

DISPOSAL OF PCB'S BY WET AIR OXIDATION

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Abstract

Raw commercial PCB was decomposed by combination of hydrolytic and wet air oxidation reactions in a laboratory autoclave. The hydrolysis was promoted by 20% solution of sodium hydroxide, the oxidation of hydrolysis reaction products was carried out by high pressure air. The decomposition of PCB was greater than 99.9975% at 295-300°C temperature and 18-20 MPa pressure during 30 min. of reaction time. The reaction rate and the degree of decomposition was found to be highly dependent on the phase transfer rate thus the stirring speed of reaction mixture.

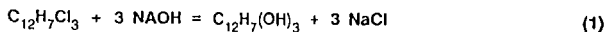
Introduction

The most common way for the disposal of out of use commercial PCB's is the high temperature incineration, however growing resistance from the local population makes it increasingly difficult to get approvals for the operation of new incinerating facilities. This phenomenon initiated the research activity in many countries for examination of low-temperature chemical processes eg. dechlorination or alkaline hydrolysis by which the PCB can be decomposed to environmentally harmless components for final disposal.

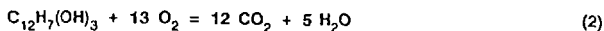
One group of chemical processes for disposal of PCB use metal sodium (or some other alkali metal) or a very reactive metal-organic compound of alkali metals at slightly elevated temperatures (50-120°C) and atmospheric pressure for dechlorination of PCB's. Dean (1) used suspension of metal sodium in toluene at 75°C temperature for dechlorination of PCB's. Similar process for dechlorination of PCB's using sodium naphthalenide at ambient temperature was described by Smith and Bulbar (2). Pytlewski et al. (3) described a dechlorination reaction using a complex of metal sodium and polyethylene glycol as a dechlorinating agent.

An other group of chemical processes for decomposition of PCB's is based on hydrolysis with aqueous solution of strong alkalies eg. sodium hydroxide at elevated temperatures (200-350°C) and high pressures (8-20 MPa).

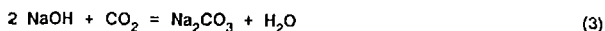
We have a relatively extensive experience in the field of wet air oxidation of technological effluents. The reaction conditions applied in wet oxidation of organic compounds are very similar to the conditions used for alkaline hydrolysis of PCB's that was the reason we tried to combine the two reactions. In first step of combined reaction the PCB's are hydrolysed with concentrated solution of sodium hydroxide at 290-300°C to corresponding polyhydroxy biphenyls as it is shown on the example of trichloro biphenyl:



Wet air oxidation is a process in which organic substances dissolved or suspended in water are oxidised to carbon oxide and water at 200-320°C and corresponding pressure needed for containing the water in aqueous phase by means of oxygen from air. In the second step of the process the polyhydroxybiphenyls formed in the hydrolysis step are oxidized to carbon dioxide and water as it shown on following example:



The sodium hydroxide is present in the reaction mixture in excess to the stoichiometric ratio thus the carbon dioxide formed reaction 2 is consumed by following reaction:



Both the reactions 1 and 2 depend on the rate of phase transfer and thus the vigorous stirring of the reaction mixture is necessary for achieving high decomposition rates for PCB in reasonable sort reaction time. In the case of reaction 1 the phase transfer is essential to promote the hydrolysis reaction between dissolved oxygen and dissolved polyhydroxy biphenyls in the aqueous phase.

Experimental

Wet air oxidation of PCB was carried out in a 2 dm³ total volume stainless steel autoclave. The autoclave was equipped with a variable speed electromagnetic stirrer and was electrically heated with build-in temperature regulation. The inside temperature of the autoclave was measured with Pt electrical resistance thermometer. The wet air oxidation experiment was initiated by measuring the sodium hydroxide solution and the raw commercial PCB mixture into the reaction vessel. The autoclave was hermetically closed and pressurised with compressed air from a gas cylinder. The heating of the autoclave was turned on and the reaction mixture was heated to reaction temperature without mixing. The typical heat-up time was approximately 1 hour. After the reaction temperature has been reached the shaking of the mixture was started by actuating the electromagnetic stirrer. Stirring of the mixture initiated the hydrolysis of PCB and the subsequent wet air oxidation of reaction products from hydrolysis by promoting the phase transfer between organic and aqueous liquid phases and enhancing the solubility of oxygen in the water phase. The wet air oxidation was stopped by turning off the stirrer and switching off the electrical heating. After the autoclave cooled down to ambient temperature it was depressurised. The typical cooling time took about 3-4 hours. The depressurised reaction vessel was opened and the reaction mixture was removed from it for further analysis. The inside walls of the reaction vessel and the stirrer blades were washed with pure n-heptane in order to remove the traces of PCB from them. The reaction mixture was extracted three times with 50 ml of pure n-heptane. The n-heptane extracts were combined with the n-heptane used for washing. The combined n-heptane solution was concentrated to 50 ml and analyzed for traces of PCB by direct injection into a GC. The GC separation was carried out on 25 m x 0.2 mm x 0.5 μm capillary column coated with 95% Me- 5% Ph- silicone and for the detection of PCB's an electron capture detector (ECD) was used. 1 μl of concentrated n-heptane solution was injected in splitless injection mode. The residual PCB concentration was determined by calibrating the response of EC detector with the same raw commercial PCB which was used for making the wet air oxidation reactions.

Results and Discussion

Several wet air oxidation reactions were carried out using raw commercial PCB for determining the Destruction and Removal Efficiency (DRE) for that type PCB. The PCB used in experiments was removed from an out-of-service industrial high voltage electric capacitor. In a typical reaction run 400 ml of 20% sodium hydroxide and 10 g of commercial PCB was measured into the autoclave. The autoclave was pressurized with air at ambient temperature to 4.0-4.5 MPa (initial pressure). Reaction temperature was maintained between 295-300°C, the pressure in the reaction vessel have risen to 18-20 MPa during heat-up. The reaction time was determined by the stirring time at the reaction temperature. The reaction time was in all cases 30 min.. The mixing speed was varied between 25 and 60 shake-ups/min. in the subsequent reaction runs. The total volume recovered after cooling down the reaction vessel was typically 390-400 ml. The wet air oxidized reaction mixture was homogeneous (no separation of organic phase was observed) aqueous solution with pale yellow colour. The observed DRE of PCB was dependent on the stirring speed of reaction mixture indicating that the reaction rate is determined by the rate of phase transfer. The greatest DRE at above described reaction conditions was achieved at maximum stirring speed of 60 shake-ups/min.. In this case the residual PCB concentration in the oxidised reaction liqeur was 0.63 mg/kg, the total mass of recovered liqeur was 0.4 kg, so the total amount of PCB remaining after wet air oxidation is 0.252 mg. Considering that the initial mass of PCB was 10 g, the DRE was calculated as follows:

$$\text{DRE} = [(10,000 - 0.252) / 10,000] * 100 = 99.9975\%$$

Based on these results this process after further modifications will be suitable for operating an equipment for continuous hydrolytic-wet air oxidation of PCB's with a capacity of 50 kg/h which is under construction. The result from continuous equipment will be available soon.

References

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2. Smith, J.G., Bulbar, G.L.; US 4,326,090; Apr. 20, 1982
3. Pytlowski, L.L., Krevitz, K., Smith, A.B.; DE 3,033,170; Oct. 22, 1981

