

Destruction of PCBs by Reaction with Potassium tert-Butoxide

Masayuki Ohno, Hisashi Kaneda

Kansai Tech Corporation, 3-1-176, Fukuzaki, Minato-Ku, Osaka 552, Japan

Kiyoshi Hirata

Kansai Electric Power Co., Inc, 3-11-20, Nakoji, Amagasaki 661, Japan

Abstract

PCB in insulating oil was dechlorinated by reactions with potassium tert-butoxide (t-BuOK) in a bench scale plant with a 150l/hr continuous treating capacity. The PCB of 120ppm in oil was reduced to ca. 0.02 ppm in a reactant time of only 6 minutes. In addition, PCDFs and PCDDs as by-products present in the PCB preparation were also completely decomposed. The advantages are (1)quick reaction (2)no solvent except for insulating oil (3)continuous reaction and (4)closed system.

1. Introduction

Various reports¹⁻³⁾ have been published on processes for a dechlorination of polychlorinated biphenyls (PCBs), which are typical environmental pollution substances. Several practical treatments have been made in the US and Europe. In 1985, the combustion of PCB was only permitted by Japanese Government. After that, however, the treatment have been prohibited, because of the fears that the environmental pollution by PCBs, PCDDs, PCDFs etc. through the combustion might occur. Hence, a bulk of insulating oil contaminated with PCBs at a level of tens to hundreds ppm has been kept stored as such without any treatments. Under such circumstances, the authors developed a very convenient process called "t-BuOK process" for dechlorination of PCBs in the insulating oil.

2. Outline of t-BuOK Process

Figure 1 is a schematic diagram of t-BuOK process. PCB in insulating oil is allowed to react with t-BuOK at 200~250°C; consequently, the chlorine in PCB is eliminated as KCl and the organic compound free of chlorine is produced.

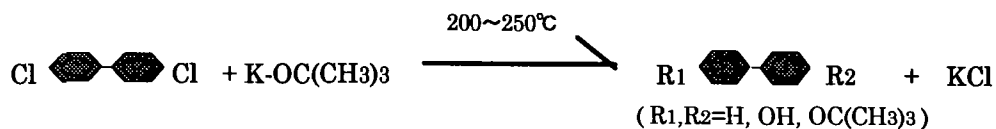


Fig.1 Schematic diagram of t-BuOK process

Dioxin '97, Indianapolis, Indiana, USA

3. Experimental

(1) Apparatus

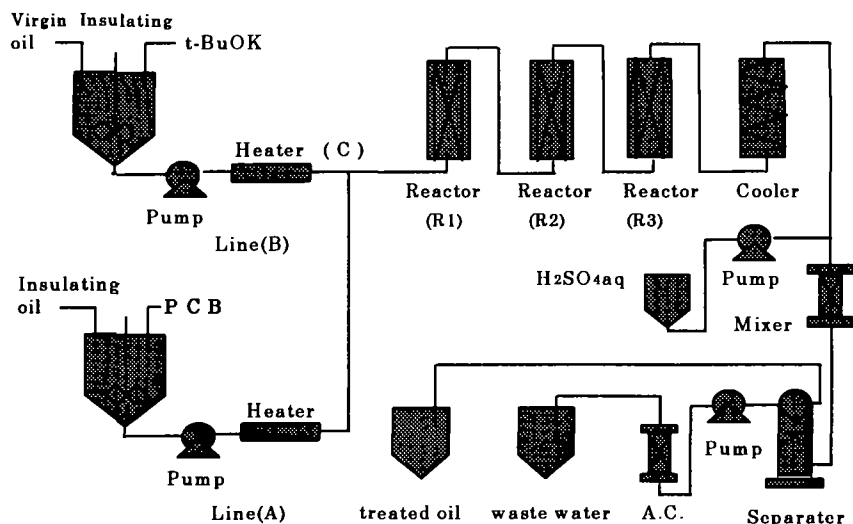


Fig.2 Outline of bench scale plant

The insulating oil mixing with PCB is fed through Line(A), and t-BuOK dissolved in virgin insulating oil with no PCBs is fed through Line(B). Both oils are preliminarily heated respectively up to near the reaction temperature, and mixed at Point C just before Reactor(R1). The mixed oil is allowed to pass through the reactors (R1~R3) and the decomposition reaction takes place therein. The oil from Reactor R3 is cooled to ca. 80°C in a cooler, and thereafter washed with dilute aqueous sulfuric acid by mixing and agitating. The separated aqueous phase together with the unreacted t-BuOK and KCl is allowed to pass through a layer of activated carbon filter.

(2) Material

PCBs were taken out of a used capacitor. The purity was 86%(w/w) with tri- and tetra-chlorinated congeners as majors (Table1). Insulating oil was obtained from a used transformer. The oil was contaminated with PCBs at a level of 11,000 ng/g (Table 2). T-BuOK was purchased from Callery Chemical company.

Table 1 Concentration of PCBs in capacitor oil

	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total
Content (wt%)	0.02	7.5	50.0	26.0	2.0	0.25	0.04	0	0	0	86.0
Ratio (%)	0.02	8.7	58.1	30.2	2.3	0.29	0.05	0	0	0	99.7

Table 2 Concentration of PCBs in insulating oil

	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total
Content (ng/g)	210	490	1,800	2,600	3,100	2,300	850	54	2	ND	11,000
Ratio (%)	1.8	4.3	15.8	22.8	27.2	20.2	7.5	0.5	0.01	0	100.1

(3) Test conditions

Oil containing PCBs with 3,500~120,000 ppb (see Table 3) were prepared by blending insulating oil and PCBs in a tank illustrated in Fig.1. The detailed test conditions were described in Table 3.

(4) Analytical procedure

According to modified methods reported by Larsen et al⁹ and Lu et al⁹, PCBs, PCDFs and PCDDs in samples of initial oil, treated oil, waste water and spent activated carbon were cleaned up and then determined in an EI-SIM mode using gas chromatograph-mass spectrometer (Shimadzu/Kratos Concept, R=10,000).

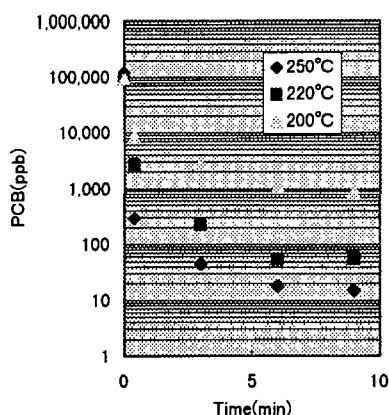
4. Results and discussion

(1) PCBs

Table 3 and Figure 3 show the concentration of PCB in the oil versus the reaction time for respective test conditions.

Table 3 Concentration of PCBs before and after reaction

Entry No.	Reaction condition				Reaction time and remaining PCBs			
	Init. PCB (ppb)	React. temp (°C)	t-BuOK (%)	treating rate (l/hr)	0.4 min (ppb)	3 min (ppb)	6 min (ppb)	9 min (ppb)
1	3,500	250	1.5	75	23	6	6	6
2	17,000	250	1.5	75	58	52	14	16
3	120,000	250	1.5	75	290	45	18	15
4	94,000	220	1.5	75	2,700	220	53	57
5	94,000	200	1.5	75	8,900	2,700	1,100	880



When the oil samples containing PCB of less than 120,000 ppb were treated for 0.4 min at 250°C, the remaining concentration were in a range of less than 290 ppb (Table 3). At lower reaction temperatures, such as 200 °C and 220 °C, the decomposition reaction became slower. When the reaction temperature was 200 °C, 9 mins. was necessary for reducing the initial PCBs concentration of 94 ppm to the level of less than 1 ppm. However, it is obvious that this process can more quickly decompose PCBs than other known chemical reactions¹⁻³.

Fig.3 Effects of reaction temperature on reaction rate

Dioxin '97, Indianapolis, Indiana, USA

(2) Coplanar PCBs, PCDDs and PCDFs

In tests of Entry Nos. 3 and 5, toxic coplanar PCBs were analyzed (Table 4). Consequently, it was revealed that all coplanar PCBs were dechlorinated to less than a detection limit of 1 ppb by our reaction. On the other hand, the generation and dechlorination of PCDDs/PCDFs were also examined in tests of Entry Nos. 2 and 3 (Table 5). As well as in case of coplanar PCBs, no PCDDs/PCDFs were detected at a detection limit of less than 0.5 ppb.

Table 4 Contents of coplanar PCBs in oil

Coplanar PCBs	Entry No.3		Entry No.5	
	Before (ppb)	After (ppb)	Before (ppb)	After (ppb)
T4CB# 77	300	ND	330	ND
P5CB#123	12	ND	21	ND
P5CB#118	270	ND	450	ND
P5CB#114	20	ND	24	ND
P5CB#105	200	ND	280	ND
P5CB#126	ND	ND	6	ND
P6CB#167	3	ND	10	ND
P6CB#156	9	ND	15	ND
P6CB#157	2	ND	5	ND
P6CB#169	ND	ND	1	ND
P7CB#180	ND	ND	ND	ND
P7CB#170	ND	ND	ND	ND
P7CB#189	1	ND	3	ND

Table 5 Contents of PCDDs,PCDFs in oil

PCDDs PCDFs	Entry No.2		Entry No.3	
	Before (ppb)	After (ppb)	Before (ppb)	After (ppb)
(1-8)CDD	ND	ND	ND	ND
M1CDF	4	ND	1.3	ND
D2CDF	ND	ND	1.6	ND
T3CDF	0.8	ND	ND	ND
(4-8)CDF	ND	ND	ND	ND

In the test of Entry Nos. 2 and 3, no PCBs, PCDDs and PCDFs were confirmed to be present in the waste water and spent activated carbon after the reaction (Table 6). This indicates our reaction is very safe for the environmental pollution. In the same tests, physical properties of oil were also determined (Table 7). As shown in this table, all values of density, kinetic viscosity and flash point were unchanged by the reaction. This indicates a possibility that the treated oil can reuse as an insulating oil.

Table 6 Contents of PCB, PCDD, PCDF in the waste water and spent A.C.

	Entry No.2		Entry No. 3	
	Water	A.C.	Water	A.C.
PCB	ND	ND	ND	ND
PCDD	ND	ND	ND	ND
PCDF	ND	ND	ND	ND

Table 7 Physical properties of oil

	before test	after test	
		Entry No.2	Entry No.3
ρ (15°C) (g/cm ³)	0.8896	0.8836	0.8862
ν (40°C)	8.326	8.374	8.458
fp (°C)	140	150	150

ρ :Density ν :Kinetic Viscosity

fp:Flash Point (The oil was sampled by eliminating the initial 5% and bottom 5%)

5. Conclusions

Decomposition tests for PCB by reactions with potassium tert-butoxide were performed in a bench scale plant with a 150 l/hr continuous treating capacity. The conclusions were as follows;

- (1) 120 ppm of PCBs in insulating oil were decomposed to less than 20 ppb during a short time of 6 minutes.
- (2) Toxic Coplanar PCBs were completely dechlorinated to an undetectable level after the reaction.
- (3) Dioxin and dibenzofuran were not formed but also decomposed.
- (4) Waste water and spent activated carbon contained no PCBs, PCDDs and PCDFs.
- (5) The physical characters of oil were unchanged by the treatment.

6. References

- 1) Fumio, Tanimoto; Kiyohiko, Tsukumoto; Tsuno, Yano, *Organohalogen Compounds*, 1994, 19, 509-516.
- 2) Alfred, Kornel; Charles Rogers, *J. Hazardous Materials*, 1985, 12, 161-176.
- 3) W. J. Janis; J. S. Ferrie; J. M. Braun, *IEEE Transaction on Power Apparatus and Systems*, 1983 Vol. PAS-102, No.12, December, 3928-3932.
- 4) B. Larsen; R. Tilio; S. Kapila, *Organohalogen Compounds*, 1990, 2, 181-182.
- 5) J.-R. Lu; H. Miyata; C.-W. Huang; H.-T. Tsai; V.-Z. Sheng; T. Nakao; Y. Mase; O. Aozasa; S. Ohta, *Chemosphere*, 1995, 31, No.3, 2959-2970.