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不同煤种燃烧生成多环芳烃的研究

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摘　要: 燃煤过程产生的多环芳烃类有机污染物烃具有强烈的致癌、致突变、致畸变等作用, 日益受到广泛的重视。本文进行了不同煤种燃烧时多环芳烃的生成研究, 比较了燃煤排放和原煤中含有的多环芳烃之间关系, 研究了煤的固定碳、挥发份、灰份等组分对燃煤过程中多环芳烃排放的影响。

关　键　词: 煤; 多环芳烃; 燃烧; 排放

中图分类号: TK229.6　　文献标识码: A

1　前　言

目前在洁净煤燃烧领域有关燃煤过程中多环芳烃的研究主要偏重于外在因素(如温度、过量空气系数、燃烧方式等)对多环芳烃生成和排放的影响, 而有关煤本身内在因素(如固定碳、挥发份、灰份、发热量等)的影响研究还很少。但实际上, 这些内在因素对燃煤过程中多环芳烃的生成和排放都有很重要的作用, 直接影响燃煤过程 PAHs 的生成与排放[1]。鉴于以上原因, 本文选取了国内主要动力用煤中的四种煤[2~3], 在自行设计的小型管式炉上进行了煤燃烧实验, 一方面比较了燃煤过程中排放的多环芳烃和原煤中含有的多环芳烃, 探讨燃煤过程中多环芳烃的主要可能来源; 另一方面, 还研究了煤的内在因素固定碳、挥发份、灰份对燃烧过程中多环芳烃排放的影响。

2　实验内容

2.1　煤种工业分析

实验选用了两种烟煤、一种无烟煤, 还有一种贫煤, 其工业分析如表 1。

表 1　实验煤种的工业分析

煤种	名称	地区	工业分析				
			M_{ad}/%	A_{ad}/%	V_{ad}/%	FC_{ad}/%	$Q_{net,ad}$/MJ·kg^{-1}
烟煤	兖州	山东	1.82	19.69	30.46	48.02	25.757
烟煤	大同	山西	4.67	13.90	26.60	54.80	27.503
贫煤	鱼矿	四川	1.71	17.76	14.90	65.63	29.880
无烟煤	晋城	山西	4.46	21.40	7.115	66.99	26.256

2.2　实验装置

实验在小型石英管式炉上进行(如图 1 所示), 由供气、管式炉加热及采样三部分组成。供气部分按照燃烧实验工况, 供给空气、氧气、氮气等不同的气氛, 本实验都在空气条件下进行; 管式炉加热部分为煤的燃烧室, 由程序升温调节和控制所需温度(温差±20 ℃); 采样部分为装有吸收有机物的 XAD－2 树脂和装有蒸馏水的吸收瓶, 两者串联用以保证能吸收烟气中的全部有机物质。

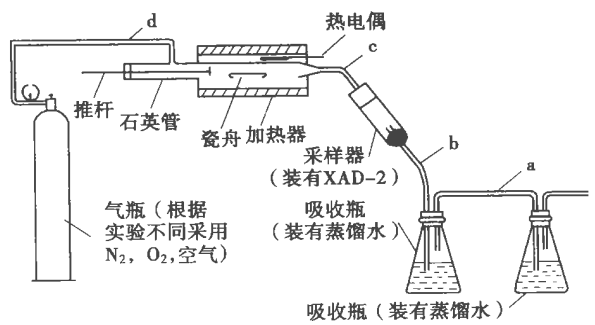

图 1　实验示意图

2.3　实验工况与样品预处理

实验时每次精确称取 0.500 0 g 的煤(80 ~ 400 目)置于瓷舟中燃烧, 气氛为空气, 空气流量为60 l/h,

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燃烧停留时间为 30 min。采样器装有适量的 XAD－2 树脂，吸收瓶装有蒸馏水。实验结束后，用二氯甲烷萃取蒸馏水，将萃取液和 XAD－2 树脂索氏抽提 20 h，然后将抽提液经旋转蒸发仪浓缩至 5 ml，最后将浓缩液经色谱分离后送气相色谱仪分析。

2.4 气相色谱仪分析测试条件

本实验采用的 ThermoQuest /Trace2000 气相色谱仪。分析 17 种（包括美国 EPA 建议优先监测的 16 种），分别为萘（Naphthalene）、苊（Acenaphthylene）、二氢苊（Acenaphthene）、芴（Fluorene）、菲（Phenanthrene）、蒽（Anthracene）、荧蒽（Fluoranthene）、芘（Pyrene）、苯并[a]蒽（Benzo[a] anthracene）、屈（Chrysene）、苯并[b]荧蒽（Benzo[b] fluoranthene）、苯并[k]荧蒽（Benzo[k] fluoranthene）、苯并[a]芘（Benzo[a]pyrene）、苯并[e]芘（Benzo[e] pyrene）、茚[123－c，d]并芘（Indeo[123－c，d] pyrene）、二苯并[a，h]蒽（Dibenz[a，h] anthracene）、苯并[g，h，i]苝（Benzo[g，h，i] perylene）。17 种 PAHs 混合标样（浓度为 100±10 μg/ml），溶剂：甲苯，编号 ES－4032）购自美国剑桥同位素实验室，采用外标法定量，通过各点绘制峰面积与浓度的标准曲线。读取色谱图上各物质的峰面积，查找对应标准曲线，得到物质浓度。

气相色谱测试条件：第一段初始温度 70 ℃，升温速率 3 ℃/min，中间温度 180 ℃；第二段升温速率 10 ℃/min，终温 270 ℃；保留 20 min。载气 He 流量为 1 ml/min，进样方式为不分流，检测器是 FID，检测器温度为 280 ℃。H_2 流量 35 ml/min，Air 流量 350 ml/min，N_2 流量 50 ml/min，进样量为 1μl。

3 结果和讨论

3.1 燃煤 PAHs 排放和原煤 PAHs 含量比较

原煤 PAHs 含量数据选自浙江大学热能工程研究所建立的部分国内原煤 PAHs 含量数据库，本文选取其中四种煤种 PAHs 含量与燃煤 PAHs 排放量进行比较，原煤 PAHs 含量见表 2。

表 2 原煤中 PAHs 含量

	山东兖州烟煤	山西大同烟煤	四川鱼矿贫煤	山西晋城无烟煤
PAHs/μg·g^{-1}	4.875	6.231 1	2.905 7	0.292 3

由图 2 和图 3 可知，虽然不同煤种燃煤 PAHs 排放量相对于相应原煤中 PAHs 含量的变化程度不同（如图 3，晋城无烟煤燃后和原煤中 PAHs 比值最高，约为 60），但是燃煤 PAHs 排放量比原煤 PAHs 含量高出很多（如图 2）。因此可以认为，燃煤 PAHs 的排放来源并不仅仅由于原煤所含有的那部分 PAHs 的挥发所致，其间必有其它途径生成，且是以其它途径为主。

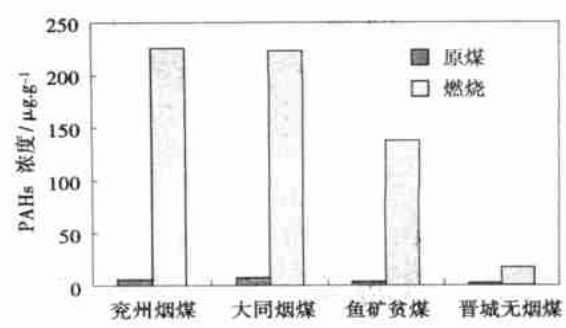

图 2 燃煤排放与原煤中 PAHs 比较

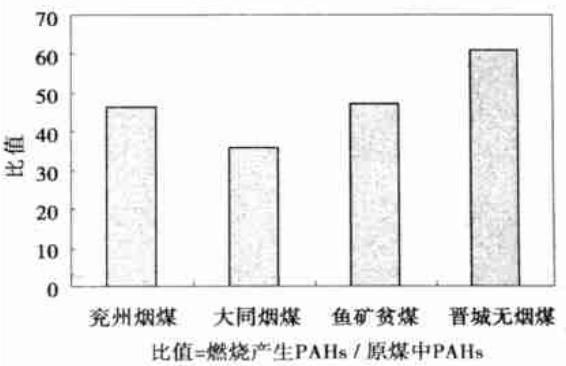

图 3 燃煤排放与原煤中 PAHs 的比值

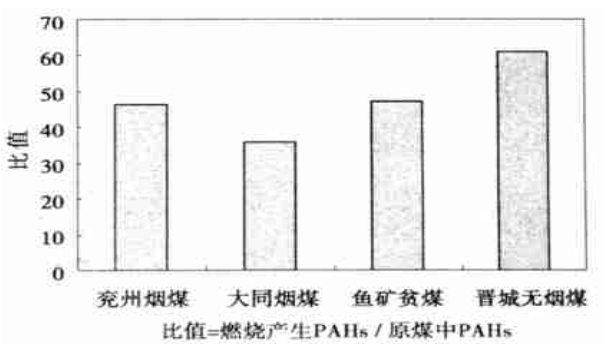

图 4 煤的单位发热量 PAHs 生成量

图 4 为选用的四种动力用煤单位发热量 PAHs 的生成量。发热量基本接近的情况下，PAHs 生成量烟煤最高，其次为贫煤，无烟煤最少。

3.2 燃煤 PAHs 排放量与煤成分的关系

煤是由有机成分和无机成分物质组成的混合

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物, 分子结构十分复杂。煤本身成分对煤燃烧有重要性, 本文分析了其与燃煤PAHs 排放量的关系。

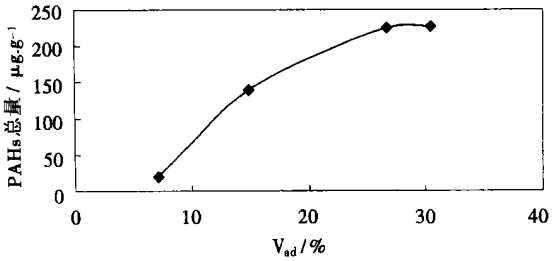

图 5　多环芳烃排放总量与煤种挥发份关系

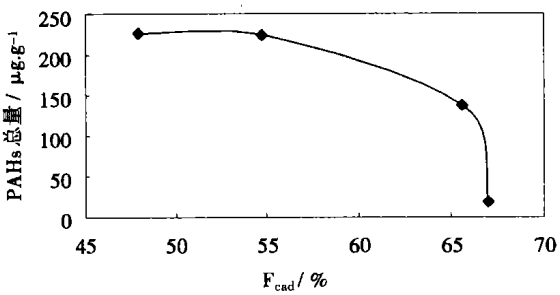

图 6　煤种固定碳含量与 PAHs 排放总量的关系

挥发份、含碳量是煤的重要成分, 煤种的煤阶特性、煤燃烧组织效果及燃烧生成和排放的产物都与其有密切的关系。本文实验选择的四种煤对挥发份含量在 7% ~30%区间的煤种有一定的代表性。图 5、图 6 为煤挥发份含量、含碳量与燃煤 PAHs 排放总量的关系, 图 7 为烟气 PAHs 排放量和底渣中 PAHs 排放量与煤挥发份含量的关系。由图 5 看出, 燃煤过程 PAHs 排放总量是随着煤种挥发份含量的增加而增加。烟气和底渣中 PAHs 排放量随煤种挥发份含量的增大, 总体上呈现上升的趋势, 但烟气和底渣中 PAHs 生成量之差有先增加后减少, 在挥发份为 30%左右又增加。分析认为, 在高温燃烧条件下烟气中挥发份的产率越高, 挥发份裂解产生的有机自由基数量也越大, 从而大大增加了燃烧炉内有机自由基反应合成的 PAHs 几率, 使得 PAHs 排放逐渐增加。底渣中 PAHs 生成主要是固定碳合成, 挥发份较低时, 气相和固相生成大体相同。随着煤中挥发份的增加, 挥发份产率增加, 在固定碳周围形成气体层, 一定程度上抑制从固相生成PAHs, 从而在挥发份为 30%时底渣中 PHAs 生成下降。另外, 从固相生成的 PAHs 部分挥发至气相。

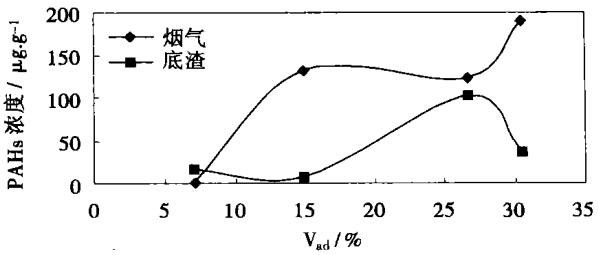

图 7　烟气、底渣中 PAHs 排放量与煤种挥发份关系

4　结　论

本文比较了四种不同煤种燃烧 PAHs 排放和原煤中 PAHs 含量, 进行了燃煤过程 PAHs 排放量与煤种内在因素关系的研究, 得出以下结论:

(1) 燃煤 PAHs 排放比原煤中 PAHs 含量高出很多, 煤燃烧 PAHs 排放来源并不仅仅由于原煤所含有的那部分 PAHs 的挥发所致, 其间必有其它途径(以高温分解和高温气相两种途径为主)生成排放 PAHs 物质;

(2) 挥发份含量在 7% ~30%的煤种, 燃烧时 PAHs 排放总量是随着煤挥发份含量的增加而增加, 其随含碳量的变化呈现相反的趋势;

(3) PAHs 排放量烟气高于底渣。

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先进微型燃气轮机的特点与应用前景＝**Specific Features of Advanced Micro Gas Turbines and Their Application Prospects** [刊, 汉] /WENG Yi-wu, SU Ming, WENG Shi-lie (Institute of Mechanical &Power Engineering under the Shanghai Jiaotong University, Shanghai, China, Post Code: 200030) //Journal of Engineering for Thermal Energy & Power. — 2003, 18(2). 111—115

A new type of heat engines, advanced micro gas turbines pertain to a category of clean, high-efficiency, low-cost and highly reliable energy supply system. They have attracted considerable attention from academics and witnessed to date a spectacular development. Concerning the worldwide research and development efforts as well as the current usage situation of these turbines, the authors have focused on their technical advances and features. Furthermore, an exploratory study was carried out of a small-sized distributed energy system with a micro gas turbine serving as its core and also of a hybrid gas turbine /fuel cell system. The usage prospects of micro gas turbines in China have been briefly evaluated. **Key words**: micro gas turbine, distributed power generation, cogeneration of cooling energy, process heat and electric power, fuel cell

无电晕高温静电除尘技术的最新进展＝**Recent Advances in the Technology of Non-corona High-temperature Electrostatic Precipitation** [刊, 汉] /YANG Ya-ping, WEI Qi-dong (Research Institute of Thermal Energy Engineering under the Southeastern University, Nanjing, China, Post Code: 210096), HUANG Hui-fen (Department of Electronics Engineering, Southeastern University, Nanjing, China, Post Code: 210096) //Journal of Engineering for Thermal Energy &Power. — 2003, 18(2). 116—119

The technology of non-corona high-temperature electrostatic precipitation involves an innovative method of dust particle removal suited for use at elevated temperatures. It utilizes the cathode emission of thermal electrons to get the dust particles in flue gases electrically charged. The electrically charged particles are then captured and collected under the action of an electric field. The most recent results of research of the above-cited technology are presented in detail. **Key words**: non-corona electrostatic precipitation, performance test, cathode poisoning

循环流化床中气固两相流动特性的可视化研究＝**A Visual Study of the Gas-solid Dual-phase Flow Characteristics in a Circulating Fluidized Bed** [刊, 汉] /TIAN Zi-ping, ZHONG Zhi-qiang, CHEN Yong-guo, CHEN Jun (Institute of Mechanical & Power Engineering under the Shanghai Jiaotong University, Shanghai, China, Post Code: 200030) //Journal of Engineering for Thermal Energy &Power. — 2003, 18(2). 120—124

Through the use of a charge-coupled device's function of fast image acquisition on a self-designed and built test rig obtained were the images of flow conditions in a fluidized bed under different airflow rates, followed by an effective processing of these initial images by using an image processing method. Furthermore, a series of phenomena were studied, including the turn-down flow adhered on a wall, gas local-diffusion coefficient, the profile of local voidage along the longitudinal and transverse axis, and the ascending velocity of bubbles. Also given is the fractal dimension of the boundary curve of bubbles during tests. As a result of the above, realized was the visualization of gas-solid dual-phase hydrodynamic characteristics in a circulating fluidized bed, thus fulfilling a fruitful attempt to use image processing techniques on a circulating fluidized bed. **Key words**: circulating fluidized bed, boiler, gas-solid two-phase flow, hydrodynamics, image processing, visual study

不同煤种燃烧生成多环芳烃的研究＝**A Study of the PAHs (Polycyclic Aromatic Hydrocarbons) Emissions Resulting from the Combustion of Different Ranks of Coal** [刊, 汉] /LI Xiao-dong, FU Gang, YOU Xiao-fang, YAN Jian-hua (National Key Lab of the Ministry of Education on Clean Utilization of Energy Sources and Environmental Engineering under the Zhejiang University, Hangzhou, China, Post Code: 310027) //Journal of Engineering for Thermal Energy &Power. — 2003, 18(2). 125—127

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The organic pollutants generated by the combustion of coal, such as polycyclic aromatic hydrocarbons (PAHs), are highly carcinogenic, mutagenic and teratogenic, and have thus attracted widespread public attention. The authors have studied the generation of PAHs during the combustion of various kinds of coal and identified the relationship existing between the PAHs emissions during coal combustion and the content of PAHs in raw coal. Also researched is the influence of the constituent content of fixed carbon, volatile substance and ash in coal on PAHs emissions during the process of coal combustion. **Key words**: coal, polycyclic aromatic hydrocarbons, combustion, pollutant emissions

管道喷射烟气脱硫的试验研究＝**Experimental Study of Flue Gas Desulfurization by Using an In-duct Sorbent Injection** [刊, 汉] /HUANG Zhen, FENG Bin, LI Da-ji (Key Lab of Education Ministry on Clean Coal Combustion and Power Generation Technology under the Southeastern University, Nanjing, China, Post Code: 210096), LU Ping (Power Engineering Institute of Nanjing Normal University, Nanjing, China, Post Code: 210042) //Journal of Engineering for Thermal Energy & Power. — 2003, 18(2). 128—131

A systematic research was conducted of the influence of various factors on the effectiveness of flue gas desulfurization. Such factors include: approach saturation temperature, SO_2 inlet concentration, atomizing airflow rate of nozzles, injected layered lime slurry and pressurized slaked sorbent, etc. The results of the study indicate that the adoption of an enhanced Ca/S ratio, a reduced ΔT, a layered water spray and pressurized slaked sorbent can be conducive to increasing the desulfurization efficiency. Under the condition of a Ca/S ratio of 2.5 the desulfurization efficiency with the use of pressurized slaked sorbent can exceed 65%. **Key words**: flue gas desulfurization, in-duct sorbent injection, desulfurization efficiency, Ca/S ratio

蜂窝体中碳黑沉积规律的实验研究＝**Experimental Investigation of Soot Carbon Deposition Mechanism in Honeycomb Regenerators** [刊, 汉] /XING Gui-ju (Anshan University of Science & Technology, Anshan, China, Post Code: 114002), HU Sheng-teng, FU Wei-biao (Department of Engineering Mechanics, Tsinghua University, Beijing, China, Post Code: 100084) //Journal of Engineering for Thermal Energy & Power. — 2003, 18(2). 132—135

Under a method of soot carbon production with the use of fuel oil cracking measured was the pressure difference generated during the passing of soot carbon-containing flue gases through a honeycomb body as well as the variation of inlet temperatures. On this basis it was discovered that the deposition of soot carbon in the honeycomb body complies with Boltzmann variation law. Such a discovery is helpful in providing valuable reference data for the applied research of high-temperature and low-oxygen regenerative combustion and for the development of new types of regenerators. **Key words**: honeycomb, soot carbon, pressure difference, deposition, regenerative combustion

强化传热管束狭窄空间内 R—11 的沸腾换热特性＝**Boiling Heat Exchange Characteristics of R-11 in the Narrow Spaces of an Intensified Heat-transfer Tube Bank** [刊, 汉] /LIU Zhen-hua, YI Jie (Institute of Power and Energy Engineering under the Shanghai Jiaotong University, Shanghai, China, Post Code: 200030) //Journal of Engineering for Thermal Energy & Power. — 2003, 18(2). 136—138

An experimental investigation was conducted of the intensified boiling heat transfer of R-11 in the narrow spaces of a compact heat-transfer tube bank consisting of rolled surfaces. The results of the investigation confirm that the full-liquid type of evaporative heat-transfer device comprising the above-cited tube bank offers a good heat-transfer performance. Its working principle is based on the utilization of the narrow spaces of the intensified heat-transfer tube bank for an early conversion of natural convection heat transfer into a thriving nucleate boiling heat transfer. The experimental results also confirm that the boiling heat-transfer intensification effect of the two kinds of intensified techniques as offered by 1) the narrow spaces formed by the tube bank and 2) the intensified heat-transfer surfaces should not be viewed as a version of simple superimposition. **Key words**: composite intensified heat transfer, boiling heat transfer, narrow space

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