煤岩生气热模拟及其对煤层气形成的示踪意义*

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摘　要　煤岩热解模拟实验为认识含煤盆地的成烃演化、煤层气地球化学特征的成因及其资源预测提供了科学依据。文章在336.8～600 ℃温度和 50 MPa压力及 20 ℃/h和 2 ℃/h升温速率条件下,对沁水盆地上古生界煤岩进行了热解生气模拟实验。结果表明,煤岩热模拟气体产物主要由甲烷(CH_4)、C_{2-5}烃类气体和二氧化碳(CO_2)非烃气体组成,氢气(H_2)和硫化氢(H_2S)含量极低;随着模拟温度的增加,气体产物中甲烷和大部分氢气(H_2)的相对百分含量呈单向增加,二氧化碳表现为单向降低,C_{2-5}烃类气体和硫化氢(H_2S)气体先增加后降低;低温速率有利于甲烷、C_{2-5}气体、氢气和二氧化碳气体的生成,并且它们的形成表现为多阶段性;相同升温速率下二氧化碳和氢气的相对产率与甲烷的相对产率变化表现为正相关,反映了它们与甲烷同是煤岩热解过程中同步进行的平行反应产物;相同模拟温度和温速条件下,山西组煤岩比太原组煤岩具有较高的产甲烷和 C_{2-5}烃类气体能力,这意味着在实际的地质环境中,山西组煤岩更有利于煤层气的形成。并且对煤岩生气热模拟实验结果在煤层气形成方面的示踪意义进行了探讨。

主题词　沁水盆地　晚古生代　煤　岩石　热模拟　升温速率　煤成气　示踪

煤岩热模拟是认识含煤沉积盆地成烃演化和煤层气资源预测的重要手段和依据[1,2]。沁水盆地作为我国重要的煤层气资源勘探开发地区,却比较缺乏煤岩热模拟实验方面的证据。另外,有关煤岩热模拟的研究内容主要集中在全煤的产烃率及产物的地球化学特征等[1,3,4],却很少考虑时间因素的作用。然而,近年来有机质成烃动力学模拟实验结果表明,地质时间在沉积盆地有机质成烃演化过程中具有非常重要的作用[5]。因此,笔者对沁水盆地上古生界煤岩进行了热模拟实验。模拟实验在 20 ℃/h和 2 ℃/h两种升温速率条件下进行,体现了时间在煤岩热解中的重要作用。研究结果对于沁水盆地煤层气生成特征的进一步认识及其资源评价提供了科学数据。

一、样品及实验方法

实验样品采自内蒙古唐公塔煤矿 6#煤层[太原组(P_1t)]和山西李雅庄煤矿 2#煤层[山西组(P_1s)],其基本分析数据见表 1。热解实验在一套高温高压热解装置中进行,方法及过程同文献[6]。

表 1　煤岩样品基本分析数据

煤岩层位	煤岩显微组分(%)				TOC(%)	R_o(%)
	镜质组	惰质组	壳质组	矿物		
P_1t	56.9	31.2	7.1	4.8	65.3	0.51
P_1s	58.4	27.2	9.4	5.0	77.5	0.94

二、结果与讨论

1.煤岩热模拟产物气体组成

分析沁水盆地煤岩热解气体产物百分含量数据可知,煤岩高温热解的主要烃类气体以甲烷(CH_4)为主,C_{2-5}烃类气体次之;非烃气体以二氧化碳(CO_2)为主,氢气(H_2)和硫化氢(H_2S)含量极低(图 1)。

图 1同时显示,相同温度条件下,对同一煤岩样品,其热模拟气体产物 CH_4、C_{2-5}气体和 CO_2 在升温速率为 20 ℃/h时的相对含量低于 2 ℃/h时的相对含量。随着温度的增大,CH_4 和大部分 H_2 的相对百分含量呈单向增加,而 CO_2 表现为单向降低;C_{2-5}气体和 H_2S先增加后降低。

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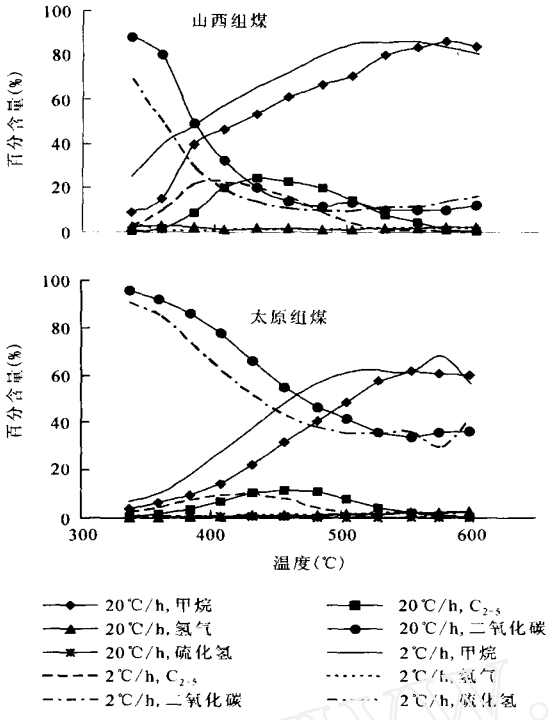


图 1　沁水盆地上古生界太原组煤和山西组煤生成

2.煤岩热模拟产物烃类气体产率演化特征

(1)烃类气体累积产率演化特征

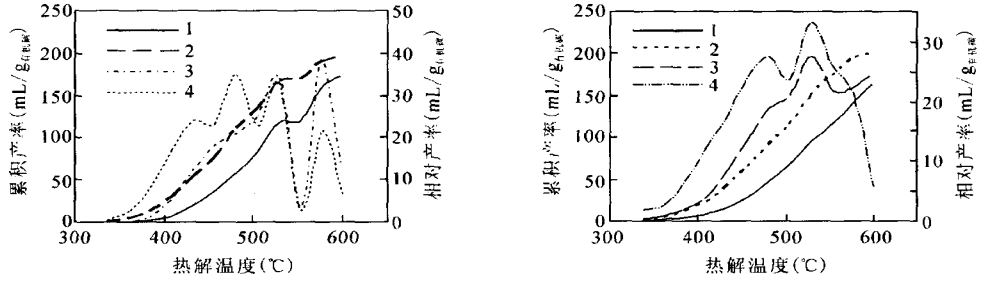
在模拟实验温度范围内,沁水盆地两组煤岩生成的 CH_4 的累计产率随着温度的增大而持续增加(图 2)。20 ℃/h温速时,CH_4 的累积产率总是低于温速 2 ℃/h时的累积产率。升温速率为 20 ℃/h和 2 ℃/h时,山西组煤岩生成的 CH_4 在 600 ℃的累积产率分别为 171和 203 mL/g TOC,而太原组煤岩分别为 163和 194 mL/g TOC,均小于山西组煤岩。

与 CH_4 相比,沁水盆地两组煤岩热解产物 C_{2-5} 气体产率较低,出现了一次累积产率的高峰,之后便逐渐降低(图 3)。相对于 2 ℃/h的升温速率,20 ℃/h升温速率条件下煤岩热解生成的 C_{2-5} 气体累积产率最高峰对应的温度值较大,明显向高温方向迁移。

相同温度和温速条件下,山西组煤岩比太原组煤岩具有较高的产 C_{2-5} 烃类气体能力,与 CH_4 的产气规律完全相同(图 3)。

(2)烃类气体相对产率演化特征

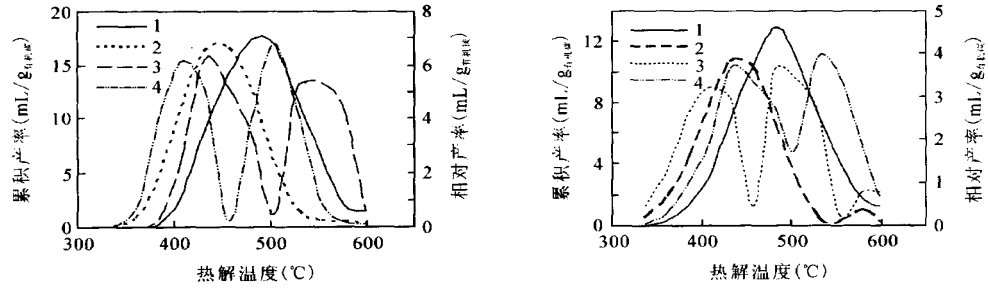
从图 2可以看出,升温速率为 2 ℃/h,山西组煤岩分别在温度为 430 ℃、470 ℃、520 ℃和 575 ℃左右处出现 4个产 CH_4 的相对产率高峰,而升温速率



(a)山西组煤　　(b)太原组煤

图 2　沁水盆地煤岩生成的甲烷气体产率

注:1表示 20 ℃/h,累积产率;2表示 2 ℃/h,累积产率;3表示 20 ℃/h,相对产率;4表示 2 ℃/h,相对产率



(a)山西组煤　　(b)太原组煤

图 3　沁水盆地煤岩生成的 C_2～C_5 烃类气体产率

注:1表示 20 ℃/h,累积产率;2表示 2 ℃/h,累积产率;3表示 20 ℃/h,相对产率;4表示 2 ℃/h,相对产率

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为 20 ℃/h时仅仅在 520 ℃和 575 ℃左右处出现两个高峰点,与 2 ℃/h时后两个 CH_4 相对产率高峰温度点重合。在两种升温速率时,太原组煤岩在 470 ℃和 540 ℃出现两个 CH_4 产率高峰温度点。由此看出,尽管不同的升温速率条件下,煤岩生成 CH_4 的演化特征是不同的。但当温度上升到 470 ℃以后,升温速率仅改变了煤岩产生 CH_4 的相对产量,但是产率峰值对应的温度点相近。

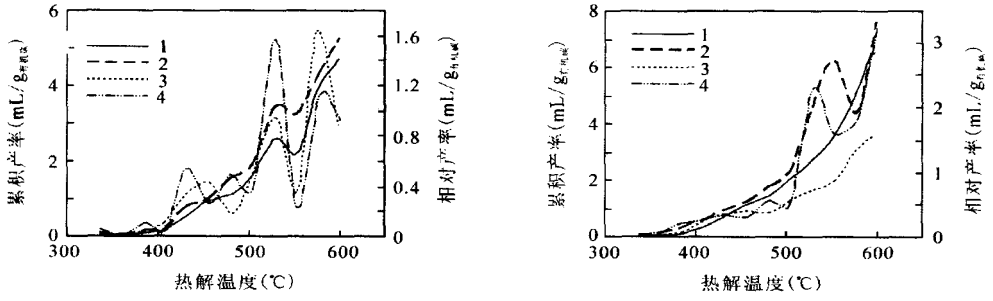
两种升温速率条件下,两组煤岩热模拟产物 C_{2-5} 气体的相对产率曲线均呈明显的双峰形态 (图 3)。在 20 ℃/h升温速率条件下,山西组煤岩生成的 C_{2-5} 烃类气体的第一相对产率高峰对应的温度点为 440 ℃,第二高峰对应的温度点为 550 ℃,而太原组煤岩生成的与山西组煤岩完全相同。相同的情况也出现在 2 ℃/h升温速率条件下。这可能反映出具有不同性质的煤岩在热演化过程中所具有的共性特征。

3. 非烃气体产率特征

随实验温度的增大, CO_2 累积产率大体保持增长态势。相同温度条件下, 2 ℃/h升温速率时的累积产率要大于 20 ℃/h升温速率时的累积产率。CO_2 成气过程基本符合化学反应动力学时间与温度互补原理。温度相同条件下,太原组煤岩热解生成的 CO_2 的累积产率高于山西组煤岩。

经过对比发现,在相同升温条件下, CO_2 的相对产率的高低变化与 CH_4 的相对产率变化完全吻合。这种关系可能证明 CO_2 和 CH_4 是煤岩热解过程种同步进行的平行反应,而不是相互独立的反应。

随着模拟实验温度的增大, H_2 的累积产率也具有增长趋势 (图 4)。H_2 的相对产率变化与 CH_4 同样具有密切的演化和生成关系。这些关系说明 H_2 生成过程基本符合化学反应动力学原理,并且与 CH_4 同属热解过程种同步进行的平行反应。



(a)山西组煤　　(b)太原组煤

图 4　沁水盆地煤岩生成的氢气产率

注:1表示 20 ℃/h,累积产率;2表示 2 ℃/h,累积产率;3表示 20 ℃/h,相对产率;4表示 2 ℃/h,相对产率

H_2S 仅在太原组煤岩的热解气体产物中被检测到,其产率变化比较复杂,与烃类气体及另外两种非烃气体的相关性差 (图 5)。

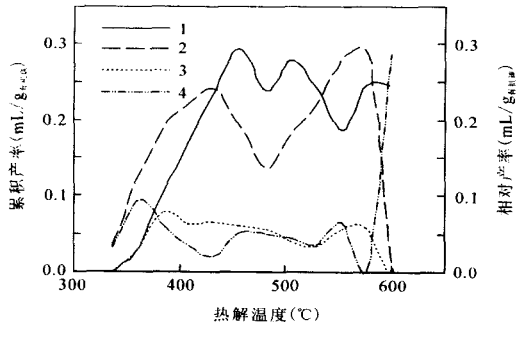


图 5　沁水盆地太原组煤岩生成的硫化氢气体产率

三、对煤层气形成的示踪意义

煤层气的成因是人们探索的热点问题,而煤岩热模拟实验研究则是了解煤层气形成的重要手段。通过上述煤岩热模拟实验研究结果可知,煤岩在模拟温度 450 ℃以前的高成熟阶段, CH_4 的累积产率较低,在实际的地质环境中,难以构成煤层气藏;大于 450 ℃的过成熟阶段, CH_4 的累积产率增长较快,特别是模拟温度达到 600 ℃ (R_o >4.0%)时, CH_4 的累积产率大于 160 mL/g有机炭,并且仍表现为快速增长趋势,这表明,从煤层气生成来说,有利的煤层气分布区应在煤岩的高演化地区。沁水盆地的煤岩演化程度较高, R_o 值一般大于 2.6%,部分地区达到 4.0%,是我国煤层气分布最好的地区,并且找到了我国最大的煤层气田,这与本文的实验模拟结果相

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吻合。

模拟实验结果表明,烃类气体产率的高低除了受到温度的控制之外,升温速率是一个不可忽视的因素,在相同的温度范围内,升温速率越慢,则烃类气体的产率越高,反映了时间和温度互补的化学动力学原理。这就意味着在实际的地质环境中,当煤岩受热程度相差不大时,经历地质时间越长,则生成的煤层气量越多。

煤层气组成是研究其成因的重要指标。由热模拟结果可知,煤岩性质极度的影响了热模拟产物是气体组成。例如,在相同模拟温度条件下,山西组煤岩生成的 CH_4 远大于太原组煤,而 CO_2 生成量远小于太原组煤;热模拟产物的气体组成还极大地受热演化程度控制,热模拟温度越高,则生成的气体中 CH_4 的含量增加, CO_2 含量减少。对于沁水盆地南部晋城地区高演化 (R_o 为 2.6%～4.0%)煤层气组成统计表明, CH_4 含量在 91%～96%之间, CO_2 为 0.03%～0.17%, C^{2+} 气体为 0.07%～0.13%。四组 600 ℃(R_o > 4.0%)热模拟产物中 CH_4 为 56.6%～84.4%, CO_2 为 12.5%～41.2%, C^{2+} 气体为 0.07%～0.46%。与沁水盆地南部煤层气组成相比,热模拟产物中 CO_2 含量很高,说明该地区原始煤层中 CO_2 已溶解在水中被带出煤层,或与 H_2 作用形成 CH_4,从而使现在煤层中 CH_4 含量很高,而 CO_2 含量极低。另外,世界上煤层气组成变化较大,重烃气体可以从 0到 70%, CO_2 可以在 0到 99%之间[7]。我们的热模拟资料为了解煤层气组成的起因提供了重要的信息。

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珠海 —中山天然气输气管道工程中山段开建

珠海 —中山天然气输气管道工程项目中山试验段于 2005年 1月 17日上午在南朗镇正式开工。该管道计划于 2006年初向珠海、中山城市居民供气。届时,它将成为广东省第一条建成的天然气管道。据了解,珠海 —中山天然气管道干线工程南起珠海市横琴岛横琴首站,北至中山市南朗镇横门末站,全长 63公里,设计输气能力 15亿立方米/年,总投资约 5.2亿元。据介绍,该天然气源来自中海油南海惠州、番禺等气田,经珠海陆上终端处理厂处理后, 2006年初向珠海、中山城市居民及沿线电厂正式供气。

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controlled by gas initial content and physicochemical property as well as coal metamorphic grade; ③ the higher the one component content in gas phase, the smaller the amount of gas's being adsorbed; and ④ the degree of affecting one component adsorption amount's being reduced by the other component is different because of the difference in adsorption property. This study provides a theoretical basis and experimental data for enhancing coalbed methane recovery by gas injection.

SUBJECT HEADINGS: Coal, Adsorption, Multicomponent gas, Experiment

Zhang Qingling *(female, senior engineer)*, born in 1962, graduated in chemistry at the Shanxi University in 1983. She is mainly engaged in the development and utilization of the minerals associated with coal measures, and the coalbed methane experimental investigation works. Add: No. 52 North Yanta Road, Xi'an, Shaanxi (710054), China Tel: (029) 87862508 E-mail: qqzhang 333@etang con

ADSORPTION OF DIFFERENT RANK COALS TO SINGLE COMPONENT GASES

Cui Yongjun, Zhang Qun, Zhang Hong and Zhang Qingling (Xi'an Branch, China Coal Research Institute). *NATUR. GAS IND.* v. 25, no. 1, pp. 61—65, 1/25/2005. (ISSN 1000 - 0976; **In Chinese**)

ABSTRACT: Through studying the single component gases (CH_4, N_2 and CO_2)' being adsorbed by long flame coal, gas coal, coking coal and anthracite respectively, their characteristics and diversities among them are discussed in the paper. It was found that the ratios of CO_2/CH_4 and CH_4/N_2 didn't show a simple relation of two times but changed along with the changes in coal rank and equilibrium pressure. The results of simulating distinct gases' being adsorbed by coals by use of several conventional adsorption models, including Langmuir, BET, D-A and D-R equations, were evaluated, and the adsorption models being more suitable for describing the behaviours of gas' being adsorbed by coal were optimized. The research results indicated that the D-A equation (n = 1) was more suitable for describing the behaviours of the adsorption of coal to CH_4; the Frendulich and Henry equations were suitable for describing the behaviours of the adsorption of low-rank coal to N_2; but all the selected models couldn't be used for interpreting reasonably the upwarping phenomenon of the isothermal line of CO_2's being adsorbed by anthracite at high pressure. These research results are of great importance to the resource evaluation and productivity prediction of coalbed methane, the technique of enhancing coalbed methane recovery by gas injection and the technique of CO_2's being sealed in coal beds, etc. **(Financed by the National Basic Research Program Project: Adsorption characteristic and gas storage mechanism of coal bed, No. 2002CB211703)**

SUBJECT HEADINGS: Coal, Adsorption, Coalbed methane, Feature, Model

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THERMAL SIMULATION OF GAS GENERATION OF COAL ROCKS AND ITS SIGNIFICANCE TRACING COALBED METHANE FORMATION

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ABSTRACT: The thermal simulation experiment of coal rock can provide a scientific basis for understanding the evolution of hydrocarbon generation in coal-bearing basin and the geochemical characteristics of coalbed methane and its resource prediction. The thermal simulation experiments of gas generation of the upper Paleozoic coal rock samples collected from Qinshui Basin were carried out at the temperatures of 336.8—600 °C, the pressure of 50 MPa and the temperature-rising rates of 20 °C/h and 2 °C/h. The results indicated that the gaseous products (relative percent content) were mainly composed of methane, C_{2-5} hydrocarbon gases and carbon dioxide, the bydrogen content and hydrogen sulfide content being extremely low; along with the increase in simulation temperature, the methane and hydrogen increased but carbon dioxide de-

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creased, and the C_{2-5} hydrocarbon gases and hydrogen sulfide increased first and decreased afterwards; the low temperature-rising rate was favourable to the generation of methane, C_{2-5} hydrocarbon gases, hydrogen and carbon dioxide, their formation being stage; the relative productivity of carbon dioxide or hydrogen was positively correlated with that of methane at the same temperature-rising rate, which reflects that they and the methane were the products of simultaneous parallel reaction in the process of the pyrolysis of coal rocks; and the ability of generating methane and C_{2-5} hydrocarbon gases of Shanxi Formation coal rocks was higher than that of Taiyuan Formation coal rocks at the same simulation temperature and temperature-rising rate, which means that the Shanxi Formation coal rocks were more beneficial to coalbed methane formation in natural conditions. Finally, the significance tracing coalbed methane formation is discussed in the paper according to the experimental results. **(Financed by the National Basic Research Program Project, No. 2002CB211701)**

SUBJECT HEADINGS: Qinshui Basin, Upper Palaeozoic, High temperature, Coal roch, High pressure, Thermal simulation, Coalbed gas

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ANALYSIS OF COAL ROCK DEFORMATION AT HIGH-TEMPERATURE AND HIGH-PRESSURE EXPERIMENTAL CONDITIONS

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ABSTRACT: The deformation experimental (at high-temperatures and high-pressures) results of the coal rock samples collected from Qinshui Basin indicated that the coal rock strengths of different ranks were of both conformity and diversity under the same experimental conditions; the effect of temperature on coal rock strength was higher than that of pressure under different experimental conditions; the stress strength of medium rank coal was lower than that of high rank coal at a certain temperature and pressure (300 ℃/300 MPa); the stress strength of high rank coal rock with low inertinite content was minimum; and the brittle-tough transition of coal rock developed between 200 ℃/200 MPa and 300 ℃/300 MPa, and, at this moment, the porosity of coal reservoir decreased but a certain number of fractures began to form, thus enhancing the permeability of coal reservoir. In the paper, the relation between coal rock deformation and its storage behaviour is discussed in combination with the test results of the maceral, permeability and specific surface of the coal rocks. **(Financed by the National Basic Research Program Project, No. 2002CB211700)**

SUBJECT HEADINGS: Coal reservoir, High temperature, High pressure, Experiment, Stree, Strength, Permeability, Maceral

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UNSTEADY PERCOLATION FLOW OF COALBED METHANE THROUGH DEFORMED COAL SEAM

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ABSTRACT: Because the coal body is easy to be deformed in the course of coalbed methane well production and the permeability has been assumed to be a constant in the conventional mathematical models of solving various coalbed methane well test problems, a relative great influence will exert on the spacial and instantaneous changes in pressure of deformation media——coal bed. In considerastion of the characteristics of coalbed's dual media, coalbed methane adsorption and medium deformation, an unsteady percolation flow model of deformed dual media was set up by introducing the permeability module. Owing to the fact that the flow equation of permeability's depending on the change in pore pressure is of strong nonlinearity, the model may be solved by use of regular perturbation method and Laplcae transform and the zero-order perturbation solution can be obtained through Laplace numerical inver-

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