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Environmental effects of supercritical water oxidation (SCWO) process for treating transformer oil contaminated with polychlorinated biphenyls (PCBs)

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ABSTRACT

Our research was carried out with an aim of the design of a commercial plant to treat "Transformer oil contaminated with polychlorinated biphenyls (PCBs)" by a supercritical water oxidation (SCWO) process. The optimal destroying conditions were determined with a lab-scale facility, then designed and manufactured a pilot plant facility of 30 kg/h capacity. After finishing pilot plant tests, dioxin, NO, NO_2 and N_2O were analyzed to estimate environmental effects of SCWO process treating transformer oil contaminated with PCBs in and around the pilot plant. As the concentration of dioxin was ~0.09 pq TEQ/m^3 at four different measuring points, we concluded that our SCWO process could be utilized to treat the transformer oil contaminated with PCBs. In addition, as we have a plan to use the oxygen made from air instead of pure oxygen as an oxidant in commercial plants, a mixed gas with 92% oxygen and 8% nitrogen was tested. The sample was collected from the exhaust system, and estimated the effects of the mixed gas on the SCWO process. The total concentrations of NO, NO_2 and NOx that were measured were less than 5 ppm and N_2O was not detected. As a result, we could ascertain the possibility of the mixed gas prepared from air as an oxidant.

1. Introduction

Due to their strong toxicity, persistence, long distance migration, bio-accumulation, etc., polychlorinated biphenyls (PCBs) are classified as POPs (persistent organic pollutants) which can cause long-term damage to the health and the environment, and thus are one of eradication compounds in the Stockholm convention. The convention effective on May 2004 requested that all the products containing PCBs are banned by 2025, and all the wastes containing PCBs must be treated environment-friendly by 2028. In accordance with the Stockholm convention, Korea has set the time schedule to complete treatments for all the wastes containing PCBs by 2015 [1,2].

Several technologies such as biological and chemical, incineration and SCWO (supercritical water oxidation) are known to treat PCBs or organic compounds contaminated with PCBs [3]. Biological treatment of PCBs is an early stage of development, and chemical treatment using a specific compound such as sodium tert-butoxide or sodium is commercializing at a medium scale in Japan and Canada. Incineration technology can be first taken into a technology to treat transformer oil contaminated with PCBs. However, PCBs is a chlorinated compound, which can lead to the formation of poly-aromatic hydrocarbons (PAHs), dioxins, and other hazardous pollutants due to incomplete miscibility with oxygen and high temperature (900–1300 °C) [3,4]. These pollutants can be avoided by the oxidation at low temperature in a solvent such as supercritical water (374 °C, 218 atm) [3–6]. SCWO can be used to destroy organic compounds in wastewater or wastes above critical point of water with a high destroying efficiency [7–9]. As the organic compounds may be destroyed almost completely, it is known that an additional secondary system is not needed to treat NOx, SOx, Dioxins, etc. Due to these advantages, we chose several SCWO methods to treat transformer oil contaminated with PCBs. We already published the optimal conditions including temperature, pressure, retention time, the amount of oxidants, etc. [10]. And also, we built and operated a pilot plant of 30 kg/h capacity.

Hydrogen peroxide can be used as an oxidant in a small size facility. However, the oxidant cost is more than 50% of total operating costs, the liquid oxygen transported by a tank lorry or pipe line is considered for a large-scale commercial plant preferentially [11–13]. There is no liquid oxygen line at the company where the commercial plant is planned to be constructed. So we tried to find other economic oxidants. Although it is known that the oxidants made from air are being used in other industry, we could not find a model commercial plant in Korea using the oxidants (~90% purity of oxygen) made from air.

The vacuum pressure swing adsorber (VPSA) is a process to get more than 93% purity of oxygen by adsorption of nitrogen and

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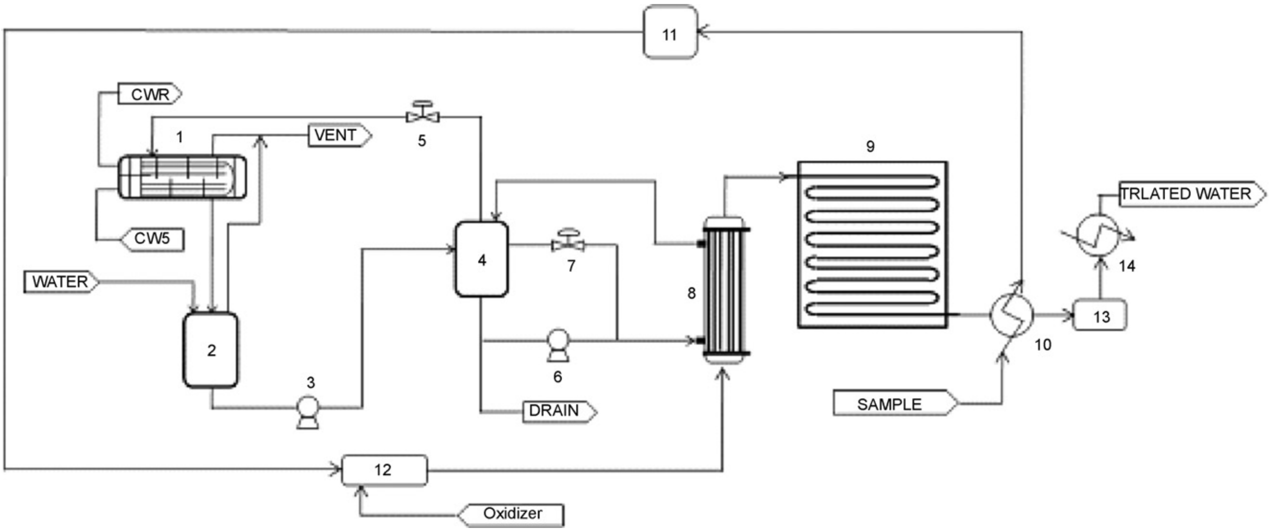

Fig. 1. Diagram of pilot plant (1: steam condenser shell and tube, 2: water feed drum, 3: water feed pump, 4: boiler water feed drum, 5: control valve, 6: boiler water feed pump, 7: control valve, 8: shell and tube reactor, 9: tubular reactor, 10: heat exchanger, 11: pre-heater, 12: mixer, 13: quencher, 14: heat exchanger).

other gases in the air. The process consists of a filtering system to eliminate the primary impurities, an adsorption system, a vacuum system, a storage system, and a utility system. The main products of VPSA process are nitrogen, air, oxygen, argon, and water. The zeolite molecular sieve (ZMS) is used as an adsorbent. In the process, a blower is used to pressurize the flow and a vacuum pump is used to desorb the adsorbed gases. Since the VPSA process is operating at a lower pressure than the pressure swing adsorber (PSA) process, the VPSA process is more economic than the PSA process. The VPSA process for oxygen production is composed of one or more adsorbent tower(s), and produces the oxygen of 92–94% purity.

Several experiments were carried out to treat transformer oil contaminated with PCBs using the pilot plant of 30 kg/h capacity, and have almost completed the detailed design of a commercial plant [14–18]. Here we intend to introduce the analysis results of the exhaust gas from the pilot plant. In particular the atmospheric samples were collected from inside and around the pilot plant, analyzed dioxin concentration to estimate environmental affects. In addition, environmental effects caused by the change of oxidants were estimated.

2. Experiments

2.1. Sample preparation and analysis

The waste transformer oil used for this study was the oil extracted from an abandoned transformer and kept for research. The PCBs concentration of the oil was 1541 ppm and the oil was diluted to 50 ppm with a new transformer oil of the same kind (Class 1, #4) as the waste transformer oil. Samples containing 3 wt.% of the diluted oil were emulsified as described in our previous works [19,20]. The samples showed 18,200 ppm of TOC, and 40,700 ppm of $\mathrm{COD_{cr}}$. The initial concentration of PCBs in the reactor was 0.6 mg/L with 427 ppb of maximum Cl ion. The destroying efficiency was measured by TOC with a detection limit of 0.1 mg/L. The experiments were repeated by the use of TOC measuring system (Shimadzu, TOC-$\mathrm{V_{CPH}}$) equipped with an auto sampler (Shimadzu ASI-V).

2.2. Pilot plant facility

The pilot plant was designed to operate at high temperature and pressure as shown in Fig. 1. The oxygen was injected by a gas booster into a buffer drum to attenuate pulsation. A preheated sample around at 300–350 °C was passed through the mixer (#12) and mixed with the oxygen, then reacted at the shell and tube reactor (#8) and the tubular reactor (#9) made by Inconel-625 successively. As the destroying reaction of the sample is an exothermic reaction, a cooling system was provided. The cooling water in the water feed drum (#2) was sent to boiler water feed (BWF) drum (#4) by BWF pump (#3). From the BWF drum (#4), the cooling water passed the shell side of a shell and tube reactor (#8) to recover reaction heats, and then returned back to BWF drum (#4). The high temperature steam in recovered cooling water was sent to tube-side of steam condenser (#1), and cooled down. The condensed cooling water was recovered in BWF (#2), and the uncondensed steam was exhausted to a vent line. After the reaction, the reaction mixture was cooled down to room temperature by a cooling system (#10, #13, #14) such as an effluent cooler and capillary condenser and to an atmospheric pressure by passing BPR (back pressure regulator). The liquid and vapor were separated in a liquid–vapor separator, and then the liquid and vapor were sent a product receiver tank and atmosphere, respectively. Fig. 2 shows the picture of the pilot plant.

2.3. Sampling of the surrounding atmosphere

The surrounding air sampling of the pilot plant was in accordance with the “measuring methods of endocrine disruptors” suggested by the National Institute of Environmental Research of

Fig. 2. Picture of pilot plant.

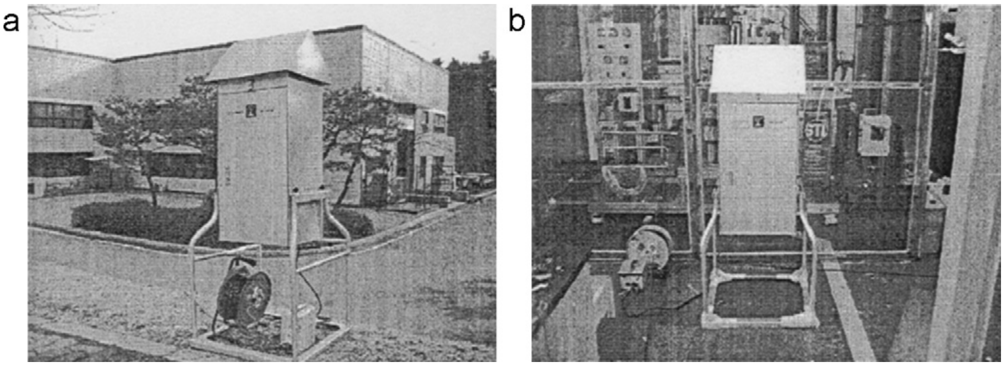

Fig. 3. Sampling at upward (a) and indoor (b).

Korea in 2002. The sampling points were chosen a point which had no obstacle such as buildings or trees in principle. When that was not possible a point was chosen where obstacles were at a distance more than two times their heights. Or the points were selected where the angle between a horizontal line and the straight line connected to upper end of obstacles were less than 30° so that the air flow around the sampling points were not obstructed. More detailed remarks are shown in Table 1. Fig. 3 shows the pictures of sampling at upward direction (a) and indoor (b).

The particulate and vaporous materials were sampled simultaneously by a high volume air sampler (SIBATA, HV-1000F). The samplers were installed far from the outer walls of the pilot plant building. Dioxin was analyzed by a high resolution mass spectrometer (HRMS, Jeol, Model JMS 700D) with a SIM (Selected Ion Monitoring), and resolution of 12,000–14,000 (10% valley standard) [21].

2.4. Modification of oxidant

As the purity of oxygen manufactured by VPSA is known as 92–93%, a mixed gas prepared 92% purity with 92% of oxygen and 8% of nitrogen. Several experiments were performed with the mixed gas as an oxidant, and analyzed $NO/NO_2/NOx$ concentration of exhausted gases by $NO/NO_2/NOx$ analyzer (Swiss, CLD 8225). The concentration of NO, $NO_{2,}$ and NOx was analyzed directly. On the other hand the concentration of N_2O was analyzed after sampling. The sample for N_2O analysis was collected in a Teddler bag at a rate of 0.5 L/min for 20 min at an exhaust pipe as shown in Fig. 4 and analyzed by GC (Shimadzu 2010) equipped with ECD (Electron Capture Detector). The analysis conditions are presented in Table 2.

3. Results and discussion

3.1. Optimal destroying conditions and destroying efficiencies

Several experiments were carried out to treat transformer oil contaminated with PCBs using the pilot plant of 30 kg/h capacity, and the reaction processes were identified by TOC concentration. The reaction was done at the range of 400–525 °C, and the optimal temperature was 500 °C. And also, the optimal reaction pressure and residence time were 3700 psi and 60 s, respectively. As the concentration of oxidant can greatly affect on the operating costs of a SCWO process, several experiments to determine minimum amounts of oxidants at given temperature and pressure were carried out. The amounts of oxidants were determined at 150%SA (stoichiometric amount) to TOC of each sample. The several destroying efficiencies at optimal conditions (500 °C, 3700 psi and oxygen 150%SA) are shown in Table 3. As shown in the table, more than 99.9% of destroying efficiencies were obtained.

Table 1
Sampling points around pilot plant facility.

Sampling points	Remarks
Upwind	North-west direction 45 m from exhaust system of pilot plant
Downwind	South-east direction 45 m from exhaust system of pilot plant
Background	West direction 290 m from exhaust system of pilot plant
Indoor	Located indoor in pilot plant

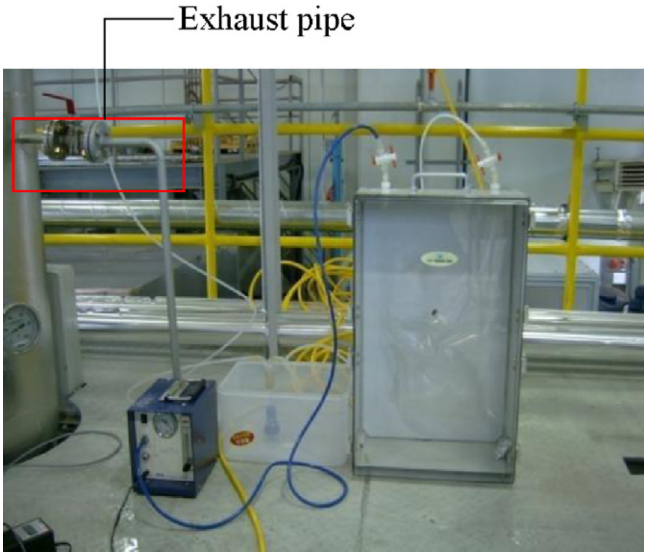

Fig. 4. Sampling at exhaust pipe for N_2O analysis.

3.2. Dioxin analysis

The samplers were installed far from the outer walls of the pilot plant building as shown in Fig. 3 and the samples were collected

Table 2
Analysis conditions for N_2O analysis.

Column	HP-PLOT/Q (J&W Scientific) 30 m × 0.53 mm × 40 μm
Injector	Temp 200 °C Split 10:1 Injection volume 150 μL
Carrier gas	N_2 2 mL/min
Oven temp.	80 °C (1 min) → 6 °C/min to 150 °C
Detector temp.	250 °C

Table 3
Destroying efficiencies at optimal conditions.

No./items	Temp (°C)	Pressure (psi)	Oxidants (%SA)	Results	
				TOC (ppm)	Destroying efficiency (%)
1	500	3700	150	14.11	99.95
2				32.18	99.98
3				28.0	99.90
4				22.74	99.98
5				2.84	99.99
6				15.34	99.94

Table 4
Concentration of dioxin.

Measuring points	Results
Upward	0.09 pg TEQ/m^3
Downward	0.09 pg TEQ/m^3
Background	0.09 pg TEQ/m^3
Indoor	0.08 pq TEQ/m^3

simultaneously from four points by a high volume air sampler as mentioned in Table 1. Dioxin was analyzed by a high resolution mass spectrometer.

The concentrations of dioxin are usually expressed as a converted concentration of the strong toxic compound, 2,3,7,8-tetrachlorodibenzodioxin (TCDD). The factor used for the concentration calculation is called TEF (toxicity equivalent factors), and there are several different TEFs made by WHO, NATO, etc. An international TEF established by official experiment methods for TEF was applied. The measured value of dioxin in atmosphere is expressed in pg TEQ/m^3. The analysis results are shown in Table 4. The concentration of dioxin in the indoor atmosphere of the pilot plant was 0.08 pq TEQ/m^3, and that of the atmosphere around exhaust pipe passed through an exhausting system including an adsorption device was 0.09 pq TEQ/m^3 in both upwind and downwind directions. On the other hand, the concentration in the atmosphere not affected by the exhaust system was 0.09 pq TEQ/m^3, which was almost the same as the concentration around exhaust pipe. Compared to Korea's environmental criteria of 0.6 pq TEQ/m^3, the dioxin concentration by SCWO process was quite low. As the concentration of PCBs in the liquid effluent of the lab-scale facility was not detected with a detection limit of 0.05 ppm and that of dioxin was 0.02 pq TEQ/m^3, the liquid effluent of the pilot plant facility was not analyzed.

3.3. *NO, NO_2, NOx and N_2O analyses by changing oxidant*

As we have a plan to use the mixed gas made from air instead of pure oxygen, a mixed gas was tested as an oxidant. The sample was collected from the exhaust pipe, and estimated the effects of the mixed gas under SCWO process. The mixed gas with 92% of oxygen and 8% of nitrogen was added at a rate of 1.20 L/min, and the experiment was lasted for about 2 h from 14:55 to 16:58. The NO/NO_2/NOx concentrations of exhausted gases were analyzed at 2 s intervals by NO/NO_2/NOx analyzer and some results are represented in Table 5. The total concentrations of NO, NO_2 and NOx were measured less than 5 ppm.

Table 5
Concentration of nitrogen oxides using a mixed gas as an oxidant.

Time/items	NO	NO_2	NOx
14:55	2.00	0.00	2.00
15:00	4.00	0.00	4.00
15:30	5.00	0.00	5.00
16:00	5.00	0.00	5.00
16:30	5.00	0.00	5.00
16:58	5.00	0.00	5.00

The sample in Teddler bag shown in Fig. 4 for N_2O concentration was analyzed by GC-ECD under the analysis conditions as mentioned in Table 2.

The retention time of N_2O peak was identified by a standard gas and the detection limit was determined to 0.4 ppm by the procedure of QA/QC handbook suggested by the National Institute of Environmental Research [22]. N_2O was not detected.

4. Conclusions

The optimal conditions (500 °C, 3700 psi, oxygen 150%SA and residence time 60 s) were confirmed by the pilot plant facility of 30 kg/h, and more than 99.9% of destroying efficiencies were obtained.

The concentration of dioxin in the indoor atmosphere of the pilot plant was 0.08 pq TEQ/m^3, and that of the atmosphere around exhaust pipe passed through an exhausting system including an adsorption device was 0.09 pq TEQ/m^3 in both upwind and downwind directions. On the other hand, the concentration in the atmosphere not affected by the exhaust system was 0.09 pq TEQ/m^3, which was almost the same as the concentration around exhaust pipe. Compared to Korea's environmental criteria of 0.6 pq TEQ/m^3, the dioxin concentration by SCWO process was low. As a result we concluded that our SCWO process could be utilized to treat the transformer oil contaminated with PCBs. Moreover a pre-treatment facility to prepare samples was established so that the environmental effects could be reduced.

As we have a plan to use the mixed gas made from air instead of pure oxygen, a mixed gas was tested as an oxidant. The sample was collected from the exhaust pipe, and estimated the effects of the mixed gas under SCWO process. The total concentrations of NO, NO_2 and NOx were measured less than 5 ppm and N_2O was not detected. As a result, we could ascertain the feasibility of the mixed gas prepared from air as an oxidant. We have almost finished a detail design of a commercial plant of 8 t/h capacity and will publish the detail design in the near future.

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