

DESTRUCTION OF USED TRANSFORMER OILS BY SUPERCRITICAL WATER OXIDATION IN A CONTINUOUS PILOT SCALE PLANT

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There is a current international commitment for eliminating the identified stock of polychlorinated byphenils (PCBs), which were widely used in the past as dielectrics in electrical transformers. For example, a preliminary inventory of PCBs in Colombia accounted for the existence of two thousand tons of transformer oils contaminated with PCBs, although this figure might be five times larger. The concentration of PCBs in contaminated transformer oils is in the 500 – 1000 ppm range, which is the result of a recurrent mixing process of fresh mineral oil in already contaminated transformers. Incineration is the only approved technology for disposal of these wastes, but because there are not facilities in Colombia, the disposal is carried out overseas, which is economically nonviable for many industries. The same situation conceivable occurs in many other countries.

In this work, the supercritical water oxidation of a PCB-free used transformer oil without is studied as a first approximation to the development of a technology for treating oils contaminated with PCBs. The physical characteristics of the used oil, such as high viscosity and poor solubility in water and methanol, make its pumping difficult. Dissolving the oil in other common organic solvents such as hexane, benzene, toluene, etc. make it possible to pump the oil, but results in higher costs due to the increased amounts of solvent and oxidant that are required. We overcame this difficulty by using and emulsifier at very low concentrations and an ultrasonic mixing process in order to create a stable emulsion of the transformer oil in water. In this way it was possible to effectively pump the oil at high pressures. We report on our experiments with hydrogen peroxide as an oxidant agent at temperatures from 450 to 500 °C and pressures from 248 to 310 bar in a continuous pilot apparatus. Conversions obtained by using an oxygen excess of 30% at residence times close to 10 seconds were higher than 97%. Destruction of used transformer oils contaminated with PCBs is a possible process whose details are to be determined.

INTRODUCTION

Persistent organic pollutants (POPs) are chemical substances that persist in the environment, bioaccumulate and pose a serious risk of causing adverse effects to human health and to the environment [3]. The United Nations Environmental Programme [4] has developed three conventions regarding environmentally sound management of hazardous chemicals like POPs throughout their lifecycles, seeking to identify the stockpiles and to promote their further elimination. One important group of the targeted POPs is conformed by the polychlorinated byphenyls or PCBs. These are halogenated hydrocarbons characterized by the byphenyl structure. Due to their chemical stability and dielectric properties, PCBs were introduced for applications in electrical equipment, heat exchangers, hydraulic systems and

several other. These compounds, thus, were manufactured from 1930 up to late 1970 when they were banned [4].

According to the outlines of the Stockholm Convention, an inventory of POPs, including PCBs [11], accounted for the existence of two thousand tons of transformer oils contaminated with PCBs in Colombia, although this figure might be five times larger. The concentration of PCBs in contaminated transformer oils is in the 500 – 1000 ppm range, which is the result of a recurrent mixing process of fresh mineral oil in already contaminated transformers. Although several treatment alternatives have been proposed for dealing with these residues [10], there are not commercial technologies available besides incineration at temperatures around 1200 °C. Unfortunately, there are not *state of the art* incineration facilities in Colombia and the disposal has to be carried out overseas. This turns out to be uneconomical for many industries because shipment of residues is charged by ton and not by concentration of PCBs in the used transformer oils, which, at most, reaches five percent of the total load.

Supercritical water oxidation (SCWO) technology has proved to be effective for destroying a large variety of industrial and high risk wastes [1,2,5,6,7] including PCBs. The SCWO process is conducted at temperatures and pressures above the critical point of water (647 K and 22.1 MPa). Under these conditions, water becomes completely miscible with organic compounds and oxygen, making possible to conduct high-temperature oxidation reactions without the mass transfer limitations imposed by multiphase systems. The high destruction efficiency in a continuous process at very short residence times makes the SCWO technology very attractive for a scale-up to industrial level. }

According to several reports, conversions near 100% have been achieved in the continuous SCWO of PCB containing mixtures [1,2,5,6,7]. In these reports, synthetic mixtures were prepared using a solid PCB congener such as monochlorobiphenyl, or a commercial PCB mixture, and an organic solvent such as methanol [1,5,6], benzene[6] or hexane. These studies have provided valuable information regarding the kinetics of the decomposition reaction and the intermediate products [5]. For example, Anitescu et al [7]. performed the SCWO of Arochlor 1248, a mixture of 76 PCB congeners, dissolved in methanol, and found that the cosolvent methanol acts to enhance the reaction rate by inducing a chain of free-radical reaction dechlorination steps.

Nevertheless, to the best of our knowledge, SCWO of an used transformer oil contaminated with PCBs has not been reported. Although the used mineral oil, commercially available as hydrotreated light naphthenic distillate, and comprised by cyclic naphthenic compounds ranging from C6 to C9, can be recycled for the soap industry, low concentrations of PCBs, resulting from the refilling of contaminated electrical transformers with fresh mineral oil, render it unusable and thus, it must be considered as a PCB waste. In fact, only few dielectric oils can be considered as pure PCBs, and the real challenge is treating mineral oils contaminated with PCBs in concentrations ranging from 50 to 1000 ppm.

In this work, the supercritical water oxidation of a PCB-free used transformer oil is studied as a first approximation to the development of a technology for treating oils contaminated with PCBs.

MATERIALS AND METHODS

A PCB-free used transformer oil was obtained from a local company. The physical characteristics of the used oil, such as high viscosity and poor solubility in water and

methanol, make its pumping difficult. By dissolving the oil in other common organic solvents such as hexane, benzene, toluene, etc. it is possible to pump the oil, but results in higher costs due to the increased amounts of solvent and oxidant that are required during the SCWO process. We overcame this difficulty by emulsifying the oil in water by means of an ultrasonic mixing process. Several emulsifiers, including *Tween 20*, *Tween 80* and *Arkopal* were tested for emulsion stability with manual agitation as follows: 1 mL of the emulsifier was added to 100 mL of distilled and deionized water in a beaker. 1 mL of the used oil was added to each beaker and was manually stirred during two minutes. After checking for the absence of the oily phase, 1 mL more of oil was added and stirred. We observed that *Arkopal* was able to emulsify 5 mL of the oil as compared to 3 mL emulsified by *Tween 20* and *Tween 80*. However, the *Arkopal* emulsion was stable only for 1 hour. In order to increase the emulsion stability, an ultrasonic mixer (Sonics, model VCX 130 with a 6 mm o.d. standart probe) was used. By sonicating the water-oil-emulsifier mixture at 60 Hz during 5 minutes, 11 mL of the oil was emulsified in 100 mL of water. The emulsion, milky in apparence, was completely stable and no phase separation took place after a week.

SCWO experiments were conducted using the continuous apparatus shown in Figure 1. This apparatus is conformed by three sections: pressurization, heating and reaction, and cooling and depressurization zones. The pressurization zone consists of two pneumatic high pressure pumps (Williams Milton-Roy, model P250V225, maximum flow rate 0.57 GPH, maximum pressure 7200 psi), each one connected to a 2 L stainless steel feeding tank. One of the pumps is used for the oxidant and the other one for the organic stream. In order to provide a constant head for the high pressure pumps and thus to achieve a constant flow in the pumps, each feeding tank is pressurized by using gaseous nitrogen. Bourdon-tube gauges (Ashcroft) were used to monitor the pressure of each feed stream.

The heating and reaction zone consists of a fluidized sand bath, two preheaters and a tubular reactor. Both preheaters were built from 0.159 cm i.d. x 0.318 cm o.d. x 5 m long 316 stainless steel tubing. The reactor was built from 0.85 cm i.d. x cm 1.27 cm o.d. x 90 cm stainless steel tubing. Temperature was measured at the inlet and exit of the reactor, and inside the sand bath by using K-type thermocouples.

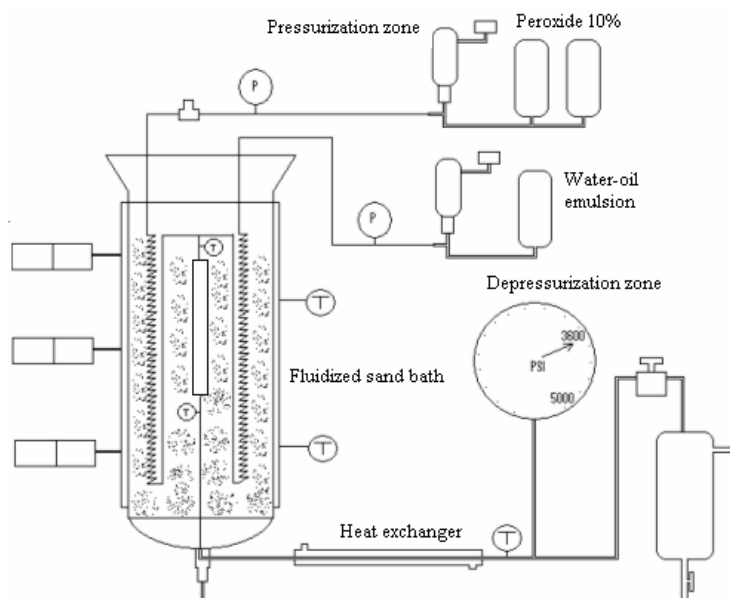


Figure 1. Supercritical water oxidation apparatus.

The cooling and depressurization zone consists of a concentric-tube heat exchanger built from 0.85 cm i.d. x 1.27 cm o.d. x 100 cm stainless steel tubing, inserted into a galvanized steel tube 2.54 cm o.d. x 1 m long. After cooling, the system pressure was determined by using a precision pressure gauge (Ashcroft, type A4A, 12 inches dial, 5000 psi maximum pressure, with 50 psi divisions). The precision pressure gauge was calibrated against a secondary standard in the Univalle metrology laboratory.

The pressure of the reaction system was regulated by a medium pressure valve (Autoclave Engineers, model 20SM4081-GY). The liquid products are collected at the exit of the apparatus in a glass kettle and the gaseous products are conducted to a scrubbing system and discharged.

For each experimental run an aqueous oxidant stream containing 10 wt% hydrogen peroxide was prepared by diluting a 30 wt% aqueous solution of hydrogen peroxide (Carlo Erba) with distilled and deionized water. Total organic carbon (TOC) analyses were carried out using a Shimadzu TIC 5050 analyzer to evaluate the decomposition of the organic matter in the liquid effluent obtained at several experimental conditions. The gaseous effluent was not collected for analyses.

RESULTS

SCWO runs were carried out at temperatures from 450 to 500 °C and pressures from 248 to 310 bar. Organic stream flowrates were set at 15 and 20 mL/min as determined at 25 °C and 14.7 bar, and the oxidant flowrate was set by assuming that the used oil is pure cyclohexane, one of the many characteristic compounds of the oil. Although a rough approximation, this allows one to calculate the theoretical hydrogen peroxide required to accomplish complete destruction of the organic matter according to the hydrogen peroxide decomposition into oxygen [12] and the oxidation of cyclohexane into carbon dioxide and water as follows:



In order to compensate for approximating the oil as cyclohexane, a 50% excess over the stoichiometric amount of oxygen required for complete destruction of the organic was used in all of the runs. The residence time of the fluids in the reactor ranged from 8 to 15 seconds. This time was calculated by dividing the reactor volume by the volumetric flow rate under supercritical conditions according to the equation:

$$\tau = \left(\frac{V}{v_L} \right) \left(\frac{\rho_{SC}}{\rho_L} \right) \quad (3)$$

where τ is the residence time in seconds, V is the reactor volume in mL, ρ_{SC} is the water density at the operating conditions in the reactor in g/mL, ρ_L is the water density at 25 °C in g/mL, and v_L is the initial flow rate of the liquid reactants in mL/s.

Experimental runs carried out at pressures over 3800 psi and temperatures ranging from 450 to 490 °C were not taken into account for TOC analysis because there was not a considerable decomposition of the organic matter. This was evidenced by a strong yellowish color of the liquid effluent that keeps the characteristic odour of the used oil. This liquid product, however, is very different from the milky emulsion fed to the apparatus and might possibly be the result of an incomplete oxidation of the oil components. Conceivably, under these operating conditions the oil components reach an intermediate oxidation stage and remain in solution without forming an oily phase.

Experimental runs carried out at 250 bar and temperatures from 450 to 500 °C showed a significant decomposition of the organic matter as evidence by the fading of the yellowish color and the characteristic odour of the oil. At these conditions an almost totally clear and odorless liquid stream was produced, especially at temperatures from 480 to 500 °C. A summary of the experimental conditions and conversions obtained for some of the runs where the effluent collected was completely clear and almost odorless are shown in Table 1. The total organic carbon (TOC) at the reactor inlet was 2497 mg/L.

Table 1. Experimental conditions and conversion for three SCWO runs

Temperature °C			Inlet flow, mL/min		TOC mg/L	Conversion
Isothermal bath	Reactor inlet	Reactor exit	Organic	Oxidant		
490	494	490	15	16.6	85.84	96.6
499	507	501	20	29.1	61.60	97.5
493	505	493	20	29.1	72.97	97.0

Note that there is a slight increase in the temperature at the reactor inlet as compared to the isothermal bath temperature due to the heat released by the exothermal oxidation of the organic matter. As evidenced by the experimental data, it is possible to obtain conversions above 97% at moderate temperatures without using a cosolvent for the used transformed oil, at residence times around 8 seconds. The results also show that that the higher the flow rate of the organic stream, the higher the conversion that is achieved. This can be explained by the increase in the reaction temperature due to the higher mass flow rate of the organic compounds being oxidized in the reactor.

CONCLUSIONS

As a first approach to the treatment of used transformer oils contaminated with PCBs, a preliminary study of the supercritical water oxidation of PCB-free transformer oils was performed. At temperatures from 450 to 500 °C and pressures from 248 to 310 bar, with residence times close to 8 seconds, an almost complete (97%) destruction of the organic matter was observed without using an organic cosolvent such as methanol, benzene or hexane. Although some studies have shown that methanol effectively increases the reaction rate by promoting a fast chain of free-radical reaction dechlorination steps of organic solutions containing PCBs, it is almost immiscible with the used dielectric oils and a different alternative must be considered. Using a small amount of an emulsifier and sonication to produce a stable emulsion of oil in water is an attractive alternative for solving the problems regarding pumping of the oil to the supercritical oxidation unit.

Nonetheless, appropriate experimental conditions regarding the reaction temperature, oxidant excess and residence time, must be addressed in order to obtain conversions of the

used dielectric oil above 97%. Due to the fact that there is uncertainty on the appropriate oxidant amount required for a complete destruction of the oil, this figure might be underestimated in our experiments. A higher oxidant excess might produce higher conversions not only because of a faster reaction rate, but also because such a faster reaction rate would increase the heat released by the oxidation and thus would increase the reaction temperature. Finally, there is a need to conduct experiments with a higher flow rate of the organic because the experimental evidence suggests that this accelerates the reaction rate due to the heat released by the intense exothermal reaction.

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