Supercritical Water Oxidation of Toxic Wastewater

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초임계산화에 의한 폐수 처리

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ABSTRACT

This study deals with the supercritical oxidation of wastewater to remove its toxic elements. A number of parameters are tested for their effects one reaction time, throughput and treated species. The supercritical oxidation kinetics of 2-butane, o-cresol, and pyridine at 276 bar and 450 - 550 °C were examined in this regard. For the conditions studied, the reaction is second-order in 2- butanone and first-order in o-cresol and their activation energies are nearly 1.4×10^4 cal/mol. Results show that toxic wastewater could be effectively handled if is treated on batch basis under the most appropriate conditions revealed by this study.

Key Words : Supercritical water oxidation, Toxic waste water

I. INTRODUCTION

The complete oxidation of organic in SCW (Supercritical Water) is an effective means of treating many organic wastes[1]. SCWO(Supercritical Water Oxidation) converts hydrocarbons to CO_2 and H_2O at reaction temperatures around 400 to 700 °C. It is most attractive economically for aqueous waste streams with organic concentrations around 1-20wt%[2]. If the organic concentrations is too low, auto-thermal operation is not possible at supercritical temperature.

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and an auxiliary fuel is required. If the organic concentration exceeds 20-25%, incineration becomes competitive because the higher incineration temperature (1,000°C) can be maintained with mineral use of auxiliary fuel. SCWO technology is an extension of wet - air oxidation, which operates at subcritical temperatures and pressures. This technology was developed to treat organics in industrial wastewater streams.

There are several advantages to conducting the oxidation reactions above, rather than below the critical point. One advantage is that higher temperatures promote faster reaction rates. A second advantage is that an single fluid phase containing organics, an oxidant, and water can exist at reaction conditions. A third advantage related to solubility is that salts have a reduced solubility in supercritical

water[3].

Therefore. salts formed from the neutralization of acid produced during SCWO can be precipitated from the solution. Many organic compounds are only sparingly soluble in water at ambient conditions. At supercritical conditions. however. nonpolar organics enjoy complete miscibility with the water. SCWO represents an innovative technology for complete and efficient destruction of hazardous wastes. without formation of harmful products. Organic compounds and oxygen are completely soluble in water above its critical point of 374 ℃ and 221bar. which provides a single – phase medium for rapid oxidation of organic to CO_2. H_2O. N_2. Cl_2. SCW exhibits characteristics of a non polar organic solvent. SCWO process produces environmentally acceptable effluents (gas. liquid and solid). lends itself to resources recovery. and can be economically competitive.

It is in the diverse applications of pollutants treatment. which can be adapted to the complete organic sludge destruction and the destruction of the mixed organic fractions in radioactive wastes. Since the 1980' s. SCWO has been considered as an innovative technology. the overall body of SCWO knowledge is rapidly expanding. The amounts of producing the sludges are continually increasing up to now. So. SCW is applicable to the treatment of these especially hazardous wastes.

One of the drawbacks to SCWO is the expense of the reaction for this higher – pressure process. which must be made of high nickel alloys such as Inconel 625 or Hastelloy C 276 to withstand the potentially corrosive SCWO conditions.

In this research. the continuous oxidization of wastewater containing respectively 2-butanone. o-cresol. pyridine in supercritical reactor was conducted. And the destructing degrees of the above components for temperature. retention time. and reynolds number were examined. This study aimed

at interpreting the kinetics of supercritical oxidations from the experimental results and examining the destructing degrees of harmful wastes.

This research was performed to investigate the supercritical continuous oxidation performance of wastewater containing such harmful wastes as 2-butanone. o-cresol. pyridine. The oxidation rates was reasonably analyzed by three-lumped model with the assumption of second order in 2-butanone and first order in o-cresol · pyridine. So the activation energies are 1.4 x 10^4 cal/mol for 2-butanone and o-cresol. 1.3 x 10^5 cal/mol for pyridine. Pyridine was less decomposed than 2-butanone and o-cresol below 500℃ because of its high activation energy. The conversions of 2-butanone were increased with the temperature. but they were decreased with the flow rates for the conditions studied. The experimental apparatus used in this research was shown in Fig. 1.
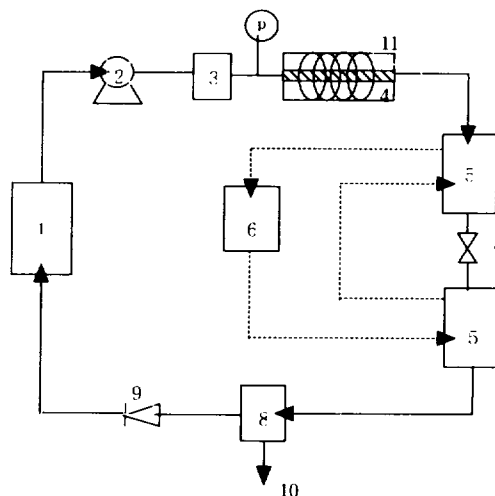
1. Feed tank
2. Feed pump
3. Pre-heater
4. PFR reactor
5. Heat exchanger
6. Freezer
7. Pressure regulator
8. Separator
9. Check valve
10. Sampling tap
11. Ceramic heater

Fig. 1. Schiamatic diagram of apparatus.

As for the dimensions of tubular reactor 10mm (ID) x 220 mm(IL). its volume was 17.3ml. The conditions of reactor design were 5000 psig and 500 ℃. The insulation of it was performed by its outside area coated with ceramic band. Continuous oxidation was carried out at a constant pressure of 276 bar to examine the effects of temperature and retention time on the destruction degree. The temperature and pressure was adjusted by PID controller.

The compositions of wastewater were 2-butanone. o-cresol. pyridne and their concentrations respectively were 6210 ppm. 10.040 ppm. 500 ppm. Dissolved oxygen concentration was 4.6 ppm and the temperatures ranged from 450 to 550 ℃ Continuous experiments were conducted under the flow ranges for 9.2 ml/min. 9.6 ml/min. 10.4 ml/min. The effluents were condensed by the refrigerator using methanol as a refrigerating fluid. Liquid effluents analysis was done by isocratic high-performance liquid chromatography(HPLC). A Rainin HPXL Solvent delivery system with an Interaction ORH-801 analysis column and Interaction Ionguard guard column was used. A Rainin Dynamax UV-/UV/ visible detector at 210 nm was also used. Peak height was used for quantification. since peak overlap occurred distorted peak area.

II. SCW'S PHYSICAL-CHEMICAL PROPERTIES AND ITS REACTION KINETICS

The physical – chemical properties of water undergo marked changes near its vapor-liquid critical point (374.2 ℃ and 22.1 MPa). Density. dielectric constant. ion product and other properties of water are altered. The density of water at 276 bar is 0.538 g/cm at 375 ℃. and 0.128g/cm at 45 0℃. Thus. diffusivity and ion mobility are higher at supercritical conditions. Specific heat capacity of water approaches infinity at the critical point. and remains orders of magnitude higher in the critical region. Higher heat capacity suggests that SCW is an excellent thermal energy carrier.

Static dielectric constant (SDC) is a measure of the hydrogen bonding and reflects the characteristics of the polar molecule in water. As the density of water decreases. the hydrogen bonding decreases. but the solvent polarity is reduced due to a density drop. Dissociation of water is a strong funtion of density and temperature.

Interpretation of the SCW properties may be summarized as : 1) high diffusivity-enhanced mass transfer rates : 2) low viscosity-better mixing : 3) high density-compact reactor size : 4) high organic and oxygen miscibility – homogeneous reaction. and 5) low inorganic solubility – unique separation opportunities.

For the evaluation of destructing degrees on the supercritical water oxidation showing the above characteristics. a treatability study involving kinetic relationship is a key requirement. Typically. an overall reaction rate constant. k. is determined. Kinetic parameter and postulated reaction path-ways for SCWO have been reported for single organic compounds.

The kinetic lumping(KL) approach is based on grouping individual constituents of feeds with simplified reaction networks between the lumps. Its concept was first developed to represent large monomolecular reaction systems(complex. first-order kinetic system) by linear differential equations involving lumps or pseudo species[5]. Such lumping analyses focussed on linear systems which can be expressed in matrix form. The KL concept has been successfully applied to many chemical process. but wastewater treatment has not been fully recognized. A unique KL situation is related to oxidative waste treatment processes. The number of initial compounds in a waste feed may be quite large.

whereas the number of oxidation and end product is known to be small. usually including carbon dioxide. water. and limited inorganic acid/salt species.

The kinetic should be obey the isothermal plug-flow design equation. A three-lump model describing simplified SCWO reaction schemes has been proposed[6]. In this case. two basic assumptions have been proposed. First. all reactions take place in a homogeneous fluid phase. Second. only carbon-containing species are considered in the lumps. For example. water is an end product of hydrocarbon oxidation. but water is not considered in Lump C.

To illustrate this model. a reaction mixture is divided into three lumps : (A) initial and unstable intermediate compounds. (B) reaction rate-controlling intermediates. and (C) carbon dioxide.

$$A \quad + \quad O_2 \quad \xrightarrow{\quad k_1 \quad} \quad C$$
$$k_2 \downarrow \qquad\qquad k_3 \uparrow$$
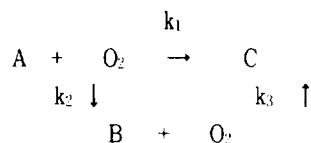$$B \quad + \quad O_2$$

Fig. 2. Three Lumped Model.

C = [oxidation end product]

B = [rate-controlling intermediate]

A = [initial and intermediate
        compounds other than B]

Lumping schemes shows how a reaction system containing a′ parent compounds. a″ unstable intermediates. b refractory intermediates. and the final oxidation product (carbon dioxide) for a total of a′ + a″ + b + 1 can be reduced to three lumps.

Li and et. al have proposed generalized reaction pathway for the oxidation of organics in near critical and supercritical water[7]. The first is direct oxidation to stable end products such as CO_2. N_2. Cl_2. The second is initial oxidation to low molecular

weight intermediates. which are then slowly oxidized to the end products. The reaction order for the organic compounds studied was nearly always close to unity. The order of oxygen appears to be more variable. That reaction rate vary with water density could also be attributed to the variation of some density-dependant property. such as the dielectric constant. that can influence reaction rate[8.9]. That the organic reaction order is typically close to unity and that the oxygen order was reported as being near zero in early SCWO kinetic studies has led to these values sometime being assumed for the analysis of data from new compounds.

From the kinetic models. several investigators have reported that elementary reaction steps were well behaved as one passed from subcritical to supercritical conditions.

Those observations at near-critical and supercritical conditions could be explained on the basis of established solution-phase kinetics. We noted here that the phenomena often associated with reactions at SC conditions(clustering. large activation volumes) appear to be most significant for dilute solutions very near the critical point. These effects are less significant as the solution becomes more concentrated and as one moves to temperatures and pressures well above Tc and Pc.

III. DESTRUCTING PERFORMANCE OF WASTES

3.1. Oxidation Kinetics

The plots of ln k to 1/T for feeds were shown at Fig.2. Assuming the reaction order. the plot of reaction constant (ln k) vs inversed absolute temperature (1/T) was an declining line. Therefore. the assumptions of the first order in such reacting species as o-cresol and pyridine except to the second

order of 2-butanone respectively were adequate for analysing the experimental results. As the temperature(T) increased. the rate constant(k) decreased. Also. the slops of the straight lines for 2-butanone and o-cresol were -6.986. -6.845. and the slope for pyridine was -12.968. And the activation energies for 2-butanone and o-cresol were nearly the same amounts as 1.4×10^4 cal/mol. and its energy for pyridine was 1.3×10^5 cal/mol. This result showed that pyridine was more difficult to activate than 2-butanone and o-cresol.
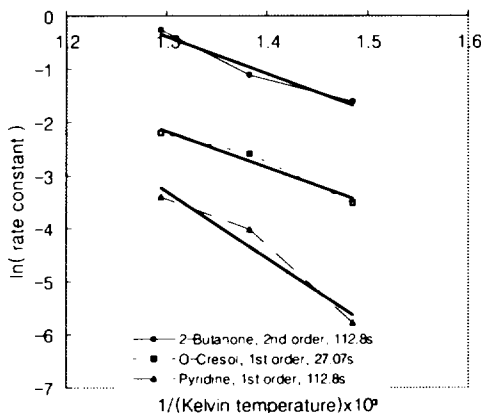
And the above results showed the destructing degrees increased with the retention time.

From these results. we were able to predicted such constituent as 2-butanone more soluble in supercritical water than o-cresol above the critical condition regardless of retention time. But pyridine was less soluble in supercritical water for 673 K and its destructing degree was 29.5 % for 673 K and 112.8s.
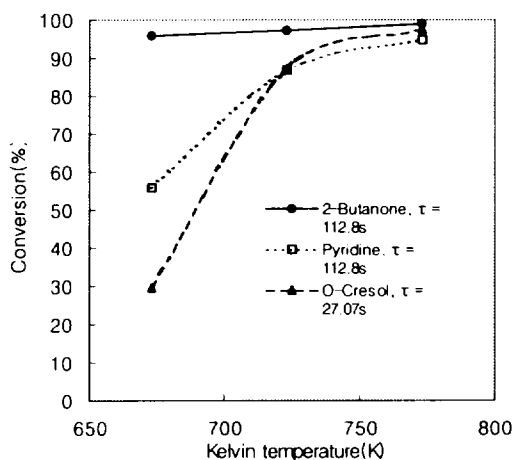

Fig. 3. Plot of rate constant vs inverse Kelvin temperature.

Fig. 4. Effect of Kelvin temperature on conversion.

3.2. Effect of absolute temperature on destructing degrees

The effects of the absolute temperature on the destructing degree (X) for feeds and retention time were shown at Fig. 3. 4. The destructing degrees (X) were increased with the temperature (T) increase regardless of feeds and their retentions. Especially. the destructing degrees were increased because the activation energy decreased with the temperature. The destructing degree of 2-butanone (retention time. 112.8s). pyridine(112.8s). and o-cresol(27.07s) respectively were 95.76 - 98.86 %. 29.5 - 97.6 %. 55.7- 94.9 % from 673 K to 773 K.

3.3. Effect of retention time on concentration profiles

The plots of concentration profile (C_f /C_{fo}) for retention time were shown at Fig. 4. The concentration profiles (C_f/C_{fo}) were decreased with the increase of retention time. The concentration profiles of 2-Butanone were decreased from 0.0404 to 0.00161 with the retention time (112.8 -338.4s). Their concentration profiles of o-cresol and pyridine were decreased with the retention time.

3.4. Effect of reynolds number on conversion

Fig. 5 shows the conversions of 2-butane. o-cresol and pyridine for reynolds number under the

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temperature of 673K. The density and the viscosity of supercritical water at 276 bar and 673K respectively was 0.7 g/cm³, 321 μ Poise. The conversion of the above wastes decreased with the retention time decrease due to increase of reynolds number. The decreasing slopes of the above wastes were nearly the same as they were shown. And the conversion of pyridine at 673K was much lower than 2-butanone and o-cresol due to its higher activation energy.
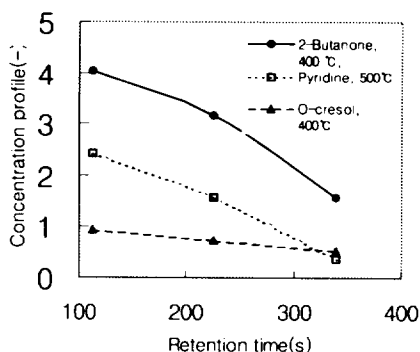

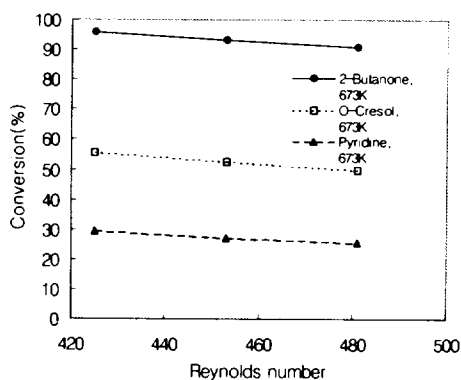Fig. 5. Effect of retention time on concentration profile.

Fig. 6. Effect of Reynolds number on conversion.

IV. CONCLUSION

The supercritical oxidation kinetics of 2-butane. o-cresol. and pyridine at 276 bar and 450 - 550 ℃

were examined from the destructing degrees of them. For the conditins studied. the reaction is second-order in 2- butanone and first-order in o-cresol and their activation energies are nearly 1.4×10^4 cal/mol. The reaction is first-order in pyridine. but its activation energy is 1.3×10^5 cal/mol. The conversions of 2-butanone. o-cresol. and pyridine from 450 ℃ to 550 ℃ were respectively 95.76 - 98.86 %. 55.7 - 94.9%. 29.5 - 97.6%. Pyridine is less decomposed than 2-butanone and o-cresol at 450 ℃ because of its high activation energy. Also conversions of them were decreased with Reynolds number.

These results indicate that the supercritical water oxidation method could handle harmful wastes effectively should the conditions are appropriately applied.

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