

Development of Wastewater Treatment Technique by Catalytic Oxidation in Superheated Steam

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Abstract The purpose of this research was the development of a wastewater treatment technique using catalytic oxidation in superheated steam. The target substance was isopropyl alcohol (IPA). The experiment was carried out using a plug-flow reactor filled with MnO₂ catalyst. The optimum decomposition condition was determined, and the kinetics of the catalytic oxidation reaction were analyzed. The experimental results were expressed as total organic carbon (TOC) removal. The dependences of the TOC removal on the reaction temperature and residence time were investigated. The TOC removal increased with the reaction temperature and residence time. It was 99.8% at 300°C, 0.9 MPa, 11 s, and oxidant ratio of 1.2. On the other hand, the TOC removal was constant for a long residence time at low reaction temperatures of 200 and 230°C. This was because acetone and acetic acid were produced via the oxidation of IPA, and they were detected as TOC. The reaction kinetics were examined using the pseudo-first-order reaction model; the TOC removal correlated well with this model. Based on the results of the kinetics, the activation energy (E_a) for TOC decomposition was determined from the Arrhenius equation; it was 56.1 kJ/mol. These results indicate that catalytic oxidation in superheated steam is useful for wastewater treatment.

1 Introduction

In semiconductor manufacturing, cleaning and drying processes are carried out to remove organic substances. The organic solvent used in these processes is amphiphilic, and a high-purity solvent is used. However, the recovered organic solvent is not high purity, and its reuse is difficult. Therefore, the wastewater is generally treated using the activated sludge method. However, this method has problems such as a long treatment time, the necessity of pre-treatment and post-treatment, and the generation of excess sludge. Therefore, a wastewater treatment technique with a short time and less environmental load is required.

Figure 1 shows the phase diagram of water. In the hydrothermal oxidation method, supercritical water and subcritical water are often used. The supercritical water oxidation (SCWO) method exhibits excellent treatment ability, allowing clean and efficient decomposition of many aqueous organic wastes. Sanchez-Oneto *et al.* (2007). studied the decomposition of different cutting fluids (Biocut and Servol) in supercritical water. The operating temperatures were 673–773 K for a wide range of residence times of 6–105 s. As a result, SCWO of both the cutting fluids achieved more than 95% removal of both

the chemical oxygen demand (COD) and total organic carbon (TOC) at 773 K. Sogut and Akgun (2007) studied a model azo dye pollutant (CI Disperse Orange 25) using SCWO in a plug-flow reactor. They achieved a removal of up to 98.52% in very short residence times of 4–12 s.

Table 1 shows the conditions for hydrothermal oxidation. The SCWO method has the drawback of severe conditions. Hence, catalytic oxidation in superheated steam is attracting attention as a new wastewater treatment technique. Cost reduction for the equipment can be expected because superheated steam oxidation is a low-temperature and low-pressure process compared with SCWO.

However, to the best of our knowledge, the oxidation reaction kinetics of wastewater in superheated steam with a catalyst has not been reported. The purpose of this research was to investigate the decomposition and analyze the kinetics. In this study, an aqueous solution of isopropyl alcohol (IPA) was selected as a model for wastewater under superheated steam conditions.

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Table 1. Conditions for hydrothermal oxidation

Method	Condition
SCWO	$T \geq 374^\circ\text{C}$ (T_c) and $P \geq 22.1$ MPa (P_c)
Superheated steam oxidation	$100^\circ\text{C} < T < T_c$ and $P < P_s$ $T \geq T_c$ and $P \leq P_c$

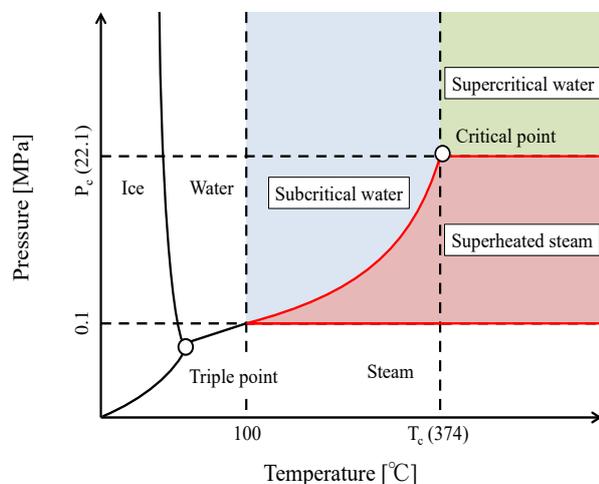


Figure 1. Phase diagram of water

2 Experimental

2.1 Apparatus

Figure 2 shows a plug-flow reactor. The two feed streams were pumped in different lines and only the H_2O_2 solution feed stream was preheated. A syringe pump (Model 500D, Teledyne Isco, USA) and a plunger pump (Model L-6000, Hitachi, Japan) were used to pump the feed to the reactor at the required flow rate, which depended on the required residence time (5–30 s) in the reactor. The reactor used was a type-316 stainless steel tube with the following dimensions: 1 in. diameter; 2.1 mm thickness; and 1 m length. The central part (86 cm) of the reactor was filled with MnO_2 particles as catalyst. Other spaces of the reactor were filled with 3 mm ϕ α -alumina balls. The preheating coil for H_2O_2 aqueous solution was made of a 1/8 in. spiral tube of type-316 stainless steel with a length of 4 m. H_2O_2 was used as the oxidant source and it was completely decomposed to oxygen and water in the preheater section. After preheating, oxygen and the model wastewater were reacted on the MnO_2 catalyst. The effluent from the reactor was rapidly cooled using a cooling coil placed in a water bath. The effluent was depressurized using a back-pressure regulator, and the liquid sample was recovered using pure water.

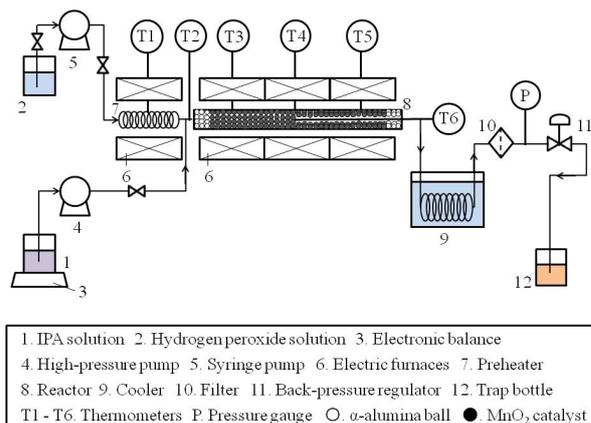


Figure 2. Experimental apparatus

2.2 Materials

IPA ($\text{C}_3\text{H}_8\text{O}$, 99.7% purity, FUJIFILM Wako Pure Chemical, Japan) was prepared as the model wastewater such that the concentration of the IPA aqueous solution was 0.5wt% at the reactor inlet. H_2O_2 aqueous solution (30wt%, FUJIFILM Wako Pure Chemical, Japan) was prepared as the oxidant source such that the oxidant ratio was 1.2. MnO_2 catalyst shows high catalytic activity and stability in SCWO. In this study, we used MnO_2 (min. 70.0% assay, particulates, FUJIFILM Wako Pure Chemical, Japan) as the catalyst in the reaction.

2.3 Calculation of residence time

The residence time (t) in the reactor packed with the MnO_2 catalyst was calculated using the following equation:

$$t [s] = \frac{\text{Void volume in the catalyst layer [mL]}}{\text{Flow rate of mixed gas [mL/s]}} \quad (1)$$

The O_2 , water, and IPA flowing in the reactor were regarded as a mixed gas, and the flow rate was calculated from the physical properties at the reaction conditions.

2.4 TOC removal

TOC removal (X_{TOC}) was used to evaluate the decomposition efficiency of catalytic oxidation in superheated steam, and it was defined as follows:

$$X_{\text{TOC}} [-] = 1 - \frac{\text{Remaining TOC [g]}}{\text{TOC in supplied IPA solution [g]}} \quad (2)$$

In this study, the condition of 99.5% was taken as the optimum decomposition condition.

2.5 Oxidant ratio

The oxidant ratio was defined as follows:

$$\text{Oxidant ratio} [-] = \frac{\text{O}_2 \text{ supplied to the reactor [mol]}}{\text{Stoichiometric amount of O}_2 \text{ [mol]}} \quad (3)$$

The oxidant ratio was 1.2, so that the TOC in IPA was completely oxidized.

2.6 Analysis

The liquid samples from the reactor were evaluated by analyzing the TOC concentration. TOC analysis was performed using a TOC-V CPH (Shimadzu, Japan). To obtain accurate data, the samples were analyzed in duplicate; the averages are reported as the results.

3 Results and Discussion

3.1 Effects of reaction temperature and residence time

In this study, the effects of the reaction temperature and residence time on the catalytic oxidation of IPA in superheated steam were investigated.

Figure 3 shows the reaction temperature and residence time dependences of the TOC removal by catalytic oxidation in superheated steam. The TOC removal increased with the reaction temperature and residence time. It was 99.8% at 300°C, 0.9 MPa, 11 s, and an oxidant ratio of 1.2. On the other hand, the TOC removal was constant for a long residence time at low reaction temperatures of 200 and 230°C. This was because acetone and acetic acid were produced via the oxidation of IPA and C-C bond cleavage. It is presumed that the oxidation decomposition rate of TOC decreases because acetone has the same amount of carbon as that in IPA, and acetic acid is stable.

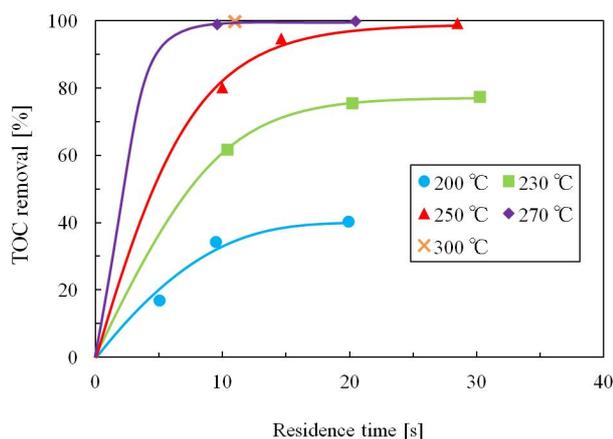


Figure 3. Reaction temperature and residence time dependences of TOC removal by catalytic oxidation in superheated steam at 0.9 MPa and oxidant ratio of 1.2

3.2 Kinetics analysis

The global reaction rate for the decomposition of TOC via hydrothermal oxidation can be expressed as follows:

$$-\frac{d[\text{TOC}]}{dt} = k[\text{TOC}]^\alpha [\text{O}_2]^\beta [\text{H}_2\text{O}]^\gamma \quad (4)$$

where $[\text{TOC}]$ is the reactant concentration (mol/L), $[\text{O}_2]$ is the O_2 concentration (mol/L), $[\text{H}_2\text{O}]$ is the H_2O concentration (mol/L), t is the residence time, k is the reaction rate constant, and α , β , and γ are the reaction orders of TOC, O_2 , and H_2O , respectively.

In this study, kinetics analysis was performed using the pseudo-first-order reaction model. H_2O was present in excess as superheated steam. In addition, O_2 was present in excess because the oxidant ratio was 1.2. As a result, the reaction order of H_2O and O_2 was assumed to be 0 ($\beta=\gamma=0$). In the pseudo-first-order reaction model, the reaction order of TOC was assumed to be 1 ($\alpha=1$). From Eq. (4), the following simplified equation was obtained:

$$-\frac{d[\text{TOC}]}{dt} = k[\text{TOC}] \quad (5)$$

Integrating Eq. (5) and using X_{TOC} , a relationship Eq. (6) between the TOC removal and residence time was obtained.

$$-\ln(1 - X_{\text{TOC}}) = kt \quad (6)$$

Figure 4 shows the kinetics of IPA decomposition via catalytic oxidation in superheated steam. The reaction correlated well with the pseudo-first-order reaction model. Using kinetics analysis, the reaction rate constants at each reaction temperature were obtained.

The temperature dependence of the reaction rate constants was expressed by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where A is the frequency factor (s^{-1}), E_a is the activation energy (J/mol), R is the universal gas constant (J/(mol · K)), and T is the reaction temperature (K). The logarithmic form of Eq. (7) is as follows:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (8)$$

Figure 5 shows the Arrhenius plot of IPA decomposition via catalytic oxidation in superheated steam. E_a was 56.1 kJ/mol and A was $6.17 \times 10^4 \text{ s}^{-1}$. Table 2 shows the reaction rate constants at each reaction temperature and the activation energy. Furthermore, the global rate expression for catalytic oxidation of IPA in superheated steam is as follows:

$$-\frac{d[\text{TOC}]}{dt} = 6.17 \times 10^4 \cdot \exp\left(-\frac{56.1 \times 10^3}{RT}\right) \cdot [\text{TOC}] \quad (9)$$

From previous research, it is known that the activation energy of IPA in SCWO is 133.5 kJ/mol (Abelleira, 2013). It is presumed that the activation energy in this study is lower due to the catalytic action. Owing to efficient contact of the activated TOC with O_2 on the catalyst surface, the reaction proceeds with low energy.

In Figure 6, the X_{TOC} predicted using Eq. (9) are plotted against the experimental values obtained in this study. The average relative error between the predicted and experimental X_{TOC} was 8.52%, which was a good agreement.

Table 2. Reaction rate constants at each reaction temperature and activation energy

T [°C]	k [s ⁻¹]	E_a [kJ/mol]
200	0.0426	
230	0.0743	56.1
250	0.176	

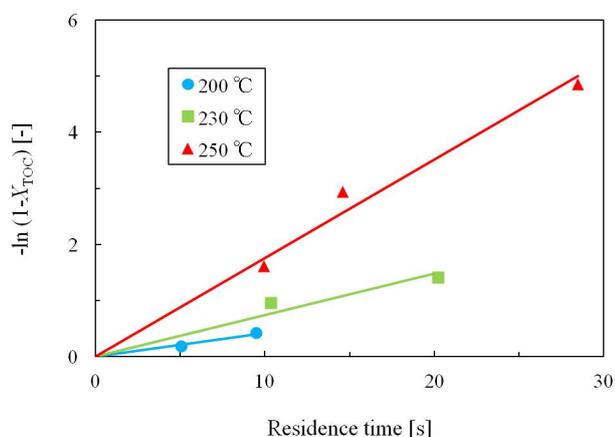


Figure 4. Kinetics of IPA decomposition by catalytic oxidation in superheated steam at 0.9 MPa and oxidant ratio of 1.2

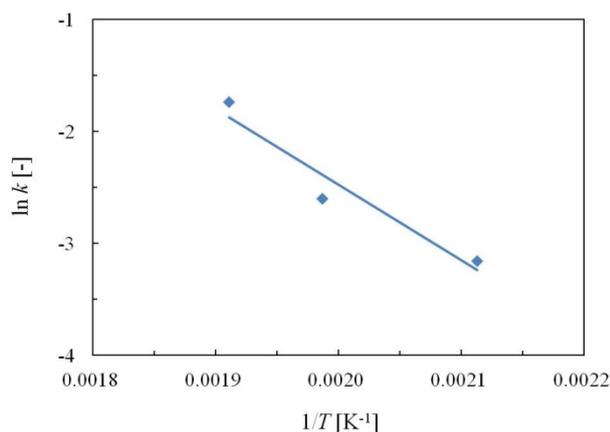


Figure 5. Arrhenius plot of IPA decomposition by catalytic oxidation in superheated steam at 0.9 MPa and oxidant ratio of 1.2

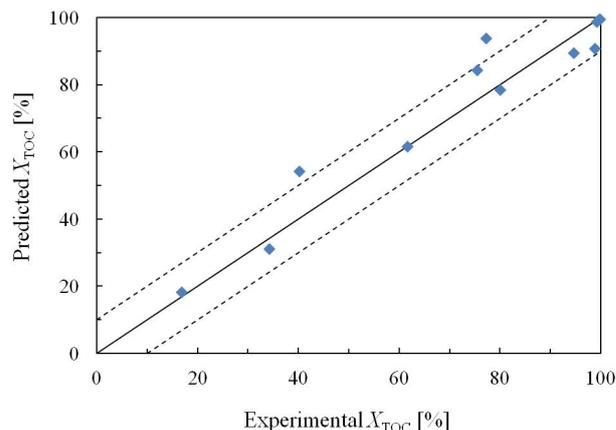


Figure 6. Comparison between predicted and experimental X_{TOC}

4 Conclusions

Catalytic oxidation of IPA in superheated steam was carried out using a plug-flow reactor filled with MnO_2 catalyst. The TOC removal achieved was 99.8% at 300°C, 0.9 MPa, 11 s, and an oxidant ratio of 1.2.

Kinetics analysis showed that the reaction correlated well with the pseudo-first-order reaction model. According to the Arrhenius plot, the activation energy was 56.1 kJ/mol. The average relative error between the TOC removal predicted using the global rate expression, and the experimental values was 8.52%. Therefore, the TOC removal at any residence time can be estimated using the global rate expression.

References

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