

# Comparison of Temperature Dependent Gas Adsorption Models and their Application to Shale Gas Reservoirs

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## **Abstract**

Significant quantities of gas are adsorbed onto the rock matrix in shale gas reservoirs. Accounting for this adsorbed gas in reservoir calculations is key for realistic estimations of gas in place, overall gas production and later as a target for enhanced gas recovery methods like thermal stimulation. Classical Langmuir isotherm fails to represent gas adsorption at multiple temperatures thereby making its application in thermal stimulation strategies limited. In this work, several temperature-dependent gas adsorption models were reviewed and grouped further into both temperature dependent and independent Langmuir volume. Application of the models to several shale gas data sets obtained from different regions show minimal differences in the successful prediction of gas adsorption using either the temperature dependent or independent Langmuir volume models. However, caution is to be exercised in the choice of

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models for use in numerical simulation studies when extrapolating to temperatures that might be outside laboratory conditions and for which no data exist. For such cases, use of the models might result in an under- or over-estimation of the volume of adsorbed gas.

## **1. Introduction**

Critical analysis and understanding of adsorption processes and its contribution to the overall recovery in shale gas reservoirs is crucial because of the high adsorption rate of most shale gas reservoirs. The large surface area of shale means more gas can be adsorbed compared to that stored by compression in the pore matrix. The process of gas adsorption in shale gas is often represented by Langmuir isotherm with many numerical simulation ignoring the temperature dependence of gas adsorption. Limited studies exist on the application of temperature dependent models on shale gas adsorption and in studies that exist, only one or two models have been successfully applied and compared. The need to incorporate temperature dependent models in numerical simulation of shale gas reservoirs is important because they are able to describe the adsorption process at multiple temperatures. However selection of these models is crucial in accounting for the right amount of adsorbed gas when conducting simulation exercises. A comparative analysis of these models and also the effect of either using temperature dependent or independent Langmuir volume is important when choosing to apply these models in numerical exercises involving shale gas reservoirs.

Shale gas as an unconventional natural gas resource has proven to be an abundant source of energy especially in the USA where it has revolutionized the energy sector. The gas is typically methane but may also be a mixture of methane and other gases such as ethane, propane and butane (1). The storage of the natural gas in shale formation is believed to occur in many forms such as free gas stored within the pores and natural/induced fractures, adsorption on internal

surface area of shale, sorbed gas in both organic and inorganic matter, and gas dissolved as a solution in the formation water (2,3).

There are different factors controlling the adsorption capacity of methane on shale. These include, but not limited to, total organic carbon, pressure, temperature, thermal maturity, moisture and shale clay minerals (4). Total Organic Carbon (TOC) is seen as a primary factor that contributes to the adsorption capacity of shale. Previous experimental studies have reported high TOC of shale resulting in a higher capacity for the adsorbed gas (5–9).

Adsorption capacity of shale can also be affected by pressure. Higher reservoir pressure corresponds to a higher adsorption capacity. Rault et al.(10) points out that with low pressure, higher binding energy is required for gas adsorption and hence the adsorbed content decreases compared with when the pressure is very high. In terms of production from shale gas reservoirs, low matrix permeability of shale reservoirs implies that considerable time will be needed for the average pressure to drop to a level where gas desorption becomes significant, by which time the economic shut in limits of the well must have been reached. Therefore dependence on pressure depletion alone for ultimate recovery of gas adsorbed on the shale matrix will contribute less towards overall gas production in the well.

One other decisive factor contributing to the adsorption capacity is temperature. The process of shale gas adsorption results in an exothermic reaction. Thereby, shale gas adsorption capacity is expected to decrease with increasing temperature. The temperature dependence of adsorption capacity is greatly controlled by the isosteric heat which also depends on the surface coverage. Many experimental studies have been conducted on the influence of temperature on adsorbed shale gas content (3,6,11–18)

According to Guo et al. (4), adsorbed gas content increased with increasing pressure under isothermal conditions whereas the gas content decreased under isobaric conditions for increases in temperature. Guo et al. (4) obtained adsorption isotherms at different temperatures

and also at different pressure points for shale samples of the Ordos Basin, China. Their studies also noted that, for low pressure and temperature zones, pressure had a much greater effect on the adsorbed gas content. For high pressure and temperature zones, however, the effect of temperature on the adsorbed gas content was dominant.

The amount of gas in shale gas reservoir is affected by the existence of geothermal gradients. There are temperature differential at different depth in the reservoir and due to the effect of temperature on the gas adsorbed, the gas in place will differ at each depth. Temperatures are usually at near critical or supercritical region of the adsorbed gas and hence, adsorption models should be able to provide reliable predictions of the temperature dependence of adsorption in these regions (13).

## 2. Description of Adsorption Models

### 2.1 Temperature dependent Langmuir volume or Saturation loading

Since gas adsorption is an exothermic reaction, the heat produced is normally dissipated towards immediate surrounding. The ratio of the change that occurs in the adsorbates enthalpy to the change in the adsorbed amount is normally referred to as the heat of adsorption. The adsorption equilibrium constant,  $b(T)$  normally represented by the van't Hoff expression, is temperature dependent (19).

$$b = b_0 \exp\left(-\frac{\Delta H_{ads}}{RT}\right) \dots\dots\dots (1)$$

$\Delta H_{ads}$  is the adsorption enthalpy change for component .

Langmuir isotherm remains one of the most commonly used adsorption model in coal/shale gas simulation with most commercial simulators such as CMG and Schlumberger Eclipse implementing gas adsorption modelling using Langmuir isotherm.

The expression for the adsorption on the microporous adsorbent is given as

$$V = V_L \frac{bp}{1+bp} \dots\dots\dots (2)$$

where  $V_L$  refers to the theoretical maximum Langmuir volume.

This equation can be written in terms of saturation loading as the temperature independent form used in this study:

$$\text{Langmuir 3: } V = q_{so} \frac{bp}{1+bp} \quad (2a)$$

where  $q_{so}$  is the saturation loading similar to the Langmuir volume.

While the adsorption equilibrium constant  $b$  is temperature-dependent as can be seen in equation (1), the Langmuir volume or saturation loading for the Langmuir isotherm is considered constant and does not change with temperature. This assumption has been made by several researchers. Zhu et al. (19) stated that saturation loading should be constant and independent of operating temperature in their studies of Zeolites. Do (20) conducted studies with the temperature dependent form of the Sips isotherm. The results from the fitting of the Sips isotherm to several temperatures showed that the saturation loading at different temperatures was the same as the reference temperature indicating the temperature independence of the saturation loading. Also, a new adsorption model was proposed by Do and Do (21) for heterogeneous solids and tested with isotherm data for various adsorbates on activated carbon and zeolites. They concluded that thermal expansion parameter for the saturation capacity is very small, implying that the saturation loading is independent of temperature.

Other researchers, however, have strongly supported the idea of temperature dependence of the saturation loading (22). According to Malek and Farooq (23), the temperature dependence of saturation loading accounts for the thermal expansion of the adsorbed phase leading to decreasing monolayer coverage at very high temperatures.

Various temperature-dependent equations have been proposed for saturation loading but the exact functional form and the thermodynamic consistency of the parameters are not completely validated (24). Hwang et al. (25) proposed the dependence of the saturation loading on temperature as

$$q_s = a_1 + a_2/T \dots\dots\dots (3)$$

An empirical equation to describe the temperature-dependent saturation loading was given (23,26) as

$$q_s = q_{so} \exp\left(\frac{-q_1}{T}\right) \dots\dots\dots (4)$$

, with  $q_1 = 0$  if the saturation loading is not temperature dependent.

$q_{so}$  is temperature independent constant.

There have been other works on petroleum applications including methane adsorption on coal and shale. Ji et al. (17) conducted experiments on shale samples from southern eastern Ordos Basin in China to ascertain the effects of TOC, maturity, clay mineral and thermodynamic conditions such as pressure and temperature on the methane sorption capacity. A positive correlation was found to exist between the sorption capacity of the samples and the TOC, whereas the clay mineralogy content of the samples had minimal effect on their adsorption capacity. Ji et al. (17) developed a computational algorithm that allowed for the calculation of methane sorption capacity as a function of TOC, temperature and pressure. They found that with the increase in temperature the Langmuir pressure increases exponentially while the Langmuir volume undergoes a linear decrease. Ye et al. (12) also proposed an exponential relation to describe the temperature dependence of the Langmuir volume based on analyzing experimental data for gas adsorption capacity on different shales. The dependence of

temperature of the Langmuir volume have been attributed to the isosteric heat of adsorption by several researchers (6,9,12,17,18) .

## 2.2 Temperature dependent Langmuir Models

Equation (1), (3) and (4) can be applied to the classical Langmuir isotherm to obtain several temperature dependent Langmuir Models. These equations can be expressed as follows

$$\text{Langmuir 1: } V = \left( a_1 + \frac{a_2}{T} \right) \left( \frac{bp}{1+bp} \right) \dots\dots\dots (5)$$

$$\text{Langmuir 2: } V = q_{so} \exp\left(\frac{-q_1}{T}\right) \left( \frac{bp}{1+bp} \right) \dots\dots\dots (6)$$

$$\text{Where } b = b_0 \exp\left(-\frac{\Delta H_{ads}}{RT}\right).$$

Due to heterogeneity of most adsorbent, the assumption of homogenous surface by Langmuir isotherm does not apply. Shale is considered to be an extremely heterogeneous adsorbent (27). In this case, the use of an adsorption model such as Freundlich equation combined with Langmuir equation can be applied by which the adsorbent heterogeneity can be represented successfully (24). However, very few works have been found on the application of combined Langmuir and Freundlich equation in modelling shale gas adsorption data. An expression for the Langmuir–Freundlich equation is given (24) as

$$\text{Langmuir Freundlich 3: } q = \frac{q_s bp^n}{1+bp^n} \dots\dots\dots (7)$$

The parameter  $n$  represents the surface heterogeneity and has been added to the Langmuir equation without any proper physical meaning ((20,24,28). Higher values of  $n$  greater than one represents a highly heterogeneous adsorbent.

By combining the temperature-dependent saturation equations (3) and (4) with equation (7), the following temperature-dependent Langmuir –Freundlich equations can be proposed which involves the temperature-dependent parameter  $b$  .

$$\text{Langmuir Freundlich 1: } V = \left( a_1 + \frac{a_2}{T} \right) \left( \frac{bp^n}{1+bp^n} \right) \dots\dots\dots (8)$$

$$\text{Langmuir Freundlich 2: } V = q_{so} \exp\left(\frac{-q_1}{T}\right) \left( \frac{bp^n}{1+bp^n} \right) \dots\dots\dots (9)$$

### 2.3 Bi-Langmuir Model

Lu et al. (6) claimed that Langmuir isotherm is insufficient in describing the adsorption in Devonian shale gas reservoirs. They noted that temperature dependence is very often ignored while it plays an important role especially during thermal stimulation as a recovery method. In fact, both pressure and temperature are major factors in determining the amount of adsorbed gas on the shale. By investigating adsorption as a function of pressure and temperature, the effects of temperature is significant (6) . They reported a general reduction in the adsorption capacity of shale at increased temperatures. Bi-Langmuir model was used to reconcile the data obtained from samples that were used in the experiment. Although Langmuir model might be suitable to represent gas/shale isotherms measured at a single temperature, Bi-Langmuir model was thought to be more suitable for representation of multiple temperatures. Lu et al. (6) argues that the assumption of homogeneous adsorbent in the Langmuir model may not be suitable for a gas/shale system due to the fact that different materials such as clay minerals and kerogen may contribute to gas desorption.

Bi – Langmuir model, written in the following form, is used to describe gas adsorption on an adsorbent having two discrete sharp peaks of adsorption energy distribution. One term of the equation describes the gas adsorption on clay minerals whiles the other term accounts for gas adsorption on kerogen.



$$\frac{N_{ads}}{N_m} = f_1 \frac{k_1(T) p}{1 + k_1(T) p} + (1 - f_1) \frac{k_2(T) p}{1 + k_2(T) p} \dots\dots\dots (10)$$

$$k(T) = k_o T^{-1/2} \exp(-E / RT)$$

Where,

$f_1$  = fraction of adsorption site

$k_{1,2}$  = adsorption equilibrium constant

$N_{ads}$  = amount of adsorbed gas per unit volume adsorbent

$N_m$  = Amount of adsorbed gas at monolayer coverage

$E_1$  = Adsorption energy

## 2.4 Exponential Model

Ye et al. (12) conducted similar studies on temperature dependence of gas adsorption. Their studies proposed a new improved Langmuir model that was used in evaluating gas adsorption capacity of shale under various pressures and temperatures.

Gas adsorption is considered as an exothermic process and hence increasing temperature will restrain the gas adsorption process thus causing a general reduction in the amount adsorbed as temperature increases (6,12).

The constant Langmuir volume ( $V_L$ ) was modified to be a function of temperature and thereby an exponential model was proposed that relate  $V_L$  to temperature as

$$V_L = V_s \exp(-D_T T) \dots\dots\dots (11)$$

The final exponential model derived, expressing a temperature-dependent Langmuir model can be defined as

$$V = \frac{V_s \exp(-D_T T) p}{p + \sqrt{T} / \left[ A \exp\left(\frac{B}{T}\right) \right]} \dots\dots\dots (12)$$

$V_s$  = theoretical maximum adsorption capacity

$D_T$  = Reduction coefficient related to temperature increase

The coefficients  $V_s$ ,  $D_T$ ,  $A$ ,  $B$  in equation (12) can be determined by fitting the experimental adsorption data.

An exponential relationship between temperature and Langmuir volume can be observed from Figure 1 where at increasing temperature, the Langmuir volume decreases exponentially.

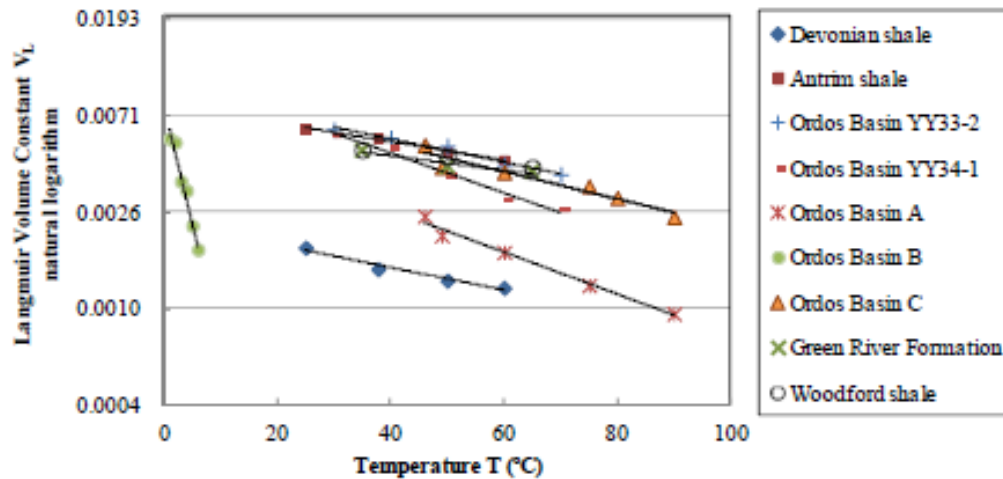


Figure 1: The Langmuir volume constant vs Temperature for typical shale samples ((12))

Ye et al. (12) analyzed published gas sorption data on shales from the USA, China, and Canada and concluded that an improved Langmuir model that incorporates the effect of temperature is able to describe shale gas sorption capacity under the effect of temperature and pressure. The exponential model was compared with both the linear model by Ji et al. (29) and also with the classical Langmuir model. The comparison was based on the use of average relative error. Their results showed exponential model as the most efficient model with the least error when predicting gas adsorption at different temperatures.

Table 1: Langmuir and Langmuir Freundlich Isotherm

| Model Name            | Model Equations                                 | Equation No. | Fitting parameters            |
|-----------------------|---|--------------|-------------------------------|
|                       | $b = b_0 \exp\left(-\frac{\Delta H}{RT}\right)$ |              |                               |
| Langmuir 3            | $V = \left(\frac{q_{so}bp}{1+bp}\right)$        | 2a           | $q_{so}, \Delta H_{ads}, b_0$ |
| Langmuir Freundlich 3 | $V = \left(\frac{q_{so}bp^n}{1+bp^n}\right)$    | 7            | $q_{so}, n, \Delta H, b_0$    |

Table 2: Variations of temperature-dependent Langmuir equation used in this study

| Model Name                         | Model Equations  | Equation No. | Fitting parameters                    |
|------------------------------------|--|--------------|---------------------------------------|
|                                    | $b = b_0 \exp\left(-\frac{\Delta H}{RT}\right)$                              |              |                                       |
| Langmuir 1                         | $V = \left(a_1 + \frac{a_2}{T}\right)\left(\frac{bp}{1+bp}\right)$           | 5            | $a_1, a_2, \Delta H_{ads}, b_0$       |
| Langmuir 2                         | $V = q_{so} \exp\left(\frac{-q_1}{T}\right)\left(\frac{bp}{1+bp}\right)$     | 6            | $q_{so}, q_1, \Delta H, b_0$          |
| Langmuir Freundlich 1              | $V = \left(a_1 + \frac{a_2}{T}\right)\left(\frac{bp^n}{1+bp^n}\right)$       | 8            | $a_1, a_2, n, \Delta H_{ads}, b_0$    |
| Langmuir Freundlich 2              | $V = q_{so} \exp\left(\frac{-q_1}{T}\right)\left(\frac{bp^n}{1+bp^n}\right)$ | 9            | $q_{so}, q_1, n, \Delta H_{ads}, b_0$ |
| Other Temperature dependent Models |  |              |                                       |

|                   |   |    |                                |
|-------------------|---|----|--------------------------------|
| Exponential Model | $V = \frac{V_s \exp(-D_r T) p}{p + \sqrt{T} / \left[ A \exp\left(\frac{B}{T}\right) \right]}$   | 12 | $V_s, D_r, A, B$               |
| Bi-Langmuir Model | $\frac{N_{ads}}{N_m} = f_1 \frac{k_1(T) p}{1 + k_1(T) p} + (1 - f_1) \frac{k_2(T) p}{1 + k_2(T) p}$<br>where $k(T) = k_i T^{-1/2} \exp(E_i/RT)$ | 10 | $N_m, k_1, k_2, E_1, E_2, f_1$ |

Selecting a model that is capable of predicting most accurately the adsorption data at different temperatures becomes essential when isotherm estimations are needed at temperatures for which no adsorption data exist. If validated based on the measurements made at laboratory conditions for certain temperatures, such a model can be used to predict gas adsorption behavior at any other reservoir temperature.

The use of temperature-dependent Langmuir volume/saturation loading when describing gas adsorption avoids the repeated matching of Langmuir constants for each isotherm (12). This can lead to more accurate representation of gas adsorption in the reservoir and also makes it easier to be applied in reservoir simulation where temperature effects are considered.

Furthermore, evaluating gas adsorption as a function of both pressure and temperature using different temperature-dependent adsorption models will allow for the possibility of employing thermal stimulation techniques to enhance the recovery of gas from shale reservoirs.

This has already being explored by several authors (30,31) by adopting Bi-Langmuir model into an unconventional simulator for thermal stimulation purposes. Their work showed that by using temperature dependent adsorption model, the potential to increase gas recovery rose significantly through thermal stimulation. This was achieved by altering the shale gas adsorption/desorption behavior through the elevation of formation temperature.

### **3. Materials and Methods**

#### **3.1 Shale gas data sets**

Experimental data of samples obtained from different shale gas reservoirs have been compiled and adsorption isotherms have been obtained for 11 different samples at different temperatures ranging from 25°C to 90°C. Four main reference sources have been used to collect the data used in this work (6,9,16,17). Lu et al. (6) obtained samples from the Devonian shale with reported mineral compositions consisting of mainly clay minerals and organic materials mainly kerogen with compositions ranging from 0 to 15% depending on the sample (32). Two shale samples from the Gas Research Institute and one illite sample was used in their adsorption measurements at four different temperatures of 25°C, 37.7°C, 50°C and 60°C.

Zhang et al. (9) collected 2 different set of samples of organic rich shales. These included the Green River Formation (Eocene, Utah) and Woodford shale (Upper Devonian) for first set of sample and second set collected from the Barnett shale cores. Methane sorption capacity for these different samples have been obtained at three different temperatures of 35.4°C, 50.4°C and 65.4°C. Samples from the Ordos Basin in china have been collected and used to obtain methane adsorption measurement at different temperatures of 30°C, 40°C, 50°C, 60°C and 90°C (16,17).

#### **3.2 Procedure for the Estimation of Parameters**

Several nonlinear regression techniques have been used to identify the optimal isotherm for gas adsorption on various adsorbents. These nonlinear regression methods involve minimizing the error distribution between the experimental data and the predicted results (33). For the selection of optimum isotherm, the use of nonlinear regression has been found to be the best (37). Among them is the method of least squares which remains one of the key techniques used by many researchers in predicting the optimum isotherm (33,34) and has also been found to be the most widely used (35,36).

Some other widely used nonlinear regression methods include Hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), Sum of the squared (ERRSQ) and Sum of the absolute errors (EABS) (33,34,38,37,39,40).

An objective function  $S$  have been used to correlate the different adsorption data with the models. The regression calculation involves minimizing the square root of the sum of the squared deviations in the predicted adsorption.

$$S = \sqrt{\left( \sum_{i=1}^N n_{ical} - n_{iexp} \right)^2} \dots\dots\dots (13)$$

Absolute average deviation (AAD %) or average relative error (ARE) have been used extensively by various researchers to find the optimum model for a set of adsorption data on coal and shale (2,11,13,41,42). Even though it has been reported to have a tendency to under or overestimate the experimental data, it minimizes the fractional error distribution across the sample concentration range (38,43).

$$\%AAD = 100 * ABS \left\{ \frac{\sum_{i=1}^N \left[ \left( \frac{n_{ical} - n_{iexp}}{n_{iexp}} \right) \right]}{N} \right\} \dots\dots\dots (14)$$

Where,

$n_{ical}$  is the calculated adsorbed concentration,

$n_{iexp}$  is the experimental adsorption data,

$N$  is the number of data points for the isotherm.

The regression analysis have been carried out simultaneously on all the temperatures provided for the experimental data to ensure accurate representation and use of the temperature dependent models. The validation and extrapolation of YY33-1 in Figure 10 and Figure 11

was, however, simulated simultaneously for only 30°C, 40°C, 50°C and 60°C of the temperatures and extrapolation carried out for temperature at 70°C.

#### **4. Results and Discussion**

Table 3 and 4 displays the results for the regression carried out on all 11 shale samples used in the study. This has been analyzed using Absolute Average Deviation (AAD %) error approach to determine which models gives the least error. The model with the least absolute average deviation error can be said to be the best model for representing the adsorption capability of the sample. Six different models based on the temperature-dependent Langmuir volume and three models of temperature-independent Langmuir volume have been compared (see Table 3 and 4).

In table 3, absolute average deviations have been obtained for models with temperature dependent Langmuir volume. By comparing these models, it can be ascertained that the Langmuir–Freundlich 2 and the Exponential model were able to give the least error for majority of the data. Langmuir-Freundlich model 2 predicted most accurately for shale samples from Green river formation, Barnett shale Tarrant A3, Blakely 1, Ordos Basin A and B in china. On the other hand, three of the shale samples from Woodford shale, Ordos Basin YY33-2, Ordos Basin YY34-1 and Antrim-7 were most accurately predicted by the exponential model.

Langmuir model 1 failed to predict most accurately the gas adsorption for any of the shale samples evaluated. The AAD% for Langmuir 1 was particularly higher in most of the results compared with the rest of the temperature dependent models ranging from 0.49 % -7.48 %. It failed to predict most accurately for any of the shale data analyzed. Similarly, Langmuir 2 could predict only one of the samples (CSW2) most accurately.

However, when the Freundlich model was combined with Langmuir model, the results of the modelling improved with Langmuir-Freundlich 2 model giving very small average absolute

deviation error for five of the samples. This could also be attributed to the extra parameter present in the Langmuir–Freundlich model. The more parameters that are present in the model, the likelihood of the model predicting more accurately. Also the Langmuir-Freundlich model is able to describe the heterogeneity of the shale sample compared with that of classical Langmuir model.

Similar comparison has been made for the models with temperature independent Langmuir volume. These models include Langmuir 3, Langmuir-Freundlich 3 and the Bi-Langmuir model (See Table 4). Comparing the values obtained for all three models, it can be observed that Langmuir-Freundlich 3 model provided the least error for six of the shale samples compared with three and two for Langmuir 3 and Bi-Langmuir model respectively.

Most of the shale data have been adequately described by the combination of both the Langmuir and Freundlich models. Thus Langmuir- Freundlich 2 and Langmuir- Freundlich 3 proved to be better models in describing the adsorption process in the shale formations. Since most of these shale are deemed to be highly heterogeneous with mixtures of clay minerals like quartz and kerogen compositions of type I or II, the combined Langmuir-Freundlich models are best used in modelling gas adsorption. Exponential model also proved to fit adequately most of the data compared with the Langmuir models. Hence the choice of model would depend on how highly heterogeneous the shale sample is and since Langmuir model assumes homogeneous surface, a preferred choice of combined Langmuir and Freundlich would best describe the adsorption process in most shales.

In order to compare how well the temperature dependent and independent form of the Langmuir volume models compare to each other when applied on the same datasets, Table 3 was combined with Table 4 and the model with the least error was chosen to be the most accurate representation of the gas adsorption data on the shale samples. By comparison, seven of the data sets were accurately described by the temperature independent Langmuir volume



models compared to only four by the temperature dependent models. However the error difference was minimal and it could be argued that minimal difference existed between results obtained from the two model equations.

Due to the large number of graphs generated for the representation of the modelling process, only results showing Woodward shale has been presented. The best fitted parameters for all the models have being provided in Supporting Document (See Table 4-11) for checking the models applicability to the data.

The  $R^2$  method to measure the level of accuracy of the fit for Woodford shale shows very close approximation to one, meaning all the models could adequately fit the gas adsorption process in Woodford shale (See Fig.2-Fig.9). This was not the case when the  $R^2$  was evaluated for the rest of the data (See Table 5-12 in Supporting document) as some of the models could not adequately describe the gas adsorption process. In particular, models like Langmuir 1 and 2 failed to describe adequately for some of the adsorption data as the  $R^2$  shows in Table 5-12.

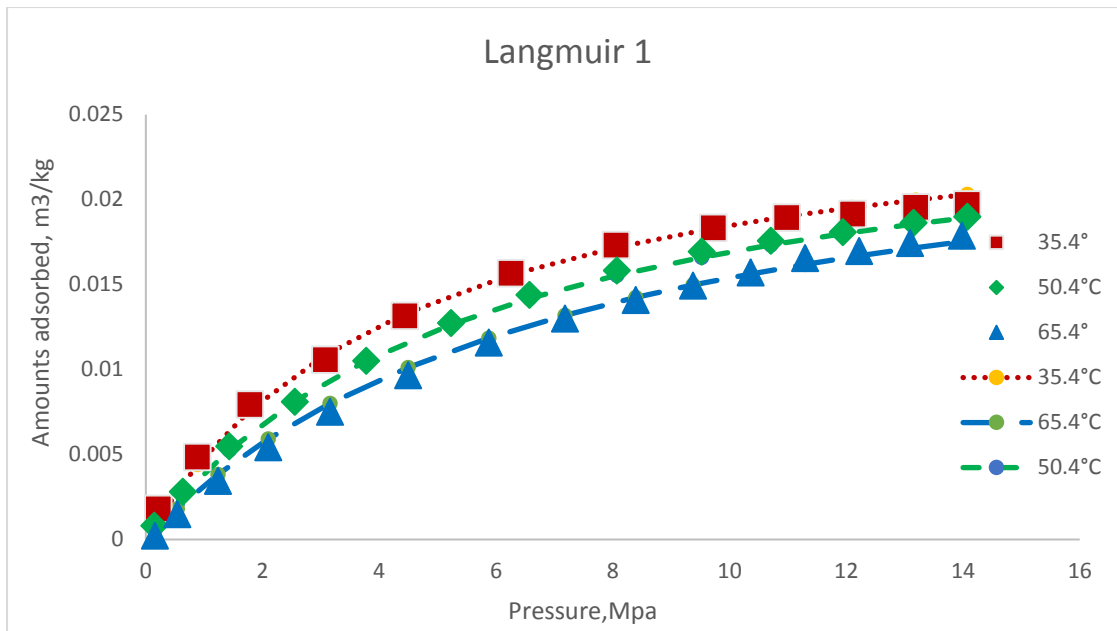


Figure 2: Modelling methane adsorption using Langmuir 1 model on experimental data of Woodford shale

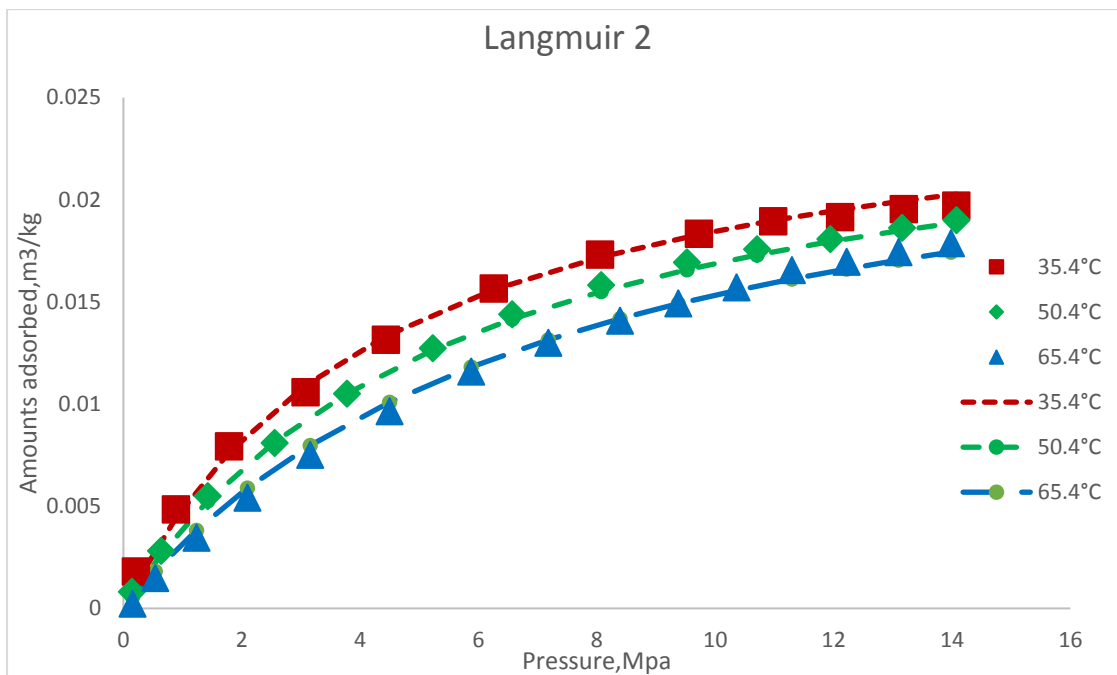


Figure 3: Modelling methane adsorption using Langmuir 2 model on experimental data of Woodford shale

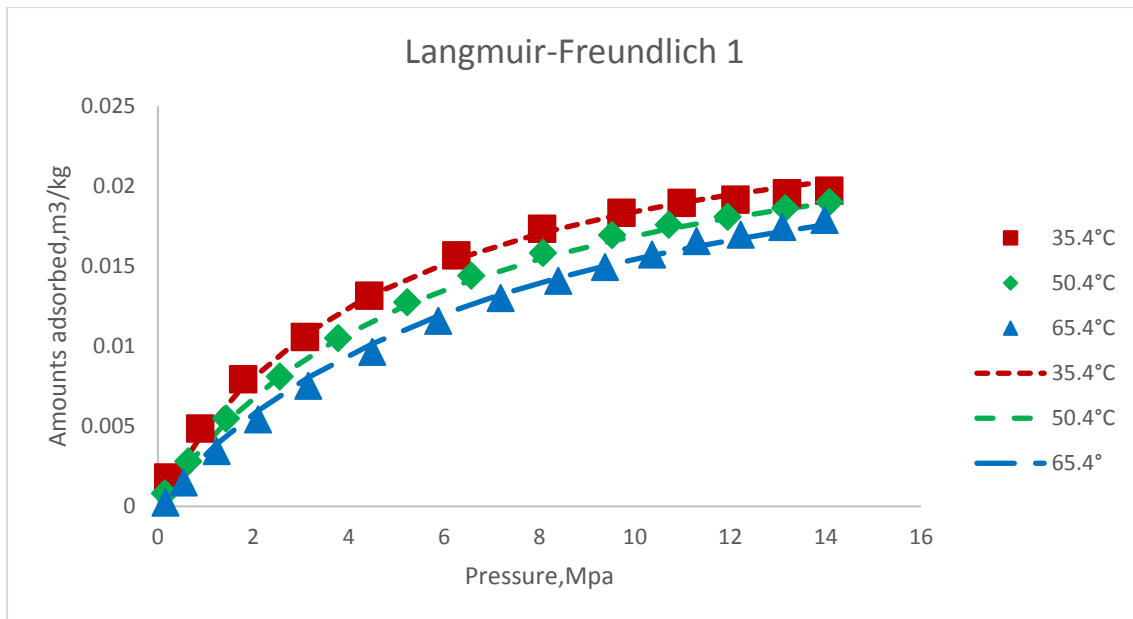


Figure 4: Modelling methane adsorption using Langmuir-Freundlich 1 model on experimental data of Woodford shale

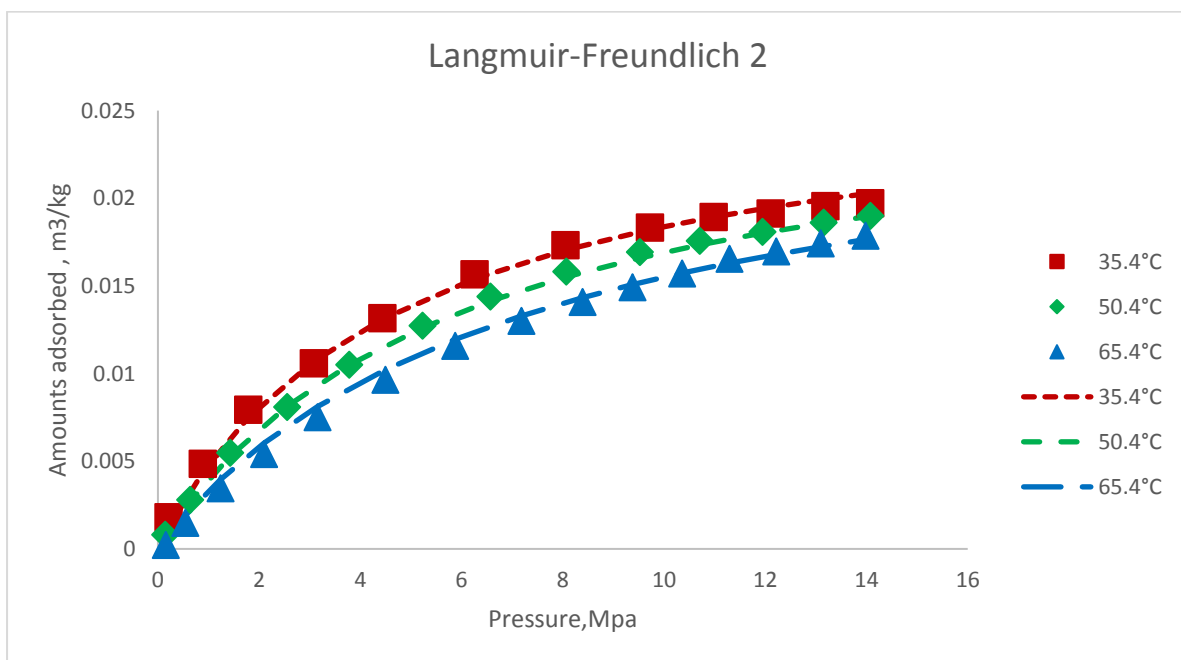


Figure 5: Modelling methane adsorption using Langmuir-Freundlich 2 model on experimental data of Woodford shale

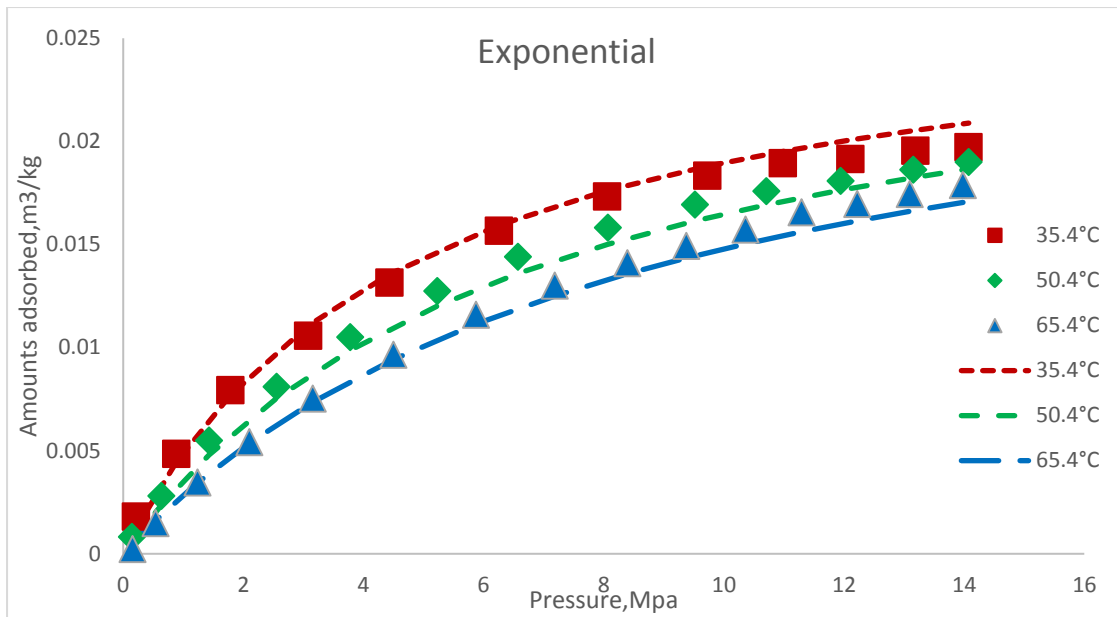


Figure 6: Modelling methane adsorption using Exponential model on experimental data of Woodford shale

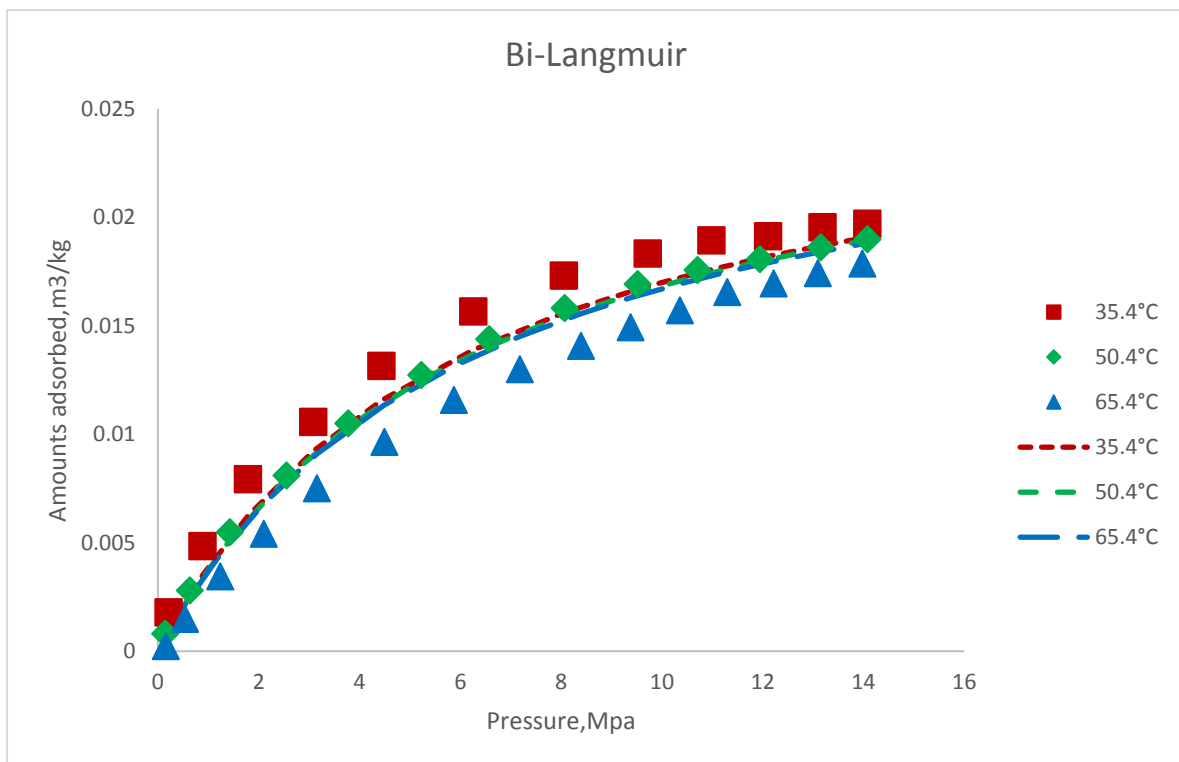


Figure 7: Modelling methane adsorption using Bi-Langmuir model model on experimental data of Woodford shale

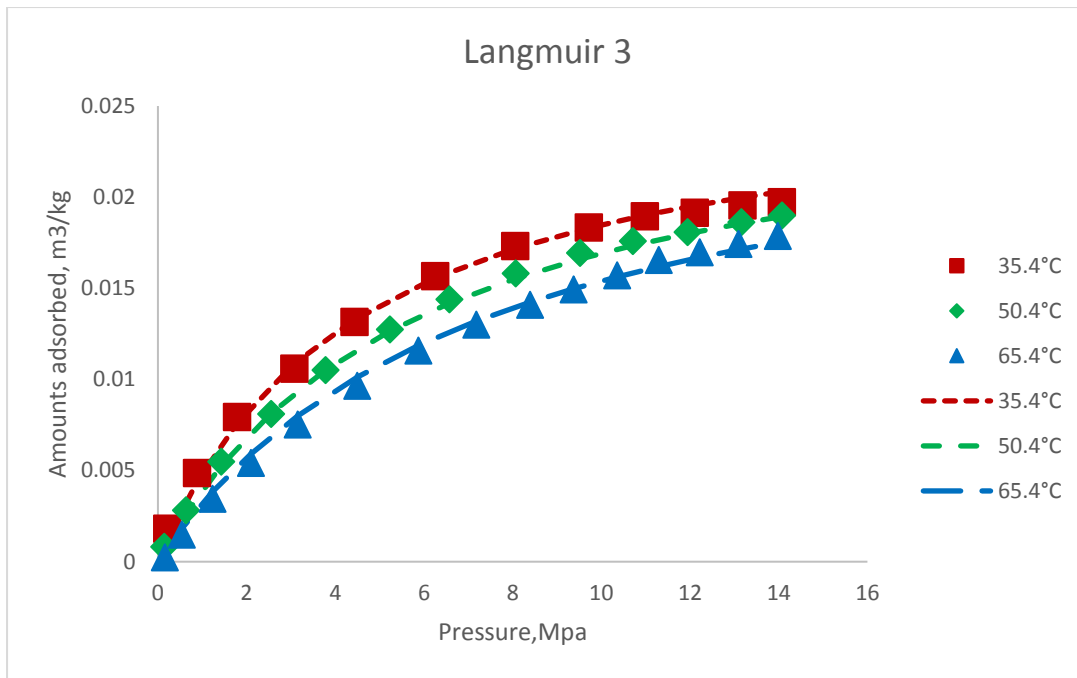


Figure 8 : Modelling methane adsorption using Langmuir 3 model on experimental data of Woodford shale

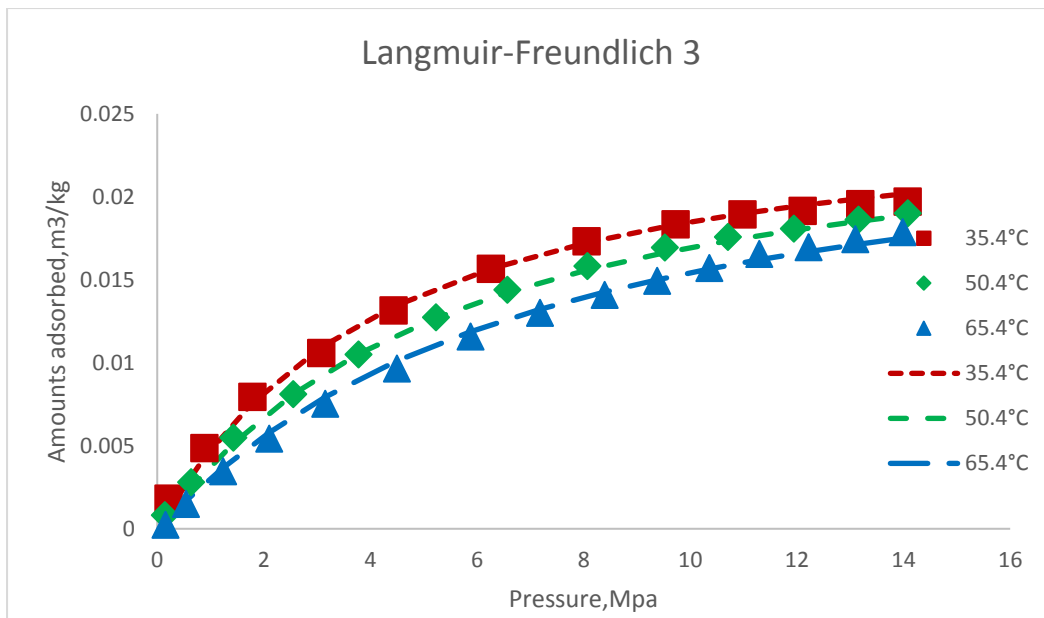


Figure 9: Modelling methane adsorption using Langmuir-Freundlich 3 model on experimental data of Woodford shale

Table 3 Absolute Average Deviation (AAD %) for models with temperature dependent Langmuir volume

| Sample                   | Reference        | Langmuir 1 | Langmuir 2 | Langmuir-Freundlich 1 | Langmuir-Freundlich 2 | Exponential | No.of Data |
|--------------------------|------------------|------------|------------|-----------------------|-----------------------|-------------|------------|
| Green River Formation    | Zhang et al 2012 | 0.49 %     | 0.48 %     | 2.66 %                | 0.07 %                | 0.33 %      | 33         |
| Woodford Shale           | Zhang et al 2012 | 2.68 %     | 2.67 %     | 2.99 %                | 3.72 %                | 1.13 %      | 40         |
| Barnett Shale Tarrant A3 | Zhang et al 2012 | 1.11 %     | 1.13 %     | 0.32 %                | 0.22 %                | 2.18 %      | 39         |
| Barnett Shale Blakeley 1 | Zhang et al 2012 | 9.28 %     | 9.23 %     | 4.07 %                | 4.00 %                | 7.82 %      | 42         |
| Ordos Basin YY33-2       | Ji et al 2014    | 1.53 %     | 2.74 %     | 5.75 %                | 2.25 %                | 0.97 %      | 35         |
| Ordos Basin YY34-1       | Ji et al 2014    | 6.95 %     | 10.63 %    | 7.57 %                | 2.00 %                | 0.76 %      | 35         |
| Ordos Basin A            | Guo 2014         | 5.57 %     | 6.81 %     | 0.46 %                | 0.25 %                | 5.76 %      | 42         |
| Ordos Basin B            | Guo 2014         | 7.14 %     | 6.30 %     | 0.63 %                | 0.45 %                | 0.94 %      | 39         |
| Ordos Basin C            | Guo 2014         | 7.48 %     | 5.74 %     | 0.11 %                | 5.82 %                | 0.26 %      | 36         |
| CSW2                     | Lu et al 1995    | 0.971 %    | 0.32 %     | 2.60 %                | 1.84 %                | 0.85 %      | 40         |
| Antrim-7                 | Lu et al 1995    | 0.976 %    | 0.83 %     | 1.71 %                | 0.77 %                | 0.66 %      | 40         |

Table 4: Absolute Average Deviation (AAD %) for models with temperature independent Langmuir volume

| Sample                   | Reference        | Langmuir 3 | Langmuir-Freundlich 3 | Bi-Langmuir | No.of Data |
|--------------------------|------------------|------------|-----------------------|-------------|------------|
| Green River Formation    | Zhang et al 2012 | 0.42 %     | 0.06 %                | 2.01 %      | 33         |
| Woodford Shale           | Zhang et al 2012 | 2.68 %     | 1.03 %                | 4.12 %      | 40         |
| Barnett Shale Tarrant A3 | Zhang et al 2012 | 1.05 %     | 0.08 %                | 1.30 %      | 39         |
| Barnett Shale Blakeley 1 | Zhang et al 2012 | 9.21 %     | 4.09 %                | 3.56 %      | 42         |
| Ordos Basin YY33-2       | Ji et al 2014    | 1.79 %     | 1.92 %                | 8.96 %      | 35         |
| Ordos Basin YY34-1       | Ji et al 2014    | 6.48 %     | 2.79 %                | 8.71 %      | 35         |
| Ordos Basin A            | Guo 2014         | 3.82 %     | 0.09 %                | 6.46 %      | 42         |
| Ordos Basin B            | Guo 2014         | 6.16 %     | 0.40 %                | 16.07 %     | 39         |
| Ordos Basin C            | Guo 2014         | 2.38 %     | 5.79 %                | 5.28 %      | 36         |
| CSW2                     | Lu et al 1995    | 0.69 %     | 2.31 %                | 0.71 %      | 40         |
| Antrim-7                 | Lu et al 1995    | 0.73 %     | 0.22 %                | 0.14 %      | 40         |

Temperatures can also be extrapolated to conditions that might be outside laboratory conditions to review how the models might predict gas adsorption. This is only possible because of the use of temperature dependent models. Extrapolation to temperatures outside laboratory condition is useful especially in simulation studies where thermal application is involved. For enhanced shale gas recovery studies, the use of temperature dependent models are key for prediction of gas where temperature variation can significantly affect the amount of gas adsorbed. To do this, validation is necessary for extrapolation of the models. The experimental adsorption data for Sample YY33-2 at 30°C, 40°C, 50°C and 60.4°C has been used for the establishment and calibration of the models.

Since extrapolation is necessary especially for numerical simulation involving thermal application, we have used isotherm data at 70°C for YY33-2 to get some idea about the importance of the model selection in extrapolation of temperature. Both temperature dependent Langmuir volume models and temperature independent Langmuir volume models have been extrapolated to 70°C to confirm how well the models predict gas adsorption for validation and extrapolation purposes (See Fig.10 and Fig.11).

Exponential model from Figure 10 shows a much more accurate fit of the extrapolation to 70°C for the shale data of YY33-2. This implies that subsequent extrapolation is more likely to give better approximation to gas adsorption at temperatures outside laboratory conditions. With the exception of Exponential model that gave a better validation, both Langmuir 1 and 2 gave an exaggerated prediction whereas the combined Langmuir and Freundlich models prediction was close to the experimental data.

For temperature independent Langmuir volume models, the validation of the extrapolation with the actual data was not very accurate. All the three models either under predicted or over predicted the results (See Fig. 11). This could be because, for the shale sample YY33-2 used,



the temperature independent Langmuir volume models does not describe the adsorption process well compared with the temperature dependent Langmuir volume models.

The results from Fig.10 and Fig.11 show that care must be taken in the choice of model and representation of temperature effects on adsorption due to the different prediction offered by the models.

Although some of the results are not exactly far off from the range of data at 70°C, caution is still expected to be exercised in the use of these models as results might be an over or under estimation of the actual adsorbed gas at temperatures for which there are no experimental data.

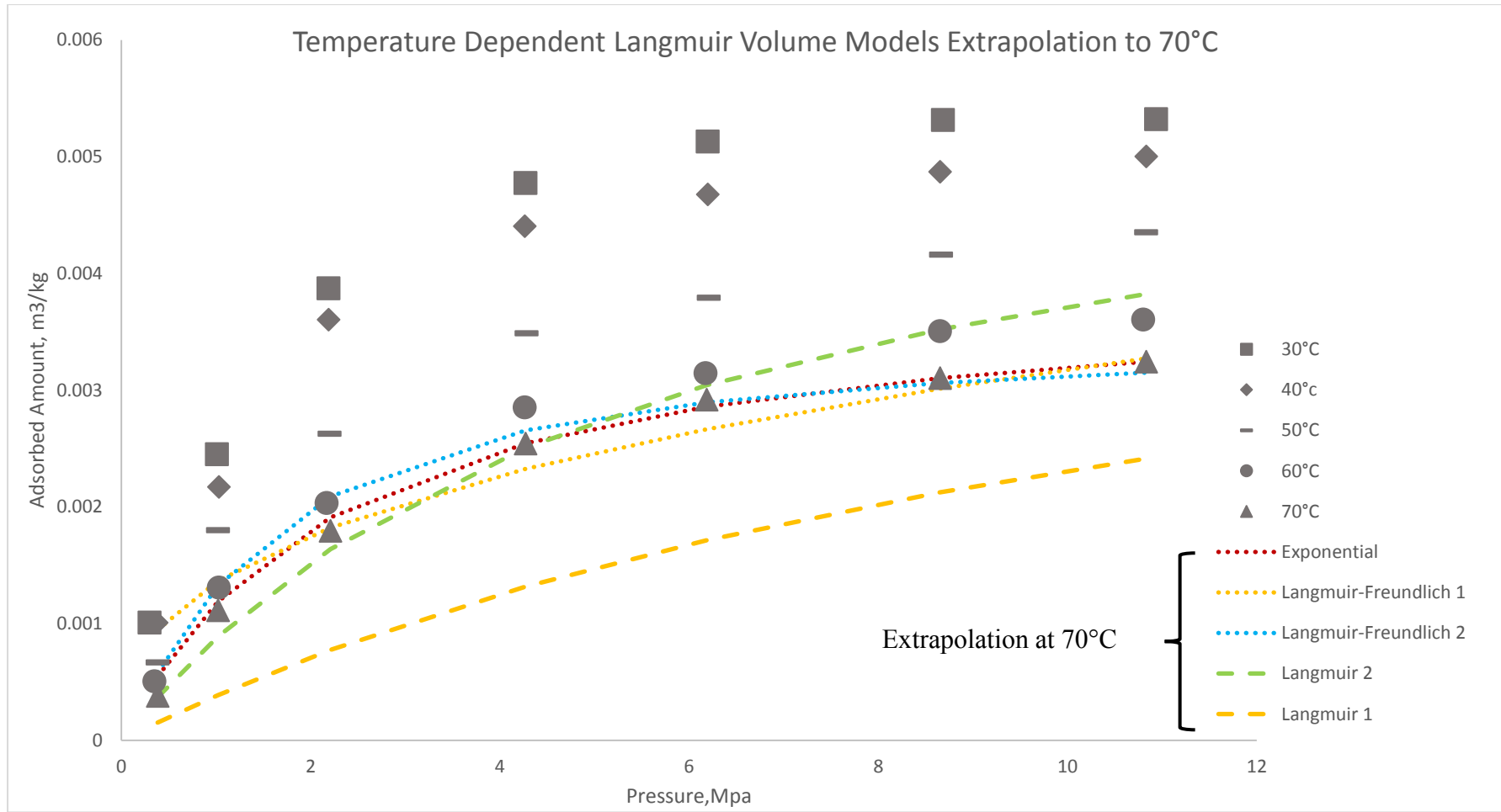


Figure 10: Extrapolation and validation at 70°C of shale sample YY33-2 using Temperature dependent Langmuir Volume models

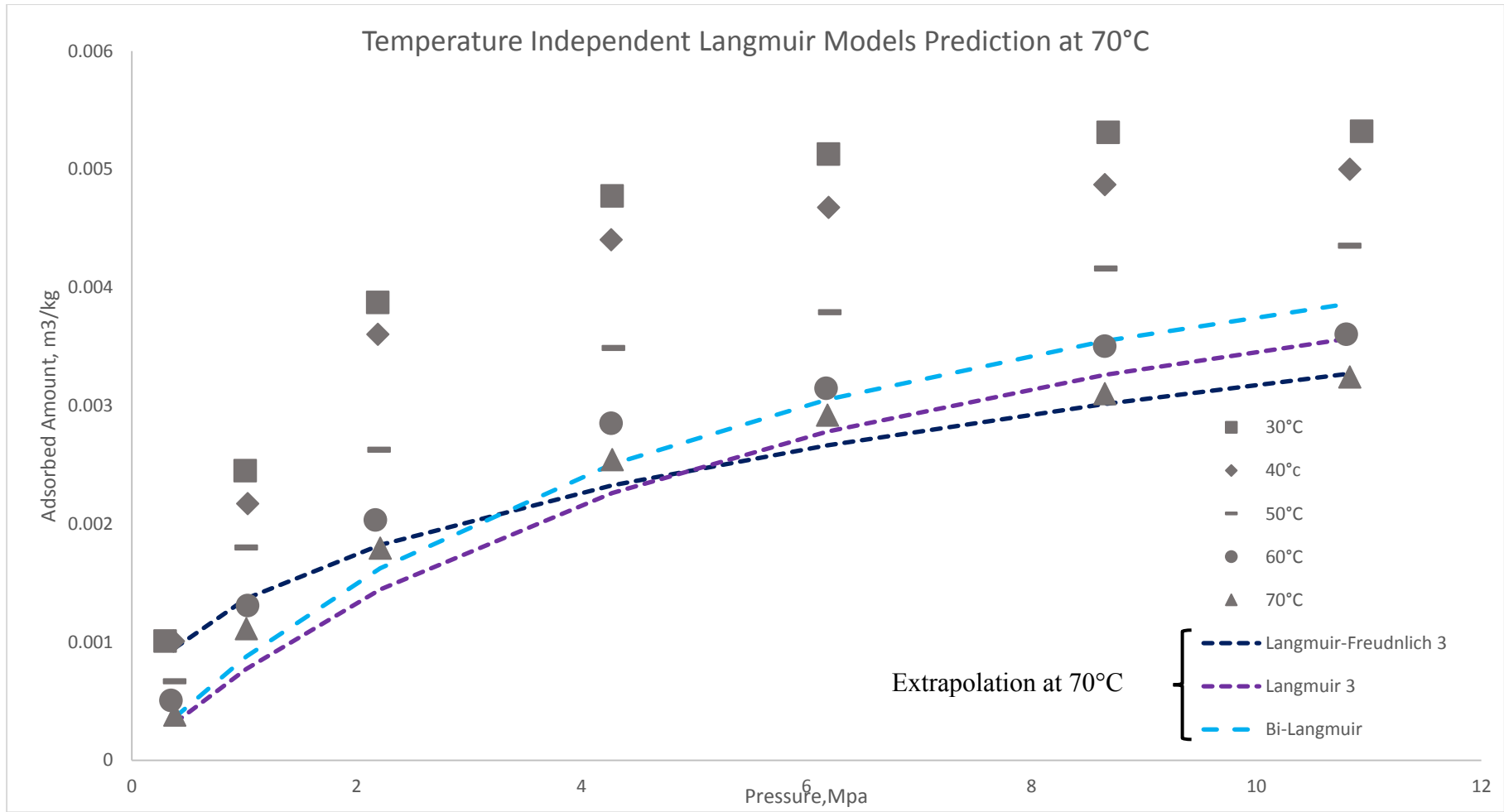


Figure 11: Extrapolation and validation at 70°C of shale sample YY33-2 using Temperature Independent Langmuir Volume models

## **Conclusion**

The present research have focused on applying 8 different temperature dependent adsorption models on a wide range of shale gas adsorption data set. Temperature dependent models have been further grouped into models that have temperature dependent Langmuir volume and those that expresses a constant Langmuir volume. Analysis of temperature dependent Langmuir volume showed that majority of the data were successfully represented when using the combined Langmuir–Freundlich 2 model and also the Exponential model. Langmuir 1 and 2 showed the least accuracy for all the data evaluated when used in modelling the gas adsorption on the experimental shale gas data studied. Temperature independent Langmuir volume also proved to be able to successfully fit the gas adsorption data presented and in some cases when compared with the temperature dependent Langmuir volume models, it predicted the most accurate of the gas adsorption. Validation and extrapolation of all the models for shale sample YY33-2 showed varying prediction to actual data at 70°C though models with temperature dependent Langmuir volume offered much closer prediction than the temperature independent Langmuir volume models. This implies that care and caution must be exercised when selecting a particular model for representation of gas adsorbed at temperatures for which no data is available. Temperature dependent models are important as they offer an ability to accurately describe gas adsorption at multiple temperatures and also to be implemented in numerical simulation studies where thermal stimulation is required for enhanced shale gas recovery process.

## **Supporting Information Available**

Best fitted parameters for Langmuir 1, Langmuir 2, Langmuir 3, Langmuir Freundlich 1, Langmuir Freundlich 2, Langmuir Freundlich 3, Exponential Model and Bi Langmuir Model.

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