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污泥的热解动力学及机理研究

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摘 要: 利用综合热分析仪对污水处理厂原始污泥进行了热分析实验, 获得了不同升温速率下污泥的 TG 和 DTG 曲线。实验结果表明, 采用一级反应模型预测污泥热解特性具有一定的局限性。利用热分析动力学, 采用最概然机理函数选择法, 提出了污泥热解的机理函数为 $f(\alpha)=(1-\alpha)[-\ln(1-\alpha)]^{-3/4}$, 分析获得的污泥活化能 E 和指前因子 A, 并给出了污泥热解动力学计算模型。

关 键 词: 污泥; 热解; 机理函数
中图分类号: TK121 文献标识码: A

1 前 言

污泥的热分解过程是污泥在气化和燃烧过程中的初始阶段, 对污泥稳定着火和燃烧过程有着重大的影响。因此, 深入研究污泥的热分解将增进对污泥的各种转换过程的理解, 对完善污泥的气化和燃烧过程的控制和设计有着一定的现实意义。

由于污泥的热解过程非常复杂, 整个热解过程既有化学变化, 也包括各种物理现象和出现许多物理化学过程的改变。尽管人们对污泥热解做了大量的研究工作, 但是在热解反应机理方面, 仍然存在着许多模糊不清之处。已有对污泥热解动力学参数研究时假设反应过程为一级反应, 研究污泥的热解特性[1~2]。然而污泥是一种非均质的复杂有机物物质的组合体, 其热解特性是许多相互竞争或平行反应的综合反映, 污泥的热解过程及其化学动力学参数必然与许多因素有关。所以, 寻找这些影响因素与热解动力学之间的关系就显得特别重要。

2 污泥热解特性的实验研究

2.1 污泥的静态特性

实验所用试样取自大庆城市污水处理厂。污泥的工业分析结果表明水分含量为 82.10%, 其干燥基工业分析数据如表 1 所示。由表可见, 污泥具有高水分, 干基挥发分较高而固定碳含量较低的特点。因此, 与煤燃烧不同的是, 在污泥的燃烧过程中, 其高水分和高挥发分将对燃烧起主要作用, 而固定碳的影响较小。

表 1 污泥的工业分析(干燥基)

挥发分 V_d/%	固定碳 FC_d/%	灰分 A_d/%	结合水 M_d/%	发热量 Q_d/MJ·kg^{-1}
40.81	6.03	47.10	6.06	10.23

2.2 污泥的热分析

采用 ZRY－2P 型热分析仪进行热重法(TG)和微商热重法(DTG)分析, 试验采用 10 ℃/min 及 20 ℃/min 不同的加热速率。典型的热重曲线分别见图 1 和图 2。

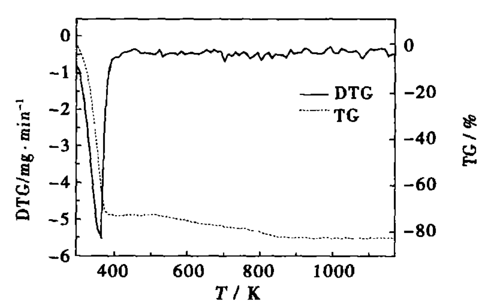

图 1 污泥热重分析曲线(10 ℃/min)

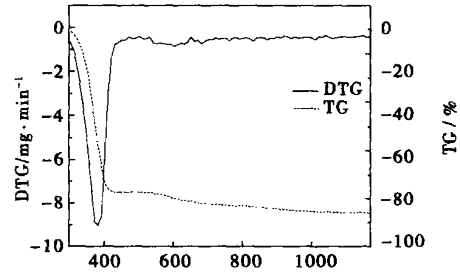

图 2 污泥热重分析曲线(20 ℃/min)

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由 TG 和 DTG 曲线可以看出，污泥整个热解过程可分两个阶段：(1) 水分析出阶段，温度范围为 312.95～433.35 K。在 372.95 K 有一峰值，此时水分析出最快。此后，温度在 433.35～503.25 K 的时间内，基本不出现失重；(2) 挥发分析出阶段，温度范围为 503.25～853.55 K。挥发分析出最大速率所对应的温度为 672.35 K。由于污泥中固定碳含量仅为 6.03%，所以曲线中没有明显表现出固定碳燃烧区。污泥在不同加热速度下的 TG 曲线两者相差很小，水分、挥发分析出规律基本相同，这说明加热速率从 10 ℃增加到 20 ℃，对热重曲线的影响不是很明显。污泥的总失重率与污泥灰分含量之和接近 100%，说明热分析实验是合理的。

3　污泥的热解动力学参数的计算

3.1　求解过程

根据热重曲线可以方便地获得污泥的动力学参数。一般气固反应的动力学方程可表示为：

$$d\alpha/dt = kf(\alpha) \tag{1}$$

式中：α—失重百分比，即某一温度下试样减少的质量与达到实验终温时试样的总损失质量之比；k—反应速率常数；$f(\alpha)$—未分解的反应物与反应速率之间的关系。假设污泥反应为一级反应，反应速率常数满足 Arrhenius 方程，则式(1)表示为：

$$d\alpha/dt = Ae^{-E/RT}(1-\alpha) \tag{2}$$

依据热重曲线和式(2)可确定频率因子 A 和活化能 E。

由图 1 和图 2 可见，污泥具有复杂的反应过程，直接采用式(2)确定反应动力学参数 E 和 A 具有较大的误差。本文采用 Harcourt－Esson 速率常数计算模型：

$$k = CT^m \tag{3}$$

代替式(1)中 Arrhenius 速率常数方程。其中，C 和 m 为常数。由式(3)确定污泥动力学参数 E 和 A。具体求解要根据热重曲线，温度变化：

$$T = T_0 + \beta t \tag{4}$$

其中：β—加热速率。将式(1)对时间进行微分，得：

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\frac{dt}{dT} = \frac{kf(\alpha)}{\beta} = \frac{CT^m f(\alpha)}{\beta} \tag{5}$$

两边取对数：

$$\ln\left[\frac{(d\alpha/dT)\beta}{f(\alpha)}\right] = \ln C + m\ln T \tag{6}$$

根据热重实验结果，求得不同温度下的 $(d\alpha/dT)$ 值，代入式(6)，作 $\ln\left[\frac{(d\alpha/dT)\beta}{f(\alpha)}\right]$ 与 $\ln T$ 的关系曲线，并采用最小二乘法确定 m 和 C 值。

对式(3)取对数：

$$\ln k = \ln C + m\ln T \tag{7}$$

由 m 和 C 值得到不同温度下得 k 值。

由 Arrhenius 公式，可表示为：

$$\ln k = \ln A - E/RT \tag{8}$$

根据不同温度下的 k 值，确定活化能 E 和频率因子 A。

3.2　机理函数的选择

在确定 m 和 C 值时需要已知反应函数 $f(\alpha)$。通常未分解的反应物与反应速率之间的关系以指数形式表示为：

$$f(\alpha) = (1-\alpha)^n \tag{9}$$

$f(\alpha)$ 又称为机理函数。当指数 n 取为 1 时反应为一级反应。

对于具有复杂的反应过程，并不能用指数形式的反应机理函数来合理描述其反应过程，采用一级反应模型将导致确定的反应动力学参数存在较大的误差。因而本文采用最概然机理函数的推断，选择能使 $\ln\left[\frac{(d\alpha/dT)_i\beta}{f(\alpha_i)}\right]$ 与 $\ln T_i$ 线性最佳，并且符合实际反应一般规律的函数为机理函数。可选择的机理函数如表 2 所示[2]。

表 2　机理函数的表达式

函数序号	机理函数
1	$\frac{1}{2}\alpha^{-1}$
2	$-[\ln(1-\alpha)]^{-1}$
3	$\frac{3}{2}[(1-\alpha)^{-1/3}-1]^{-1}$
4, 5	$\frac{3}{n}(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-(n-1)}$ $(n=2, 1/2)$
6	$4(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]^{1/2}$
7	$\frac{3}{2}(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$
8	$\frac{3}{2}(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$
9	$1-\alpha$
10～16	$\frac{1}{n}(1-\alpha)[-\ln(1-\alpha)]^{-(n-1)}$ $(n=\frac{2}{3}, \frac{1}{2}, \frac{1}{3}, 4, \frac{1}{4}, 2, 3)$
17～22	$\frac{1}{n}(1-\alpha)^{-(n-1)}$ $(n=\frac{1}{2}, \frac{1}{3}, 4, \frac{1}{4}, 2, 3)$
23～27	$\frac{1}{n}\alpha^{-(n-1)}$ $(n=1, \frac{3}{2}, \frac{1}{2}, \frac{1}{3}, \frac{1}{4})$
28	$(1-\alpha)^2$
29	$2(1-\alpha)^{3/2}$

根据热重实验结果, 计算结果表明当采用机理函数为:

$$f(\alpha)=\frac{1}{4}(1-\alpha)[-\ln(1-\alpha)]^{-3} \tag{10}$$

时 $\ln\left[\frac{(\mathrm{d}\alpha/\mathrm{d}T)_i\beta}{f(\alpha_i)}\right]$ 与 $\ln T_i$ 之间相关程度最高, 线性相关系数为 0.97。该机理函数表示的反应机理为随机成核和随后成长, 并且每个颗粒上有 4 个核心, 对于污泥这种成份复杂的混合物, 在热解过程中出现这种反应机制是合理的, 因而可以认为此机理函数是正确。表 3 给出不同升温速率下污泥的动力学参数。由表可见, 对于所用的城市污泥, 采用一级反应的机理函数, 线性相关系数较低, 由此获得的动力学参数具有较大的误差, 难以合理反映污泥的热解特性。

表 3　动力学参数(活化能、频率因子和相关系数)

升温速率 /℃·min^{-1}	机理函数	相关系数 r	活化能 E/kJ·mol^{-1}	频率因子 A/min^{-1}
10	$1-\alpha$	0.735 2	17.622	760.49
10	$\frac{1}{4}(1-\alpha)[-\ln(1-\alpha)]^{-3}$	0.968 4	23.474	693.5
20	$1-\alpha$	0.754 9	39.433	1 683.5
20	$\frac{1}{4}(1-\alpha)[-\ln(1-\alpha)]^{-3}$	0.971 2	57.067	1 536.4

3.3　污泥挥发分析出过程的反演

将所得到的污泥动力学参数 E 和 A 代入挥发分析出模型, 可进行挥发分析出过程的反演。由机理函数式(10)可得污泥挥发分析出过程为:

$$v=v^*\{1-\exp[(-\int_0^t A\exp(-\frac{E}{RT})\mathrm{d}t)^{1/4}]\} \tag{11}$$

若机理函数 $f(\alpha)=1-\alpha$, 则挥发分析出模型为:

$$v=v^*\{1-\exp[-\int_0^t A\exp(-\frac{E}{RT})\mathrm{d}t]\} \tag{12}$$

式中: v—对应于一定数量的污泥到 t 时为止热解反应所释放出的挥发物; v^*—$t\to\infty$时热解反应所释放出的挥发物。挥发分析出过程的反演过程如图 3 和图 4 所示。由图可见, 采用机理函数 $f(\alpha)=\frac{1}{4}(1-\alpha)[-\ln(1-\alpha)]^{-3}$ 与 $f(\alpha)=1-\alpha$ 相比, 与实验值吻合更好。表明采用机理函数式(10)能够正确反映污泥热解特性。

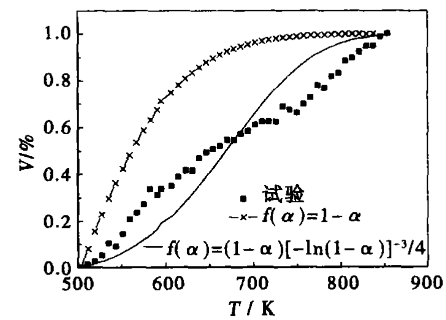

图 3　湿污泥升温速率为 10 ℃/min 反演曲线

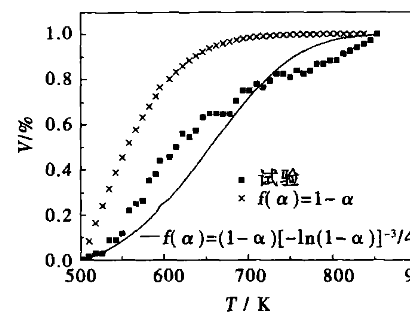

图 4　湿污泥升温速率为 20 ℃/min 反演曲线

4　结　论

(1) 污泥具有高水分、高挥发分、低固定碳含量的特点, 在固定碳含量较低的情况下, 污泥有两个明显的失重过程, 即水分析出区和挥发分析出区。

(2) 用最概然机理函数的选择方法, 得出污泥热解过程的反应机理以随机成核和随后成长的反应为主, 其机理函数可以表示为: $f(\alpha)=\frac{1}{4}(1-\alpha)[-\ln(1-\alpha)]^{-3}$。

注: 本文第四作者的工作单位为哈尔滨工业大学市政环境工程学院。

参考文献:

[1] 奉　华, 张衍国, 邱　天, 等. 城市污水污泥的热解特性[J]. 清华大学学报, 2001, **41**(10): 90—92.

[2] 蒋旭光, 池　涌, 严建华, 等. 污泥的热解动力学特性研究[J]. 环境科学学报, 1999, **19**(2): 221—224.

[3] 胡荣祖, 史启祯. 热分析动力学[M]. 北京: 科学出版社, 2001.

(辉　编辑)

power plant. **Key words**: load of coal-fired power plant, genetic algorithm, chaos, variable step-length gradient drop method, optimized dispatching

超临界水葡萄糖制氢中的多元气液相平衡＝**Multiple Vapor-liquid Phase Equilibrium in Hydrogen Preparation from Glucose in Supercritical Water**[刊, 汉] /LIU Yong (Energy Source and Power College under the Nanjing University of Aeronautics and Astronautics, Nanjing, China, Post Code: 210016), ZHANG Jun, XU Yi-qian (Power Engineering Department, the Southeast University, Nanjing, China, Post Code: 210096) // Journal of Engineering for Thermal Energy & Power. — 2006, 21(5). —521～524

By using a PC-SAFT (perturbed chain statistical associating fluid theory) model, a study was conducted of the specific features of vapor-liquid equilibrium located at the gas-liquid separator of a hydrogen preparation system involving glucose gasification in supercritical water. A comparison with the experimental data shows that the theoretical calculation results are rational. Under a same material-feeding condition, CO, H_2 and CH_4 gas phase share in the vapor-liquid equilibrium system will gradually decrease with a rise in pressure. However, CO_2 and H_2O gas phase share will gradually increase. Therefore, a low-pressure separation will contribute to a purer combustible gas-phase product. The experimental results show that the operating pressure has little influence on the glucose-gasified product. However, in summing up the effect of pressure on solubility, one can conclude that a high pressure can virtually be favorable to the gasification of glucose. **Key words**: multiple phase equilibrium, PC-SAFT (perturbed chain statistical associating fluid theory), equation of state, glucose, hydrogen preparation under a supercritical condition

基于粗糙集理论的除氧系统智能控制器设计＝**Design of an Intelligent Controller in a Deaerating System Based on a Rough Sets Theory**[刊, 汉] /QU Yan-bin, ZHANG Yang (Weihai Information Science and Engineering College under the Harbin Institute of Technology, Weihai, China, Post Code: 264209) // Journal of Engineering for Thermal Energy & Power. — 2006, 21(5). —525～528

Expounded is the control tactic and establishment of a knowledge database for an intelligent controller in a deaerating system. With a rough sets theory serving as a basis, redundant attributes have been simplified, resulting in a most simplified knowledge database. A method is presented for designing an intelligent controller and establishing a knowledge database by making use of the rough sets theory. The intelligent controller thus designed was once used in the modification of a deaerating system for a power-supply station affiliated to an oil refinery. The practical operation shows that the controller under discussion can guarantee the stable operation of the system during a start-up and switching-over process with operating indexes of the deaerating system being fulfilled. **Key words**: deaerating system, intelligent control, expert system, rough sets

污泥的热解动力学及机理研究＝**An Investigation of Sludge Pyrolytic Dynamics and Its Mechanism**[刊, 汉] /LIU Wen-tie, WANG Shu-yan, LU Hui-lin, et al (Energy Source Science and Engineering College under Harbin Institute of Technology, Harbin, China, Post Code: 150001) // Journal of Engineering for Thermal Energy & Power. — 2006, 21(5). —529～531

By using an integrated thermal analyzer, a thermal analytic experiment was conducted of the initial sludge in a waste water treatment factory with TG (thermogravimetric) and DTG (derivative thermogravimetric) curves at different rates of temperature rise being obtained. The experimental results indicate that the use of a single-stage reaction model to predict the pyrolytic properties of the sludge has its definite limitations. By making use of thermal analytic dynamics and through the adoption of a selection method featuring the most probable mechanism function, the mechanism function of sludge pyrolysis may be proposed to be $f(\alpha) = (1-\alpha)(-\ln(1-\alpha)^{-3})/4$. Through an analysis, the activation energy E and pre-exponential factor A of the sludge were obtained and the pyrolytic dynamics calculation model of the sludge was also given.

Key words: sludge, pyrolysis, mechanism function

汽轮发电机组远程智能故障诊断系统= **An Intelligent Remote Fault-diagnosis System for a Turbogenerator Set**
[刊, 汉] /HE Qing, DU Dong-mei, LI Hong (Education Ministry Key Laboratory on Condition Monitoring and Control of Power Plant Equipment Affiliated to Energy and Power Engineering College under the North China Electric Power University, Beijing, China, Post Code: 102206) //Journal of Engineering for Thermal Energy & Power. — 2006, 21(5). —532～535

Analyzed and studied are the techniques of intelligent fault diagnosis of vibration for turbogenerator sets. By combining artificial neural network technology with object-oriented one, a four symptom neural network has been established. The four symptoms are vibration frequency spectrum, axial-center trajectory, speeding-up-and-down characteristics and load characteristics. Meanwhile, constructed was an intelligent fault-diagnosis neural network for sensing vibrations of steam turbogenerator sets with incomplete symptom inputs. With the frequency spectrum symptoms of turbogenerator set vibrations serving as an example, a method for the automatic acquisition of frequency spectrum symptoms was studied and a specific case was given of comprehensive fault diagnosis with an incomplete symptom based on the frequency spectrum symptom. On this basis, by using a Browser/Server mode and Java technology, an intelligent remote fault-diagnosis system for turbogenerator sets was developed along with a description of the structure composition of the system, functional modules, servers and client-terminal program design and implementation method. **Key words**: turbogenerator set, vibration, neural network, intelligent fault diagnosis, remote diagnosis

类热机结构优化特征及其论证= **Structure Optimization Features of Quasi-heat Engines and Their Demonstration Justification**[刊, 汉] /ZHANG Xiao-hui (Thermal Energy Department of the Soochow University, Suzhou, China, Post Code: 215006) //Journal of Engineering for Thermal Energy & Power. — 2006, 21(5). —536～538

Based on the analysis of the configuration optimization characteristics of an existing heat engine and a quasi-heat engine device, the model of a quasi-heat engine has been extended to a general transmission-process model. Through a variational method, the configuration optimization criterion for general transmission processes was derived, proving that with respect to a linear transmission model and under the condition of a finite-dimension constraint, with the entropy production in the transmission process (or device) being at its minimum, an equipartition of the configuration will be its basic characteristics. In the meanwhile, also described is the application of the configuration optimization of transmission processes in the analysis of quasi-heat engines and in the study of generalized thermodynamics optimization theory. Moreover, the configuration optimization feature under discussion has been preliminarily verified along with a brief exposition of the development trend of its applications. **Key words**: engineering thermodynamics, quasi-heat engine, transmission process, configuration optimization

彼尔姆发动机制造联合体的燃气轮机技术= **Gas Turbine Technology of Perm Engine Manufacturing Complex**
[刊, 汉] /ALEXANDER Yinojamchef, DANIYL Sulimof ("Perm Engine Manufacturing Complex Stock Corp". Managine Company, Perm, Russia, Post Code: 614000) //Journal of Engineering for Thermal Energy & Power. — 2006, 21(5). —539～540

Key words: gas turbine; performance; power plant