Chemical Engineering Journal 165 (2010) 170–174

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

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

Kyeongsook Kim[a,*], Soon Hwan Son[a], KwangSin Kim[a], Kyungbok Kim[a], Yeong-Cheol Kim[b]

[a] Green Growth Laboratory, Korea Electric Power Corporation (KEPCO) Research Institute, 65 Munji-Ro, Yuseong-Gu, Daejeon 305-760, Republic of Korea
[b] Supercritical Fluid Engineering Laboratory, Korea Research Institute of Chemical Technology (KRICT), P.O. Box 107, Yuseong-Gu, Daejeon 305-380, Republic of Korea

ARTICLE INFO

Article history:
Received 7 July 2010
Received in revised form 6 September 2010
Accepted 6 September 2010

Keywords:
Supercritical water oxidation (SCWO)
Polychlorinated biphenyls (PCBs)
Transformer oil
Environmental effects
Mixed gas
Dioxin

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

---

* Corresponding author. Tel.: +82 42 865 5239; fax: +82 42 865 5204.
E-mail addresses: kskim@kepri.re.kr, 96801025@kepco.co.kr (K. Kim).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.09.012

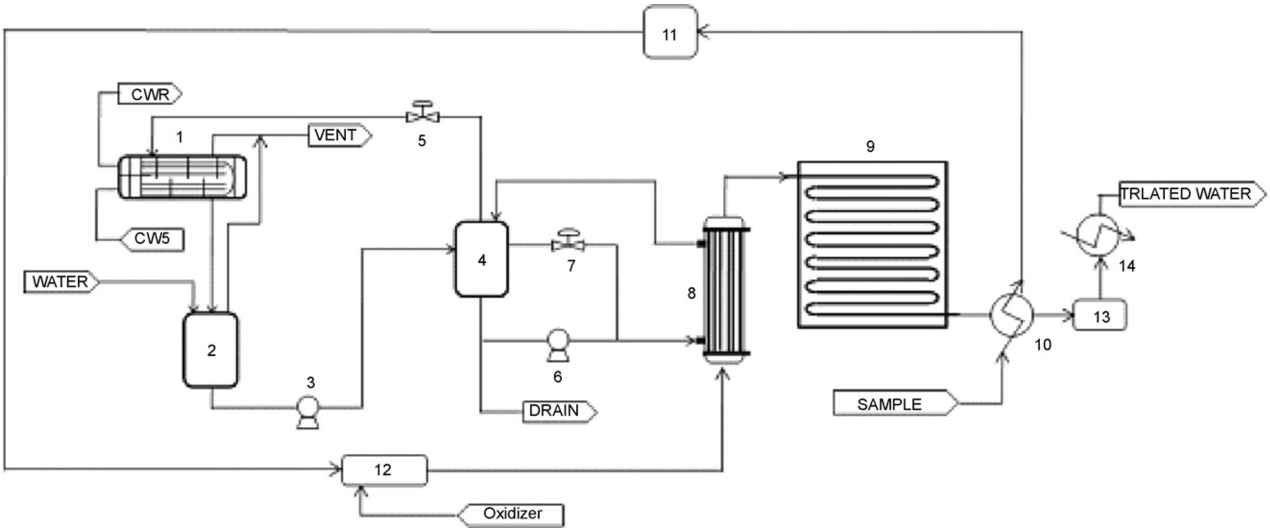

Fig. 1. Diagram of pilot plant (1: steam condenser shell and tube, 2: water feed drum, 3: water feed pump, 4: boiler water feed drum, 5: control valve, 6: boiler water feed pump, 7: control valve, 8: shell and tube reactor, 9: tubular reactor, 10: heat exchanger, 11: pre-heater, 12: mixer, 13: quencher,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