초임계수에서 유사화학작용제(DMMP)의 산화반응 연구

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Supercritical water oxidation of chemical agent simulant (dimethyl methyl phosphonate)

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Introduction

Contemporary environment problem is being expandied to whole global problem beyond the range of a individual or a nation. When we consider that especially internal environment problem in military threats people's life and safety now, we think it is natural that the military should deal actively with threats from the interior. Through the 1st War, the 2nd War, Korean War and Vietnam War, explosives have largely been used as materials of main conventional weapons and/or nuclear weapons. But after the end of cold war, the quantity of unused explosive materials has rapidly increased. Therefore demilitarization problem have been seriously considered. As a part of these endeavors, CWC (Chemical Weapons Convention), to destroy all chemical weapons in the world forever, was effective in April 29, 1997 and 169 nations signed and 121 nations ratified except some nations including North Korea now dated on Nov., 1998. This treaty about developing, producing, reserving, forbidding use and discharging chemical weapons regulates to discharge chemical weapons by 2007, within 10 years since after it was effective.[1]

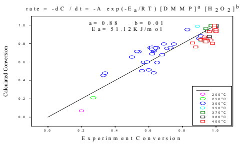
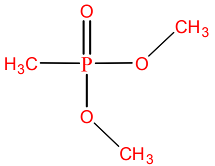
Now, The processing of military chemical weapon treatment are Biological method, Incineration, Wet Air Oxidation, Chemical Oxidation and etc.[1,2] However, as the recognition of environment problem is raised, the technology for higher treatment effectiveness is being requested. Supercritical Water Oxidation (SCWO) is an emerging technology capable of essentially complete destruction of toxic and hazardous organic waste. When reaction temperature and pressure is over 374℃ and 220bar, oxidant and organic material exist in homogeneous phase, then, the mass transfer problem is idealistically solved and so the reaction rate becomes fast. The chemical weapons in the supercritical condition can be converted to environmental friendly material like H_2O and CO_2.[3,4]

In this study, supercritical water oxidation of chemical agent simulant (DMMP) has been studied. DMMP is similar to the nerve agent GB, Sarin in structure , miscible in water and relatively non-toxic in comparison to the actual chemical agents.[5] It will be confirmed that supercritical water oxidation technology is applicable for military chemical weapons.

Experiment

Fig.1 shows a schematic diagram of SCWO experimental apparatus. This experiment system consists of two feeding pumps, DMMP/hydrogen peroxide storage, preheater, reactor, heat exchanger, filter, back pressure regulator and so on. The model compound of this study, the physical property of GB and DMMP is shown to table 1.

Table 1. Physical properties of GB and DMMP

property	Nerve agent (GB)	Chemical agent simulant (DMMP)
structure	 (toxic)	 (non-toxic)
molecular weight (g/mol)	140.01	124.08
boiling/melting point (℃)	158/-56	181
density at 35 ℃ (g/ml)	1.145	1.09
solubility in distilled water (g/100) at 25 ℃	miscible	miscible

Each of the DMMP and the hydrogen peroxide solution was preheated in 1/16 -in O.D. x 2 m length and 1/16 -in. O.D. x 4 m length of SS 316 tube. The length of DMMP line was designed shorter than that of oxidant line to minimize destruction by pyrolysis during preheating. The reactor was made of a SS316 (15 cm length x 3/8-in O.D.). The effluent was cooled rapidly in a counter current heat exchanger of 12 cm length and then, the system pressure was reduced by using back- pressure regulator (Tescom co. 26-1721-24). The depressurized reactor effluent was separated into gas and liquid phase. The concentration of DMMP in the liquid effluent was analyzed by a Hewlett-Packard 4890 GC (Gas Chromatography) with a 0.32 mm ID×30 m length, 5 µm film thickness capillary column AT-1. The gas samples were analyzed using a Hewlett-Packard 5890 GC with a thermal conductivity detector. A Rheodyne injection valve was used for on-line sample injection into a 10 -ft length x 1/8 -in OD Supelco Carboseive S-II permanent gas column.

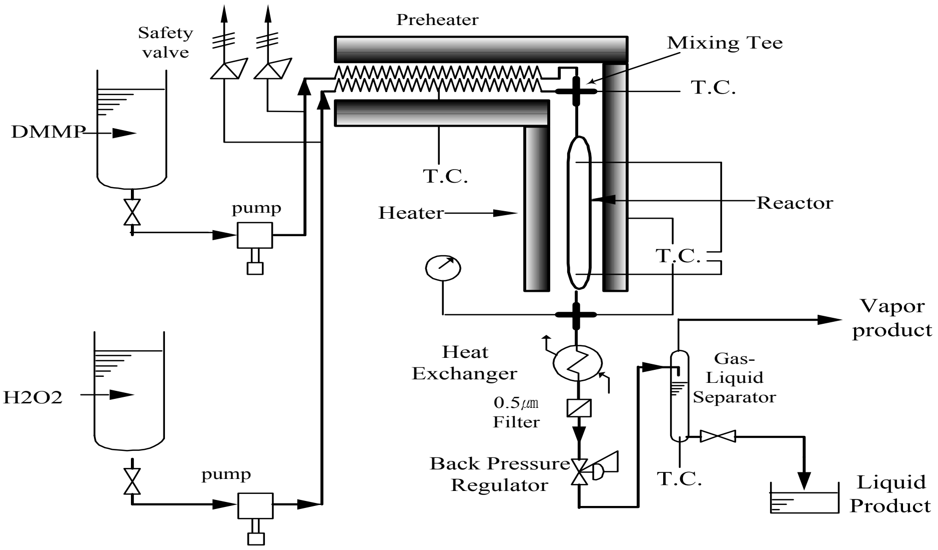


Figure 1. Schematic diagram of experiment apparatus

Result and Discussion

The description of the reaction would be :

$$C_3H_9O_3P + 10H_2O_2 \rightarrow 3CO_2 + H_3PO_4 + 13H_2O$$

Seventy oxidation experiments were performed for DMMP in an isothermal, isobaric condition in a continuous flow tubular reactor. The oxidation of DMMP in SCW was investigated at 250 to 400 ℃ and 200 to 270 bar with residence times of 2 to 30 sec. The hydrogen peroxide concentrations were between 850 and 4800 mmol/L (Excess H_2O_2 = 200～1400 %). The initial concentration of DMMP ranged from 20 to 100 mmol/L.

Figures 2 and 3 show the effect of feed DMMP concentration and H_2O_2 concentration on the DMMP conversion at a given residence time in sub and supercritical condition. These results represent that reaction rates in supercritical condition are faster than at liquid phase. Figure 4 shows the effect of water concentration (by changing pressure) on DMMP conversion with constant temperature, DMMP and H_2O_2 concentrations. As it can be seen from this figure. there is no appreciable change in DMMP conversion at the pressure between 200 and 270 bar. Figure 5 shows the effect of temperature on DMMP conversion. the conversion of DMMP was over 90 % at 380 ℃. Destruction effectiveness of supercritical region was four times in comparison to that of subcritical region. It was caused by fast reaction

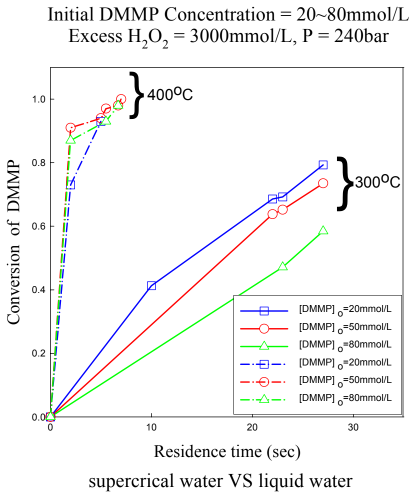


Figure 2. Effect of the initial feed concentration on DMMP conversion

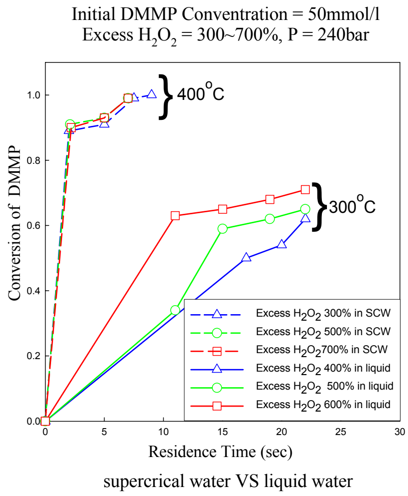


Figure 3. Effect of hydrogen peroxide feed concentration on DMMP conversion

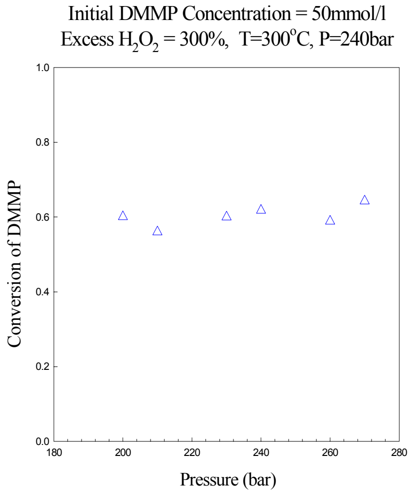


Figure 4. Effect of water concentration on DMMP conversion

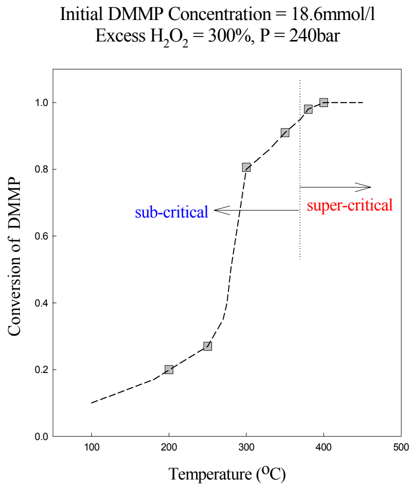


Figure 5. Effect temperature on DMMP conversion

rate due to homogeneous phase in supercritical water.

The global rate for DMMP decomposition may be expressed as

$$\text{rate} = k(T)[DMMP]^a[H_2O_2]^b \quad (1)$$

Equation (1) can be solved analytically with the initial condition X=0 at τ=0. The relationship between the DMMP composition conversion and the relevant process variables is follows:

$$X = 1-(1-(1-a)k_0\exp(-E_a/RT)[DMMP]_o^{a-1}[H_2O_2]^b t)^{1/1-a} \quad \text{if} \neq 1 \quad (2)$$

We performed a non-linear regression analysis to fit the DMMP decomposition conversions. The hydrogen peroxide concentration is assumed constant throughout the reaction since H_2O_2 was always present in at least 200% excess of the stoichiometric requirement. These 70 data sets led to reaction orders of a=0.88 (±0.09) for DMMP and b=0.01 (±0.1) for hydrogen peroxide. The values of the Arrhenius parameters A and Ea were 3.64×10^3 s^{-1} and 35.66 KJ/mol, respectively. Figure 7 shows a parity plot of the rate predicted from the global rate law using the parameters in Equation (2) against the rate obtained experimentally. Our model fits reasonably well experimental data.

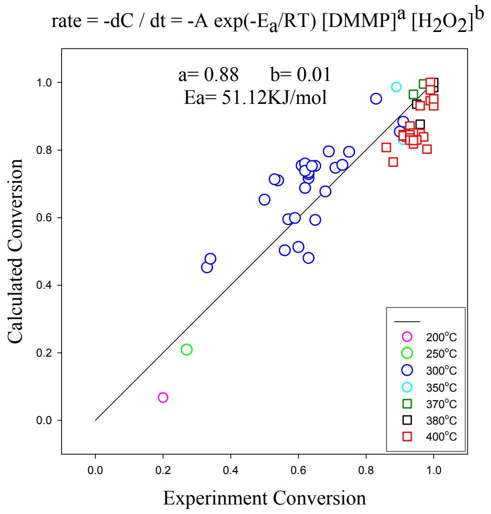


Figure 7. Parity plot for power-law rate equation
for DMMP decomposition rates

Reference

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[4] P.E. Savage, Chem. Rev.99 (1999) 603.

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