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# Chemical Treatment of Polychlorinated Biphenyls in Waste Insulating Oil by Using Chromium Oxide Catalyst†

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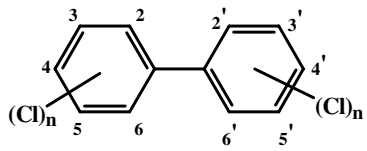
A study on the removal of polychlorinated biphenyls in waste insulating oil by using a chromium oxide catalyst was conducted through changing catalyst reaction temperatures, air injection rates and concentrations of polychlorinated biphenyls. As a result of this study, in the case of using chromium oxide as a catalyst in reductive dechlorination, treatment of high concentrations (over 1,000 ppm of polychlorinated biphenyls) contained in waste insulating oil was possible. Also, the optimal reaction conditions were the reaction temperature 400 °C of the tubular reactor (diameter 5 cm, length 30 cm, catalyst 400 g), air injection rate 400 mL/min and insulating oil injection rate 5 mL/min. As it is possible to treat high concentrations of over 1,000 ppm of polychlorinated biphenyls contained in waste oil when using a chromium oxide catalyst in reductive dechlorination mechanism by utilizing the efficiency, it is considered to be usable for continuous and movable multi-stage reactors.

**Keywords: Polychlorinated biphenyls, Waste insulating oil, Chromium oxide.**

## INTRODUCTION

Polychlorinated biphenyls (PCBs hereafter) include 209 species of chlorine compounds of 2-10 chlorines substituted biphenyl formed with combination of 2 benzene rings, of which 130 species were used.




These polychlorinated biphenyls are insoluble in water but soluble in oil or organic solvents and are one form of persistent organic pollutants (POPs hereafter), which are toxic, have slow decomposition and remain in the ecosystem for long period of time. In 1997, the world wide fund for nature (WWF) designated endocrine disruptors along with 43 species of pesticides and 42 species of toxic chemicals, including phenol. In particular, polychlorinated biphenyls have been known to have powerful carcinogenic effects and cause birth defects while remaining in the body. Further, with the revelation that they are harmful to the human body merely upon contact (without being absorbed), their production and use have recently been prohibited and products containing polychlorinated biphenyls are not being produced.

However, in the past, polychlorinated biphenyls were used widely as insulating oil for transformers and condensers because they have good electrical insulating properties, large heat capacity and are chemically stable. Up to this day, polychlorinated biphenyls contaminated with insulating oil within waste transformers have been a problem.

Although damage cases caused by polychlorinated biphenyls have not been reported domestically, contamination incidents are widely known, such as the Kanemi rice bran oil contamination incident of 1968 in which 1,800 people were harmed by coloration, rash symptoms in Japan and an incident in Belgium in 1999, in which contaminated animal feed brought about 36 trillion Won worth of damage to European stock farms. In order to reduce such damage, the Stockholm convention on persistent organic pollutants (which regulates POPs) is requiring each nation to check and remove all kinds of devices containing polychlorinated biphenyls until 2025 and up to the present date, about 200 nations have signed[1].

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At present, as a chemical treatment method to remove polychlorinated biphenyls, reductive dechlorination and alkaline dispersion are mainly being used. In reductive dechlorination, Pd, Mg and Ca are used as single catalysts; or, Mg/Pd are being used as complex catalysts. However, this method is used for waste fluid with a relatively low concentration of polychlorinated biphenyls. Also, for alkaline dispersion, KOH/PEG (polyethylene glycol) metallic sodium is used. In case of the metallic sodium method, it is applied not only to insulating oil but also to soil, dioxin and pesticides because of its low disposal cost of polychlorinated biphenyls and a broad application. However, there is difficulty in applying it to commercial technology due to its low dechlorination efficiency and risk of explosion[2].

Making polychlorinated biphenyls (PCBs) innoxious is achieved through removal of chlorine by the following dechlorination reaction mechanism:

$$\text{Waste Oil (PCBs)} + \text{CrOx/TiO}_2\cdot\text{SO}_4^{2-} + \text{Air} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{HCl}$$

Polychlorinated biphenyls reactant of the above removal process are oxidized through reacting with lattice oxygen by absorption onto Cr(VI), the activation point of reaction. Chromium(VI), which consumed lattice oxygen, supplements lattice oxygen by reacting with gaseous oxygen after being reduced to Cr(III). On the other hand, the products, which finished reacting at the reaction activation point, complete a cycle of oxidation-reduction reaction by desorption. Cl element could be removed by introducing $H_2O$ into the contact with reaction products and making them into the form of HCl[3,4].

Thus, this study intends to delineate the results of evaluating removal efficiencies of polychlorinated biphenyls through changing catalyst reaction temperatures, air injection rates and concentrations of polychlorinated biphenyls by using chromium oxide as catalyst in order to safely treat high concentration polychlorinated biphenyls that have been a problem in chemical treatment of the existing polychlorinated biphenyls.

## EXPERIMENTAL

**Preparation of catalyst:** Chromium oxide catalyst for removing polychlorinated biphenyls was prepared by the incipient wetness method. $TiO_2$ [titanium(IV) oxide, a mixture of rutile and anatase, nanopowder, < 100 nm particle size (BET), 99.5% trace metals basis (Aldrich)], which is used as a supporter was put on filter paper and after an aqueous solution of 1N $H_2SO_4$ 10 times the mass of $TiO_2$ was added and dried in the air. It was treated at a temperature of about 400 °C for 1 h; then, $TiO_2$ surfaces were reformed. The reformed $TiO_2$ was designated by $TiO_2\cdot SO_4^{2-}$.

Chrome was prepared in an aqueous state by making reagents $Cr(NO_3)_3\cdot 9H_2O$ soluble in distilled water of about 40 °C. Then, after $TiO_2\cdot SO_4^{2-}$ and chrome aqueous solution were mixed and stirred for 12 h, it was dried at approximately 100 °C and chromium oxide catalyst was prepared in powder form. The prepared chromium oxide catalyst was treated at 450 °C for 6 h and 10-15 wt% of chrome-supported chromium oxide catalyst was obtained.

In reforming $TiO_2$ surface with $H_2SO_4$, the oxidation state of sulfur becomes +6 and the temperature at which amorphous metastasizes into anatase form rises to about 100 °C compared to pure $TiO_2$; also, the specific surface area increases[5].

**Catalytic removal systems:** In order to reduce the pressure drop of the reactor, 50-60 mesh powders were selected and filled inside the sus 304 tubular reactor. The reactor was a 5 cm inner-diameter tube, 60 cm in length and designed to be filled with about 400 g of catalysts.

For measuring temperature inside the reactor, thermocouple was installed inside the reactor and air was supplied at flow velocity of 400 mL/min by connecting compressor and air-inlet to supply air. Waste insulating oil containing polychlorinated biphenyls was fed at a flow velocity of 20 mL/min through polychlorinated biphenyls oil inlet by using a controlled volume pump.

The oil used in the experiment was waste insulating oil used for waste transformers. By using this oil containing over 1,000 ppm of polychlorinated biphenyls and in order to find removal efficiency and the operating condition of chromium oxide catalyst, experiments measuring the removal efficiencies by reaction temperatures, by flow rates of injected oxygen and by concentrations of polychlorinated biphenyls content were conducted.

**Measurement of polychlorinated biphenyls concentration:** The results of the experiment on treatment of polychlorinated biphenyls using chromium oxide catalyst were measured by the polychlorinated biphenyls-gas chromatography-mass spectrometry; after refining pre- and post-treatment insulated oil using the multilayered silica gel column, a fixed quantity of refined oil was taken, then analyzed and compared using the internal standard substances (Aro 1242, 1254, 1260).

Quantitative analysis, which checks polychlorinated biphenyls according to peak patterns, was used by using gas-chromatography (Agilent Technologies, 6890N)[6].

## RESULTS AND DISCUSSION

**Removal efficiencies of polychlorinated biphenyl by catalytic reaction temperatures:** In order to find the optimal reaction temperature condition for removal reaction of polychlorinated biphenyls take place in the reactor in Fig. 1, air supply flow rate and injection flow rate of insulating oil containing polychlorinated biphenyls (raw material 100 ppm) were fixed at 5 mL per min. Also, the catalytic reactions were carried out by varying isothermal reaction temperatures at 100, 200, 300, 400 and 500 °C. After reactions, the levels of polychlorinated biphenyls in insulating oil coming out through the reactor were analyzed. The results are shown in Table-1.

TABLE-1
ANALYSIS RESULTS OF REMOVAL EFFICIENCY BY CATALYTIC REACTION TEMPERATURES

| No. | Reaction temperature | Concentration before treatment | Concentration after treatment |
|---|---|---|---|
| (a) | Raw sample | 100 ppm | – |
| (b) | 100 °C | 100 ppm | 99 ppm |
| (c) | 200 °C | 100 ppm | 96 ppm |
| (d) | 300 °C | 100 ppm | Below 0.5 ppm |
| (e) | 400 °C | 100 ppm | Below 0.5 ppm |
| (f) | 500 °C | 100 ppm | Below 0.5 ppm |

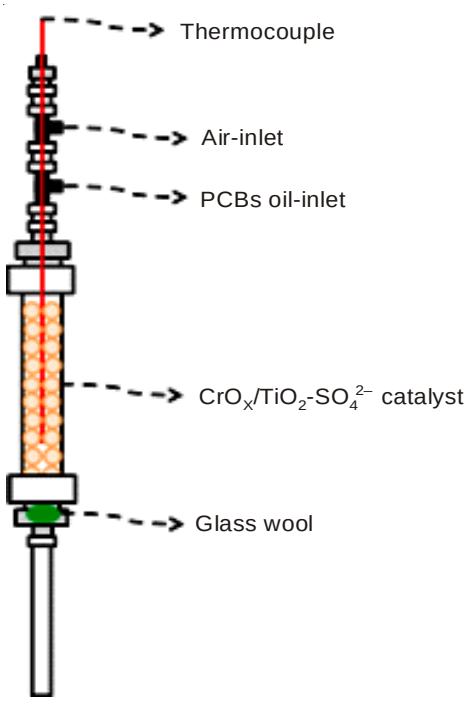


Fig. 1. Catalyst reactor

Since the boiling point of biphenyl is 256 °C and the boiling points of polychlorinated biphenyls are in range of 285-456 °C, it is presumed that the temperature of the reactor should be maintained at over 250 °C in order to remove Cl element by coming into contact with the catalyst[7].

**Removal efficiency of polychlorinated biphenyl by flow rates of injection air:** Since removal reaction of polychlorinated biphenyls in oil occurs as chromium oxide catalyst is oxidized from 3 valence to 6 valence by using surrounding oxygen on the catalyst surface and again reduced from 6 valence to 3 valence, air should be sufficiently supplied during reaction and used in the reaction. However, if supplied with more than the proper flow rate, the contact time of substrate with catalyst shortens and the removal capability could fall generously.

In order to verify it, removal efficiency of polychlorinated biphenyl was evaluated by changing flow rate of air supply to 100-500 mL/min while having the injection rate of insulating oil containing polychlorinated biphenyls (raw sample 100 ppm) fixed at 5 mL per min and reaction temperature of the reactor had maintained at 400 °C. The results are shown in Table-2. As shown in the results, removal capabilities were analyzed to be at its best when air was supplied more than 300 mL/min and less 500 mL/min.

TABLE-2
ANALYSIS RESULTS OF REMOVAL EFFICIENCY BY FLOW RATES OF INJECTION AIR

| No. | Flow rate (mL/min) | Concentration before treatment | Concentration after treatment |
|---|---|---|---|
| (a) | Original sample | 100 ppm | – |
| (b) | 100 | 100 ppm | 5 ppm |
| (c) | 200 | 100 ppm | 2 ppm |
| (d) | 300 | 100 ppm | Below 0.5 ppm |
| (e) | 400 | 100 ppm | Below 0.5 ppm |
| (f) | 500 | 100 ppm | Below 0.5 ppm |

**Removal efficiency by concentrations of polychlorinated biphenyls:** Removal efficiencies were obtained as a result of experimenting by changing concentration of polychlorinated biphenyls to 100, 200, 380, 460, 600, 800, 1000, 3000 ppm, while maintaining air supply flow rate at 400 mL/min, raw sample feeding rate at 5 mL/min and reaction temperature at 400 °C to evaluate removal efficiency of chromium oxide catalyst. These results are shown in Table-3. The results given in Table-3 suggest that for chromium oxide catalyst complete removal was possible even in the case of waste oil containing a high concentration of polychlorinated biphenyls.

TABLE-3
ANALYSIS RESULTS OF REMOVAL EFFICIENCY BY CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS

| No. | Concentration before treatment (ppm) | Concentration after treatment (ppm) |
|---|---|---|
| (a) | 100 | Below 0.5 |
| (b) | 200 | Below 0.5 |
| (c) | 380 | Below 0.5 |
| (d) | 460 | Below 0.5 |
| (e) | 600 | Below 0.5 |
| (f) | 800 | Below 0.5 |
| (g) | 1000 | Below 0.5 |
| (h) | 3000 | Below 0.5 |

In GC analysis, the peaks between 18-19 min on the graphs of more than 600 ppm of polychlorinated biphenyls were showing the benzene, which were verified through GC-mass. In the analysis results obtained from the treatment of waste oil of less than 460 ppm concentration of polychlorinated biphenyls, benzene peaks were not observed and it is considered that chromium oxide catalyst disintegrated benzene by cracking it.

**Generating optimum polychlorinated biphenyl treatment condition:** It is presumed that the optimum reaction condition for treating waste insulating oil containing polychlorinated biphenyls is an economical process condition while satisfying the legally permitted standards of polychlorinated biphenyl concentration of below 0.5 ppm.

In this light, based on the results of the experiment, the optimum catalytic reaction conditions are identified as follows. That is, that insulating oil containing polychlorinated biphenyls is injected inside a reactor at 5 mL/min flow rate under a reaction condition, in which air is supplied at the rate of 400 mL/min while being heated at 400 °C in a tubular reactor (5 cm in diameter, 30 cm in length and 400 g of chromium oxide catalyst is filled inside).

In this case, as polychlorinated biphenyls in insulating oil coming out of the under part are detected to be below 0.5 ppm, the legal standards regarding polychlorinated biphenyl emissions are satisfied and it can be reused as insulating oil in a safe condition.

## Conclusion

As a result of experiments on the methods to chemically treat and remove polychlorinated biphenyls contained in waste insulating oil by using chromium oxide catalyst, the conclusions obtained are as follows:

• In the case of using chromium oxide as catalyst in reductive dechlorination, treatment of high concentration polychlorinated biphenyls of more than 1,000 ppm contained in waste insulating oil was possible. The optimum reaction conditions were a reaction temperature of 400 °C of tubular reactor (diameter 5 cm, length 30 cm, catalyst 400 g), air intake rate 400 mL/min and injection rate of insulating oil containing polychlorinated biphenyls at 5 mL/min.

• As it is possible to treat high concentration polychlorinated biphenyls of more than 1,000 ppm contained in waste insulating oil in a case of using chromium oxide catalyst in reductive dechlorination, it has the merit of being usable for continuous and movable multi-stage reactors by applying the efficiency.

## ACKNOWLEDGEMENTS

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