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废物衍生燃料(RDF)加压热解特性及其动力学研究

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摘　要: 利用加压热重分析仪对城市固体废弃物衍生燃料(RDF)中厨余物等典型有机组份进行了加压热分析研究, 实验载气为高纯氮气, 加热速率为 20 K/min, 终温 773 K。通过对热重(TG)、微分热重(DTG)曲线的深入分析, 得出了加压条件下 RDF 中几种典型有机组份的热解反应动力学参数, 并提出相应的热解机理。

关　键　词: 废物衍生燃料; 热解特性; 动力学参数; 热重分析

中图分类号: X705; O642　　文献标识码: A

符号说明

α—— 样品热解转化率
k—— 反应速度常数
n—— 反应级数
t—— 反应时间 / s
T—— 绝对温度 / K
W_0—— 样品初始重量 / mg
W_t—— $T(t)$ 时样品重量 / mg
W_∞—— 最终样品重量 / mg
A—— 频率因子 / min^{-1}
E—— 活化能 / $kJ \cdot mol^{-1}$
ΔW—— 样品重量差 $(W_t - W_0)$ / mg
ΔW_∞—— 样品重量 $(W_\infty - W_0)$ / mg

1　引言

纵观国内外城市垃圾的处理方式, 随着垃圾中可燃物所占比例的上升, 以焚烧为代表的处理方式迅猛发展。同时也暴露出许多问题, 如热效率低、产生的烟气易造成设备损坏和形成二次污染。

燃气－蒸汽联合循环发电技术能较大幅度提高发电效率, 已在燃煤电厂获得了成功应用, 特别是带前置式裂解炉的第二代增压流化床联合循环和第二代整体煤气化联合循环发电技术, 不仅发电效率达 45% 以上, 而且对环境污染很小[1~3]。同样, 采用基于加压气化思想的垃圾联合循环发电技术, 既可提高综合发电效率, 又可通过在流化床气化炉内和对产生的燃气添加脱除剂去除大量的气相污染物, 燃烧室内的高温燃烧使飞灰熔融后骤冷固化可消除重金属和有机致癌物质对环境的不良影响, 同时也达到了除尘效果。其中加压气化是决定该技术先进性和实用性的重要因素之一, 本文针对中国 RDF 的某些典型有机组份, 着重研究了加压对各物料热解特性的影响, 并提出相应的热解动力学模型。

2　实验

2.1　实验物料

城市固体废弃物是多种废物的混合物, 其组成随季节、地区等因素变化很大, 比较典型的组份如表 1, 其中厨余物含量最高。城市固体废弃物衍生燃料(RDF)中可燃物的元素与热值分析(表 2)可知废塑料热值最高, 其余依次为废橡胶、废木料、废织物和废纸, 厨余物热值最低(约为 4 650 kJ/kg, 高位发热量)。本文选取 RDF 中有代表性的厨余物以及废木料和废纸作实验物料。

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(复　编辑)

表 1 城市固体废弃物的分类

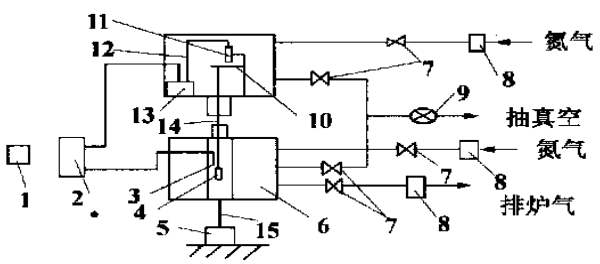
组份类别	平均重量分额/%
厨余物	23.80
废纸	7.43
塑料与橡胶	6.11
木材与竹料	2.97
纤维	1.03
灰土	47.93
砖头、石料	4.50
金属	1.19
玻璃	2.48
其它	2.56
总计	100

表 2 RDF 中可燃物的元素与热值分析

组份	C	H	O	N	S	A	Total	热值
类别	干基/(W)%							Q_{GW}/kJ·kg^{-1}
厨余物	48.0	6.4	37.6	2.6	0.4	5.0	100	4 650
废纸	43.5	6.0	44.0	0.3	0.2	6.0	100	16 750
塑料	60.0	7.2	22.8			10.0	100	32 570
橡胶	78.0	10.0		2.0		10.0	100	23 260
木材与竹料	49.5	6.0	42.7	0.2	0.1	1.5	100	18 000
纤维	55.0	6.6	31.2	4.6	0.15	2.5	100	17 450

2.2 加压热解实验方法

使用东南大学自行设计制造的加压热重分析仪，该仪器采用悬臂式电涡流称重原理，主要由高压容器、温控加热炉(控温精度 1 250±1 ℃，最高使用温度 1 600 ℃)、连续称重和测温系统(位移传感器灵敏度 8 mv/μm，精度为 0.5%，称重最大值 400 mg，温度稳定性小于 0.05%/K)、升降系统、数据采集处理系统(单片机采用 12 位 A/D 转换器，软件包最快采样速度为 30 次/秒)及环境气氛控制系统等组成。



1— 打印机；2— 精密控温仪；3— 热电偶；4— 坩埚；5— 电动机；6— 加热炉；7— 单向阀；8— 常压流量计；9— 真空泵；10— 弹簧片；11— 传感探头；12— 高压容器；13— 位移传感器；14— 吊丝；15— 电动推杆

图 1 加压热重分析仪结构示意图

常压情况文献[4]已有叙述，本实验只研究 RDF 在氮气氛围中，升温速率 20 K/min，终温 773 K，压力分别为 0.3 MPa、0.6 MPa、0.9 MPa 条件下的热解特性。实验过程中，将干燥后并称重的样品放入坩埚，并将坩埚悬挂于悬臂的自由端，待测重系统稳定后，加热炉升起使坩埚平稳进入加热炉的反应区，密封高压容器，抽真空，充入惰性气体氮气。达到压力要求，通过温控仪加热升温，采样频率为 1 次/秒，反应结束后放下加热炉，取出坩埚称重。

2 实验结果与讨论

观察图 2～图 11 为几种有代表性的 RDF 典型

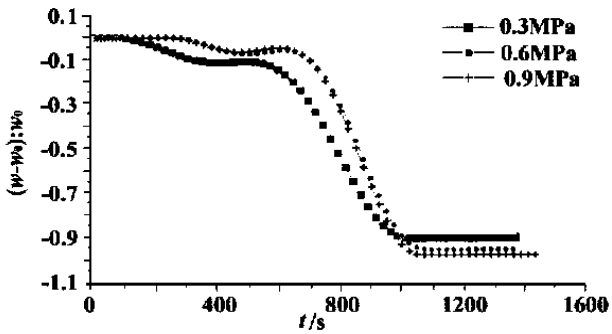


图 2 脂肪热解热重曲线

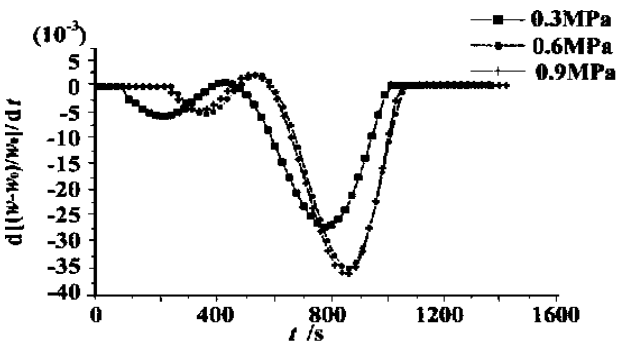


图 3 脂肪热解微分热重曲线

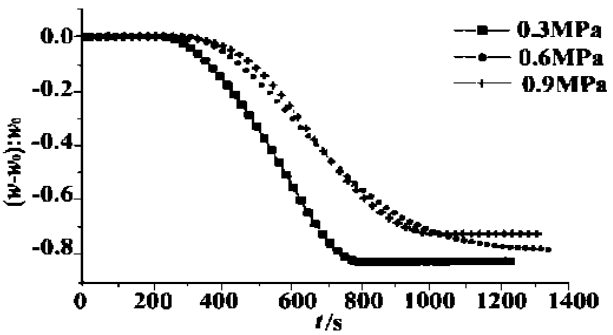


图 4 牛肉热解热重曲线

常压情况文献[4]已有叙述，本实验只研究 RDF 在氮气氛围中，升温速率 20 K/min，终温 773 K，压力分别为 0.3 MPa、0.6 MPa、0.9 MPa 条件下的热解特有机组份的热解曲线。由曲线与分析可知，牛肉、米饭(0.6 MPa、0.9 MPa)和木材的 DTG 曲线只有一个峰，这表明这些组份中的有机质在该压力下可直接

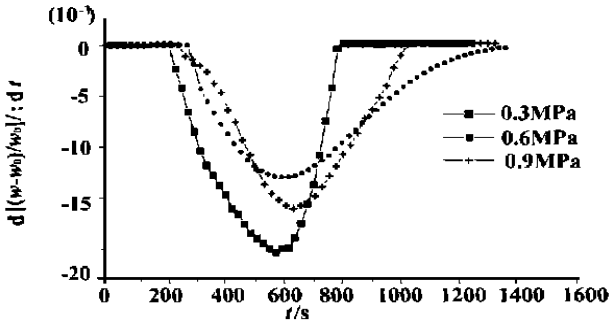


图 5　牛肉热解微分热重曲线

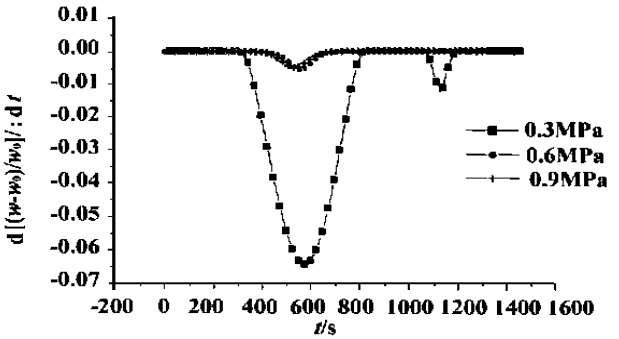


图 9　米饭热解微分热重曲线

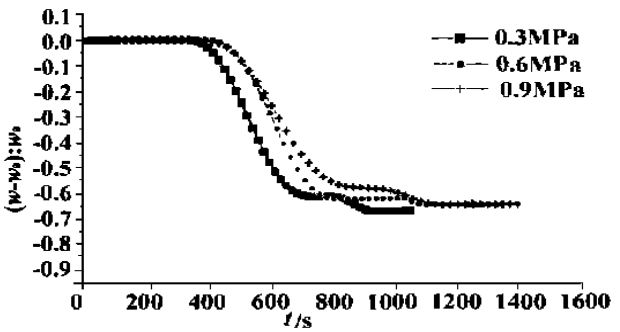


图 6　纸热解热重曲线

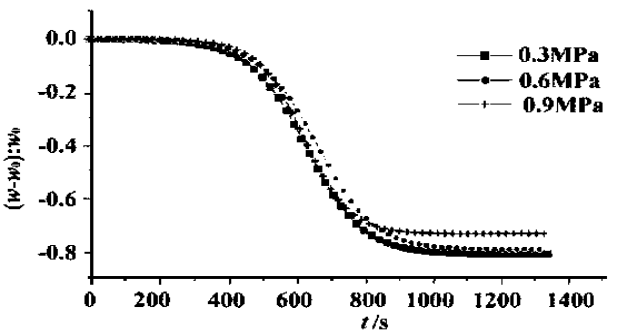


图 10　木材热解热重曲线

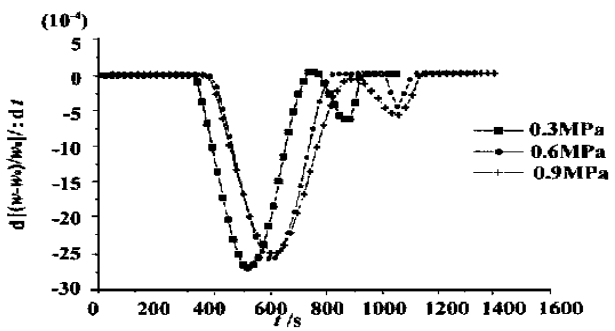


图 7　纸热解微分热重曲线

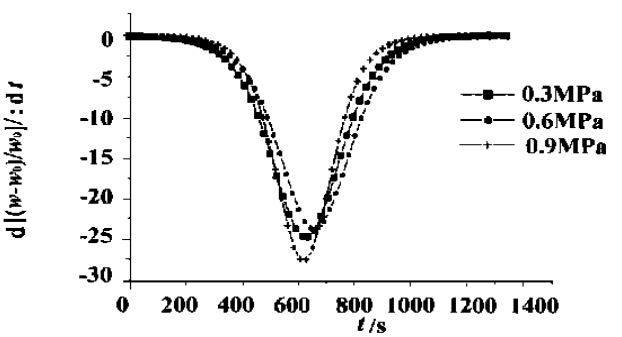


图 11　木材热解微分热重曲线

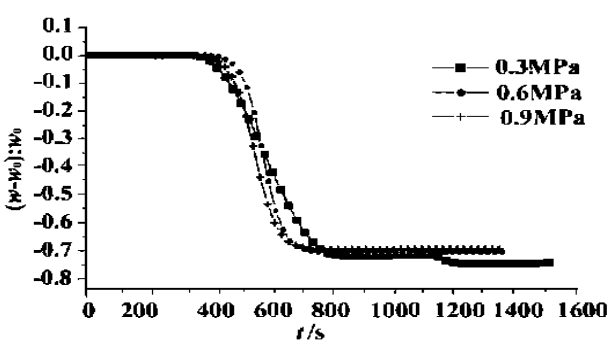


图 8　米饭热解热重曲线

受热分解为直链烷烃、直链烯烃、固定碳和低级燃料气。脂肪是双峰反应并在反应初期 DTG 曲线即出现第一个峰值，随压力升高该峰值后移。脂肪主要是由三甘油脂组成，实验前脂肪在空气中放置 24 小时，随时间和细菌的增长三甘油脂会分解成短链的脂肪酸和其它类别有机物。脂肪酸比相应的三甘油脂更易挥发，因此在裂解反应初期即挥发出来，同时由于压力的升高使小分子挥发份不易逸出，故而第一个峰值出现较早，且随压力升高后移。随温度的升高，脂肪的 DTG 曲线出现第二个峰，对低分子量脂肪酸可能发生脱水反应生成脂肪酸酐：$2RCOOH \rightarrow (RCO)_2O + H_2O$，对高分子量脂肪酸可能变为烃类或酮基：$RCOOH \rightarrow RH + CO_2$，$2RCOOH \rightarrow R_2CO + CO_2 + H_2O$。羟基脂肪酸脱水反应过程中内脂化、聚合和断链反应竞相发生。同时脂肪酸受热还可能发生脱羧反应。纸、米饭(0.3 MPa)在 673～773 K 温度区域 DTG 曲线出现第二个峰值，即有机物中某些官能团在受热时发生键断裂，异构成较稳定的小分子析

出。有机物中可能存在的官能团如羟基、醛基、酮基、羧基、氨基、硝基在 673—773 K 易发生去氧去氮反应。而随压力升高,米饭(0.6 MPa、0.9 MPa)在此温度范围不再出现第二个峰值,即官能团中键的断裂还受压力的影响。裂解过程中各实验物料可能发生以下反应:有机物大分子的裂解;异构反应,即构成分子的原子数量不变而结构发生变化;去氧去氮反应;环化、热聚合等反应。

由表 3 可见,物料随压力升高,裂解初始温度升高,除木材外,压力进一步升高,裂解初始温度下降,如脂肪、牛肉、纸、米饭在 0.9 MPa 压力下比 0.6 MPa 压力下的裂解初始温度低,而比 0.3 MPa 压力下的裂解初始温度高。除木材外,随压力升高,裂解开始时间后移,压力进一步升高,裂解开始时间前移。随压力升高,裂解持续时间可能增加也可能减少,如牛肉、纸、米饭裂解持续时间增加,而脂肪、木材则持续时间减少。除脂肪外,随压力升高裂解失重率下降,即气态产物减少,液态和固态产物增加。热解开始温度范围在 460 ~ 542 K;热解持续时间 7 ~ 15 min,除脂肪外,热解失重率在 65% ~ 83% 之间,所以当 RDF 中有机物比率发生变化时,总的热解百分率变化不大(相同压力下),与文献[4]结论一致。

根据热解曲线及数据,可拟合出相应的热解动力学曲线。由质量作用定律可列出热解速率方程:

$$d\alpha/dt = A[\exp(-E/RT)](1-\alpha)^n \quad (1)$$

其中:$\alpha = -TG/\Delta W_\infty = \Delta W/\Delta W_\infty$,

两边取对数,则有:

$$\ln[(d\alpha/dt)/(1-\alpha)^n] = (-E/R)\times((1/T)+\ln A \quad (2)$$

令 $Y = \ln[(d\alpha/dt)/(1-\alpha)^n]$, $A' = \ln A$, $B = -E/R$, $X = 1/T$

则 $Y = A' + BX$ (3)

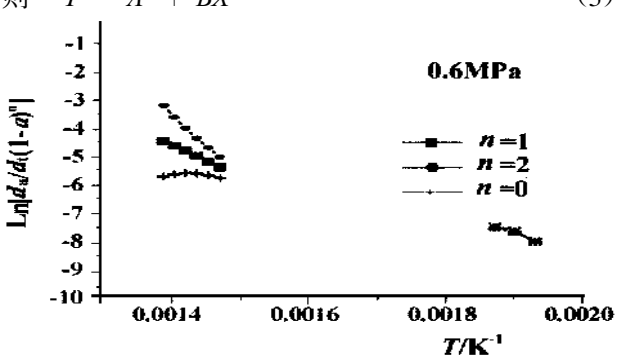


图 12 脂肪在不同反应级数 n 下的热解动力学参数拟合曲线

因为由实验测得数据可作出 TG、DTG 曲线,所以可方便地得到不同 X 坐标下的 Y 值,由方程(3)可得出 A' 和 B 的值,从而求出活化能 E 与频率因子 A。图 12 给出了脂肪在不同反应级数下的拟合曲线。由图可见,反应级数 $n = 1$ 时曲线拟合最好。其它 4 种 RDF 的热解动力学参数拟合曲线也与脂肪相似。5 种物料活化能与频率因子可由方程(2)和方程(3)得出,结果见表 4。

表 3 各组份发生裂解的初始温度、初始时间、持续时间、质量变化

组份类别	压力/MPa	热解初始温度 T_i/K	热解开始时间 t_i/s	热解持续时间 Δt/min	热解最大失重率 α
脂肪	0.3	460.213 0867	141.639 26	14.696 351	−0.908 361 204
	0.6	521.676 136 7	326.028 41	12.550 300 17	−0.957 814 553
	0.9	514.771 44	305.314 32	12.529 992 33	−0.982 741 913
牛肉	0.3	510.973 4	293.920 32	9.583 371 833	−0.828 957 239
	0.6	541.811 623 3	386.434 87	13.086 328	−0.777 860 327
	0.9	538.177 453 3	375.532 36	12.155 779 83	−0.727 350 427
纸	0.3	543.718 936 7	392.156 81	9.201 909 167	−0.672 118 959
	0.6	566.610 7	460.832 1	11.006 974 67	−0.650 055 866
	0.9	563.233 333 3	450.7	11.66	−0.646 265 56
大米	0.3	539.697 073 3	380.091 22	7.113 810 667	−0.720 778 928
	0.6	562.711 863 3	449.135 59	7.095 480 333	−0.708 641 975
	0.9	546.858 756 7	401.576 27	7.788 983	−0.698 252 07
木材	0.3	537.657 12	373.971 36	14.234 919 17	−0.813 824 885
	0.6	543.222 246 7	390.666 74	11.606 235 67	−0.796 435 272
	0.9	549.810 316 7	410.430 95	13.433 656 67	−0.736 150 235

表 4 各组份热解动力学参数

组分	压力/MPa	第一阶段			第二阶段		
		E: R	A'	A	E: R	A'	A
脂肪	0.3	3 445	−0.413 13	0.661 576	8 776.167	7.755 548	2 334.489
	0.6	8 629.833	8.582 788	5 338.972	11 947.8	12.115 08	182 604.2
	0.9	4 327.833	0.451 058	1.569 973	10 972.5	10.771 63	47 649.38
牛肉	0.3	5 010.5	2.524 76	12.487 9			
	0.6	3 822	−0.182 88	0.832 868			
	0.9	7 422.875	5.771 91	321.150 5			
纸	0.3	3 387.178	−0.137 46	0.871 572	41 667	52.783 08	8.38E+22
	0.6	11 071.38	12.479 6	262 919.3	60 080	71.459 58	1.08E+31
	0.9	11 807	13.752 88	939 290.4			
米饭	0.3	7 533.2	10.253 04	28 368.65			
	0.6	28 212.4	42.524 73	2.94E+18			
	0.9	24 665.2	37.238 22	1.49E+16			
木材	0.3	8 136.6	7.694 288	2 195.77			
	0.6	10 198	10.855 6	51 823.55			
	0.9	11 604	13.568 78	781 351.2			

3 结论

(1)由五种 RDF 典型有机物组份的加压热解试验曲线可以看出,热解曲线形状略有差异,在相同压力下(相同温升速率),不同物料单峰或双峰出现在不同温度区域;随压力升高,同种物料双峰反应可能转化为单峰反应。

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5 结论

(1) 弹性转子—轴承系统在一定偏心质量作用下随转速的增加具有产生混沌运动的能力, 混沌运动容易引起转子—轴承系统产生疲劳破坏并可能导致系统失稳, 因此在设计过程中应避开该区域。

(2) 偏心质量和非线性油膜力是导致混沌运动的根本原因, 倍周期运动是通向混沌的道路。数值计算结果表明, 该类转子—轴承系统在四倍周期分叉后产生混沌运动。

(3) 在一定偏心质量下, 该类系统运动状态随转速的升高超过某一值后混沌运动消失。

(4) 改变基础参数可以有效避开混沌运动区域, 计算结果表明, 增加基础刚度、阻尼, 可以消除混沌运动, 保证系统安全运行。

上述结论可以为该类转子—轴承系统的设计和安全运行提供定性参数。

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(2) 加压对城市生活垃圾典型有机物组份裂解初始时间、持续时间和失重率的影响:

(a) 随压力升高, 裂解初始温度升高, 达到一定压力后, 当压力进一步升高时, 裂解初始温度反而下降。

(b) 随压力升高, 裂解初始时间后移, 但随压力进一步升高时, 裂解初始时间反而前移。

(c) 随压力升高, 对不同物料的裂解持续时间有不同的影响, 可能加快也可能减慢。

(d) 随压力升高, 裂解失重率下降。

(3) 由五种 RDF 典型有机组份加压热解试验数据及动力学模型得出其热解反应可视为一级反应, 即 $d\alpha/dt = A[\exp(-E/RT)](1-\alpha)$。

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活性矾土与烟气污染物的脱除＝**Removal of Pollutants in Flue Gases through the Use of Activated Alumina** [刊, 汉] / HAN Chun-li, ZHANG Jun, YAN Zheng, LIU Kun-lei, XU Yi-qian (Thermal Energy Research Institute under the Southeastern University, Nanjing, China, Post Code: 210096) //Journal of Engineering for Thermal Energy & Power. — 2001, 16(4). —355 ~358

A brief account was given of the research results on the technology for removing a variety of pollutants, such as alkali metals, SO_x and NO_x through the use of activated alumina. The valuable information provided may benefit the further probe of the role of the activated alumina as a pollutant-removal agent. **Key words**: activated alumina, alkali, SO_x, NO_x

燃煤电厂飞灰碳含量与 PAHs 有机污染物吸附量之间相关性研究＝**A Study of the Correlation between the Carbon Content in Fly-ash of Coal-fired Power Plants and Adsorption Quantity of PAHs (Polycyclic Aromatic Hydrocarbons) Organic Pollutants** [刊, 汉] / LIU Hui-yong, XU Xu-chang, YAO Qiang (Thermal Energy Engineering Department, Tsinghua University, Beijing, China, Post Code: 100084), ZHANG Ai-yun (China National University of Geology, Beijing, China, Post Code: 100083) //Journal of Engineering for Thermal Energy &Power. — 2001, 16(4). —359 ~362

With five coal-fired power plants serving as objects of study an experimental analysis was conducted of the content of total carbon, elemental carbon and organic carbon in fly ash. On this basis a study has been performed of the correlation of the content of the above items and the adsorption quantity of polycyclic aromatic hydrocarbons (PAHs) in fly ash. Furthermore, also studied was the correlation of PAHs given off by the burned coal and the PAHs in coal located at the furnace front. From the perspective of coal chemistry and coal combustion science discussed and explored was the adsorption reaction mechanism of the PAHs organic pollutants. As a result, proposed was a kind of major mechanism of PAHs formation during the burning of pulverized coal, the so-called adsorption reaction mechanism of unburned carbon particles. It is noted that the carbon in fly ash serves not only as a major adsorption location but also as an important reaction location for PAHs. **Key words**: polycyclic aromatic hydrocarbons (PAHs), adsorption and reaction mechanism of unburned carbon particles

洁净燃煤发电系统热力性能计算软件编制＝**Preparation of a Thermodynamic Performance Calculation Software for a Clean Coal-fired Electrical Power Generation System** [刊, 汉] / XIAO Jun, CAI Ning-sheng, CUI Li (Thermal Energy Research Institute under the Southeastern University, Nanjing, China, Post Code: 210096) //Journal of Engineering for Thermal Energy &Power. — 2001, 16(4). —363 ~366

Based on the thought of process system engineering and through the use of a modularization model building method the authors have set up a method for mathematical modeling of typical equipment for a clean coal-fired electrical power generation system. Moreover, also established for the above-cited system were the mathematical model base of a typical equipment and function base for the calculation of thermodynamic properties of various working mediums. With the use of a development tool, i.e., Visual Basic program, a software for calculating the thermodynamic performance of a clean coal-fired electrical power generation system has been developed. Featuring a friendly interface, ease of use, configuration flexibility and a high potential for expandability, the proposed software is of high practical value for the type selection, design and optimization analysis of Chinese-made clean coal-fired electrical power generation systems. **Key words**: thermodynamic calculation, modularization, software

废物衍生燃料(RDF)加压热解特性及其动力学研究＝**A Study of Pressurized Pyrolysis Characteristics of Refuse Derived Fuels (RDF) and Their Kinetic Parameters** [刊, 汉] / JIN Bao-sheng, DONG Chang-qing, ZHONG Zhao-ping (Thermal Energy Research Institute under the Southeastern University, Nanjing, China, Post Code: 210096) //Journal of Engineering for Thermal Energy &Power. — 2001, 16(4). —367 ~370, 374

With the help of a pressure thermogravimetric analyzer a pressurized thermal analytical study was conducted of kitchen refuse and other typical organic components of municipal refuse derived fuels (RDF). The RDF pyrolysis tests were carried out under the ambient condition of high-purity N_2 with a heating rate of 20 K/min and a final temperature of 773 K. Through an analysis of thermogravimetric and differential thermogravimetric curves obtained were the pyrolysis reaction kinetic parameters of several kinds of typical organic components in RDF under pressurized conditions. In addition, also

presented is a relevant pyrolysis mechanism. **Key words**: refuse derived fuel, pyrolysis characteristics, kinetic parameter, thermogravimetric analysis

滑动轴承支撑转子系统混沌响应计算＝**The Calculation of Chaotic Response of a Journal Bearing-supported Rotor System** [刊, 汉] / WU Xin-hua, ZHANG Xin-jiang (Energy College under the Harbin Institute of Technology, Harbin, China, Post Code: 150001), YU Zeng-bo (Harbin Turbine Works, Harbin, China, Post Code: 150046) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(4). —371 ~ 374

On the basis of the theory of rotor dynamics and nonlinear dynamics and in the light of the specific features of a nonlinear rotor-bearing system set up was a model of elastic rotor-bearing system with the use of a short bearing model. Moreover, through the use of a numerical integration and Poincaré mapping method a nonlinear vibration study was conducted of the above rotor-bearing system in the domain of certain parameters. As a result, obtained for the system in the above domain were bifurcation diagrams, Poincaré mappings and speed-varied three-dimensional spectral diagram. The results of calculation indicate that the rotor-bearing system may be subject to chaotic motions. An analysis was conducted of the nonlinear behavior of the system dynamics characteristics, which may vary with the change of certain parameters. A visual display is thereby obtained of the influence of parameter variation on the system dynamics characteristics. The above work can provide some theoretical reference data for the design of elastic rotor-bearing systems. **Key words**: turbomachinery, rotor dynamics, rotor-bearing system, nonlinear vibration, chaotic response

分离式热管换热器的工作原理及其在电厂余热回收中的应用＝**Working Principle of a Separation-type Heat-Pipe Heat Exchanger and Its Use in the Heat Recovery System of a Power Plant** [刊, 汉] / LIU Xiao-zhou, HUI Shi-en, XU Tong-mo, et al (Boiler Research Institute under the Xi'an Jiaotong University, Xi'an, Shaaxi Province, China, Post Code: 710049) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(4). —375 ~ 376, 379

Described is the working principle of a separation-type heat-pipe heat exchanger along with its use in a separation-type heat-pipe economizer installed on a 670 t/h boiler of a 200 MW power plant. A comparison of the above-cited heat exchanger with a conventional low-pressure economizer shows that the recommended heat exchanger enjoys tremendous superiority in terms of heat recovery efficiency. **Key words**: separation type heat pipe, working principle, low-pressure economizer, economic benefit

水平管内油气水三相间歇流向环状流转换的研究＝**An Investigation on the Intermittent-to-Annular Flow Transition of Oil-gas-water Three-phase Flow in a Horizontal Tube** [刊, 汉] / ZHOU Yun-long, CAI Hui, HONG Wen-peng, LI Yan (Power Engineering Department, Northeastern Electric Power Institute, Jilin, China, Post Code: 132012) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(4). —377 ~ 379

An experimental and theoretical study was conducted of the intermittent-to-annular flow transition of oil-gas-water three-phase flow in a horizontal tube. Proposed was a boundary equation featuring the transition of the intermittent-to-annular flow. The experimental study results show that the major factor governing the transition of the intermittent-to-annular flow is the gas-phase reduced speed and the liquid-phase reduced one with the effect of oil fraction and tube diameter playing an insignificant role. The results of calculation have been found to be basically in agreement with those of experiment. **Key words**: horizontal tube, oil-gas-water three-phase flow, flow pattern transition.

火床炉风室内横向配风特性的理论分析＝**Theoretical Analysis of the Characteristics of Air Transverse Flow Distribution in a Stoker-boiler Air Compartment** [刊, 汉] / MIAO Zheng-qing, DOU Wen-yu, ZHOU Qu-lan, et al (Power and Energy College under the Xi'an Jiaotong University, Xi'an, China, Post Code: 710049) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(4). —380 ~ 382

Presented is an enclosed set of equations, which describes the air flow in a flow stabilized section of a stoker boiler dual lateral-side full-section air feed compartment and a full lateral-side air feed compartment. Through a theoretical deduction obtained was an analytical solution along with the deduction of a theoretical expression of the stoker surface flow-rate deviation. On this basis the limiting flow rate deviation location and the flow rate deviation limiting ratio were compared for the following cases: the dual lateral-side air feed mode and the single lateral-side air feed mode. Moreover, an analysis was performed of influence of air compartment construction and stoker grate layer structure on the flow rate deviation. **Key words**: stoker boiler, stoker air compartment, flow characteristics, flow distribution, flow deviation