A Novel On-Site System for the Treatment of Pharmaceutical Laboratory Wastewater by Supercritical Water Oxidation

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For the on-site treatment of laboratory waste, we have been developing a compact-sized reaction system for the treatment of laboratory wastewater using supercritical water oxidation (SCWO) technology. Pharmaceutical laboratory wastewater is one of the most difficult wastewaters to treat because of its high concentration of halogenated organic compounds. We proposed a new cascade process in which two reactors are consecutively combined, carrying out hydrolysis in the first reactor followed by SCWO in the second reactor, for the complete removal of halogenated organic compounds. Dichloromethane was chosen as a representative model of chlorinated compounds. There have been many previous studies on the hydrolysis of dichloromethane, which results in the coproduction of formaldehyde and HCl. However, there has been less investigation on the kinetics of formaldehyde oxidation in supercritical water. In this study, we focus on the oxidation of formaldehyde in supercritical water with and without a catalyst. As a result, formaldehyde can be completely decomposed at 400°C and 25 MPa within a very short contact time in a heterogeneous system with a MnO2 catalyst.

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1. Introduction

The laboratory wastes generated from scientific research sometimes contain various hazardous chemicals, and present a serious problem for universities. Supercritical water oxidation (SCWO) technology has been widely studied and applied to wide variety of hazardous wastes. Most organic compounds have been reported to be converted into CO$_2$ and H$_2$O by SCWO within a very short residence time at conditions above the critical point of water (374°C, 218 atm).\(^{(1,2)}\) In our group, we have recently developed a compact reactor for the on-site treatment of laboratory wastewater, which we expect will meet the two important and fundamental concepts of such waste treatment, “treatment at the origin” and “self-responsibility for waste.”

Among laboratory wastes, the wastewater from pharmaceutical laboratories is one of the most difficult wastewaters to treat with SCWO because it usually contains several types of halogenated compounds such as chloroform, barium chloride and dichloromethane. In this study, dichloromethane was chosen as a representative model of chlorinated compounds. In order to avoid the problem of corrosion by chlorine, we proposed a new cascade process in which two reactors are consecutively combined, carrying out hydrolysis in the first reactor followed by SCWO in the second reactor, for the complete removal of halogenated organic compounds. The schematic outline of the cascade process is shown in Fig. 1.

There have been many previous studies of the hydrolysis of dichloromethane. Marrone \textit{et al.}\(^{(3,4)}\) investigated the hydrolysis of CH$_2$Cl$_2$ in subcritical water, and reported that the main products were formaldehyde and HCl. Salvatierra \textit{et al.}\(^{(5)}\) studied the hydrolysis kinetics of CH$_2$Cl$_2$ in liquid water 100–250°C. They proposed an empirical first-order rate expression using a standard Arrhenius equation for the rate constant. Oshima \textit{et al.}\(^{(6)}\) designed a corrosion-resistant flow reactor with a rapid-heating system and obtained kinetic information on CH$_2$Cl$_2$ hydrolysis in sub- and supercritical water. Compared with the abundance of previous research on dichloromethane hydrolysis, there has been less investigation on the kinetics of formaldehyde oxidation in supercritical water. Therefore, we investigated the SCWO of formaldehyde in order to obtain kinetic information.

![Schematic diagram of the proposed cascade process](image)

Fig. 1. Schematic outline of proposed cascade process with consecutive performance of hydrolysis and SCWO for pharmaceutical laboratory wastewater treatment.
2. Materials and Methods

The water used in this study was commercially obtained distilled water that was deoxygenated by N2 gas bubbling prior to use. The oxidant was oxygen that was produced by the thermal decomposition of H2O2, a solution of which was prepared from 30 wt% H2O2/water for initial stock solutions. A formaldehyde solution was prepared from 37 wt% commercial aqueous solutions that also contained about 8% methanol as a preservative.

For homogeneous SCWO (without using a catalyst), the experiments were conducted using a plug flow reactor (PFR). The experimental apparatus is shown in Fig. 2. A fluidized sand bath was used for heating the reactor and preheating line, and the temperature was monitored at the inlet and outlet of the reactor using thermocouples. The reactor was made of Hastelloy C-276 tubing (o.d., 0.16 cm; i.d., 0.11 cm). H2O2 solution, which completely decomposed into O2 and H2O in the preheating line, and formaldehyde solution were separately fed into the reactor using two HPLC pumps. The fluid emitted from the reactor was cooled and depressurized, followed by gas-liquid separation. The gas products, as well as the formaldehyde in the liquid, were analyzed by GC-TCD. Methanol in the liquid phase was quantified by GC-FID. Reaction temperatures and pressure were 400–500°C and 25 MPa, respectively.

For heterogeneous SCWO, we used the “compact” apparatus, which was 0.45 × 0.45 × 1.10 m³. The flow sheet for the apparatus was almost the same as that shown in Fig. 2, except for the fixed bed reactor (stainless steel; o.d., 0.95 cm; volume, 14.3 ml) with the loading of 12 g of MnO2, surrounded by an electric heater. The concentration of formaldehyde in the original solution was 0.50 mol/l.
3. Results and Discussion

3.1 Homogeneous SCWO of formaldehyde

The time profiles of formaldehyde conversion at 400, 450 and 500°C are shown in Fig. 3. The initial concentrations of formaldehyde in the reactor inlet were 2.7, 1.7 and 1.3 mmol/l at 400, 450 and 500°C, respectively. Excess H₂O₂ (480% of the stoichiometric requirement) was supplied; thus, we can assume a pseudo first-order reaction of formaldehyde in the kinetic analysis. In Fig. 3, the conversion rate of formaldehyde increased with increasing temperature, and formaldehyde was completely converted at 500°C, with a residence time of 4 s. The pseudo first-order rate constant calculated from the data is shown in Table 1. As previously mentioned in Materials and Methods, the commercial formaldehyde solution we used in this study contained about 8% methanol as a preservative. Therefore, we need to take the contribution of not only the formaldehyde oxidation, but also the formaldehyde formation from methanol oxidation into consideration, because formaldehyde was presumed to be the primary product in the SCWO of methanol. Rice et al. reported that methanol oxidation produces formaldehyde with a maximum yield of about 20% in the temperature range of 440–500°C. Since the ratio of methanol to formaldehyde in the original solution was about 1:4.5, the maximum yield of formaldehyde from methanol oxidation is estimated to be less than 4% of the initial formaldehyde concentration. Thus, we consider the contribution of formaldehyde production from methanol oxidation to be negligible.

Fig. 3. Formaldehyde conversion in homogeneous system for SCWO at 400°C (□), 450°C (□) and 500°C (△), at 25 MPa.
From the temperature dependence of the rate constants in Table 1, the calculated activation energy of formaldehyde oxidation in supercritical water was about 51 kcal/mol. In previous studies, the direct experimental measurement of the activation energy of this reaction has not been carried out, and the only available value to compare with our data is $90.6 \pm 42.9$ kcal/mol, obtained from the oxidation of methanol by Brock et al.\cite{Brock7} In their study, the rate constant of formaldehyde oxidation was estimated under the assumption that the carbon mass balance was dependent only on CO, CO$_2$, methanol and formaldehyde, although formaldehyde was not quantitatively analyzed by their experimental method. Despite the large uncertainty in the reported activation energy, the value obtained in this study is still in agreement with that of the previous study within the stated uncertainty.

The carbon yield of formaldehyde oxidation in supercritical water at each reaction temperature is shown in Fig. 4. Higher yields for CO and CO$_2$ were obtained at longer residence times and higher temperatures, but complete oxidation could not be achieved even at 500°C and 13.4 s. Figure 4 also shows that a very good carbon yield balance can be achieved at each reaction temperature.

### Table 1
The pseudo first order rate constants of formaldehyde oxidation in supercritical water at 400–500°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate constant (s$^{-1}$)</th>
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<tbody>
<tr>
<td>400</td>
<td>0.02</td>
</tr>
<tr>
<td>450</td>
<td>0.08</td>
</tr>
<tr>
<td>500</td>
<td>2.30</td>
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</tbody>
</table>

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#### 3.2 Heterogeneous oxidation of formaldehyde in SCWO

From the experimental results of homogeneous oxidation in the previous section, it was suggested that further modification of the system to achieve 100% conversion of formaldehyde at a lower temperature and shorter residence time is required for the practical application of SCWO technology to laboratory waste treatment. In this study, we also investigated the heterogeneous catalysis to enhance the conversion of formaldehyde.

The experimental result at 400°C and 25 MPa is shown in Fig. 5. The contact time was defined as catalyst bulk volume divided by fluid volumetric flow rate, on the assumption that the flow in the reactor was isothermal at 400°C. The result in Fig. 5 shows that formaldehyde was completely converted at 400°C and 25 MPa in a contact time shorter than 0.8 s. In addition, no total organic carbon (TOC) was observed in the effluent, suggesting that all the carbon atoms in the original solution had been converted to CO$_2$ in the catalytic oxidation of formaldehyde. From these results, we can conclude that heterogeneous SCWO is effective for the complete and efficient conversion of formaldehyde.
Fig. 4. Carbon yields of formaldehyde oxidation in SCW in homogeneous system at 400°C (A), 450°C (B) and 500°C (C), at 25 MPa.
4 Conclusion

We investigated the oxidation of formaldehyde in supercritical water with and without catalysts at temperatures of 400–500°C and a pressure of 25 MPa. In homogeneous SCWO, about 77% conversion of formaldehyde was achieved at 450°C and 16 s. The conversion was completed at 500°C within a residence time of 4 s. When MnO₂ was used as a catalyst in the heterogeneous system, formaldehyde was completely converted at 400°C and 0.8 s. Our experimental results suggest that heterogeneous SCWO is a promising technique for the complete conversion of formaldehyde.

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References


