

Supercritical Water Oxidation for Harmful Wastes

Koh, Young-Hwan, Yoon, Chang-Hoon, Hyun, Young-Jin

Environmental Research Institute, Cheju National University
690-756, 1, Ara Dong, Cheju City, Cheju Do, Korea

Abstract

This study was carried out to investigate the performance of supercritical water oxidation. Such harmful waste as poly chloro bipenyl, penta chloro phenol, p-chloro phenol, o-cresol, pyridine are easily oxidized to unharful constituents as CO_2 , H_2O , Cl_2 , NO , etc.

The enhanced breakage of harmful wastes come from the physical-chemical properties of supercritical water, that is to say, diffusivity, ion mobility, specific heat capacity and static dielectric constant of the water.

The oxidation rates is reasonably analyzed by three-lumped model. The reaction rate was density dependant. So the rate was increased with water density. Considering the great increasement of harmful wastes up to now, supercritical water oxidation is applicable to the effective treatment of them.

I . Introduction

The complete oxidation of organic in SCW (Supercritical Water) is an effective means of treating many organic wastes.[Modell, M, 1989]

SCWO(Supercritical Water Oxidation) converts hydrocarbons to CO_2 and H_2O at reaction temperatures around 400 to 700 $^{\circ}\text{C}$. It is most attractive economically for

aqueous waste streams with organic concentrarions around 1-20wt%. [Thomson, T, 1984]

If the organic concentrations is too low, auto-thermal operation is not possible at supercritical temperature, 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 minimal 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 a 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.

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 °C and 221 bar, which provides a single-phase medium for rapid oxidation of organic to CO₂.

H₂O, N₂, Cl₂. 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.

II. Theoretical Survey

The physical - chemical properties of water undergo marked changes near its vapor-liquid critical point (374.2 and 22.1MPa). Density, dielectric constant, ion product and other properties of

water are altered. At a typical SCWO process pressure of 27.6MPa, the density of water is 0.538 g/cm at 375°C and 0.128g/cm at 450°C.

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.

Also, the enhancement of the heat transfer coefficient, as water approaches the critical region, is largely due to changes in the specific heat capacity.

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.

SDC is about five at SCWO conditions as contrasted to 78.5 at standard temperature and pressure(STP). [Frank, E, U, 1963]

Dissociation of water is a strong function of density and temperature. At 450°C and 25MPa, the ion product decreases to $10^{21.6}$ from the ambient value of 10^{14} . [Marshall,W,L, 1987]

Thus, fewer ions exist and electrolyte associations is favored over dissociation in the SCW region.

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 reacton, and 5) low inorganic solubility - unique separation opportunities.

Specific heat capacity suggests that SCW is an excellent thermal energy carrier. Also, the enhancement of the heat transfer coefficient, as water approaches the critical region, is largely due to changes in the specific heat capacity.

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.

For evaluation of complex wastes, 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 a complex feed into broad but measurable pseudo-species (lumps)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. [Wei, j, 1969]

Such lumping analyses focussed on linear systems which can be expressed in matrix form. The KL concept has been successfully applied to many chemical processes, but its potential benefit in 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:

$$\tau / Cr^0 = \int_0^{X_i} dX_i / -r_i \quad (1)$$

where,

- X_i = conversion of reactant
- $-r_i$ = rate of reaction for reactant i
- Cr^0 = initial concentration of reactant
- τ = reactor residence time

The reaction rate of PCP (Penta Chloro Phenol) is assumed in the form of below rate expression,

$$-r_{\text{reactant}} = k [\text{reactant}]^a [\text{O}_2]^b [\text{H}_2\text{O}]^c \quad (2)$$

Where k is the rate constant, which

can be expressed in the Arrhenius form as

$$k = A \exp (- E_a / RT) \quad (3)$$

Where, A = Collision frequency

E_a = activation energy

R = gas constant

T = Kelvinb Temperature

$$\begin{aligned} & [\text{reactant}]^{a+b-1} (k \tau) \\ & = \int_0^X dX_i / (1 - X_i)^a [C_{O_2} / C_{T0} \\ & - (\text{mol of O}_2 / \text{mol of reactant}) X_i] \quad (4) \end{aligned}$$

With such an overall first-order assumption, Eq. 4 reduced to

$$k = - \ln (1 - X) / \tau \quad (5)$$

A three-lump model describing simplified SCWO reaction schemes has been proposed. [Kuo, j, 1969]

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, such as acetic acid, methanol, and carbon monoxides ; and (C) carbon dioxide.

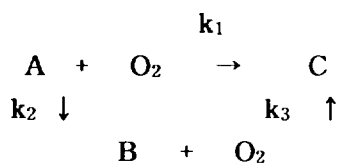


Fig. 1 Three Lumped Model

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.

Lumping models involving more detailed classifications of reaction steps have been reported. [Li,L, 1993]

III. Result and Discussion

Li et have proposed generalized reaction pathway for the oxidation of organics in near critical and supercritical water. [Li,L,1993]

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 to date was nearly always close to unity. The order of oxygen appears to be more variable.

Values around 0.5 were reported for phenol, 2-chlophenol, CO, and methane, whereas values of zero were reported for methanol, and 4-chlophenol. The rection rate was clearly density dependent, and the rate was increased with increasing density.

The water order of 0.7 for phenol oxidation, 1.5 for CO oxidation, and 0.34 for 2-chlophenol oxidation were reported.

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.

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.

This effect can also be exploited to form a single homogeneous fluid phase for a reaction and thereby overcome interphase transport limitations that might exist at subcritical conditions. SCF makes itself attractive as media for chemical reactions.

Its properties vary with density, which is a strong function of temperature and pressure in the critical region. The pressure dependence can be also to integrate and separation steps in a process-sheet.

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 T_c and P_c .

IV. Conclusion

The diversity in this field is also evident where the wide range of potential applications include biochemical reactions, material processing, fuel processing, catalysis, pollution prevention, and environmental control.

The diffusivity of a molecule in a SCF falls between that in a liquid and gas. Thus, reactions that are diffusion limited in the liquid phase could become faster in a SCF phase. SCF also have unique solubility properties. Compounds that are largely insoluble in the fluid at ambient conditions can become soluble in the fluid at supercritical conditions. This enhanced

solubility can lead to higher reactant concentrations and hence accelerated reaction rate at supercritical conditions. And high diffusivity, high heat capacity and low viscosity of supercritical water have brought the easy oxidation of harmful wastes.

Therefore SCF Oxidation is useful for treating toxic waste.

Acknowledgement

This research is performed by the assistance of funding for R&D at Cheju National University on the April, 1999.

We will acknowledge for the support of the above institution.

References

1. Modell, M., Supercritical Water Oxidation, in Standard Handbook of Hazardous Waste Treatment and Disposal, H.M. Freeman, ed., McGraw-Hill, New York (1989)]
2. Thomason, T. B., & M. Modell, Haz. Waste, 1, 453 (1984)
3. Franck, E. U., Pure. Appl. Chem., 37, pp.339 (1963)
4. Marshall, W, L., & J. D. Frantz, Electrical Conductance Measurements of Dilute, Aqueous Electrolytes at Temperatures to 800 and 4264 Bars, Ed. G.C. Ulmer and H.L. Barners, New York,

- John Wiley & Sons, pp.2612(1987)
5. Wei, j., & J. C. Kuo, I & EC Fundam., 8(1), pp.114-133,(1969)
 6. Kuo, J. C. W., & J. Wei, I & EC Fundam., 8(1), 124-133,(1969)
 7. Li, L., Chen, P., & E. F. Gloyna, AIChE J., 37, (11), PP. 1687-97(1991)
 8. Li, L., Chen, P.& E. F. Gloyna, Kinetic Model for Wet Oxidation of Organic Compounds in Subcritical and Supercritical Water, Supercritical Fluid Engineering Science No.514 : Chater 24, pp.306-313
 9. Boock, L. T., & M. T. Klein, Ind. Eng. Chem. Res., 33, pp. 2554-2562(1994)