %AAD does not include the highlighted isotherms for which parameters were regressed.

Table 8. Modified SLD Model Parameters for Gas Adsorption on Coals (Data from (Sakurovs et al., 2008))

Adsorbent	Adsorbate	Model Parameters			
		SA (m ² /g)	L (nm)	$\epsilon_{ss/k}$ (K)	δ (1/R)
Pocahontas	CH ₄	71.6	1.02	33.7	1.91E-03
	N ₂	53.2			2.74E-03
	CO ₂	79.3			2.02E-03
Illinois-6	CH ₄	61.5	1.21	26.1	1.81E-03
	N ₂	50.2			2.24E-03
	CO ₂	93.3			1.02E-03
Beulah Zap	CH ₄	51.5	1.31	39.5	4.10E-03
	N ₂	38.2			3.51E-03
	CO ₂	85.3			1.96E-03

Table 9. Modified SLD Model Representations on Coals

Adsorbent	Adsorbate	Temperature (K)	NDP	Modified SLD Model		Reference
				%AAD	Overall	
Pocahontas	CH ₄	308	10	1.9	1.4	(Sakurovs et al., 2008)
		328	10	1.0		
	N ₂	298	10	1.1	1.1	
		328	10	1.0		
	CO ₂	308	10	6.7	6.7	
		328	10	6.6		
Illinois-6	CH ₄	308	10	1.9	2.5	
		328	10	3.1		
	N ₂	298	10	2.3	2.2	
		328	10	2.1		
	CO ₂	308	10	5.7	4.6	
		328	10	3.6		
Beulah Zap	CH ₄	308	10	2.4	1.6	
		328	10	0.7		
	N ₂	298	10	1.2	1.3	
		328	10	1.5		
	CO ₂	308	10	5.8	5.4	
		328	10	4.9		
Overall			180		3.0	

Table 10. Modified SLD Model Parameters for Gas Adsorption on Coals (Data from Li et al. (2010))

Adsorbent	Adsorbate	Model Parameters*			
		SA (m ² /g)	L (nm)	$\epsilon_{ss/k}$ (K)	δ (1/R)
Hulun Buir	CH ₄	69.6	1.24	31.3	7.45E-03
	CO ₂	98.9			1.94E-03
Pingdingshan	CH ₄	58.2	1.27	30.5	2.22E-03
	CO ₂	62.4			1.37E-03
Jingcheng	CH ₄	105.3	0.93	34.5	1.77E-03
	CO ₂	115.2			2.86E-03

*Model parameters were obtained from SLD model regression using adsorption data of methane and CO₂ at 308 and 318 K from Li et al. (2010). These sets of parameters were used for predicting adsorption at 328 K.

Table 11. Modified SLD Model Representations and Predictions for Gas Adsorption on Coals

Adsorbent	Adsorbate	NDP	Temperature (K)	%AAD* in Excess Adsorption	Reference
Hulun Buir	CH ₄	12	308	1.0	(Li et al., 2010)
		15	318	0.6	
		14	328	2.2	
	CO ₂	27	308	4.2	
		26	318	2.6	
		27	328	2.5	
Pingdingshan	CH ₄	12	308	2.3	
		15	318	1.8	
		16	328	2.3	
	CO ₂	24	308	4.9	
		25	318	3.9	
		22	328	2.3	
Jingcheng	CH ₄	16	308	0.6	
		15	318	0.6	
		17	328	0.8	
	CO ₂	24	308	4.3	
		22	318	2.9	
		21	328	2.7	
Overall		117		2.2	

*%AADs in the highlighted rows are percentage average absolute deviation for SLD model representations with respect to experimental data at 308 and 318 K. Overall %AAD does not include the highlighted isotherms for which parameters were regressed.

Table 12. Modified SLD Model Parameters for Gas Adsorption on Shales

Adsorbent	Adsorbate	Sample#	Model Parameters			
			SA (m ² /g)	L (nm)	$\epsilon_{ss/k}$ (K)	δ (1/R)
Posidonia Shales	CH ₄	WIC7145	8.7	1.85	26.4	1.93E-03
		WIC7155	8.9	1.79	21.6	2.31E-03
		HAR7038	11.81	0.71	8.45	2.08E-03
		HAR7060	9.3	0.70	8.6	1.40E-03
		HAD7090	10.0	1.14	29.3	1.75E-03
		HAD7119	9.6	1.04	20.5	1.43E-03

Table 13. Modified SLD Model Representations on Shales

Adsorbent	Adsorbate	Sample#	NDP	Temperature (K)	Modified SLD Model		Reference
					%AAD	Overall	
Posidonia Shales	CH ₄	WIC7145	26	318	5.3	5.3	(Rexer et al., 2014)
				338	5.6		
				358	5.2		
		WIC7155	28	318	3.2	3.6	
				338	4.0		
				358	3.8		
		HAR7038	25	318	6.6	5.7	
				338	5.2		
				358	5.5		
		HAR7060	14	318	3.9	5.0	
				338	6.2		
				358	4.6		
		HAD7090	23	318	4.1	3.7	
				338	2.9		
				358	4.0		
		HAD7119	29	318	3.7	2.7	
				338	2.8		
				358	1.7		
Overall			145			4.2

Figure 1(a). Deviations of SLD Model Representations for Methane Adsorption on Maxsorb II (Points are Data from Wang et al. (2010))

Figure 1(b). Deviations of SLD Model Representations for Methane Adsorption on Columbia Grade G (Points are Data from (Payne et al., 1968))

Figure 1(c). Deviations of SLD Model Representations for CO₂ Adsorption on Norit-RB1
(Points are Data from Van Der Vaart et al. (2000))

Figure 2(a). Modified SLD Model Representations for Methane Adsorption on F30/470
(Points are Data from Berlier and Frère (1997))

Figure 2(b). Modified SLD Model Representations for Nitrogen Adsorption on F30/470
(Points are Data from Berlier and Frère (1997))

Figure 2(c). Modified SLD Model Representations for CO₂ Adsorption on F30/470
(Points are Data from Frère and De Weireld (2002))

Figure 2(d). Modified SLD Model Representations for Methane Adsorption on Maxsorb III
(Points are Data from Loh et al. (2010))

Figure 2(e). Modified SLD Model Representations for Ethylene Adsorption on Nuxit-Al
(Points are Data from Szepeszy (1963))

Figure 3. Temperature Effect on Adsorbed-Phase Volume (Points are based on Data from Ray and Box (1950))

Figure 4(a). Generalized Predictions of the Modified SLD Model for Ethane Adsorption on Templated Carbon
(Points are Data from Chen et al. (2011))

Figure 4(b). Generalized Predictions of the Modified SLD Model for Ethylene Adsorption on Nuxit-Al (Points are Data from Szepesy (1963))

Figure 4(c). Generalized Predictions of the Modified SLD Model for Ethylene Adsorption on Maxsorb III
 (Points are Data from Loh et al. (2010))

Figure 5(a). Generalized Predictions of the Modified SLD Model for Methane Adsorption on Coconut shell-derived carbon (Points are Data from Zhou et al. (2000))

Figure 5(b). Generalized Predictions of the Modified SLD Model for Nitrogen Adsorption on CO-64
(Points are Data from Dundar et al. (2012))

Figure 6(a). Deviations of Modified DA, MPTA-MDP and SLD Model Representations for Methane Adsorption on CNS-201 (Points are Data from Dundar et al. (2012))

Figure 6(b). Deviations of Modified DA, MPTA-MDP and SLD Model Representations for Nitrogen Adsorption on CO-64 (Points are Data from Dundar et al. (2012))

Figure 7(a). Modified SLD Model Predictions for Methane Adsorption on F30/470 Based on a Single Adsorption Isotherm (Points are Data from Berlier and Frère (1997))

Figure 7(b). Modified SLD Model Predictions for Nitrogen Adsorption on F30/470 Based on a Single Adsorption Isotherm (Points are Data from Berlier and Frère (1997))

Figure 7(c). Modified SLD Model Predictions for CO₂ Adsorption on F30/470 Based on a Single Adsorption Isotherm (Points are Data from Frère and De Weireld (2002))

Figure 8. Modified SLD Model Representations for Methane, Nitrogen and CO₂ Adsorption on Pocahontas Coal (Points are Data from Sakurovs et al. (2008))

**Figure 9. Modified SLD Model Predictions for Methane and CO₂ Adsorption at 328 K on Hulun Buir Coal
(Points are Data from Li et al. (2010))**

Figure 10(a). Modified SLD Model Representations for Methane Adsorption on Posidonia Shale (WIC7115)
(Points are Data from Rexer et al. (2014))

Figure 10(b). Modified SLD Model Representations for Methane Adsorption on Posidonia Shale (HAD7090)
(Points are Data from Rexer et al. (2014))

Figure 10(c). Modified SLD Model Representations for Methane Adsorption on Posidonia Shale (HAD7119)
(Points are Data from Rexer et al. (2014))

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