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Destruction of chemical agent simulants in a supercritical water oxidation bench-scale reactor

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Abstract

A new design of supercritical water oxidation (SCWO) bench-scale reactor has been developed to handle high-risk wastes resulting from munitions demilitarization. The reactor consists of a concentric vertical double wall in which SCWO reaction takes place inside an inner tube (titanium grade 2, non-porous) whereas pressure resistance is ensured by a Hastelloy C-276 external vessel. The performances of this reactor were investigated with two different kinds of chemical warfare agent simulants: OPA (a mixture of isopropyl amine and isopropyl alcohol) as the binary precursor for nerve agent of sarin and thiodiglycol [TDG, $(HOC_2H_4)_2S$] as the model organic sulfur heteroatom. High destruction rates based on total organic carbon (TOC) were achieved (>99.99%) without production of chars or undesired gases such as carbon monoxide and methane. The carbon-containing product was carbon dioxide whereas the nitrogen-containing products were nitrogen and nitrous oxide. Sulfur was totally recovered in the aqueous effluent as sulfuric acid. No corrosion was noticed in the reactor after a cumulative operation time of more than 250 h. The titanium tube shielded successfully the pressure vessel from corrosion.

Keywords: Supercritical water oxidation; OPA; Thiodiglycol; Double wall reactor

1. Introduction

Supercritical water oxidation (SCWO) is an environment-friendly waste treatment technology that produces disposable clean liquid (pure water), clean solid (metal oxides), and clean gas (carbon dioxide and nitrogen) [1–5]. SCWO uses supercritical water ($T_c = 374\,^\circ C$ and $P_c = 22.1$ MPa) as a reaction medium and exploits the unique solvating properties to provide enhanced solubility of organic reactants and permanent gases (such as oxygen and carbon dioxide). This single-phase environment makes free of interphase mass-transfer limitations, faster reaction kinetics, and an increased selectivity to complete oxidation products [6–10]. SCWO has most often been used to treat dilute organic waste streams that can be otherwise difficult to remediate.

Studies of SCWO for treating and destroying stockpiles chemical warfare agents (CWAs) are underway in support of an international program for the destruction of these CWAs stockpiles [11]. SCWO is an attractive treatment choice for treating and destroying stockpiles CWAs because the oxidation is carried out in a closed, controlled system that can be easily shut down should problems arise. Also, it does not produce the toxic or undesirable byproducts such as NO_x, as might be experienced with combustion based technologies [12]. Despite the high potential of the SCWO process, the significant corrosion of equipment, including reactor, heat exchanger and tubing, due to acidic byproduct has been obstacles for the successful application of CWAs stockpiles destruction by SCWO process [2,13–19]. Recently, many researchers have attempted to solve this problem using a variety of new or modified reactor designs. Design modifications include the dual-shell pressure-balanced

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vessel, the transpiring wall reactor, and the reactor concept of a film-cooled coaxial hydrothermal burner [11,19–27]. However, it was reported that the reactor can age including corrosion of the core tip and coaxial tubes when exposed to acidic conditions [18–22].

The primary goal of this study is to determine the optimum operational conditions to achieve high destruction efficiencies of >99.99% for the different types of CWA simulant in our newly designed bench-scale SCWO reactor. Thus, the present study examines the performance of the new reactor design to treat high-risk wastes resulting from munitions demilitarization. As a start, OPA, a mixture of isopropyl amine and isopropyl alcohol was oxidized first in order to verify the efficiency of the reactor. OPA was also chosen because it is well studied in our previous works [28,29] and classified as the binary precursor for nerve agent of sarin.

After the preliminary studies, for the concern of corrosive species, thiodiglycol [TDG, $(HOC_2H_4)_2S$], a well-known compound as a model organic sulfur heteroatom [11,30] was studied. Hydrothermal decomposition of TDG in supercritical water has been studied; however, there remained intermediate products, mainly hydrogen sulfide (H_2S) even at high temperature of 530 °C [17]. TDG oxidation in a SCWO reactor yields sulfuric acid, which is corrosive [16], which may lead to system operational shutdown because of corrosion. This study will contribute to the database of potential reactor design of SCWO for the hydrolysates of sulfur mustard in the larger-scale chemical agent destruction.

2. Experimental

2.1. The experimental apparatus design

The experiments were conducted in a bench-scale, continuous-flow SCWO reactor system. A schematic diagram of the system including the SCWO reactor is shown in Fig. 1. The system involves three parallel sets of feed line that are almost identical: one for delivering the waste feed solution, another for the oxidant solution, and the other for the distilled water. All hot sections of the system were insulated in boxes of ceramic board and the temperature was monitored directly using thermocouples (K-type). The system temperature was controlled by temperature controllers (Hanyoung Electronics, model DX 7). Oxygen, which was the oxidant used in these experiments, was prepared by heating an aqueous solution of hydrogen peroxide (H_2O_2) so that the H_2O_2 decomposed to form oxygen gas (O_2) and water (H_2O). Complete conversion of H_2O_2 to O_2 and H_2O in the preheater line was verified experimentally [31,32].

The reactor consists of a concentric vertical double wall. The external vessel with an inside diameter (ID) of 52 mm, an outer diameter (OD) of 102 mm, and an internal volume of 1274.74 cm^3 is made of Hastelloy C-276. The external vessel contains a reaction chamber limited by a non-porous wall, which was constructed by a 590 mm length of 22 mm ID and 25.4 mm OD titanium grade 2 tubing. An annular gap is created between the external vessel and the reaction chamber. The inner tube confines the reacting medium inside the tubular space; thus, the Hastelloy C-276 vessel has no contact with the aggressive solutions generally treated by SCWO. The detailed scheme of the reactor is shown in Fig. 2.

The distilled water, generally under supercritical condition around 25 MPa and 400 °C, is introduced in the annular gap by its lower part, and it heated up to reaction temperature by two cast heaters (2 kW each) located at the outer side reactor. In the top of annular gap, its direction is reversed entering the reaction chamber, and then, it flow downward, mixing with the waste and oxidant solution that enters into the reactor by the inlet dip pipe at the upper part. The products leave the reactor by its lower part. As the inner and outer flows are at the same pressure, no pressure constrains have to be considered.

Oxidant solution, waste solution, and distilled water were pumped separately into the reaction system using high-pressure pumps. Oxidant solution was fed by a Milton Roy (model 92014903) piston pump with flow rates ranging from 6 to 13 $cm^3\ min^{-1}$. The oxidant solution was preheated in 6 m of 1/8 in. (3.175 mm) OD coiled stainless steel (SS316) tubing by two cast heater (1.6 kW each) prior to its reactor input. Waste solution was delivered by a chromatographic pump (Young Lin, model M930) with flow rates ranging from 4 to 14 $cm^3\ min^{-1}$. The waste solution was injected directly into the reactor by the inlet dip pipe without being preheated, to avoid making any degradation of the waste. Distilled water was pumped by a Milton Roy (model MBPAF1-16) metering pump with flow rates ranging from 20 to 145 $cm^3\ min^{-1}$. The distilled water was preheated in 12 m of 1/8 in. (3.175 mm) OD coiled SS316 tubing by cast heater (6 kW) prior to its reactor input.

The products of the reaction were cooled in a cooling unit after leaving the reactor and, afterward, it were filtered to separate the solid particles through a 0.5 μm in-line metal filter and finally depressurized to ambient condition by a back-pressure regulator (Tescom Co., model 26-1721-24). After the product exited the regulator, it flashed to atmospheric pressure and the two-phase mixture was separated into two streams by the gas–liquid separator. The gas flow rate was measured using a wet gas meter, while the liquid flow rate was measured by recording the time required to fill a volumetric flask. The gaseous effluent was injected into the two gas chromatographs while the liquid effluent samples were collected in a glass sample vials and analyzed using a total organic carbon (TOC) analyzer and an ion chromatography (IC).

2.2. Materials and analytical methods

The materials used and analytical methods were already published in the previous papers [16,28]. Therefore, only a short description is given below.

OPA feed was prepared by mixing isopropyl alcohol, C_3H_8O (Daejung, 99% purity) with isopropyl amine, C_3H_9N (Acros, 99% purity) by weight percentage of 71.7:28.3. OPA was premixed with distilled and dionized (DDI) water as feed. TDG feed was prepared by making an aqueous solution of TDG (Aldrich, 99+% purity), which was used as received and dissolved in DDI water. The H_2O_2 feed solution was prepared by diluting a 35% (w/v) aqueous solution H_2O_2 (Junsei Chemical Company) with