Complete Destruction of PCB by Using A Catalytic Hydrogenation-Dechlorination Reaction and t-BuOK Method in A Bench Scale Plant

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Abstract

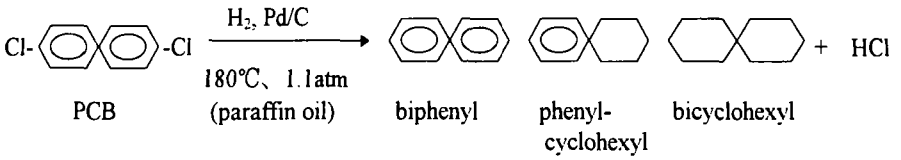
The catalytic hydrodechlorination (C.H.D.) of PCBs was studied in a bench scale plant using a 5%Pd/C catalyst. The plant consists of a closed and hydrogen-circulating system. Paraffin oil was used as a solvent. 2Kg of PCBs in 18kg of paraffin oil was converted to non-chlorinated hydrocarbons (conversion rate : above 99.9%) for 5 hours at 180℃ under 1.1 atm of H_2. Complete destruction(>99.9999%) of the remaining PCB in the solution after C.H.D. was accomplished by using the reaction with potassium tert-butoxide(t-BuOK) at 250℃ in the other flow reaction system. The advantages of our combined decomposition system are (1) almost complete dechlorination of high concentration of PCB such as a 10% solution, (2) closed system, (3) no product of hazardous chemicals such as PCDD and PCDF, and (4) easy recovery of solvent, catalyst and products.

1. Introduction

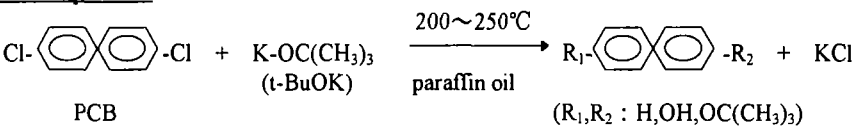
PCB has long been used as dielectric fluids in transformers and capacitors. In 1972, however, it was prohibited to manufacture and to use in Japan because of its toxicity and high accumulation for organisms. Japanese government permitted only once incineration disposal treatment of used PCBs, in which about 5,000kg of used PCBs was incinerated during a period of 1985 to 1986 in Hyogo prefecture. After that, however, such incineration has not been done, because of the fears that incineration of PCBs might cause the environmental pollution by PCBs, PCDDs, PCDFs etc. From these reasons, many techniques for destroying PCBs have been investigated, for examples, supercritical water oxidation[1], plasma-fired destruction[2] and ultraviolet-ray dechlorination[3] etc. In actually, one of the important points in treating PCB is that the reaction or the treatment does not cause the environmental pollution, therefore, it should be carried in a closed system. Another important point is that a large volume of PCBs can be treated with the system. In view of these reasons, we studied a catalytic hydrodechlorination (C.H.D.) of PCBs using a closed bench scale plant system. To achieve the complete dechlorination in a shorter time, "t-BuOK reaction" was adapted after C.H.D.. "t-BuOK reaction" was previously developed[5] by us as a destruction method for a low concentration PCB in the oil using a potassium tert-Butoxide. In this study, we confirmed that PCB can be completely dechlorinated by using C.H.D. followed by t-BuOK reaction.

2. Outline of C.H.D. and t-BuOK process

C.H.D.



t-BuOK process



3. Experimental

(a) Apparatus

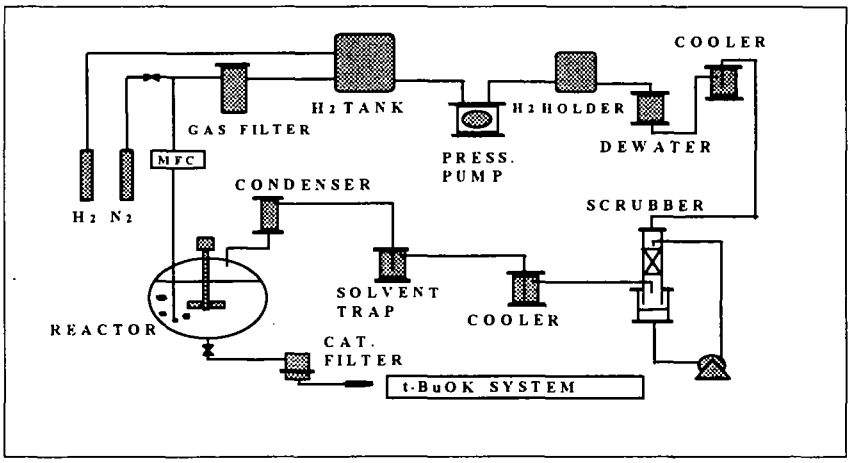


Fig.1 Outline of Test plant for C.H.D.

(b) Procedure of the test

2kg of PCBs taken out from a used condenser and 18kg of paraffin oil were poured into the reactor and 100g of Pd/C catalyst was dispersed into the solution. Air evacuation was primarily done to remove oxygen, and hydrogen was introduced into the plant finally at the pressure of 1.1 atm. Hydrogen gas circulated in the plant at a rate of 20 little/min through a mass flow controller (MFC), with bubbling the solution in the reactor. Hydrogen was consumed with the proceeding of the reaction. To keep the constant hydrogen pressure of 1.1atm during the reaction period, a fresh hydrogen was introduced into the H_2 tank from hydrogen cylinder. The solution was heated with stirring at 800rpm and the temperature was kept constant at 180℃. HCl gas produced by the reaction was carried with the hydrogen stream and was absorbed into the NaOH solution at the scrubber. After C.H.D reaction, the solution separated from catalyst was treated with t-BuOK to accomplish the complete dechlorination. t-BuOK reaction was proceeded with a flow reaction

system. The schematic flow diagram is shown in figure 2. Reaction conditions are as follows : reaction temperature:250℃, flow rate of oil: 20l/hr, t-BuOK:1.5%,

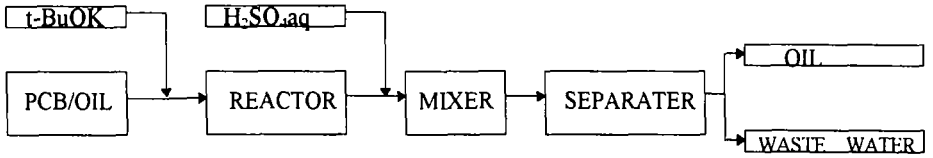


Fig.2 t-BuOK process for treatment of oil contaminated PCB

(c) PCBs and reagent

The content of PCBs used in the test is shown in Table 1. 5%Pd/C was purchased from Degussa Japan Co., Paraffin oil (Whiterex-205) was obtained from Mobil (Osaka, Japan). t-BuOK was purchased from Callery Chemical Company(Pittsburgh,US). Each was used without any treatment.

Table1 Content of PCBs

	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total
content (g/kg)	0.37	130	470	270	24	7.3	1.5	0.14	0.02	0	900
portion (%)	0.03	14.4	51.9	30.0	2.7	0.8	0.16	0.01	0	0	100.0

(d) Analytical procedure

According to modified methods reported by Larsen et al[5] and Lu et al[6], PCBs ,PCDFs and PCDDs in the original oil and treated oil were cleaned up and then determined in an EI-SIM mode using gas chromatography-mass spectrometer (VG Autospec Ultima R=10,000).

4. Results and discussion

(a) PCB destruction

Table 2 shows the concentration of PCBs and destruction efficiency after the C.H.D.. 10% PCB was reduced to 15 ppm after 5 hrs, and the destruction efficiency was 99.983%. Weight of chlorine caught in the scrubber was 696g, 744g and 759g in the test Nos. 1-1 to 3-1, respectively. The initial weight of chlorine was calculated as 774g (2kg × 90% × 43%). Therefore, the percentages of dechlorination were 89.9%, 96.1% and 98.1%. Biphenyl and phenyl-cyclohexyl produced in C.H.D. were 375g and 658g, respectively, and bicyclohexyl was not detected in the test No.3-1. From this result, the total mol amount of the products was 6.57mols, while, original PCB was 6.86mols on the basis

Table 2 Destruction of PCBs by C.H.D

Test No	React. time (hr)	PCB conc. (ppm)	Destruct. efficiency (%)
1-1	3	5,500	93.889
2-1	4	550	99.389
3-1	5	15	99.983

init.PCB:90,000ppm, react. temp:180℃, paraffin oil:18kg, PCB:2kg(90%conc.), Pd/C:100g, H2:20l/min

of the content of each congener group shown in Table 1. Therefore, 96% of productions was quantitatively identified. Table 3 shows the PCBs concentration after t-BuOK reaction. Initial PCBs in Table 3 correspond to them after C.H.D shown in Table 2.

Table 3 Destruction PCBs by the t-BuOK reaction

No	Init PCB Conc. (ppm)	PCB after t-BuOK React. (ppb) Reaction time (min)			Destruct.effici. by t-BuOK at 15min. (%)	Total Destruct.effici. by C.H.D. and t-BuOK (%)
		5	10	15		
1-2	5,500	24,000	5,100	900	99.997	99.99900
2-2	550	4,300	280	210	99.962	99.99976
3-2	15	85	49	36	99.760	99.99996

t-BuOK reaction condition: React. temp.=250℃, t-BuOK=1.5wt%

PCBs were decreased quickly by t-BuOK reaction, for example,15ppm of PCB after C.H.D reaction (No.3-2) was reduced to 36ppb in 15 mins. Consequently, it was revealed that 90,000ppm(9%) of PCBs was reduced to 36ppb (0.036ppm) by 5 hrs. of C.H.D. and 15 mins. of t-BuOK reactions, showing the destruction efficiency to be 99.99996%.

(b) Co-PCBs

Recently, Co-planer PCBs are getting much attention of their high toxicity caused from its plane structure. Concentrations of 13 Co-PCB in the initial solution, after C.H.D reaction (No.3-1) and after t-BuOK reaction (No.3-2) are listed in Table 4.

Table 4 Concentration of Co-PCB congeners (μ g/kg)

congener	Initial	after C.H.D	after t-BuOK
33'44'------T4CB	370,000	13	ND
33'44'5-----P5CB	ND	ND	ND
33'44'55'--H6CB	ND	ND	ND
2'344'5-----P5CB	7,500	ND	ND
23'44'5-----P5CB	290,000	20	ND
2344'5------P5CB	13,000	ND	ND
233'44'-----P5CB	160,000	14	ND
2344'55'---H6CB	11,000	ND	ND
233'44'5---H6CB	6,900	ND	ND
233'44'55'-H7CB	1,700	ND	ND
22'344'55'-H7CB	42,000	3.0	ND
22'33'44'5-H7CB	31,000	2.1	ND
total Co-PCB	960,000	54	ND
μ g-TEQ/kg	260	0.011	ND

ND<0.5 μ g/kg

The total concentration of Co-PCBs present in PCB taken out from the used condenser was about 1%. The concentration of Co-PCBs was reduced to 54 μ g /kg (54ppm) after 5 hrs. of C.H.D. reaction, indicating the destruction rate to be 99.994%. After subsequent t-BuOK reaction of 10 mins., Co-PCBs were completely destructed.

(c) PCDDs and PCDFs

Concentrations of PCDDs and PCDFs in the initial solution, after C.H.D reaction (No.3-1) and after t-BuOK reaction (No.3-2,10minutes) are listed in Table 5.

PCDDs and PCDFs are present in the PCB as by-product. (PCDDs+PCDFs) was reduced from 200ng/g in the initial to 0.63ng/g after C.H.D. reaction, and they were seemed to be slightly increased after t-BuOK reaction (however, TEQ was decreased to less than a detection limit.).

Table 5 Concentration of PCDDs and PCDFs

PCDDs/PCDFs	Init. (ng/g)	After C.H.D (ng/g)	After t-BuOK (ng/g)
T4CDDs	0.11	ND<0.5	0.31
P5CDDs	0.08	ND<0.5	0.54
H6CDDs	0.14	ND<0.5	0.49
H7CDDs	ND	ND<0.5	ND<0.2
O8CDD	0.03	0.41	ND<0.2
PCDDs	0.36	0.41	1.3
T4CDFs	93	ND	1.7
P5CDFs	28	ND	0.24
H6CDFs	11	ND	0.51
H7CDFs	5.2	ND	ND
H8CDF	0.84	0.22	ND
PCDFs	200	0.22	2.5
PCDDs+PCDFs	200	0.63	3.8
ng-TEQ/g	5.2	0.00063	<0.0002

5. Conclusion

Decomposition tests for PCBs by C.H.D. were performed in a bench scale plant consisted of a closed and hydrogen circulate system, followed by t-BuOK reaction for reducing PCB completely. The conclusions were as follows:

(1)9% (90,000ppm) of PCBs in paraffin oil was decomposed to less than 15ppm for 5 hrs. by C.H.D., and then the remaining PCBs (15ppm) was reduced to 0.036ppm (36ppb) within 15 mins. by t-BuOK reaction.

(2)Highly toxic Co-PCB congeners were also dechlorinated from 960ppm of the initial to less than a detection limit of 0.0005ppm (0.5ppb).

(3)PCDDs + PCDFs were also decreased from 5.2 ng-TEQ/g of the initial to less than a detection limit of 0.0002 ng-TEQ/g.

(4)Almost all of chlorine bound with PCB was released and converted into inorganic chlorine (HCl). In addition, PCBs were almost completely dechlorinated and converted into biphenyl and phenylcyclohexyl.

6. References

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