REACTION CHARACTERISTICS OF PCBs DECHLORINATION UTILIZING SDMA AND ORGANO METALLIC CATALYSTS

Dong J-I*[1], Yeo S-G[1], Park P-M[1], Lee W-C[1], Seo S-S[1]

[1] 163 Seoulsiripdae-ro, Dongdaemun-gu, Seoul, Korea, Department of Environment Engineering, University of Seoul, Korea

Introduction

The Stockholm Convention is a global treaty to protect human health and the environment from persistent organic pollutants(POPs). The convention was adopted in May 2001 and entered into force in May 2004. Polychlorinated biphenyls(PCBs), One of the most important compounds of POPs, should be managed in an environmentally sound manner and every country should take actions to remove PCBs found above certain thresholds by the year 2025[1)]. In Korea, appropriate and adequate destruction facilities are limited, and the costs associated with proper treatment are very expensive. As a result, all of high-level PCBs containing equipments and waste had to be shipped to developed countries for destruction mostly by high temperature incineration. At present, the PCBs containing equipments and waste have been recovered and stored without any detoxifying treatments because feasible techniques for disposing PCBs have not been established. There exist two technologies(thermal treatment and chemical treatment) to destroy PCBs. In Korea, Chemical treatment is more favored than incineration or high-temperature pyrolysis because of possible secondary environmental impacts. Lots of investigations have been carried out on chemical decomposition. [2)]

This objectives of this study were: (1) to determinate the optimal operation condition and major variables of PCBs dechlorination by applying different SDMA and catalyst loads, various catalysts, hydrogen donors and temperatures; (2) to understand the dechlorination mechanism of PCBs thorugh more reliable decomposition characteristic data by analyzing 209 PCB isomers.

Materials and methods

The dechlorination reaction experiments were performed under a nitrogen atmosphere in the presence of a standard solution of Arochor 1242, 1254(50mg, neat), SDMA, cobalt and nickel catalyst($Co(C_5H_7O_2)_2$, $Ni(C_5H_7O_2)_2$) in toluene with a total volume of 30 ml.

PCBs were analyzed by GC-Electron Capture Detector(ECD) on a CP-Sil Capillary column (50 x 0.25mm x 0.12um, Varian 3400X Ltd). For the analytical conditions, injector temperature was 270℃ at 1℃ min^{-1} and increasing to 300℃, at 3℃ min^{-1} held for 5min. The carrier gas was nitrogen at 20psi.

In a typical experiment, a reaction vessel kept under nitrogen was charged with the known amount of Aroclor 1248 and then toluene and the known volume of catalyst solutions were subsequently added. The magnetically stirred reaction mixture was then heated to the reaction temperature at which SDMA solution was added. The samples withdrawn at a fixed time interval were injected in the vessel and then the internal reference(PCBs-209) was added and the samples were treated with aqueous sulfuric acid. The solution was applied to silica-gel treatment and concentrated and then the sample was analyzed as described above. Details of reaction conditions are shown in Table 1.

*Corresponding author: Jong-In Dong, The University of Seoul, Korea (E-mail: jidong@uos.ac.kr)

Table 1 Experimental conditions of Aroclor 1242 and 1254 PCBs decomposition

Test No.	SDMA[Na:Cl]	Catalyst		Temp.(℃)	Reaction time(min)	Hydrogen donor
		Type	**[Catalyst:Cl]**			
42A	**50:1**	x	x	**90**	**0~60**	x
42B	**50:1**	**Cobalt**	**0.1:1**	〃	〃	x
42C	**50:1**	**Nickel**	**0.1:1**	〃	〃	x
42D	**50:1**	**Cobalt**	**0.1:1**	〃	〃	**Mineral oil**
54A	**50:1**	x	x	〃	〃	x
54B	**50:1**	**Cobalt**	**0.1:1**	〃	〃	x
54C	**50:1**	**Nickel**	**0.1:1**	〃	〃	x
54D	**50:1**	**Cobalt**	**0.1:1**	〃	〃	**Mineral oil**

Results and discussion

Experimental results of Aroclor 1242 and 1254 PCBs decomposition with the consideration of all are variables shown Fig1~Fig4.

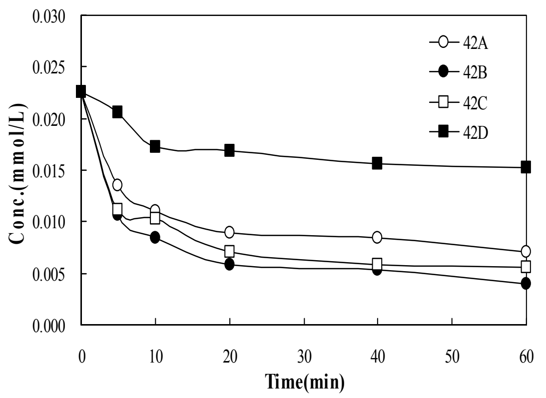

Fig 1. Experimental results of Aroclor 1242 decomposition PCBs

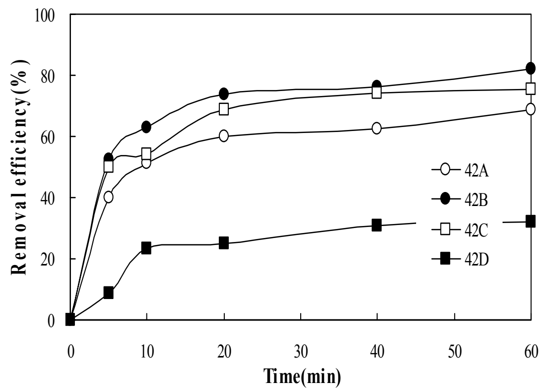

Fig 2 . Removal efficiency of Aroclor 1242 PCBs

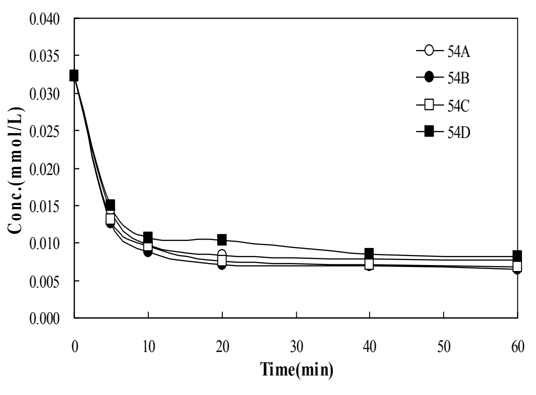

Fig 3. Experimental results of Aroclor 1254 decomposition PCBs

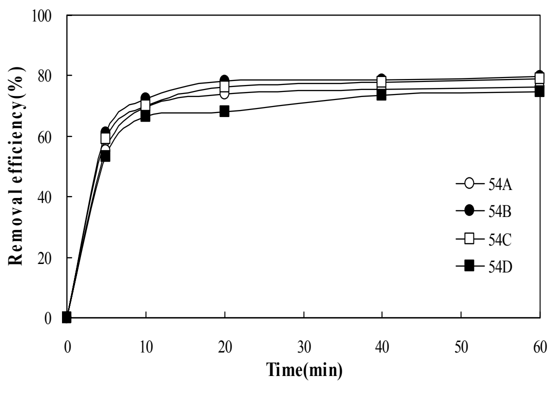

Fig 4 . Removal efficiency of Aroclor 1254 PCBs

Decomposition Characteristics by catalyst and SDMA injection is shown table 2~table 3.

Table 2 Experimental condition and results of Aroclor 1254PCBs decomposition with different SDMA loads

Text No.	SDMA		Temp(℃)	RXN Time (min)
	Molar ratio [Na: Cl]	Loading (mL)		
S 1	**5:1**	**0.057**	**110**	**5**
S 2	**50:1**	**0.571**	〃	〃
S 3	**100:1**	**1.142**	〃	〃

Total Concentration (mmol/L) [Decomposition Efficiency(%)]			TEQ Concentration(mmol-TEQ/L) [Decomposition Efficiency(%)]		
S 1	S 2	S 3	S 1	S 2	S 3
0.94 [11.2]	**0.28 [73.3]**	**0.23 [78.3]**	**15.09 x 10^{-6} [95.5]**	**4.07 x 10^{-6} [98.8]**	**1.14 x 10^{-6} [99.7]**

Table 3 Experimental conditions and results of Aroclor 1254PCBs decomposition with different catalyst loads

Text No.	Catalyst [Co(acac)2 : Cl]	SDMA [Na : Cl]	Temp(℃)	RXN Time (min)
C 1	**0.05 : 1**	**50: 1**	**110**	**5**
C 2	**0.1 : 1**	〃	〃	〃
C 3	**0.5: 1**	〃	〃	〃

Total Concentration (mmol/L) [Decomposition Efficiency(%)]			TEQ Concentration(mmol-TEQ/L) [Decomposition Efficiency(%)]		
C 1	**C 2**	**C 3**	**C 1**	**C 2**	**C 3**
0.012 [97.7]	**0.010 [98.0]**	**0.007 [98.5]**	**0.03 x 10^{-6} [99.9]**	**0.15 x 10^{-6} [99.9]**	**2.48 x 10^{-6} [98.4]**

Conclusions

Chmical destruction method using SDMA and organo metallic catalysts is suitable for fast, safe and complete dechlorination of PCBs. As a result of experiments, The optimal operation temperature was selected 110℃ with the use of SDMA in a certain mole ratio ($n_{NA}:n_{Cl}$ = 50:1) and with $Co(acac)_2$ with less than the stoichiometric amount of Cl($n_{Co(acac)^2}:n_{Cl}$=0.1:1).

The target compounds showed different results in decomposition efficiency by adding catalyst and mineral oil. Decomposition efficiency of Aroclor 1254 PCBs was higher whereas those of Aroclor 1242 was lower. The PCBs decompositions were affected strongly by the nature of the homolog distribution. With mineral oil, decomposition efficiencies of Aroclor 1242 PCBs was dramatically lower than those without mineral oil but showed no substantial changes of decomposition efficiency in Aroclor 1254 PCBs. The influence of catalysts was the most effective in Aroclor 1242 PCBs.

The dechlorination method reported in the present styudy may be considered a useful alternative of chemical treatment alternative of PCBs in Korea..

Acknowlegement

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