TRJ Vol. 9 Issue 4 July-August 2023 ISSN: 2454-7301 (Print) | ISSN: 2454-4930 (Online)

A MATHEMATICAL ANALYSIS OF LOW-RANK COAL ADSORPTION BEHAVIOR

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Abstract: This paper discusses the limitations of the Langmuir isothermal adsorption equation, then proposes the theoretical significance of the temperature-pressure-adsorption equation (TPAE). The series isothermal adsorption data of low-rank coal from Yangpoquan 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-100°C and pressure between 0-30 MPa can be arbitrarily calculated, with an average relative error of less than 8.0 %, 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 Yangpoquan 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 1900 m underground, the critical adsorption pressure is 19 MPa, the critical adsorption temperature is 75°C, and the critical adsorption capacity is 7.68cm^3/g.

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

I. 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. It is a consensus that there is a maximum value for the adsorption of coalbed methane in coal reservoirs, and the academic community calls it the "critical adsorption". The description of this phenomenon is: 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.

II. DATA AND TEMPERATURE-PRESSURE-ADSORPTION EQUATION

A. Sample

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

TABLE 1: THE DATA AND PARAMETERS OF YPQ COAL SAMPLE [1]

parameter	data
$R_{0,\ max}$/%	0.57
Vitrinite/%	55.7
Inertinite/%	37.7
Exinite/%	4.9
Mineral/%	1.76
Ash/%	5.2
Moisture/%	8.1

B. The Langmuir adsorption equation

The Langmuir adsorption equation can be represented as:

$$V = \frac{abP}{1+bP} \tag{1}$$

here

a is the Langmuir volume.

b is the reciprocal of the Langmuir pressure.

The YPQ coal under different testing temperatures is listed in Table 2. The temperature range is 30~100℃ and pressure is 0~30 MPa.

TABLE 2: THE LANGMUIR VOLUME AND THE RECIPROCAL OF LANGMUIR PRESSURE OF YPQ COAL [1]

Experimental temperature/°C	a/cm^3g^{-1}	b/MPa^{-1}
30	17.89	0.1094
50	15.34	0.0909
70	11.1	0.0995
85	12.25	0.0722
100	11.09	0.069

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.

C. 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

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

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 (cm^3/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].

D. 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:

$$\delta_i = \frac{|V_{TP}-V_{LA}|}{V_{LA}} x100\% \tag{3-1}$$

The average relative error is defined as:

$$\bar{\delta} = \frac{1}{n}\sum_{i=1}^{n}\frac{|V_{TP}-V_{LA}|}{V_{LA}} x100\% \tag{3-2}$$

here:

n is the total numbers of testing at different temperatures and pressures. There are 5 Langmuir’s temperatures, and for each temperature, 16 pressure values are chosen, from 1 to 31 MPa with a fixed interval of 2.0 MPa. The n is equal to 80.

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）.

E. 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

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

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:

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

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

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

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

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

Under isothermal condition, because all parameters, B, M, T, P and β 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:

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

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

$$dT = T_2 - T_1 \qquad (9\text{-}1)$$

$$dP = P_2 - P_1 \qquad (9\text{-}2)$$

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

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

III. RESULTS AND DISCUSSIONS

A. TPAE

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

TABLE 3: THE TPAE PARAMETERS REGRETTED FROM ISOTHERMAL ADSORPTION MEASUREMENTS OF YPQ COAL

Parameter	value
A	0.168
B	0.0001728
Δ/K	1562
β	0.5847
$\bar{\delta}$/%	7.92

The final average relative error of low-rank coal is 7.92%. 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 5 rows' points are corresponding 5 Langmuir's temperatures.

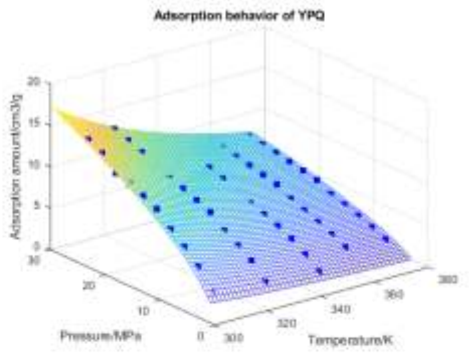

Figure 1: Visibility of TPAE cured surface and Langmuir points.

From Figure 1, the 5 rows' Langmuir points are agreed with the TPAE cured surface. This approves that TPAE treats accurately a series of isothermal adsorption.

B. 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 REULTS OF TOTAL DIFFERENTIAL AND PARTIAL DIFFERENTIAL OF YPQ COAL UNDER THE TESTED TEMPERATURE AND PRESSURE

T_1/K	T_2/K	P_1	P_2	$\left(\frac{\partial V}{\partial T}\right)_P$	$\left(\frac{\partial V}{\partial P}\right)_T$	dT	dP	dV	V*
291	294	1	2	-0.0496	1.30202	3	1	1.1533	3.8433
294	297	2	3	-0.0625	1.00779	3	1	0.8203	4.6636
297	300	3	4	-0.0713	0.83946	3	1	0.6257	5.2893
300	303	4	5	-0.0774	0.72511	3	1	0.4930	5.7823
303	306	5	6	-0.0817	0.64024	3	1	0.3952	6.1775
306	309	6	7	-0.0846	0.57376	3	1	0.3199	6.4974
309	312	7	8	-0.0865	0.51979	3	1	0.2601	6.7575
312	315	8	9	-0.0877	0.47481	3	1	0.2118	6.9693
315	318	9	10	-0.0882	0.43660	3	1	0.1720	7.1413
318	321	10	11	-0.0882	0.40365	3	1	0.1390	7.2802
321	324	11	12	-0.0879	0.37489	3	1	0.1113	7.3915
324	327	12	13	-0.0872	0.34954	3	1	0.0879	7.4794
327	330	13	14	-0.0863	0.32702	3	1	0.0681	7.5475
330	333	14	15	-0.0852	0.30686	3	1	0.0512	7.5987
333	336	15	16	-0.0840	0.28872	3	1	0.0368	7.6356
336	339	16	17	-0.0826	0.27230	3	1	0.0245	7.6601
339	342	17	18	-0.0812	0.25738	3	1	0.0139	7.6740
342	345	18	**19**	-0.0796	0.24376	3	1	**0.0048**	**7.6788**
345	348	19	20	-0.0781	0.23128	3	1	-0.0030	7.6758
348	351	20	21	-0.0765	0.21982	3	1	-0.0097	7.6661
351	354	21	22	-0.0749	0.20925	3	1	-0.0154	7.6507
354	357	22	23	-0.0733	0.19948	3	1	-0.0204	7.6303
357	360	23	24	-0.0717	0.19043	3	1	-0.0246	7.6057
360	363	24	25	-0.0701	0.18203	3	1	-0.0282	7.5775
363	366	25	26	-0.0685	0.17421	3	1	-0.0312	7.5463
366	369	26	27	-0.0669	0.16692	3	1	-0.0338	7.5125

Here V_0=2.69

First, under testing temperature range (18~93℃, 291 ~366K), for YPQ coal with Δ=1562K, 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 (0~30 MPa), YPQ 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 YPQ is zero, along with the buried depth increasing.

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

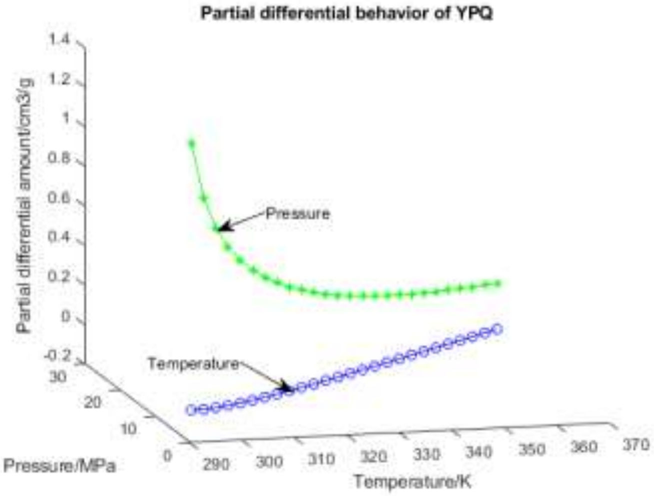

Figure 2: Partial differential of temperature and pressure

C. 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 ＜345K, P＜ 19MPa. 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 ＞345K, P＞19MPa.

Assuming the temperature of the constant temperature layer at YPQ coal was 15℃， the ground temperature gradient of 3℃ /100m and the pressure gradient of 1MPa / 100m, the relationship between the buried depth and the adsorption amount of YPQ coal is depictured in Figure 3.

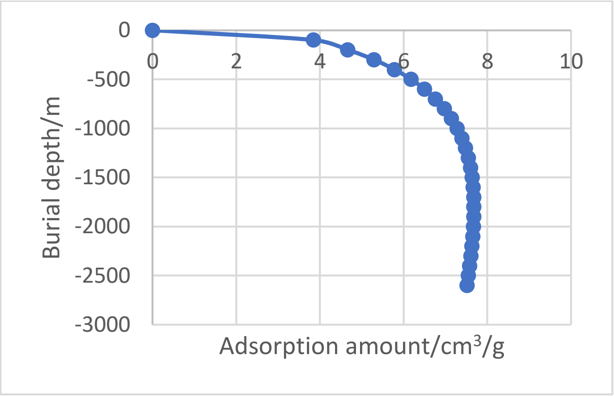

Figure 3: The relationship between the burial depth and the adsorption amount of YPQ coal

Based on the assumption of the ground temperature gradient of 3℃ /100m and the pressure gradient of 1MPa / 100m, the critical depth is predicted at 1900m with a maximum adsorption amount of 7.6788 cm^3/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.

IV. CONCLUSIONS

The set of five temperatures' isothermal adsorption data of YPQ 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-absorbing) equation with the average relative errors is 7.92%. 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-absorbing) equation, its partial differential of temperature， partial differential of pressure and total differential can be numerically calculated. All calculation results of the YPQ coal sample in the measured temperature range (30~100℃) and pressure range (0~30 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℃ /100m and the pressure gradient of 1MPa / 100m, the critical depth is predicted at 1900m with a maximum adsorption amount of 7.6788 cm^3/g.

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