

A Mathematical Simulation of low-rank Coal Adsorption Behavior

Wu Bing¹, Wang Liyan², Wei Yaling³, Zhang Xuemei⁴, Ma Qinghua⁴, Li Dong⁴,

¹Xinjiang Coalfield Geology Bureau, Urumqi, Xinjiang, China

²121 Geological Brigade of Fujian Province, Longyan, Fujian, China

³Ningxia Sanfang Coal Quality Testing Technology Co., Ltd., Yinchuan, Ningxia, China

⁴Energy and Chemical Engineering Research Center, Xi'an Siyuan University, Xi'an, China

Abstract: This paper presents the theoretical significance of the temperature-pressure-adsorption equation (TPAE) over the limitations of the Langmuir isothermal adsorption equation. The series isothermal adsorption data of low-rank coal from Wangtian coal mine in Shanxi Province, China were used to verify the practicality of the TPAE, and four parameters were obtained. According to the TPAE sought, the adsorption value of any tests between 30°C-70°C and pressure between 0-30 MPa can be arbitrarily calculated, with an average relative error of less than 8.82 %, and expressed by a three-dimensional adsorption surface. According to the total differential of the multivariate function is the sum of the differentials of each independent variable, assuming that the ground temperature gradient of Wangtian coal mine is 3°C/100 m and the ground pressure gradient is 1.0 MPa/100 m, it can be precisely calculated that both partial deviations of temperature and pressure. It can be approximately calculated that the critical adsorption depth of the low-rank coal is about 1300~1400 m underground, the critical adsorption pressure is about 13 MPa, the critical adsorption temperature is about 54°C, and the critical adsorption capacity is 10.8cm³/g.

Keywords: temperature-pressure-adsorption equation; Langmuir isothermal adsorption equation; partial deviations of temperature; partial deviations of pressure; the critical burial depth.

1. Introduction

Coal bed gas is usually defined as a hydrocarbon gas absorbed mainly on the surface of coal matrix particles, free in coal pores or dissolved in coal seam water. The adsorption amount of gas on solid is a function of both temperature and pressure[1-4]. At constant pressure, the curve which describes the relationship between adsorption amount and equilibrium temperature, is called isobaric adsorption. At constant adsorption amount, the curve which describes the relationship between adsorption pressure and equilibrium temperature, is called isosteric adsorption. At constant temperature, the curve which describes the relationship between adsorption amount and equilibrium pressure, is called isothermal adsorption.

The Langmuir isothermal adsorption equation is the most famous equation to treat the data between adsorption amount and equilibrium pressure [5-8]. All those three "iso adsorption" have transformed the three variables adsorption into two variables adsorption by fixing one variable. This kind of operation can make the understanding of the relationship between two variables easy, but not complete. Therefore, Langmuir parameters of a serials isothermal adsorptions at different temperatures cannot be used to mathematically explain why the absorption capacity of coal decreases with the increase of temperature, and its' relationship regarding the phenomenon of with the increase of the buried depth, the adsorption capacity of coalbed methane gradually increases until it reaches a critical depth, and then decreases with the further increase of the buried depth. This paper will try to use a TPAE to overcome the limitation of Langmuir isothermal adsorption equation, and mathematically explain why the absorption capacity of coal decreases with the increase of temperature, why the adsorption gas content has a maximum value and what are the necessary and sufficient conditions for the adsorption gas content to appear at a maximum value.

2 Data and Temperature-Pressure-Adsorption Equation

2.1 Sample

A low-rank coal from Wangtian(WT) coal mine in Shanxi Province, China is used to verify the practicality of the TPAE, and its' mathematical derivations. The data and parameters of WT coal samples are listed in Table 1.

Table1: The data and parameters of WT coal sample [1]

parameter	data
R _{0,max} /%	0.84
Vitrinite/%	76.6
Inertinite/%	11.3
Exinite/%	10.1
Mineral/%	1.95
Ash/%	10.4
Moisture/%	7.2

2.2 The Langmuir adsorption equation

The Langmuir adsorption equation can be represented as:

$$V = \frac{abP}{1+bP} \quad (1)$$

here

a is the Langmuir volume.

b is the reciprocal of the Langmuir pressure.

The WT_{coal} under different testing temperatures is listed in Table 2. The temperature range is 30~100°C and pressure is 0~30 MPa.

Table2: The Langmuir volume and the reciprocal of Langmuir pressure of WT coal [1]

Experimental temperature/°C	a/cm ³ g ⁻¹	b/MPa ⁻¹
30	23.09	0.1348
50	23.04	0.1056
70	14.81	0.1011

Mathematically, the Langmuir equation only deals with a function between adsorption amounts and pressures under isothermal condition, therefore, it is not a function of the temperature.

2.3 Temperature-pressure-absorbing equation (TPAE) [9-14]

Using the temperature and pressure as independent variables and adsorption amount as dependent variable, the TPAE can be expressed as

$$V = \frac{1}{\sqrt{MT}} \left[A + BP^\beta T^{1.5} \exp\left(\frac{\Delta}{T}\right) \right] \quad (2)$$

here:

A is a constant of microporous geometric shape for a fixed porous medium, dimensionless.

B is the adsorption flow coefficient, which is related to the adsorption area, dimensionless.

M is a molecular weight, and the molecular weight of methane is 16.

P is pressure (MPa).

T is the absolute temperature (K).

V is the adsorption amount (cm³/g).

β is a parameter which measures the relative influence of adsorption pressure, dimensionless.

Δ is the energy difference between the lowest potential energy and the activation energy of an adsorbed

molecule in the adsorbed mass flow, which mainly measures the relative influence of the adsorption temperature, K.

The details regarding the regression of TPAE from series Langmuir adsorption has been presented early [9].

2.4 Verification

It is very necessary to verify the suitability of TPAE by comparing the adsorption amount of TPAE V_{TP} and that of the Langmuir equation V_{LA} under the exact same temperature and pressure. The relative error is defined as:

$$\delta_i = \frac{|V_{TP} - V_{LA}|}{V_{LA}} \times 100\% \quad (3-1)$$

The average relative error is defined as:

$$\bar{\delta} = \frac{1}{n} \sum_{i=1}^n \frac{|V_{TP} - V_{LA}|}{V_{LA}} \times 100\% \quad (3-2)$$

here:

n is the total numbers of testing at different temperatures and pressures. There are 3Langmuir's temperatures, and for each temperature, 10 pressure values are chosen, from 1 to 20 MPa with a fixed interval of 2.0 MPa. The n is equal to 30.

V_{TP} is the calculated adsorption amount of TPAE at i conditions (temperature and pressure) .

V_{LA} is the calculated adsorption amount of Langmuir at i conditions (temperature and pressure) .

2.5 Partial differential equations of TPAE

As the influence of pore geometry constant, A is directly related to Knudsn diffusion, and is rather small comparing to rest part of TPAE. Therefore, the TPAE can be simplified as

$$V = \frac{B}{\sqrt{M}} T \exp\left(\frac{\Delta}{T}\right) P^\beta \quad (4)$$

The equation (4) indicates that the adsorption amount still is a function of both temperature and pressure. For a trinary equation, its total differential of adsorption amount should be presented as the sum of the differentials of each independent variable, temperature and pressure:

$$dV = \left[\frac{\partial V}{\partial T}\right]_P dT + \left[\frac{\partial V}{\partial P}\right]_T dP \quad (5)$$

here:

$\left(\frac{\partial V}{\partial P}\right)_T$ is the partial differential with respect to pressure under isothermal condition, and $\left(\frac{\partial V}{\partial T}\right)_P$ is the partial

differential with respect to temperature under the isobaric condition.

The partial differential equation of temperature is

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{B}{\sqrt{M}} P^\beta \exp\left(\frac{\Delta}{T}\right) \left(1 - \frac{\Delta}{T}\right) \quad (6)$$

According to the equation (6), under the isobaric condition, $\left(\frac{\partial V}{\partial T}\right)_P$ could be either negative or positive. If $\frac{\Delta}{T}$ is larger than 1, $\left(\frac{\partial V}{\partial T}\right)_P$ is negative, less than zero. Then the right-hand side of equation (6) must be less than zero, which means that increasing temperature has negative effect. If $\frac{\Delta}{T}$ is smaller than 1, $\left(\frac{\partial V}{\partial T}\right)_P$ is positive, larger than zero. Then the right-hand side of equation (6) must be larger than zero, which means that increasing temperature has a positive effect. Therefore, equation (6) illustrates that, for most coal samples' isothermal adsorptions, as Δ larger than T , the adsorption volume will decrease with temperature increasing. Even under isobaric condition, according to the equation (6), both pressure "P" and parameter "β" have contributed to the value of the partial differential with respect to T.

The partial differential equation of pressure is

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{B}{\sqrt{M}} T \exp\left(\frac{\Delta}{T}\right) \beta P^{\beta-1} \quad (7)$$

Under isothermal condition, because all parameters, B, M, T, P and b are positive, never being negative by any chance, the right side of equation (7) is always positive. Therefore, the adsorption pressure always has a positive influence, which has been approved by all isothermal adsorptions. Even under isothermal condition, both temperature "T" and parameter "Δ" have contributed into the value of the right-hand side of equation (7).

From Equations (5), (6), and (7), The total differential and partial differentials can be calculated if the following equations being used in the calculation:

$$T = \frac{T_1 + T_2}{2} \quad (8-1)$$

$$P = \frac{P_1 + P_2}{2} \quad (8-2)$$

$$dT = T_2 - T_1 \quad (9-1)$$

$$dP = P_2 - P_1 \quad (9-2)$$

$$V_i = V_{i-1} + dV_i \quad (10)$$

Based on the coal samples isothermal adsorption temperature and pressure range, both increase integral of temperature and pressure are designed.

3. Results and Discussions

3.1 TPAE

The four parameters of TPAE regressed from Table 2 parameters of WT coal are listed in Table 3.

Table 3: The TPAE parameters regressed from isothermal adsorption measurements of WT coal

Parameter	value
A	0.168
B	0.0001207
Δ/K	1817
β	0.5641
δ/%	8.82

The final average relative error of low-rank coal is 8.82%. It is reasonable to conclude that TPAE treats accurately a series of isothermal adsorption. Since the TPAE is a mathematical expression of temperature-pressure-adsorption, it could be presented in a three-dimensional picture as shown in Figure 1. The 3 rows' points are corresponding 3 Langmuir's temperatures.

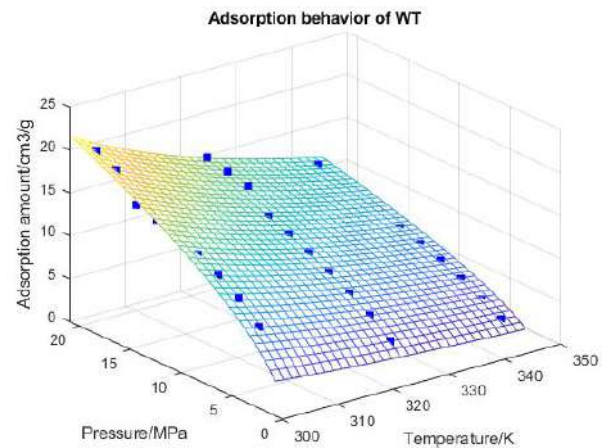


Figure 1: Visibility of TPAE cured surface and Langmuir points

From Figure 1, the 3 rows' Langmuir points are agreed with the TPAE cured surface. This approves that TPAE treats accurately a series of isothermal adsorption.

3.2 Partial differentials

The results of total differential and partial differentials are listed in Table 4. There are three phenomena that should be noticed.

Table 4: The results of total differential and partial differentials of YPQ coal under the tested temperature and pressure

T1/K	T2/K	P1	P2	$\left(\frac{\partial V}{\partial T}\right)_P$	$\left(\frac{\partial V}{\partial P}\right)_T$	dT	dP	dV	V
291	294	1	2	-0.0986	2.0806	3	1	1.7849	6.3049
294	297	2	3	-0.1220	1.5795	3	1	1.2136	7.5185
297	300	3	4	-0.1370	1.2953	3	1	0.8844	8.4029
300	303	4	5	-0.1468	1.1037	3	1	0.6633	9.0663
303	306	5	6	-0.1531	0.9624	3	1	0.5032	9.5695
306	309	6	7	-0.1568	0.8526	3	1	0.3821	9.9515
309	312	7	8	-0.1587	0.7639	3	1	0.2878	10.2393
312	315	8	9	-0.1592	0.6906	3	1	0.2130	10.4524
315	318	9	10	-0.1586	0.6287	3	1	0.1529	10.6053
318	321	10	11	-0.1572	0.5757	3	1	0.1041	10.7094
321	324	11	12	-0.1552	0.5297	3	1	0.0642	10.7735
324	327	12	13	-0.1527	0.4895	3	1	0.0314	10.8050
327	330	13	14	-0.1498	0.4539	3	1	0.0044	10.8093
330	333	14	15	-0.1468	0.4224	3	1	-0.0179	10.7914
333	336	15	16	-0.1435	0.3941	3	1	-0.0363	10.7551
336	339	16	17	-0.1401	0.3687	3	1	-0.0515	10.7036
339	342	17	18	-0.1366	0.3458	3	1	-0.0640	10.6395
342	345	18	19	-0.1331	0.3250	3	1	-0.0743	10.5652
345	348	19	20	-0.1296	0.3060	3	1	-0.0827	10.4825
348	351	20	21	-0.1261	0.2887	3	1	-0.0894	10.3931
351	354	21	22	-0.1226	0.2729	3	1	-0.0949	10.2982
354	357	22	23	-0.1192	0.2583	3	1	-0.0991	10.1991
357	360	23	24	-0.1158	0.2449	3	1	-0.1024	10.0966
360	363	24	25	-0.1125	0.2325	3	1	-0.1049	9.9917
363	366	25	26	-0.1092	0.2211	3	1	-0.1067	9.8850
366	369	26	27	-0.1061	0.2104	3	1	-0.1079	9.7772
369	372	27	28	-0.1030	0.2006	3	1	-0.1085	9.6687
372	375	28	29	-0.1000	0.1914	3	1	-0.1088	9.5599
375	378	29	30	-0.0971	0.1828	3	1	-0.1086	9.4512
378	381	30	31	-0.0943	0.1748	3	1	-0.1082	9.3430
381	384	31	32	-0.0916	0.1673	3	1	-0.1075	9.2355
384	387	32	33	-0.0890	0.1603	3	1	-0.1066	9.1289
387	390	33	34	-0.0864	0.1537	3	1	-0.1055	9.0234
390	393	34	35	-0.0839	0.1476	3	1	-0.1043	8.9192
393	396	35	36	-0.0815	0.1418	3	1	-0.1029	8.8163

V=4.52 at 291K and 1 MPa.

First, under testing temperature range (18~93°C, 291~366K), for WT coal with Δ=1817K, its partial differential of temperature should be always less than zero. This proves the observation of the adsorption volume decreases as the temperature increases.

Second, under testing pressure range (1~36 MPa), WT coal's partial differential of pressure is always greater than zero. This proves the observation of the adsorption volume increase as the pressure increases.

Since the total differential of the multivariate function is the sum of the differentials of each independent variable, then a partial differential of temperature (being always less than zero) adds a partial differential of pressure (being always greater than zero) could produce a turning point, at where the total differential of WT is zero, along with the buried depth increasing.

The partial differential of both variables can be seen in Figure 2.

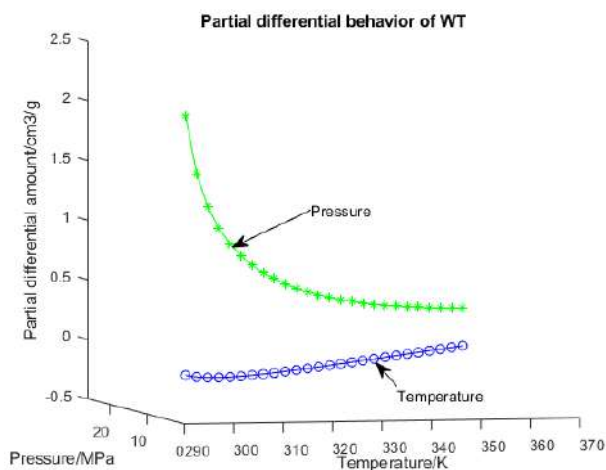


Figure 2: Partial differential of temperature and pressure

3.3 Buried depth

When the buried depth of coal is increased, both temperature and pressure are increased. Therefore, the total differential of adsorption amount is positive, the adsorption amount is increased, as shown in Table 4, $T < 330\text{K}$, $P < 14\text{MPa}$. When the buried depth of coal is increased, both temperature and pressure are increased, the total differential of adsorption amount is approaching zero, the adsorption amount is approaching a maximum. After this critical depth, even if the buried depth of coal is increased, both temperature and pressure are increased, but the total differential of adsorption amount is negative, the adsorption amount is reducing, as shown in Table 4, $T > 330\text{K}$, $P > 14\text{MPa}$.

Assuming the temperature of the constant temperature layer at WT coal was 15°C , the ground temperature gradient of $3^\circ\text{C}/100\text{m}$ and the pressure gradient of $1\text{MPa}/100\text{m}$, the relationship between the buried depth and the adsorption amount of WT coal is depicted in Figure 3.

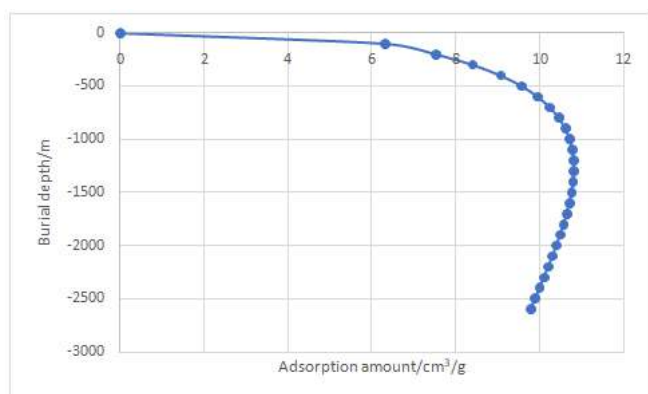


Figure 3: The relationship between the burial depth and the adsorption amount of WT coal

Based on the assumption of the ground temperature gradient of $3^\circ\text{C}/100\text{m}$ and the pressure gradient of $1\text{MPa}/100\text{m}$, the critical depth is predicted at the depth between 1300m and 1400m with a maximum adsorption amount of $10.8093\text{ cm}^3/\text{g}$. Before reaching the critical depth, the total differential of adsorption amount is positive, the adsorption amount is increased. After passing the critical depth, the total differential of adsorption amount is negative, the adsorption amount is reducing.

4 Conclusions

The set of five temperatures' isothermal adsorption data of WT coal of Shanxi, China have been used to regress and to calculate the parameters of TPAE. This operation has transformed the Langmuir equations into trinary (temperature-pressure-adsorbing) equation with the average relative errors is 8.82% . The TPAE curvature surface and adsorption points match very well. Both numerical and graphical evidence approved that TPAE is applicable to interpreting the series isothermal adsorption data.

TPAE is a trinary (temperature-pressure-adsorbing) equation, its partial differential of temperature, partial differential of pressure and total differential can be numerically calculated. All calculation results of the WT coal sample in the measured temperature range ($30\sim 70^\circ\text{C}$) and pressure range ($0\sim 20\text{ MPa}$) have been presented in a table format.

Under the isobaric condition, the partial differential with respect to $T, \left(\frac{\partial V}{\partial T}\right)_P$, is negative, so the adsorption amount is decreasing with increasing temperature. Under the isothermal condition, the partial differential with respect to $P, \left(\frac{\partial V}{\partial P}\right)_T$, is positive, so the adsorption amount is increasing with increasing pressure.

Assuming that the ground temperature gradient of $3^\circ\text{C}/100\text{m}$ and the pressure gradient of $1\text{MPa}/100\text{m}$, the critical depth is predicted at the depth between 1300m and 1400m with a maximum adsorption amount of $10.8093\text{ cm}^3/\text{g}$.

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