Organic Process Research & Development **2010,** *14,* 1140–1146

# Pilot-Plant Study of the PCB Degradation at Ambient Temperature and Pressure

Yasunari Monguchi,[†] Shinji Ishihara,[†] Akiko Ido,[‡] Miki Niikawa,[‡] Koichi Kamiya,[§] Yoshinari Sawama,[†] Hisamitsu Nagase,[‡] and Hironao Sajiki*,[†]

*Laboratory of Organic Chemistry, Department of Organic and Medicinal Chemistry, Gifu Pharmaceutical University, 1-25-4 Daigaku-nishi, Gifu 501-1196, Japan, Laboratory of Hygienic Chemistry and Molecular Toxicology, Department of Biopharmaceutical Sciences, Gifu Pharmaceutical University, 1-25-4 Daigaku-nishi, Gifu 501-1196, Japan, and Ogaki Plant Sangyou, 3-38-1 Mangoku, Ogaki-shi, Gifu 503-0812, Japan*

## Abstract:

**A continuous pilot plant for the degradation of polychlorinated biphenyls (PCBs) by the palladium on carbon (Pd/C)-catalyzed hydrogenation in the presence of triethylamine was designed and constructed. Both undiluted PCBs obtained from a capacitor and diluted PCBs with desulfurized trans oil were smoothly decomposed at ambient temperature and pressure. Desulfurization of the trans oil was found to be essential for the efficient degradation due to the possible deactivation of the Pd/C by catalysis poisoning due to the sulfur-containing materials in the oil. The combined use of the present degradation method and the catalytic desulfurization technology for the purification of gasoline and kerosene could be used in practical applications.**

## Introduction

Polychlorinated biphenyls (PCBs), which consist of 209 congeners possessing different numbers and substitution patterns of chlorine atoms on the biphenyl nucleus, used to be globally employed as an electric insulating oil, lubricant, and coolant in electrical devices such as transformers and capacitors due to their high resistance to acids, bases and heat, nonflammability, and electrical insulation. However, their production and novel use were banned in the mid 1970s since the chemical and physical stabilities of PCBs as well as their highly lipophilic property were found to cause a serious persistent environmental pollution, including bioaccumulations and biomagnifications through the food chain.[1] The toxicity of PCBs in living animals is responsible for skin and liver damages, cancer, and endocrine disruption.[2] The PCBs in general could be decomposed by combustion using high-temperature incinerators (above 1100 °C), while the combustion below 1100 °C creates the possibility to generate dioxins;[3] hence, it is even difficult to reach an agreement by local communities for the construction of the incinerator. Therefore, tons of PCBs have been stored by each facility under the strict conditions of each country's laws. However, a huge expense and fear of improper disposal and accidental leaking of PCBs by an earthquake, unexpected war, etc., have increased with the longer periods of storage.[4] To avoid further expansion of pollution, the United Nations Environment Programme Global Treaty adopted at the Stockholm Convention on Persistent Organic Pollutants in 2001 stipulated that the elimination of all liquids and equipment containing PCBs would be completed by 2028.[5] The remediation techniques of PCBs currently under development are hydride reduction,[6] hydrodechlorination,[7] dechlorination using metals,[8] photolysis[9] and $\gamma$-radiation,[10] oxidation,[11] electrolysis,[12] mechanochemical degradation,[13] etc. However, most processes require harsh reaction conditions such as high temperature and pressure, radiation, stoichiometric reagents, and strongly basic conditions; in addition, many of the reported remediation methods could not achieve the complete degradation of PCBs.

---

* Author for correspondence. Telephone/Fax: 81-58-230-8109. E-mail: sajiki@gifu-pu.ac.jp.

[†] Laboratory of Organic Chemistry, Department of Organic and Medicinal Chemistry, Gifu Pharmaceutical University.

[‡] Laboratory of Hygienic Chemistry and Molecular Toxicology, Department of Biopharmaceutical Sciences, Gifu Pharmaceutical University.

[§] Ogaki Plant Sangyou.

(1) (a) Erickson, M. D. In *Analytical Chemistry of PCBs*, 2nd ed.; CRC Press: Boca Raton, 1997; p 1. (b) Blais, J. M.; Schindler, D. W.; Muir, D. C. G.; Kimpe, L. E.; Donald, D. B.; Rosenberg, B. Nature **1998**, *395*, 585. (c) *Toxicological Profile for Polychlorinated Biphenyls;* U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry: Atlana, GA, 2000; http://www.atsdr.cdc.gov/toxprofiles/tp17.pdf.

(2) (a) Nelson, J. A. Biochem. Pharmacol. **1974**, *23*, 447. (b) Gilbertson, M.; Kubiak, T. J.; Ludwig, J. P.; Fox, G. A. J. Toxicol. Environ. Health **1991**, *33*, 455. (c) Arnold, S. F.; Klotz, D. M.; Collins, B. M.; Vonier, P. M.; Guillette, L. J., Jr.; McLachlan, J. A. Science **1996**, *272*, 1489. (d) Mayes, B. A.; McConnell, E. E.; Neal, B. H.; Brunner, M. J.; Hamilton, S. B.; Sullivan, T. M.; Peters, A. C.; Ryan, M. J.; Toft, J. D.; Singer, A. W.; Brown, J. F., Jr.; Menton, R. G.; Moore, J. A. Toxicol. Sci. **1998**, *41*, 62.

(3) Erikson, M. D.; Cole, C. J.; Flora, J. D., Jr.; Gorman, P. G.; Haile, C. L.; Hinsshaw, G. D.; Hopkins, F. C.; Swanson, S. E. Chemosphere **1985**, *14*, 855.

(4) Meharg, A. A.; Osborn, D. Nature **1995**, *375*, 353.

(5) (a) *PCB Transformers and Capacitors: From Management to Reclassification and Disposal. The United Nations Environment Programme*, 2nd issue; UNEP Chemicals: Geneva, Switzerland, 2002; http://www.chem.unep.ch/Pops/pdf/PCBtranscap.pdf. (b) *Inventory of World-Wide PCB Destruction Capacity. The United Nations Environment Programme*, 2nd issue; UNEP Chemicals: Geneva, Switzerland, 2004; http://www.chem.unep.ch/pops/pcb_activities/pcb_dest/PCB_Dest_Cap_SHORT.pdf.

(6) (a) Roth, J. A.; Dakoji, S. R.; Hughes, R. C.; Carmody, R. E. Environ. Sci. Technol. **1994**, *28*, 80. (b) Liu, Y.; Schwartz, J.; Cavallaro, C. L. Environ. Sci. Technol. **1995**, *29*, 836. (c) Liu, Y.; Schwartz, J. Tetrahedron **1995**, *51*, 4471. (d) Lassova, L.; Lee, H. K.; Hor, T. S. A. J. Org. Chem. **1998**, *63*, 3538. (e) Pittman, C. U., Jr.; Yang, C. J. Hazard. Mater. **2001**, *B82*, 299.

(7) (a) Anwer, M. K.; Spatola, A. F. Tetrahedron Lett. **1985**, *26*, 1381. (b) Anwer, M. K.; Sherman, D. B.; Roney, J. G.; Patola, A. F. J. Org. Chem. **1989**, *54*, 1284. (c) Marques, C. A.; Selva, M.; Tundo, P. J. Org. Chem. **1994**, *59*, 3830. (d) Ghattas, A.; Abu-Reziq, R.; Avnir, D.; Blum, J. Green Chem. **2003**, *5*, 40.

10.1021/op100107r

The Japan Environmental Safety Corporation (JESCO) was established in April, 2001, by the Japanese government to eliminate PCBs and owns five commercially operating PCB degradation facilities in Hokkaido, Tokyo, Toyota, Osaka, and Kitakyushu. The methods adopted at the five facilities, which are sodium dispersion (Hokkaido, Toyota, and Kitakyushu), hydrothermal decomposition (Tokyo), and hydrodechlorination (Osaka) methods, require strongly basic conditions, high temperature or/and high pressure. Accidental leakage and exposure of PCBs have taken place at least in the Toyota and Tokyo facilities,[14] and the elimination of PCBs in Japan is very slow in spite of the looming deadline established by the Stockholm Convention on Persistent Organic Pollutants. We recently established an efficient method for the palladium on carbon (Pd/C)-catalyzed hydrodechlorination of aromatic chlorides using triethylamine ($Et_3N$) as a single electron donor at ambient temperature and pressure.[15] The method has been successfully applied for the detoxification of DDTs[16] and PCBs[17] (especially highly toxic coplanar PCBs) based on the removal of the chlorine atoms from the biphenyl nuclei. In this contribution, the design and construction of a continuous pilot plant and its verification tests for the PCB degradation using our Pd/C−$Et_3N$ method are described.

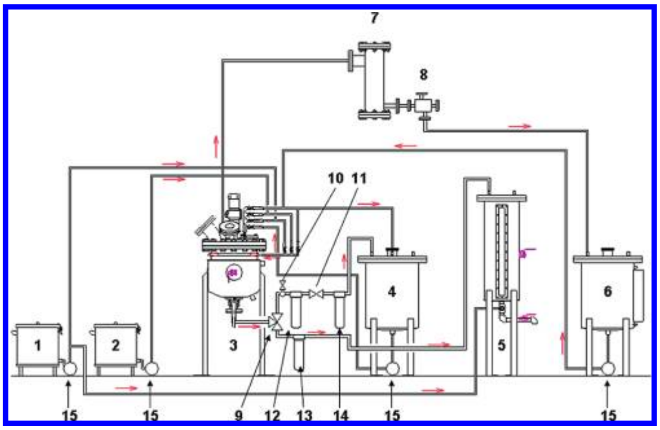


***Figure 1.*** **Schematic diagram of the reaction mixture. 1, water tank; 2, heptane tank; 3, stirred reactor; 4, receiver; 5, separator; 6, methanol tank; 7, condenser (5 °C); 8, condenser (−20 °C); 9, in-line three-way valve; 10, valve; 11, in-line valve; 12, stainless steel filter (2 $\mu$m); 13, cotton filter (1 $\mu$m); 14, cotton filter (0.5 $\mu$m); 15, pump.**

## Results and Discussion

**Design of the Pilot Plant.** The pilot plant mainly consists of four stainless steel vessels as shown in Figure 1: **3**, 50 L-stirred reactor; **4**, receiver; **5**, separator; **6**, methanol tank. The Pd/C-catalyzed degradation reaction of the PCBs in MeOH is carried out in the reactor (**3**) under a hydrogen atmosphere, and then the reaction mixture is transferred to the receiver (**4**) through a stainless steel 2 $\mu$m filter (**12**) and a subsequent 0.5 $\mu$m cotton filter (**14**) which effectively remove and recover the Pd/C. The filtrate is returned to **3** using the pump (**15**) and concentrated under reduced pressure (150 Torr) around 35 °C (60 °C water jacket temperature). The MeOH vapor is cooled in two serially cascaded refrigeration condensers (**7** and **8**) at different temperatures (**7**: 5 °C; **8**: −20 °C), therefore, efficiently condensed and nearly quantitatively collected in the MeOH tank (**6**). The residue in **3** is dissolved with $H_2O$ and heptane charged from the water (**1**) and heptane (**2**) tanks, respectively. The resulting two-phase mixture is passed through a 1 $\mu$m cotton filter (**13**) and transferred to the separator (**5**), where the generated triethylammonium chloride and biphenyl are separated in the $H_2O$ and heptane layers, respectively.

The reactor (**3**, see Figure 2) is equipped with a stirrer (**16**) connected to a rotary impeller, a drain (**17**) leading to the receiver (**4**), a sampling valve (**18**) for withdrawing a small amount of the reaction mixture to confirm the reaction progress, and four spray nozzles (**19**). Each nozzle (**19**), which is directed obliquely upward, produces a cone-shaped fog spray with an angle of more than 100°, and the inside wall of **3** can be washed

---

(8) (a) Yak, H. K.; Wenclawiak, B. W.; Cheng, I. F.; Doyle, J. G.; Wai, C. M. *Environ. Sci. Technol*. **1999**, *33*, 1307. (b) Chuang, F.-W.; Larson, R. A.; Wessman, M. S. *Environ. Sci. Technol*. **1995**, *29*, 2460. (c) Grittini, C.; Malcomson, M.; Fernand, Q.; Korte, N. *Environ. Sci. Technol*. **1995**, *29*, 2898. (d) Wang, C.-B.; Zhang, W.-X. *Environ. Sci. Technol*. **1997**, *31*, 2154. (e) Jackman, S. A.; Knowles, C. J.; Robinson, G. K. *Chemosphere* **1999**, *38*, 1889. (f) Yak, H. K.; Wenclawiak, B. W.; Cheng, I. F.; Doyle, J. G.; Wai, C. M. *Environ. Sci. Technol*. **1999**, *33*, 1307. (g) Arienzo, A.; Chiarenzelly, J.; Scrudato, R.; Pagano, J.; Falanga, L.; Connor, B. *Chemosphere* **2001**, *48*, 1339. (h) He, F.; Zhao, D. *Environ. Sci. Technol*. **2005**, *39*, 3314. (i) Wu, W.; Xu, J.; Zhao, H.; Zhang, Q.; Liao, S. *Chemosphere* **2005**, *60*, 944.

(9) (a) Zhang, P.; Scrudato, R.; Pagano, J.; Roberts, R. *Chemosphere* **1993**, *26*, 1213. (b) Huang, I. W.; Hong, C. S.; Bush, B. *Chemosphere* **1996**, *32*, 1869. (c) Lin, Y.; Gupta, G.; Baker, J. *J. Hazard. Mater*. **1996**, *45*, 259. (d) Huang, Q.; Hong, C. S. *Chemosphere* **2000**, *41*, 871. (e) Manzano, M. A.; Perales, J. A.; Sales, D.; Quiroga, J. M. *Chemosphere* **2004**, *57*, 645. (f) Lin, Y. J.; Teng, L. S.; Lee, A.; Chen, Y. L. *Chemosphere* **2004**, *55*, 879.

(10) (a) Arbon, R. E.; Mincher, B. *J. Environ. Sci. Technol*. **1994**, *28*, 2191. (b) Arbon, R. E.; Mincher, B. *J. Environ. Sci. Technol*. **1996**, *30*, 1866. (c) Schmelling, D. C.; Poster, D. L.; Chaychian, M.; Neta, P.; Silverman, J.; Al-sheikhly, M. *Environ. Sci. Technol*. **1998**, *32*, 270. (d) Chaychian, M.; Silverman, J.; Al-Shieikhly, M. *Environ. Sci. Technol*. **1999**, *33*, 2461.

(11) (a) Sediak, D. L.; Andren, A. W. *Environ. Sci. Technol*. **1991**, *25*, 1419. (b) Brubaker, W. W., Jr.; Hites, R. A. *Environ. Sci. Technol*. **1998**, *32*, 3913. (c) Duffy, J. E.; Anderson, M. A.; Hill, C. G., Jr. *Environ. Sci. Technol*. **2000**, *34*, 3199.

(12) (a) Connors, T. F.; Rusling, J. F. *Chemosphere* **1984**, *13*, 415. (b) Zhang, S.; Rusling, J. F. *Environ. Sci. Technol*. **1993**, *27*, 1375. (c) Huang, Q.; Usling, J. F. *Environ. Sci. Technol*. **1995**, *29*, 98.

(13) (a) Zhang, Q.; Saito, F.; Ikoma, T.; Tero-kubota, S.; Hatakeda, K. *Environ. Sci. Technol*. **2001**, *35*, 4933. (b) Pizzigallo, M. D. R.; Napola, A.; Spagnuolo, M.; Ruggiero, P. *Chemosphere* **2004**, *55*, 1485.

(14) Japanese reports are only available on the Web. (a) *Ministry of the Environment of the Japan Goverment, Basic Plan of the Treatment of Polychlorinated Biphenyl Wastes*, **2007**; http://www.env.go.jp/recycle/poly/plan/191018.pdf. (b) *Japan Environmental Safety Corporation, Environmental Report;* **2007**; http://www.jesconet.co.jp/company/pdf/environrep2007m.pdf. (c) *Japan Environmental Safety Corporation, Regarding the Accidental Leakage of PCBs in the Toyota Facility;* **2006**; http://www.jesconet.co.jp/facility/toyota/pdf/toyotajikohoniinkai.pdf. (d) *Japan Environmental Safety Corporation, Report of the Accident: Regarding the Accidental Leakage of a Trace Quantity of PCB-containing Liquid Waste at the Tokyo Facility* ; **2006**; http://www.jesconet.co.jp/facility/tokyo/pdf/tokyojikorep060331.pdf. (e) *Japan Environmental Safety Corporation, Report of the Accident: Regarding the Accidental Leakage of a Trace Quantity of PCB-containing Exhaust Emission at the Tokyo Facility;* **2006**; http://www.jesconet.co.jp/facility/tokyo/pdf/tokyojikorep060602.pdf.

(15) (a) Sajiki, H.; Kume, A.; Hattori, K.; Hirota, K. *Tetrahedron Lett*. **2002**, *43*, 7247. (b) Monguchi, Y.; Kume, A.; Hattori, K.; Maegawa, T.; Sajiki, H. *Tetrahedron* **2006**, *62*, 7926.

(16) Monguchi, Y.; Kume, A.; Sajiki, H. *Tetrahedron* **2006**, *62*, 8384.

(17) (a) Sajiki, H.; Kume, A.; Hattori, K.; Nagase, H.; Hirota, K. *Tetrahedron Lett*. **2002**, *43*, 7251. (b) Kume, A.; Monguchi, Y.; Hattori, K.; Nagase, H.; Sajiki, H. *Appl. Catal., B* **2008**, *81*, 274.

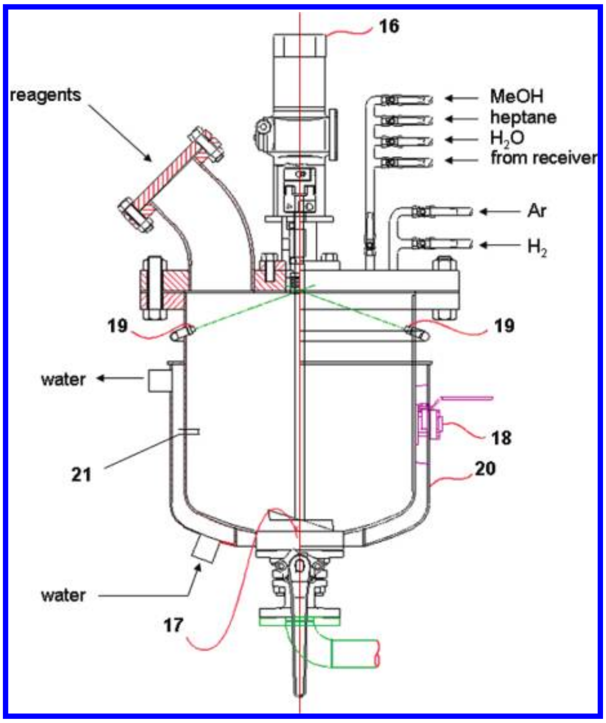


*Figure 2.* **Schematic diagram of planned reactor (3). 16, stirrer equipped with a rotary impeller; 17, drain; 18, sampling valve; 19, spray nozzle; 20, heating jacket; 21, temperature sensor.**

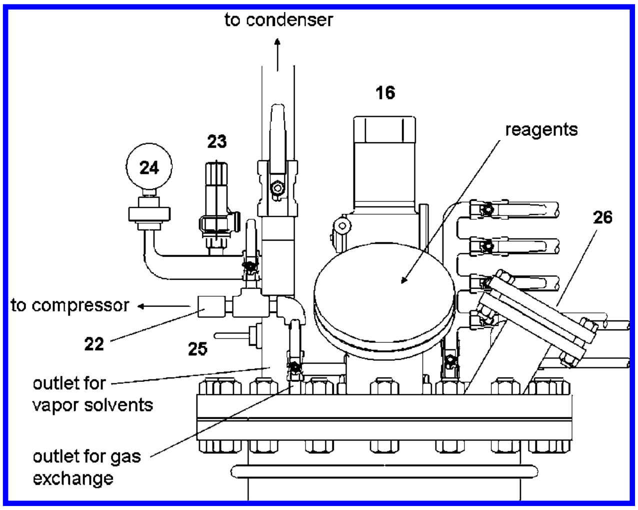


*Figure 3.* **Upper part of reactor 3. 22, aspirator; 23, safety valve; 24, pressure gauge; 25, temperature sensor; 26, window.**

with a fine mist (approximately 140−160 μm) of MeOH, heptane, and water carried from each tank (**1**, **2**, and **6**). A heating jacket (**20**) is designed to control the temperature of the reaction mixture during the reductive dechlorination and heat the filtered reaction mixture for the distillation of MeOH under reduced pressure in the reactor (**3**). The reaction temperature is monitored by a temperature sensor (**21**). As shown in Figures 3 and 4, two inlets for gases (Ar and $H_2$) and solvents are provided, which can be regulated by separate valves, and gas exchange and vapor solvents removal outlets are also provided on the top of **3**. The outlet for the gas exchange is connected to an air compressor which serves as an aspirator (**22**) and the inside air (oxygen gas) is efficiently exhausted. The stainless steel pipe from the outlet for the vapor solvents (Figures 3 and 4) to methanol tank (**6**) via condensers (**7** and **8**) is equipped with a safety valve (**23**), a pressure gauge (**24**), and a temperature sensor for the vapors (**25**). The stirring of the impeller and amount of the solvent can be checked from an inspection window (**26**) by shining a light through another window (**27**).

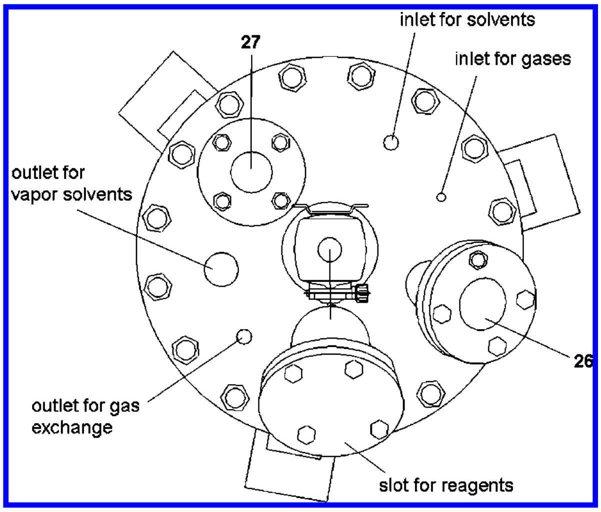


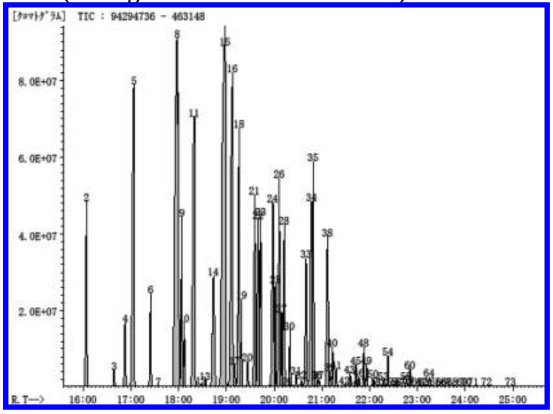
*Figure 4.* **Top of the reactor 3. 26 and 27, inspection windows.**

The plant was also designed with the safety of the personnel and the public in mind. Three different types of valves for the filtration system (**9**, **10**, and **11** in Figure 1) are installed. After the filtration of the reaction mixture through **12** and **14**, the pipe line is first closed using a three-way cock (**9**) to prevent back-flow of the Pd/C-suspended solvents from the filter (**12**) to the reactor (**3**), and the valve (**10**) is then opened. The stainless steel filter is filled with water through **10** to avoid ignition of the Pd/C. The cotton filter (**14**) can also be filled with water through the valve on top of the filter (**14**, the valve is not shown in Figure 1) bottle in a similar manner. A huge stainless steel pan, which can contain more than the total volume of the reactor contents is installed under the entire plant to avoid accidental spillage of the PCBs. Two exhaust pipe lines are also installed in the pilot plant, and emission gases are exhausted through a −50 °C cold trap and activated carbon filters. The pilot plant was finally constructed as designed (Figure 5), and verification tests were carried out.

**Degradation of PCBs.** Undiluted PCBs obtained from an old capacitor manufactured by the Nichicon Corporation, Kyoto, Japan, in 1964, which was previously in practical use at our university, was first examined as a high-concentration PCB substrate for the pilot scale degradation. The GC/MS analysis indicated that the average chlorine number is 3.42 according to Hor's calculation method (see Table 1 in the Experimental Section). The PCBs (1.49 kg) were dissolved in MeOH (15 L, $1.11 \times 10^5$ ppm of PCBs) in the 50 L-reactor (**3**), and $Et_3N$ (3.67 L, 1.28 equiv vs chlorine number) and 10% Pd/C (wet-type, 450 g, 30 wt % of the PCBs) were added in sequence. The mixture was mechanically stirred at 255 rpm and 25−30 °C under 1 atm of $H_2$. After 24 h, the mixture was filtered and concentrated at 60 °C in vacuo (450−160 Torr). The resulting residue was partitioned between heptane (8 L) and water (5 L) and then transferred to the separator (**5**), and the reactor was

***Figure 5.*** **Continuous pilot plant for the degradation of PCBs under mild conditions.**

***Table 1.*** **Distribution of PCB congeners obtained from capacitor (average chlorine numbers: 3.42)**



| chlorine number | 1 | 2 | 3 | 4 | 5 | 6 | 7−10 |
|---|---|---|---|---|---|---|---|
| abundance ratio (%) | − | 7.2 | 40.8 | 33.3 | 17.8 | 0.9 | trace |

also washed using additional heptane (8 L) and water (5 L). The combined heptane and water layers were clearly separated and analyzed by GC/MS. When the GC/MS was operated in the split mode (split ratio, 100:1), no peaks for the PCBs, but totally dechlorinated biphenyl were detected from both layers as shown in panels b and d of Figure 6. However, the use of splitless mode showed a peak for 2,2′,6,6′-tetrachlorobiphenyl with a very weak intensity together with other small peaks possibly derived from nonchlorinated benzene oligomers [Figure 6c], the formation of which was suggested from GC/MS. The PCB concentration contained in the heptane layer was measured by high-resolution mass spectrometry using a JEOL MStation (JMS-700) spectrometer; the total concentration of the PCBs was 26 ppm, and 2,2′,6,6′-tetrachlorobiphenyl was virtually the only product. Although 2,2′,6,6′-tetrachlorobiphenyl is extremely hindered and a stable compound and, hence, resists the present hydrodechlorination,[17b] it is quite less toxic than other PCB congeners and excluded from the concept of the toxicity equivalency factor, since two benzene rings cannot be located on the same plane unlike the highly toxic coplanar PCBs and dioxins.

The detoxification of the dilute PCBs was next investigated using the continuous pilot plant. Huge amounts of PCBs diluted by trans oil, which were used as insulators for transformers and capacitors, have been stored by each facility for a prolonged period, and too much obligation and accountability have been imposed on the PCB-waste owners. Therefore, the construction of secure, safe, and convenient PCB degradation plants is an urgent issue.

To determine the applicability of the present pilot-plant scale method for the degradation of commercial PCBs, Aroclor 1248 (450 mg, Monsanto Chemical Co., average chlorine number: 3.93), diluted (100 ppm) by commercial trans oil (5 L, purchased from Matsumura Sekiyu, Osaka, Japan), the reaction was performed in MeOH using the continuous pilot plant in a manner similar to the degradation of highly concentrated PCBs. However, the PCBs were not completely consumed even after a 24-h reaction at room temperature as shown in Figure 7c. The low conversion was attributed to the contamination of sulfur-containing materials in the trans oil derived from petroleum (180 ppm by the oxygen bomb combustion ion chromatography), which could deactivate the Pd/C and lead to an incomplete reaction. On the other hand, the Aroclor 1248 diluted (100 ppm) with the desulfurized trans oil, which was washed with concentrated sulfuric acid prior to use, was effectively hydrodechlorinated, and virtually no PCBs were detected in the heptane extracts by GC/MS (Figure 7d), although it was clarified that 2.0 ppm of the PCBs was still contained in the extracts based on the high-resolution mass spectrometry analysis. Since 25 ppm of the sulfur contaminants was still detected in the desulfurized trans oil, the more efficient desulfurization of the trans oil prior to the reaction would be expected to allow the complete decomposition.

## Conclusion

The continuous pilot plant for the degradation of the PCBs based on the hydrodechlorination technique using 10% Pd/C and triethylamine in MeOH was designed with personnel and public health safety in mind. Both high- and low-concentrated PCBs were smoothly decomposed under ambient temperature and pressure in the pilot plant. The pilot plant would be useful for the practical degradation, in particular, of diluted PCBs by the establishment of an efficient desulfurization system.

## Experimental Section

**Reagents.** Aroclor 1242 was manufactured by the Monsanto Chemical Co. (St. Louis, MO). Concentrated (nondiluted) used PCBs were drained from a capacitor manufactured by the Nichicon Corporation (Kyoto, Japan, TPA-66050R, manufactured in 1964), and the average chlorine numbers were found to be 3.42 by Hor's calculation.[6d] From the N.E. Chemcat Co. (Tokyo, Japan), Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and Kanto Chemical Co., Inc. (Tokyo, Japan) were purchased 10% Pd/C (wet-type), which contains 50 wt % water, $Et_3N$, and MeOH, respectively. Concentrated $H_2SO_4$ was obtained from Wako Pure Chemical Industries, Ltd. The trans oil (Barrel trans M) was purchased from Matsumura Sekiyu (Osaka, Japan).

**Degradation of Highly Concentrated (Undiluted) PCBs [PCBs from a Capacitor (Average Chlorine Number: 3.42)].** MeOH (15 L) was transferred from the MeOH tank to a 50-L stainless steel reactor by an electric pump, and the PCBs (1.49

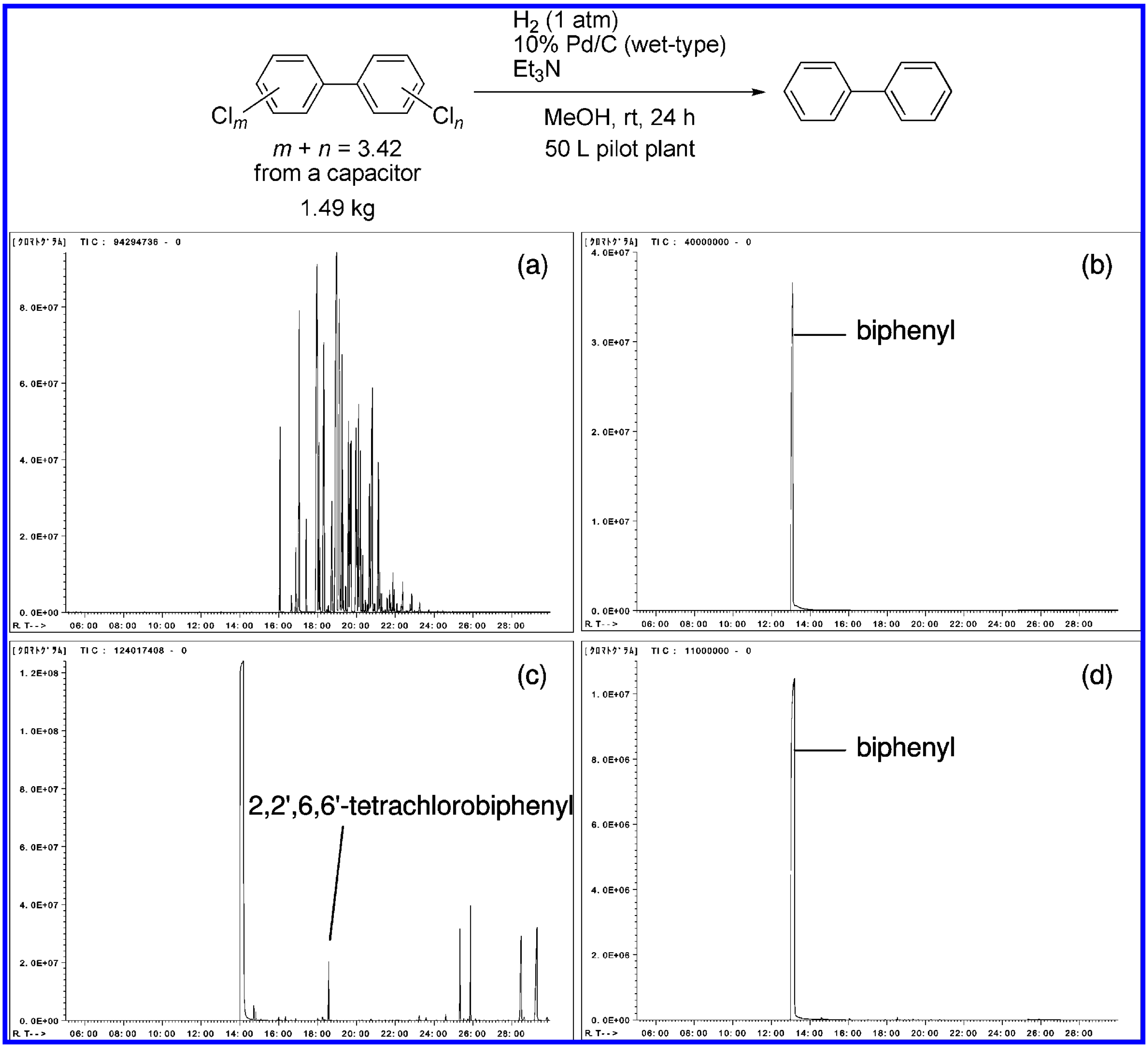


***Figure 6.*** **Pilot-plant study for the undiluted PCB degradation for the Pd/C−$H_2$−$Et_3N$ system. GC charts: (a) before the degradation of PCBs from a capacitor; (b) heptane extracts after the degradation, split mode; (c) heptane extracts after the degradation, splitless mode; (d) aqueous extracts after the degradation, splitless mode. (No PCB peaks were also detected in the split mode.)**

kg, 5.50 mol), $Et_3N$ (3.67 L, 26.3 mol), and 10% Pd/C (wet-type, 450 g) were successively added. The air inside the reactor was replaced with hydrogen (1 atm), and the pressure was maintained at 1.0−1.1 atm. The mixture was then kept at 25−30 °C by regulated water in the jacket around the reactor, and stirred at 255 rpm. After 24 h, the hydrogen was replaced with argon, and the 10% Pd/C was removed by successive in-line filtration through a 2 $\mu$m stainless steel filter and a 0.5 $\mu$m cotton filter using medium pressure argon. The filtrate collected in a transit tank was transferred to the reactor, and concentrated under reduced pressure (450−160 Torr) until the formation of solid was observed. The reactor was cooled to 10 °C by the chilled water in the jacket, and heptane (8 L) and water (5 L) were then added using pumps. The mixture was stirred at 400 rpm for 15 min, and then transferred to a separatory tank. The reactor was washed again with more heptane (8 L) and water (5 L) in the same way. The two layers were separated and assayed using GC/MS (split and splitless modes) and high resolution GC/MS analyses. While the GC/MS of the heptane layer showed no PCB peaks in the split mode, a weak peak derived from the PCBs, for 2,2′,6,6′-tetrachlorobiphenyl, was observed in the splitless mode. No PCBs, except for biphenyl, were detected in the aqueous layer. The quantitative analyses of the heptane layer using high resolution mass spectrometry, which were carried out at the Nihon Environmental Services, Co., Ltd. (Tokyo, Japan) using a JEOL JMS-700 spectrometer, clarified that the total PCB concentration was 26 ppm and that 2,2′,6,6′-tetrachlorobiphenyl accounted for 96% (25 ppm out of 26 ppm) of the product.

**Degradation of Diluted Aroclor 1248 with Trans Oil.** Nonsulfurized trans oil (7 L), MeOH (7 L), Aroclor 1248 (630 mg, 2.18 mmol), $Et_3N$ (11.9 mL, 85.4 mmol), and 10% Pd/C (wet-type, 280 g) were successively added to a 50-L stainless steel reactor. The air inside the reactor was replaced with hydrogen (1 atm), and the pressure was maintained at 1.0−1.1 atm. The mixture was then kept at 25−30 °C, by regulated water

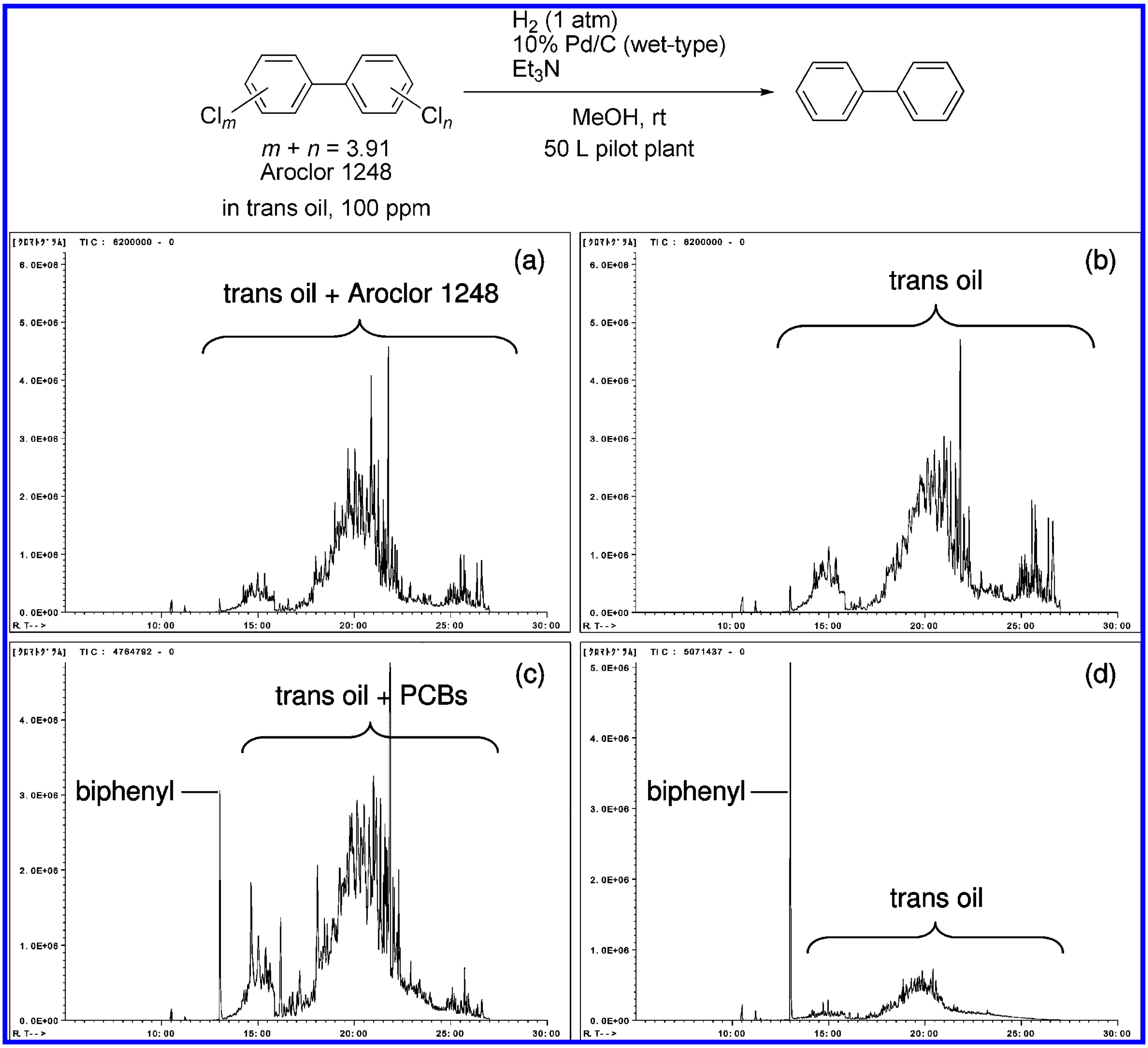


*Figure 7.* **Pilot-plant study for the diluted PCB degradation for the Pd/C−$H_2$−$Et_3N$ system. GC charts: (a) before the degradation of Aroclor 1248 diluted with trans oil; (b) trans oil; (c) heptane extracts after the degradation of Aroclor 1248 diluted with nondesulfurized trans oil; (d) heptane extracts after the degradation of Aroclor 1248 diluted with desulfurized trans oil, measured by GC/MS-selective ion monitoring (GC/MS-SIM) in the splitless mode. Since the GC peaks of trans oil overlapped with those of PCBs, the heptane extracts for (c) and (d) were washed by simple extraction using DMSO to remove the oil components as much as possible before the GC measurements (see Experimental Section).**

in the jacket around the reactor, and stirred at 320 rpm. After 6 h, the mixture was filtered, concentrated, and partitioned between the heptane and water layers in the same manner as described for the degradation of the undiluted PCBs. Since the obtained heptane layer contained a large amount of trans oil, the GC peaks, which overlapped with those of the PCBs, was washed by the simple extraction using DMSO to remove the oil components as much as possible. An aliquot of the heptane layer (1 mL) was sampled and diluted with hexane (20 mL), and then the mixture was extracted with DMSO (25 mL × 4). The combined DMSO layers were washed with hexane (40 mL), diluted with $H_2O$ (100 mL), and extracted with hexane (75 mL × 3). The combined hexane layers were concentrated to 1 mL and then used as a sample for the GC/MS-SIM (see in the GC/MS analyses below). The quantitative high-resolution GC/MS analyses of the heptane layer in the separator (**5**) indicated that the PCB concentration was 31 ppm.

**Desulfurization of Trans Oil.** To a 10-L separatory funnel equipped with a Teflon propeller were added trans oil (3 L) and conc. $H_2SO_4$ (1 L), and the mixture was electrically stirred at 500 rpm for 30 min and then allowed to stand for 30 min. The $H_2SO_4$ layer was removed, and the oil was successively washed with more conc. $H_2SO_4$ (1 L) and hot water (1 L × 3) in the same manner. This oil was used as desulfurized trans oil.

**Degradation of Diluted Aroclor 1248 with Desulfurized Trans Oil.** Desulfurized trans oil (5 L), MeOH (10 L), Aroclor 1248 (450 mg, 1.56 mmol), $Et_3N$ (8.5 mL, 61.0 mmol), and 10% Pd/C (wet-type, 50 g) were successively added to a 50-L stainless steel reactor. The air inside the reactor was replaced with hydrogen (1 atm), and the pressure was maintained at 1.0−1.1 atm. The mixture was kept at 25−30 °C by regulated water in the jacket around the reactor, and stirred at 360 rpm. After 24 h, the mixture was filtered, concentrated, and partitioned between the heptane and water layers, and then the sample for the GC/MS-SIM was prepared in the same manner described for the degradation of the diluted Aroclor 1248 by the nondesulfurized oil (see the GC/MS analyses below). The quantitative high resolution GC/MS analyses of the heptane layer in the separator (**5**) indicated that PCB concentration was 2 ppm.

**GC/MS Analysis.** An aliquot of the heptane extracts was analyzed using a JEOL JMS Q1000GC Mk II Quad GC/MS and an InertCap 5MS/Sil+GD capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness, GL Science) in the split (split ratio: 100: 1) and splitless modes for the highly concentrated PCBs and in the splitless mode for the dilute PCBs with trans oil. Helium was employed as the carrier gas at the flow rate of 1.5 mL/min. The injector and detector temperatures were both 280 °C. The column temperature was programmed to ramp from 70 °C (5 min hold) to 280 °C (4 min hold) at the rate of 10 °C/min and then to be held at 280 °C for 4 min. The injected sample amount was 1 μL. The highly concentrated PCBs were measured in both the split (split ratio, 100: 1) and splitless modes. The GC/MS-selected ion monitoring (GC/MS-SIM) method was adopted for the analysis of the diluted PCBs containing trans oil due to the difficult identification of the PCB peaks by overlapping with the trans oil peaks even after the oil-component removal process. The selected ions derived from the PCBs were as follows: 154, 188, 190, 222, 224, 256, 258, 290, 292, 324, 326, 360, 362, 394, 396, 428, 430, 462, 464, 498, and 500.

## Acknowledgment

We sincerely appreciate the strong support by the New Energy and Industrial Technology Development Organization (NEDO), Japan.

Received for review April 19, 2010.

OP100107R