화학 및 열적 처리를 이용한 폴리염화바이페닐(PCB)의 제거

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Disposal of Polychlorinated Biphenyls(PCBs) by a Combined Chemical with Thermal Treatment

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요 약. 변압기 오일에 함유되어 있는 폴리염화바이페닐(PCB)의 제거를 위해서 화학적 처리와 제어된 산화반응에 의한 열적처리를 상호 결합시킨 한 포괄적인 공정이 이루어 졌다. 화학시약을 이용한 화학처리에서 완전히 처분할 수 없었던 폴리염화바이페닐은 오일의 순환중에 적절한 흡착제로 걸러진 후 열처리되었다. 열처리에 의해서 폴리염화바이페닐은 99.99% 이상 파괴 되었으며 독성 부산물인 PCDDs나 PCDFs는 처리과정 중에 형성되지 않았다. 변압기에 있는 오일이나 무기지지체는 공정 후에 재회복 되었다. 화학 및 열적처리를 결합시킨 이 공정은 환경적으로 유익하며, 다른 유용한 기술보다도 사용하기 쉽고 효과적이며 경제적 이었다.

ABSTRACT. A comprehensive process which combines chemical with thermal treatment by controlled counterflow oxidation has been developed for disposal of PCBs in transformer oil. PCBs which not completely removed by chemical treatment, after being filtered with appropriate adsorbent during the oil circulations, was thermally treated. Destruction efficiencies of better than 99.99% was obtained, with no measurable formation of PCDDs (polychlorinated dibenzo-p-dioxins) or PCDFs (polychlorinated dibenzofurans). The combination also permits high recovery of oil and inorganic supports from scrap power transformers. The process is environmentally benign, easy to use and less capital intensive than other available technologies.

INTRODUCTION

Polychlorinated biphenyls (PCBs) consist of 209 discrete compounds, termed congeners, in which one to ten chlorine atoms are attached to the two phenyl rings. These chemicals were commercially produced in large quantities over 40 years for the period 1930 to 1977. The total production of PCBs in the world has been estimated to be 1.1×10^9 kg, of which about 93% were produced by Monsanto in the United States.[1] Complex mixtures of PCBs by Monsanto were marketed under the registered trade-mark of Aroclor. The principal application of PCBs was as insulating fluid in electrical equipments such as transformers and capacitors, due to their chemical and thermal stability as well as their high dielectric property.[2] However, the extensive use and improper disposal of PCBs, coupled with their high persistence to environment, have led these chemicals to ubiquitous environmental pollutants.[3,4] They have been found through the bioaccumulation in marine organism, fish, bird, terrestrial animal, and, of course, human.[5,6] It has been recently reported in the newspapers that PCBs act as a pseudo-hormone in reducing the sperm in male and turning male into female, by disrupting transference of natural hormone in organism.

With the mounting evidence of environmental

damage, federal regulation of PCBs began in 1976 with the passage of the Toxic Substances Control Act(TSCA).[7] Similar regulatory directives were issued by the European Communities. These regulations prohibited manufacture, processing, commercial distribution or use of PCBs in open system.[8] However, large numbers of PCB containing devices still remain in operation. It was reported that, in the United States and European Community, approximately 500,000 transformers contained askarel (an international electrochemical commission designation for dielectric fluids with PCB/trichlorobenzene).[9] Furthermore, it is estimated that more than 2 million transformers contain mineral oil or other dielectric fluids with PCB concentrations exceeding the regulatory limits (25-50 ppm). The numbers are much larger worldwide. The askarel contaminated materials results from cross contamination during manufacturing of equipments, processing of dielectric fluids, refilling, service and maintenance as well as disposal of fluids or recovery of materials. The vast majority (99%) of the PCB contamination in mineral oil falls between 50-2,000 ppm, above the 25-50 ppm limits set by regulatory agencies. The PCB contaminated mineral oil thus represents a significant environmental problem.

The problem has been so far addressed through two approaches. The most common approach is high temperature incineration, whereby the PCB contaminated oil is drained and incinerated at high temperature in rotary kiln.[10,11] The process is straightforward; however, it is hampered by the disposal costs and problems with transportation of contaminated material and destruction of reusable materials. The second approach involves chemical reaction of PCBs with poly(ethylene glycols) and alkali metal under the basic condition.[12,13] The process has become the most used treatment technology for PCB-laden transformer oils. The process, in its original form, was introduced by scientists at General Electric Company.[14] Many improvements have since been incorporated.

The objective of the present study is to evaluate the efficiency of a combined chemical with thermal treatment for disposal of PCBs in transformer oil and recovery of resources such as mineral oils and adsorbents, as well as to monitor the possible formation of toxic by-products such as dioxin and furan.

EXPERIMENTAL

Analysis and Materials. Analysis of PCBs was carried out on a gas chromatograph equipped with a ^{63}Ni electron capture detector and an auto-injection sampler. Chromatographic separations were performed on a 0.25 mm (i.d.)$\times$30 m long capillary DB-5 column. The GC oven was temperature programmed through a two step ramp, an initial ramp from 80 to 180 °C at 10 °C/min followed by a final ramp rate of 3 °C/min to 265 °C. Helium was used as the carrier gas. A four point calibration curve was established over the 30 pg to 10 ng. Chromatographic peaks were identified by relative retention time, with pentachlorobenzene (PCBz) as a retention time marker. Identification of dioxin and furan, after spiking with stable labeled isotopes as surrogate standards, was accomplished by GC/quadruple mass spectrometry, operating in selected ion monitoring (SIM) mode. Separations were achieved with a OV-17 column. Quantitation of HCl was conducted using an ion chromatograph with conductivity detector. The ratios of CO/CO_2 gas were determined with a gas chromatograph/thermal conductivity detector, by measuring the response relative to standard gas mixtures. The gases were separated with a carbosieve (60-80 mesh) packed column at 80 °C oven temperature. Surface area was measured by a Quantasorb Surface Area Analyzer (QS-10, Quantachrome Corp. Syosset, NY), using a N_2 BET method.

Analyte standards (Aroclor 1242, Aroclor 1260, and dioxin and furan) were obtained from Ultra Scientific Incorporation at a nominal concentration of 1 mg/mL and were serially diluted with isooctane for chromatographic calibration. The solvents were all pesticide grade, used without further purification. Askarel fluid, PCB-contamin-

ated transformer oil was obtained from Sea Marconi Technology, Torino, Italy. Activated carbon (Darco, 20-40 mesh) and silica gel (Davisil, Grade 923, 80-100 mesh) were purchased from Aldrich Chemical Incorporation.

Experimental Procedures. Chemical reagents consisting of a polyethylene glycol (PEG), an aluminum (Al), and a potassium hydroxide (KOH) were prepared for PCB disposal by chemical treatment. Polyethylene glycol (molecular weight; 600) was used to remove chlorines from PCBs in transformer oils under the basic condition. Aluminum was utilized as a dechlorination accelerator. The solid KOH was ground to a powder before use. To optimize the process, the mole ratio of PEG and total chlorine content of PCBs in oil was 1:1. The concentration of Al in the reaction mixture was 0.1-0.2 weight percent relative to oil. Initial concentration of PCBs in the transformer oil was approximately 700 ppm. *Fig.* 1 depicts experimental design for disposal of PCBs from transformer oil. A glass reactor was utilized. Two bladed impellers were installed to provide efficient mixing of the chemical reagents and oil. A pump was provided for circulations of oil. Nitrogen was used to prevent oxidative degradation of the oil. The reaction mixture was heated to 80-100 °C by adjusting the temperature of the hot water. As the
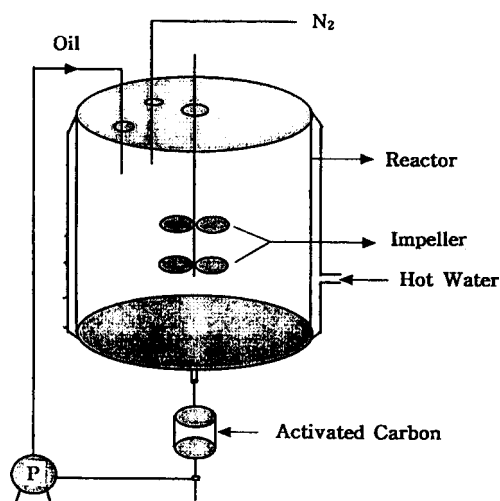
reaction progresses, reaction mixture gradually turned to a darkening color and sludge. The reaction time required was maintained for 1 hr. During the circulation, the product oils were filtered through activated carbon. After each cycle, the circulated oil and activated carbon were removed and submitted for PCB analysis.

Thermal treatment by counterflow oxidation process (COP) was carried out using a reactor, as shown in *Fig.* 2. The reactor was constructed with a 5 cm i.d.×45 cm long quartz tube. The fittings were placed on the top and bottom side of the tube, and then was connected to a gas cylinder and an exhaust gas line. The reactor was filled with activated carbon which adsorbed PCBs in oil during the oil circulations. The O_2 was used as an oxidant. Oxygen was forced to flow from the top of the reactor to the bottom. The flow rates of oxygen were controlled using a needle valve on a pressure regulator and monitored with a calibrated rotameter. Combustion of activated carbon was ignited at the bottom of the tube until flame was generated, using a torch or a resistive heater. The self-propagating flame was then moved counter to the oxygen flow, coincidently burning a portion of the carbon and destructing adsorbed PCBs. The flow rates were operated at 60~600 mL per min. The oxygen flow was shut off when the flame

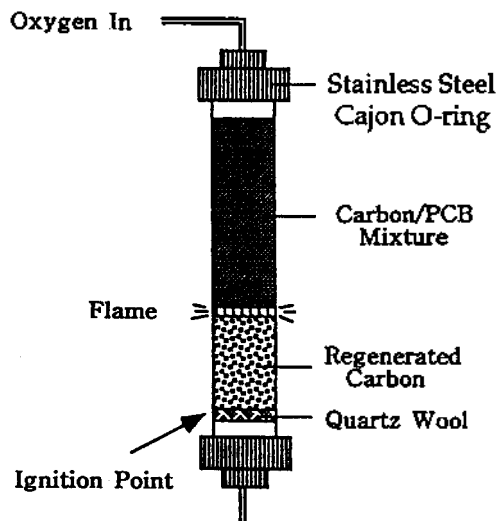*Fig.* 1. A Reactor design for PCB disposal.

Fig. 2. A Schematic diagram of PCB reactor.

reaches the top of the reactor. During the COP, a portion of gas evolved was sampled at intervals for gas compositions such as CO, CO_2, CH_4, H_2 and etc. Other portion was allowed to pass through a series of impinger traps that filled with water and iso-octane, respectively, to trap HCl and PCBs/dioxin/furan. After COP was completed, aliquots of carbon were withdrawn from the reactor and Soxhlet extracted with CH_2Cl_2, and then silica gel column clean-up was introduced to remove interferents from the extract. The final extract was concentrated to 2 mL volume using a rotavapor and a stream of N_2 gas. Soon after, analysis of PCBs and dioxin/furan was followed.

RESULTS AND DISCUSSION

Chemical Treatment. The disposal of PCBs in transformer oil was conducted with chemical reagents. A sample used, PCBs in transformer oil, was Aroclor 1260 (mixture of PCBs with mostly five and six chlorines on biphenyl frame). During the reaction of PEG/Al/KOH with PCBs, PEG serves as a nucleophile under the basic condition which attack a partially positive charged carbon on benzene, resulting in leaving a chlorine. Aluminum plays a role in accelerating dechlorination. The 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. The oil was circulated for 25 number of cycles, via a bed of activated carbon, by a pump. Most of the oils ($\geq 95\%$) were easily recovered from the reaction mixture because the oil was insoluble in the mixture.

The oils, before being filtered by activated carbon, were analyzed for PCB residue per cycle of the treatment. The analytical procedures to determine PCBs were, however, extremely tedious and time-consuming because the oil product was unclean and, such a case, the cleaning step is required, in addition due to the large number of PCB isomers present in commercial mixtures. The
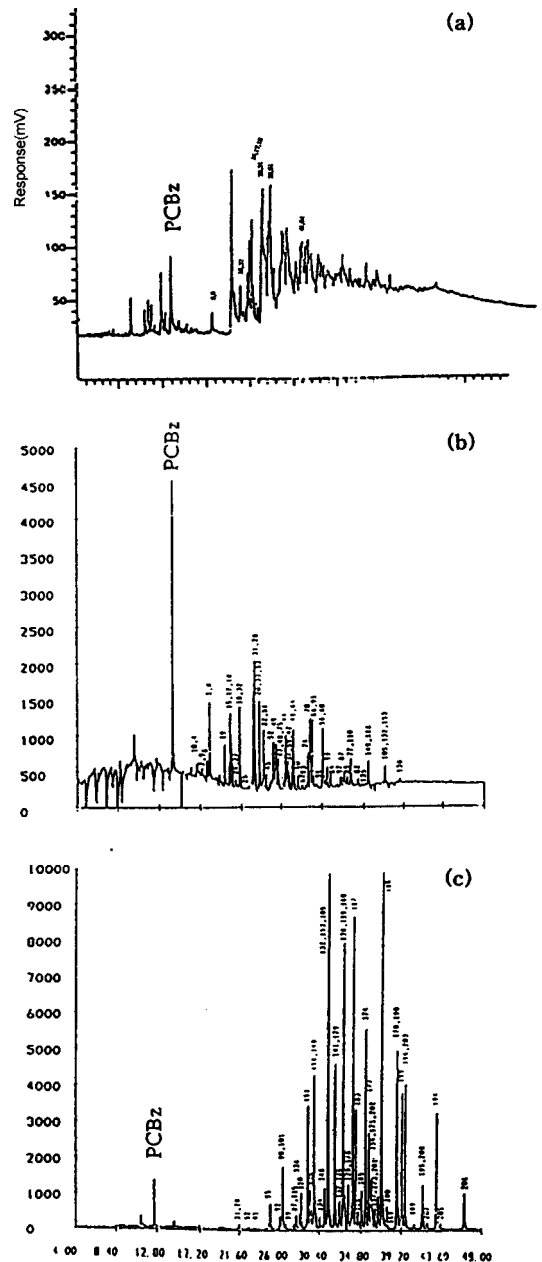

Fig. 3. Chromatograms of (a) residual PCBs in oil, (b) Aroclor 1242, and (c) Aroclor 1260.

result of analysis is shown in *Fig.* 3(a). The chromatogram of *Fig.* 3(a) was no longer similar to that of the composition of Aroclor 1260, shown in *Fig.* 3(c), as a starting material. It is clear that higher chlorinated PCBs were transformed into

lower chlorinated PCBs (Aroclor 1242), shown in *Fig.* 3(b), due to the continuous dechlorination reaction in a PEG/KOH/PCBs system. Generally, the retention time of individual PCBs in Aroclor 1242 by GC-ECD is earlier detected than Aroclor 1260. The concentration of PCBs was thus determined on the basis of percent contribution of individual PCBs to Aroclor 1242 (mixture of PCBs composed of mostly 3 and 4 chlorine atoms) reported by Schulz *et al.*[15] The total concentration of PCBs was approximated by aggregating the concentration of individual PCBs. The PCB removal after each oil circulation was summarized in *Table* 1. The reaction of PEG/KOH/PCBs resulted in reducing the level of PCBs from 700 ppm to 80 ppm in first cycle and 20 ppm after 12 cycles. After 24 number of cycles, any PCBs were not detected in oil.

Activated carbon was sampled for analysis of PCBs immediately after oil circulations were over. The PCBs were found in the carbon. The amount of PCBs in carbon was almost equivalent to that of PCBs in oil before oil circulation. It points out that acivated carbon is highly effective in adsorbing PCBs from PCB-contaminated oil. More detailed study was reported on a paper by K. S. Ryoo.[16] Anyway, there arises a perplexing issue about how to treat PCB-contaminated carbon. Such a carbon still poses disposal problem. Ideally one would want a process that destroys PCBs by leaving the carbon intact. Up to date, wet air oxidation (WAO) has been typically introduced for reuse of spent carbon. WAO is geneally conducted when carbon contains substances that volatilize at temperatures below 150 °C,[17] besides it is highly energy intensive and is not useful in cases when very strongly adsorbing or highly toxic compounds are present. It is apparent that WAO is not suitable for the current study because PCBs are thermally stable. Therefore, one alternative process has been

Table 1. PCB removal by oil circulations

Number of oil circulation	0	1	12	25
Residual PCBs in mixture (ppm)	700	80	20	0

developed in my laboratory and signifies its *modus operandi*, termed counterflow oxidation.

Counterflow Oxidation Process (COP). The entire process of counterflow oxidation utilizes a self-sustained flame which propagates itself in a direction counter to the flow of oxygen. The flame destroys the substances adsorbed on the carbon, together with the loss of carbon. Particularly, the destruction of PCBs by thermal treatment requires very high temperature because PCBs are very difficult to burn due to their thermal stability. A few scientists have studied experimentally and theoretically that, at temperatures higher than 800 °C, PCBs are thermodynamically unstable.[18] Therefore, destruction of PCBs could be achieved by maintaining temperature ≥ 800 °C at least. However, in the process of counterflow oxidation, direct measurement of flame temperature by temperature transducers was actually impossible in spite of a numerous attempt, due to the nature of the flame which moves slowly upward against a stream of oxygen. The flame temperature was, hence, determined both by the relative ratios of the CO and CO_2 gas exhausting from the reactor and by the loss of carbon at such ratios.

The following procedures were introduced to calculate the flame temperature. A known amount of carbon was placed in a quartz tube of cross-sectional area A and length L. The number of carbon moles per cm^3 is C_c=weight/(12AL). In a section of this tube of length(L), the carbon and oxygen at T are converted to carbon(C), CO(g), and $CO_2(g)$ at temperature T, with loss of some of the carbon(Δn_C). All of the oxygen delivered at a volumetric flow rate(F, cm^3/sec) and pressure P (atm) is assumed to be consumed. The amount of oxygen consumed depends on the total burn time. This calculation neglects oxygen which is present in the interparticle pore and intraparticle pore space at the beginning of the burn. The flame advances through this section at a linear burning rate(B, cm/sec). The time required is $t=L/B$. The volume of O_2 burned is: $V_{O2}=Ft=FL/B$. Moles of O_2 burned are: $\Delta n_{O2}=kFPL/BT$, where k(reciprocal number of gas constant)=1/R=0.001/0.08205=
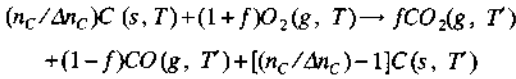
$0.01219(\text{mol} \cdot \text{K/cm}^3 \cdot \text{atm})$. The ratio of carbon to oxygen burned is: $\Delta n_C/\Delta n_{O2}=2/(1+f)$, and $\Delta n_C= 2kFPL/BT(1+f)$. f=mole fraction of CO_2 in product stream. The total moles of carbon involved is

$$n_C = AC_cL, \quad so \quad \Delta n_C/n_c = 2kFP/AC_CBT(1+f)$$

The process is

$$(n_C/\Delta n_C)C\,(s, T)+(1+f)O_2(g, T) \rightarrow fCO_2(g, T')$$
$$+(1-f)CO(g, T')+[(n_C/\Delta n_C)-1]C(s, T')$$

and is assumed to occur adiabatically, so that

$$O = f[\Delta_f H_{CO2}+\int_T^T C_{P_{co2}}\,dT]+(1-f)$$
$$[\Delta_f H_{CO}+\int_T^T C_{P_{co}}\,dT]+[(n_C/\Delta n_C)-1]\int_T^T C_{P_c}\,dT]$$

with enthalpies of formation $\Delta_f H$ at T, which is taken as 298.15 K.

The final flame temperatures, T', were estimated from both enthalpies of formation and heat capacities of CO and CO_2 gas and the loss of carbon at different oxygen flow rates. The gas products from the combustion reaction of carbon with oxygen by COP were observed as CO, CO_2, CH_4, and H_2, and CO, CO_2, and CH_4 were identified as the primary products. The ratios of CO and CO_2 were roughly varied from 1:0.7 to 1:1 according to increasing the oxygen flow rates from 60 to 600 mL per min. The loss of carbon ranged from 7% to 15% at such flow rates. The flame temperatures based on the thermodynamic calculation were found to be strongly dependent on oxygen flow rate. The range of flame temperature was between $800\,^{\circ}C$ to $1500\,^{\circ}C$.

Thermal Treatment by Counterflow Oxidation Process. Activated carbon was employed as an adsorbent to adsorb PCBs from PCBs-containing oil during the chemical treatment process. It was shown that activated carbon was highly effective for removal of PCBs from transformer oil. Thermal treatment by COP was conducted for destruction of PCBs that adsorbed on activated carbon. In case of the thermal degradation of PCBs, the possible products or by-products leading to decomposition of PCBs are as follows:
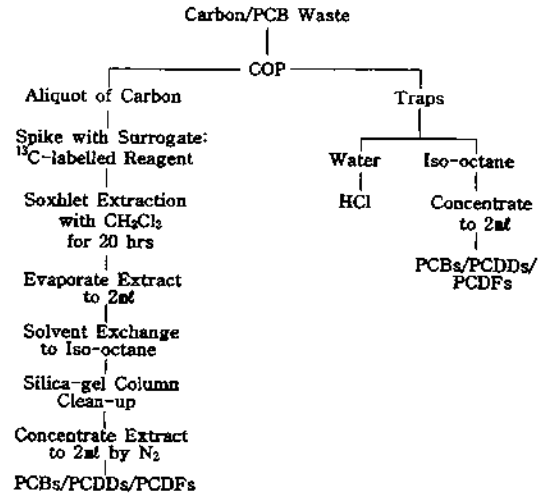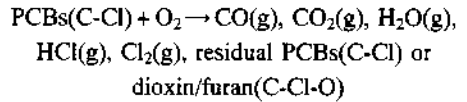

Fig. 4. A Flow schematic of experimental protocol.

$$PCBs(C\text{-}Cl) + O_2 \rightarrow CO(g), CO_2(g), H_2O(g),$$
$$HCl(g), Cl_2(g), \text{residual } PCBs(C\text{-}Cl) \text{ or}$$
$$\text{dioxin/furan}(C\text{-}Cl\text{-}O)$$

A comprehensive experimental procedure was presented in *Fig.* 4 as a flow schematic. The schematic was subjected to removal and destruction efficiency of PCBs in a quantitative manner and characterization of dioxin/furan. The relative concentration of the PCBs in carbon before and after treatment, or the ultimate mineralized product such as HCl in the impinger traps was employed to determine the removal and destruction efficiency of PCBs. The process was run in successive cycles. Removal and destruction efficiecy of 95.56% was achieved at first cycle. The efficiency was more or less low due to the flame occuring inconsistently at times because of high amounts of PCB-laden oil. At second cycle, destruction efficiency of PCBs showed 97.59%, increased slightly over the first cycle. Destruction efficiency at third cycle was considerably higher with the value of $\geq$ 99.99%. The result convinces that complete destruction of PCBs can be achieved with three successive COP cycles and, in view of results achieved, it proves that the COP is very effective thermal treatment method for disposal of PCBs.

The possible formation of other toxic chlor-

inated compounds not originally present in the oil was monitored because of the fact that the formation of dioxin/furan from pyrolysis-combustion of PCBs at 300 °C in the presence of air was reported by many papers.[19,20] Other potentially toxic chemicals such as dioxin/furan in this study
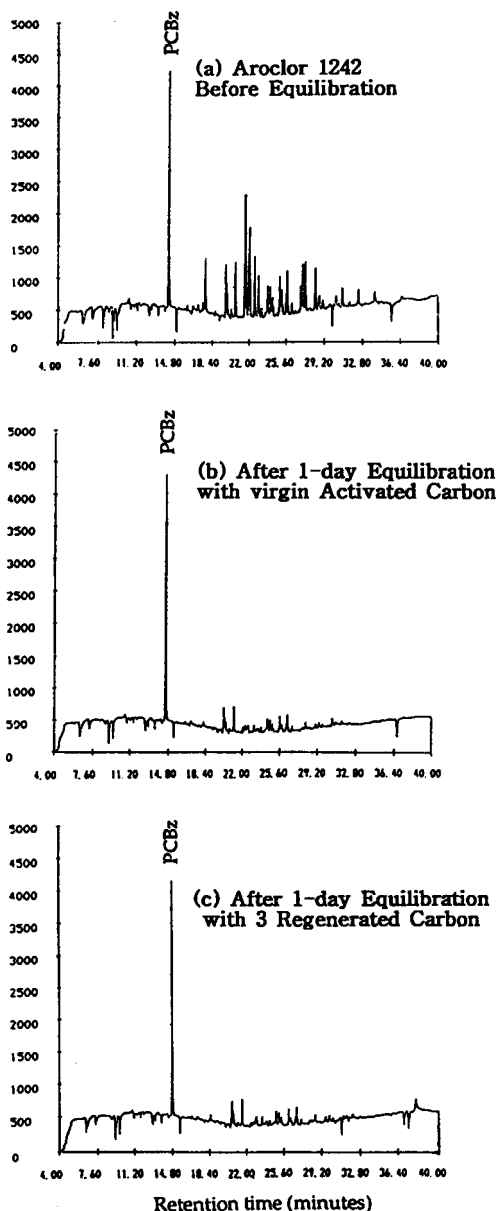

Fig. 5. Chromatograms of (a) Aroclor 1242 before equilibration, (b) after 1-day equilibration with virgin activated carbon, and (c) after 1-day equilibration with 3 regenerated carbon.

were not found above a detection limit of 5 ppb in the thermal treatment residues and exhaust gases. This result is attributed to the extremely high flame temperature and the presence of appreciable hydrogen which combines with the released chlorine.

The efficiency of COP is affected by restoration of carbon's adsorptive capacity for the further adsorption. Virgin activated carbon and carbon regenerated by COP were therefore examined to compare the behavior of adsoptive capacity. Adsorption experiments were carried out with the oil containing a mixture of PCBs (Aroclor 1242). Fig. 5(a) shows the chromatogram of Aroclor 1242 before equilibration of carbon and PCB-containing oil. Fig. 5(b, c) represents the chromatograms after 24 hr equilibration. The results showed that the adsorption efficiencies of virgin and regenerated carbon were $\geq 95\%$. It means that the adsorptivity of regenerated carbon remains largely intact compared with that of virgin activated carbon. The confidence was also supported by the surface area measurement which showed little change in surface area of regenerated carbon even after three successive cycles. Conclusively, it is thought that a combination of chemical and thermal treatment by COP is quite effective in completely destroying PCBs without permitting any toxic by-products, allowing the reuse of adsorbent.

CONCLUSION

The destruction of PCBs in transformer oil was conducted with a combined chemical with thermal treatment by COP. The destruction of PCBs suspended on appropriate adsorbent after oil circulations was practically complete, showing destruction efficiency $\geq 99.99\%$. Furthermore, no unwanted by-products such as PCDDs or PCDFs were detected at concentration greater than 5 ppb in the process residues or off gases. Another interesting feature of the process is that it permits high recovery of oil and resource materials such as inorganic supports and metals from transformer, as well as the adsorbent used in the thermal treatment.

Thus, a combination of these two treatment processes appears to be highly effective and economical.

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