

Destruction and Removal of PCBs in Waste Transformer Oil by a Chemical Dechlorination Process

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A practical and efficient disposal of PCBs (polychlorinated biphenyls) in waste transformer oil by a chemical dechlorination process has been reported. The transformer oil containing commercial PCB mixtures (Aroclor 1242, 1254 and 1260) was treated by the required amounts of PEG 600 (polyethylene glycol 600), potassium hydroxide (KOH) and aluminum (Al), along with different reaction temperatures and times. The reaction of PEG with PCBs under basic condition produces arylpolyglycols, the products of nucleophilic aromatic substitution. The relative efficiencies of PCB treatment process were assessed in terms of destruction and removal efficiency (DRE, %). Under the experimental conditions of PEG600/KOH/Al/100 °C/2hr, average DRE of PCBs was approximately 78%, showing completely removal of PCBs containing 7-9 chlorines on two rings of biphenyl which appear later than PCB no. 183 (2,2',3,4,4',5',6-heptaCB) in retention time of GC/ECD. However, when increasing the reaction temperature and time to 150 °C and 240 min, average DRE of PCBs including the most toxic PCBs (PCB no. 77, 105, 118, 123 and 169) in PCB family reached 99.99% or better, with the exception of PCB no. 5 and 8 (2,3-diCB and 2,4'-diCB). In studying the reaction of PEG with PCBs, it confirmed that the process led to less chlorinated PCBs through a stepwise process with the successive elimination of chlorines. The process also permits complete recovery of treated transformer oil through simple segregating procedures.

Key Words : PCBs, Chemical dechlorination process, Transformer oil, Aroclor, Polyethylene glycol

Introduction

PCBs are structurally defined by chlorine substitution of one to ten on the two rings of biphenyl. These chemicals were considered commercially valuable and produced in large quantities for the period 1929 to 1976. The total worldwide production through 1976 has been estimated to be 6.1×10^8 kg, of which about 93% were produced by Monsanto corporation in the United States.¹ Commercial PCB mixtures by Monsanto corporation were marketed under the registered trade-mark of Aroclor and used in a wide variety of applications, including dielectric fluids in transformers and capacitors, heat transfer fluids, plasticizers, lubricant inks, paint additives, and adhesives.²⁻⁵ However, their physicochemical properties related with the resistance to breakdown by acids, bases, heat, and hydrolysis have led these chemicals to ubiquitous environmental pollutants. Not surprisingly, they have been identified in almost every compartment of the global ecosystem.⁶⁻⁹

A PCB-containing product class used in transformers is askarel. The most common transformer askarel was mainly consisted of 60% Aroclor 1260/40% trichlorobenzene (type A) and 70% Aroclor 1254/30% trichlorobenzene (type B).⁹ It was reported that approximately 300,000 waste transformers have been discharged in Korea since 2000. In addition, a large number of transformers with the cross-contamination of mineral oil with PCBs still remain in operation. As a

party to an agreement of Stockholm on May 17, 2005 by the United Nations Environment Program (UNEP), the Korean government recently passed the Act of the Waste Management, which specifically regulates the PCB-contaminated materials. The regulation prohibited manufacture, processing, commercial distribution or use of PCBs in open system and promulgated that such waste transformers with PCB concentrations exceeding the regulatory limit set (2 ppm) must be disposed of properly.

Disposal of PCBs has been so far addressed through various approaches. The most conventional approach is high temperature controlled incineration.^{10,11} The incineration technology is quite effective for destruction of PCBs. However, it is hampered by the disposal costs and the exclusion of reusable materials, as well as by highly toxic by-products such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Another approaches involve pyrolysis, chemical methods (adsorption, catalytic hydrodechlorination, ozonation, ultrasonic, photolytic, wet air oxidation, reaction with a sodium salt in amine solvent, and etc.),¹²⁻¹⁵ supercritical water oxidation (SWO),¹⁶ and microbial degradation.^{17,18} Among these methods, catalytic hydrodechlorination has been recognized as a promising technology due to its easy and simple procedures.¹⁹⁻²¹ However, most of the catalytic hydrodechlorination processes have been carried out in various organic solvents. Such process consumes plenty of organic solvents that are volatile

and toxic. Moreover, the removal efficiency of PCBs is still far from satisfaction.

The present study is concerned about a comprehensive evaluation of an alternative chemical dechlorination process. Chlorines from PCBs are removed, as shown in below, by poly(ethylene) glycol acting as a nucleophile in reaction with PCBs under the basic condition. This process has proven to be practical and highly cost-effective for disposal of PCBs directly in transformer oil and the recovery of the treated oil. Furthermore, the process avoids the use of potentially dangerous alkali metals and alkali metal oxides being generally employed as catalysts.

Experimental Section

Materials and methods. A sample of waste transformer oil was obtained from a power plant in Korea. An aliquot of oil was withdrawn and analyzed for PCBs according to the procedures described in Figure 1. It was observed that any PCBs were not present in transformer oil above 5 ppb of detection limit. For this reason, chemical dechlorination process was accomplished with fresh transformer oil artificially loaded with commercial PCB mixtures of Aroclor 1242, 1254, and 1260 (Accustandard, Inc., USA). Transformer oil was contaminated with 100 ppm of PCB mixtures. Chemical

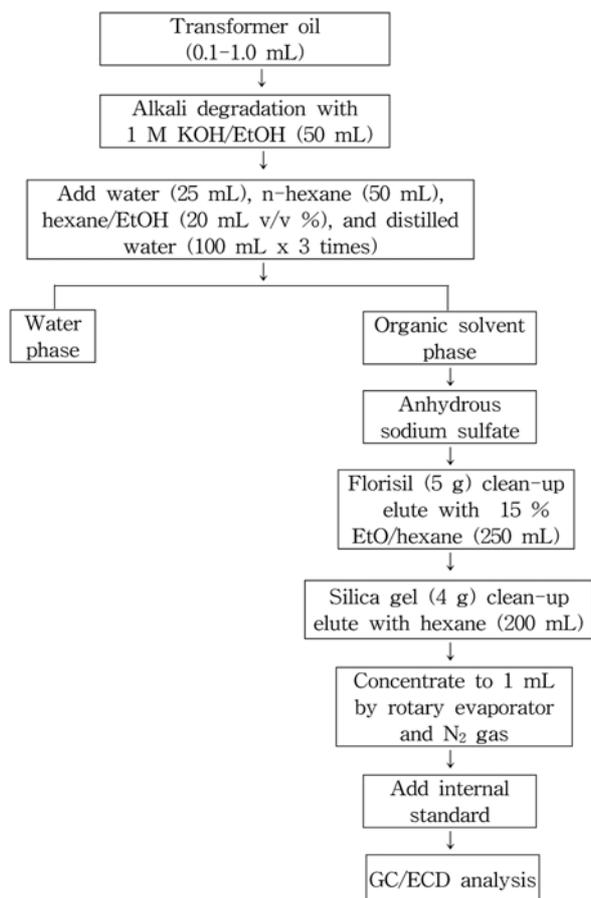
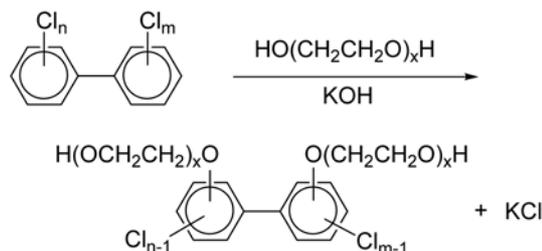


Figure 1. Flow chart of standard process test for PCBs analysis in transformer oil.

reagents consisting of a polyethylene glycol 600 (PEG 600), a potassium hydroxide (KOH), and an aluminum (Al), purchased from Samchun Pure Chemical Co. Ltd., Korea, were prepared for decontamination of PCB-laden transformer oil. PEG was used to remove chlorines from PCBs in oil under basic condition. The solid KOH was ground to a powder before use. Al was utilized as a dechlorination accelerator. The chemical dechlorination process reported here is as follows:



During the process, the mole ratios of PEG 600 and chlorine content of PCBs in oil were varied from 11.42:1 to 57.1:1. The concentrations of KOH and Al were 3.0% and 2.0% (w/w basis) relative to oil, respectively. Figure 2 presents a batch-type reactor, which was made of a double jacketed glass, for disposal of PCBs. A magnetic stirrer with two bladed impellers was installed to provide efficient mixing of the chemical reagents and oil. Nitrogen was used to prevent oxidative degradation of the transformer oil. The reaction mixture was heated to the desired reaction temperatures by adjusting the temperature of the hot oil in the outer jacket. As the reaction runs, reaction mixture gradually turned to a darkening color and sludge. Aliquots of the reactor content were removed periodically and submitted for PCB analysis.

Analysis. A gas chromatograph (Trace GC 2000, Italy) equipped with an electron capture detector (ECD) and a 30 m × 0.25 mm, 0.25 μm 5% phenylpolysiloxane Zebtron ZB-5 column (Torrance, CA) was used for separation and quantification of PCBs. The GC oven program was the following: initial temperature 170 °C, retained for 2 min, then

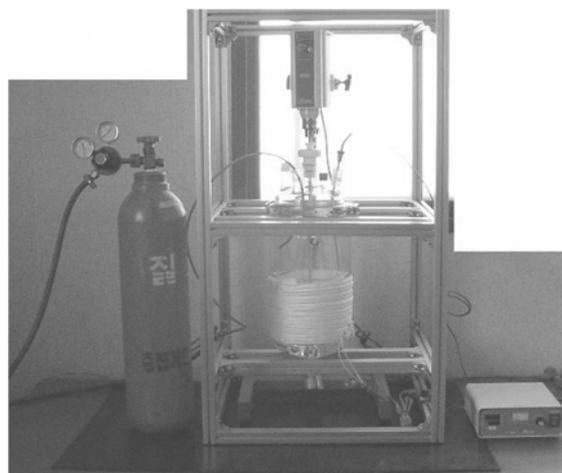


Figure 2. Schematic diagram of a batch-type reactor for PCB destruction process.

increased at a rate of 5 °C/min to 230 °C, retained for 2 min, then increasing at a rate of 5 °C/min to 300 °C, and finally retained for 10 min. The injection was performed in a splitless mode. A 10% CH₄ in Ar was used as the carrier gas. Chromatographic peaks were identified by relative retention time, with pentachlorobenzene (PCBz) as a retention time marker.

Results and Discussion

Identification of PCB congeners in PCB mixtures. A GC chromatogram of commercial PCB mixtures (Aroclor 1242, 1254, and 1260) added into transformer oil was obtained with a ZB-5 column and an ECD, as shown in Figure 3. Previous to instrumental analysis of PCBs, sample treatment of transformer oil containing PCBs was extremely tedious and time-consuming because the oil was unclean, therefore the cleaning steps such as florisil and silica gel were required. Furthermore, qualitative analysis of each PCB congener was also significantly complicated due to the large number of PCB congeners and/or isomers present in commercial PCB mixtures.

In total, 74 chromatographic peaks were identified, each of which contained either a well-resolved peak or a cluster of unresolved peaks. A total of 123 PCB congeners including the presence of co-eluted congeners were found in PCB mixtures on the basis of the relative retention times and listed on the chromatographic peak to which they belong. Out of these congeners, any congeners gave hardly any detectable signal. The numbers listed here were in accordance with IUPAC rules.²² The individual PCB mixtures are different in substitution patterns and the degree of chlori-

nation. For instance, Aroclor 1242 comprises almost entirely congeners with between 2 and 5 chlorine atoms on the two rings of biphenyl, whereas the PCB congeners consisting Aroclor 1254 and Aroclor 1260 have 4-7 and 5-9 chlorine atoms, respectively. In addition, the retention times of each PCB mixture by GC/ECD were typically detected in order of Aroclor 1242, Aroclor 1254, and Aroclor 1260.

Disposal of PCBs by chemical dechlorination process at different reaction conditions. In this work, the effect of reaction temperature assisted chemical dechlorination process was studied for removal of PCBs in transformer oil. Therefore, amounts of reactants, reaction time, and rate of mixing were all kept constant during the run. During the reaction of PEG/KOH with PCBs, PEG serves as a nucleophile under basic condition which attack a partially positive charged carbon on benzene, resulting in leaving a chlorine. Aluminum plays a role in accelerating dechlorination. The chemical reaction process was somewhat slow due to the high viscosity of transformer oil, despite vigorous mechanical stirring for the indicated time. The reaction mixture gradually appeared to be a homogeneous and black sludge during the process runs.

Figure 4 shows the residual PCBs in transformer oil after reaction of PCBs with chemical reactants as stated earlier for 120 min at different temperatures. Compared with Figure 3 representing the PCB concentration level of 100 ppm, it was observed that, when increasing the temperature from 25 °C (Fig. 4A) via 50 °C (Fig. 4B), to 100 °C (Fig. 4C), the numbers and height of PCB peaks have a tendency to gradually diminish. The results clearly demonstrated that removal of PCBs in transformer oil by chemical reaction was highly dependant on the reaction temperature.

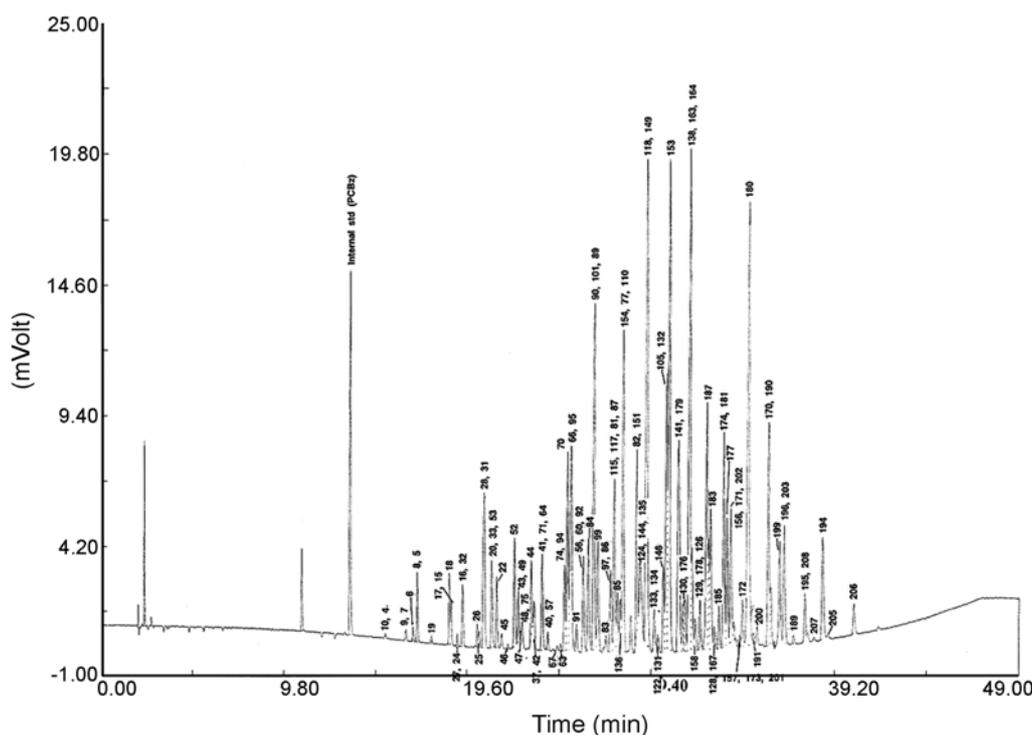


Figure 3. GC/ECD chromatogram of PCB mixture (Aroclor 1242, 1254, and 1260) on a ZB 5 column.

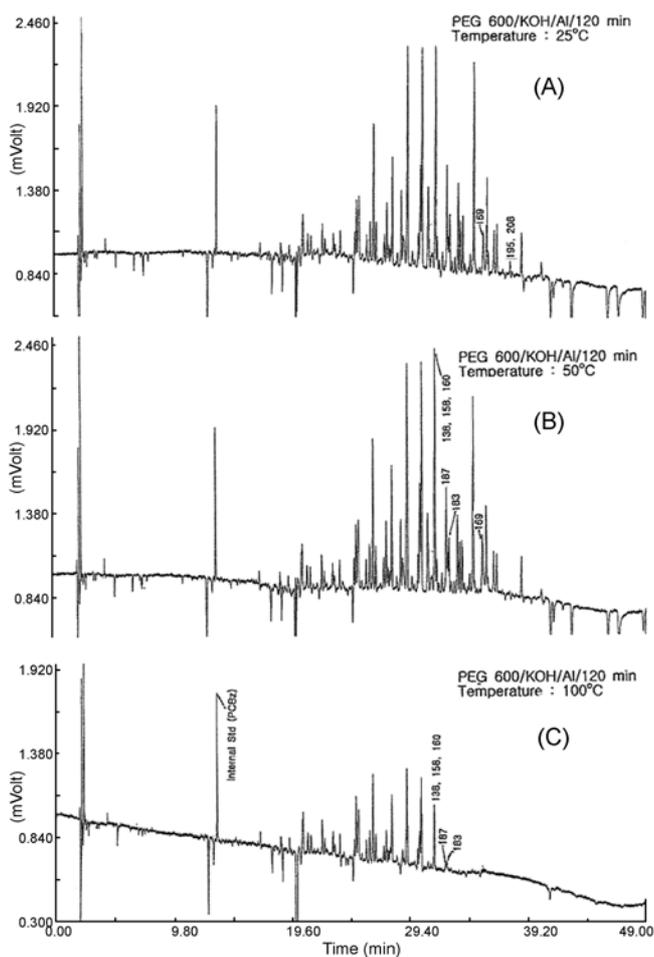


Figure 4. GC/ECD chromatogram of PCB congeners remained in transformer oil after chemical treatment with PEG 600, KOH, and Al for 2 hours at different temperatures.

The performance of this study was assessed in terms of the destruction and removal efficiency (DRE) of PCBs. DRE value was expressed as percentage. Average DREs of PCBs were determined by comparison of relative peak area corresponding to the starting PCB mixtures. The numbers and height of PCB congeners in Figure 4B achieved from experimental condition at 50 °C were nearly identical to those of Figure 4A at 25 °C, except for disappearing only PCB no. 195 and 208. At 50 °C, % average DRE of PCB congeners, as listed in Table 1, was 29.67%, while % average DRE at 25 °C was 28.91%. The experimental results show that reaction temperature of 50 °C is not still enough to remove PCBs directly in transformer oil.

However, when increasing the reaction temperature to 100 °C, the PCB compositions of Figure 4C obtained were no longer similar to those of Figure 4A and 4B, and Figure 3 as a starting composition of PCB mixtures. The % average DRE achieved at 100 °C reached 77.94%, showing complete removal of PCB congeners containing mostly 7-9 chlorines on two rings of biphenyl which appear later than PCB no. 183. The trend suggests that Aroclor 1260 could be more rapidly removed, along with significantly reducing the concentration of PCBs, than Aroclor 1242 in a PEG/KOH/

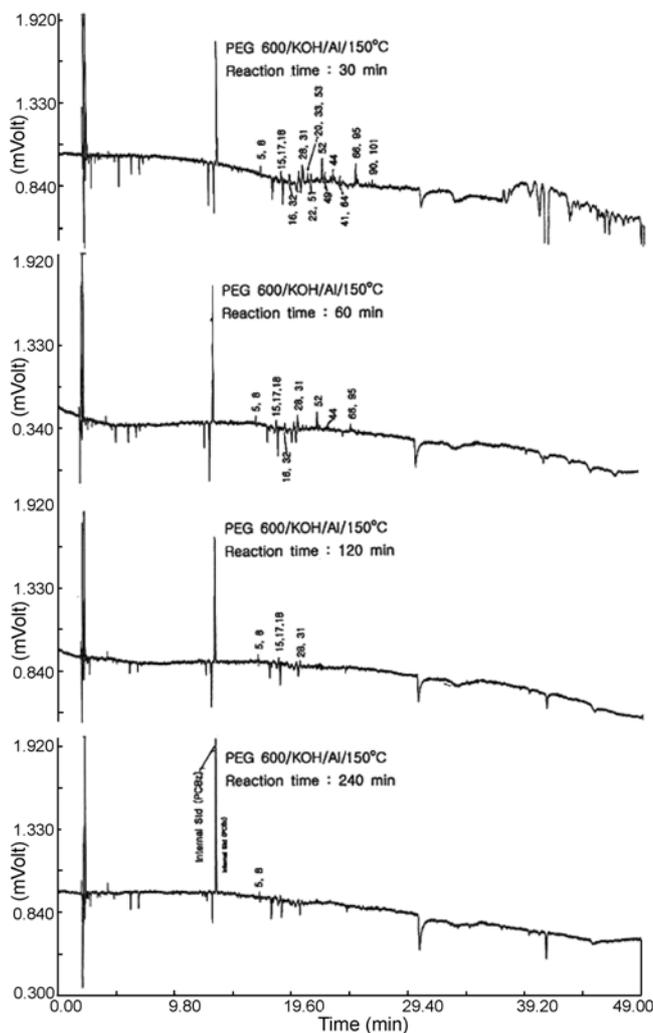


Figure 5. GC/ECD chromatogram of PCB congeners remained in transformer oil after chemical treatment with PEG 600, KOH, and Al at 150 °C for different reaction times.

PCBs system. Such patterns obviously confirmed that the chemical reaction of PCBs and PEG under basic condition takes place essentially through the successive elimination of higher chlorinated PCBs preferentially.

Certain non- and mono-ortho PCB congeners, which possess coplanar geometry, are responsible for their high toxicity.²³ Throughout the commercial PCB mixtures, the toxic PCB congeners such as PCB no. 77 (3,3',4,4'-tetraCB), 105 (2,3,3',4,4'-pentaCB), 118 (2,3',4,4',5-pentaCB), 123 (2',3,4,4',5-pentaCB) and 169 (3,3',4,4',5,5'-hexaCB) were identified. The DRE of each toxic PCB congener was increased with increasing the reaction temperature. However, when compared Figure 4A, 4B, and 4C each other, it was interesting that the peak height of PCB no 169 became taller at temperature condition of 50 °C and then completely disappeared at 100 °C.

The performance of PEG/PCB system in basic medium was also evaluated with different reaction time. The following parameters such as the rate of mixing, reaction temperature, and amounts of reagents therefore remained constant

Table 1. Dechlorination of PCB mixtures (Aroclor 1242, 1254, 1260) in transformer oil by chemical reagents (PEG 600, KOH, Al) for 2 hours at different temperatures

PCB Mixture (Aroclor 1242, 1254, 1260)		Before Chemical Treatment	After Chemical Treatment		
IUPAC No. ^a	Structure	Peak Area	25 °C Peak Area (DRE ^b %)	50 °C Peak Area (DRE %)	100 °C Peak Area (DRE %)
8	2,4'	3421	2252 (34.17)	2260 (33.94)	556 (83.75)
5	2,3				
18	2,2',5	4231	1899 (55.17)	1876 (55.66)	518 (87.76)
17	2,2',4				
15	4,4'				
16	2,2',3	4847	2108 (56.51)	2176 (55.11)	627 (87.06)
32	2,4',6				
26	2,3',5	2009	1073 (46.59)	1084 (46.04)	174 (91.34)
31	2,4',5	12031	10124 (15.85)	11584 (3.72)	10829 (14.48)
28	2,4,4'				
20	2,3,3'		4989 (28.78)	4703 (32.86)	3577 (48.94)
33	2',3,4	7005			
53	2,2',5,6'				
51	2,2',4,6'	4964	3740 (24.66)	3569 (28.10)	3108 (37.39)
22	2,3,4'				
45	2,2',3,6	1081	534 (50.60)	573 (46.99)	n.d. ^c
52	2,2',5,5'	11168	7623 (31.74)	5077 (54.54)	8755 (21.61)
49	2,2',4,5'	5077	3324 (34.53)	2561 (49.56)	579 (88.60)
47	2,2',4,4'	2144	466 (78.26)	488 (77.24)	n.d.
48	2,2',4,5				
75	2,4,4',6				
35	3,3',4	2009	231 (88.50)	162 (91.94)	n.d.
44	2,2',3,5'	8590	5245 (38.94)	5077 (40.90)	4975 (42.08)
37	3,4,4'	5203	2176 (58.18)	2084 (59.95)	161 (96.91)
59	2,3,3',6				
42	2,2',3,4'				
41	2,2',3,4	9442	7013 (25.73)	7529 (20.26)	4529 (52.03)
64	2,3,4',6				
40	2,2',3,3'	1574	619 (60.67)	679 (56.86)	160 (89.83)
74	2,4,4',5	9221	6910 (25.06)	6886 (25.32)	3303 (64.18)
70	2,3',4',5	22869	18018 (21.21)	19586 (14.36)	16748 (26.77)
66	2,3,4,4'	34697	24119 (30.49)	25186 (27.41)	21420 (38.27)
95	2,2',3,5',6				
91	2,2',3,4',6	2964	1062 (64.17)	1091 (63.20)	152 (94.88)
60	2,3,4,4'	9950	6881 (30.84)	6739 (32.27)	4332 (56.46)
56	2,3,3',4				
84	2,2',3,3',6	15284	11145 (27.08)	12632 (17.35)	4523 (70.41)
90	2,2',3,4',5	49039	39657 (19.13)	43650 (10.99)	26001 (46.98)
101	2,2',4,5,5'				
99	2,2',4,4',5	13989	11481 (17.93)	11678 (16.52)	3840 (72.55)
83	2,2',3,3',5	1572	496 (68.45)	515 (67.24)	n.d.
97	2,2',3',4,5	10033	7461 (25.64)	7028 (29.95)	2581 (74.27)
87	2,2',3,4,5'	23369	16542 (29.21)	17401 (25.54)	3994 (82.91)
115	2,3,4,4',6				
85	2,2',3,4,4'	7229	3217 (55.50)	3199 (55.75)	236 (96.74)
136	2,2',3,3',6,6'	6955	2658 (61.78)	2576 (62.96)	198 (97.15)
77 ^c	3,3',4,4'	47165	30366 (35.62)	33688 (28.57)	17299 (63.32)
110	2,3,3',4',6				
82	2,2',3,3',4	27065	20280 (25.07)	18629 (31.17)	1234 (95.44)
151	2,2',3,5,5',6				
135	2,2',3,3',5,6'	9943	6176 (37.89)	4469 (55.05)	157 (98.42)
107	2',3,3',4',5	1997	1238 (38.01)	988 (50.53)	n.d.
123 ^d	2,3,4,4',5	90863	58672 (35.43)	57379 (36.85)	33305 (63.35)
149	2,2',3,4',5',6				
118 ^d	2,3',4,4',5				

Table 1. Continued.

PCB Mixture (Aroclor 1242, 1254, 1260)		Before Chemical Treatment	After Chemical Treatment		
IUPAC No. ^a	Structure	Peak Area	25 °C Peak Area (DRE ^b %)	50 °C Peak Area (DRE %)	100 °C Peak Area (DRE %)
134	2,2',3,3',5,6	6034	2278 (62.25)	2361 (60.87)	n.d.
131	2,2',3,3',4,6	2086	1068 (48.80)	822 (60.59)	n.d.
122	2',3,3',4',5				
146	2,2',3,4',5,5'	13160	9568 (27.29)	9473 (28.02)	1081 (91.79)
132	2,2',3,3',4,6'	79851	58218 (27.18)	58424 (26.59)	21746 (73.01)
153	2,2',4,4',5,5'				
105 ^d	2,3,3',4,4'				
141	2,2',3,4,5,5'	43655	32514 (25.52)	30882 (29.26)	286 (99.34)
179	2,2',3,3',5,6,6'				
130	2,2',3,3',4,5'	1187	660 (44.40)	668 (43.72)	n.d.
176	2,2',3,3',4,6,6'	875	543 (37.94)	549 (37.26)	n.d.
137	2,2',3,4,4',5				
160	2,3,3',4,5,6	89800	63237 (29.58)	65723 (26.81)	17902 (80.06)
138	2,2',3,4,4',5'				
158	2,3,3',4,4',6				
129	2,2',3,3',4,5	7766	4427 (43.00)	3276 (57.82)	n.d.
178	2,2',3,3',5,5',6				
187	2,2',3,4',5,5',6	42440	24513 (42.24)	23805 (43.91)	381 (99.10)
183	2,2',3,4,4',5',6	22671	11241 (50.42)	11691 (48.43)	378 (98.33)
128	2,2',3,3',4,4'	3929	1688 (57.04)	1472 (62.53)	n.d.
185	2,2',3,4,5,5',6	6840	2136 (68.77)	1908 (72.11)	n.d.
174	2,2',3,3',4,5,6'	35864	26122 (27.16)	23350 (34.89)	n.d.
177	2,2',3,3',4',5,6	20372	10103 (50.41)	13473 (33.87)	n.d.
202	2,2',3,3',5,5',6,6'	21723	10118 (53.42)	12587 (42.06)	n.d.
171	2,2',3,3',4,4',6				
156	2,3,3',4,4',5				
173	2,2',3,3',4,5,6	3025	1274 (57.88)	1296 (57.16)	n.d.
157	2,3,3',4,4',5'				
201	2,2',3,3',4,5',6,6'				
172	2,2',3,3',4,5,5'	7395	3661 (50.49)	3062 (58.59)	n.d.
180	2,2',3,4,4',5,5'	80452	41828 (48.01)	42213 (47.53)	n.d.
193	2,3,3',4',5,5',6	4082	253 (93.80)	161 (96.06)	n.d.
191	2,3,3',4,4',5',6	1563	247 (84.20)	226 (85.54)	n.d.
200	2,2',3,3',4,5,6,6'	2526	422 (83.30)	187 (92.60)	n.d.
169 ^c	3,3',4,4',5,5'	194	11459 (-5,806.70)	13788 (-7,007.22)	n.d.
170	2,2',3,3',4,4',5,	34794	27586 (20.72)	19208 (44.80)	n.d.
190	2,3,3',4,4',5,6				
199	2,2',3,3',4,5,5',6	19187	11488 (40.13)	10750 (43.97)	n.d.
203	2,2',3,4,4',5,5',6	20621	12880 (37.54)	11259 (45.40)	n.d.
196	2,2',3,3',4,4',5',6				
189	2,3,3',4,4',5,5'	1605	304 (81.06)	174 (89.16)	n.d.
208	2,2',3,3',4,5,5',6,6'	8399	2620 (68.81)	175 (97.92)	n.d.
195	2,2',3,3',4,4',5,6				
194	2,2',3,3',4,4',5,5'	19817	12702 (35.90)	11273 (32,73543.11)	n.d.
206	2,2',3,3',4,4',5,5',6	5764	2824 (51.01)	1247 (78.37)	n.d.
Sum		995,677	707,777	700,285	219,649
Average DRE (%)			28.91	29.67	77.94

^aIUPAC No.: K. Ballschmiter and M. Zell, Analytical Chemistry, 302, 1980. ^bDRE : destruction and removal efficiency. ^c77 and 169: coplanar PCB congeners. ^d123, 118, 105 and 169: monoortho coplanar PCB congeners. ^en.d.: no detection above concentration level of 0.05 ppm.

Table 2. Dechlorination of PCB mixture (Aroclor 1242, 1254, 1260) in transformer oil by chemical reagents (PEG 600, KOH, Al) and different reaction times at 150 °C

PCB Mixture (Aroclor 1242, 1254, 1260)		Before Chemical Treatment	After Chemical Treatment			
IUPAC NO. ^a	Structure	Peak Area	30 min Peak Area (DRE ^b %)	60 min Peak Area (DRE %)	120 min Peak Area (DRE %)	240 min Peak Area (DRE %)
8	2,4'	3421	324 (90.53)	295 (91.38)	252 (92.63)	185 (94.60)
5	2,3					
18	2,2',5	4231	369 (91.28)	297 (92.98)	266 (93.71)	n.d. ^c
17	2,2',4					
15	4,4'					
16	2,2',3	4847	337 (93.05)	213 (95.61)	n.d.	n.d.
32	2,4',6					
26	2,3',5	2009	n.d.	n.d.	n.d.	n.d.
31	2,4',5	12031	752 (93.75)	577 (95.20)	205 (98.30)	n.d.
28	2,4,4'					
20	2,3,3'		378 (94.60)	n.d.	n.d.	n.d.
33	2',3,4	7005				
53	2,2',5,6'					
51	2,2',4,6'	4964	299 (93.98)	n.d.	n.d.	n.d.
22	2,3,4'					
45	2,2',3,6	1081	n.d.	n.d.	n.d.	n.d.
52	2,2',5,5'	11168	817 (92.68)	612 (94.52)	n.d.	n.d.
49	2,2',4,5	5077	294 (94.21)	154 (96.97)	n.d.	n.d.
47	2,2',4,4'	2144	n.d.	n.d.	n.d.	n.d.
48	2,2',4,5					
75	2,4,4',6					
35	3,3',4	2009	n.d.	n.d.	n.d.	n.d.
44	2,2',3,5'	8590	396 (95.39)	242 (97.18)	n.d.	n.d.
37	3,4,4'	5203	n.d.	n.d.	n.d.	n.d.
59	2,3,3',6					
42	2,2',3,4'					
41	2,2',3,4	9442	258 (97.57)	n.d.	n.d.	n.d.
64	2,3,4',6					
40	2,2',3,3'	1574	n.d.	n.d.	n.d.	n.d.
74	2,4,4',5	9221	n.d.	n.d.	n.d.	n.d.
70	2,3',4',5	22869	n.d.	n.d.	n.d.	n.d.
66	2,3,4,4'	34697	842 (97.57)	265 (99.24)	n.d.	n.d.
95	2,2',3,5',6					
91	2,2',3,4',6	2964	n.d.	n.d.	n.d.	n.d.
60	2,3,4,4'	9950	n.d.	n.d.	n.d.	n.d.
56	2,3,3',4					
84	2,2',3,3',6	15284	n.d.	n.d.	n.d.	n.d.
90	2,2',3,4',5	49039	269 (99.45)	n.d.	n.d.	n.d.
101	2,2',4,5,5'					
99	2,2',4,4',5	13989	n.d.	n.d.	n.d.	n.d.
83	2,2',3,3',5	1572	n.d.	n.d.	n.d.	n.d.
97	2,2',3',4,5	10033	n.d.	n.d.	n.d.	n.d.
87	2,2',3,4,5'	23369	n.d.	n.d.	n.d.	n.d.
115	2,3,4,4',6					
85	2,2',3,4,4'	7229	n.d.	n.d.	n.d.	n.d.
136	2,2',3,3',6,6'	6955	n.d.	n.d.	n.d.	n.d.
77 ^c	3,3',4,4'	47165	n.d.	n.d.	n.d.	n.d.
110	2,3,3',4',6					
82	2,2',3,3',4	27065	n.d.	n.d.	n.d.	n.d.
151	2,2',3,5,5',6					
135	2,2',3,3',5,6'	9943	n.d.	n.d.	n.d.	n.d.
107	2',3,3',4',5	1997	n.d.	n.d.	n.d.	n.d.
123 ^d	2,3,4,4',5	90863	n.d.	n.d.	n.d.	n.d.
149	2,2',3,4',5',6					
118 ^d	2,3',4,4',5					
134	2,2',3,3',5,6	6034	n.d.	n.d.	n.d.	n.d.

Table 2. Continued

PCB Mixture (Aroclor 1242, 1254, 1260)		Before Chemical Treatment	After Chemical Treatment			
IUPAC NO. ^a	Structure	Peak Area	30 min Peak Area (DRE ^b %)	60 min Peak Area (DRE %)	120 min Peak Area (DRE %)	240 min Peak Area (DRE %)
131	2,2',3,3',4,6	2086	n.d.	n.d.	n.d.	n.d.
122	2',3,3',4',5					
146	2,2',3,4',5,5'	13160	n.d.	n.d.	n.d.	n.d.
132	2,2',3,3',4,6'	79851	n.d.	n.d.	n.d.	n.d.
153	2,2',4,4',5,5'					
105 ^d	2,3,3',4,4'					
141	2,2',3,4,5,5'	43655	n.d.	n.d.	n.d.	n.d.
179	2,2',3,3',5,6,6'					
130	2,2',3,3',4,5'	1187	n.d.	n.d.	n.d.	n.d.
176	2,2',3,3',4,6,6'	875	n.d.	n.d.	n.d.	n.d.
137	2,2',3,4,4',5					
160	2,3,3',4,5,6	89800	n.d.	n.d.	n.d.	n.d.
138	2,2',3,4,4',5'					
158	2,3,3',4,4',6					
129	2,2',3,3',4,5	7766	n.d.	n.d.	n.d.	n.d.
178	2,2',3,3',5,5',6					
187	2,2',3,4',5,5',6	42440	n.d.	n.d.	n.d.	n.d.
183	2,2',3,4,4',5',6	22671	n.d.	n.d.	n.d.	n.d.
128	2,2',3,3',4,4'	3929	n.d.	n.d.	n.d.	n.d.
185	2,2',3,4,5,5',6	6840	n.d.	n.d.	n.d.	n.d.
174	2,2',3,3',4,5,6'	35864	n.d.	n.d.	n.d.	n.d.
177	2,2',3,3',4',5,6	20372	n.d.	n.d.	n.d.	n.d.
202	2,2',3,3',5,5',6,6'	21723	n.d.	n.d.	n.d.	n.d.
171	2,2',3,3',4,4',6					
156	2,3,3',4,4',5					
173	2,2',3,3',4,5,6	3025	n.d.	n.d.	n.d.	n.d.
157	2,3,3',4,4',5'					
201	2,2',3,3',4,5',6,6'					
172	2,2',3,3',4,5,5'	7395	n.d.	n.d.	n.d.	n.d.
180	2,2',3,4,4',5,5'	80452	n.d.	n.d.	n.d.	n.d.
193	2,3,3',4',5,5',6	4082	n.d.	n.d.	n.d.	n.d.
191	2,3,3',4,4',5',6	1563	n.d.	n.d.	n.d.	n.d.
200	2,2',3,3',4,5,6,6'	2526	n.d.	n.d.	n.d.	n.d.
170	2,2',3,3',4,4',5,	34794	n.d.	n.d.	n.d.	n.d.
190	2,3,3',4,4',5,6					
199	2,2',3,3',4,5,5',6	19187	n.d.	n.d.	n.d.	n.d.
203	2,2',3,4,4',5,5',6	20621	n.d.	n.d.	n.d.	n.d.
196	2,2',3,3',4,4',5',6					
189	2,3,3',4,4',5,5'	1605	n.d.	n.d.	n.d.	n.d.
208	2,2',3,3',4,5,5',6,6'	8399	n.d.	n.d.	n.d.	n.d.
195	2,2',3,3',4,4',5,6					
194	2,2',3,3',4,4',5,5'	19817	n.d.	n.d.	n.d.	n.d.
206	2,2',3,3',4,4',5,5',6	5764	n.d.	n.d.	n.d.	n.d.
Sum		995,483	5,335	2,655	723	185
Average DRE (%)			99.46	99.73	99.93	99.99

^aIUPAC No.: K. Ballschmiter and M. Zell, Analytical Chemistry, 302, 1980. ^bDRE: destruction and removal efficiency. ^c77: coplanar PCB congener. ^d123, 118 and 105: monoortho coplanar PCB congeners. ^en.d.: no detection above concentration level of 0.05 ppm.

throughout the experiment. Our previous studies showed that % average DRE of PCBs could be enhanced with increasing the temperature. However, the results obtained were not still adequate for disposal of PCBs due to the

stipulation for requiring 99.9999% of PCB destruction and removal efficiency and/or less than 2 ppm.

GC chromatograms of PCB congeners remained in transformer oil after chemical reaction of PCBs with PEG/KOH

for different reaction times at 150 °C are represented in Figure 5. Figure 5A (150°C, 30 min) was no longer analogous to their original formulation of starting PCB mixtures as shown in Figure 3. Only lower chlorinated 12 PCB peaks, such as PCB no. (90, 101), PCB (65, 95), (PCB 41, 84), and etc. consisting of Aroclor 1242, were found in treated transformer oil, together with a significant decrease in peak height of PCBs and the average DRE obtained was 99.46%, as listed in Table 2. At 150 °C and 60 min, the numbers and peak height of residual PCBs in transformer oil were more decreased than those of the conditions above-mentioned. The average DRE reached 99.73%, and it showed that some PCB congeners such as PCB no. (90, 101), (41, 64), (49), (22, 51), and (20, 33, 53) disappeared preferentially.

In order to improve the destruction and removal efficiency of PCBs, the reaction time was further extended. As a result, a little higher % DRE (99.93%) was achieved at conditions of 120 min and 150 °C compared to that in the case of 60 min and 150 °C. All the remaining PCB peaks in treated transformer oil were the following: PCB no. (5, 8), (15, 17, 18), and (28, 31). The best results were attained under conditions of 240 min and 150 °C, where only a peak (PCB no. 5, 8) was found in treated transformer oil as a result of consecutively dechlorinating reaction. Average DRE of PCBs, as shown in Table 2, was 99.99% or better. It was observed that complete destruction of PCBs in transformer oil could be achieved by conducting the reaction for a longer period of time at higher temperature.

In this report, we have completed a laboratory evaluation of the chemical reaction of PCBs with PEG and KOH in transformer oil. Several key points were made: (1) The reaction was carried out in transformer oil directly. In the case of PCB-laden transformer oil, from the practical view-point, dechlorinating PCBs directly in oil is a suitable disposal method. To the best of our knowledge, most of the dechlorinating processes for transformer oil containing PCBs have implemented in various organic solvents. Recently, nanometric sodium hydride (nano-NaH) and transition metal catalysts have been directly used to dechlorinate PCBs in transformer oil¹⁹; (2) The chemical reagents PEG and KOH used in this study are common and fairly inexpensive. Hence, the cost of oil decontamination might be below any available alternative disposal costs; (3) Certain PCB congeners, PCB no. 77, 105, 118, 123 and 169, are approximate isosteromers of the most toxic 2,3,7,8-TCDD (2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin) in their coplanar conformation. It is apparent that such toxic PCB congeners are easily removed by PEG under basic condition; (4) The operation of reactor system is simple and safe, requiring no special precautions.

Recovery of the treated transformer oil. After completion of the experiments, the reactor content was drained into a vessel and cooled to room temperature. The treated transformer oil was segregated from the contents by filtering, washing with water, dehydrating under vacuum, and centrifuging; this resulted in precipitation of PEG, KOH, Al, and reaction products. Such segregating steps described above constitute standard treatment of treated transformer oil before reuse.

Conclusion

We have developed a safe, inexpensive, and efficient chemical dechlorinating process for the disposal of PCBs directly in transformer oil. The numbers and peak height of residual PCBs in treated oil were gradually decreased in order of Aroclor 1260, 1254, and 1242 with increasing the reaction temperature and time, which is the characteristic of consecutive reaction. In PCBs/PEG/KOH system under experimental conditions of 150 °C and 4 hr, the destruction and removal efficiency of PCBs including certain PCBs (PCB no. 77, 118, 105, 123 and 169), which are responsible for their toxicity, was equivalent to or better than 99.99%. Furthermore, another interesting feature of the process is that it permits high recovery of the treated oil through simple segregating procedures.

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