ANALYSIS OF PCDD/PCDF IN SOLID RESIDUE PRODUCED IN THE PYROLYSIS OF MIXED WASTE PLASTICS BY AN ADDITIONAL CLEAN-UP METHOD WITH DIMETHYL SULFOXIDE.

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Introduction

Pyrolysis process for recycling of mixed waste plastics under the various operating conditions has been carried out, and the technology is being settled in many countries according to what kinds of material is the product that they wants[1]. We have developed low temperature pyrolysis for mixed waste plastics to enhance oil production. This pyrolysis process produces solid residue that accounts 14-25% of feeding material, but, what is the most reliable method to dispose the solid residue is not yet known. Incineration bottom ash is classified as a general waste that can be landfilled; otherwise pyrolysis residue has not even been discussed whether it can be considered as a general waste or a hazardous waste, or how much it contains hazardous material. Besides, it has even been ignored simply because it is a waste left behind from a recycling of waste. The solid residue contained so much plastic degrades, that is, long chain hydrocarbons and wax type material, so that the clean up procedure for waste such as incineration ash described in the US EPA method 8290[2] was not feasible. In this study we developed a clean up procedure using dimethyl sulfoxide (DMSO) for the heavily contaminated sample by wax type material and analyzed PCDDs/PCDFs. The efficiency of this sole DMSO extraction method for 13C-labeled PCDDs/PCDFs compounds was 85.8% on the average.

Methods and Materials

Materials and Experiments

Pyrolysis residue sample was obtained from the mixed waste plastic pyrolysis plant for mainly oil production, grounded and sieved on 100/120 stainless mesh. Waste plastics consisted of different kinds of plastics including PE films used at the agriculture field and as grain bags, PP, PS and PVC.

Standard solution of labeled and unlabeled PCDDs/PCDFs was obtained from Cambridge Isotope Laboratories (CIL, Andover, Mass). Pyrolysis residue sample was extracted, concentrated, washed with sulfuric acid and water by the method described in the USEPA Method 8290, followed by two different cleaning up procedures including DMSO. The first method was as follows. Sulfuric acid washed sample was applied to multi-layer silica and alumina column and concentrated. Then the sample was reextracted with hexane after extraction with DMSO three times to remove precipitated material during concentration step, washed with water, concentrated and analyzed on GC/MS immediately after adding labeled standard. The second method was as follows. Sulfuric acid washed sample was applied to the extraction with DMSO and then applied to the multi-layer silica and alumina column, concentrated and analyzed on GC/MS after adding labeled standard.

For the estimation of the DMSO extraction procedure developed here, next experiment was carried out. Labeled standard mixture used for the estimation of extraction efficiency was spiked into 20 ml of normal hexane and extracted with 50 ml of DMSO three times. The DMSO extract was reextracted with 50 ml of hexane three times after adding 150 ml of water, washed 50 ml of water three times, concentrated after removing water and then analyzed.

Instruments

The mass spectrometer used was an Autospec Ultima (Micromass, UK) instrument equipped with a Carlo Erba Gas Chromatograph (GC8000) with a SP2331 capillary column (60m x 0.32mm x 0.2μm film thickness). Oven temperature was started at 120°C, held for 1 min, and programmed to 200°C with 10°C/min, hold for 2 min, then programmed to 260°C with 3°C/min and held for 20 min. Interface temperature was 270°C.

Results and Discussion

Extraction and clean-up procedure for the incineration ash described in many literature[2-3] was not adequate for solid residue sample produced from the mixed waste plastic pyrolysis process because of large amount of wax and long chain plastic degrade. This wax type material could not be removed in spite of washing with sulfuric acid nine times, so they were precipitated during concentration step after passing through a multi-layer silica and alumina column. Similar clean-up method with DMSO, that had been used for oily sample[4-5] was modified and employed to the eluant which had been passed through a multi-layer silica column. This additional extraction with DMSO made PCDDs/PCDFs analysis successfully done. The result of PCDDs/PCDFs analysis was shown in Table 1-2 and the efficiency of DMSO extraction procedure was shown in Table 3. Average recovery of 15 ^{13}C-labeled standards was 85.8% ranging from 70.6% to 98.5%. The

recovery of hepta- or octa-PCDD/PCDF compounds heavily substituted with chlorine by DMSO extraction procedure was lower than that of compounds less substituted with chlorine due to lower water solubility. The concentration of PCDDs/PCDFs in the plastic derived pyrolysis solid residue analyzed by the first and second method developed here was 0.172 ng-TEQ/g and 0.185 ng-TEQ/g, respectively. These amounts were within the limits for landfill, but the sample surely contained PCDDs/PCDFs.

Table 1. Recovery Efficiency of $^{13}C_{12}$-Internal Standards in the Solid Residue Sample

Dioxins	Labeled $^{13}C_{12}$-Internal Standards	Recovery Efficiency(%)	
		1st Method	2nd Method
PCDFs	$^{13}C_{12}$-2,3,7,8-TCDF	70.4	60.5
	$^{13}C_{12}$-1,2,3,7,8-PeCDF	48.4	54.3
	$^{13}C_{12}$-2,3,4,7,8-PeCDF	82.0	63.0
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	37.2	49.9
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	38.7	48.8
	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	76.6	37.5
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	65.1	54.1
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30.9	42.0
	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	46.7	40.7
PCDDs	$^{13}C_{12}$-2,3,7,8-TCDD	60.8	53.7
	$^{13}C_{12}$-1,2,3,7,8-PeCDD	51.6	53.3
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	51.9	52.4
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	56.8	53.5
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	62.4	54.7
	$^{13}C_{12}$-OCDD	61.7	51.4
Average recovery(%)		56.1	51.3

Table 2. Concentration of PCDDs/PCDFs in the Pyrolysis Residue

Dioxins		1st Method		2nd Method	
		Concentration		Concentration	
		pg/g	ng-TEQ/g	pg/g	ng-TEQ/g
PCDFs	2,3,7,8-TCDF	319.701	0.032	372.145	0.037
	1,2,3,7,8-PeCDF/2	175.406	0.009	176.814	0.009
	2,3,4,7,8-PeCDF	215.953	0.108	228.033	0.114
	1,2,3,4,7,8-HxCDF/2	54.488	0.005	50.075	0.005
	1,2,3,6,7,8-HxCDF	108.370	0.011	106.697	0.011
	2,3,4,6,7,8-HxCDF	54.709	0.005	45.620	0.005
	1,2,3,7,8,9-HxCDF	12.072	0.001	10.917	0.001
	1,2,3,4,6,7,8-HpCDF	78.374	0.001	73.775	0.001
	1,2,3,4,7,8,9-HpCDF	16.416	0.000	16.273	0.000
	OCDF	0.000	0.000	0.000	0.000
Total PCDFs		1,035.489	0.172	1,080.348	0.183
PCDDs	2,3,7,8-TCDD	0.000	0.000	2.250	0.002
	1,2,3,7,8-PeCDD	0.000	0.000	0.000	0.000
	1,2,3,4,7,8-HxCDD	0.000	0.000	0.000	0.000
	1,2,3,6,7,8-HxCDD	0.000	0.000	0.000	0.000
	1,2,3,7,8,9-HxCDD	0.000	0.000	0.000	0.000
	1,2,3,4,6,7,8-HpCDD	12.639	0.000	23.386	0.000
	OCDD	34.773	0.000	80.318	0.000
Total PCDDs		47.412	0.000	105.953	0.002
Total (PCDFs+PCDDs)		1,082.901	0.172	1,186.302	0.185

Table 3. DMSO Extraction Efficiency for $^{13}C_{12}$-Labeled Internal Standards

Dioxins	Labeled $^{13}C_{12}$-Internal Standards	Recovery Efficiency(%)
PCDFs	$^{13}C_{12}$-2,3,7,8-TCDF	93.1
	$^{13}C_{12}$-1,2,3,7,8-PeCDF	93.7
	$^{13}C_{12}$-2,3,4,7,8-PeCDF	98.5
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	80.0
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	79.9
	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	83.7
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	78.4
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	70.6
	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	70.8
PCDDs	$^{13}C_{12}$-2,3,7,8-TCDD	93.1
	$^{13}C_{12}$-1,2,3,7,8-PeCDD	92.2
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	90.6
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	88.2
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	91.0
	$^{13}C_{12}$-OCDD	83.2
Average recovery(%)		85.8

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