

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, CaCl₂ 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:1Cl₂ 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. © 2005 Elsevier B.V. All rights reserved.

Keywords: PCB destruction; Thermo-chemical treatment; Quicklime; Mineralization; Reactor

1. Introduction

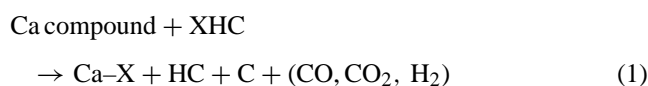
Polychlorinated biphenyls (PCBs) have widely been used over 40 years in many industrial applications, such as capacitors and transformers [1]. The commercial use of the PCBs began to be prohibited since 1977, and thus transformers containing PCBs are no longer in production [2]. While PCB production 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

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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 ($\sim 600^\circ\text{C}$), 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]:



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 ($25\text{ m} \times 0.25\text{ mm}$ inner diameter). The column was temperature programmed from an initial temperature of $160\text{--}200^\circ\text{C}$ at $2^\circ\text{C}/\text{min}$, to 240°C at $8^\circ\text{C}/\text{min}$ 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 ($\varnothing 10\text{ mm}$) 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.

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