



Full Length Article

The adsorption heat of methane on coal: Comparison of theoretical and calorimetric heat and model of heat flow by microcalorimeter



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ABSTRACT

Various methods have been proposed to determine the heat of adsorption indirectly from adsorption isotherms or directly through calorimeter, whereas authors rarely compared different models for calculating isosteric heat of methane adsorption on coal and seldom studied adsorption thermodynamics related to calorimetric heat flux. In this work, for better probing thermodynamics of adsorption of methane on coal, seeking a reliable model to describe adsorption heat, and predicting the adsorption heat at given temperatures and pressures from heat flow, isothermal adsorption experiments of methane on anthracite at temperatures of 298 K, 308 K and 318 K were conducted, with both calorimetric and volumetric method. The calorimetric results indicate that isosteric heat decreases with the increase of adsorption capacity and temperature. Then the calorimetric heat was compared with the isosteric heat using four adsorption models, in the fitness sequence of D-A > Toth > C-C > Virial. To be noted that the heat flux measured calorimetrically increases to the crest rapidly, then gradually decreases to the initial state. This tendency is proposed to be described by the exponential function with the fitting parameters estimated by empirical formulas proposed. The predicted heat flows were thus acquired, agreeing well with the experimental data except for the low coverage or pressure stage. Furthermore, it is revealed that the temperature evolution of adsorption can also be expressed by an exponential-like polynomial solution, induced from the proposed thermal flux prediction model based on the Tian's equation.

1. Introduction

Coal bed methane (CBM), as a clean nonconventional natural gas resource, has been an intense research topic with wide engineering applications, such as the resource exploitation and development, coal degasification and dynamic gas disasters control for underground mining, CBM reserve estimation, CO₂ sequestration to enhance CBM recovery and global warming amelioration [1–3]. Hence, characteristics of methane adsorption in coal were extensively studied, which a variety of methods and theories have been and continue to be proposed for better interpreting adsorption isotherm data. For example, there were Langmuir model based on monolayer [4], empirical three-parameter Langmuir-modification (Langmuir-Freundlich, extended Langmuir and Toth model) [5], BET model of multilayer theory [4], and adsorption potential model (D-R or D-A) [6,7]. These isotherm models were widely used to describe the experimental adsorption isotherms in other fields of activated carbon or molecular sieves, but were seldom

used in CBM adsorption except for the most common used Langmuir model [8].

In contrast to the sorption kinetics, less attention has been focused on the thermodynamic behavior (especially in the experimental aspect) which is closely correlated to the mechanism of gas adsorption or desorption process. As one of the most fundamental thermodynamic parameters, the adsorption heat is the conversion energy between free gas and adsorbed gas, revealing macroscopic performance of adsorbate-adsorbent molecules interacting on the surface [9]. To some extent, the heat can characterize the properties of adsorption capacity on coal, site energy distribution, surface energetic heterogeneity and temperature involvement, which in turn will affect the adsorption kinetics from the viewpoint of thermodynamics [3,10,11]. Moreover, the heat of adsorption can be used to predict the adsorption isotherms at different temperatures and pressures with less restrictions of experiment, providing a possible basis for evaluating the adsorption of coal reservoir under complex conditions such as high temperature, high pressure and

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deep mining [12,13,39].

As one of the most presentative heats of adsorption [14], the isosteric heat of adsorption can be estimated by two commonly established techniques, i.e. the indirect adsorption isotherm method (AIM) or the direct calorimetric isotherm method (CIM). The adsorption heat of AIM is mathematically derived by using the sorption isotherm models at various temperatures using Clausius–Clapeyron (C-C) relation [15], which was widely utilized however reported not to fit the experimental data well [16]. Strenuous efforts have been made to improve the accuracy of AIM with strict consideration on factors of adsorbed phase volume, non-ideality gas, proper isotherm models, higher pressure and homogeneity [17–19]. They were yet lacking in persuasion and universality on accurate estimation of adsorption heat, unless the comparisons among various AIM models are added rather than the only comparisons of AIM and CIM results. That is why this research made the optimized comparisons among the four resultant heat prediction models based on equations of C-C, Virial, Toth and D-A. As for the CIM, it is available to acquire the adsorption heat quantitatively in a more accurate way by calorimeter. Whereas, calorimetry was arduous to demand the synchronization of the heating signal from reacting cells and to demand an unerring accounting of the adsorbate retention time [14]. In addition, an additional volumetric system is required for the determination of calorimetric heat to contrast with the heat of AIM. Due to the extra complexity and limitations above, CIM turned out to be less popular used in comparison with other simpler techniques like AIM, chromatography, and molecular simulation [20,21].

In the past few years, to improve measurement accuracy of thermal parameters via sundry types of calorimeter, the theory of calorimetric systems, calorimetric principles and the generalized equations of the heat balance and dynamics have been considerably developed [22,23]. But most of calorimetry cases only discussed the static equilibrium method like calorimetric isotherm analysis, lacking in the added analysis of dynamic equilibrium especially on the thermal signal. Only if the heat flow at the given pressure and temperature can be expressed explicitly (studied in this paper), it would be likely to predict accurate adsorption heat avoiding the troublesome of time-consuming and labor-intensive calorimetric measurement.

In this paper, to take merits of both AIM and CIM, the C80 microcalorimeter was utilized to simultaneously determine the adsorption and calorimetric isotherms at different temperatures. Then the appropriate resultant isosteric heat equation was obtained for engineering calculation after comparing heats from AIM and CIM. Moreover, a new formula of heat flux prediction and the temperature evolution of adsorption process is proposed and verified as well.

2. Experimental methodology

2.1. Samples and preparation

The coal sample for this research is the anthracite coal collected from 3# coal seam of Chengzhuang Coal Mine, Shanxi Province, China. Following Chinese National Standard GB474-1996, the coal was milled and screened by a 60–80 mesh strainer (0.18–0.25 mm) and then was placed into the drying chamber at 105–110 °C for 10 h. After that, these

prepared specimens were stored in the vacuum dehydrator at 5 °C for experimental use. The gas purity of methane and helium sample was 99.999% and 99.99%, respectively. The proximate and ultimate analysis was performed in the compliance with GB/T212-2008 and GB/T 476-2001, respectively. While the determination of $R_{o, \max}$ and the maceral analysis followed the relevant national standard GB/T 6948-2008 and GB/T 8899-2013, respectively. The key properties of coal were measured in detail as shown in Table 1.

2.2. Testing apparatus

Experimental system for simultaneous measurement of adsorption heat and isotherms is sketched in Fig. 1, comprising both microcalorimetric and volumetric/manometric units of gas adsorption expatiated below.

A Tian-Calvet type microcalorimeter (C80) was applied to the synchronous determination of adsorption isotherms and heats of adsorption, which mainly consists of two twin cylinders: a sample cell and a reference cell. Cells are surrounded by approximate 496 pairs of 3D thermocouples in a connecting way of series-opposing, by which at least 95% heat changed slightly from adsorption can be measured. For the whole process, it is notable that the pressures, temperatures, gas flow and other conditions should be seriously equal at the two cells in consideration of testing accuracy.

Apart from the adsorption heat, we can obtain the adsorption isotherms varying from the room temperature to 100 °C and pressure up to 30 MPa. The maximum precision of pressure sensor is up to 10^{-6} MPa. The charging tank, as an intermediate vector linked between the gas supply cylinder and the C80, is immersed in the water at a stable temperature monitored by the temperature sensor to ensure the isothermal condition. And the flow rate could be altered by adjusting the valves set on vessels automatically. Moreover, temperatures at adsorption cell should be guaranteed to always equal to temperatures of charging tank. Thermal compensation is thus needful from wire heater installed on the calorimeter under the automatic control of computer.

2.3. Measurement of methane adsorption and calorimetric isotherms

The experiment was carried out to determine adsorption characteristics and thermodynamics of methane on coal at three temperatures (298 K, 308 K, and 318 K). For the readers' verification and reproduction, the detailed experimental procedure is provided as follows.

- (1) Check of gas tightness and dispersion of residual gas. First of all, weigh 4 g the pre-treated coal sample and place it into the sample cell. Then by charging helium into the cells and tank by 2–3 MPa, we can check the gas tightness from the observation on whether the pressure inside would be stabilized for 3 h or more. At the same time, since the characteristics on non-adsorption and small atomic radius, helium is a better choice to dispel the other gas originally adsorbed onto coal sample.
- (2) Measurement of dead volume and calibration. Evacuate the whole apparatus to a vacuum level of 10^{-6} MPa. Afterwards, inject helium again to the charging tank up to a suggested pressure of 2–3 MPa

Table 1
Properties of coal samples.

| Chengzhuang Coal Mine | Proximate (wt %) | | | | | Ultimate (wt %) | | | | | Maceral analysis (vol %) | | | | $R_{o, \max}$ |
|-----------------------|------------------|----------|----------|-----------|----------|-----------------|----------|----------|------------|------------|--------------------------|------|-----|-----|---------------|
| | M_{ad} | A_{ad} | V_{ad} | FC_{ad} | C_{ad} | H_{ad} | O_{ad} | N_{ad} | $S_{t,ad}$ | $P_{t,ad}$ | V | I | E | M | |
| Anthracite | 0.76 | 13.78 | 7.51 | 77.95 | 77.64 | 2.85 | 3.48 | 1.2 | 0.23 | 0.06 | 81.7 | 15.7 | 1.5 | 1.1 | 2.53 |

Note: wt – Weight percentage; vol – Volume fraction; the subscript “ad” identifies the air dried basis. M_{ad} – Moisture; A_{ad} – Ash yield; V_{ad} – Volatile matter; FC_{ad} – Fixed carbon content. C_{ad} – Content of carbon; H_{ad} – Content of hydrogen; O_{ad} – Content of oxygen; N_{ad} – Content of nitrogen; $S_{t,ad}$ – Content of sulphur; $P_{t,ad}$ – Content of phosphorus. V – Vitrinite; I – Inertinite; E – Exinite; M – Minerals.

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