Thermo-chemical destruction of polychlorinated biphenyls (PCBs) in waste insulating oil

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Abstract

The feasibility of thermo-chemical destruction of polychlorinated biphenyls (PCBs) was investigated using a batch reactor and two different (vertical and horizontal) types of continuous reactor. A simple batch reactor was first designed and constructed to examine applicability of thermal–chemical destruction of PCBs. It was evidenced from the batch test results that the destruction of PCBs in the insulating oil (40% PCBs, w/w) was accomplished via abiotic dechlorination and mineralization of PCBs with quicklime at 600 °C under nitrogen environment. PCB destruction efficiencies were obtained about 99.95%. The reaction was exothermic resulting release of heat by which the reactor temperature suddenly increased up to 750 °C at the incipient 30 min of the experiment. Two major end products, $CaCl_2$ and carbon, were identified. For a practical purpose, two continuous reactors were developed and tested. The observed continuous test results indicate that over 99.99% of PCB destruction efficiencies were achieved when excess quicklime ($>3Ca:1Cl_2$ as a molar basis) was used. Specifically, the horizontal continuous reactor was suitable in view of ease of solid transfer, which is essential for complete destruction of PCBs and for full-scale applications.
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1. Introduction

Polychlorinated biphenyls (PCBs) have widely been used over 40 years in many industrial applications, such as capacitors and transformers [1]. The commercial use of the PCBs began to be prohibited since 1977, and thus transformers containing PCBs are no longer in production [2]. While PCB production was completely banned in 1979, existing devices continue to use large amounts of PCBs in many countries including Korea [3,4]. It has been estimated, for example, that approximately 2 million transformers containing PCBs exist in US and Europe and thereby exceeding the regulatory limits (25–50 ppm) [4]. Furthermore, it has been reported that some developing countries can continue running electrical transformers using PCBs until 2025, provided they protect against leaks [5].

For several decades, PCBs have been recognized as hazardous material and pose a pollution threat mainly due to their recalcitrant, carcinogenic and endocrine disruptive properties [6,7,8]. Incineration is currently the most widespread disposal technique of these waste streams as it provides relative ease of construction and operation. The applicability of the incinerator is straightforward; however, it is significantly restricted by high construction and operational costs. This is mainly because these wastes can safely be destructed without dioxin concerns at considerably high temperature over 800–1200 °C [9], and such systems generally require accompanying facility in association with off-gas treatment. Several alternative methods for treatment of these compounds

have been suggested and tested over the last few decades [10,11]. Although some of the principles of these alternative methods are well established, the chemicals used are considerably expensive to limit their applications to the full-scale systems. Thermo-chemical treatment is a promising process for the destruction of aromatic chlorinated compounds. Here, chlorinated hydrocarbons are degraded to salt and inorganic compounds with addition of alkali at moderately high temperatures. For example, at an elevated temperature ($\sim$600 °C), halogenated hydrocarbons (XHC) in the presence of calcium compounds can be converted into calcium halogenides (Ca–X), hydrocarbons (HC), carbon (C) and some gaseous compounds such as carbon monoxide (CO), carbon dioxide and molecular hydrogen (H_2) shown by the following relationship [12]:

$$Ca\,compound + XHC$$
$$\rightarrow Ca\text{–}X + HC + C + (CO, CO_2, H_2) \quad (1)$$
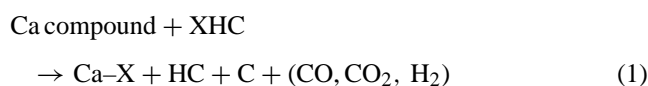
Since there are three phases (e.g, solid, liquid and gas phases) involved in this process, the extreme mechanistic complexity of the reactor still requires more knowledge for optimal and safe operation. In addition, the major end product, $CaCl_2$, can be fused at high temperature resulting in problematic solid removal, i.e. clogging, and thus, the temperature in the reactor should be carefully controlled below the melting point of $CaCl_2$ (782 °C).

In view of seeking a potential clean-up option for safe disposal of PCBs, we developed the reactors and performed sets of experiments to evaluate the availability of the aforementioned reaction to full-scale systems. We herein report the result of our studies on the development of a practical thermo-chemical reaction process, which makes possible the complete destruction of PCBs.

2. Materials and analytical procedures

The waste insulating oil was obtained in viscous liquid form (40 and 59% as PCBs, w/w) at the hazardous waste treatment facility, Whasung, Korea. The oil was then sealed in 20-l buckets and stored at 20 °C in the ventilation hood until use. Granular quicklime (CaO, average diameter: 1.0 mm, s.g.: 3.3) was used as the sole dechlorination agent. *n*-Hexane was selected as a solvent for extraction of PCBs from the oil (Aldrich Chemical Inc., Milwaukee, WI). *n*-Hexane extracts were quantified with a gas chromatograph equipped with an electron capture detector (ECD, 300 °C; HP 5890II, Avondale, DE), utilizing HP-1 column (25 m × 0.25 mm inner diameter). The column was temperature programmed from an initial temperature of 160–200 °C at 2 °C/min, to 240 °C at 8 °C/min and held for 10 min. Helium was used as a carrier. Standards were run in duplicate each time when samples were analyzed using Arochlor 1254. Total mass of PCBs was solely counted because the composition of PCBs could change over time via chemical transformation. Cl anion concentration in

solid mixture was quantified according to the silver nitrate titration in the standard methods [13].

3. Reactors and experimental methods

The reactors under study are shown schematically in Fig. 1. Three reactor systems in series, having the different size and features, were constructed with either stainless steel for bench-scale systems or carbon steel for pilot-scale system. Experiments were conducted under nitrogen atmosphere to prevent by-product formations, such as dioxin.

3.1. Batch reactor

A batch reactor (R_I) was developed in bench-scale (390 mm height and 2.5 mm diameter; Fig. 1(a)). The reactor was prepared by adding 20 ml insulating oil (40% PCBs, w/w) using a pipette. Ceramic balls (Ø 10 mm) were then placed over the oil, above which quicklime was carefully piled. The reactor was carefully placed inside the oven except the bottom part of the reactor (50 mm) filled with oil, and heated up to 600 °C. The typical heat-up period required to raise the reactor temperature to 600 °C was equal to or less than 5 min. The bottom part of the reactor was cooled down by the heat exchanger to prevent PCBs from evaporating before the reaction temperature is reached. Once the reaction temperature was achieved, the experiment was initiated by stopping the cooling water circulation and purging the nitrogen gas into the reactor. The experiment continued for 6 h. The off-gas from the vessel is passed through a condenser and a solvent bottle in stepwise to entrap the residual PCBs contained in the off-gas. Solvent was sampled and analyzed at 0.5–1.0 h intervals. After the reaction was terminated, the solid mixtures were collected at three positions (uppermost, middle, bottommost) and analyzed for PCBs and Cl ions.

3.2. Vertical type continuous reactor

The bench-scale continuous reactor (R_{II}) consists of a vertical reaction vessel (600 mm *H*, 90 mm *D*), a hopper and a product storage tank, respectively. Five in-line thermocouples were placed in the reactor at 5 cm intervals to allow continuous monitoring of temperature and to control the system to the desired set points (600 °C). Granular quicklime was then continuously supplied at 7.2 g/min with the flow of nitrogen gas at 0.5 l/min having 22.4 s of detention time (DT). The waste oil was placed in a 2-l jar and fed to the reactors via a peristaltic pump, as a result of which the molar ratio of quicklime (as Ca) and total chlorine anion (as Cl_2) was maintained at 10:1. Samples were collected at 0.5–1.0 h intervals from the sampling port of the solvent trap and analyzed to determine destruction efficiencies of PCBs.
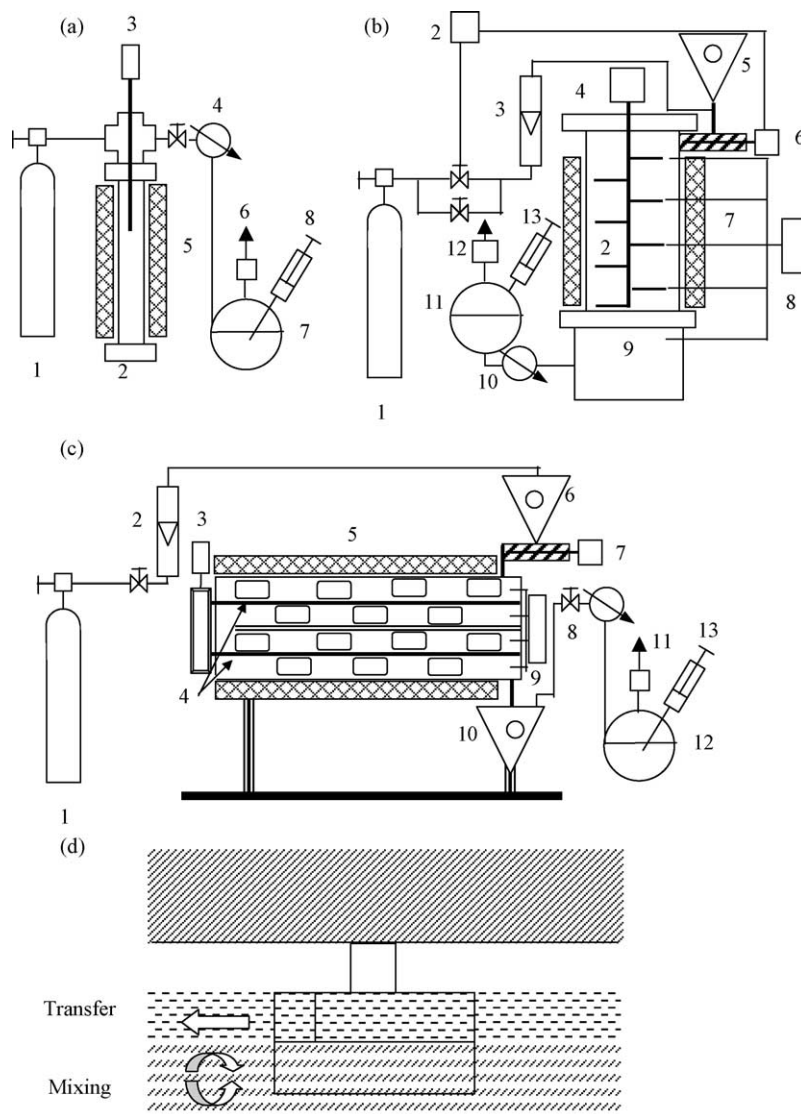
Fig. 1. Schematic diagram of the experimental setups. (a) Batch reactor—(1) N$_2$ cylinder, (2) reactor, (3) thermocouple and temperature controller, (4) condenser, (5) heater, (6) to ventilating hood, (7) solvent trap and (8) sampling syringe. (b) Vertical type continuous reactor—(1) N$_2$ cylinder, (2) timer and on/off controller, (3) flow meter, (4) motor and speed controller, (5) hopper, (6) motor and speed controller, (7) heater, (8) thermocouple and temperature controller, (9) product chamber, (10) condenser, (11) solvent trap, (12) to ventilating hood and (13) sampling syringe. (c) Horizontal type continuous reactor—(1) N$_2$ cylinder, (2) flow meter, (3) motor and speed controller, (4) shafts and vanes, (5) heater, (6) hopper, (7) motor and speed controller, (8) condenser, (9) thermocouple and temperature controller, (10) product chamber, (11) to ventilating hood, (12) solvent trap and (13) sampling syringe. (d) Vane structure.

3.3. Horizontal type continuous reactor

The reactor (R$_{III}$) was constructed similar to the vertical continuous system except that the flow of the reactant stream was horizontal. In this reaction vessel, the mixing and moving of oil–quicklime mixture avoided clogging of the solid mixture at the bottom of the reactor. The novel structure of the vanes specifically designed for mixing and transferring solid mixture is shown in Fig. 1(d). The vane is mainly divided into two parts; the upper part of the vane fixed to be vertical to the wall of the reactor so that the mixture can be well mixed, while the slanted area in the bottom part of the vane (10°) allows the mixture to move forward with mixing only when

the mixture is accumulated enough and reach the bottom part of the vane.

Experiments were conducted to compare three different load conditions (3–5Ca:1Cl$_2$ as molar basis). The reactors were first half filled with quicklime and heated up to 600 °C. The experiment was then initiated by rotating the vanes at 400 rpm and pumping oil into the reactor at the variable flow rates (15–37.5 g/min) with the continuous supply of the quicklime to match the reaction stoichiometry. Experiments were terminated after 5-h continuous operations. During the experiments, the nitrogen gas was purged into the reactor at 3 s of DT. To analyze the reactants, residual solid mixtures were carefully transferred from the storage container (8 l)
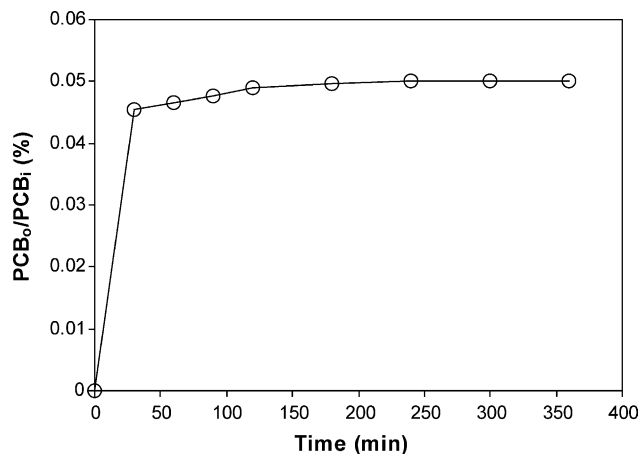
Fig. 2. Cumulative PCB concentrations over time in the batch reactor.

Fig. 3. Amount of PCB remained in the reactants inside the batch reactor.

under nitrogen atmosphere. At the lower end of the reactor, the product was collected in a funnel and discharged in a decanter.

4. Results and discussion

4.1. Batch reactor

This experiment was performed in an attempt to obtain basic data for the complete destruction of PCBs for development of continuous treatment system. Initially, the molar ratio of Ca to Cl_2 was set at 5:1 based on the stoichiometry. The experiments were conducted in duplicate at identical conditions. The experimental results were averaged and summarized in Fig. 2. The amounts of PCBs measured at the outlet account for 0.05% of the total PCBs supplied, and mostly appeared in the first 30 min of the experiment. This implies that during the incipient experimental period, a certain amount of the PCBs got evaporated at ranges of 365–390 °C [14] before the reaction temperature was reached. This was confirmed by the fact that the temperature inside the reactor suddenly increased up to 750 °C at the incipient 30 min and slowly decreased and reached the set point.

Less than 0.02% of the PCBs supplied were measured in the reaction products taken equally at three different positions (top, middle and bottom sections of the reactor) after the termination of the experiment and mostly measured in the bottom part of the reactor (Fig. 3). The Cl anion concentration in the mixture accounts for over 92% of Cl content in the total PCBs supplied and 24, 36 and 40% was distributed at the top, middle and bottom parts of the reactor, respectively. Carbon particles were identified in the mixture located mostly in the upper part of the reactor. Although gaseous compounds were not analyzed, calcium chloride and carbon were identified as the major reaction end products in the aforementioned reaction. The stoichiometric relationship can then be determined
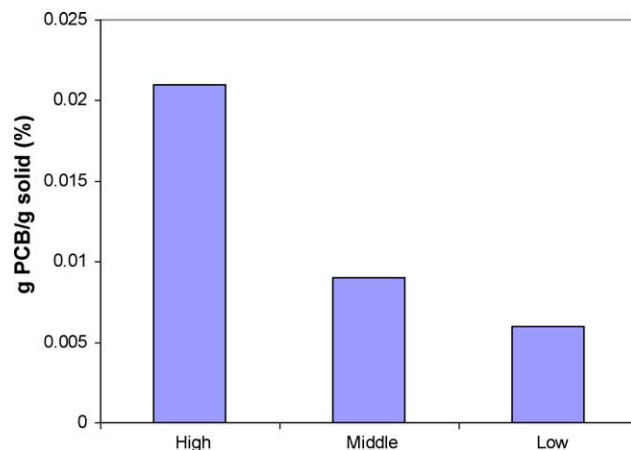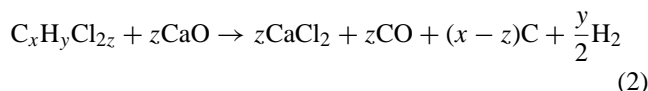
by the following equation:

$$C_xH_yCl_{2z} + zCaO \rightarrow zCaCl_2 + zCO + (x-z)C + \frac{y}{2}H_2$$

(2)

At an elevated temperature (~600 °C), chlorinated hydrocarbon along with calcium oxide is converted into harmless inorganic compounds such as calcium chloride, carbon, carbon monoxide and hydrogen.

4.2. Vertical type continuous reactor

With vertical type continuous reactor, we could control the flow rate of both PCBs and quicklime and thus could operate the reactor at the desired temperature (Fig. 1(b)). As shown in Fig. 4, the solid feeder specifically designed for quicklime supply showed stable performance regardless of the initial height of the quicklime in the hopper.

The experimental results were depicted in Fig. 5. Since the oil contains 40% PCBs, the flow rate of net PCBs was 21.7 g/h. PCB destruction efficiency (PDE) was calculated
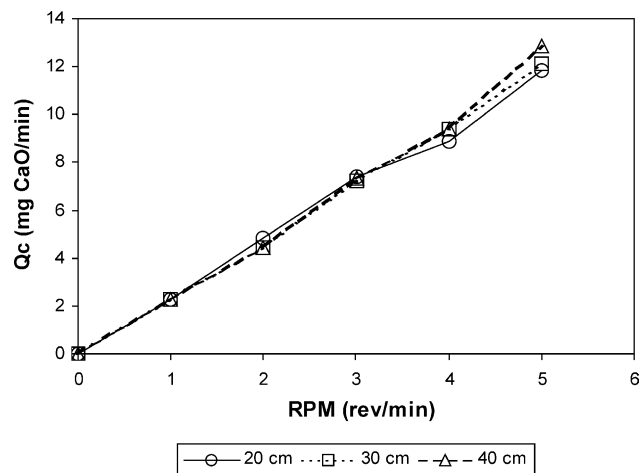

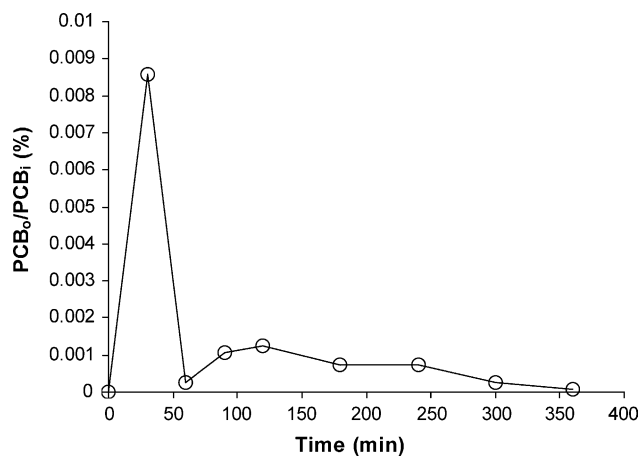Fig. 4. Powder supply as a function of shaft revolution.

Fig. 5. Destruction of PCBs with quicklime at the ratio of $10Ca:1Cl_2$ in the vertical type continuous reactor.

from the equation described below:

$$\text{PDE}\,(\%) = \frac{100 \sum_i m_e}{\sum_i m_i} \qquad (3)$$

where m_e is the amount of PCBs held captive in the solvent trap measured between sampling time intervals and m_i is the amount of PCBs supplied to the reactor between sampling time intervals. The figure suggests that approximately 99.99% of PDE can be achieved in this continuous system. Overall PDE was over 99.99%. High pressure of the ventilation system could result in initial leakage of PCBs at 30 min after the onset of the experiment. Slight increase in the reactor temperature (up to 45 °C in 90 min) was observed during the experiment (Table 1). This represents that relatively small amounts of PCBs were supplied in unit time compared to the batch system, resulting in suppression of the abrupt releasing of reaction heat.

Although a high PDE could be achieved, a problem was found in the process of product removals during the experiment; the powders often clogged the product outlet where the temperature suddenly dropped resulting in the liquefaction of the gaseous oil.

4.3. Horizontal type continuous reactor

Improvements were carried out on the design of the vertical reactor in order to facilitate solid removals and to apply to the design of a full-scale system. To prevent the possible leakage of volatilized PCBs, the hopper was enclosed with a cover on the inlet port for nitrogen flow. Each set of

Table 1
Reactor temperatures at various points over time

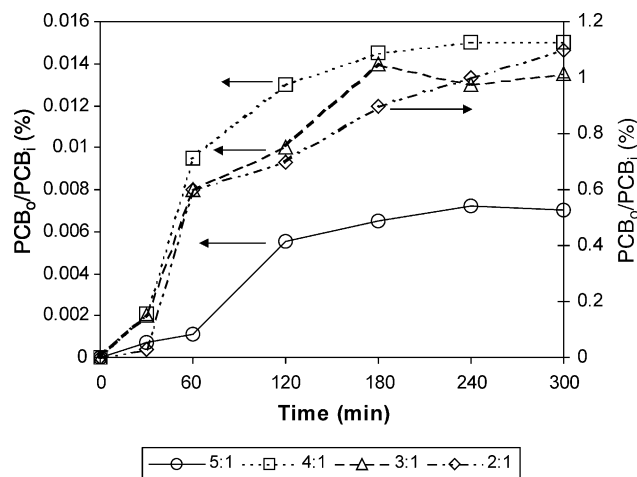| Time (min)	Reactor temperature (°C)					
	H_5	H_{20}	H_{25}	H_{30}	H_{35}	H_w
0	314	514	580	608	615	620
90	303	559	600	620	620	624
240	290	554	597	618	619	618

Fig. 6. Destruction of PCBs with quicklime at the ratio of $3–5Ca:1Cl_2$ in the horizontal type continuous reactor.

experiment was therefore conducted for 5 h with the limited hopper capacity. Unlike the vertical type reactor, no clogging was observed in the experiments. This is mainly because the vanes can completely mix the solid mixture and mechanically force the mixture to move forward preventing the mixture from coagulating inside the reactor.

The effects of the molar ratio between PCBs and quicklime on the removal efficiency are shown in Fig. 6. Steady states were achieved after about 3 h in all the experiments. At the 5:1 ratio, 99.99% of PDE was achieved at the steady state. No PCBs were detected in the product mixtures analyzed after the experiment was terminated. Similar performance was observed at both the 4:1 and the 3:1 ratios. Most of the PCBs supplied to the reactor were mineralized. No residual PCBs were measured in the solid mixtures. The Cl anion concentration and carbon particles in the collected mixture were in agreement with the reaction stoichiometry where the PCBs are mineralized to $CaCl_2$ and carbon. In the 2:1 ratio experiment, however, PDE was 98.90% and was not satisfactory in view of perfect destruction of PCBs. Including PCBs contained in the product mixture, overall removal efficiency was 98.40%. It was found that excess lime is required to maintain at least three times calcium anion concentration (more than stoichiometric demand of the Cl content in PCBs) in the system to achieve near perfect destruction of PCBs (>99.99% PDE).

5. Conclusion

Thermo-chemical reaction has been successfully demonstrated at the laboratory-scale bench and continuous reactors with insulating oils contaminated with PCBs.

Batch test results reveal the feasibility of the proposed process and it appears that the reaction proceeds quickly once the reaction temperature is achieved. Based on the results in the batch tests, PCB destruction efficiency was about 99.95%.

Volatilized PCBs before reaction temperature reached were not completely destructed. Exothermic reaction increased temperature up to 750 °C inside the reactor. The analyses of the reaction residues indicate that chlorine in PCBs was transformed to two major solid products, calcium chloride and carbon.

Horizontal continuous rector showed better performance in view of the operation (e.g. anti-clogging structure) than the vertical reactor. Over 99.99% of PCBs were found to be decomposed at least three to five times more than the stoichiometric demand of calcium ions.

Further study is clearly required to ascertain the applicability of technology on various other sources including contaminated sediments and soils and assess the performance of system.

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