

CHLORINATION EFFECTS ON PCBzs, PCPhs, PCDD/DFs AND PAHs BY DIOXIN-FREE FLYASH AND UNBURNT HYDROCARBON: 2. EFFECT OF HCL CONCENTRATION

Takumi Takasuga¹, Norihito Umetsu¹, Tetsuya Makino² and Katsuya Tsubota²

¹Shimadzu Techno-Research Inc., 1, Nishinokyo-Shimoaicho, Nakagyo-ku, Kyoto 604-8436, Japan

²Japan PVC Environmental Affairs Council, Uchisaiwaicho 2-1-1, Chiyoda-ku, Tokyo 100-0011, Japan

Introduction

Formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) during municipal waste incineration was discovered in 1977¹. The presence of these compounds in incinerator fly ash has led to laboratory-scale modeling of the formation process. Recent reviews summarized the most important trends and results²⁻³. Our earlier report we demonstrated the formation of dioxin during burning of newspaper, kerosine, paraffin, and plastics with dioxin-free flyash⁴. In general practice, HCl was formed from the NaCl during heating of NaCl which contain waste along with clay. In order to understand the formation of dioxins from HCl, baseline study is needed for the confirmation. Not only dioxins, but also chlorinated chemicals (CCs) such as chlorobenzenes (PCBzs) and chlorophenols (PCPhs) also evolved during heating of dioxin-free flyash catalytic reaction. Besides, the burning experiment suggested that polycyclic aromatic hydrocarbons (PAHs) also a major chemical evolved during these complex reactions. In addition, the presence of metal chloride in the fly ash and hydrocarbons in the gas stream is the major contributors for the increased dioxin chlorinated compounds and concentration.

With continued research activities on fly ash samples, in present study we conducted research on dioxin-free fly ash samples as a catalyst for the dioxin formation with the presence hydrogen chloride (HCl) at different concentrations. Further, the homologue pattern, chlorine percentage, of PCBzs, PCPhs, PCDD/DFs and PAHs has been determined and evaluated.

Materials and Methods

Dioxin-free fly ash

Fly ash was obtained from the electrostatic precipitator of municipal solid waste incinerator and subjected into thermal heat of 500 °C for 2 hours with the presence of nitrogen stream that removed 99.99 % of dioxin. This dioxin-free fly ash was analyzed to confirm the levels of organic compounds as a catalyst.

Experiment

The experiment was conducted using experimental apparatus shown elsewhere⁴. Briefly, the paraffin powder of 1 g was dusted 100 times with 10 mg for the duration of 2 hour. CO, CO₂, O₂ were also monitored simultaneously during the entire period of experiment. The hydrogen chloride concentration was changed as 10 ppm, 50 ppm, 100 ppm, 500 ppm and 1000 ppm in the paraffin powder. The experiment also conducted with dioxin-free paraffin powder and newspaper. Extraction and cleanup procedures and analysis were same as JIS K 0311 methods established by our team with minor modifications⁴.

FORMATION AND SOURCES

HRGC/HRMS analysis

The identification and quantification of PCDD/DFs were performed using Micromass Autospec Ultima. Additionally chlorobenzenes, (PCBzs) and chlorophenols (PCPhs) and 16 compounds PAHs were analyzed in HRGC-HRMS at a resolution of > 10, 000 using ¹³C-internal standards. The concentrations of PCBzs and PCPhs and PCDD/DFs were ng/g while, PAHs expressed as mg/g unless otherwise specified.

Table 1. Formation of PCBzs, PCPhs, PCDDs, PCDFs, PAHs and TEQ with varied concentrations of HCl¹ and

| Sample | Paraffin | Paraffin | Paraffin | Paraffin | Paraffin | Nothing | Paraffin | Paraffin |
|---------------------------------------|----------|----------|----------|----------|----------|------------------|------------------|------------------|
| HCl ¹ concentration stream | 10 ppm | 50 ppm | 100 ppm | 500 ppm | 1000 ppm | 100ppm | 100ppm | 1000ppm |
| Chlorobenzene (Cl%/MW) | | | | | | | | |
| MoCBZ (0.316/112.5) | 120 | 490 | 130 | 23 | 200 | 10 | 10 | 85 |
| DiCBZ (0.483/147) | 2600 | 16000 | 8500 | 4400 | 8800 | 230 ^a | 450 ^a | 670 ^a |
| TrCBZ (0.587/181.5) | 1800 | 22000 | 33000 | 20000 | 34000 | 22 | 10 | 95 |
| TeCBZ (0.657/216) | 830 | 1400 | 20000 | 25000 | 33000 | 10 | 20 | 21 |
| PeCBZ (0.705/250.5) | 250 | 4500 | 7300 | 17000 | 20000 | 10 | 10 | 10 |
| HxCBZ (0.747/285) | 170 | 920 | 1300 | 4800 | 4300 | 59 | 130 | 130 |
| PCBzs | 5800 | 58000 | 70000 | 71000 | 100000 | 310 | 600 | 1000 |
| Cl% | 55 | 58 | 61 | 64 | 63 | | | |
| Chlorophenols (Cl%/MW) | | | | | | | | |
| MoPCPhs (0.276/128.5) | 5100 | 15000 | 37000 | 2200 | 2600 | 100 | 150 | 600 |
| DiPCPhs (0.436/163) | 1300 | 14000 | 47000 | 6800 | 5500 | 200 | 250 | 1200 |
| TrPCPhs (0.539/197.5) | 330 | 11000 | 30000 | 24000 | 28000 | 100 | 100 | 520 |
| TePCPhs (0.612/232) | 110 | 7100 | 26000 | 27000 | 31000 | 130 | 100 | 570 |
| PeCPCPhs (0.666/266.5) | 150 | 1500 | 4200 | 9500 | 9800 | 120 | 100 | 270 |
| PCPhs | 7000 | 49000 | 144000 | 70000 | 77000 | 450 | 400 | 3200 |
| Cl% | 33 | 44 | 45 | 57 | 57 | | | |
| PCDDs (Cl%/MW) | | | | | | | | |
| TeCDDs (0.441/322) | 6 | 250 | 290 | 290 | 250 | 0.006 | 0.0099 | 0.39 |
| PeCDDs (0.498/356.5) | 2.5 | 210 | 310 | 630 | 980 | 0.006 | 0.009 | 0.096 |
| HxCDDs (0.545/391) | 0.86 | 150 | 240 | 830 | 1100 | 0.0097 | 0.016 | 0.1 |
| HpCDDs (0.584/425.5) | 0.3 | 53 | 86 | 570 | 790 | 0.0095 | 0.017 | 0.065 |
| OCDD (0.617/460) | 0.17 | 13 | 18 | 250 | 320 | 0.014 | 0.017 | 0.12 |
| PCDDs | 10 | 680 | 940 | 2600 | 3400 | 0.046 | 0.069 | 0.77 |
| Cl% | 47 | 50 | 50 | 54 | 54 | | | |
| PCDFs (Cl%/MW) | | | | | | | | |
| TeCDFs (0.464/306) | 94 | 1800 | 2400 | 2900 | 2900 | 0.016 | 0.03 | 5.0 |
| PeCDFs (0.521/340.5) | 29 | 1000 | 1400 | 2500 | 2900 | 0.016 | 0.025 | 0.72 |
| HxCDFs (0.568/375) | 5.5 | 390 | 610 | 1500 | 1400 | 0.014 | 0.021 | 0.17 |
| HpCDFs (0.607/409.5) | 0.94 | 130 | 200 | 710 | 730 | 0.01 | 0.012 | 0.089 |
| OCDF (0.640/444) | 0.3 | 21 | 29 | 180 | 170 | 0.01 | 0.01 | 0.067 |
| PCDFs | 130 | 3300 | 4600 | 7800 | 8100 | 0.056 | 0.088 | 6.0 |
| Cl% | 48 | 50 | 50 | 52 | 52 | | | |
| Sum PCDD/DFs | 140 | 4000 | 5540 | 10000 | 12000 | 7.4 | 28 | 7200 |
| TEQ | 1.8 | 62 | 99 | 170 | 170 | 0.12 | 0.2 | 95 |

¹hydrochloric acid; * indicates mg/g concentration levels;^adenotes blank background concentrations.

PCBz, PCPhs, PCDDs, PCDFs, TEQ and PAHs respectively, polychloro benzene, polychlorophenols, polychlorinated dibenzo-*p*-dioxins, dibenzofurans, toxic equivalency and polycyclic aromatic hydrocarbons.

Results and Discussion

Very drastic increase of PCBzs, PCPhs, PCDDs, PCDFs, TEQ and PAHs with the presence of dioxin-free fly ash has been noticed at 10 to 50 ppm HCl concentrations along with paraffin powder and newspaper (Tables 1 and 2). Considerably, more than 100 to 1000 ppm HCl concentrations, there was not much effect in increased formation of any the chemicals and their homologue pattern we determined (Table 1). We also conducted the 3 black test with the absence of flyash but with and without presence of paraffin at 100 and 1000 ppm HCl concentrations. The results provided very less pronounced increase of all the chemicals we determined except dichlorobenzenes which showed slightly greater levels and these trend clearly shows the external contamination (Table 1).

Table 2. Formation of PCBzs, PCPhs, PCDDs, PCDFs, PAHs and TEQ with varied concentrations of HCl and dioxin-free flyash as a catalyst with the presence of newspaper.

| Sample | Newspaper HCl ¹ concentration stream 10 ppm | Newspaper 50 ppm | Newspaper 100 ppm | Newspaper 500 ppm | Newspaper 1000 ppm |
|-------------------------------|--|---------------------|----------------------|----------------------|-----------------------|
| Chlorobenzene (Cl%/MW) | | | | | |
| MoCBZ (0.316/112.5) | 330 | 290 | 380 | 120 | 130 |
| DiCBZ (0.483/147) | 3600 | 7200 | 1900 | 4600 | 2600 |
| TriCBZ (0.587/181.5) | 2600 | 13000 | 11000 | 9800 | 4200 |
| TeCBZ (0.657/216) | 1300 | 9200 | 13000 | 10000 | 6500 |
| PeCBZ (0.705/250.5) | 470 | 4600 | 8100 | 8000 | 7500 |
| HxCBZ (0.747/285) | 140 | 1300 | 2400 | 2900 | 3800 |
| PCBzs | 8400 | 36000 | 37000 | 35000 | 25000 |
| Cl% | 55 | 60 | 64 | 63 | 65 |
| Chlorophenols (Cl%/MW) | | | | | |
| MoPCPhs (0.276/128.5) | 16000 | 5800 | 6500 | 9200 | 7400 |
| DiPCPhs (0.436/163) | 2200 | 4500 | 7400 | 10000 | 9400 |
| TriPCPhs (0.539/197.5) | 550 | 10000 | 18000 | 18000 | 35000 |
| TePCPhs (0.612/232) | 180 | 7500 | 10000 | 11000 | 7400 |
| PePCPhs (0.666/266.5) | 55 | 1700 | 2800 | 3500 | 4200 |
| PCPhs | 19000 | 30000 | 45000 | 52000 | 63000 |
| Cl% | 31 | 50 | 51 | 50 | 51 |
| PCDDs (Cl%/MW) | | | | | |
| TeCDDs (0.441/322) | 37 | 62 | 61 | 57 | 32 |
| PeCDDs (0.498/356.5) | 28 | 130 | 200 | 140 | 98 |
| HxCDDs (0.584/391) | 16 | 210 | 350 | 350 | 290 |
| HpCDDs (0.584/425.5) | 6.7 | 170 | 320 | 380 | 480 |
| OCDD (0.617/460) | 3.5 | 140 | 290 | 450 | 910 |
| PCDDs | 91 | 710 | 1200 | 1400 | 1800 |
| Cl% | 49 | 55 | 56 | 57 | 59 |
| PCDFs (Cl%/MW) | | | | | |
| TeCDFs (0.464/306) | 95 | 730 | 1100 | 800 | 490 |
| PeCDFs (0.521/340.5) | 35 | 530 | 840 | 730 | 510 |
| HxCDFs (0.568/375) | 11 | 310 | 530 | 510 | 460 |
| HpCDFs (0.607/409.5) | 2.8 | 170 | 320 | 390 | 470 |
| OCDF (0.640/444) | 0.34 | 53 | 130 | 210 | 420 |
| PCDFs | 140 | 1800 | 2900 | 2600 | 2400 |
| Cl% | 49 | 52 | 52 | 53 | 56 |
| Sum PCDD/DFs | 230 | 2500 | 4141 | 4100 | 4200 |
| TEQ | 2.6 | 36 | 57 | 51 | 44 |

¹hydrochloric acid; * indicates mg/g concentration levels.

PCBz, PCPhs, PCDDs, PCDFs, TEQ and PAHs respectively, polychloro benzene, polychlorophenols, polychlorinated dibenzo-*p*-dioxins, dibenzofurans, toxic equivalency and polycyclic aromatic hydrocarbons.

Isomer profiles of chlorinated compounds was found similar at all HCl concentration levels (results not shown). For example, dichlorophenols had no influence of HCl concentration dependent variations especially for the 23-, 24-, 25, 26-, 34- and 35-DCPhs. These results indicated that *ortho* and *para*-orient reaction in chlorophenol ring might be a possible explanation. On the whole, paraffin powder increased greater formation of all target chemicals rather than newspaper by 2 to 10 orders particularly PCBzs, PCPhs and PAHs.

Concentrations of PAHs were several hundred times greater than chlorinated chemicals. This may be due to the greater proportion of hydrocarbons in gas stream of the test apparatus rather than chlorinated compounds. Particularly, naphthalene, acenaphthalenes, phenanthrene concentrations was predominated, while, acenaphthene and dibenzo[a,h]anthrathene showed lower concentration levels (Table 3). Maximum increase of concentrations have been observed with the HCl concentrations of 10 to 50 ppm and then remained constant. Comparatively, paraffin powder produced 30-times greater concentrations of PAHs than newspaper (Table 3).

Based on the results it can be explained that chlorinated compounds formation was greatly influenced by the catalytic reaction of flyash. Furthermore, presence of hydrocarbons may lead to form chlorinated compounds at some extent. Therefore, flyash is responsible in the formation of analyzed chemicals rather than HCl source. Particularly the "active site control type reaction" in fly ash is a critical point for the formation of chlorinated compounds. For example, in the heating chamber, the

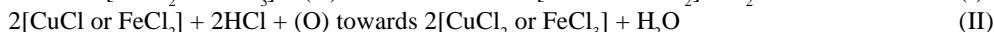
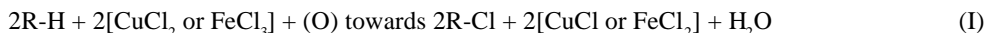
FORMATION AND SOURCES

Table 3. Concentrations of PAHs* during burning of paraffin powder/newspaper with HCl¹ and dioxin-free flyash as a catalyst.

| HCl ¹ concentration stream Fly ash Sample | 10 ppm Presence | | 50 ppm Presence | | 100 ppm Presence | | 500 ppm Presence | | 1000 ppm Presence | |
|--|--------------------|-----------|--------------------|-----------|---------------------|-----------|---------------------|-----------|----------------------|-----------|
| | Paraffin | Newspaper | Paraffin | Newspaper | Paraffin | Newspaper | Paraffin | Newspaper | Paraffin | Newspaper |
| Naphthalene | 9,000 | 550 | 11,000 | 910 | 8,400 | 960 | 8,000 | 940 | 13,000 | 770 |
| Acenaphthylene | 6,700 | 96 | 3,600 | 390 | 6,700 | 710 | 6,200 | 380 | 3,700 | 320 |
| Phenanthrene | 4,500 | 190 | 3,400 | 250 | 4,100 | 480 | 4,600 | 250 | 4,200 | 210 |
| Pyrene | 2,500 | 78 | 1,900 | 160 | 2,300 | 99 | 2,600 | 150 | 2,200 | 120 |
| 9H-Fluorene | 1,800 | 7 | 1,700 | 100 | 1,800 | 140 | 1,700 | 100 | 1,900 | 76 |
| Fluoranthene | 1,600 | 130 | 1,500 | 140 | 1,500 | 280 | 2,100 | 140 | 1,700 | 110 |
| Anthrathene | 1,400 | 15 | 1,100 | 61 | 1,500 | 130 | 1,600 | 44 | 1,400 | 36 |
| Benzo[a]pyrene | 1,100 | 15 | 580 | 31 | 1,100 | 67 | 1,300 | 15 | 670 | 3 |
| Benzo[a]anthrathene | 700 | 8 | 540 | 36 | 620 | 61 | 690 | 33 | 640 | 26 |
| Benzo[g,h,i]perylene | 520 | 22 | 320 | 24 | 440 | 50 | 550 | 23 | 390 | 14 |
| Indeno[1,2,3-cd]pyrene | 430 | 19 | 290 | 25 | 370 | 53 | 480 | 24 | 360 | 18 |
| Benzo[b]fluoranthene | 410 | 29 | 230 | 40 | 360 | 86 | 430 | 41 | 300 | 34 |
| Crysene | 350 | 21 | 240 | 38 | 320 | 75 | 350 | 38 | 320 | 32 |
| Acenaphthene | 230 | 2.8 | 170 | 5.8 | 220 | 11 | 240 | 5.5 | 230 | 3.8 |
| Benzo[k]fluoranthene | 240 | 6 | 150 | 16 | 220 | 30 | 260 | 15 | 210 | 12 |
| Dibenzo[a,h]anthrathene | 37 | 0.96 | 21 | 3.5 | 30 | 6.4 | 36 | 3.3 | 29 | 2.8 |
| Sum PAHs | 31,517 | 1,190 | 26,741 | 2,230 | 29,980 | 3,238 | 31,136 | 2,202 | 31,249 | 1,788 |

*Concentrations on ng/sample used;¹hydrochloric acid; The values rounded for two significant digit.

flyash was greatly attracted by hydrocarbons rather than HCl. The time of reaction by hydrocarbons might comparatively longer than chlorinated compounds. Consequently, heavier chlorinated compounds had less chance to contact with active reaction site in flyash. Basically in flyash active site, the Deacon type of reaction can be expected;



in which the continuous back reaction of both CuCl₂ and FeCl₃ play a chlorine source in experimental instrument. For instance, in case of absence of chlorine source (HCl), the Deacon reaction will be restricted thus, formation of chlorinated compounds expected to limited. Especially, 10-50 ppm HCl concentration was not so enough to expect any chlorinated compounds formation. It can be also explained that the stable nature of chlorinated compounds at greater HCl concentrations, the active site of flyash is limited for chlorine reaction therefore, formation. In addition, during benzene phenol chlorination reaction, the reaction speed highly reduced when higher chlorinated species formed. The observations of mono- through hexachlorobenzenes, suggested that the time factor of reaction in heating chamber. Because chlorine source may stay for few seconds and further mobilized to impinger. Therefore the time limitation for reaction in heating chamber may reduce any formation but homologue pattern had not much variation. Altogether, our results also co-incided to the organic electron theory and homolytic radical reaction.

References

1. Olie K., Vermeulen P.L. and Hutzinger O. (1977) *Chemosphere* 6, 455
2. Addink R. and Olie K. (1995) *Environ Sci Technol.*, 29, 1425
3. Altwicker E.R. (1996) *J Hazard Mater.*, 47, 137
4. Takasuga T., Makino T., Tsubota K. and Takeda N. (2000) *Chemosphere* 40, 1003