DESTRUCTION OF INSULATING OILS CONTAINING PCBS AND PCDD/FS IN A TWO-STAGE MOLTEN SALT OXIDATION REACTOR SYSTEM

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Abstract

The characteristics of a destruction of PCBs and PCDD/Fs in waste insulating oils were investigated under various molten salt oxidation (MSO) reactor operating temperatures. The emissions of dioxin-like PCBs and PCDD/Fs were measured for four different temperatures of a two-stage MSO reactor system during the destruction of a real PCBs-contaminated waste oil (0.035% PCBs, w/w). The destruction of PCBs in a molten Na_2CO_3-Li_2CO_3 eutectic salt at over 1173K was substantial and the determined destruction efficiency (DE) was over 99.9999% for each of the dioxin-like PCBs. DEs for the PCDDs were also determined from a mass balance of their feed and emission streams across the MSO reactors. Determined DEs were in the range of 99.92-99.97% for 123478-H6CDF, 123678-H6CDF and O8CDF, while those for the other 6 kinds of PCDFs were determined as over 99.99999%.

Introduction

Incineration is an effective method for the destruction of PCBs[1, 2]. While an incineration has been considered as an effective destruction process for a PCBs-containing waste, the environmental acceptability for the potential formation of PCDD/Fs is a major criterion for an the application of the incineration to PCBs destruction process1.[1-3] Molten salt oxidation (MSO) is one of the promising alternative destruction technologies for PCBs because it is capable of trapping chlorine during an organic destruction. In hot molten sodium carbonate, for example, hydrogen chloride or chlorine is first released at the stage of a catalytic destruction of the chlorinated organics and it is trapped in the form of sodium chloride.[4-7] This study investigated the PCBs destruction performance of two MSO reactors in series. Investigated operating parameter in this study is the MSO reactor temperature. The purpose of this study is to establish the characteristics of a MSO of the PCBs and PCDD/Fs.

Materials and Methods

A schematic diagram of a bench-scale MSO system with a designed capacity of 1 kg/h is shown in Fig. 1. A binary carbonate salt mixture was used as a molten salt to extend the range of the investigating temperature of the MSO reactors. The salt mixture consisted of 50 mol% Li_2CO_3 and 50 mol% Na_2CO_3. The selected waste oils used in this study were insulating oils contaminated with PCBs and PCDD/Fs. Experimental conditions are shown in Table 1. During the test runs, the concentrations of O_2, CO and NOx in the off-gas released from each MSO reactor were measured by using a combustion efficiency analyzer (TESTO-300). About 3 Nm^3 of the off-gas samples was taken for each test run and the feeds and emissions of dioxin-like PCBs and PCDD/Fs were analyzed by HRGC/HRMS (Jeol-700D, Resolution: >10000, SIM mode).

Results and Discussion

In the MSO reactor, as shown in Fig. 1, the vaporized oil-air mixtures form bubbles when they enter the molten salt at the bottom of the MSO reactor. These bubbles rise throughout the salt and disappear at the surface of the molten salt. Gas-phase organic destruction and chlorine-capturing surface reactions occur simultaneously in the rising bubbles. The overall reaction in a Li_2CO_3-Na_2CO_3 eutectic salt reactor is given by the following equation.

$$C_aH_bCl_c + \frac{c}{2}\mathrm{Na(or\ Li)_2CO_3} + \left(a + \frac{b-c}{4}\right) O_2 \rightarrow \left(a + \frac{c}{2}\right) CO_2 + \frac{b}{2} H_2O + \mathrm{Na(or\ Li)Cl} \quad (1)$$

The emissions of dioxin-like PCBs for the K sample (345 ppm PCBs) under various operating temperatures are shown in Table 2. Based on each congener concentration in the feed waste oil and that in the gas emission from the secondary MSO reactor, the DE of the tested MSO system for each dioxin-like PCB was determined. It should be noted that no PCBs were detected for the samples of the molten salt after each test run. As shown in Table 2, there was no significant difference in the destruction efficiency for different kinds of dioxin-like PCB. In addition there's no significant difference in the destruction efficiencies with the tested temperature. Overall destruction efficiency of the tested two-stage MSO system for the dioxin-like PCBs in the waste insulating oils was determined as over 99.9999%.

It was found that the tested waste oils had some PCDD/Fs as well as PCBs. Destruction efficiencies for the PCDD/Fs were determined based on the mass concentrations of the PCDD/Fs in the feed oil and those in the gas emission. It should also be noted that there were no PCDD/Fs detected in the molten salt after each test runs. As shown in Table 3, the determined DEs for 123478-H6CDF, 123678-H6CDF and O8CDF were in the range of 99.92-99.97. However, emissions of the other 6 kinds of PCDFs and those of the 7 kinds of PCDDs were not detected and the determined DEs for those 13 kinds of PCDD/Fs were determined as over >99.99999%.

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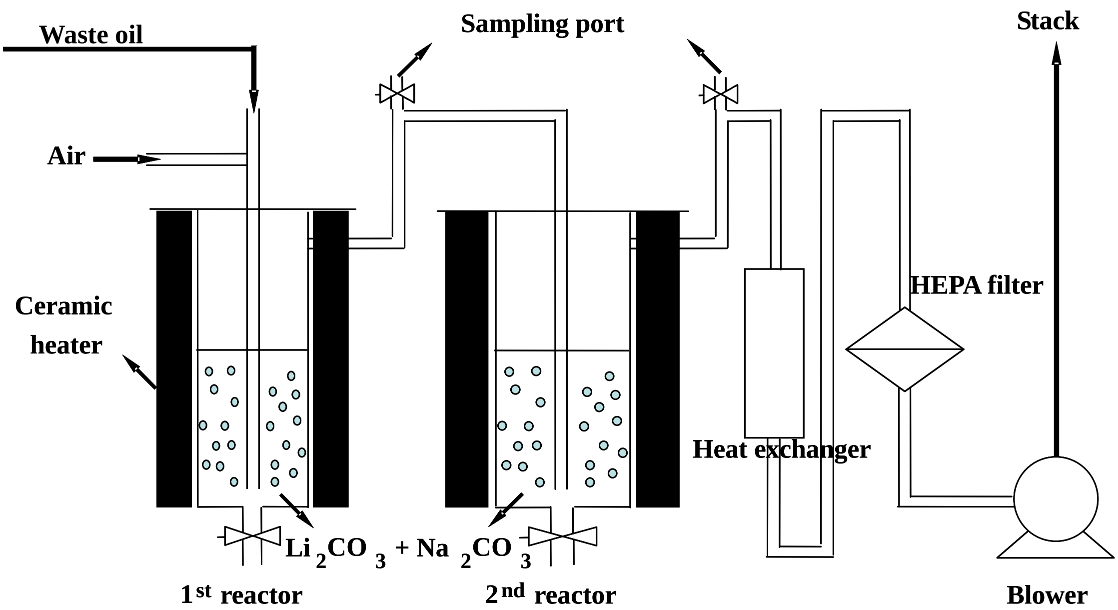

Fig. 1. Schematic diagram of a two-stage molten salt oxidation reactor system

Table 1. Test conditions for PCBs-containing insulating oils and the emissions of carbon monoxide

Test No.		1	2	3	4	5	6
Waste insulated oil		W	Y	K	K	K	K
Feed rate of insulated oil (L/hr)		0.9	0.92	1	1	1	1
PCBs concentration in oil (mg/L)		4.54	61.08	344.71	344.71	344.71	344.71
Feed rate of PCBs, (mg/hr)		4.086	56.12	344.71	344.71	344.71	344.71
Primary MSO Reactor Temperature (K)	Minimum	1133	1133	1133	1148	1163	1178
	Maximum	1154	1155	1155	1164	1177	1193
	Average	1148	1149	1149	1157	1164	1183
Secondary Reactor Temperature (K)	Minimum	1173	1173	1173	1173	1173	1173
	Maximum	1179	1179	1180	1180	1180	1180
	Average	1176	1177	1177	1176	1177	1176
CO emission (ppm, 12% O_2)	Average	270	106	38	32	6	5
	Maximum	658	530	208	180	24	14
	Minimum	42	0	0	0	0	0

Table 2. Mass balance and determined destruction efficiency for each dioxin-like PCB

Com-pounds	Congener	Feed rate (μg/h)	Test 4		Test 5		Test 6		Test 7	
			Emission, (μg/h)	DE, (%)	Emission, (μg/h)	DE, (%)	Emission, (μg/h)	DE, (%)	Emission, (μg/h)	DE, (%)
Non -ortho	344’5	187	0.0001	99.99998	<0.0001	99.99999	<0.0001	99.99999	0.0004	99.9998
	33’44’	174	0.0008	99.9999	0.0008	99.9996	0.0005	99.9997	0.0008	99.9995
	33’44’5	65	0.0001	99.9999	<0.0001	99.99999	<0.0001	99.99999	<0.0001	99.99999
	33’44’55’	0	-	-	-	-	-	-	-	-
Mono -ortho	2’3344’5	1,196	0.0007	99.99994	0.0011	99.99991	0.0009	99.9993	0.0011	99.99991
	23’44’5	11,325	0.0142	99.9999	0.0143	999998	0.0122	99.9999	0.0101	99.99991
	2344’5	225	0.0002	99.9999	0.0004	99.9998	0.0004	99.9998	0	100
	233’44’	2,643	0.0056	99.9998	0.0039	99.9999	0.0042	99.9998	0.0038	99.9999
	23’44’55’	881	0.0006	99.99994	0.0007	99.99992	0.0009	99.9999	0.0009	99.9999
	233’44’5	2,155	0.0012	99.99994	0.0012	99.99994	0.0015	99.99993	0.0029	99.9999
	233’44’5’	269	0.0002	99.99991	0.0005	99.9998	0.0005	99.9998	0.0006	99.9998
	233’44’55’	296	<0.0001	99.99999	<0.0001	99.99999	<0.0001	99.99999	<0.0001	99.99999
Total dioxin-like PCBs		19,415	0.0237	99.9999	0.0230	99.9999	0.0212	99.9999	0.0207	99.9999

Table 3. Mass balance and determined destruction efficiency for PCDD/Fs in waste insulating oil (Test 4)

Compounds	Congener	pg/mL	feed (μg/h)	Emission (pg/Sm^3)	DE (%)
PCDDs	2378-T4CDD	129.555	0.1295550	<0.001	>99.99998
	12378-P5CDD	548.049	0.5480490	<0.001	>99.99999
	123478-H6CDD	282.075	0.2820750	<0.001	>99.99999
	123678-H6CDD	272.301	0.2723010	<0.001	>99.99999
	123789-H6CDD	338.737	0.3387370	<0.001	>99.99999
	1234678-H7CDD	191.326	0.1913260	<0.001	>99.99999
	O8CDD	401.239	0.4012390	<0.001	>99.99999
	total	2163.282	2.1632820	0.007	>99.99999
PCDFs	2378-T4CDF	427.122	0.427122	<0.001	>99.99999
	12378-P5CDF	337.128	0.337128	<0.001	>99.99999
	23478-P5CDF	891.088	0.891088	<0.001	>99.99999
	123478-H6CDF	169.513	0.169513	25.641	99.95778
	123678-H6CDF	227.72	0.227720	27.778	99.96597
	123789-H6CDF	352.11	0.352110	<0.001	>99.99999
	234678-H6CDF	261.71	0.261710	<0.001	>99.99999
	1234678-H7CDF	291.375	0.291375	213.675	99.79540
	1234789-H7CDF	307.388	0.307388	<0.001	>99.99999
	O8CDF	444.974	0.444974	123.504	99.92256
	total	3710.128	3.7101280	390.604	99.97063
Total (PCDDs+PCDFs)		5873.41	11.7468200	390.611	>99.99072