

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, (HOC₂H₄)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.

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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 ($T_c = 374\text{ }^\circ\text{C}$ and $P_c = 22.1\text{ MPa}$) 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 kinet-

ics, 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, (HOC₂H₄)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 (H₂S) 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 (H₂O₂) so that the H₂O₂ decomposed to form oxygen gas (O₂) and water (H₂O). Complete conversion of H₂O₂ to O₂ and H₂O 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 cm³ 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 cm³ 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 cm³ 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 cm³ 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, C₃H₈O (Daejung, 99% purity) with isopropyl amine, C₃H₉N (Acros, 99% purity) by weight percentage of 71.7:28.3. OPA was pre-mixed 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 H₂O₂ feed solution was prepared by diluting a 35% (w/v) aqueous solution H₂O₂ (Junsei Chemical Company) with

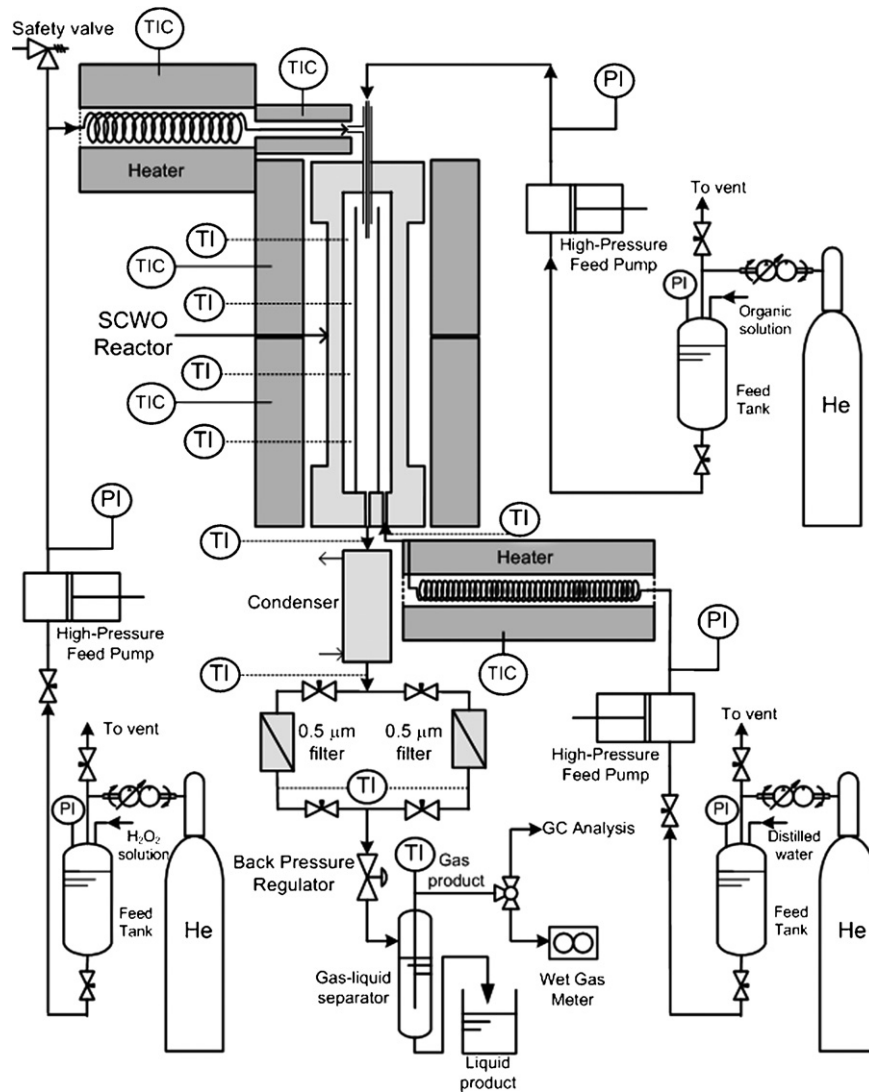


Fig. 1. Schematic diagram of the new bench-scale reactor for the supercritical water oxidation (SCWO) experiment.

DDI water to the desired concentration. All of the standard solutions for calibration and identification in liquid analytical methods were prepared using high-purity chemicals (Aldrich, ACS grade).

Gas samples were analyzed online using two Hewlett-Packard model 5890 Series II gas chromatographs with a thermal conductivity detector (TCD) and helium as the carrier gas, with detection limits ranging from 0.1 to 0.5 vol.%. The TOC concentration of the waste solution and the liquid-phase reactor effluent were analyzed using a TOC analyzer (Shimadzu, model TOC-VCSH), with a detection limit of 0.01 mg/L. The concentration of sulfate ion was determined by an ion chromatography (Dionex, model DX-100), which was equipped with an anion column (Dionex, model IonPac AS14) and an anion self-regenerating suppressor (Dionex, model ASRS-UltraII), with a detection limit of 0.1 mg/L. An inductively couple plasma (ICP) spectrometer with detection limit ranging from 0.02 to 0.1 was used to determine the concentration of metals contained in the liquid phase effluents.

2.3. Calculations

2.3.1. Residence times

The residence time is calculated by using the following equation:

$$t = \frac{A_R \times L_R}{M_{\text{total}}} \rho(P, T) \quad (1)$$

where A_R is the inside, cross-sectional area of the reaction chamber, L_R is the useful length of the reaction chamber as shown in Fig. 2, $\rho(P, T)$ is the density of fluid at reaction pressure and temperature, and M_{total} is the total feed mass flow rate including the water, the wastewater mixture, and the oxidant fed into the system. The density of the fluid was taken from steam tables for pure water [33] since the investigations were performed with dilute solutions of wastewater in the water and no data were available for density of water–wastewater–oxygen mixtures at supercritical condition.

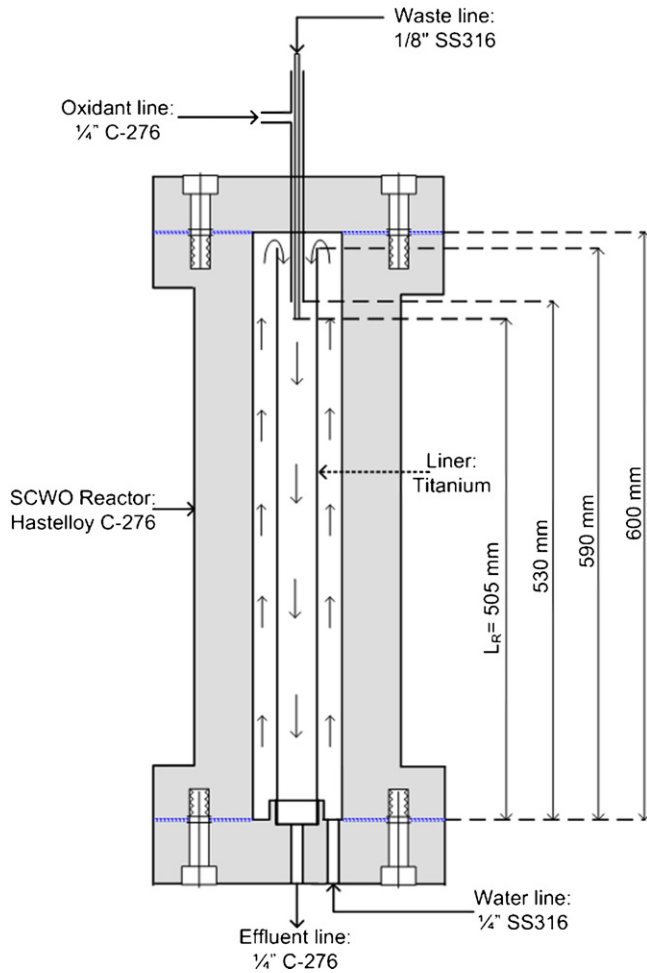


Fig. 2. Detailed scheme of the reactor.

2.3.2. TOC conversion

TOC conversion, noted as X , is defined as:

$$X = 1 - \frac{[\text{TOC}]_f}{[\text{TOC}]_i} \quad (2)$$

where $[\text{TOC}]_i$ and $[\text{TOC}]_f$ are the concentrations at the reactor inlet and outlet.

2.3.3. Initial concentration at reaction conditions

The initial concentration of reactant at reaction condition was calculated from the measured feed stock concentrations and flow rates of the feed streams with the process condition, assuming that the fluid has the density of water [34]. For initial concentration of TOC:

$$N_{\text{TOC}} = \frac{C_{\text{TOC}}}{12} \times \frac{M_{\text{TOC}}}{M_{\text{total}}} \times \rho(P, T) \quad (3)$$

where N_{TOC} is the initial concentration of TOC in mol/L, C_{TOC} is the TOC concentration in the wastewater feed tank in g/L, M_{TOC} is the wastewater feed flow rate to reactor in g/min, M_{total} is the total feed mass flow rate including the water, the wastewater mixture, and the oxidant fed into the system in g/min, and $\rho(P, T)$ is the density of water at reaction pressure and temperature.

For initial concentration of oxidant:

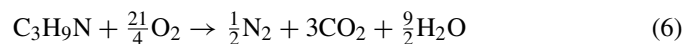
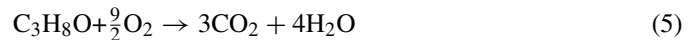
$$N_{\text{O}_2} = \frac{[\text{H}_2\text{O}_2]}{2} \times \frac{M_{\text{H}_2\text{O}_2}}{M_{\text{total}}} \times \rho(P, T) \quad (4)$$

where N_{O_2} is the initial concentration of O_2 in mol/L; $[\text{H}_2\text{O}_2]$ is the H_2O_2 concentration in the feed tank in mol/L, $M_{\text{H}_2\text{O}_2}$ is the H_2O_2 feed flow rate to reactor in g/min, M_{total} is the total feed mass flow rate including the water, the wastewater mixture, and the oxidant fed into the system in g/min, and $\rho(P, T)$ is the density of water at reaction pressure and temperature. In the calculation of initial concentration of the oxidant, the equation is divided by two because 1 mol of H_2O_2 is decomposed into 0.5 mol of O_2 and 1 mol of H_2O .

3. Results and discussion

3.1. OPA oxidation

The reactor performances were first tested using OPA as a model compound. Twenty-six SCWO experiments were conducted at different temperatures, residence times, and initial concentrations of TOC and oxygen at a fixed pressure of 25 MPa in the new reactor system under the experimental conditions as shown in Table 1. The destruction of OPA was expressed in terms of TOC conversion, as shown in Eq. (2). A stoichiometric level of oxygen was determined using the assumption of the complete oxidation of isopropyl alcohol and isopropyl amine:



The reaction products include gaseous and liquid components. The gas analysis indicated the absence of methane (CH_4) and carbon monoxide (CO) in the gaseous effluent. Oxygen (O_2), nitrogen (N_2), nitrous oxide (N_2O), and carbon dioxide (CO_2) were only the reaction products detectable.

A mass balance for both carbon and nitrogen species were conducted for all experiments, based on the measured inlet concentration and outlet product. As for the carbon balance, the incoming carbon was based on carbon in the feed OPA, and the outgoing carbon was the sum of the carbon in the liquid and gas

Table 1

Experimental conditions for oxidation of OPA and TDG in supercritical water

Experimental variable	Range of values	
	OPA	TDG
Pressure (P)	25 MPa	25 MPa
Temperature (T)	609–660 °C	555–609 °C
Residence time (τ)	11–15 s	11–13 s
Initial total organic carbon (TOC) concentration ^a	3.52–9.83 mmol/L	2.69–4.63 mmol/L
Initial oxygen (O_2) concentration ^a	27.65–41.96 mmol/L	16.83–19.66 mmol/L

^a The TOC and O_2 concentration at the reaction conditions was calculated from the feed stock concentration and flow rates of the feed streams with the process condition.

effluents. The only detectable carbon-containing product was CO₂, measured in the gas phase. Therefore, Henry's law was used to calculate the dissolved CO₂ concentration in the liquid effluent, based on the concentration in the off-gas [34]. The carbon balances had an average value of 98.1% ± 1.7%, with a range of 95.2%–101.1%.

As for the nitrogen balance, the incoming nitrogen was based on nitrogen in the feed OPA, and the outgoing nitrogen was based on the sum of the nitrogen in the liquid and gas effluents. The detectable nitrogen-containing products were N₂ and N₂O, all measured in the gas phase. Henry's law was also used to calculate the dissolved N₂ and N₂O in the liquid effluent, based on the concentration in the off-gas [34]. In all cases, no nitrites and nitrates were observed in the liquid effluents analysis at a detection limit of 0.1 mg/L. On the basis of this calculation, the nitrogen balances had an average value of 99.3% ± 3.3%, with a range of 94.2%–105.7%.

The effect of temperature and oxidant concentration on TOC conversion were determined by a set of 10 experiments at two concentration of oxygen excess (227% and 283%), with residence times of 12 s, and an initial TOC concentration of 5.19 mmol/L. Fig. 3 shows that the conversion of TOC increases with higher reaction temperature and oxidant concentration. TOC conversions were all >99.7% and the TOC concentrations at the reactor outlet were all <3 ppm. The influence of the TOC concentrations on the TOC conversion were determined by conducting five experiments at a temperature of 645 °C and residence times of 15 s at a fixed pressure of 25 MPa. The results of the experiments shown in Fig. 4 reveal that the TOC conversion at a given oxidant concentration increases with higher TOC concentration of the feed, in good agreement with our previous experiments [28].

These experimental results validate and confirm the performance of the reactor. High destruction rates based on total organic carbon were achieved (>99.99%) without production of chars or undesired gases such as CO and CH₄ in the gaseous effluent in the particular case of OPA destruction. No leakage was detected during the experiments. In addition, a visual control of the inner tube after the experiments revealed its perfect

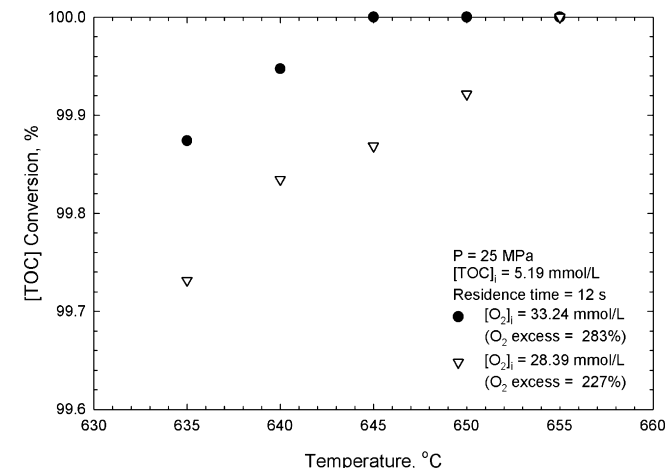


Fig. 3. Effect of temperature and oxygen excess on TOC conversion in the destruction of OPA.

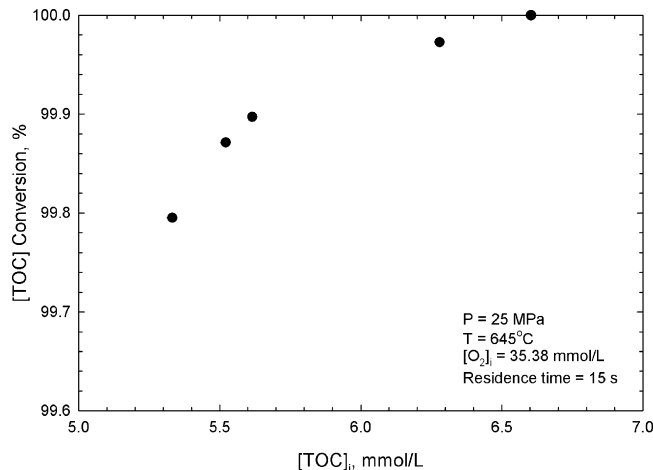
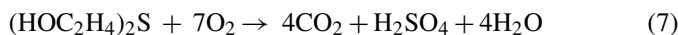


Fig. 4. Effect of TOC feed concentration on TOC conversion in the destruction of OPA.

compatibility with extreme conditions during oxidation, in terms of high concentration of oxidant and high reaction temperature. In regard to the corrosive species, the investigation whether the inner tube really performed its protective role against corrosion was performed. This was examined by the oxidation experiments involving the thiodiglycol (TDG).

3.2. Thiodiglycol oxidation

The oxidation experiments involving the TDG were conducted under the experimental conditions shown in Table 1. Oxygen was introduced with a large excess, approximately twice as much as the stoichiometric required. A stoichiometric level of oxygen was determined using the assumption of the complete oxidation of TDG (as follows):



The destruction of TDG was expressed in terms of TOC conversion, as shown in Eq. (2). In regard to elemental sulfur, its oxidation would yield sulfuric acid. Consequently, the amount of this acid in the aqueous output stream was measured by an ion chromatography. In addition, sulfur balance was defined to quantify the ability to remove elemental sulfur. The sulfur balance based on the measured sulfur in the inlet and outlet reactor. The incoming sulfur was based on sulfur in the feed of TDG, and the outgoing sulfur was based on the sum of the sulfur in the liquid.

Figs. 5 and 6, in good agreement with our previous experiments [16], show that the TOC conversion increases with higher reaction temperature, oxidant concentration, and TOC concentration of the feed. According to the experiments, the reactor proved to be very efficient to oxidize the TDG. High conversion (>99.99%) were obtained at a temperature of 605 °C, a pressure of 25 MPa, an oxygen concentration of 200% stoichiometric requirement, and residence times of 11 s, with a very good quality of gaseous effluent. This gaseous effluent was composed of carbon dioxide and oxygen. Hydrogen sulfide, carbon monoxide, and methane were not detected in the gaseous products. The carbon balance had an average value of 100.4% ± 2.5%,

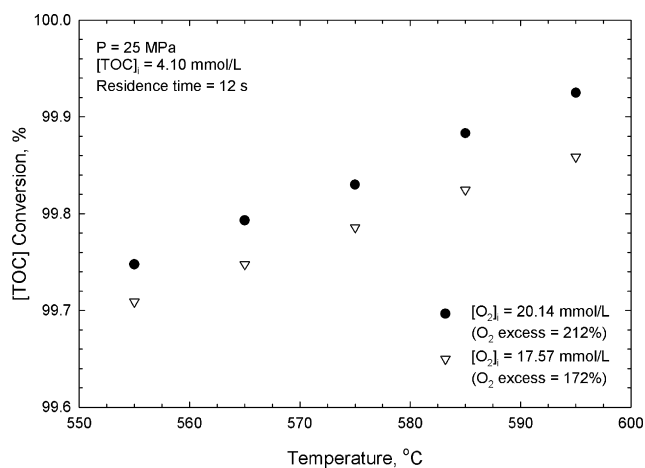


Fig. 5. Effect of temperature and oxygen excess on TOC conversion in the destruction of TDG.

with a range of 96.1%–105%. In regard to elemental sulfur, it was totally recovered in the output stream as sulfuric acid. The sulfur balance had an average value of $98.8\% \pm 1.8\%$, with a range of 95.5%–103.9%.

The reactor was opened after every 100 h experiment to control whether the inner tube was still intact. No damage was observed, neither crack, nor pit: it suffered no corrosion. The inner tube perfectly withstood extreme conditions during oxidation, in terms of both thermal gradients and corrosion. There are no deposits on the pressure vessel or on the filter, which means that the titanium tube shielded successfully the pressure vessel from corrosion. In addition, inductively coupled plasma analysis result showed that nickel, molybdenum, and titanium were not detected in the liquid phase effluents, which led us to believe that corrosion did not occur during the experiments. The entire reactor worked perfectly during each experiment; therefore, it could be employed in a SCWO process for the treatment of the organic wastes without corrosion problems. Further researches are being proceeded with feed materials containing acid and salts.

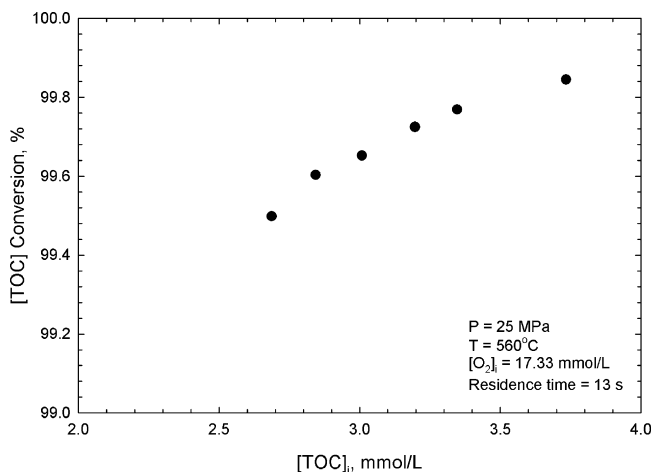


Fig. 6. Effect of TOC feed concentration on TOC conversion in the destruction of TDG.

4. Conclusions

A new design of SCWO bench-scale reactor has been developed to overcome the corrosion problem for the treatment of chemical agent simulants. The reactor consists of a concentric double wall with an inner non-porous titanium tube. Experiments with two different types of organic feeds, OPA and TDG, were performed to investigate the destruction performance and corrosion of the reactor under oxygen excess condition.

Experimental data of OPA oxidation showed that TOC conversion were all >99% at temperatures in the range of 609–660 °C at a fixed pressure of 25 MPa with a reactor residence time of 11–15 s. Conversion efficiency was significantly improved with temperature. The higher conversion was obtained at higher temperature and oxidant concentration. As the result of OPA oxidation, nitrogen, nitrous oxide, and carbon dioxide were formed in the gas-phase effluents. No leakage was detected during the experiments. The carbon and nitrogen balances of this experiment had average values of $98.1\% \pm 1.7\%$ and $99.3\% \pm 3.3\%$, respectively.

Based on the TDG oxidation experiments results, the inner titanium tube was proven to be very efficient in protecting the pressure vessel from corrosion by sulfuric acid. There was no corrosion damage observed, either on the pressure vessel or on the inner tube. Oxidation of TDG was also performed with a very high conversion (>99.99%), which signifies an elemental sulfur was almost removed as sulfuric acid. The carbon and sulfur balances had average values of $100.4\% \pm 2.5\%$ and $98.8\% \pm 1.8\%$. The reactor system can be successfully operated for extended periods of time without corrosion.

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