

高温/中温两相厌氧消化反应中有机酸的变化

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摘要 为了深入考察高温/中温两相厌氧消化反应器系统用以处理混合基质(分别同时处理污泥与其他高浓度有机废物)时有机酸的变化特性, 采用蒸馏-滴定法测定挥发有机酸总量, 并在系统达到相对稳定时出色质联机确定有机酸的组成及各自含量。研究结果表明, 混合基质经高温消化后挥发有机酸含量有所增加, 平均在 3346—5529 mg/L, 进一步经中温消化且系统达到稳定后其含量平均为 43—433 mg/L; 乙酸、丙酸、丁酸和戊酸是进料混合基质和高温消化后基质中主要的有机酸种类。

关键词 高温/中温, 厌氧消化, 有机酸。

随着城市污水和工业废水处理程度的不断提高, 越来越多的污泥有待于得到有效的处理, 以防止造成二次污染。另一方面, 随着工业发展和人民生活水平的提高, 涌现出越来越多的加工业诸如食品加工、屠宰场与肉类加工及罐肠加工等, 无疑将产生大量的高浓度有机废物, 若直接排至城市污水管道, 既增加污水处理厂的有机负荷和运行难度, 又增加建厂造价及运转费用。为了将污泥和不同种类高浓度有机废物一并进行消化处理, 并缩短传统的污泥消化工艺所需的较长停留时间, 采用高温/中温两相厌氧消化反应器系统, 使产酸菌与产甲烷菌均生长在较佳的环境条件中。由于有机酸是厌氧消化反应过程中有机物分解时产生的重要中间产物, 大部分甲烷气都是由有机酸的进一步分解而产生的, 故这里着重讨论有机酸的变化情况。

1 试验设施与方法

本试验研究采用的是高温/中温两相厌氧消化处理的中试规模试验设施, 即产酸相(兼灭活病原菌)的高温消化作为第一段消化反应器(有效容积为 0.65 m^3 , 停留时间为 2.5 d, 温度控制在 $75 \pm 1^\circ\text{C}$), 而产甲烷相的中温消化作为第二段反应器(有效容积为 1.95 m^3 , 停留时间为

10 d 或 14 d, 温度控制在 $37 \pm 0.5^\circ\text{C}$)。2 个反应器的中心轴上装有螺旋桨搅拌器进行机械搅拌混合。待处理的混合基质是由联邦德国 GOCH 污水处理厂二沉池剩余污泥和各不同加工厂的高浓度有机废物所组成, 先后用于本试验研究的有马铃薯加工废物(主要含碳水化合物), 屠宰场的猪血(主要含蛋白质)和罐肠加工废物(主要含脂类)。基质投配采用半连续形式, 即污泥和高浓度有机废物每日分别由储泥罐和废物罐每隔 8 h 分 3 次由泵再经流量计计量投配至高温消化反应器, 经其消化的一级消化污泥在容器储存 15—30 min 再由泵经流量计计量投配至中温消化反应器, 经其消化的二次消化污泥经容器后排至地面污泥井, 再由泵抽至室外污泥堆放场, 整个过程均自动进行, 试验流程见图 1。按照污泥与其他高浓度有机废物的投加比例情况, 本试验研究分为 4 个系列连续进行, 试验进程及各系列持续时间如图 2 所示, 只有在系列 3-2 中混合基质在中温消化反应器中的停留时间为 14 d, 其余皆为 10 d。

在本试验研究中, 有机酸的测定采用 2 种方式。第一种方式是用蒸馏-滴定法^[1]测定挥发性有机酸(VFA)的含量, 每周进行 2 次, 测定

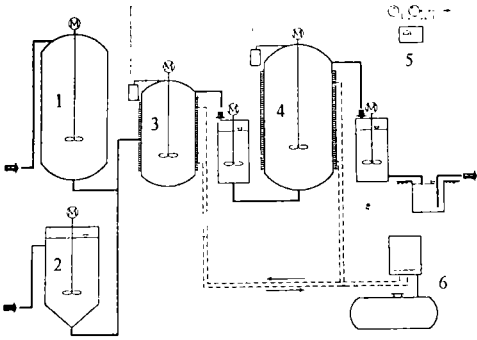


图 1 高温/中温两相厌氧消化中试试验流程

1. 污泥储存罐 2. 有机废物储存罐 3. 高温消化 4. 中温消化 5. 气表与 CH₄ 测定装置
6. 加热装置与丙烷气罐

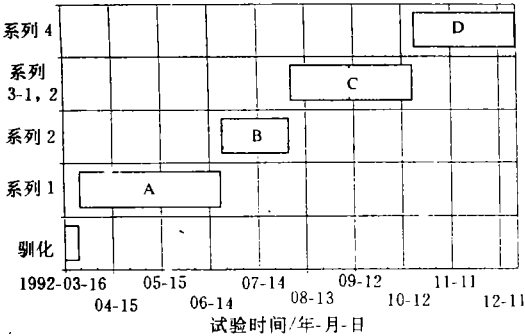


图 2 厌氧消化试验进程

- A. 50%污泥+50%马铃薯废物 B. 80%污泥+20%马铃薯废物 C. 90%污泥+10%猪血
D. 90%污泥+10%罐肠加工废物

样品包括污泥与各高浓度有机废物的比例组合样,高温消化后基质和中温消化后基质.另一种方式是用 GC-MS 法,当高温/中温两相厌氧消化系统相对于各试验系列达到稳定运行状态后,采集 3 个样品(同第一种方式),首先进行预处理,即取一定量的样品加入丙酮并高速搅拌,过滤后加入戊烷,然后加入氯化钠的酸溶液进行相分离,戊烷相用旋转蒸发器将样品浓缩至 1 ml,然后进行色谱-质谱联机分析.由此可具体了解混合基质经第一段高温消化和第二段中温消化以后有机酸的组成及各自含量.

2 试验结果

2.1 挥发性有机酸含量的变化

将用蒸馏-滴定法测定的挥发性有机酸(VFA)含量(以 mgHAc/L 表示)的分析结果绘制成曲线,结果示于图 3. 从图 3 可以看出:混合基质经高温消化后的 VFA 的平均浓度,在系列 1 和 2 中与其在进料混合基质的浓度相差不多,分别为 3746 mg/L 和 4369 mg/L;在系列 3 中大幅度升高,平均为 5529 mg/L;而在系列 4 中比其在进料混合基质的浓度略高,平均为 4121 mg/L. 经高温消化后的基质进一步经中温消化后,VFA 的浓度大幅度降低,在稳定状态下其平均浓度介于 43—433 mg/L. 有资料表明^[2,3],运行良好的厌氧消化反应器,VFA 的浓度通常应小于 500 mg/L,最好是低于 300 mg/L. 挥发酸的浓度在 200—400 mgHAc/L 通常认为是正常的良好消化^[4]. 从这些观点来看,高温/中温两相厌氧消化系统基本处于满意运行状态.

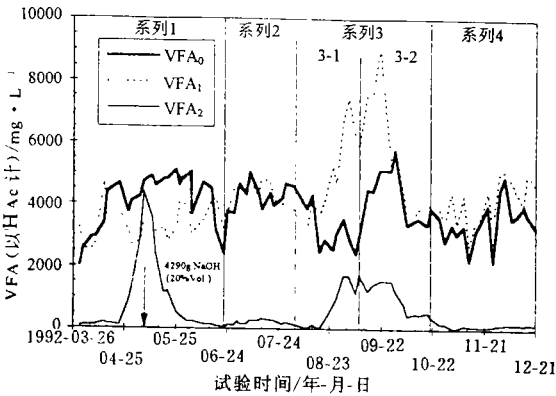


图 3 挥发性有机酸的浓度变化曲线

在系列 1 中,因 04-12 及 04-23 2 天停电而发生加热干扰,再则是 04-27 因更换投配污泥至中温消化反应器的流量计而只投配马铃薯加工废物,致使中温消化反应器消化后基质的 VFA 的浓度逐渐升高,达到 4397 mg/L,但是在向反应器系统中投加碱后,经过 10 d 后 VFA 浓度降低至常态,并保持相对稳定.而在系列 3-1 中,由于系统接受混合基质的有机负荷逐渐增高,因而经中温消化后基质的 VFA 浓度也逐渐增加,高达 1712 mg/L,当延长中温消化反应器的水力停留时间至系列 3-2 中的 14 d 后,尽

管有机负荷仍在增加,但是反应器中 VFA 的浓度下降至 433 mg/L. 由此可见,投加碱或适当延长 HRT(或减少负荷)是恢复中温消化反应器正常运行的弥补措施.

2.2 有机酸各组分及含量的变化

在各试验系列运行达相对稳定时,将混合基质、高温消化和中温消化后基质的 3 个样品进行 GC-MS 的有机酸检测分析,结果见表 1. 从表 1 中可以看出,乙酸、丙酸、丁酸和戊酸是进料混合基质和经高温消化后基质中的主要有机酸种类,其次是软脂酸和硬脂酸. 当混合基质经高温消化 2.5 d 以后,复杂的有机物水解

并产酸,因而大部分有机酸呈浓度增加趋势,而当进一步经中温消化 10 d 或 14 d(系列 3-2)后,C2 至 C18 酸的所有有机酸的浓度均大幅度降低,这表明了在中温消化反应器内以这些有机酸作为基质的甲烷菌进行了有效的甲烷发酵与产气过程. 一般来讲,碳水化合物、蛋白质和脂肪等复杂有机物的厌氧代谢分解要经过酸性和碱性发酵两个阶段,最后产生主要由甲烷和二氧化碳组成的沼气^[5]. 就上述 3 种化合物的分解速度而言,碳水化合物是有机物中最易分解的,分解速度为最高,脂肪次之,蛋白质为最低.

表 1 各试验系列中混合基质消化前后酸的变化对比/mg · L⁻¹

样 品	系 列 1						系列 3-1		
	06-03			06-16			09-09		
	A	B	C	A	B	C	A	B	C
C2 酸(乙酸)	3052	993		1495	427		2921	5685	1626
C3 酸(丙酸)	8078	7967	191	2874	1620	174	1838	2875	955
C4 酸(丁酸)	8272	9864	3906	4200	7910	1964	1724	1712	49
C5 酸(戊酸)	4254	1289	33	400	504	25		547	536
C6 酸(己酸)	44	30	1	53	20	1		13	10
C7 酸(庚酸)	2	2		1	1			4	3
C8 酸(辛酸)	1	1		0	0			1	1
C9 酸(壬酸)									
C10 酸(癸酸)	2	3			1				7
C11 酸(十一酸)									
C12 酸(十二酸)	7	16	0	5	4	1		12	13
C13 酸(十三酸)									
C14 酸(十四酸)	36	34	0	12	13	1		32	40
C15 酸(十五酸)	23	32	1	9	6	1			5
C16 酸(十六酸)	131	362	4	117	67	5	9	36	61
C17 酸(十七酸)		33							
C18 酸(十八酸)	87	519	3	57	86	3	4	15	21

样 品	系列 3-2			系列 4					
	10-08			12-03			12-16		
	A	B	C	A	B	C	A	B	C
C2 酸(乙酸)	2719	2328	600	3986	4412	442	2910	3730	559
C3 酸(丙酸)	1720	2302	89	2425	2591	45	1909	2285	68
C4 酸(丁酸)	598	1142	20	1363	1349	8	968	1000	3
C5 酸(戊酸)	249	1674		1669	1198	2	583	645	4
C6 酸(己酸)		5		11	20	0	11	9	0
C7 酸(庚酸)	2	2		0	5	0	2	2	
C8 酸(辛酸)	1			1	1		1	1	
C9 酸(壬酸)					0		0	0	
C10 酸(癸酸)				2	3		3	5	
C11 酸(十一酸)				2	2	0	5	0	0
C12 酸(十二酸)	28	15		7	9	0	11	14	0
C13 酸(十三酸)				5	3		1	3	0
C14 酸(十四酸)	132	113		59	62	1	126	111	1
C15 酸(十五酸)	20	20		43	39	2	5	12	0
C16 酸(十六酸)	853	580	32	316	226	17	1138	1178	31
C17 酸(十七酸)				25	12	1	7	8	0
C18 酸(十八酸)	276	327	34	221	111	16	326	296	33

A. 进料混合基质 B. 高温消化后基质 C. 中温消化后基质

由表 1 可知,在系列 1 处理污泥与马铃薯加工废物中,由于碳水化合物含量相对较高,且其分解速度又快,在其贮存未投入高温消化池前已大部分水解与产酸,故在 06-03 和 06-16 的 2 次检测中发现高温消化后基质中乙酸、丙酸和丁酸的浓度都比进料混合基质中相应各酸的浓度为低,这意味着进料基质中的这些酸在高温反应器中即得以分解,这也是在系列 1 中在高温反应器里测得较大量气体的原因;基质进一步经中温消化后,乙酸未检出,丙酸分别降至 191 和 174 mg/L,而丁酸浓度却异常高,这有可能是由于丁酸转化成乙酸、甲烷和二氧化碳较慢的缘故。在系列 3 用于处理污泥和猪血的试验中,表现出了高温消化产酸而中温消化产气,再对比系列 3-1 和系列 3-2 发现,当停留时间由 10 d 延长至 14 d 后,中温消化后基质中由原来可检测出 13 种有机酸到只能检测出 5 种有机酸,这进一步说明了适当延长中温消化反应器的停留时间可以使酸分解产甲烷更有效,尤其是在投加猪血负荷较高时,适当延长停留时间可避免有机酸在产甲烷反应器中累积。在系列 4 用以处理污泥和罐肠加工废物的试验中,亦表现出了高温消化反应器水解与产酸、中温消化反应器酸进一步分解有机物而产气的过程,最终消化基质中乙酸的浓度为 442—559 mg/L,而其他有机酸的含量均较低。由于油脂的主要成分是多种高级脂肪酸甘油酯的混合物,而油脂组成中常见的饱和脂肪酸为十二酸(月桂酸)、十四酸(豆蔻酸)、十六酸(软脂酸)和十八酸(硬脂酸),因而在整个试验系列中均检测出以上各有机酸,但尤以投加罐肠加工废物的系列 4 检测出上述各有机酸平均浓度为最高。在各试验

系列中混合基质经高温消化后乙酸和丙酸浓度多超过 2000 mg/L,但似乎并未对中温消化反应器造成任何抑制作用^[6],这与文献中结论不太一致^[7]。

3 试验结论

对高温/中温两相厌氧消化反应器系统用以处理混合基质时有机酸变化特性的研究结果表明,高温消化后有机酸含量增加,中温消化后有机酸被分解去除而产生沼气。采用蒸馏-滴定法测定的挥发性有机酸总量,在系统达到相对稳定时最终消化基质中含量为 43—433 mg/L;通过采用 GC-MS 法确定有机酸的组成及各自含量发现,乙酸、丙酸、丁酸和戊酸是进料混合基质和高温消化后基质中主要的有机酸种类,而其他酸含量相对较少。

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15%. At the conditions of the residence time of 5.9 s for the flue gas in reactor and specific energy of 4 Wh/Nm³, the removal efficiency of NO and NO_x are 42% and 29% respectively.

Key words: pulsed corona discharge, denitrification, flyash, NO, NO_x.

Calculation of Effective Refractive Index of Atmospheric Aerosol and the Effect of Relative Humidity on It. Tian Wenshou et al. (Dept. of Atmospheric Science of Lanzhou Univ., Lanzhou 730000); *Chin. J. Environ. Sci.*, 17(3), 1996, pp. 31–34

Based on the scattering and absorbing characteristic of aerosol, a effective medium approximative method was given, and the effective refractive index of aerosol was calculated. The calculated effective refractive index of the winter aerosol of Beijing is 1.561–0.057i, which is agreed with the observational value (1.550–0.057i). Using this method, the effects of soot content contained in atmospheric areosol and the relative humidity on the effective refractive index were further discussed, and some useful conclusions were obtained.

Key words: aerosol, effective refractive index, relative humidity.

Study on Allocating Permissible Pollutants Discharge Based on Axioms System. Lin Wei et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(3), 1996, pp. 35–37

In this paper the unfairness hidden in the previous fair allocation of permissible pollutant discharge was pointed out, the axioms system about fair allocation was established and a new allocation rule subject to the axioms system was designed using environmental conflict analysis theory. The fruit of this research is practical significant to resolve environmental conflict fairly and improve the traditional environmental planning and management.

Key words: fair allocation, total quantity control of pollutant discharge, environmental conflict analysis.

Study on the Balance of Increasing Pollutants after Closed-Looped Circulation of Wastewater of Coal Gas. Liu Jingjin et al. (Environ. Protection Research Institute, Hunan University, Changsha 410012); *Chin. J. Environ. Sci.*, 17(3), 1996, pp. 38–40

A large amount of experiments and monitoring data showed that after circulation of coal gas washwater, the concentration of pollutants (mainly valatile phenol) does not increase unlimitedly, but reaches a dynamic equilibrium. The concentration of phenol is 1300–2000 mg/L, cyanide is 4–20 mg/L, sulfide is 35–70 mg/L at the range of equilibrium. The result showed that it is completely feasible to use the routine technological treatment of closed-looped circulation of pretreatment of coal gas washwater removing suspended solids and tar.

Key words: closed-looped circulation, washwater of coal gas, dynamic equilibrium.

A Study on the Conversion of Waste Settlings from the Production of Furfural into Complex Fertilizer. Liu Junfeng et al. (Xiang Tan Mineral Institute, Hunan 411201); *Chin. J. Environ. Sci.*, 17(3), 1996, pp. 41–43

The results showed that the waste settlings is almost neutral and contains effective phosphorus and potassium, which are all satisfied to the quality standard for the complex fertilizer in furfural formation from straw of rice (or straw of wheat), and the yield of furfural exceeded 9% (as abs dry raw material) by the addition of the materials under the conditions of hydrolysis which showed as following: the temperature 110°C–140°C, the ratio of the additions to straw: 1 : 2–1 : 3 by weight, the ratio of the liquid to the solid: 3 : 1–4 : 1 by weight, time of hydrolysis: 2–3 h, and 1 atm.

Key words: modification of sulfuric acid catalysis, production of furfural, conversion of waste settlings, complex fertilizer containing phosphate and potassium.

Organic Acid Changes in Two-phase Thermophilic/Mesophilic Anaerobic Digestion Process. Qingliang Zhao and Baozhen Wang (Harbin University of Architecture & Engineering, Harbin 150001), G. Kugel (Niersverband, 41747 Viersen, F. R. Germany); *Chin. J. Environ. Sci.*, 17(3), 1996, pp. 44–47

In order to investigate the changes of organic acids in the two-phase thermophilic/mesophilic anaerobic digestion which was designed for the treatment of mixed substrates from sewage sludge and other high-concentration organic waste, distillation-titration method was adopted for the analyses of volatile organic acids, and GC-MS for

their composition and concentration. The experimental results showed that the concentration of volatile organic acids increased after the thermophilic digestion of the mixed substrates and decreased greatly after their further digestion in the second mesophilic digester, which were averagely 3346—5529 mg/L and 43—433 mg/L, respectively. Acetic acid, propionic acid, butyric acid and valeric acid are the main acids in the mixed substrates and in the effluent of thermophilic digester.

Key words: thermophilic/mesophilic, anaerobic digestion, organic acids.

Study on the Effect of Tourism on the Ecological Environment of Mountain Emei and Protective Strategies.

Jiang Wenju et al. (Dept. of Environ. Sci. and Eng., Sichuan Union Univ., Chendu 610065); *Chin. J. Environ. Sci.*, **17** (3), 1996, pp. 48—51

With development of tourism and increase of visitors, the ecological environment of Mt. Emei has been seriously damaged. SO_2 concentrations in the atmosphere in some places have exceeded the national standard and NO_x concentrations are increasing gradually. The acidization of rain, fog and soil are getting more serious. *Abies fabri*, main scenic forest at high altitudes, have also been on the way to decline. The damaged extent at tourist spots is obviously higher than that in other places. In this paper, the policy of protection prior to development was proposed, with strategies of increasing capacity of tourism, rationally dispersing tourists, advocating electricity in replacement of coal, concentratedly disposing sewage and solid wastes, devoting major efforts to plant vegetation, controlling residential population and emphasizing consciousness of environmental protection.

Key words: Mountain Emei, tourism, ecological environment, protective strategy.

Catalytic Combustion of Pyridine Over Metal Oxides Catalysts. Luo Mengfei et al. (Institute of Catalysis, Hangzhou University, Hangzhou 310028); *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 52—53

The Oxidation activity of pyridine and NO_x control in pyridine oxidation over metal oxides catalyst were studied. As the temperature increased, the content of nitrogen oxide generated by pyridine oxidation went through a maximum value.

Oxidation activity of catalysts was found to be in direct proportion to their NO_x control ability. Ag-Mn and Ag-Co bi-metal oxides catalysts exhibit higher activity and NO_x control ability than the individual composition catalyst. The oxidation mechanism of pyridine was discussed.

Key words: pyridine catalytic oxidation, metal oxide catalyst, NO_x control.

The Photolysis Character of HCFC-22 in Presence of Hydrogen Peroxide. Zhong Jinxian et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Chen Dazhou (Chinese Center for Certified Reference Materials, Beijing 100013); *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 54—56

Under simulated atmospheric condition, the HCFC-22 + H_2O_2 in the presence or absence of oxygen was irradiated by low pressure mercury lamp and the products of photolysis were determined by a Fourier Transform Infrared Spectroscopy with a 20 m long path cell. The products are COF_2 , CO_2 , HF and HCl for HCFC-22 + H_2O_2 system, CO_2 , H_2O , HF and HCl for HCFC-22 + $\text{H}_2\text{O}_2 + \text{O}_2$ system. Based on these results, the mechanisms of photolysis were suggested.

Key words: photooxidation, HCFC-22, H_2O_2 .

Study on the Catalytic Removal of Phenols from Aqueous Solution by Immobilized Enzyme. Hu Longxing (Dept. of Chem. & Chem. Eng., Shanghai University, Shanghai 200072); *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 57—60

The removal of phenols from aqueous solution by immobilized enzyme catalytic oxidation was studied. The immobilized enzyme was prepared by containing horseradish peroxidase with calcium alginate gel, and hydrogen peroxide was used as oxidizing agent. For 100 ml phenol or o-aminophenol aqueous solution containing 100 mg/L phenol, under the following appropriate conditions: 3% sodium alginate solution 30 ml, gel particle diameter 1 mm, immobilization time 1 h, containing amount of enzyme 50 u, reaction time 1h, pH 6 and hydrogen peroxide dose 2 mmol, the removal rates of phenol and o-aminophenol exceeded 80% and 70% respectively. There was synergistic effect between various phenols in the treatment of mixed phenol aqueous solution. The treatment result after mixing dif-