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Chemical Dechlorination of PCBs by the Base Catalyzed Decomposition Process

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1. Introduction

The Base Catalyzed Decomposition Process (BCD process), developed by the US EPA in 1989, is a chemical destruction method for persistent and hazardous organic chlorine compounds such as PCBs, PCPs, etc. Such organic chlorine compounds become destroyed within a short time and under mild conditions, in the presence of alkali, a carboneous compound catalyst, and a hydrogen donor. The products are dechlorinated organic compounds, alkali chloride and water. Fig. 1 shows the outline of the BCD reaction.



The BCD process has been applied for the dechlorination of PCBs in various matrices such as transformer oils and soil in Australia and the US. The BCD process has potential as an alternative to incineration, as obtaining community approval for the latter is hard in Japan.

The authors carried out bench scale of BCD experiments to clarify the relationship among reaction rates, alkali amounts, and reaction temperatures. Pilot-scale PCB treatment at low ppm levels were also carried out. The following discusses findings obtained from bench scale, as well as

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pilot scale experiments.

2. The Reaction Rate in BCD Reaction

2.1 Apparatus and experimental method

Fig. 2 shows a schematic diagram of the bench-scale experimental apparatus. PCBs, hydrogen donors, alkali and catalysts were placed in a 300ml threenecked-flask ,which was heated to 255-355°C under a nitrogen atmosphere at normal pressure. During the reaction, the PCB level was monitored by GC/MS for checking the progress of reaction.



Fig.2 Bench- scale experimental apparatus

2.2 Results

2.2.1 The relation between the reaction rate and temperature

The influence of reaction temperature on the reaction rate was studied at different temperatures $(255^{\circ}C, 285^{\circ}C, 315^{\circ}C, 325^{\circ}C)$ and $355^{\circ}C$). The following were employed in a series of experiments: Kaneclor KC300 (initial concentration: 20,000 ppm) as the PCB, C-heavy oil as the hydrogen donor, and NaOH. Fig.3 shows the effect of reaction temperature on the reaction rate. It is shown that a reaction temperature higher than $300^{\circ}C$ was needed for a complete reaction, and that the decomposition proceeded at the first order reaction.

2.2.2 The relation between the reaction rate and dosage of alkal

A previous report by the authors discussed





Fig.4 Relationship between amont of KOH added and k of KC-400

the relationship between the amount of NaOH and destruction reaction rate, and indicated that the use of KOH significantly improved the reaction rate, much more than when using NaOH $^{1)}$. In this

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research, the effect of alkali dosage on the reaction rate was studied using 10,000 ppm of KC-400, transformer oil as the hydrogen donor, and KOH. The results are shown in Fig. 4. This study revealed that the decomposition reaction rate of KC-400 became higher along the increase in alkali dosage.

2.2.3 The relationship between the reaction rate and the hydrogen donor

Influences of hydrogen donors on the reaction rate was studied using an industrial fluid paraffin, fuel oil, and two types of transformer oil. Experiments were carried out at a temperature range of 310° C- 360° C. Fig. 5 shows the effect of hydrogen donors on the reaction rate. The transformer oil was found to be most effective in accelerating the reaction.

2.3 Dechlorination reaction

Previous experiments had revealed that consecutive dechlorination occurred during PCB decomposition in the BCD process ²⁾. In this study, a finding was made that the recovery of



inorganic chloride generated after the BCD reaction of 2,3,4-trichlorobiphenyl was nearly 100%. This indicates that the BCD reaction accomplished complete dechlorination.

Experimental results showed that transformer oil and KOH are the most applicable chemicals for the BCD process, in terms of cost effectiveness and high decomposition reaction rate.

3. Pilot-scale Experiment of High Concentration PCB Treatment

3.1 The apparatus and experimental conditions

Fig. 6 shows an outline of a pilot-scale plant used for the experiments. The main equipment of this plant are a reactor, a cooling tank for the treated oil, and supplying units of hydrogen donors and alkali. Volatile compounds were returned to the reactor from the condenser, and the water was removed from the reactor.

The experimental conditions for the PCB are shown in Table 1. The PCB level was monitored during the reactions by GC/MS to check the progress of reaction.

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Fig.6 Outline of batchwise pilot-scale plant

Table1 Experimental condition and resultsof high concentration PCB treatment

		** **	
Run No.	No.1	No.2	No.3
Initial concentration	KC-300	KC-300	KC-300
of PCBs	50,000(ppm)	100,000[ppm]	150,000[ppm]
Hydrogen donor	Transformer oil	Transformer oil	Transformer oil
	801	801	801
кон	10.9 kg	12.5 kg	15.6 kg
Additive	0.81	0.81	0.81
Reaction temperature	325°C	325°C	325°C
Reaction time	4 hrs.	4 hrs.	4 hrs.
Total POB concentration in treated oil	0.062[ppm]	0.04[ppm]	0.26(ppm)
PCB decomposition ratio	99.9998%	99.9999%	99.9998%

3.2 Experimental results

3.2.1 PCB destruction rate

Table 1 also shows the experimental results. PCBs in the transformer oil was reduced, from 150,000 ppm to 0.26 ppm, after four hours of treatment, and the PCB destruction rate of 99.9998% was accomplished. The PCB destruction rate of over 99.9999% was accomplished for the cases where the PCB concentrations in the transformer oil were 50,000 ppm and 100,000 ppm (to 0.062 ppm and 0.040ppm, respectively).

3.2.2 PCDDs/PCDFs and coplanar PCBs in the treated oil

The results of high resolution GC/MS analysis following a thorough clean up showed that neither PCDDs/PCDFs nor coplanar PCBs were present in the treated oils. This indicated that the BCD process destroyed PCDDs/PCDFs as well as coplanar PCBs, also that the reaction conditions for this experiment did not lead to the generation of these compounds.

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4. Treatment of insulating oils contaminated by low level PCBs

Continuous treatment was carried out for transformer oil contaminated by low concentrations (less than 50 ppm) PCBs.

4.1 Bench-scale test

A schematic diagram of the benchscale experimental apparatus used is shown in Fig. 2. The reaction was carried out using a transformer oil containing 50 ppm of KC-300 and KOH. Fig. 7 shows the time course of the PCB residual ratios. The concentration of residual PCBs was 0.013 ppm after 20 ^G minutes. We found that the decomposition proceeded at an first order reaction, which was similar to that for the case of treating high-concentration PCBs.



Fig.7 Time - course of PCB residual ratio at a low concentration

4.2 Pilot-scale tests

Run No.	No.1	No.2
Throughput	60 kg/hr	120 kg/hr
Initial concentration of PCBs	50 ppm	
KOH feed rate	0.2 kg/hr	0.4 kg/hr
Additive feed rate	0.6 kg/hr	1.2 kg/hr
Reaction temperature	320 °C	
Retention time	30 min	15 min

Table2 Experimental condition for treatment of low concentration PCBs

The pilot-plant used for the tests constituted a reactor, a continuous feeder for contaminated oil and alkali, and a treated oil cooling tank. Tests were carried out using transformer oil containing 50 ppm of KC-300. Experimental conditions are shown in Table 2. During the reaction, PCB levels were monitored by GC/MS to check the progress of reaction.

4.3 Experimental results

Test results for different retention times revealed that a PCB decomposition of 99.9% was reached. Post-treatment analysis on coplanar PCB concentration revealed that the concentration was below the limit of detection.

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5. Conclusions

Studies were made on the BCD process for PCB treatment using a bench-scale apparatus and a pilot-scale plant. The results obtained were as follows:

1) The most appropriate reaction temperature for PCB decomposition was above 320 °C.

2) The optimum dosage of KOH for PCB decomposition was determined to be 6-fold the stoichiometric ratio.

3) The most applicable combination for effective treatment by the BCD process was transformer oil (as the hydrogen-donor) and KOH (as the alkali) in the BCD process.

4) PCBs were completely dechlorinated.

5) Both PCDDs and PCDFs were decomposed and no formulation occurred during the reaction.

6) The BCD process is a cost-effective system due to the use of less expensive and safe chemicals.

6.References

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