A Chemical Agent Simulant Oxidation Kinetics in Supercritical Water

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Abstract

Supercritical Water Oxidation (SCWO) has been proved to be a powerful technology to eleminate a wide range of wastes, but there are few references in the literature about the application of SCWO to chemical weapon agents wastes. In this work, SCWO have been tested to treat chemical agent simulant Dimethyl methylphosphonate (DMMP), which is similar to the nerve agent VX and GB (Sarin) in structure. All experiments were performed in an isothermal tubular reactor with a H_2O_2 oxidant, at temperature from 300 to 405 ^{o}C, and pressure 240 bar. The total organic carbon (TOC) concentration of DMMP in feed tank were between 1800 and 10000 ppm. The initial concentration of H_2O_2 were between 1.4 and 4.4 M, which were the stoichiometric amount needed to oxidize DMMP completely to carbon dioxide. It is found that the oxidative decomposition of DMMP proceeded rapidly and a high TOC decomposition up to 90% was obtained within 7 second at 400 ^{o}C. As the result of experiment, the power-law rate expression that best correlates the experimental results for the conversion of TOC was determined to be:

$$rate = -1.2 \times 10^2 \exp(-46.5071/RT)[TOC]^{0.96}[H_2O_2]^{0.27}.$$

Introduction

Under the provision of the 1993 International Chemical Weapons Convention, all stockpiled chemical warfare agents (CWAs) are to be irreversibly destroyed. Studies of degradation of CWAs at various temperatures are underway in support of an international program [1] for the destruction of these CWA stockpiles.

For the last decade a lot of studies have been carried out for the oxidation in supercritical water of various organic compounds including toxic organic materials like PCBs and dioxins [2-5]. Nowadays, SCWO is being applied in pilot plants and a few commercial scale plants and has been successfully demonstrated for complete destruction of organic wastes efficiently. To understand the reaction rate for a practical operating condition, the decomposition of military chemical weapons at SCWO is significant. The effectiveness of the SCWO must also be examined. Thus, in this paper we describe experiments designed to identify kinetic reaction rate in the supercritical water oxidation of DMMP.

Experiments

A schematic diagram of the SCWO experiment apparatus is shown to Figure 2. The reactant solutions
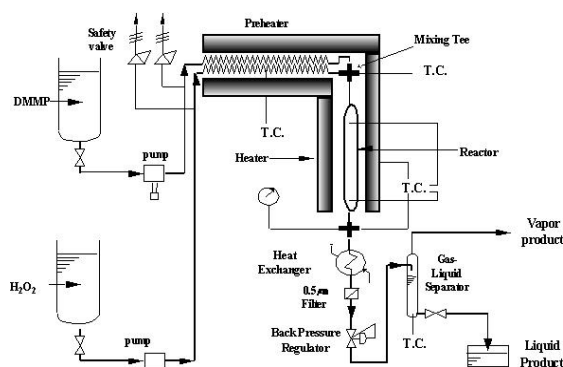
Figure 2. Schematic diagram of the continuous-flow reactor system for SCWO

were pumped to the desired operating volumetric flow rate using individual high-pressure pump. Each of the DMMP and oxidant solution is preheated in 1/16-in. OD of SS 316 tube. The reactor was made of a stainless steel 316 (280 mm long×18 mm OD×9.5 mm ID). The reactor effluent is cooled by passing through a shell and tube heat exchanger of 12 cm length and then is depressurized by a back-pressure regulator (Tescom co. 26-1721-24). After depressurized the liquid products were collected in a graduated cylinder. The gas samples were analyzed using a Hewlett-Packard 5890 gas chromatography with a thermal conductivity detector. A Rheodyne single mode injection valve provided on-line sample injection into a 10-ft length×1/8-in. OD Supelco Carboseive S-II permanent gas column. The concentration of DMMP was analyzed by a Hewlett-Packard 4890 GC Gas Chromatography with a Flame Ionization Detector and a 0.32mm ID×30m length, 5μm film thickness capillary column AT-1. The liquid-phase reactor effluents were analyzed by Shimadzu 5050 TOC Analyzer which is based on combustion and subsequent non-dispersive infrared (NDIR) gas analysis, respectively. Destruction efficiency of TOC, X, defined as follows, was used to evaluate the extent of oxidative decomposition, where $[TOC]_i$ is the initial TOC and $[TOC]_f$ is the residual TOC after reaction.

$$X = \left(1 - \frac{[TOC]_f}{[TOC]_i}\right) \tag{1}$$

Results and discussion

Forty-nine oxidation experiments were performed for DMMP in an isothermal, isobaric packed-bed flow reactor and the experiments were carried out in the sub and supercritical state. All experiments were performed in an isothermal tubular reactor with a H_2O_2 oxidant, at temperature from 300 to 405 °C, and pressure 240 bar. The TOC concentrations of DMMP in feed tank were between 1800 and 10000 ppm. The initial concentration of H_2O_2 were between 1.4 and 4.4 M, which were the stoichiometric amount needed to oxidize DMMP completely to carbon dioxide. The oxidation reaction in this study can be represented to following stoichiometric equation (2).

$$C_3H_9O_3P + 10H_2O_2 \rightarrow 3CO_2 + H_3PO_4 + 13H_2O \tag{2}$$

In order to investigate the effect of temperature, concentration of TOC, H_2O_2 and water one by one on the decomposition rate of TOC, we carry out a series of experiments in which one concentration was changed while the other three remained constant during the experiment. Figure 3 shows the effect of temperature on TOC conversion and we found that TOC was decomposed (> 90 %) near 400°C and its conversion was increased slightly with increasing temperature. It was reported that DMMP adsorb

dissociatively on aluminum oxide as methoxy methylphosphonate at temperatures below 300℃ and as methylphosphonate at temperatures above 500℃ [5].
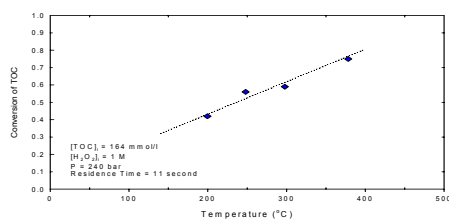
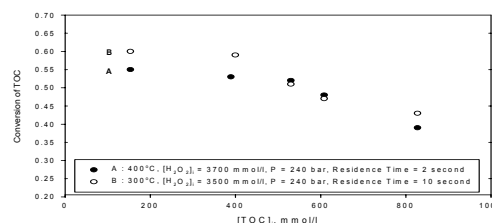Figure 3.Effect of temperature on TOC conversion

Figure 4. Effect of initial TOC concentration on TOC conversion
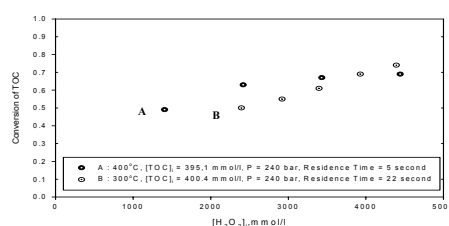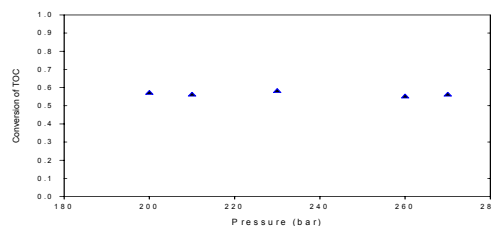
Figure 5. Effect of oxidant feed conc. on TOC conversion

Figure 6. Effect of pressure on TOC conversion

Figure 4 shows that TOC conversion was decreased with increasing initial TOC concentration at both sub and supercritical state. TOC conversion in the supercritical was approximately five times than in subcritical region since for getting the same value of TOC conversion in subcritical, we need residence time five times longer than in supercritical region. Figure 5 shows that TOC conversions are enhanced by increasing oxidant concentrations in the feed. This implies that the global reaction order for hydrogen peroxide as oxidant is greater than zero. Figure 6 shows that when the pressure is increased from 200 to 270 bar with constant temperature, TOC and oxidant concentrations, the TOC conversion does not appreciably change. Since the pressure is related to the water density, so we can conclude that water concentration did not effect the TOC conversion.

Figures 4-6 show that the TOC disappearance rate is a function of the COD and oxygen concentrations but not the water concentration. The global power-law reaction rate can be described as equation (3).

$$\text{Rate} = -k[TOC]^a[H_2O_2]^b \tag{3}$$

where a and b are the reaction orders of TOC and H_2O_2, respectively. k is the rate constant, which can be expressed in Arrhenius form in equation $k = A \exp(-E_a/RT)$; where A and E_a are the pre-exponential factor and activation energy, respectively. Equation (3) can be solved analytically with the initial condition X=0 at τ=0 to provide equation (4) as the relationship between the TOC removal efficiency and the experiment variables.

$$X=1-[1-(1-a)k(T)\tau[TOC]_o^{a-1}[H_2O_2]_o^b]^{1/(1-a)} \quad \text{if } a\neq1 \tag{4}$$

The hydrogen peroxide concentration was assumed constant throughout the reaction since H_2O_2 was always present in at least 200% excess of the stoichiometric requirement.

We used a non-linear regression analysis to fit the rate of reaction, and made estimates of the parameter values in order to predict the rate of reaction. We can search for those values that will minimize the sum of the squared differences of the experimental initial rates, and the predicted initial rates. We want to find the sum of

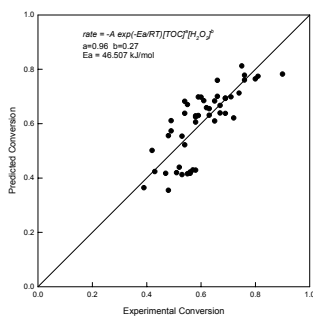$$S = \sum_{i}^{N_{exp}} \left(X_{exp} - X_{pred} \right)$$ for all data points to be minimum.

Figure 7. Parity plot for power-law

rate equation for TOC conversion

These 49 data sets led to reaction orders of a=0.96 ($\pm$0.09) for TOC, and b=0.27 ($\pm$0.15) for oxidant, respectively. The values of the Arrhenius parameters, A and E_a are 1.203 ($\pm$0.561)$\times 10^2$ $l^{1.23}$/(mmol$^{0.23}$ s) and 46.507 ($\pm$2.24) kJ/mol, respectively. The uncertainties reported here are the 95% confidence intervals.

Figure 7 shows a parity plot of the rate predicted from the global rate law using the parameters from experiments data in equation (5) against the rate obtained experimentally. A perfect fit of the model to the data would result in all the points lying on the 45° line. Our model fits reasonably well experimental data

Conclusion

Decomposition of DMMP in supercritical water was studied in a continuous flow tubular reactor. It is found that TOC conversion increased with increasing temperature, H_2O_2 concentration and residence time, on the other hand, it will be decreased with increasing initial TOC concentration. The kinetics of DMMP decomposition were best fit by the global rate law : rate = -1.2 x 10^2 exp(-46.507/RT)[TOC]$^{0.96}$[H_2O_2]$^{0.27}$.

where the reaction rate has unit of mmol/s, TOC and H_2O_2 are in mmol/l and the activation energy is in kJ/mol. DMMP could be completely destructed at supercritical temperature and pressure with sufficient amount of oxidant.

Reference

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