

## Use of methanol and oxygen in promoting the destruction of deca-chlorobiphenyl in supercritical water

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### Abstract

The destruction of the well-known PCB, deca-chlorobiphenyl (10-CB), by oxidation and methanolysis in supercritical water (SCW), has been studied in a micro-reactor hydrothermal diamond-anvil cell (DAC, 50 nL) and in larger batch reactors (6 mL). The DAC was coupled to optical and infrared microscopes. In the DAC experiments, 10-CB proved to be stable under pyrolytic conditions, whereas in water, it was hydrolyzed and actually dissolved at temperatures above 475 °C. When partial oxygen was added to the 10-CB/water system, the solubility of 10-CB increased slightly as compared to the pure water experiments, and 10-CB was further decomposed by oxidation. The addition of methanol resulted in further decomposition by methanolysis, as confirmed by FT-IR spectroscopy, and lowered the dissolution temperature to 419 °C. Both oxygen and methanol (25 vol.%) were then used to destroy 10-CB in batch reactors, in which the supercritical water experiments permitted a detailed study of the reaction products of the 10-CB destruction. In the absence of methanol, more than 12 intermediate products were detected by GC-MS, and 99.2% of the 10-CB was destroyed in the presence of 225% excess oxygen at 450 °C within 20 min. When methanol was used in the absence of any excess oxygen, a destruction rate of 100% was achieved at 450 °C within 10 min and only three intermediate products were detected. The enhanced destruction of 10-CB in the presence of methanol is attributed to the homogenous reaction conditions employed and the generation of free radicals.

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### 1. Introduction

Polychlorinated biphenyls (PCBs;  $C_{12}H_{10-m}Cl_m$ ) are mixtures of synthetic chlorinated aromatic hydrocarbons with the same basic chemical structure and similar physical properties ranging from oily liquids ( $m = 1-4$ , light, oily

fluids;  $m = 5$ , heavy, honey-like oils) to waxy solids ( $m > 5$ , greases and waxy substances;  $m = 10$ , solid) [1,2]. Because of their non-flammability, chemical and thermal stability, high boiling points and low electrical conductivities, PCBs have been used in hundreds of industrial and commercial applications, including electrical equipment (e.g., transformers and capacitors), plasticizers, hydraulics and lubricants, and carbonless copy paper. PCBs are considered to be probable human carcinogens [1–3] and, consequently, their destruction is crucial owing to the potential health risks involved. Technologies to destroy PCB wastes include chemical and biological treatment,

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incineration [4], and supercritical water oxidation. Chemical processes are proven technologies, but are used to destroy lower concentrations of PCBs in contaminated oils. Biological treatment is still at an early stage of development and is not commercially available. Conventional flame-based incineration, however, seems to be ineffective due to the inflammability and chemical stability of PCBs [1]. We propose here a new process involving the oxidation and methanolysis of PCBs in supercritical water (SCW;  $>374\text{ }^{\circ}\text{C}$  and 22.1 MPa) which should result in the complete destruction of PCBs. In the supercritical water oxidation (SCWO) process employed ( $450\text{--}600\text{ }^{\circ}\text{C}$ ; 27 MPa [5–7]), PCBs, water, methanol and oxygen form a single phase in which the PCBs are homogeneously and completely destroyed without generating pollutants (e.g.,  $\text{NO}_x$ , PAHs). In particular, we now report the results of an investigation of the oxidation and methanolysis in supercritical water for the most stable PCB, deca-chlorobiphenyl (10-CB;  $\text{C}_{12}\text{Cl}_{10}$ ,  $m = 10$ ), in a hydrothermal diamond-anvil cell micro-reactor and in batch reactors.

## 2. Experimental

Solid deca-chlorobiphenyl powder (10-CB;  $100\text{--}500\text{ }\mu\text{m}$ , 99.0% purity) was used as received from Supelco-Aldrich, Bellefonte, PA. It had a melting point  $T_m = 302.5\text{ }^{\circ}\text{C}$  and a density of  $1200\text{ kg/m}^3$ . Methanol (99.9% purity) was obtained from Sigma-Aldrich (St. Louis). Hydrogen peroxide 50 wt.% (Fisher ACS certified) was used as an oxygen supplier. Two types of reactors were used in the experiments: (i) a micro-reactor (50 nL), hydrothermal diamond anvil cell (DAC) for visual observation of the phase changes; (ii) larger batch reactors (6 mL) to determine the products of decomposition and the destruction rates of 10-CB.

### 2.1. Micro-reactor, hydrothermal diamond anvil cell

The phase behavior of 10-CB in supercritical water was investigated using a hydrothermal DAC micro-reactor that has been described earlier [8]. The reaction chamber (50 nL;  $500\text{ }\mu\text{m}$  i.d.,  $250\text{ }\mu\text{m}$  thickness) was sealed by the compression of two opposing diamond anvils and was heated by two electric micro-heaters. The initial density of water (or pressure) was adjusted by changing the applied force to the diamond anvils. Little change was observed in the chamber volume during the reaction process [8]. The temperature of the two diamond anvils was measured with the aid of a data acquisition unit (Strawberry Tree, Model DS-12-8-TC, Sunnyvale, CA). After loading the sample (10-CB +  $\text{H}_2\text{O}$  + methanol/ $\text{H}_2\text{O}_2$ ), the mixture was heated and the progress of the reaction was monitored using a stereo-microscope (Olympus SZ11). The images (110X magnification) were recorded on a Panasonic 3 CCD camera (AW-E300) and a VHS recorder (Panasonic AG-5720). Digital imaging analysis of the sample area was achieved using a commercial soft-

ware package (Scion Image, Frederick, MD). After the reaction was complete, the solid residues that had been deposited on the diamond faces were analyzed by FT-IR microscopy (UMA 500, Bio-Rad, Cambridge, MA). Fuller details of the experimental set-up and procedures for these measurements are given in previously published work [9–11].

### 2.2. Batch reactors

Tubular stainless-steel (316-SS) batch reactors (6 mL; length = 105 mm, o.d. = 12.7 mm) were used to study the oxidation of 10-CB in SCW. Both temperature and pressure were measured with a pressure transducer fitted with a J-type thermocouple (Dynisco E242). In the experiments, approximately 1 and 10 mg of 10-CB, and a 1-mL mixture of  $\{\text{H}_2\text{O} + \text{methanol} + \text{H}_2\text{O}_2\}$  were loaded into the reactor. After sealing and connecting to the data acquisition system, the reactor was submerged in a fluidized sand bath (Omega FSB-3) and was heated at a rate of  $3.5\text{ }^{\circ}\text{C/s}$  up to  $450\text{ }^{\circ}\text{C}$ . After a pre-determined period (10–20 min), the reactor was quenched in cold water and the reaction mixture was emptied into a flask. The reactor was washed with water (9 mL) and benzene (10 mL), and the washings were transferred into the same flask. The resulting solution was filtered through a membrane filter. The benzene phase was decanted off from the aqueous phase. The aqueous phase was then analyzed using ion chromatography (Dionex DX-100) to determine the  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{Cl}^-$  anion concentrations. For each ion, three concentrations, blank, 20 ppm and 50 ppm, prepared from standards were used for calibration. The benzene phase was analyzed by gas chromatography-mass spectrometry (GC-MS; GCQ Packages: Polaris MS, Trace 2000 GC, ThermoQuest, Austin, TX). A calibration coefficient for the 10-CB analyses was obtained using blank, 1, 10 and 50 ppm (or 500 ppm for experiments with 10 mg 10-CB) 10-CB standards, and tetradecane was used as an internal standard. Other products were identified using library data without any standard material calibrations.

## 3. Results and discussion

Experiments concerning the phase behavior of 10-CB in the DAC were conducted under conditions of pure water, {25% vol. methanol + water} solution, at partial (insufficient) oxygen and excess oxygen concentrations. Fig. 1 shows IR spectra of the solid residues obtained from 10-CB decomposition in SCW using pure water, partial oxygen and methanol. Fig. 2 shows visual observation of 10-CB phase transition in SCW when methanol was used.

In the batch experiments, oxidation of 10-CB in SCW was performed at  $450\text{ }^{\circ}\text{C}$ , 30 MPa, and 10 or 20 min reaction times, using  $-36.0$ ,  $93.1$ ,  $159.5$  and  $225\%$  excess oxygen concentrations (with 1 mL solution of  $0.8\text{--}4.2\text{ wt.}\%$

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