Supercritical Water Oxidation for Toxic Organic Wastewater Disposal

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The destruction of toxic organic wastewaters from munitions demilitarization and complex industrial chemicals clearly becomes an overwhelming problem if left to conventional treatment processes. Two options, incineration and supercritical water oxidation (SCWO), exist for the complete destruction of toxic organic wastewaters. Incinerator, on the one hand, has associated problems such as very high cost and public resentment; SCWO, on the other hand, has proven to be a very promising method for the treatment of various types of wastewaters with its extremely efficient organic waste destruction of 99.99% with none of the emissions associated with incineration. In this review, the concepts of SCWO, the results of and present perspectives on its applications, as well as the industrial status of SCWO are critically examined and discussed.

Keywords: Industrial status of SCWO, industrial wastewater, supercritical water oxidation (SCWO), *and* toxic wastewater treatment.

INTRODUCTION

The world is facing a waste crisis from organic and toxic wastes. Every year the amount of wastes generated by industrial and domestic sources increase rapidly. Moreover, the treatment of organic and toxic waste is becoming more difficult and costly because of more stringent treatment standards and discharge limitations.

Public health concerns are the driving force for the continued legislation aimed at providing a cleaner and safer environment. Furthermore, Environmental Protection Agency (EPA) goals suggest destruction levels of up to 99.9999% for some compounds and the use of totally enclosed treatment facilities. Increased environmental concerns and unfavorable public opinion have challenged the continuing application of conventional waste management techniques (Li et al. 1991).

The conventional methods currently being used to treat the different types of organic and toxic wastes include adsorption, biological oxidation, chemical oxidation, land-based, and incineration technologies. Each treatment method has its shortcomings and, therefore, may not be the best option for treating organic and toxic wastes. Therefore, additional treatment of the adsorbent is required to destroy the contaminant and to regenerate the adsorbent.

Supercritical water oxidation (SCWO) has been proposed as a technology capable of destroying a wide range of hazardous organic waste. It has drawn much attention because it

effectively destroys a large variety of high-risk wastes resulting from munitions demilitarization and complex industrial chemicals.

The primary advantage of the SCWO process over such land-based alternatives as land filling, deep-well injection, and lagooning is the destruction method. Land-based disposal does not address the ultimate destruction of toxic waste components and can result in the contamination of the surrounding soil and groundwater. Deep-well injection systems are subject to plugging or fouling if an organic concentration of 1% or higher is allowed. Landfills and lagoons can contribute to the contamination of the air by volatile organics. Increased public concern and regulatory action will restrict or prohibit the land-based disposal of many organic wastes in the future.

Destruction methods based on oxidation of organic content for aqueous wastes include activated carbon treatment, biological treatment, incineration, wet air oxidation and supercritical oxidation. For very dilute aqueous waste whose organic ·contents are less than 1%, activated carbon treatment or biological treatment is often an effective destruction method. In activated carbon treatment, organics are first adsorbed onto carbon and then oxidized during regeneration of carbon. Partially oxidized materials are perfectly destroyed by after-burner treatment. Main cost is proportional to the organic content. So this method is not economically useful for waste containing more than 1% organic. Biological treatment systems often become poisoned and cannot be sustained for many wastes with organic concentrations of 1% or more.

Incineration, on the other hand, is restricted for economic reasons to waste streams relatively high organic concentrations. To attain high destruction efficiency for hazardous and toxic wastes, incineration must be operated at very high temperatures at $900\sim1100‡$ and often with excess air of $100\sim200\%$. With aqueous wastes, the energy required to bring the water component of the waste to this temperature is substantial. For the aqueous wastes with organic content more than 25%, the heat required for high temperature can be generated from wastes. With decreasing organic content, the supplemental fuel required to satisfy the energy balance becomes a major cost. Thus, controlled incineration of aqueous waste with less than 20% organics is only

consideration in extenuating circumstances (Thomason and Modell 1984). Incineration is also being regulated to restrict stack gas emissions to the atmosphere. Extensive equipment must now be used downstream of the reaction system to remove NO_x, acid gasses, acid gases, and particulates from the stack gases before discharge. The cost of this equipment often exceeds that of the incinerator itself.

In the range of concentration of 1 to 20% organic, wet air oxidation or supercritical water oxidation is far less costly than incineration or active carbon treatment. Wet air oxidation (WAO) has been offered as a method to treat wastewater, industrial wastes and sludge. From a public perception standpoint, WAO is more favorable than incineration, land application, deep well injection and ocean dumping because the waste products can be completely converted to inert materials and the process can be conducted as a closed system which does not produce any hazardous byproducts. Capital costs are often higher than incineration; however, operating costs are lower. It is possible to recover energy and inorganic in WAO. Wet air oxidation, commonly associated with sludge conditioning and some organic destruction is a low-temperature process (Boock 1996).

The Zimpro-Passavant's wet air oxidation process is typically operated in a temperature range of 150‡ to 350‡ and pressure range of 2 to 20 MPa. The operating pressure is maintained well above the saturation pressure corresponding to the operating temperature so that the reaction is carried out in the liquid phase. Residence times may range from 15 min to 120 min, and the chemical oxygen demand (COD) removal may typically be about 75% to 90%. Volatile acids constitute a substantial portion of remaining COD. The formation of volatile acids, particularly acetic acid, is a limitation for WAO. Furthermore, the effluent from incomplete (partial) wet oxidation of some wastewaters may be intensely colored and toxic (Li et al. 1991).

The above examples illustrate the utility of WAO as an alternative to incineration for the treatment of dilute aqueous wastes. However, a number of compounds, including m-xylene and acetic acid are refractory towards oxidation at these conditions. Additionally, WAO often cannot achieve the 99.9+% destruction efficiencies that
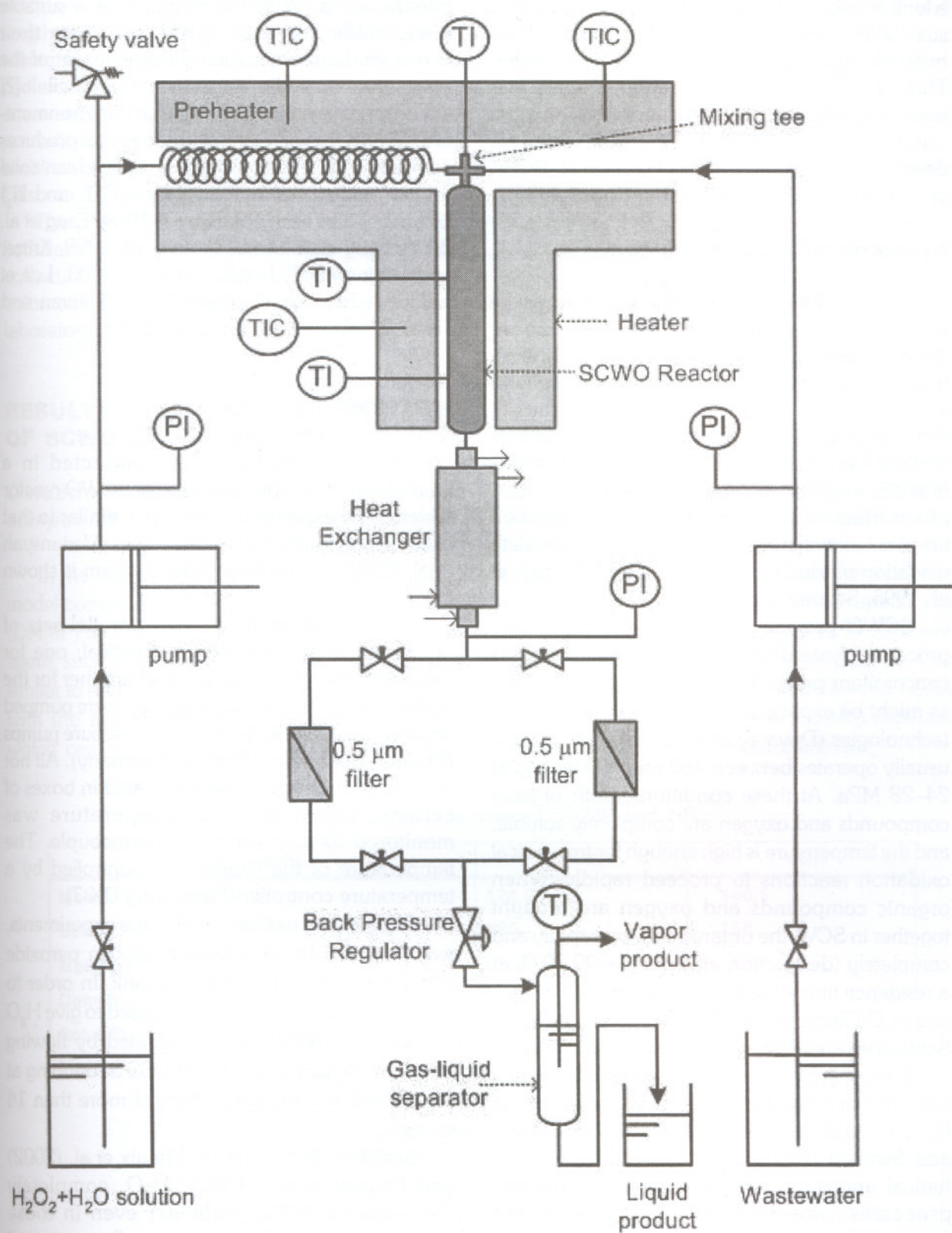
Figure 1. Simplified Flow Diagram of SCWO System

many newer regulations require. This motivated a look at oxidation under more severe conditions, such as higher temperatures and pressures, which bring the reaction mixture above its critical point. Thus, the supercritical oxidation process was born. Supercritical water oxidation, on the other hand, is known to attain nearly complete destruction of various organics, such as PCBs, and dioxins in a very short time (Boock 1996).

Supercritical water oxidation

Supercritical water oxidation is defined as the oxidation process which occurs in water above its critical point ($T_c = 374$°C and $P_c = 22.1$ MPa). It uses supercritical water as a reaction medium and exploits its unique solvating properties to provide enhanced solubility to organic reactants and permanent gases such as oxygen and carbon dioxide, single-phase environment free of inter-phase mass transfer limitations, faster reaction kinetics, and increased selectivity to complete oxidation products (Tester et al. 1993, Savage et al. 1995, Schimeider and Abeln 1999).

SCWO provides a potential alternative for processing hazardous military wastes without the concomitant production of noxious by-products as might be experienced with combustion-based technologies (Downey et al. 1995). The process usually operates between 450 and 600 °C and at 24–28 MPa. At these conditions, both organic compounds and oxygen are completely soluble, and the temperature is high enough for free radical oxidation reactions to proceed rapidly. When organic compounds and oxygen are brought together in SCW, the organic oxidizes rapidly and completely (destruction efficiency > 99.99 % at a residence time of less than one minute) to CO_2 and H_2O (Tester et al. 1993, Savage et al. 1995, Schmieder and Abeln 1999, Modell et al. 1989).

If any nitrogen is present, either introduced with the waste or if air is used as the source of O_2, the resulting product is N_2 or N_2O (Killilea and Swallow 1992). NO_x and SO_x gases, the typical undesired by-products of combustion processes, are not formed because the temperature is too low for these oxidation pathways to be favored.

Any N_2O found can be catalytically converted to N_2. Heteroatoms (e.g., chlorine, phosphorous,

and sulfur) react to form their corresponding mineral acids. With the addition of a suitable base, acids are neutralized and form their corresponding salts which precipitate out of the reacting mixture allowing for their removal. It [?] already proved that SCWO is an environment-friendly waste treatment technology that produces disposable clean liquid (pure water), clean solid (metal oxides), and clean gases (CO_2 and N_2) [Bianchetta et al. 1999, Burner 1994, Fang et al. 2000, Fang et al. 2005, Goto et al. 1999, Kritzer and Dinjus 2001, Kronholm et al. 2003, Lee et al. 2004, Rice and Steeper 1998, Sullivan and Tester 2004, Veriansyah et al. 2005].

METHOD

The experiments were conducted in a laboratory-scale, continuous-flow SCWO reactor system. The experimental set-up is similar to that used in previously published works (Veriansyah et al. 2005). A simplified flow diagram is shown in Figure 1.

The system involved two parallel sets of equipment that were almost identical: one for delivering the waste solution and another for the oxidant. Waste and oxidant solution were pumped separately into the system by high pressure pumps (Thermo Separation Product Company). All hot sections of the system were insulated in boxes of ceramic board and the temperature was monitored directly using a thermocouple. The temperature of the system was controlled by a temperature controller (Hanyoung DX 7).

Oxygen, the oxidant used in the experiments, was prepared by dissolving hydrogen peroxide with deionized water in a feed tank. In order to assure that all of H_2O_2 is decomposed to give H_2O and O_2, the oxidant was preheated by flowing through 6 m coiled 1/8-in O.D. SS 316 tubing at 600°C and at a residence time of more than 14 seconds.

Based on the studies of Phenix et al. (2002) and Croiset et al. (1997), H_2O_2 completely decomposed in the preheater even in those experiments carried out at a high flow rate and at low temperature. Waste solution was preheated by flowing through 0.5 m 1/8-in O.D. SS 316 tubing. The solutions mixed at the reactor

entrance in a SS 316 cross and then entered the reactor, which was constructed from a 300 mm length of 12.7-mm O.D. and 9.4-mm I.D. SS 316 tubing. Upon leaving the reactor, the effluent was cooled rapidly in a shell and tube heat exchanger; afterwards, the particles were filtered out by a 0.5-μm inline filter before being depressurized to ambient condition by a back-pressure regulator (Tescom Co. 26-1721-24).

The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder, and their volumetric flow rates were measured at ambient laboratory conditions.

RESULTS AND DISCUSSIONS OF SCWO EXPERIMENTS

Oxidation of toxic organic model compound

In the SCWO experiment with toxic organic model compound, dimethyl methylphosphonate (DMMP) was chosen as a simulant for the never agent, such as VX and GB, since it is structurally similar to and has physical properties comparable with the actual agent. The chemical structure which can be described DMMP, VX and GB is shown in Figure 2 where R_1 and R_2 are differing functional groups. For DMMP, $R_1 = OCH_3$ and $R_2 = CH_3$; for GB, $R_1 = F$ and $R_2 = CH(CH_3)_2$; and for VX, $R_1 = SCH_2CH_2N(C_3H_7)_2$, and $R_2 = CH_2CH_3$. Select physical properties of DMMP and Agent GB are listed in Table 1 (Akzo Nobel Function Chemical 2002).

The experiments were performed at 24 MPa with H_2O_2 as oxidant. The reaction temperatures ranged from 398 to 633 °C. Table 2 provides the experimental ranges and variables. The oxidation reaction in this study can be represented by following stoichiometric Eq. (1).

$$C_3H_9O_3P + 10H_2O_2 \rightarrow 3CO_2 + H_3PO_4 + 13H_2O \quad (1)$$

The conversion was monitored by analyzing the total organic carbon (TOC) in the liquid effluent samples using TOC Analyzer (Shimadzu TOC-VCPN). The results obtained from the SCWO of DMMP gave a TOC conversion value of 58.0–99.99%. It was found that the oxidative decomposition of DMMP proceeded rapidly and that a high TOC conversion of up to 99.99% was obtained within 11 seconds at 555°C. Gas analyses using GC-TCD (Hewlett-Packard 5890) showed that O_2 and CO_2 were the only products detected in the gaseous reactor effluent.

Table 1. Physical Properties of DMMP and GB

Property	DMMP	GB
Molecular Weight	124.08	140.1
Boiling Point, $^{\circ}C$	180	158
Melting Point, $^{\circ}C$	Pour point: < - 50	- 56
Density at 25°C, g/ml	1.17	1.09
Solubility in Distilled Water (g/100g) at 25°C	miscible	miscible

Table 2. Experimental Variables and Ranges

Experimental Variable	Range
Pressure, P	24 MPa
Temperature, T	398–633°C
Residence Time, t	4–15 s
TOC Concentration at Reactor Inlet	2–32 mmo/l
H_2O_2 Concentration at Reactor Inlet	38–300 mmol/l

Table 3. Property of LCD Wastewater
in Its Concentrated Form

Description	Value (mg/ℓ)
COD	37,191–41,323
BOD	26,250–81,287
Total Cr	3,495–3,622
Total N	10,987–54,306

Figure 2. Structure of Chemical Agent Welfare

Oxidation of real wastewater

Wastewater from an LCD manufacturing plant was treated with SCWO. The original wastewater contained a wide variety of organic pollutants and heavy metal chromium, as shown in Table 3. Experiments were carried out between 400 and 605 °C at a pressure of 25 MPa, a residence time of 15 s, and an oxidant excess of 132%.

The oxidative decomposition of wastewater was evaluated by chemical oxygen demand (COD) analysis according to Standard Method 5220D. The results of the experiments are shown in the Figures 3 and 4. These figures show that the conversion of COD increases and that the color changes gradually with the reaction temperature. Likewise, a COD conversion of up to 99.99% and a clear effluent were obtained a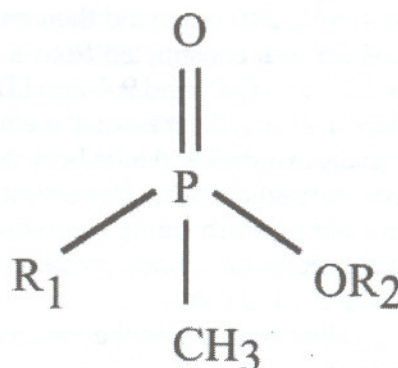t a reaction temperature 605°C. This was an indication that most organic compounds disappear as reaction temperature increasd.

Gas analyses using GC-TCD showed that O_2, N_2, and CO_2 were the only reaction products detected in the gaseous reactor effluent. There was no evidence of hydrogen, carbon monoxide, and methane being formed. In addition to the destruction of organic matter, in situ formation of chromium oxide nanoparticles by decomposition of heavy metal chromium contained in the wastewater was found during the SCWO process.

CONCLUSIONS

The studies performed on state-of-the-art laboratory scale showed that SCWO technology is a very promising method for the treatment of toxic organic wastewaters. Furthermore, for
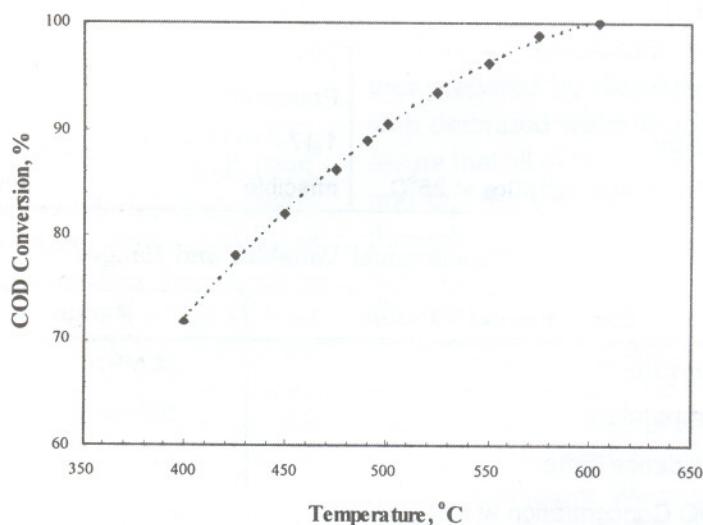

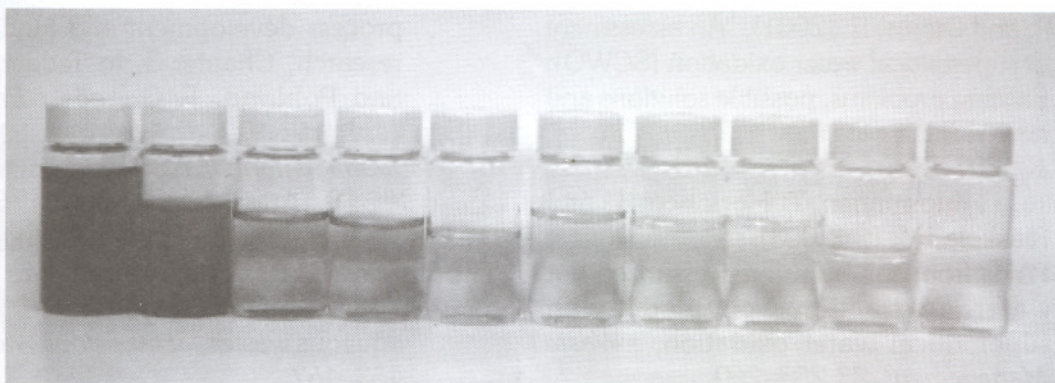Figure 3. Experimental Results of SCWO on Real Wastewater

Figure 4. Samples of Real Wastewater Before and After SCWO Treatment

wastes like LCD wastewater that contain valuable . heavy metals, SCWO treatment offers, besides an extremely clean effluent, the possibility of recovering these important compounds. The extremely clean inorganic material recovered through SCWO ought to increase interest in this treatment method. This type of waste may very well be the breakthrough of SCWO.

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