

## **Oxidation rate of OPA in Supercritical Water Oxidation**

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### **Introduction**

Supercritical Water Oxidation (SCWO) reaction is effective in destruction of hazardous wastes both for the complex industrial chemicals and military wastes. SCWO of organic compounds is especially drawing much attention due to effectively destroy a large variety of high-risk wastes resulting from munitions de-militarization and thus regarded as one of the promising technologies for alternative to incineration[1].

An important design consideration in the development of SCWO is the oxidation rate. The SCWO process is conceptually simple [2-4]. Organic waste in aqueous solution, typically ranging from 1-10 wt.%, is pressurized and heated to conditions above the critical point of water (374°C, 221 bar). At these conditions, the organic material can function as a fuel in an oxidation reaction. An oxidizer is added to this mixture, and given adequate reaction time, the organic waste reacted with oxygen is converted to CO<sub>2</sub> and H<sub>2</sub>O as the ultimate products.

To understand the oxidation rate for a practical operating condition, the decomposition of a target material in SCWO reactor is significant. The effectiveness of the SCWO must also be examined. Thus, in this paper we describe experimental results of OPA, a mixture of isopropyl alcohol and isopropyl amine designed to identify kinetic oxidation rate in the supercritical water oxidation. OPA is a highly volatile and flammable liquids, readily foaming oxides of nitrogen as well as explosive mixtures with air. When it comes to contact with organo phosphorous halides, it can produce extremely toxic organophosphate compounds[5]. Thus one of the aim of this paper is to find the optimum destruction conditions for the material in the experimental SCWO system.

## Experiments

Figure 1 shows a schematic diagram of laboratory scale SCWO experimental apparatus. All wetted parts, from the high pressure pumps to the back-pressure regulator, were made of stainless steel 316. The reactor was constructed from a 28 cm length of 9.5 mm i.d. tubing. The oxidant stream were prepared by dissolving hydrogen peroxide with deionized water in an oxidant storage tank. Another feed tank was loaded with OPA. The two feed streams were pressurized in two different lines by two high-pressure pumps and then separately preheated. In order to assure that all  $\text{H}_2\text{O}_2$  is decomposed to give  $\text{H}_2\text{O}$  and  $\text{O}_2$ , the oxidant was preheated by flowing through 6 m coiled 1/8 in. o.d. tubing. The OPA feed stream was preheated by flowing through 0.5 m 1/8 in. o.d. tubing. After preheating, two streams were mixed in the mixing tee. Upon exiting the

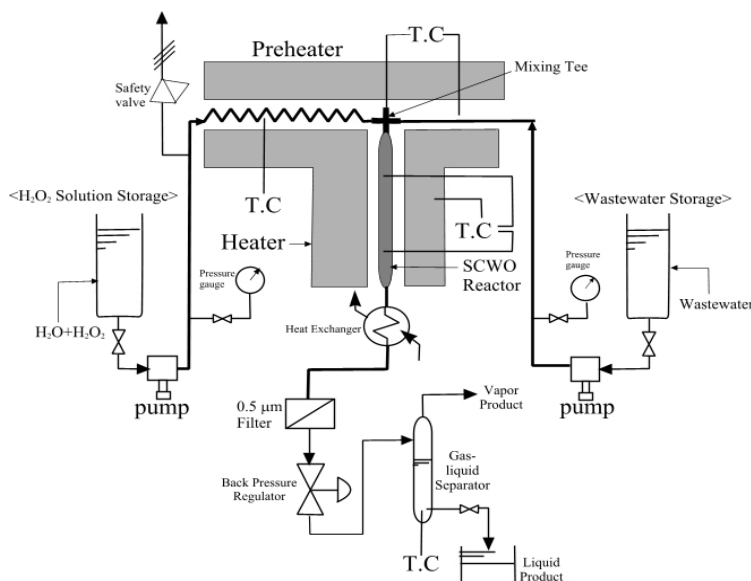


Figure 1. Schematic diagram of the continuous-flow reactor system for SCWO

reactor, the effluent was cooled rapidly by passing through a shell and tube heat exchanger and afterwards, depressurized by a back-pressure regulator. The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder. The concentration of OPA and liquid-phase reactor effluents were analyzed by TOC Analyzer(Shimadzu TOC-VCPN) which is based on combustion catalytic oxidation method and highly sensitive non-dispersive infrared (NDIR) gas analysis, respectively. Destruction efficiency of OPA(X) based on TOC was defined as

Destruction efficiency of OPA(X) = OPA conversion

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

where  $[\text{TOC}]_i$  and  $[\text{TOC}]_f$  are the OPA concentrations at the reactor inlet and outlet based on TOC respectively. X was used to evaluate the extent of oxidative decomposition in this reaction.

## Results and discussion

Oxidation experiments were performed for the waste water in an isothermal, isobaric continuous-flow reactor and the experiments were carried out in the supercritical state.

The global rate for the OPA decomposition may be expressed as

$$\text{rate} = -k [\text{OPA}]^a [\text{H}_2\text{O}_2]^b \quad (2)$$

where  $a$  and  $b$  are the reaction orders for OPA and  $\text{H}_2\text{O}_2$ , respectively.  $k$  is the reaction rate constant, which can be expressed in the 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 (2) can be solved analytically with the initial condition  $X=0$  at  $\tau=0$  to provide equation (3) as the relationship between the TOC removal efficiency and the experiment variables.

$$X = 1 - [1 - (1-a)k(T)\tau[\text{OPC}]_0^{a-1}[\text{H}_2\text{O}_2]_0^b]^{1/(1-a)} \quad \text{if } a \neq 1 \quad (3)$$

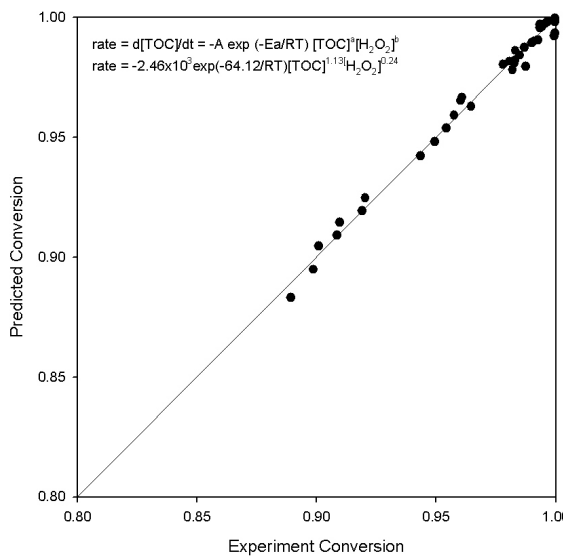


Figure 2. Parity plot for power-law rate equation for OPA conversion

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. The hydrogen peroxide concentration is assumed constant throughout the reaction since  $\text{H}_2\text{O}_2$  was always present in at least 200% excess of the stoichiometric requirement. 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  $S = \sum_i^{N_{\text{exp}}} (X_{\text{exp}} - X_{\text{pred}})^2$  for all data points to be minimum. Where  $N_{\text{obs}}$  is the the number of experiments,  $X_{\text{exp}}$  is the experimental OPA conversion and  $X_{\text{pred}}$  is model predicted OPA conversion.

These 37 data sets led to reaction orders of  $a=1.13 (\pm 0.02)$  for OPA, and  $b=0.24 (\pm 0.01)$  for oxidant, respectively. The values of the Arrhenius parameters,  $A$  and  $E_a$  are  $2.46 (\pm 0.71) \times 10^3 \text{ l}^{1.36}/(\text{mmol}^{0.36} \text{ s})$  and  $64.12 (\pm 2.11) \text{ kJ/mol}$ , respectively. The uncertainties reported here are the 95% confidence intervals.

Figure 2 shows a parity plot of the rate predicted from the global rate law using the parameters 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 this experimental data.

### **Conclusion**

Decomposition of OPA in supercritical water was studied in a continuous-flow reactor. The rate of OPA decomposition by supercritical water oxidation were best fit by the global rate law.

$$\text{rate} = -2.46 \times 10^3 \exp(-64.12/RT)[\text{OPA}]^{1.13}[\text{H}_2\text{O}_2]^{0.24}.$$

where the reaction rate has unit of mmol/s, [OPA] and [H<sub>2</sub>O<sub>2</sub>] are in mmol/l and the activation energy is in kJ/mol. OPA could be completely destructed at the experimental conditions with 200% excess H<sub>2</sub>O<sub>2</sub>.

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