

OPA oxidation rates in supercritical water

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Abstract

Supercritical water oxidation can effectively destroy a large variety of high-risk wastes resulting from munitions demilitarization and complex industrial chemical. An important design consideration in the development of supercritical water oxidation is the information on the oxidation rate. In this paper, the oxidation rate of isopropyl amine (OPA), one of high-risk wastes resulting from munitions demilitarization, was investigated under supercritical water oxidation (SCWO) conditions in an isothermal tubular reactor. H₂O₂ was used as the oxidant. The reaction temperatures were ranged from 684 to 891 K and the residence times varied from 9 to 18 s at a fixed pressure of 25 MPa. The conversion of OPA was monitored by analyzing total organic carbon (TOC) on the liquid effluent samples. The initial TOC concentrations of OPA varied from 7.21 to 143.78 mmol/l at the conversion efficiencies from 88.94 to 99.98%. By taking into account the dependence of reaction rate on oxidant and TOC concentration, a global power-law rate expression was regressed from 38 OPA experimental data. The resulting pre-exponential factor was $2.46(\pm 0.65) \times 10^3 \ell^{1.37} \text{mmol}^{-0.37} \text{s}^{-1}$; the activation energy was $64.12 \pm 1.94 \text{ kJ/mol}$; and the reaction orders for OPA (based on TOC) and oxidant were 1.13 ± 0.02 and 0.24 ± 0.01 , respectively.

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1. Introduction

Under the provisions of the 1993 International Chemical Weapon Convention, all stockpiled chemical warfare agents (CWAs) are to be irreversibly destroyed [1]. Studies of supercritical water oxidation (SCWO) for treating and destroying CWAs are underway in support of an international program for the destruction of these CWAs stockpiles. SCWO has been drawing much attention due to effectively destroy a large variety of high-risk wastes resulting from

munitions demilitarization and complex industrial chemical and regarded as one of the promising technologies for alternative to incineration [2–16]. SCWO uses water above its critical point (674 K, 22.1 MPa) as a reaction medium where both gas and liquid form a homogeneous single phase, thus avoiding interfacial mass transfer limitations. At supercritical operation conditions, oxidation proceeds quickly and completely for most H–C–N compounds with water, carbon dioxide, and molecular nitrogen as the main products [17,18].

One of the classes of CWAs stockpiles is a ‘binary chemical weapons’, which includes isopropyl alcohol and isopropyl amine (OPA), methylphosphonic difluoride (DF), and ethyl 2-diisopropylaminoethyl methylphosphonite (QL) [19,20]. Information of binary chemical weapons oxidation rate is an important design consideration in the development of

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SCWO process. Knowledge of the reaction kinetics allows one to calculate the residence times required for desire destruction and removal efficiency in a commercial SCWO reactor [4,5,21,22]. Several researchers have studied oxidation kinetics of CWAs and chemical agent simulant in SCWO [4,5,15,16,21]. However, there are no references in the literature about kinetic reaction rate of OPA. Thus, in this study we report experimental oxidation result of OPA designed to identify kinetic oxidation rate in supercritical water oxidation.

2. Experimental

2.1. Apparatus and procedure

The experiments were conducted in a laboratory-scale, continuous-flow SCWO reactor system. The experimental set-up is similar to previous published works [3]. The system involved two parallel sets of equipment that are almost identical, one for delivering the OPA solution and the other for the oxidant. OPA 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 thermocouple. The temperature of the system was controlled by a temperature controller (Hanyoung DX 7). Oxygen, the oxidant used in these experiments, was prepared by dissolving hydrogen peroxide with deionized water in a feed tank. In order to assure all of H_2O_2 is decomposed to give H_2O and O_2 , the oxidant was pre-heated by flowing through 6 m coiled 1/8 in. o.d. SS 316 tubing at 873.15 K and residence time of more than 14 s. Based on the studies of Phenix et al. [23] and Croiset et al. [24], it has been evidenced that H_2O_2 completely decomposed in the pre-heater even in those experiments carried out at high flow rate and low temperature. OPA solution was pre-heated 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 280 mm length of 18 mm o.d. and 9.5 mm i.d. SS 304 tubing. Upon leaving the reactor, the effluent was cooled rapidly in a shell and tube heat exchanger and then 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.

2.2. Materials and analytical methods

OPA was prepared by mixing isopropylalcohol (Daejung, 99% purity) with isopropylamine (Acros, 99% purity) by weight percentage of 71.7:28.3 in water. Hydrogen peroxide (Junsei, 35%, w/v aqueous solution) was used as a source

of oxygen. Diluted oxidant solutions were prepared using deionized water.

Gas samples were analyzed using a Hewlett-Packard 5890 gas chromatography with a thermal conductivity detector (TCD). A Rheodyne single mode injection valve provided on-line sample injection into a 3 m length \times 0.318 cm o.d. Supelco Carbosieves-II gas chromatograph column. The system was calibrated with a standard gas mixture containing H_2 , O_2 , N_2 , CO , CO_2 , and CH_4 .

The concentration of OPA and the liquid-phase reactor effluents were analyzed by total organic carbon (TOC) analyzer (Shimadzu TOC-VCPN), which is based on combustion catalytic oxidation method and highly sensitive non-dispersive infrared (NDIR) gas analysis, respectively. In order to provide precision data, samples were analyzed in duplicate. The relative standard deviation (R.S.D.) for the TOC measurement falls between 0.2 and 4.5% and the averages are reported as result.

2.3. Calculations

2.3.1. Residence times

The residence time is calculating using the following equation:

$$t = \frac{V_R}{M_{total}} \rho(P, T) \quad (1)$$

where V_R is the reactor volume, $\rho(P, T)$ the density of fluid at reaction pressure and temperature, and M_{total} is the total feed mass flow rate including both the waste–water mixture and the oxidant fed into the system. The density of the fluid is taken from steam tables for pure water [25] since the kinetic investigations performed with dilute solutions of OPA in water and no data were available for density of water–OPA–oxygen mixtures at supercritical condition. Koda et al. [26] have estimated the influence of 4.86 mol% O_2 on the mixture density. At 683.15 K and 24.7 MPa, the ratio of the steam table density to the value calculated was 1.20. Therefore, in more diluted systems the error in density and consequently in the residence time is thus smaller than 20%.

2.3.2. TOC decomposition

Destruction efficiency of OPA, X , based on TOC decomposition was defined as follows:

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

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

2.3.3. Initial concentration

The initial concentration of reactants used to determine the global reaction rates were 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 [27]. 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} the TOC concentration in the feed stock in g/l, M_{TOC} the TOC feed flow rate to reactor in g/min, M_{total} the total feed mass flow rate including both the waste–water 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:

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

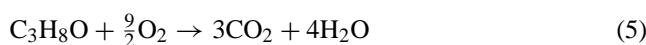
where $N_{\text{H}_2\text{O}_2}$ is the initial concentration of H_2O_2 in mol/l, $[\text{H}_2\text{O}_2]$ the H_2O_2 concentration in the feed stock in mol/l, $M_{\text{H}_2\text{O}_2}$ the H_2O_2 feed flow rate to reactor in g/min, M_{total} the total feed mass flow rate including both the waste–water 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.

3. Results and discussion

Thirty-eight supercritical water oxidation experiments were conducted at temperatures ranging from 684 to 891 K and a pressure of 25 MPa, with residence times of 9–18 s. The initial concentration of OPA based on TOC was ranged from 7.21 to 143.78 mmol/l and the initial oxygen concentration ranged from 122 to 1685% of stoichiometrically required amount for complete oxidation of the reactant. A summary of each experimental condition and the measured conversions are shown in Table 1.

3.1. OPA decomposition

Decomposition of OPA in the SCWO can be expected to follow the reactions for complete oxidation of isopropylalcohol and isopropylamine:



The gas analysis indicated the absence of hydrogen, carbon monoxide, and methane in the gaseous reactor effluent. Oxygen, nitrogen, and carbon dioxide were the only reaction products detected. As can be seen in Table 1, OPA was easily oxidized in the supercritical water oxidation; up to 99.98% of TOC decomposition.

3.2. Rate expression for oxidation of OPA

In order to develop reliable reaction rate expression, 38 data were taken under various conditions. The global power-

law reaction rate can be described as follows:

$$\text{rate} = -\frac{d[C_n]}{dt} = k[C_n]^a[\text{O}_2]^b[\text{H}_2\text{O}]^c \quad (7)$$

where $[C_n]$ is the concentration of reactant (mmol/l); $[\text{O}_2]$ the concentration of oxidant (mmol/l); $[\text{H}_2\text{O}]$ the concentration of water; t the reaction time; a – c are the reaction orders of C_n , O_2 , and H_2O , respectively. k is the rate constant, which can be expressed in Arrhenius form in equation as follows:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

where A and E_a are the pre-exponential factor and activation energy, respectively.

In this study, we assumed the global oxidation of OPA depends only on the temperature, the reactant concentration, and the oxidant concentration. The water concentration was assumed to have no explicit effect on the reaction rate, as is the case in many reported SCWO kinetic studies [3,5,7–9,14,21,27–31], so the global power-law reaction rate can be expressed as:

$$\text{rate} = -\frac{d[C_n]}{dt} = k[C_n]^a[\text{O}_2]^b \quad (9)$$

Substituting C_n with $[\text{TOC}]$ and rearranging the equation with respect to the TOC decomposition, X , defined by Eq. (2), the relationship obtained is,

$$-\frac{d(1-X)}{dt} = k[\text{TOC}]_i^{a-1}(1-X)^a[\text{O}_2]^b \quad (10)$$

In order to investigate the effect of the concentrations of TOC and oxidant one by one on the decomposition rate of TOC, a series of experiments were carried out in which one concentration was changed while the other remained constant during the experiment.

Fig. 1 shows that decomposition of TOC at a given oxidant concentration was increased with higher TOC concentration in the reactor feed. This is the indication of the fact

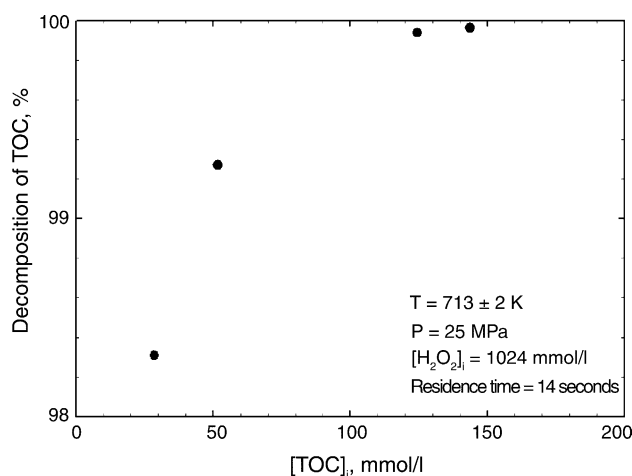


Fig. 1. Dependence of TOC decomposition on the initial TOC concentration.

Table 1
Summary of OPA oxidation experiments conducted in the SCWO flow reactor

Reaction temperature (K)	Residence time (s)	Initial concentration at reactor inlet*		Oxygen excess (%)	TOC decomposition (%)
		TOC (mmol/ℓ)	H ₂ O ₂ (mmol/ℓ)		
684	18	21.2	217.5	445	92.04
684	18	20.9	108.9	175	89.87
684	18	20.7	174.6	344	90.97
684	18	20.7	87.3	122	88.94
684	18	20.9	130.4	228	90.10
684	18	20.7	152.4	287	90.86
684	18	20.7	196.5	404	91.92
711	14	124.5	1038.6	307	99.94
712	14	28.6	1031.2	1686	98.31
716	14	143.8	1020.5	269	99.96
718	14	51.7	1005.3	843	99.27
729	14	15.2	95.8	233	94.93
729	13	15.0	80.1	183	94.36
730	13	15.1	111.2	290	95.44
730	14	15.3	126.6	338	95.75
731	14	16.2	154.0	380	96.03
732	14	15.4	140.1	404	96.08
751	12	120.2	853.3	244	99.97
771	12	12.1	94.2	271	98.49
771	13	12.4	106.9	311	98.70
773	11	11.5	67.9	183	98.19
773	12	11.8	80.8	227	98.31
775	12	12.2	118.6	362	99.01
776	12	12.1	131.8	421	99.10
801	10	76.6	790.8	406	99.98
807	10	97.6	729.5	267	99.98
828	10	10.4	58.6	180	99.35
828	10	10.3	70.6	241	99.44
828	10	10.1	106.4	422	99.58
828	10	10.7	115.9	437	99.67
829	10	10.5	81.6	285	99.36
829	10	10.4	93.5	348	99.57
887	9	7.6	92.4	380	99.95
888	9	7.5	102.8	436	99.95
888	9	7.3	83.1	347	99.92
889	9	7.2	62.3	239	99.90
890	9	7.3	51.7	179	99.86
891	9	7.5	71.5	274	99.91

* TOC and H₂O₂ concentration at the reactor inlet were calculated from the feed stock concentrations and flow rates of the feed streams with the process condition.

that the global reaction order for TOC is greater than zero. Fig. 2 shows the effect of oxidant concentration on the TOC decomposition at given TOC concentration. The decomposition of TOC is also enhanced by higher oxidant concentration. This implies that the global reaction order for oxidant is also greater than zero.

In this study, all of experiments were performed at a short contact time, between 9 and 18 s, therefore the method of initial rates can be used to all data [32,33]. If the method of initial rate is applied to Eq. (10) with the initial condition $X=0$ at reaction time $t=0$, it can be solved analytically to provide Eq. (11) as the relationship between the TOC removal efficiency and the experiment variables.

$$X = 1 - [1 - (1 - a)kt[\text{TOC}]_i^{a-1}[\text{O}_2]_i^b]^{1/(1-a)} \quad (11)$$

for $a \neq 1$

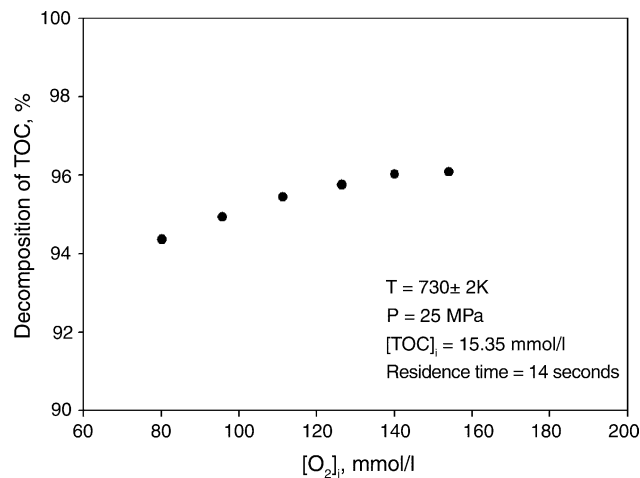


Fig. 2. Dependence of TOC decomposition on the initial oxidant.

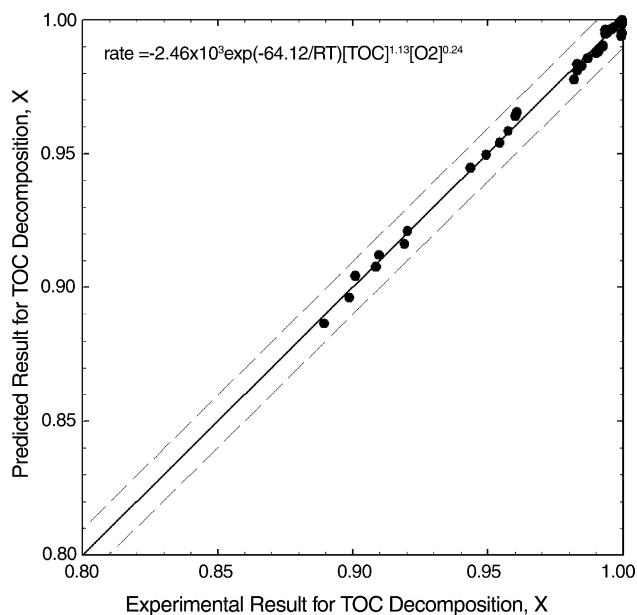


Fig. 3. Parity plot for power-law rate equation on decomposition of TOC.

A multi variable non-linear least squares technique was used to estimate the kinetic parameters A , E_a , and the reaction orders. The best-fit values were obtained by minimizing the sum of squares error

$$s^2 = \sum_i^{N_{\text{exp}}} (X_{\text{exp}} - X_{\text{pred}})^2 \quad (12)$$

where N_{exp} is the number of experiments, X_{exp} the experimental conversion, and X_{pred} is the model predicted OPA conversion. The quality of data fitting was evaluated by R^2 in ANOVA routine [34]. It has algorithms to estimate 95% confidence interval on each parameter and on the predicted response. Using this procedure and considering all data points, the best-fit global rate expression for TOC of OPA oxidation in supercritical water was obtained as

$$-\frac{d[\text{TOC}]}{dt} = 2.46(\pm 0.65) \times 10^3 \exp\left(\frac{-64.12 \pm 1.94}{RT}\right) \times [\text{TOC}]^{1.13 \pm 0.02} \times [\text{O}_2]^{0.24 \pm 0.01} \quad (13)$$

Fig. 3 shows a good comparison between the experimental and prediction TOC decomposition with $R^2 = 0.992$. The dashed line, indicating a deviation of $\pm 1\%$ TOC decomposition from the 45° line (perfect match), contain all data points. This model fits very well with our experimental data.

4. Conclusions

The oxidation kinetics of OPA was examined from 684 to 891 K at 25 MPa, residence times of 9–18 s with the initial concentration of OPA based on TOC was ranged from

7.21 to 143.78 mmol/l and the initial oxygen concentration ranged from 122 to 1685% of stoichiometrically requirement. Experimental data showed that TOC decomposition greater than 99.9% can be obtained within 10 s at temperature 801 K.

By taking into account the dependence of reaction rate on oxidant and TOC concentration, all experimental data were used to fit the reaction rate in a non-linear regression analysis, assuming a zero-order dependence on water concentration. Reaction parameter values were determined to be $2.46(\pm 0.65) \times 10^3 \ell^{1.37} \text{mmol}^{-0.37} \text{s}^{-1}$ for the pre-exponential factor, $64.12 \pm 1.94 \text{ kJ/mol}$ for the activation energy, and for the reaction orders, 1.13 ± 0.02 for OPA (based on TOC), and 0.24 ± 0.01 for oxidant.

Acknowledgements

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