DIOXIN FORMATION AND PCBs EMISSIONS IN A POOL COMBUSTION OF PCBs MIXED OILS
- SIMULATION OF FIRES IN PCBs DEGRADATION FACILITIES -

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Introduction

Polychlorinated biphenyls (PCBs) are knows as dioxin families (DXNs), and more than 1,000,000 tons of PCBs are still in use or storage in the world. The Stockholm Convention requests to eliminate PCBs by 2028. Recently, incineration of PCBs has difficulties to get an agreement of local residents for the risks of DXNs. In Japan, 55,000 tons of PCBs had been produced, but only 5,500 tons of PCBs were incinerated for 1988 - 1989. PCBs degradations in chemical methods were authorized in 1998 as an alternative to incineration, and PCBs degradations are enforced by 2016 in Japan. A combined technique using photochemical- and catalystic- dechlorinations (UV / catalyst method) [1] has excellent features such as atmospheric pressure, low temperature below 75 C (degrees centigrade), no DXNs formations, closed system, less or no waste water. Figure 1 shows a system diagram of PCBs degradation facility using UV / catalyst method and washing with decane ($C_{10}H_{22}$). PCBs in capacitors, transformers, *etc.* are extracted by disassembling and distilling the PCBs / decane oils in the washing machines. Extracted PCBs are dissolved in isopropyl alcohol (IPA) with NaOH, and dechlorinated by UV / catalyst dechlorination processes.

For the "safety net" and "risk communication" of the PCB degradation facility, we investigated a fire disaster as a severe accident, where decane or IPA leaked on a sump accidentally gets fire by electrostatic or flint sparks. So far, a damage of building due to a fire involving PCBs [2], and DXNs formation in incinerators for the domestic wastes [3] were reported. Studies on "pool combustion", similar to the fires on a sump, were performed by Akita *et al.*[4], Nishida *et al.*[5], and Lee *et al.*[6]. In this work, we firstly investigated pool combustion of PCBs / decane mixture oil for the study of PCBs emission and DXNs formation in the fire. The results of this work will provide a basic knowledge on fires in other
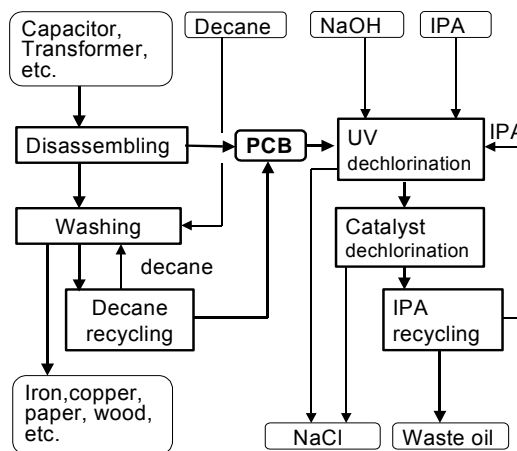
Figure 1: System diagram of PCBs degradation facility including UV / catalyst method and decane washing.
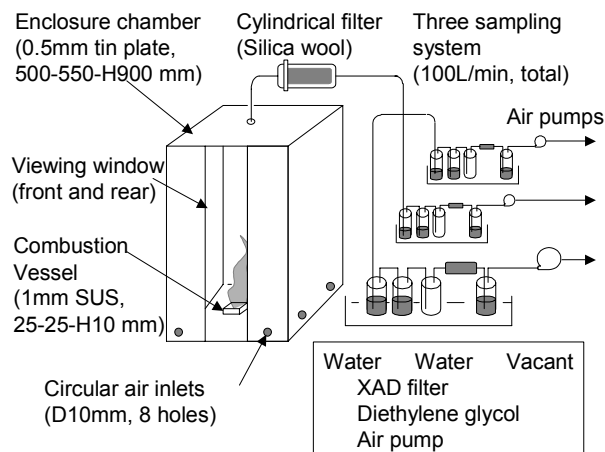
PCBs degradation facilities using inflammable solvents.

Methods and Materials

The experimental set-up is shown in Fig. 2. The oil combustion vessel, made of stainless steel with 1mm thickness, has dimensions of 25 mm square and 10 mm depth, filled with PCBs / decane mixture oil, manually kept at full vessel. The temperature of the flame and the vessel were measured by thermocouples (CA type). The enclosure chamber made of tin with 0.5 mm thickness, which covers the combustion vessel, has dimensions of 550 mm square and 900 mm height. It has two viewing windows, and eight circular air inlets with 10 mm diameter at 20 mm above the bottom. Combustion gas was pumped out in 1.67×10^{-3} [m³/s] from an air outlet with 10 mm diameter at the top panel. The suction wind speed of 2.65

Figure 2: Experimental setup for PCBs / decane pool combustion. All combustion gas is conducted to three identical sampling systems.
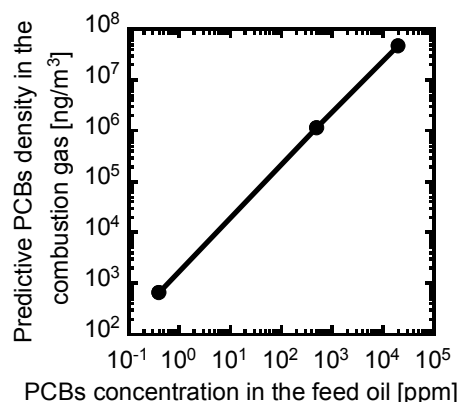
[m/s] at the air inlet is sufficiently high to conduct all combustion gas to the sampling system. Particulate materials (PMs) were collected by the cylindrical filter made of silica wool. PMs attached to the enclosure chamber were also collected for PCBs and DXNs analysis. The combustion gas was collected in parallel by three identical sampling systems with two water impingers, a vacant pot, XAD filter, a diethylene glycol impinger, and an air pump. The determination limits for PCBs and DXNs are about 0.02 [ng/m³] and 0.01 [pg-TEQ/m³], respectively. Three concentrations of PCBs (KC-300, Kanegafuchi Chemical Co.) / decane were provided for this experiment, *i.e.,* 0.4 ppm, 410 ppm, and 20,000 ppm. 0.4 ppm is just below the regulation of degraded waste oil in Japan (0.5 ppm), and 20,000 ppm is equivalent to the maximum PCBs concentration in the facility.

Results and Discussion

The flame of PCBs / decane mixed oils had a length of 100 - 150 mm, which was similar to the open air combustion without the enclosure chamber. The oxygen density in the combustion gas was 18.8 - 19.9 %. The flame had a temperature of 600 C (degrees centigrade) up to 60 mm above the oil surface. The temperature decreased down to 200 C, 100 C, at 100 mm, 300 mm, 900mm (outlet position) above the oil surface, respectively. The temperature of the combustion vessel rose up to 75 C, within 5 minutes after ignition, and became stable. The combustion durations were 40 min (0.4 ppm) and 30 min (410 and 20,000 ppm). Oil consumption rate during the combustion was 6.74 [mg/s]. Figure 3 shows predictive PCBs vapor densities in the enclosure chamber
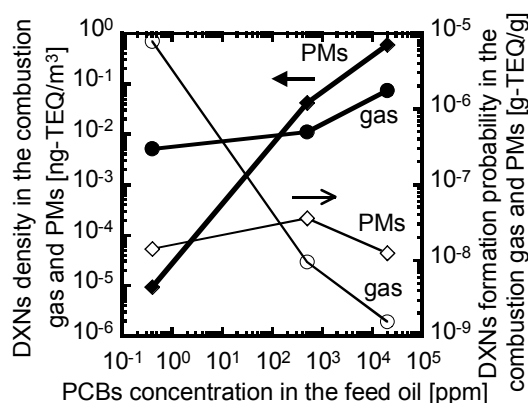

Figure 3: Predictive PCBs vapor density in the enclosure chamber.
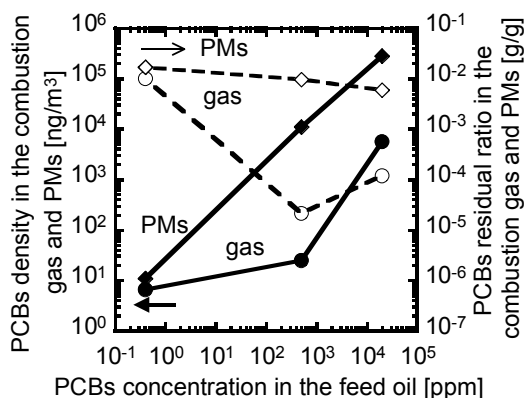
Figure 4: PCBs density and PCBs residual ratio in the combustion gas and PMs.
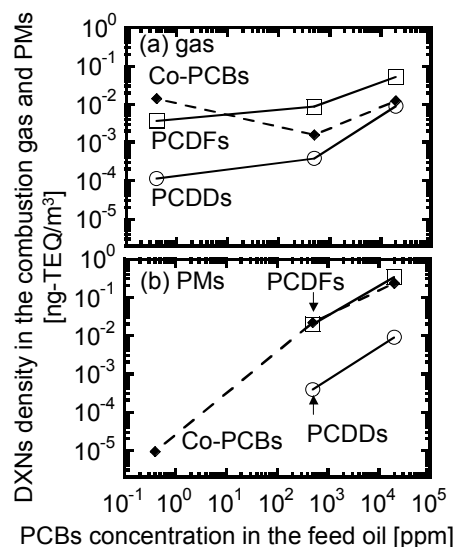
Figure 5: DXNs density and DXNs formation probability in the combustion gas and PMs.

assuming no combustion, defined as total evaporated PCBs [g] / total sampled gas volume [m^3]. PCBs in the combustion vessel after the fire extinction were condensed by 2.5 times due to the different boiling points, *i.e.,* 340 - 375 C (KC-300), and 172 C (decane). Since PCBs contain various isomers with different boiling points, the ratio of PCBs with >5 chlorines (higher boiling point) / total PCBs increased by 20 - 40 %. The ratio of mono-chlorinated biphenyls / total PCBs, however, increased by 50 %, which would be due to the thermal dechlorinations of PCBs in the oil or gas phase.

PCBs densities in the gas and PMs (per unit gas volume), and PCBs residual ratio defined as PCBs densities / predictive PCBs density are shown in Fig. 4. Here, PCBs densities in the PMs are defined as PCBs weight in the PMs / total sampled gas volume. PCBs densities in PMs were always larger than those in the gas. PCBs residual ratio in PMs were almost constant at 10^{-2} [g/g], which suggests that PCBs trapped in PMs were not degraded because of low temperature and / or lack of oxygen. PCBs residual ratios in the gas varied in the range of 10^{-2} - 10^{-4} [g/g] for 0.4 - 20,000 ppm PCBs concentrations in the feed oil. It would be necessary here to consider thermodynamic equilibrium of PCBs formation and degradation in the gas.

In the combustion gas and PMs, DXNs can be formed from PCBs, decane and impurities in the air such as NaCl. DXNs densities in the combustion gas and PMs are shown in Fig. 5. DXNs densities in PMs were larger than those in the gas for the PCBs concentration in the feed oil above 410 ppm. DXNs formation probabilities, defined as DXNs densities in the combustion gas and PMs / predictive PCBs vapor densities in the non-combustion gas, are also shown

Figure 6: DXNs densities of PCDDs ( ), PCDFs ( ), and Co-PCBs ( ) in the combustion gas (a) and PMs (b). PCDFs and PCDDs densities in the PMs at 0.4 ppm PCBs concentration are below the determination limits.

in this figure. DXNs formation probabilities in PMs were almost constant at 10^{-8} - 10^{-7} [g-TEQ/g] regardless to the PCBs concentrations in the feed oil, while that in the gas varied in wide range of 10^{-5} - 10^{-9} [g-TEQ/g]. Figure 6 shows the densities of three types of DXNs, i.e., polychlorinated dibenzo-para-dioxin (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar PCBs (Co-PCBs). Co-PCBs are important in the PCBs combustion, since PCBs in the feed oil originally contains Co-PCBs. In PMs, Co-PCBs densities were close Co-PCBs concentrations in the original PCBs (1.3×10^{-6} [g-TEQ/g]) x residual PCBs density in PMs [g/m^3] within a factor of two. This suggests PCBs trapped in the PMs were hardly transformed to Co-PCBs. In the combustion gas, Co-PCBs / PCBs density ratios varied very wide range by the orders of 3 - 1 for 0.4 - 20,000 ppm PCBs concentrations in the feed oil. Transformations or formations of Co-PCBs from the PCBs or PCBs fragments would be important in the combustion gas especially in low PCBs concentrations in the feed oil. PCDFs densities in the combustion gas and PMs were always larger than PCDDs densities by 1 - 2 orders. One of the reasons for this result would be the thermal transformations of PCDFs from PCBs in the presence of oxygen. DXNs formations in the combustion involving decane and NaCl in the air would be important especially in low PCBs concentrations. Quantitative investigations of PMs density in the gas, and PCBs and DXNs densities per PMs weight are also important for further discussions.

Early fire extinction is important for the safeties, as a matter of course, if we consider the fact that PCBs are condensed in the sump. We should pay an extra attention to DXNs and PCBs in the combustion gas and PMs. The PCBs vapor after the fire extinction can be very high as shown in Fig. 3. For the fireman's safety, ventilation is important, since it lowers PCBs and DXNs densities in the working environment and it may suppress the production of PMs. A chemical-cartridge respirator would be effective for the removing PCBs and DXNs. Removal efficiencies of 99 % (PMs) and 95 % (PCBs and DXNs) are sufficient to reduce PCBs and DXNs densities shown in Figs. 4 and 5 below the regulations for worker's safeties in Japan (PCBs: 10^5 ng/m^3, DXNs: 2.5×10^{-3} [ng-TEQ/m^3]). For the environmental safety, even a wire mesh filter trapping PMs is effective to suppress DXNs emission below the level of regulation in large incinerators in Japan (0.1 [ng-TEQ/m^3]).

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