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# **DECOMPOSITION OF SELECTED ORGANICS IN**

# SUPERCRITICAL WATER

By Sikun Xu

# A THESIS SUBMITTED TO THE DEPARTMENT OF MINING, METALS AND MATERIALS ENGINEERING IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

McGill UNIVERSITY, MONTREAL March 2003



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#### Decomposition of Selected Organics in Supercritical Water

# By

# Sikun Xu

Submitted to the Department of Mining, Metals, and Materials Engineering on November 2002 in partial fulfillment of the requirements for the degree of Doctor of Philosophy

#### ABSTRACT

Supercritical water (SCW; above 374°C & 22 MPa) possesses the characteristics of non-polar solvents. It has been studied as a promising medium for decomposition of hazardous organics. Experimental research has been conducted to determine the phase behavior of SCW and organics in an oxidative environment via a Diamond Anvil Cell, coupled with a Fourier Transformed Infrared Spectrometer, an optical stereomicroscope and a high-resolution 3CCD camera. Homogeneous phases in H<sub>2</sub>O-O<sub>2</sub>, H<sub>2</sub>O-naphthalene and H<sub>2</sub>O-O<sub>2</sub>-naphthalene systems were identified. Flameless oxidation was observed to take place in the homogeneous phases. The chemical evolution and destruction rates of naphthalene/decachlorobiphenyl/cellulose during supercritical water oxidation (SCWO) were established using a batch reactor-based system, simulating practical conditions. Reaction pathways in SCWO were established for naphthalene, decachlorobiphenyl and the industrial sludge. They suggest the involvement of radicals in the reaction mechanism. In the proposed mechanism, ionic reactions were coupled with radical reactions. A significant role of intermediates during SCWO of organics is postulated and explained for the first time. A high activation energy of 139 kJ/mol indicated that the homogeneous SCWO of naphthalene was kinetic-controlled rather than diffusion-controlled. Complete elimination of typical noxious products NO<sub>x</sub> associated with hydrocarbon-air flames was confirmed in the SCWO of sludge wastes.

A new function describing  $H_2O-O_2$  interactions under SCW conditions has been determined. It allows for calculations of the critical properties and phase behavior of SCW-O<sub>2</sub> system. This function can be applied to determine the effect of pressure on the reaction rate constants in supercritical water.

Thesis Supervisor: Janusz A. Kozinski

Title: Associate Professor of Energy and Environmental Engineering

#### Décomposition de Composés Organique dans de l'Eau Supercritique

Par

#### Sikun Xu

Soumis au département de génie des mines, métaux et matériaux au mois de novembre 2002, pour la rencontre partielle des pré-requis pour le titre de docteur de philosophie

#### Résumé

L'eau supercritique (SCW, au dessus de 374°C & 22MPa) possède les caractéristiques de solvants non-polaires. Elle a été étudié comme un médium prometteur pour la décomposition de produits organiques dangereux. Les expériences ont été conduites pour déterminer le comportement des phases entre SCW et certains composés organiques dans un environnement oxydant par une cellule d'Anvil en diamant, associé à un spectromètre infra-rouge à transformée de Fourier et un stéréomicroscope optique relié à une camera à haute résolution. Des phases homogènes ont été identifiées dans les systèmes H<sub>2</sub>O-O<sub>2</sub>, H<sub>2</sub>O-naphtalène et H<sub>2</sub>O-O<sub>2</sub>-naphtalène. L'oxydation observée dans les phases homogènes se produit sans la présence de flamme. L'évolution chimique et le taux de destruction du naphtalène/décachlorobiphenyl/ cellulose durant l'oxydation de l'eau supercritique (SCWO) a été établis utilisant un réacteur en lot, simulant des conditions pratiques. La séquence des réactions a été établies pour le naphtalène, le décachlorobiphenyl et des boues industrielles. Les réactions démontrent l'implication des radicaux dans les mécanismes de réactions. Dans le mécanisme proposé, des réactions ioniques sont couplées aux réactions des radicaux. Un rôle significatif des intermédiaires durant SCWO de produits organiques est postulé et expliqué pour la première fois. Une énergie d'activation élevée, de l'ordre de 139 kJ/mol indique que la SCWO homogène du naphtalène est contrôlé par la cinétique de réaction et non par diffusion. L'élimination complète de produits typiquement nocifs tel NO<sub>x</sub>, associé a des flammes hydrocarboneair, a été confirmé par la SCWO de déchets boueux.

Une nouvelle fonction décrivant les interactions  $H_2O-O_2$  sous des conditions SCW a été déterminé. Celle-ci permet le calcul des propriétés critiques et du comportement des phases du système SCW-O<sub>2</sub>. Cette fonction peut être appliquée pour déterminer de façon précise les effets de la pression sur les taux de réactions en eau supercritique.

Superviseur de thèse: Janusz A. Kozinski

Titre: Professeur associe, Génie de l'énergie et environnent

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#### **1** INTRODUCTION

Modernization of today's society is often associated with the generation of diversified wastes. These materials can threaten public health and the global environment if improperly disposed of. Hence, the treatment and disposal of these wastes become of importance. Wastes can be classified into two categories: inorganic and organic wastes. Inorganic wastes, such as heavy metals, can be immobilized or recovered using known techniques [Bowe et al. 2002, Bajza et al. 1998]. Their treatment and disposal have been proved safe in the majority of recorded cases [Karius et al. 2001, van der Sloot 2002].

Organic wastes are present in more complex forms, consisting of hundreds of hydrocarbons, or even hydrocarbon-heavy metal mixtures. For example, polycyclic aromatic hydrocarbons (PAHs), chemicals harmful to the human respiratory system, may be found in micro-size aero-gel and fly ash; polychlorinated biphenyls (PCBs) circulate in the environmental water reserves, contaminating drinking water. Food wastes are mixed with complex solid-liquid components, from which secondary pollutants, e.g. dioxins and furans, are emitted if not properly treated.

Land-filling and combustion are currently used to dispose of organic wastes. Initially, organic wastes were land-filled and decomposed *via* bacteria. However, research in this field has indicated the formation of hazardous dioxins and furans during the degradation of PCBs and salty food wastes after land-filling, indicating that this method could not be successfully applied to more complex organic components present in modern organic wastes [Schecter 1991]. High-temperature combustion is considered as an efficient method to convert wastes in a relatively harmless way. However, high-temperature combustion of rubber, PCBs, polystyrene, polyvinyl chloride (PVC), and other organics may result in secondary hazardous emissions of PAHs, NO<sub>x</sub>, SO<sub>x</sub> and particulates

1

[Ledesma et al. 2000]. As a result, new technologies have emerged to offer alternatives to the existing technologies of treatment. One of the newer technologies, biodegradation, is based on decomposition of organic wastes via selected bacteria, simulating the natural bioprocess. Hence, biodegradation is time-consuming and costly to maintain proper surveillance. Another method, supercritical water oxidation (SCWO), has shown the possibility of destruction of a wide variety of wastes. Such pollutants as  $NO_x$  and  $SO_x$  can be avoided in supercritical water oxidation due to relatively low processing temperatures (380~700°C) and high-pressures (>22MPa). The unique properties of supercritical water (SCW) contribute to the efficiency of this method. Above water's critical point (374.2°C and 22 MPa), the heterogeneity of liquid water is disabled, allowing gaseous phases and liquid phases to merge into a unique supercritical fluid (supercritical water), forming a homogeneous phase. Therefore, the properties of supercritical water differ substantially from those of its liquid form. Its transport properties, diffusivity, viscosity, thermal conductivity, and dielectric constants allow it to behave like a non-polar solvent rather than a polar liquid water (see Table 1-1) [Gebhart 1993, Clifford 1999]. This gives rise to many of the advantages of the supercritical water-based approaches. For example, the diffusion coefficient of benzene in water increases one hundred times from that in ambient water to that in supercritical water at 400°C and 25MPa (see Table 1-1). This significant increase in diffusivity of organics in water would reduce diffusion-controlled reactions, and enable kinetic-controlled reactions. Structural study, using Raman spectrometry [Franck and Weingartner 1999] and computer calculations of molecular dynamic models [Bellosent-Funel 2001, Liew 1998], revealed that hydrogen-bonded clustered water molecules dissociate at supercritical conditions, forming dimers or monomers. The dissociation of clustered molecules of liquid water enables organic

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compounds to be attracted and dissolved. Fast diffusion of organics in supercritical water and the rapid self-diffusion of supercritical water promote the formation of homogeneous mixtures of organics and supercritical water. When oxygen is added to the mixtures of supercritical water and organics, forming homogeneous ternary systems, the oxidation of organics is immediate. Kinetic-controlled, rather than diffusion-controlled reactions dominate SCWO processes. Therefore, supercritical water oxidation, which stimulates the destruction of non-biodegradable organic wastes, proceeds much faster than oxidation in both liquids and gases. Heat is released during exothermic reactions and utilized [Modell et al 1982].

| Compounds | T (°C) | Density<br>(kg/m <sup>3</sup> ) | Pressure<br>(bar) | Dielectric<br>constant | Diffusivity<br>(m <sup>2</sup> /s)<br>(Benzene<br>into water) | Kinematic<br>viscosity<br>(m <sup>2</sup> /s) |
|-----------|--------|---------------------------------|-------------------|------------------------|---|---|
|           | 25     | 997                             | 0.1               | 78                     | 1.2E-09   | 8.93E-07                                      |
|           | 300    | 743                             | 25                | 23                     | 7.4E-09   |   |
| Water     | 400    | 166                             | 25                | 3                      | 160E-09   | 1.20E-07                                      |
| Benzene   | 25     | 880                             | 0.1               | 2.3                    |   | 0.70E-07                                      |

Table 1-1 Thermal conductivity, diffusivity and viscosity of water and benzene

Data taken from references [Gebhart 1993] [Clifford 1999]

Conversion of organics in SCWO is achieved in excess of 99% at the reacting time less than 60s. Heteroatoms of Cl and S are converted to acids [LaGrega et al. 2001, Thomason and Modell 1984], while N is converted to  $N_2$  [Timberlake et al. 1982]. For aqueous wastes containing from 1 to 20wt% organics, supercritical water oxidation is less costly than controlled incineration or activated carbon treatment, and more efficient than wet oxidation [Thomason and Modell 1984]; it has been further confirmed by the first commercial scale of SCWO plant in the world that SCWO costs less than other alternatives such as autothermal thermophilic aerobic digestion and more traditional forms of digestion that still require dewatering and final disposal [Griffith and Raymond 2002]. SCWO had been observed to efficiently destroy both complex substances such as urine and feces, as well as simple organics such as methane and ammonia. Therefore, the supercritical water oxidation process is particularly suited to recycling wastewater in a closed environmental life support system, in which human metabolic wastes can be completely decomposed to  $CO_2$  and  $N_2$  [Timberlake et al. 1982, Hong and Fowler 1987].

Most recently, supercritical water oxidation has been shown to convert heavy organic wastes, e.g., rubber, cellulose, and polychlorinated biphenyls (PCBs) to liquid fuels [Fang and Kozinski 2002, Sasaki 1998]. In particular, the partial supercritical water oxidation of rubber and cellulose produced light organics (alcohol species), which can be used as alternative fuels for an internal combustion engine [Fang and Kozinski 2002, Sasaki 1998]. This type of "recycling" of industrial organic wastes may thus generate future revenues by using supercritical water-based technologies.

The disappearance rate of organics in supercritical water hydrolysis/oxidation has been extensively documented in literature. Rate equations indicate that water is clearly involved in oxidation reactions [Gopalan 1995a, Krajnc 1996, Oshima 1998]. One of the possible reasons is that the density of water affects reaction rates. However, the indexes of reactants and activation energies in rate equations have not been consistent after taking water concentrations into account [Gopalan 1995a, Krajnc 1996, Oshima 1998], restricting detailed considerations of reaction mechanisms in supercritical water oxidation. Thus, the application of the kinetic data is limited, not allowing for proper design of industrial reactors.

A set of model compounds, such as methane, methanol, ammonia, hydrogen, carbon monoxide, benzene and phenol, has been investigated to set up kinetics and reaction mechanisms for the destruction of practical organic wastes. The existing combustion models of methane and benzene were adapted to supercritical water oxidation based on the assumption of the similarity between combustion and supercritical water oxidation of the same organics [DiNaro 2000a, Holgate 1994]. Intermediates were well predicted in the modified combustion models, but the production of  $CO_2$  and CO was under-predicted in the benzene model [DiNaro 2000a], which revealed differences existing between the combustion mechanism and the mechanism of supercritical water oxidation. Modeling of phenol oxidation in supercritical water [Gopalan 1995b] was used to study the evolution of intermediates in supercritical water oxidation. Both the predicted intermediates and CO<sub>2</sub>/CO in the model followed, qualitatively, the general trend, but quantitative matching with the experimental data was poor. The deviation between the modeling prediction and the experimental data suggests that the mechanism of supercritical water oxidation of phenol was not complete. In both combustion and SCWO mechanisms, free radical reactions are considered to dominate processes, in which water is in the form of free radicals OH, HO2 and H [DiNaro 2000a, Gopalan 1995b]. In general, little information is available on these mechanisms that come directly from SCWO researches. This is due to sampling difficulty from high-pressure systems, very fast reactions, and low concentrations of feed materials. However, obtaining reliable experimental data from SCWO systems is the first critical step towards proper modeling of the chemistry and kinetics of these processes.

Intermediates, such as furans and dioxins, are formed in the supercritical water oxidation of benzene and phenol. Ammonia is formed in the SCWO of N-containing heterocyclic compounds such as pyridine, aniline and acetonitrile. Presence of these intermediates requires longer residence time in reactors prior to discharge into the environment [Crain et al. 1993, Cocero et al. 2000, Aki and Abraham 1999]. The use of catalysts has been investigated as an optional route to improve the reaction rates in supercritical water. In the SCWO of ammonia,  $MnO_2/CeO_2$  catalyst [Aki and Abraham 1999] was found to increase the reaction rate 600 times.  $Pt/\Box$ -Al<sub>2</sub>O<sub>3</sub> works more efficiently than  $MnO_2/CeO_2$  in the supercritical water oxidation of pyridine. Transitionmetal oxide catalysts (e.g. TiO<sub>2</sub>) substantially enhance the oxidation of phenol in supercritical water [Krajnc and Levec 1997, Yu and Savage 2000]. However, Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, CuO/zeolites, Cu(II)-tetrafluoroborate and  $MnCl_2$  increase the reaction rates of 2– chlorophenol by only a minor degree [Yang and Eckert 1988]. Both homogeneous and heterogeneous catalytic mechanisms are suggested in supercritical water [Krajec and Levec 1997, Yang and Eckert 1988]. The stability of catalysts is a main issue in such severe conditions (oxidative and acidic environments).

In this dissertation, three types of organic wastes are studied in SCWO: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and de-inking sludge residue (DISR). Several PAHs, e.g. benzo(a)pyrene and fluoranthene, are considered carcinogenic and mutagenic. They contaminate off-gases from energy and petroleum industries, and other industrial wastes, e.g. de-inking sludge. PCBs are the notorious precursors of dioxins during their biodegradation in the environment. Reactive hydroxylated PCBs metabolites, the products of PCB biotransformation, bind DNA and RNA in hamsters, causing subsequent gene damage and carcinogenesis [ATSDR 1996]. De-inking sludge residue is produced in large quantities by the pulp and paper industry. The sludge consists mainly of cellulose and ash, accompanied by high concentrations of heavy metals and PAHs [Zheng and Kozinski, 1998].

Our research will try to theoretically resolve the inconsistency in the kinetic equations while emphasizing both the chemical and the phase evolution of PAHs, PCBs,

and industrial wastes (DISR) during supercritical water oxidation, hydrolysis and pyrolysis. This research, the first such comprehensive approach, will start with a simple compound, pure naphthalene, as a representative of PAHs. Its oxidation mechanism, investigated using a batch reactor and a diamond anvil cell, will help in understanding the SCWO of complex PAHs. The behavior of a more complex compound, decachlorobiphenyl, will be subsequently studied. Decachlorobiphenyl is the most difficult to be destroyed of all PCBs. Its SCWO is helpful in determining the role of water by tracing hydrogen atoms in the products, and in understanding the evolution of chloride. A real industrial waste, de-inking sludge residue, will be used to verify the practicality and to perform the parametric study of SCWO.

The evolution of organic wastes in SCWO will be determined using a batch reactor coupled with on-line pressure and temperature sensors. The kinetics, conversion and destruction rates of the selected compounds will be determined from the batch reactor data and from the equations of state. We will subsequently investigate the phase behavior of organics in supercritical water and water-oxygen systems using a diamond anvil cell (DAC). The visual images and on-line temperature measurements will be collected to identify the phase changes. Predictions of the phase evolution in the batch reactor (contrary to DAC, phase changes are not visible) will be made using theoretical equations of state (EOS). Peng-Robinson equation and Franck Critical equation will be adapted to determine the critical properties of mixtures of oxygen and water. Pressure effects on the reaction rates will be considered in the Arrhenius equation based on the above equation of state (EOS). Complete SCWO models and database of organics, including more reliable and consistent parameters, will be then available for future studies.

### 2 FUNDAMENTALS OF SUPERCRITICAL FLUIDS

#### 2.1 Concept of Supercritical Fluid

Early in 1822, Baron Charles Caginard de la Tour discovered that there was a critical temperature. Above the critical temperature, only a single substance existed as a uniform phase, not as either a liquid or a gas. Below this temperature, condensation to a liquid or evaporation to a gas was possible. The phase transformations of a pure substance are schematically illustrated in Figure 2-1.



Temperature

#### Figure 2-1 The phase diagram of a single substance

In Figure 2-1, at low temperature, a substance probably exists as a solid or a gas or both along the coexisting curve. The gas/solid curve ends at a triple point once a liquid is forming, where the liquid, the solid and the gas coexist. The triple point develops, with increasing temperature and pressure, to the coexisting curve of the gas & the liquid and the coexisting curve of the solid & the liquid. In Figure 2-1, the distinction between the gas and the liquid finally disappears, and the gas-liquid border ends at a critical point. The critical temperature  $T_c$  and the critical pressure  $p_c$  coordinate the critical point on the phase diagram, where the critical molar volume  $v_c$  is established ( $v_c$ : a dependant variable of  $T_c$  and  $p_c$ , and the molar volume of the liquid is equal to the molar volume of the gas at  $T_c$  and  $p_c$ ). Each particular substance has its particular values of  $T_c$ ,  $p_c$ , and  $v_c$ . Therefore, the term "supercritical fluid" has been coined to describe the media around/above their critical points.

Supercritical fluids exhibit important characteristics such as compressibility, homogeneity, and continuous changes of properties from the gases to the liquids. The important media, such as  $CO_2$ ,  $N_2$ , and  $O_2$ , have low critical temperatures and pressures. As their critical states are easily achieved, they are widely used.  $CO_2$  is the most popular supercritical medium. It is chemically/radioactively stable, non-flammable, and inexpensive. Its non-polar molecules are like organic molecules; thus, it has been classified as a good non-polar solvent. However, the solubility of hydrocarbons with high molar masses is limited in supercritical  $CO_2$ .

Supercritical water (SCW, above 374.2°C & 22 MPa) is distinguished from the critical fluids such as CO<sub>2</sub>, N<sub>2</sub> and propane. It is a clean, powerful, and stable solvent for organics even though its molecules show a similar polarity to the ambient water [Westacott 2001]. However, the molecular network of the ambient water is "crashed" in supercritical water. About 80% of hydrogen bonding is dissociated; dimers are formed in supercritical water instead of the tetrahedral structure in liquid water [Bellissent-Funel 2001]. The dissociation of water molecule-network enables non-polar organic molecules

to enter supercritical water. Hence, a unique homogeneous environment containing water molecules with strong polarity is formed in supercritical water.

#### 2.2 Physical Properties of Supercritical Water

#### 2.2.1 Ion products and dielectric constants

Sub-critical and supercritical water existing between  $300^{\circ}$ C- $700^{\circ}$ C are of the main research interest. The typical density of supercritical water ranges from 0.7g/ml to 0.05g/ml [Li et al. 1993a and 1993b, Thornton et al. 1991, Smith 1995, Tester 1993]. The dissociation constant K<sub>w</sub> ranges from  $10^{-10}$  to  $10^{-25}$  (see Figure 2-2) [Marshall and Franck 1981, Haar et al. 1984, Uematsu and Franck 1980]. The higher the pressure, the higher the dissociation constants K<sub>w</sub> [Marshall and Franck 1981]. Near the critical point of water between 50 bar (5MPa) and 500bar (50MPa), K<sub>w</sub> rises up to  $10^{-10}$  (see Figure 2-2), 100 times higher than that of the ambient water (K<sub>w</sub>= $10^{-14}$  for the ambient water at 25°C and 0.1013 MPa). Dielectric constants of supercritical water are about 1.0~15.0 while for the ambient water at 25°C & 0.1 MPa it is about 78 (see Figure 2-3). Supercritical water acts like an acidic medium, near the critical point. However, its non-polar-like solvent properties have more desired values above its critical point.





Figure 2-2 Ion products of water vs. temperature and pressure (note:  $1bar = 10^5 Pa \approx 1atm$ ) [Marshall and Franck 1981]



Figure 2-3 Dielectric constants of water vs. temperature and pressure (note: 1MPa = 10 bar) [Uematsu and Franck 1980]

#### 2.2.2 Structural transformation

The low dielectric constants and the variations in dissociation constants indicate the structural evolution of supercritical water. The neutron diffraction data and site-site pair distribution function  $g_{OH}$  of molecular dynamics [Posttorino et al. 1993] suggested that hydrogen bonding would be completely broken. However, other authors [Scoper et al. 1997] disproved the above results using the simulation of molecular dynamics; a part of molecules was still hydrogen bonded. The association between supercritical water molecules was confirmed later *via* the experimental data of IR and X-ray [Gorbaty and Kailinichev 1995]. Water molecular dimers were found in the supercritical water *via*  Raman Spectroscopy. They were present as bifurcated hydrogen bonding (BHB) [Liew et al. 1988, Ikushima 1997]. Calculations of simulated molecule dynamics were also conducted to clarify water molecular structure [Kalinichev and Churakov 1999]. The calculations indicated that no water rings were present in the supercritical water. These results were actually contrary to the explanation of water cage-effect in the supercritical water oxidation of methane [Helling and Tester 1987]. However, the research of the molecule dynamics (MD simulation) [Marti 1999] showed that the presence of hydrogen bonding was detected at every supercritical state; two hydrogen-bonded molecules, which allowed cavities, substituted the tetrahedral structure, typical of liquid water at room temperature (see Fig.2-4). Therefore, the cage-effect in SCW [Helling and Tester 1987] might actually be caused by cavities of two hydrogen-bonded molecules.

The stretch motion of O—D bond vibration has specific frequency if hydrogen (H) is replaced by deuterium (D) of its isotope. O—D bonds' stretch motion would shift after the formation of O—D…H. The intensity of O—D vibration reflects the intensity of hydrogen bonding. The isotropic Raman spectra data of O—D stretch motion show that more than 80% hydrogen bonding is dissociated in supercritical water with density 0.8 g.cm<sup>-3</sup> at 400°C [Kohl et al. 1991]. A structural transformation of water has been concluded in Figure 2-5 in this work.



Liquid Water

Supercritical Water





Figure 2-5 Structural transformation of water (concluded from literature review)

#### 2.2.3 Thermal conductivity, diffusion coefficient and viscosity

Molecular network "crashing" in supercritical water brings significant changes of physical properties of water, such as thermal conductivity, diffusion coefficient and viscosity. The thermal-conducting behavior of sub-critical & supercritical water (>300°C) is similar to that of dissociating gases, the dissociating reaction equilibria of which are strongly shifted by temperature changes. Thus, the dissociation energy is transported along a temperature gradient in addition to the amount of energy if no dissociation occurs. Hence, hydrogen bonding dissociation and ion dissociation of sub/supercritical water result in much higher thermal conductivity than other critical fluids without dissociation occurring. However, the thermal conductivity ( $\lambda$ ) of supercritical water is lower than that of the ambient water (see Table 2-1) because most of hydrogen bonding no longer exists. The temperature dependence of high thermal conductivity of supercritical water is positive, which enables fast heat transfer and facilitates temperature control in chemical processing.

The viscosity of supercritical water ( $\eta$ ) at 500°C and 500bar (50MPa) is about 20 times lower than that of liquid water (see Table 2-1). At low density, momentum transport is dominated by translational transfer, and viscosity slightly depends temperature of water. At high density, collisional transfer prevails; viscosity strongly decreases with increasing temperature. In the scope of 400°C ~ 800°C and 0.2 g.cm<sup>-3</sup> ~ 0.8 g.cm<sup>-3</sup>, momentum transport is composed of translational transfer and collisional transfer, the viscosity  $\eta$  weakly depends on temperature and density. The low viscosity causes high mobility of both water and solute molecules. As the consequences of high mobility, solute diffusion coefficients, self-diffusion coefficients and ionic mobility are much larger in

supercritical water than in liquid water (see Table 2-1), which help to form homogeneity

in mixtures of supercritical water and solutes.

| Ambient water   |  |  | Supercritical water   |  |  |
|---|--|--|---|--|--|
| Viscosity, $\eta$<br>cP (centipoises= $10^3$<br>$\mu$ N.s.cm <sup>-2</sup> )  | Thermal<br>conductivity, λ<br>J.s <sup>-1</sup> .cm <sup>-1</sup> .K <sup>-1</sup> | Diffusion, D<br>cm <sup>2</sup> .sec <sup>-1</sup> | Viscosity, $\eta$<br>cP (centipoises=10 <sup>3</sup><br>$\mu$ N.s.cm <sup>-2</sup> ).   | Thermal conductivity, $\lambda$ J.s <sup>-1</sup> .cm <sup>-1</sup> .K <sup>-1</sup> | Diffusion, D<br>cm <sup>2</sup> .sec <sup>-1</sup> |
| Viscosity: $\eta = 1.787$ cP (0°C, 1 atm), 1.0020 cP (20°C, 1 atm), 0.2829 cP (100°C, 1 atm), decreasing with increasing temperature; increasing with increasing pressure [Bett and Cappi 1965]   |  |  | Viscosity: 0.0848 cP (350°C, 500bar), 0.0688 cP (400°C,<br>500 bar), 0.042 cP (500°C, 500 bar), 0.045 cP (800°C,<br>500 bar), slightly dependent on temperature; increasing<br>with increasing pressure   |  |  |
| Thermal conductivity: $\lambda = 5.6 \times 10^{-3}$ joule.s <sup>-1</sup> .cm <sup>-1</sup> .K <sup>-1</sup><br>(0°C, 1 atm), 6.0 x 10 <sup>-3</sup> (20°C, 1 atm), 7.7 x 10 <sup>-3</sup> (100°C,<br>1 atm); reaching maximum at 130°C, no pressure effect<br>given |  |  | Thermal conductivity: $\lambda = 4.83 \times 10^{-3}$ joule.s <sup>-1</sup> .cm <sup>-1</sup> .K <sup>-1</sup><br>(350°C, 250bar), 1.62 x 10 <sup>-3</sup> (400°C, 250bar), 0.995 x<br>10 <sup>-3</sup> (500°C, 250bar); 1.36 x 10 <sup>-3</sup> (800°C, 250bar),<br>reaching minimum at 500°C for 250 bar, increasing with<br>pressure rising. |  |  |
| Self-diffusion: $D = 2.5 \times 10^{-5} \text{ cm}^2 \text{.sec}^{-1}$ (25°C, 1 atm)  |  |  | Self-diffusion: $D = 6.0 \times 10^{-4} \text{ cm}^2 \text{.sec}^{-1} (370^{\circ}\text{C and } 218 \text{ atm})$   |  |  |
| Benzene diffusing<br>(25°C, 1 atm)  | ; in water: $D = 1.2 \times 10^{-1}$   | $^{-3}$ cm <sup>2</sup> .sec <sup>-1</sup>         | Benzene diffusing in water: $D = 7.4 \times 10^{-3} \text{ cm}^2 \text{.sec}^{-1}$<br>(300°C, 248 bar), 1.6 x 10 <sup>-1</sup> cm <sup>2</sup> .sec <sup>-1</sup> (400°C, 249 bar),   |  |  |

Table 2-1 Comparison of transport properties [Franks 1972]

Note: 1 atm = 1.01325 bar = 0.101325 MPa.

#### 2.3 Solubility of Organics in Supercritical Water

#### 2.3.1 Solubility of small organic molecules

The solubility of several organic compounds near the critical point of water was measured [Connolly 1966, Tsonopoulos and Wilson 1983]. They are shown in Figure 2-6 A, B, C, D, and E. The solubility of benzene, n-heptane, n-pentane, 2-methyl pentane, and toluene shows similar profiles against temperature and pressure. Increasing pressure reduces the solubility of organics while higher temperature promotes their dissolution in water. It is because the higher pressure at lower temperature results in a larger density, subsequently the larger density increases hydrogen bonding, which reduces the organic dissolution. Between 200-400atm (20.3-40.5 MPa), benzene is miscible with water at 300°C, n-heptane at 355°C, n-pentane at 352°C, 2-methyl pentane at 355°C, and toluene at 310°C. These temperatures constitute thresholds where the solubility curves separate

into two branches. The miscible regions are located between the two branches. For aromatic and alkane species, the miscible temperature increases with larger molar weight. The miscible temperatures of aromatic compounds are lower than those of their corresponding alkane (e.g. toluene, aromatic hydrocarbon containing 7 carbons, vs. nheptane, alkane containing 7 carbons). Therefore, aromatic compounds have higher solubility than alkanes at the same condition because they have relatively lower dielectric constants. Figure 2-6 shows that the solubility of organics stays constant vs. different pressures at the certain temperatures: 281°C for benzene, n-heptane at 330°C, n-pentane at 300°C, 2-methyl pentane at 300°C, and toluene at 300°C. The invariable solubility suggests that water density does not significantly change its physical properties at or below those temperatures. At 250 atm (25.3 MPa) and 100-350°C, a transformation of the insolubility to the miscibility of benzene and n-pentane with water has been observed [Uematsu and Franck 1980]. When higher temperature is reached, the decomposition of organics is dominant.

#### 2.3.2 Dissolution of large organic molecules

Polystyrene, cellulose, and polyethylene were found soluble in supercritical water, and they are hydrolyzed to form small molecular units (e.g. styrene, glucose, ethylene). The hydrolysis of solid organics in supercritical water is of importance for recycling the organic wastes. Varieties of reactions, such as hydrolysis, pyrolysis, condensation (polymerization) and isomerization, occur during the dissolution of solid organics in supercritical water. Raman spectroscopy data [Fang et al 1999] confirmed hydrolysis and pyrolysis taking place during dissolution processes. The dissolution of polyethylene terephthalates (PET plastics), cellulose and PAHs in supercritical water had been visually observed through Diamond Anvil Cell [Fang and Kozinski 2000a; Sasaki 2000; Sobhy et al. 2002]. The cooling-down products were terephthalic acid, ethylene glycol, oligomer and polyethylene terephthalates [Fang et al 1999; Fang et al. 2000b; Sobhy et al. 2002]. The hydrolysis and dissolution of PET in supercritical methanol produced similar products [Yang et al. 2002]. Terephthalic acid would constitute 76%wt of the final products of PET in the supercritical water at 1800s residence time. Other plastics, such as PEN (polyethylene naphthalates), bylon-6, nylon-66, and polyurethane, also dissolved in supercritical water [Arai 1999]. Liquid methanol [Grunschke 1968], liquid ethylene glycol [Baliga and Wong 1989], and alkaline water solution [Datye and Vaidya 1984] were used to dissolve PET, then converting the PET into monomers in order to recycle it. However, supercritical water is more secure and cleaner solvent than organic solvents. Biomass (typically cellulose-based) was converted into smaller molecules in supercritical water [Minowa 1998, Sasaki 1997]. HPLC analysis showed that final products contained 1,6-anhydroglucose, cellobiose, acids, glucose, fructose, erythrose, and 5-(Hydroxymethyl)-2-(formylfuran) (5-HMF). Rubber and polypropylene are strongly resistant to dissolution in supercritical water. A partial oxidation technology was used in order to dissolve them [Kocher 1996, Fang and Kozinski 2002a]. Although PVC is a degradation-resistant and strong dissolution-resistant plastic, the supercritical water and oxygen had been successfully used to decompose PVC. The final products were oxalic acid (0.45kg), benzenecarboxylic acid (0.28kg) and CO<sub>2</sub> if a 1.0kg of PVC was processed at 250°C and oxygen partial pressure of 5MPa after 5 hours [Yoshioka 2000]. The results on the decomposition of large molecule organics in supercritical water are encouraging. Therefore, waste organics are also considered as a potential energy source.

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#### 2.4 Solubility of Inorganic Compounds

The behavior of inorganic compounds in supercritical water is dramatically different from their behavior in the ambient water. Supercritical water behaves like a non-polar fluid near or above its critical point. Therefore, the solubility of metal salts is greatly reduced in supercritical water whereas organic compounds become soluble. The typical solubility of chloride salts and nitrate salts in SCW is about 100mg per kilogram while their solubility in the ambient water is about 100 gram per kilogram. The solubility decreases in a factor of  $10^3$  from the ambient water to supercritical water, as seen in Table 2-2.

The solubility of salts (see in Table 2-2) is in the range of a hundred ppms. NaOH and Na<sub>2</sub>SO<sub>4</sub>, separately having solubility of 2.5g per 100g water at 400°C & 28.3MPa and 7g per 100g water at 350°C and 27.4MPa, are considered soluble in SCW. Therefore, NaOH is often used to enhance hydrolysis of organics in supercritical water. It is found that increasing pressure increases the solubility of salts in SCW (see Table 2-2). The pressure dependence of solubility results from higher dielectric constants and ion products at higher pressures. The solubility of both organics and inorganics mainly depends on the solvent environment, where solute molecules are attracted or excluded. For example, the solubility of NaCl changed from 63 mg/kg to 250 mg/kg when the pressure changed from 20MPa to 25MPa at 450°C. Nevertheless, increasing temperature apparently inhibits the dissolution of salts in SCW. For example, the solubility of NaCl decreases to 299mg/kg from 824mg/kg if the temperature rises to 509°C from 408°C at 29.8MPa.

For metal oxides and salts, such as  $Al_2O_3$ , CuO, and CaCO<sub>3</sub>, not soluble in the ambient water, their solubility is further reduced in SCW in comparison with that in the

ambient water (see Table 2-3). Silica has a different behavior from metal salts and oxides in SCW. The solubility of amorphous silica is about 58.8mg/kg and the crystal SiO<sub>2</sub>, such as chalcedony and crystal quartz, has even lower solubility of 11.1mg/kg in the ambient water (see Table 2-3). In supercritical water, the solubility of silica increases to 216 mg/kg water at 34.5 MPa and 500°C. Silica dissolves to form H<sub>4</sub>SiO<sub>4</sub> in supercritical water. The dissociation of H<sub>4</sub>SiO<sub>4</sub> is weak with  $K_1 = 3.0 \times 10^{-10}$  and  $K_2 = 3.0 \times 10^{-12}$ , which is very close to that of supercritical water near the critical point. Therefore, such low ion products of H<sub>4</sub>SiO<sub>4</sub> result in higher solubility of silica in supercritical water.

The insolubility of inorganic oxides and salts is a considerable disadvantage in the SCWO of organic wastes containing inorganic impurities. These solid inorganic compounds cause problems related to the device design and operation, such as the corrosion of instruments and the clogging of pipes. The solid separation technology had been tested to remove inorganic compounds in SCWO. Two cross-flow filters were tested in conjunction with 150L/hr SCWO pilot plant [Goemans 1995a, 1995b]. The filter elements were made of sintered stainless steel 316L tubes with a pore size about 0.5µm. Sodium nitrate and  $\alpha$ -alumina were feed as solids. The separation efficiency (SE, defined as  $SE = \frac{\text{weight retained by filter}}{\text{feed weight}} x100\%)$  for sodium nitrate ranged from 60% to 85% at 420°C, 470 °C and 27.6MPa. The separation efficiency for α-alumina was between 97.3% and 99.90% at the same conditions. The low SE for NaNO<sub>3</sub> resulted from the salt's solubility. Two hydro-cyclones with 10mm and 25.4mm diameter, respectively, were tested [Dell'Orco 1993a 1993b, Gloyna 1993]. The particulates were  $\alpha$ -alumina [Gloyna 1993], silica, titania and zirconia, [Dell'Orco 1993a and 1993b] with particle sizes from below 1.0 µm to 10.0 µm. Feed flow rates ranged from 0.012L/sec to
0.031L/sec with particle concentrations from 500mg/L to 2000mg/L. The high solid removal efficiency, up to 99.95%, was achieved at 420°C and 27.6MPa.

Heavy metals, such as chromium, lead and cadmium are "pollutants" in supercritical water oxidation. In SCWO, heavy metal salts or oxides are investigated by doping the SCW with heavy metals at high concentrations. Chromium valence in the effluents depends on the pH values of the effluents. At pH<7, valence of Cr was +3; at pH>7,  $Cr^{3+}$  equilibrates with  $Cr^{6+}$ . The results showed that hexa-valence chromium were effectively removed by the precipitation of chromate at SCW conditions [Rollans 1992]. Lead was found to precipitate as PbCO<sub>3</sub> during SCWO with large excess of oxygen [Zimet 1995].

In the recently conducted experiments by our research group, PbCrO<sub>4</sub> was found as a main precipitate at SCWO conditions with excess of oxygen. Cadmium was relatively stable in both solid residues and solutions during SCWO. Experimental results showed that Pb was removed at high efficiency (above 99.9%) by precipitating as lead chromate and lead carbonate. It is expected that lead and chromate would be completely removed from aqueous phases during the combustion of de-inking sludge residue if the molar ratio between lead and chromium was properly made [Fang, Xu and Kozinski 2000c].

However, the insolubility of inorganics in supercritical water and supercritical water oxidation may occur as an advantage in the field of materials science and engineering. For example, the insolubility of metal oxides and salts in SCW has helped to recover precious metals, as well as proved useful in preparation and production of fine particle powder with high purity [Lvov and Machdonald 1997]. Supercritical water dissolves organics and precipitate inorganic compounds. Therefore, it would also serve as

an extracting solvent for separating organics and inorganics [Ogunsola and Berkowitz 1995, Hartonen et al. 1997].

| Compound                        | Pressure(MPa) | Temperature(°C) | Solubility(mg/kg) | Reference       |
|---------------------------------|---------------|-----------------|-------------------|-----------------|
| K <sub>2</sub> HPO <sub>4</sub> | 26.8          | 450             | <7                | Wofford 1994    |
|                                 | 29.5          | 450             | 17                | Wofford 1994    |
| КОН                             | 27.7          | 450             | 331               | Wofford 1994    |
|                                 | 25.3          | 475             | 154               | Wofford 1994    |
|                                 | 22.1          | 525             | 60                | Wofford 1994    |
| KNO <sub>3</sub>                | 24.8          | 475             | 275               | Dell-Orco 1992  |
|                                 | 27.6          | 475             | 402               | Dell-Orco 1992  |
| LiNO <sub>3</sub>               | 24.7          | 475             | 433               | Dell-Orco 1992  |
|                                 | 27.7          | 475             | 1175              | Dell-Orco 1992  |
| NaNO <sub>3</sub>               | 27.6          | 450             | 991               | Dell-Orco 1992  |
|                                 | 27.6          | 475             | 630               | Dell-Orco 1992  |
|                                 | 27.6          | 500             | 540               | Dell-Orco 1992  |
| NaCl                            | 27.0          | 450             | 500               | Ölander 1950    |
|                                 | 27.6          | 500             | 304               | Morey 1951      |
|                                 | 30.0          | 500             | 200               | Martyanova 1976 |
|                                 | 25.0          | 450             | 250               | Bischoff 1986   |
|                                 | 20.0          | 450             | 63                | Armellini 1991  |
|                                 | 29.8          | 408             | 824               | Dell-Orco 1993b |
|                                 | 29.8          | 509             | 299               | Dell-Orco 1993b |
| $Na_2SO_4$                      | 27.4          | 350             | 70,000            | Ravich 1964     |
|                                 | 29.8          | 407             | 136               | Dell-Orco 1993b |
|                                 | 30.0          | 450             | 0.02              | Martyanova 1976 |
| NaOH                            | 28.3          | 400             | 25,000            | Urusova 1974    |
| NaHCO <sub>3</sub>              | 29.8          | 509             | 86                | Dell-Orco 1993b |
| Mg(OH) <sub>2</sub>             | 24.0          | 440             | 0.02              | Martyanova 1964 |
|                                 |               |                 |                   |                 |

Table 2-2 Solubility of inorganic salts in supercritical water

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| Compound                       | Pressure (MPa) | Temperature | Solubility     | Reference       |
|--------------------------------|----------------|-------------|----------------|-----------------|
|                                |                | (°C)        | (mg/kg)        |                 |
| Fe <sub>2</sub> O <sub>3</sub> | 100            | 500         | 90             | Matson 1989     |
| $Al_2O_3$                      | 100            | 500         | 1.8            | Matson 1989     |
| NiO                            | 100            | 500         | 20             | Matson 1989     |
| PbO                            | 28             | 500         | 684            | Yokoyama 1993   |
| CuO                            | 25.0           | 450         | 0.010          | Martyanova 1976 |
|                                | 31.0           | 320         | 0.015          | Pocock 1963     |
| CaCO <sub>3</sub>              | 24             | 440         | 0.02           | Martynova 1964  |
| SiO <sub>2</sub> (amorphous)   | 0.1            | 25          | 55.8           | Advovat 1991    |
| $SiO_2$ (quartz)               | 0.1            | 25          | Ammed<br>Ammed | Stumm 1981      |
|                                | 25.0           | 450         | 55             | Martynova 1976  |
|                                | 28             | 500         | 250            | Yokoyama 1993   |
|                                | 30.0           | 450         | 160            | Martynova 1976  |
|                                | 34.5           | 400         | 637            | Morey 1951      |
|                                | 34.5           | 500         | 216            | Morey 1951      |
|                                | 100            | 500         | 2,600          | Matson 1989     |

| Table 2-3 | Solubility | of oxides | in | supercritical | water |
|-----------|------------|-----------|----|---------------|-------|
|-----------|------------|-----------|----|---------------|-------|

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# 2.5 Chemistry and Kinetics in Supercritical Water Reactions

# 2.5.1 Radical reactions in supercritical water oxidation

Hydroxyl radicals are considered as primary oxidizing species in SCWO processes. Initial models have shown to be inadequate in describing SCWO of simple compounds. Nevertheless, the analogy between combustion and SCWO chemistry was strengthened with comprehensive research on reaction mechanisms. Brock et al. [Brock 1996] proposed a reaction pathway of SCWO of methanol in the range 500~600°C, and have found that only eight elementary reaction steps are needed to describe the system adequately (see Figure 2-7). The path analysis showed that the fastest reactions, consuming methanol, involved OH attack and the resulting radicals producing formaldehyde, which was attacked by OH to form CO eventually. CO was oxidized to CO<sub>2</sub> via OH reacting with CO. DiNaro [DiNaro 2000a] has set up a reaction mechanism model of benzene in SCWO by modifying benzene combustion mechanism. All intermediates in the SCWO of benzene were accurately predicted but CO<sub>2</sub>/CO yields were under-predicted. It suggests that a similar mechanism exist in both the benzene combustion and the SCWO of benzene. The reason for under-predicted CO<sub>2</sub>/CO yields is that the kinetic constants of some reaction steps in the combustion model of benzene have been likely changed with pressure since a high pressure of water is applied in the SCWO of benzene. An analysis of reactions indicated that HO<sub>2</sub> and OH radicals play main roles (see Table 2-4). When the combustion model of benzene is used, the kinetic parameters of the reaction 1, 4, 6, 25~27, 56, 59, 70~77, and 81 in Table 2-4 have been recalculated. This modification reveals the discrepancy that might be caused by pressure effects.



Figure 2-7 Relative net reaction rates of the fastest reactions for the SCWO of methanol at 538 °C, 246 atm, 1.5 s, [H<sub>2</sub>O]<sub>0</sub> = 4.49 × 10<sup>-3</sup>, [O<sub>2</sub>]<sub>0</sub> = 4.64 × 10<sup>-6</sup>, [CH<sub>3</sub>OH]<sub>0</sub> = 7.27 × 10<sup>-7</sup> (mol/cm<sup>3</sup>). The numbers near the arrows are relative net reaction rates. Thicker arrows denote faster reactions. (A, top) Carbon-containing species; (B, bottom) free-radical species [Brock et al. 1996]. Note: 1 atm = 1.01325 bar = 0.101325 MPa.

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Table 2-4 Reduced elementary reaction mechanisms for benzene oxidation in supercritical water (Mechanism developed for the Pressure of 246 bar (1 bar = $10^5$ Pa) and Temperatures around 540 °C;

the Rate Coefficient used is identical to that used by Shandross [1996a, b]) ( [DiNaro 2000a])

| No.  | Reaction $A (cm^3 mol s)$                      |                        | n     | $\begin{bmatrix} E_{a} \\ (cal/mol) \end{bmatrix}$ | Ref.                       |
|--|--|------------------------|-------|--|----------------------------|
| H <sub>2</sub> /O <sub>2</sub> reactions   |  |                        |       |  |                            |
| 1  | $H + O_2 \iff HO_2$                            | $2.07 \times 10^{18}$  | -1.69 | 890  | QRRK                       |
| 2  | $O_2 + HO_2 \iff H_2O_2 + O_2$                 | $2.22 \times 10^{11}$  | 0.    | -1 629   | a                          |
| 3  | $H_2O_2 + OH \iff H_2O + HO_2$                 | $7.83 \times 10^{12}$  | 0.    | 1 331.4  | [Baulch et al. 1992]       |
| 4  | $OH + OH \iff H_2O_2$                          | $2.96 \times 10^{28}$  | -5.26 | 2 980  | QRRK                       |
| 5  | $OH + HO_2 \iff H_2O + O_2$                    | $1.91 \times 10^{16}$  | -1.0  | 0  | [Kim et al. 1994]          |
| 6  | $H + O_2 \iff OH + O$                          | $2.10 \times 10^{15}$  | -0.3  | 20 200   | QRRK                       |
| 7  | $OH + OH \iff O + H_2O$                        | $1.50 \times 10^{9}$   | 1.14  | 99.4   | [Baulch et al. 1992]       |
| 8  | $O + HO_2 \iff OH + O_2$                       | $3.25 \times 10^{13}$  | 0.    | 0  | [Baulch et al. 1992]       |
| C <sub>7</sub> H <sub>7</sub> reactions    |  |                        |       |  |                            |
| 9  | $C_{5}H_{5} + C_{2}H_{2} \iff C_{7}H_{7}$      | $3.72 \times 10^{11}$  | 0.    | 8 300  | [Zhang 1995]               |
| 10   | $C_7H_8 + OH \iff C_7H_7 + H_2O$               | $1.26 \times 10^{13}$  | 0.    | 2 583  | [Emdee et al. 1992]        |
| C <sub>6</sub> H <sub>6</sub> reactions    |  |                        |       |  |                            |
| 11   | $OH + C_6H_6 \iff C_6H_5OH + H$                | $1.34 \times 10^{13}$  | 0.    | 10 592   | [He et al. 1988]           |
| 12   | $OH + C_6H_6 \iff C_6H_5 + H_2O$               | $1.63 \times 10^{8}$   | 1.42  | 1 454  | [Baulch et al. 1992]       |
| 13   | $O + C_6H_6 \iff C_6H_5O + H$                  | $2.40 \times 10^{13}$  | 0.    | 4 668  | [Ko et al. 1991]           |
| C <sub>6</sub> H <sub>5</sub> OH reactions |  |                        |       |  |                            |
| 14   | $H + C_6H_5O \iff C_6H_5OH$                    | $2.50 \times 10^{14}$  | 0.    | 0  | [He et al. 1988]           |
| 15   | $OH + C_6H_5OH \iff H_2O + C_6H_5O$            | 1.39 × 10 <sup>8</sup> | 1.43  | -962   | [Shandross 1996a]          |
| 16   | $C_6H_5OH + O \iff C_6H_5O + OH$               | $1.28 \times 10^{13}$  | 0.    | 2 891  | [Tan 1996, Baulch<br>1994] |
| 17   | $C_6H_5OH + HO_2 \iff C_6H_5O + H_2O_2$        | $3.00 \times 10^{13}$  | 0.    | 15 000   | [Bittker 1991]             |
| 18   | $C_6H_5OH + CH_2CHCHCH \iff C_4H_6 + C_6H_5O$  | $6.00 \times 10^{12}$  | 0.    | 0  | [Emdee et al. 1992]        |
| 19   | $C_6H_5OH + CH_2CHCCH_2 \iff C_4H_6 + C_6H_5O$ | $6.00 \times 10^{12}$  | 0.    | 0  | [Emdee et al. 1992]        |
| 20   | $C_6H_5OH + C_6H_5 \iff C_6H_6 + C_6H_5O$      | $4.91 \times 10^{12}$  | 0.    | 4 400  | [Emdee et al. 1992]        |

| Table 2-4 (Continued)                                  |  |                           |       |                   |                     |  |
|--|--|---------------------------|-------|-------------------|---------------------|--|
| No.  | Reaction   | A (cm <sup>3</sup> mol s) | n     | $E_{a}$ (cal/mol) | Ref.                |  |
| C <sub>6</sub> H <sub>5</sub> O reactions              |  |                           |       |                   |                     |  |
| 21   | $C_6H_5O + C_5H_6 \iff C_5H_5 + C_6H_5OH$                                | $3.16 \times 10^{11}$     | 0.    | 8 000             | [Emdee et al. 1992] |  |
| 22   | $C_6H_5O \iff C_5H_5 + CO$   | $7.40 \times 10^{11}$     | 0.    | 43 853            | [Frank et al. 1994] |  |
| 23   | $C_6H_5O + O \iff C_6H_4O_2 + H$   | $3.00 \times 10^{13}$     | 0.    | 0                 | [Tan 1996]          |  |
| C <sub>6</sub> H <sub>5</sub> reactions                |  |                           |       |                   |                     |  |
| 24   | $C_6H_5 + O \iff C_5H_5 + CO$  | $9.00 \times 10^{13}$     | 0.    | 0                 | [Frank et al. 1994] |  |
| 25   | $C_6H_5 + O_2 \iff C_6H_5O + O$  | $2.57 \times 10^{-29}$    | 12.73 | -5 699            | QRRK                |  |
| 26   | $C_6H_5 + O_2 \iff C_6H_5OO$   | $1.85 \times 10^{13}$     | -0.15 | -159              | QRRK                |  |
| C <sub>6</sub> H <sub>5</sub> OO reactions             |  |                           |       |                   |                     |  |
| 27   | $C_6H_5OO \iff C_6H_5O + O$  | $4.27 \times 10^{15}$     | -0.7  | 33 027            | QRRK                |  |
| 28   | C <sub>6</sub> H₅OO + H <del>↔</del> C <sub>6</sub> H₅OOH                | $2.50 \times 10^{14}$     | 0.    | 0                 | b                   |  |
| 29   | C <sub>6</sub> H <sub>5</sub> O + OH ⇔ C <sub>6</sub> H <sub>5</sub> OOH | $1.00 \times 10^{12}$     | 0.    | 0                 | c                   |  |
| 30   | $C_{6}H_{5}OO + C_{6}H_{5}OH \iff C_{6}H_{5}OOH + C_{6}H_{5}O$           | $1.00 \times 10^{11.5}$   | 0.    | 6 961             | d                   |  |
| 31   | $C_6H_5OO + HO_2 \iff C_6H_5OOH + O_2$                                   | $1.87 \times 10^{12}$     | 0.    | 1 540             | e                   |  |
| 32   | $C_6H_5OO \iff C_6H_4O_2 + H$  | $4.00 \times 10^{8}$      | 0.    | 0                 | f                   |  |
| 33   | $C_6H_5OO \iff C_5H_5 + CO_2$  | $1.60 \times 10^{8}$      | 0.    | 0                 | ſ                   |  |
| C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> reactions |  |                           | ,     |                   |                     |  |
| 34   | $C_6H_4O_2$ $\iff$ $C_5H_4O + CO$  | $3.70 \times 10^{11}$     | 0.    | 59 000            | [Alzueta 1998]      |  |
| 35   | $C_6H_4O_2$ $\iff$ $C_5H_4 + CO_2$                                       | $3.50 \times 10^{12}$     | 0.    | 67 000            | [Alzueta 1998]      |  |
| 36   | $C_6H_4O_2 + H \iff C_5H_5O + CO$  | $2.50 \times 10^{13}$     | 0.    | 4 700             | [Alzueta 1998]      |  |
| 37   | $C_6H_4O_2 + H \Longrightarrow C_6H_3O_2 + H_2$                          | $2.00 \times 10^{12}$     | 0.    | 8 100             | [Alzueta 1998]      |  |
| 38   | $C_6H_4O_2 + OH \Rightarrow C_6H_3O_2 + H_2O$                            | $1.00 \times 10^{6}$      | 2.0   | 4 000             | [Alzueta 1998]      |  |
| 39   | $C_6H_4O_2 + O \Longrightarrow C_6H_3O_3 + H$                            | $1.50 \times 10^{13}$     | 0.    | 4 530             | [Alzueta 1998]      |  |
| 40   | $C_6H_4O_2 + O \Rightarrow C_6H_3O_2 + OH$                               | $1.40 \times 10^{13}$     | 0.    | 14 700            | [Alzueta 1998]      |  |
| C <sub>6</sub> H <sub>3</sub> O <sub>2</sub> reactions |  |                           |       |                   |                     |  |
| 41   | $C_6H_3O_2 + H \Rightarrow 2C_2H_2 + 2CO$                                | $1.00 \times 10^{14}$     | 0.    | 0                 | [Alzueta 1998]      |  |
| 42   | $C_6H_3O_2 + O \Rightarrow C_2H_2 + HCCO + 2CO$                          | $1.00 \times 10^{14}$     | 0.    | 0                 | [Alzueta 1998]      |  |
| 43   | $C_6H_3O_3 \Longrightarrow C_2H_2 + HCCO + 2CO$                          | $1.00 \times 10^{12}$     | 0.    | 50 000            | [Alzueta 1998]      |  |
| C <sub>5</sub> H <sub>5</sub> O reactions              |  |                           |       |                   |                     |  |
| 44   | C <sub>5</sub> H <sub>5</sub> O ⇔CH <sub>2</sub> CHCHCH + CO             | $7.50 \times 10^{11}$     | 0.    | 43 900            | [Alzueta 1998]      |  |
| C <sub>5</sub> H <sub>4</sub> O reactions              |  |                           |       |                   |                     |  |
| 45   | $C_5H_4O \iff C_4H_4 + CO$   | $1.00 \times 10^{12}$     | 0.    | 0                 | [Tan 1996]          |  |
| 46   | $C_5H_4O + O \Longrightarrow C_4H_4 + CO_2$                              | $1.00 \times 10^{13}$     | 0.    | 2 000             | [Alzueta 1998]      |  |
| 47   | $C_5H_4O + H \iff CH_2CHCCH_2 + CO$                                      | $2.50 \times 10^{13}$     | 0.    | 4 700             | [Alzueta 1998]      |  |
| 48   | $C_5H_4O \iff 2C_2H_2 + CO$  | $1.00 \times 10^{15}$     | 0.    | 78 000            | [Alzueta 1998]      |  |
| 49   | C₅H₄OH ⇐⇐C₅H₄O + H   | $2.13 \times 10^{13}$     | 0.    | 48 000            | [Emdee et al. 1992] |  |

\* \* A 4 (0) . د \*

| No.                                     | Reaction                                     | $A (\text{cm}^3 \text{ mol s})$   | n     | $\begin{bmatrix} E_{a} \\ (cal/mol) \end{bmatrix}$ | Ref.  |
|---|--|---|-------|--|---|
| $C_5H_4$ reactions                      |  |   |       |  |   |
| 50                                      | $C_5H_4+H \iff C_5H_3+H_2$                   | $1.00 \times 10^{6}$  | 2.5   | 5 000  | [Alzueta 1998]  |
| 51                                      | $C_5H_4+O \iff C_5H_3+OH$                    | $1.00 \times 10^{6}$  | 2.5   | 3 000  | [Alzueta 1998]  |
| 52                                      | $C_5H_4$ + OH $\iff$ $C_5H_3$ + $H_2O$       | $1.00 \times 10^{7}$  | 2.0   | 0  | [Alzueta 1998]  |
| $C_5H_3$ reactions                      |  |   |       |  |   |
| 53                                      | $C_5H_3 + O_2 \iff C_2H_2 + HCCO + CO$       | $1.00 \times 10^{12}$   | 0.    | 0  | [Alzueta 1998]  |
| C <sub>5</sub> H <sub>6</sub> reactions |  | C. Subschligt of the second s<br>Second second se<br>Second second sec<br>second second sec |       |  | C. C. Conserver, et al. C. Conserver, Internet internet control of a subsection of the conserver of the c |
| 54                                      | $C_5H_6+H \iff C_2H_2+C_3H_5$                | 7.14 × 10 <sup>-34</sup>  | 15.1  | 14 617   | [Zhong 1997], QRRK  |
| 55                                      | $C_5H_6+H \iff C_5H_5+H_2$                   | $1.20 \times 10^{5}$  | 2.5   | 1 492  | [Zhong 1997]  |
| 56                                      | $C_5H_6+O \iff C_5H_5O_{1-2}+H$              | $1.00 \times 10^{15}$   | -0.6  | 3 669  | [Zhong 1997], QRRK  |
| 57                                      | $C_{5}H_{6}+O \iff C_{5}H_{5}+OH$            | $4.77 \times 10^{4}$  | 2.7   | 1 106  | [Zhong 1997]  |
| 58                                      | $C_{5}H_{6}+OH \iff C = CC \cdot C = COH$    | $4.40 \times 10^{10}$   | 0.82  | 2 914  | [Zhong 1997], QRRK  |
| 59                                      | $C_{5}H_{6}+OH \iff C_{5}H_{5}+H_{2}O$       | $3.10 \times 10^{6}$  | 2.0   | 0  | [Zhong 1997]  |
| 60                                      | $C_5H_6+O_2$ $\leftrightarrow$ $C_5H_5+HO_2$ | $4.00 \times 10^{13}$   | 0.    | 37 150   | [Zhong 1997]  |
| 61                                      | $C_5H_6+HO_2$ $C_5H_5+H_2O_2$                | $1.10 \times 10^{4}$  | 2.6   | 12 900   | [Zhong 1997]  |
| 62                                      | $C_5H_6$ + HCO $\iff$ $C_5H_5$ + $CH_2O$     | 1.10 × 10 <sup>8</sup>  | 1.9   | 16 000   | [Zhong 1997]  |
| 63                                      | $C_5H_6+CH_3 \iff C_5H_5+CH_4$               | 0.18  | 4.0   | 0  | [Zhong 1997]  |
| 64                                      | $C_5H_6+C_2H_3 \iff C_5H_5+C_2H_4$           | 0.12  | 4.0   | 0  | [Zhong 1997]  |
| 65                                      | $C_5H_6+C_3H_5 \iff C_5H_5+C_3H_6$           | 0.20  | 4.0   | 0  | [Zhong 1997]  |
| 66                                      | $C_5H_6 + CH_2CH CHCH \iff C_5H_5 + C_4H_6$  | 0.12  | 4.0   | 0  | [Zhong 1997]  |
| 67                                      | $C_5H_6+C_6H_5 \iff C_5H_5+C_6H_6$           | 0.10  | 4.0   | 0  | [Zhong 1997]  |
| 68                                      | $C_5H_6 + CH_2CHCCH_2 \iff C_5H_5 + C_4H_6$  | $6.00 \times 10^{12}$   | 0.    | 0  | [Emdee et al. 1992]   |
| $C_5H_5$ reactions                      |  |   |       |  |   |
| 69                                      | C₅H₅+ H ⇔C₅H <sub>6</sub>                    | $3.20 \times 10^{14}$   | 0.0   | 0  | [Zhong 1998], (k 🗂 🔿  |
| 70                                      | $C_5H_5+O$ $\iff$ $C_5H_5O$                  | $5.20 \times 10^{30}$   | -5.96 | 3 445  | [Zhong 1998], QRRK  |
| 71                                      | $C_{5}H_{5}+O$ $\iff$ $C_{5}H_{4}O+H$        | $4.25 \times 10^{15}$   | -0.56 | 1 230  | [Zhong 1998], QRRK  |
| 72                                      | C₅H₅+ O ⇔CH₂CHCHCH + CO                      | $1.45 \times 10^{1}$  | 3.76  | 2 213  | [Zhong 1998], QRRK  |
| 73.                                     | $C_{5}H_{5}+OH \iff C_{5}H_{4}OH + H$        | $3.63 \times 10^{-48}$  | 18.18 | -3 853   | [Zhong 1998], QRRK  |
| 74                                      | $C_5H_5+HO_2$ $\iff$ $C_5H_5O+OH$            | $6.19 \times 10^{-31}$  | 13.81 | -4 130   | [Zhong 1998], QRRK  |
| 75                                      | $C_5H_5+HO_2 \iff C_5H_4O+H_2O$              | $9.46 \times 10^{-32}$  | 13.13 | -4 803   | [Zhong 1998], QRRK  |
| 76                                      | $C_5H_5+O_2$ $\iff$ COC=CKET + H             | $4.35 \times 10^{7}$  | 1.08  | 16 737   | [Zhong 1998], QRRK  |
| 77                                      | $C_5H_5+O_2$ $C=CC=C=O+HCO$                  | $1.31 \times 10^{-3}$   | 4.41  | 16 472   | [Zhong 1998], QRRK  |

### Table 2-4 (Continued)

| No.                      | Reaction                               | $A (\text{cm}^3 \text{ mol s})$ | n     | $E_{a}$ (cal/mol) | ref                                     |
|--------------------------|--|---------------------------------|-------|-------------------|---|
| C <sub>4</sub> reactions |  |                                 |       |                   |   |
| 78                       | $CH_2CHCCH_2 + O_2 \iff C_4H_4 + HO_2$ | $1.20 \times 10^{11}$           | 0.    | 0                 | [Emdee et al. 1992]                     |
| 79                       | $C_4H_4 + OH \iff H_2CCCCH + H_2O$     | $7.50 \times 10^{6}$            | 2.0   | 5 000             | [Miller 1992]                           |
| C <sub>2</sub> reactions |  |                                 |       |                   |   |
| 80                       | $C_2H_3 + O_2 \iff CH_2O + HCO$        | $4.00 \times 10^{12}$           | 0.    | -250              | [Miller 1992]                           |
| 81                       | $C_2H_2 + H \iff C_2H_3$               | $7.85 \times 10^{14}$           | -0.22 | 1 770             | QRRK                                    |
| C <sub>1</sub> reactions |  |                                 |       |                   |   |
| 82                       | $CH_2O + OH \iff HCO + H_2O$           | $3.43 \times 10^{15}$           | 1.18  | -447              | [Miller 1992]                           |
| 83                       | $HCO + M \iff H + CO + M$              | $2.50 \times 10^{14}$           | 0.    | 16 802            | [Miller 1992]                           |
| 84                       | $CO + O \iff CO_2$                     | $1.80 \times 10^{10}$           | 0.    | 2 438             | [Westmoreland 1986,<br>Troe 1974] (kpp) |
| 85                       | $CO + OH \iff CO_2 + H$                | $3.09 \times 10^{11}$           | 0.    | 735               | [Dixon-Lewis 1972]                      |

Table 2-4 (Continued)

<sup>*a*</sup> Hippler et al.[1990] fit to single exponential for temperatures around 800 K. <sup>*b*</sup> Estimated from C<sub>6</sub>H<sub>5</sub>O + H  $\Leftrightarrow$ C<sub>6</sub>H<sub>5</sub>OH [He et al. 1988]. <sup>*c*</sup> Rate coefficient assumed to have a pre-exponential factor for diffusion controlled reactions ( $A = 10^{12}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) and no energy barrier ( $E_a = 0$ ). <sup>*d*</sup> Estimated from the reaction of poly(peroxystyrl)peroxyl radical with phenol using the measurement of  $k = 10^7$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at 65°C [Howard 1963] and assumed  $A = 10^{11.5}$  to infer  $E_a$ . <sup>*e*</sup> Estimated from HO<sub>2</sub> + HO<sub>2</sub>  $\Leftrightarrow$ H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> [Baulch et al. 1992]. <sup>*f*</sup> Treated as adjustable parameters. QRRK seen in [Robinson 1792]. 1 cal/mol = 4.18 Joule/mol.

### 2.5.2 Ionic reactions in supercritical water

Ionic reactions are the main pathways in the ambient water, where the solvation of water molecules attracts solute molecules and promotes ionic dissociation of reactants. Molecular dynamic simulation of *tert*-butyl chloride hydrolysis in supercritical water reveals that the ionic nature of *tert*-butyl chloride remains up to  $0.04g/cm^3$  of water density [Westacott 2001]. The single nucleophilic substitution (S<sub>N</sub>1) is responsible for the hydrolysis. The experimental study of methoxynaphthalene in SCW [Penninger and Kolmschate 1989] clearly showed that water density favored the selectivity to hydrolysis. Addition of NaCl increased the conversion of methoxynaphthalene. This result confirms the ionic mechanism of hydrolysis in SCW. According to Debye-Huckel limiting law for dilute solutions, the activity coefficient obeys the equation:

$$\ln \gamma_i = -Z_i^2 \alpha(\mu)^{0.5}$$
(2-1)

where  $Z_i$  = charge of ion i;  $\mu$  = the ionic strength of the solution which is defined as  $0.5\sum C_i Z_i^2$  with  $C_i$  = concentration of ion i, mole/liter. The parameter  $\alpha$  is defined as:

$$\alpha = \frac{e^{3} (2\pi N)^{0.5}}{\underline{k}^{1.5}} \bullet \frac{1}{(\epsilon T)^{1.5}}$$
(2-2)

where N = Avogadro number, e = charge of electron and  $\underline{k}$  = Boltzmann constant, which are independent of solvent properties and temperature. Dielectric constant  $\varepsilon$  is a function of both solvent density and temperature. The hydrolysis of methoxynaphthalene in supercritical water has the following sequence [Penninger and Kolmschate 1989]:

$$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

Assuming the first order reaction for the hydrolysis of methoxynaphthalene, the rate is obtained as:

Hydrolysis rate: r = k[E] (r in M/s; [E] = [methoxynaohthalene], in M)

$$\mathbf{k} = \mathbf{k}_0 \bullet [\mathbf{H}_3 \mathbf{O}^+] \bullet \rho_{\mathbf{W}} / [\mathbf{H}_2 \mathbf{O}]$$
(2-4)

$$[H_3O^+] = k_w^{0.5} / \gamma_{\pm} (\gamma_{\pm}, \text{ mean ionic activity coefficient of water})$$
(2-5)

$$k_{w} = [H_{3}O^{+}] \bullet [OH^{-}] \bullet \gamma_{+} \bullet \gamma_{-}$$
(2-6)

 $[H_3O^+] = [OH^-], \gamma_+ = \gamma_-, \gamma_{\pm}^2 = \gamma_+ \bullet \gamma_-$  ( $\gamma_+$  and  $\gamma_-$ , ionic activity coefficients of cation and anion).

By combining (2-1)~(2-6), the following equation is given:

$$\epsilon^{1.5} (\log k - \log k^*) = C^* (\mu)^{0.5}$$
(2-7)

where  $k^* = \log(k_0) + \log(\rho_w) + 0.5 \log(k_w) - \log([H_2O]); C^* = Z_i e^3 (2\pi N)^{0.5} / (\underline{k}T)^{1.5}$ 

(proportionality constant); k = constant of hydrolysis rate

Equation 2-7 can be used to predict the effect of ionic strength on the hydrolysis reaction rates of ether. It is clear that increasing ionic strength in supercritical water results in the increasing of hydrolysis rates as well (see Figure 2-8) [Penninger and Kolmschate 1989].



Figure 2-8 Correlation calculated from equation (2-7) [Penninger and Kolmschate 1989] Note: pw = density of supercritical water.

### 2.5.3 Pressure effects on kinetics

In SCWO systems, only either pressure or temperature is an independent variable. The other one must be a dependent function. The inconsistency of reactant indexes of reaction rates has been discovered in different researches without taking pressure effects into account [Webley 1989a, Brock 1996, Anitescu 1999, Helling 1987, Anitescu 1999] (see Table 2-5). Hence,  $H_2O$  is included as a reactant in order to counter the pressure effect by the researchers because the changes of water concentrations would reflect the change of pressure. However, the discrepancy could not be resolved as seen in Table 2-6.

| System                      | Rate equation                          | Pre-exponential                        | Activation energy          | Peference |
|-----------------------------|--|--|----------------------------|-----------|
| System                      | $k = A_0 \exp(-E_a/RT)$                | factor (A <sub>0</sub> )               | (E <sub>a</sub> ) (kJ/mol) | Reference |
| $CH_{2}OH + H_{2}O + O_{2}$ | $d[CH_3OH] = -k[CH_0H]$                | 10 <sup>26.2±5.8</sup> e <sup>-1</sup> |                            | Webley    |
|                             | dt dt                                  | 10 5                                   | 408.4                      | 1989a     |
| CHOH + HO + O               | d[CH <sub>3</sub> OH]                  | 1021 3+53 c <sup>-1</sup>              |                            | Brock     |
|                             | $\frac{dt}{dt} = -\kappa[CH_3OH]$      | 1021.3-33 5                            | 326 ± 83                   | 1996      |
| $CH_OH + H_O + H_O$         | d[CH <sub>3</sub> OH] MCH OHI          | 1011 8 c <sup>-1</sup>                 |                            | Anitescu  |
|                             | dt                                     | 1011.0.5                               | 177.6                      | 1999      |
| $CO + H_{2}O + O_{2}$       | $\frac{d[CO]}{d[CO]} = -k [CO]^{1.87}$ | 10 <sup>17.5</sup>                     |                            | Helling   |
|                             | $dt = k_2 [00]$                        | 10                                     | 237.8                      | 1987      |
| $CO+H_{2}O+H_{2}O_{2}$      | $\frac{d[CO]}{d[CO]} = -k[CO]$         | 1010.8 s <sup>-1</sup>                 | 171.4                      | Anitescu  |
|                             | dt dt                                  | 1010.0 5                               | 1/1.4                      | 1999      |

#### Table 2-5 Equations of reaction rates of methane and CO

#### Table 2-6 Global disappearance rate of phenol

|                | Global Disappearance Rate of Phenol  |  |  |  |  |
|----------------|--|--|--|--|--|
| Oshima, et al. | $((2.82\pm0.0017) \times 10^4) \times \exp((50.4\pm14.6)/\text{RT}) \text{ [phenol] } [O_2]^{0.48\pm0.15} \text{ [H}_2\text{O}]^{-0.45\pm0.18}$                                      |  |  |  |  |
| (1998)         | between 370-430°C  |  |  |  |  |
| Gopalan and    | $(218.78\pm1.90) \text{ x exp}((51.83\pm4.18)/\text{RT}))$ [phenol] <sup>0.85\pm0.04</sup> [O <sub>2</sub> ] <sup>0.5\pm0.05</sup> [H <sub>2</sub> O] <sup>0.42\pm0.05</sup> between |  |  |  |  |
| Savage (1995a) | 420-480°C  |  |  |  |  |
| Krajnc and     | $((4.903\pm0.064) \times 10^8) \times \exp((-124.776\pm93)/RT) \times ([H_2O] + [O_2] + [phenol])^{0.422\pm0.005} \times 10^{-10}$   |  |  |  |  |
| Levec (1996)   | $Y_{ph}^{1.041\pm0.002} \times Y_{O2}^{0.381\pm0.003}$ between 380-450°C   |  |  |  |  |

Note:  $Y_{ph}$  and  $Y_{O2}$  are mol fraction of phenol and oxygen; activation energy in kJ/mol

According to the transition state theory, a thermodynamic equilibrium is achieved between reactants and the transition state:

$$A + B \leftrightarrow A * B[\text{transition state}] \leftrightarrow \text{products}$$
 (2-8)

From the standard thermodynamic relationships, the pressure effect on the reaction rate constant can be written as [Hamann and Bradley 1963]:

$$RT\left(\frac{\partial \ln k}{\partial p}\right)_{T} = -\Delta v^{\#} - RT * k_{T}$$
(2-9)

where k is a bimolecular rate constant (M<sup>-1</sup>s<sup>-1</sup>) in equation (2-9),  $\Delta v^{\#} = \bar{v}_{A*B} - \bar{v}_{A} - \bar{v}_{B} =$ reaction activation volume,  $\bar{v}_{i}$  = partial volume,  $k_{T}$  = isothermal compressibility. The pressure effect is simply the difference in partial molar volume of the transition state and the two reactants minus a compressibility term. If integrating Eq. (2-9) from a standard pressure "p<sub>\u03c9</sub>" to a pressure "p", the modification of Arrhenius equation is proposed in supercritical water:

$$k = A * \exp(\frac{-E_a}{RT}) * \exp(\int_{p_a}^{p} (\frac{-\Delta v^{\#} - RT * k_T}{RT}) dp)$$
(2-10)

The amount of the transition state (A\*B) is negligible and it is short-lived. Hence, its formation and loss has a minor effect on the bulk volume:  $\left(\frac{\partial V}{\partial n_{A^*B}}\right)_n = \overline{v}_{A^*B} \approx 0$ . For example, an equilibrium system is stationary in the term of bulk volume where the reaction rate of reactants is equal to that of products. Thus, equation (2-10) can be simplified as:

$$k = A * \exp(\frac{-E_{a}}{RT}) * \exp(\int_{p_{4}}^{p} (\frac{\overline{\nu}_{A} + \overline{\nu}_{B} - RT * k_{T}}{RT}) dp)$$
(2-11)

The partial molar volumes of reactants A and B can be calculated using Peng-Robinson equation with proper mixing rules. The integration part of Equation (2-11) is considered in Chapter 5.

### **3 OBJECTIVES**

Currently, many of SCWO researches are focused on the classical kinetics and the testing of catalysts. This work intends to develop new knowledge of the physical and chemical behavior of various organic compounds in SCW oxidation processes, and explore the phase behavior of the SCW-O<sub>2</sub> system. Another objective is to theoretically resolve the existing disagreement in the SCW kinetics by considering pressure effects in the Arrhenius equation.

A number of basic equations of state (EOS) can be used to calculate the thermodynamic properties of a binary water- $O_2$  system. However, it is important to test their adaptability before application. This work will determine the parameters of the EOS necessary for calculations of the water- $O_2$  system. These parameters can be used to predict critical properties, and further calculate kinetic constants and thermodynamic properties of the system.

This research uses polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and de-inking sludge residue (DISR) containing heavy metals as experimental materials.

Following are the main objectives of this dissertation:

- Determine SCWO pathways of naphthalene (Nap) representing PAHs; decachlorobiphenyl representing PCBs, and de-inking sludge residue (DISR) representing industrial organic wastes.
- Understand the reactive role of water by tracking hydrogen atom and chloride during the SCWO of PCBs.
- Propose, for the first time, the reaction mechanism of naphthalene in SCWO.
- > Determine the destruction rates of PCBs and naphthalene in supercritical water.

- Investigate the SCWO of de-inking sludge residue as an alternative technology for its treatment.
- Verify the feasibility of SCWO as a practical treatment method for PCBs and deinking sludge residues, containing PAHs, heavy metals and ash.
- Explore the basic phase behavior (PVT parameters) of a supercritical water-oxygen system via performing fugacity calculations and determining its thermodynamic properties.
- Propose the equation for determining the reaction rate constant including pressure effect, derived from the equation of the transition state theory and the equation of state (EOS).

#### 4 METHODOLOGY

#### 4.1 Chemicals

Polycyclic aromatic hydrocarbons (PAHs) are usually formed during incomplete combustion of organic materials [Kozinski 1994] and during pharmaceutical production. Some PAHs, e.g. benzo(a)pyrene (BaP; C<sub>20</sub>H<sub>12</sub>), are considered carcinogenic. Therefore, even fractionally small amounts of PAH emissions may become substantial health hazards. Thus, their destruction is of practical importance. PAHs are often emitted into the atmosphere as condensed species adsorbed on fine solid particles [Kozinski 1994]. These particles also contain heavy metals released during combustion. Thus, the fine particulate acts as a carrier of both the PAHs and toxic metals. It can penetrate deep into the respiratory system, being harmful to human health. As PAH-particulate-metal aerosol is known to be mutagenic to bacterial and human cells [Rhofir and Hawari 2000], a research directed toward their formation and destruction during SCWO becomes of interest to public health and industries generating contaminated wastes. It is particularly meaningful when residual materials, e.g. de-inking sludge residue, containing aromatic hydrocarbons and heavy metals, are recycled. Naphthalene (Nap) was selected as a representative of the PAHs. Naphthalene, containing two fused benzene rings, was used in a form of transparent crystals (99% purity, 1.178g/cm<sup>3</sup> density, 80.1°C melting point, 217.9°C boiling point). Naphthalene is the simplest of PAHs. It may be converted to other PAHs via polymerization [Arey 1989]. The investigation of naphthalene reaction chemistry will provide a necessary database for in-depth study of mechanisms of PAH oxidation.

Polychlorinated biphenyls (PCBs) are formed due to substituting chlorine for hydrogen. There are 209 possible PCB compounds based on the number of chlorine atoms and their isomers. Polychlorinated biphenyls (PCBs) were widely used in civil life and industrial activities, e.g. pulp and paper, pesticide and herbicide products (PCBs had been prohibited since 1979) [ATSDR 1996]. About 200 million kg PCBs had been discharged to the global environment by different paths and found in every body of water in the United States [EPA 1996]. They are hydrophobic with a solubility of about 0.001 to 0.01 mg/kg in the ambient water. However, they are lipophilic, tending to absorb on organics [ATSDR 1996]. They can travel as an aerosol in the air and can stay airborne for 10 days [ATSDR 1996]. PCBs are regulated since they are fatal to both humans and animals [EPA 1996]. They biodegrade slowly. It is known that dioxins are formed during the transformation and oxidation of PCBs during their natural degradation and combustion [Schecter 1991]. A waste stream may contain PCBs over 200ppm, and the bio-treatment has been proved ineffective [Shaw et al. 1991, R.O.C. EPA 1996, Suntio et



al. 1988, Lin et al. 1998]. Therefore, the oxidation of PCBs in supercritical water is of practical interest. Decachlorobiphenyl (10-CB, C<sub>12</sub>Cl<sub>10</sub>) was selected as

**Figure 4-1 Molecular** a representative of PCBs. In the 10-CB molecule, 10 chlorides replace 10 hydrogen atoms of biphenyl (as seen Fig.4-1). It is the most "*difficult*" PCB to be destroyed. The SCWO of 10-CB will reflect the behavior of both an inorganic element "Cl" and hydrocarbon-based compounds. Usually, organics contain heterogeneous elements of "N", "S" and "Cl" etc. Therefore, it is essential to understand the role of chlorides during the SCWO of organics (Cl is the most reactive of these heteroatoms).

Industrial de-inking sludge residue (DISR) is generated by pulp & paper industry. Significant amounts of this residue are produced (about 70 million dry tons per year in North America) [Blaney et al. 1995]. It is anticipated that increased paper recycling will stimulate increase in the production of this waste and enlarge heavy hydrocarbon portion of its chemical composition [Fang and Kozinski 2000a]. The solid portion of the sludge is cellulose-based and contains ink, pigments and clay fillers, as well as enough combustibles to be considered as a low-grade fuel.



DISR is a mixture of individual fragments composed of fine fibers (2-50  $\mu$ m in width and 300-500  $\mu$ m in length as seen in Fig.4-2) [Fang, Xu and Kozinski 2000]. The fibers are intertwined with each other and randomly distributed with no preferential alignment. Fine fibers (<20  $\mu$ m) make up the bulk of the cellulosic matrix, while large fibers

Figure 4-2 Morphology of DISR [Fang, Xu and Kozinski 2000]

(>30  $\mu$ m) are trapped inside the matrix. The matrix appears rather dense and non-uniform in comparison with the individual fibers. An ash elemental analysis shows the dominance of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO (about 56%, 29% and 4%, respectively), with high levels of alkalis (Na<sub>2</sub>O+K<sub>2</sub>O > 2%) (see Table 4-1). The sludge is usually contaminated by heavy metals and polycyclic aromatic hydrocarbons (PAHs), which can be formed from other hydrocarbons at ambient conditions (e.g. naphthalene concentrations may reach 3.7 wt% while Pb amount may reach 4.5 wt% in de-inking sludge). The properties of the DISR used in this work are listed in Table 4-1.

Combustion is usually used to treat de-inking sludge residue, and recover energy from it. However, secondary emissions, such as PAHs, NO<sub>x</sub> and particulates, are formed during combustion. Thus, the SCWO of de-inking sludge residue is investigated as an alternative technology for its treatment.

| Ultimate Analyses of Sludge (Wt%)  |  |   |                                    |  |
|--|--|---|------------------------------------|--|
| Carbon   | 40.10  | Moisture  | 10.00                              |  |
| Hydrogen   | 2.11   | Nitrogen  | 0.60                               |  |
| Sulfur   | <0.10  | Oxygen  | 26.72                              |  |
|  |  |   |                                    |  |
| Ash<br>Ash Element   | 20.37<br>tal Analyses (wt%                                   | , based on ash of bu  | ırnt sludge)                       |  |
| Ash<br>Ash Element   | 20.37<br>tal Analyses (wt%<br>56.47                          | , based on ash of bu<br>Na2O  | irnt sludge)<br>1.4                |  |
| Ash<br>Ash Element<br>SiO <sub>2</sub><br>Al <sub>2</sub> O <sub>3</sub>               | 20.37<br>tal Analyses (wt%<br>56.47<br>29.43                 | , based on ash of bu<br>Na <sub>2</sub> O<br>K <sub>2</sub> O   | 1.4<br>0.61                        |  |
| Ash<br>Ash Element<br>SiO <sub>2</sub><br>Al <sub>2</sub> O <sub>3</sub><br>CaO        | 20.37<br>tal Analyses (wt%<br>56.47<br>29.43<br>4.49         | , based on ash of bu<br>Na <sub>2</sub> O<br>K <sub>2</sub> O<br>Fe <sub>2</sub> O <sub>3</sub>                                   | 1.4<br>0.61<br>0.96                |  |
| Ash<br>Ash Element<br>SiO <sub>2</sub><br>Al <sub>2</sub> O <sub>3</sub><br>CaO<br>TiO | 20.37<br>tal Analyses (wt%<br>56.47<br>29.43<br>4.49<br>3.11 | b, based on ash of bu<br>Na <sub>2</sub> O<br>K <sub>2</sub> O<br>Fe <sub>2</sub> O <sub>3</sub><br>P <sub>2</sub> O <sub>3</sub> | 1.4<br>1.4<br>0.61<br>0.96<br>0.14 |  |

| <b>Table 4–1 Physicochemica</b> | l properties | of sludge waste | [Fang, 2 | Xu and Kozinsk | i 2000c]. |
|---------------------------------|--------------|-----------------|----------|----------------|-----------|
|---------------------------------|--------------|-----------------|----------|----------------|-----------|

Selected Metals Identified (mg/kg, based on sludge)

| Si | 49,000 | Ca | 6,200 |
|----|--------|----|-------|
| Al | 29,500 | Na | 2,000 |

In order to achieve high concentrations of oxygen in the experimental systems, 49wt% H<sub>2</sub>O<sub>2</sub> (from Fisher) was used as a source of oxygen. Pb(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O, and Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O (all 99%purity, Fisher) were selected to represent heavy metals present in ash. Naphthalene and pure PCBs were purchased from Sigma-Aldrich Chemical Company. De-inking sludge residue was obtained from Bowater Canada in Gatineau, Quebec. Chemicals listed below, which were used as standards for various analysis, were obtained from Sigma-Aldrich Chemical Company:

Acids: formic acid, acetic acid, salicylic acid, phthalic acid, benzoic acid, citric acid, oxalic acid, 2-acetylbenzoic acid.

Other organics: coumarin, fluorenone, phthalic anhydride, dibenzofuran, salicylaldehyde, phthlide, chromone, 1-naphthol, 2-naphthol, benzene, and acetone Other inorganic compounds:  $Al_2Si_2O_3(OH)_4$  (kaolin), ,  $K_2CrO_4$ , amorphous aluminum synthetic (AAS)  $(SiO_2)_{1.37}(Al_2O_3)_{0.093}(Na_2O)_{0.127} = 82wt\% SiO_2 +$ 9.5wt%  $Al_2O_3 + 8wt\% Na_2O$ ).

#### 4.2 Instrumentation

A diamond anvil cell (DAC) system (Figure 4-3) and a batch reactor (Figure 4-4) were used to study SCWO processes.

Visual observations were conducted in DAC [Bassett 1993 and 1996, Xu 2001a] (see Fig. 4-3). It is designed to carry out tests in fluids at pressure up to 2.5 GPa and temperature up to 1200°C. The DAC was heated by two micro-heaters, which transferred heat to the diamond anvils. Temperature was measured by two K-type micro-thermocouples and was recorded by a computer through a data shuttle (Strawberry Tree, Model DS-12-8-TC, Sunnyvale, California). Pressure is produced by two opposing diamond anvils inside the 50 nL chamber hole (ID 508 µm, thickness 250 µm) made of inconel gasket. Pressure was determined from the equation of state of water [Saul 1989] based on an isochore (described later) [Bassett 1993]. The sample was heated and observed at 110x magnification by a microscope (Olympus SZ11). A mixture of argon + 1%H<sub>2</sub> flows around the diamond to prevent oxidation damage. The images were recorded by a Panasonic 3CCD camera (AW-E300). 2-D apparent concentrations of naphthalene from the images were calculated with digital image analysis (Scion Image, Frederick, MD, USA).

K-type thermocouples were attached each of the diamond anvils by ceramic cement (sealing ceramic paste) and temperature was recorded every 0.1s. The thermocouples were calibrated by loading powder from samples contained in a gasket of reference metals tin ( $T_m = 232.00^{\circ}$ C) and zinc ( $T_m = 419.58^{\circ}$ C), and observing their melting points at a slow heating rate (<2°C/min) [Fang et al. 1999]. The accuracy of temperature reading from thermocouples was estimated to be ±1.0°C up to 600°C. The temperature difference between two anvils was generally lower than 10°C. Thus, the reported temperatures were the average of the both anvils.

The pressures are estimated using the equations of water [Bassett 1993], correlated to the recorded temperature profiles and phase changes. When a sample and water are loaded, an air bubble is introduced to determine a temperature of homogeneity ( $T_h$ ). Heating the DAC causes the liquid to expand and the air bubble to shrink until it disappears, at which point the chamber is filled with the homogeneous fluid at the temperature of homogeneity ( $T_h$ ) and the density of the fluid can be calculated ( $1/v_h$ ) [Bassett 1993]. The pressure at this point is the vapor pressure along the two-phase L-V curve at  $T_h$ . If heated further, the pressure will increase according to the P\_T path of ioscore( $v = v_h$ ). Thus, the pressure can be calculated knowing T and  $v_h$ . In the case of H<sub>2</sub>O<sub>2</sub> being present,  $v_h$  was estimated without considering an air bubble. Pressure was calculated only by considering water contribution after H<sub>2</sub>O<sub>2</sub> had decomposed. The calculated values are lower than actual pressures. Thus, the estimated pressures in H<sub>2</sub>O<sub>2</sub> systems were considered as only references during the DAC experiments.

Recorded images were changed to 24-bit RGB bitmap files *via* a video capture board, and analyzed with digital imaging software (scion image, Scion Corporation, MD,

USA) to calculate the apparent concentration of the sample [Fang and Kozinski 2002a]. The areas of the sample and the chamber were determined by counting the number of pixels of the corresponding defined zone. The apparent area concentration was obtained from the sample/chamber area ratio by normalizing to water area in the chamber at room temperature with the density of water at  $T_h$  (the homogeneous temperature of gas-water in DAC) [Bassett 1993 and 1996]. The mass concentration can be calculated by the apparent area concentration along with the known organics and water densities. In order to avoid area changes caused by the organic melting and orientation during heating, the solubility was defined as the difference between the apparent concentration at the very beginning of the dissolution process and the concentration when the organic dissolution was completed divided by the initial concentration. Since the image analysis is two-dimensional, the calculated results are semi-quantitative. However, the depth of the reaction chamber (250  $\mu$ m) corresponded to the sample's thickness, thus allowing for minimizing inaccuracies associated with the 3D structure of the organics.

After reaction, the residues were analyzed by an FT-IR microscopy (UMA 500, Bio-Rad, Cambridge, MA). The advantages of the DAC are (i) clear visualization of samples; (ii) access to *in-situ* spectroscopic monitoring of reactions; (iii) high heating and cooling rates ( $\pm 20^{\circ}$ C/s) due to the small volume; and (iv) using relatively inert materials in contact with samples (diamonds, ruby, and inconel).







Figure 4-4 A batch reactor with accessories

A tubular batch reactor (TBR, volume 6 ml, length 105mm, OD 12.7mm, ID 8.5mm) is made of inconel stainless steel (see Figure 4-2). It is connected to a Data Acquisition System (DAS, consisting of a pressure transducer with a J-type thermocouple (Dynisco E242, Sharon, MA, USA)) and a flue gas outlet. A Fluidized Sand Bath (FSB, Omega FSB-3, <1.0°C difference in the sand) was used to heat and maintain reaction temperatures by submerging the reactor into the hot sand bath. When the temperature inside the reactor increased, the pressure was built up because of evaporation, both of the

temperature and pressure were monitored *via* the DAS. Reactions were stopped by quenching the reactor in cold water. A volumetric syringe (1000 ml) connected through the flue gas outlet was used to collect gaseous samples. Residual ash was filtered while liquids were washed into organic solvents and deionised water. Sampling ports and quenching reactors allow for the collection of samples at various stages of SCW oxidation processes.

Quenching the reactors in 10 liter cold water at 20°C took 2  $\sim$ 3 seconds to lower the reactor temperature to below 100°C. Therefore, it minimized the errors of residence time (<3 s). The pressure and thermocouple sensors were in contact with the fluids during reactions. Thus, the errors of T and P mostly resulted from the instrumental accuracy and sensitivity, a 0.25% error for Dynisco-transducer pressure and a 0.2% error for J-type thermocouple. Loss of samples during collection resulted in errors in the material balance (details are discussed in section 4-3).

The main analytical instruments in the thesis are following:

- Model DC-80 Total Organic Carbon Analyzer and Model 183 TOC sampler (TOC, Folio Instruments, Inc., Rosemount, Dohrmann): analysis of TOC in aqueous samples.
- Dionex 100 Ion Chromatograph (IC, Dionex Corp., Sunnyvale, CA. USA): identification and quantification of organic acids and anions.
- PE40 Inductively Coupled Plasma emission spectrometer (ICP, Perkin-Elmer, UT): quantification of heavy metals.
- Hewlett Packard 4890 Gas Chromatography with Thermal Conductivity Detector (GC/TCD, Hewlett Packard Canada): analysis of gases.

- Hewlett Packard 4890 Gas Chromatograph with Flame Ion Detector (GC-FID, Hewlett Packard Canada): quantification of intermediates in organic phases, naphthalene and PCBs.
- Gas Chromatograph plus Quadrupole Ion Trap (GCQ-plus/Polaris: equal to GC-MS, Thermo Quest/Finnigan, USA): identification and quantification of intermediates.
- JEOL 840A Scanning Electron Microscope with Electron Derived X-rays (SEM-EDX, JEOL LTD., Japan): chemical analysis and observation of ash morphology.
- DMAX-III Rigaku rotating anode diffractometer (X-rays Diffractometer: XRD, Rigaku, Japan): identifications of ash structures.
- UMA 500 Infrared Microscope (IRM, Bio-RAD, Cambridge MA)): identification of organic structures within DAC.

#### 4.3 Experimental Procedures

#### Conducting experiments in the diamond anvil cell (DAC)

The samples are fed into the diamond anvil cell (DAC) as seen in Figure 4-3. After the upper part of the DAC is assembled, the thermocouples and heating wires are connected. Once the temperature of the DAC is increased at predetermined rates (5°C/min to homogeneous  $T_h$  [Bassett 1993 and 1996], 1~2°C/min to 300°C and 10°C/min to higher temperature in order to avoid the oxidation of diamond and gasket), incident white light traverses the cell and the images of phase evolution are recorded through the highresolution 3CCD camera. The reflecting-mode FTIR monitors the reactions in the cell. Ar+1%H<sub>2</sub> flows continuously to prevent the DAC from being oxidized. The other information of experimental conditions is summarized in Section 6.1.



Figure 4-5 Sample loading in DAC



Figure 4-6 Sample flow in the batch reactor

# **Batch** experiments

A set of experiments with different  $H_2O_2$  concentrations and molar volume has been carried out from room temperature to 400°C in the batch reactor (Table 4-2). P, V and T data of water- $O_2$  systems are used to determine the interaction parameter in the mixing rule used for Peng-Robinson equation discussed in Chapter 5. Mole percent of naphthalene, 10-CB and cellulose is less than 0.6mol% in all systems. Therefore, pressures in the reactor are estimated using water- $O_2$  systems. The errors of the calculated pressures are less than 8% for water- $O_2$  systems (see Chapter 5).

|   | H <sub>2</sub> O <sub>2</sub> | H          | O <sub>2</sub>      |                     |
|---|-------------------------------|------------|---------------------|---------------------|
| Mol volume of water- $O_2$<br>(m <sup>3</sup> /mol) | Weight (g)                    | Weight (g) | Mol fraction<br>(%) | Mol fraction<br>(%) |
| 3.32 x 10 <sup>-4</sup>                             | 0.175                         | 0.182      | 85.54               | 14.46               |
| 8.95 x 10 <sup>-5</sup>                             | 0.175                         | 1.054      | 96.10               | 3.90                |
| $1.99 \times 10^{-4}$                               | 0.292                         | 0.304      | 85.54               | 14.46               |
| 8.73 x 10 <sup>-5</sup>                             | 0.292                         | 0.992      | 93.67               | 6.33                |
| $1.33 \times 10^{-4}$                               | 0.438                         | 0.456      | 85.54               | 14.46               |
| 8.46 x 10 <sup>-5</sup>                             | 0.438                         | 0.915      | 90.81               | 9.19                |
| 9.96 x 10 <sup>-5</sup>                             | 0.584                         | 0.608      | 85.54               | 14.46               |
| 8.21 x 10 <sup>-5</sup>                             | 0.584                         | 0.837      | 89.11               | 11.89               |
| 7.97 x 10 <sup>-5</sup>                             | 0.730                         | 0.758      | 85.54               | 14.46               |

Table 4-2 Experimental matrix for determining PVT of water-O2 systems

# General procedure

The experimental procedure using the batch reactor started from feeding the materials (e.g. naphthalene, decachlorobiphenyl, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, and inorganic additives) into the reactor, heating the fluidized sand bath temperature reserve (FSB, Omega FSB-3) to a pre-determined temperature and maintaining this temperature ( $\geq$ 400°C). The reactor was subsequently immersed in the Fluidized Sand Bath in order to build up the temperature and pressure inside the reactor. After the reaction was completed, the reactor was quenched at 160 °C/s in cold water, and the top of the reactor was connected to a 1000 ml

syringe for the collection and volume measurements of the gas phase. In order to obtain an adequate material for further analysis, both liquid and solid samples were collected into a 10ml-water and a 10ml-benzene solution. The mixture of 10ml water and 10ml benzene was left to separate in the refrigerator (temperature  $2\sim8^{\circ}$ C, 48 hours). Benzene on the top of the mixture was removed to new glass bottles by a pipette. Hydrophobic organics were extracted from water through C<sub>6</sub>H<sub>6</sub>.

The total volume of the gas sample was a sum of volume of gas syringe and the reactor. There was about 5% difference between the actual volume and the ideal gas volume. It was confirmed that 99.9% of naphthalene could be recovered by first washing the reactor with benzene solvent, and next washing it with deionised water. The mass balance during the batch processes achieved  $85\% \sim 99\%$  in weight.

The experiments of the DISR were different and described after Table 4-6. The entire design of the experimental program carried out in this dissertation is summarized in Table  $4-3 \sim$  Table 4-6.

|                                  | Diamond Anvil<br>Cell                             | Batch Reactor  |
|----------------------------------|---|--|
| Naphthalene (Nap)                | Dissolution in pure<br>SCW                        | Hydrolysis in pure SCW   |
|                                  | Oxidation<br>(Nap+H <sub>2</sub> O <sub>2</sub> ) | Oxidation:<br>Nap+H <sub>2</sub> O <sub>2</sub> +H <sub>2</sub> O: System A<br>Nap+H <sub>2</sub> O <sub>2</sub> +H <sub>2</sub> O+Cr(NO <sub>3</sub> ) <sub>3</sub> +Kaolin: System B<br>Nap+H <sub>2</sub> O+K <sub>2</sub> CrO <sub>4</sub> +(SiO <sub>2</sub> ) <sub>1.37</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>0.093</sub> (Na <sub>2</sub> O) <sub>0.127</sub> : System C |
| Decachlorobiphenyl<br>(10-CB)    |   | Oxidation:<br>$10-CB+H_2O_2$<br>$10-CB+H_2O_2+Na_2CO_3$  |
| De-ink Sludge<br>Residues (DISR) |   | Oxidation with Pb, Cr, Cd  |
| Heavy metals                     |   | Oxidation:<br>Heavy metals + DISR<br>$Cr(NO_3)$ +Nap+H <sub>2</sub> O <sub>2</sub> +Kaolin<br>Nap+H <sub>2</sub> O <sub>2</sub> +Kaolin  |

 Table 4-3 Experimental matrix for supercritical water tests

|         |                         | Naphthalene<br>(C <sub>10</sub> H <sub>8</sub> , Nap) | $H_2O_2$ and $H_2O$                       | Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> (kaolin)<br>(SiO <sub>2</sub> ) <sub>1.37</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>0.093</sub> (Na <sub>2</sub> O) <sub>0.127</sub><br>(amorphous aluminum<br>synthetic: AAS) | $Cr(NO_3)_3 \bullet 9H_2O / K_2CrO_4 (Cr^{3^+}/Cr^{6^+})$ |
|---------|-------------------------|---|---|--|---|
| DAC     | Dissolution             | 43~44wt%  | Pure H <sub>2</sub> O                     |  |   |
| DAC     | Oxidation               | 17~27wt%  | 10~49 wt% H <sub>2</sub> O <sub>2</sub>   |  |   |
|         | Hydrolysis <sup>b</sup> | 50 mg   | 1000 g pure H <sub>2</sub> O              |  |   |
|         | Oxidation               |   |   |  |   |
| Batch   | System A                | 50 mg   | 1.0ml 49wt% H <sub>2</sub> O <sub>2</sub> |  |   |
| Reactor | System B                | 50mg  | 1.0ml 49wt% H <sub>2</sub> O <sub>2</sub> | 100mg kaolin   | 20mg Cr(NO <sub>3</sub> ) <sub>3</sub> •9H <sub>2</sub> O |
|         | System C                | 50mg  | 1.0ml H <sub>2</sub> O                    | 50mg AAS   | 10mg K <sub>2</sub> CrO <sub>4</sub>                      |

### Table 4-4 Naphthalene experiments <sup>a</sup>

Note: <sup>a</sup> the reactor was quenched in 10-liter-25°C cold water at 15s, 25s, 45s, 60s, 75s, 90s, 120, 150s, 180s, 300s, and 1800s while the temperature of the sand bath is maintained at 400°C. Density of 49wt%  $H_2O_2 = 1.19226g/cm^3$ . <sup>b</sup> the reactor was purged using an argon gas for the hydrolysis experiments of naphthalene.

#### Table 4-5 Decachlorobiphenyl (10-CB) experiments

|         |           | 10-CB | H <sub>2</sub> O <sub>2</sub>                                     | Na <sub>2</sub> CO <sub>3</sub> |
|---------|-----------|-------|---|---------------------------------|
| Batch   | Oxidation | 10mg  | 1.0 ml 0.83, 2.5, 3.33,<br>4.16 wt% H <sub>2</sub> O <sub>2</sub> |                                 |
| Keactor |           | 10mg  | 1.0 ml 0.83, 2.5, 3.33,<br>4.16 wt% H <sub>2</sub> O <sub>2</sub> | 10.6mg                          |

Note:  $T = 450^{\circ}C$ , time: 10mins, 20mins. Density for  $0wt\% \sim 5wt\% H_2O_2$  is  $0.997 \sim 1.0145 \text{g/cm}^3$ . The density of  $H_2O_2$  was obtained using interpolation.

| Table 4-6 Experiments for | determining in | nteraction of | metals and | inorganics |
|---------------------------|----------------|---------------|------------|------------|
|---------------------------|----------------|---------------|------------|------------|

| ID   | T(°C)      | Doped metals |          |          | Orconica           | Others                |  |
|--|------------|--------------|----------|----------|--------------------|-----------------------|--|
| IJ   | I(C)       | Cd           | Pb       | Cr       | Organics           | Outro                 |  |
| <sup>a</sup> DISR doped<br>with $Cd^{2+}$ , $Pb^{2+}$ ,<br>$Cr^{3+}$ | 525<br>450 | 2030 ppm     | 2080 ppm | 2080 ppm | 75~100mg Cellulose | Inorganic<br>residue  |  |
| *DISR  | 525<br>450 |              |          |          | 75~100mg Cellulose | Inorganic<br>residue  |  |
| <sup>a</sup> DISR with Cr <sup>3+</sup>                              | 525<br>450 |              |          | 2000 ppm | 75~100mg Cellulose | Inorganic<br>residue  |  |
| <sup>a</sup> DISR with Pb <sup>2+</sup>                              | 525<br>450 |              | 2000 ppm |          | 75~100mg Cellulose | Inorganic<br>residue  |  |
| <sup>a</sup> DISR with<br>Cd <sup>2+</sup>                           | 525<br>450 | 2000 ppm     |          |          | 75~100mg Cellulose | Inorganic<br>residue  |  |
| <sup>b</sup> Nap with Cr <sup>6+</sup>                               | 400        |              |          | 2075 ppm | 50mg Naphthalene   | 50mg<br>Amorphous ash |  |
| <sup>b</sup> Nap with Cr <sup>3+</sup>                               | 400        |              |          | 1940 ppm | 50mg Naphthalene   | 100mg Kaolin          |  |
| Nap  | 400        |              |          |          | 50mg Naphthalene   | 100mg Kaolin          |  |
| <sup>b</sup> Nap with Cr <sup>3+</sup>                               | 400        |              |          | 2148 ppm | 50mg Naphthalene   |                       |  |

Note: Heavy metals in the DISR: 97 ppm Cr, 343 ppm Cd and 493 ppm Pb.<sup>a</sup> the doped concentrations of metals in the DISR; <sup>b</sup> the concentrations of metals in total materials in the batch reactor.

Experimental time was up to 1800s for all experiments, and reactions were stopped between 0s and 1800s, depending on data required.

## Experimental details for Table 4-6

The DISR was doped and well mixed with lead, cadmium, and chromium. Aqueous solutions of metal nitrates such as Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O, and Pb(NO<sub>3</sub>)<sub>2</sub> were used. A sample from 70 to 150 mg of the dried DISR and 0.7 to 1.5 ml aqueous solutions containing Pb, Cd and Cr nitrates were loaded to the reactor. The reactor was then sealed and held at room temperature for 12 hours to saturate the DISR. It was then opened and dried at 100°C for 24 hours. After that, an oxidant from 0.7 to 1 ml 49 wt% H<sub>2</sub>O<sub>2</sub> was loaded. Both the added metals (Cd, Cr, Pb) and metals naturally present in the sample (Si, Al, K, Na) were randomly dispersed inside the feed material prior to combustion [Kozinski and Zheng 1998]. In addition, no influence of the DISR pre-drying and re-hydration on combustion profiles was observed [Zheng and Kozinski 2000]. The reactor was submerged into the fluidized sand bath, where the temperature can be controlled up to 600°C within 1°C. The uniformity of sand temperature was within 0.5°C. The sample was heated at a rate of 3.5 °C/s. After the reaction was completed, the reactor was removed from the bath, quenched in water and placed into a -18°C refrigerator to freeze the liquid products. The reactor was subsequently opened slowly to collect the exhaust gas and sealed again until it reached room temperature. The mixture of products, after collecting gaseous samples, was separated into three phases: (1) by washing with deionised water through a 1-µm-pore-size filter, a 25 ml aqueous phase was obtained; (2) the remainder was washed with 99.6% acetone (Certified, A.C.S., Fisher), and a 10 ml acetone phase was obtained; and (3) the insoluble fraction on the filter paper was dried at 100°C for 24 hr, and an ash phase was obtained.

The sampling of the SCWO of the DISR is more complicated than that of pure compounds. Additional techniques were used in the preparation of sludge samples. The gaseous sample was analyzed using GC-TCD (HP 4890). The 25 ml aqueous phase and the 10 ml acetone phase were filtered again through a 0.2µm GS or GTTP membrane filter and metals were analyzed by an Inductively Coupled Plasma spectrometer (PE40, Perkin-Elmer, UT). TOC (Total Organic Carbon) levels were analyzed by Total Organic Carbon Analyzer (Model DC80). The levels of acetate, chloride, sulfate, chromate and nitrate were determined by Ion Chromatograph (Dionex 100). The acetone phase samples were injected GC-MS to detect the formation of PAHs and other organic phases. The acetone phase samples were diluted 10 times with de-ionized water before the ICP analyses were conducted.

The metal distributions of the ash phase were analyzed by Scan Electron Microscopy with Electron Derived X-rays (Model JEOL 840A). The chemical structure was determined by an X-ray diffractometer (DMAX-III, Rigaku rotating anode diffractometer). The ash was also tested for its leachability applying a method similar to the Toxic Characteristic Leaching Procedure (TCLP) [LEP 1998, Later 1997]. In the test, a 0.5 M acetic solution was added to the ash samples at solid to liquid ratio of 1:10 and mixed for 24 hours. The mixture was then diluted and filtered using the similar procedure as before. Concentrations of Cr, Cd, and Pb were analyzed by the ICP.

Naphthalene is one of PAHs in the DISR. It was also burnt with heavy metals and simulated ash and without the DISR. Aqueous phases and solid ashes were collected and analyzed by the same procedures as in the analysis of the DISR samples.

# The analysis of gases and intermediates in organic phases

After the gaseous samples were collected from the batch reactor, the gases were analyzed, identified and quantified by Hewlett Packard 4890 Gas Chromatograph coupled with Thermal conductivity Detector (GC-TCD). A standard gas mixture was used to set up the calibration curves. The mixture consisted of 2.80 vol.% oxygen, 10.53vol.% nitrogen, 6.67 vol.% methane and 6.67 vol.% CO<sub>2</sub> with an internal standard of 6.67 vol.% N<sub>2</sub>O and 66.66 vol.% helium of a carrier gas. A Hyesop DB 100/120 stainless steel packed column with 76.2cm (L) x 0.3175cm (OD) x 0.2159cm (ID) was used for the analysis of gaseous phases. The column was initially heated up to 50°C and held at this temperature for 300s. It was subsequently heated to 120°C at 10°C/min. heating rate and held for 300s. The injected volume of gas samples was 100µl. Helium was used as a carrier gas. The temperatures were optimized to be low enough to retain gases in order to separate their peaks, and high enough to fast flow all gases out the column. The peaks of different gases were clearly separated and all gases flowed out in 15 min. using the above method. No errors resulted from overlapping of peaks. About 5% error resulted from the instrumental sensitivity and repeatability. Total errors of gas yields are in the range of 10% (after considering the sampling loss). CO<sub>2</sub> yield was calculated as:

$$CO_2$$
 yield =  $\frac{\text{moles of } C \text{ in } CO_2}{\text{moles of } C \text{ in feed material}} \times 100\%$ 

Naphthalene conversion was determined from the GC data. After the extraction, the analysis of the aqueous samples by GC-FID (HP 4890) showed that no naphthalene was detected in the aqueous phase. Analytical results confirmed that the extraction could completely remove naphthalene from the aqueous phase to the benzene phase. Four standard benzene solutions were prepared for the measurements of naphthalene in the

products: (1) 0.5 wt.% naphthalene (Nap) + 1 wt.% Tetradecane (TD); (2) 0.5 wt.% Nap + 2 wt.% TD; (3) 2 wt.% Nap + 1 wt.% TD; (4) 5 wt.% Nap + 1 wt.% TD. The linear correlating factor was above 99%. The GC was programmed to be preheated to 80°C for 120 s, heated to 240°C at 20°C/min. heating rate, and held at 240°C for 600s. The preheating was used to remove impurities from the column. The injection temperature and the temperature of the Flame Ion Detector (FID) were maintained at 275°C to clean the reception cell and ignite the organics, respectively. A 0.3µl injection volume was used to avoid the saturation of the Flame Ion Detector. A Tenax TA 60/80 packed column (porous polymer based on 2,6-dipheny-p-phenylene oxide) with size of 15.24cm (L) x 0.3175cm (OD) was used for organic solution analysis. Helium was the carrier gas. This program was used to obtain naphthalene (Nap) data only. The naphthalene conversion was determined as:

Nap conversion =  $\frac{\text{(total moles of Nap)} - \text{(moles of unreacted Nap)}}{\text{(total moles of Nap)}} \times 100\%$ 

A Gas Chromatography plus Quadrupole Ion Trap (GCQ-plus/Polaris, equal to GC-MS) (Thermo Quest/Finnigan) was applied for identification/quantification of compounds present in the benzene phase during the SCWO of naphthalene. Standard intermediates of 500ppm concentration were used to set up one level calibration. A 1.0µl benzene solution (to avoid the saturation of the mass detector) was injected, benzene solution evaporated into column with splitless mode, helium flowed at a 1.0ml/min rate as the carrier gas in the DB5 capillary column, while a mass spectrum detector received mass fragments to quantify and identify the compounds. The GCQ program started at 40°C initial temperature, 1 minute initial time, reached 250°C final temperature at a 20.0°C/min temperature rate, maintained 250°C for 5 min.; the temperature 250°C was

sustained in the ion source while 275°C was retained at the transfer line between the column and the mass detector. GCQ was cleaned at 250°C for 300s after the completion of one injection. The yields of intermediates are defined as:

Intermediate yields of naphthalene SCWO =  $\frac{\text{moles of } C \text{ in intermediates}}{\text{moles of } C \text{ in naphthalene}} \times 100\%$ 

The concentrations of 10-CB and the identification of intermediates in 10-CB supercritical water oxidation were analyzed using the same methods as the analysis of naphthalene intermediates. The 10-CB conversion is calculated as:

 $10-CB \text{ conversion} = \frac{(\text{total moles of } 10-CB) - (\text{moles of unreacted } 10-CB)}{\text{total moles of } 10-CB} \times 100\%$ 

Errors for GC-FID and GCQ analysis resulted from the quantitative errors of sample injection and instrumental instability. The combined relative error from both sources for naphthalene analysis was about 1% for high concentration (>1000ppm), 5% for low concentration (<100ppm), 1~5% between 100-1000ppm. The relative error using the GCQ for 10-CB and intermediates analysis was about 5%.

#### The analysis of aqueous phases

A Ultra-Violet Rays Analyzer (Varian, Inc., Cary 1 UV spectrophotometer) was used to qualitatively verify species in the aqueous phases at 25°C. A 1.0 ml of aqueous phases was injected into Dionex 100 Ion Chromatograph (IC, Dionex Corp., Sunnyvale, CA, USA) with an electric conductivity detector for further identification and quantification. In the IC analysis, an eluent (working as a carrier) was a mixture of 0.3mM NaCO<sub>3</sub> and 0.29 mM NaHCO<sub>3</sub> with a flow rate of 1.5 ml/min; the experimental conditions were 25°C and one atmospheric pressure, two levels of calibration were used for the quantification. The standards are listed in Table 4-7. Samples were diluted if the concentrations in the samples were larger than the standards. A 1.0ml injection volume has minimized the errors of injection quantity to 0.1%. The relative error of IC analysis was 5%, which mainly resulted form instrumental sensitivity and repeatability.

Table 4-7 Standard concentrations of solvable anions

|                | Acetic ion | Formic ion | Nitrate | Chloride |
|----------------|------------|------------|---------|----------|
| Level I (ppm)  | 20         | 10         | 20      | 20       |
| Level II (ppm) | 50         | 20         | 50      | 30       |

Note: Acetic ion, formic ion, nitrate and chloride are in the form of acetic acid, formic acid, sodium nitrate and hydrogen chloride (or NaCl), respectively. Sulphate in the form of sodium sulphate with standard concentrations: 20 and 50 ppm.

During the combustion of sludge, TOC (total organic carbon) was determined using Total Organic Carbon analyzer (Model: DC-80 Total Organic Carbon analyzer and Model 183 TOC sampler, Folio Instruments, Inc., Rosemount, Dohrmann). A 200 $\mu$ m sample was injected into the reception cell. Pressurized oxygen (>0.1MPa) was used to carry the sample into the oxidation chamber, where the sample was oxidized using UV-K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> technique. The working conditions of TOC were room temperature and one atmosphere. The relative error for TOC analysis was about 1%, which contained 0.9% instrumental errors and 0.1% injection volume errors.

A PE40 (ICP, Perkin-Elmer, UT) Inductively Coupled Plasma spectrometer was used to analyze metals in aqueous samples. Two levels of calibration were used, and the correlation coefficients were usually above 99.8%. Each measurement was an average of data from three-times detection by the UV detector. Each sample was analyzed twice (results were reported as average). After analyzing 3-4 samples, the ICP stability was verified using various standard solutions. During ICP calibration, three standard solutions with different concentrations (including a blank: de-ionized water) were used to obtain calibration characteristics (lines). The standard concentrations of elements are shown in Table 4-8. The relative errors of ICP analysis were in the range between 1% (>50ppm) and 5% (<5ppm).

|                | Cd  | Cr  | Pb  | Na | Al | Si | Fe |
|----------------|-----|-----|-----|----|----|----|----|
| Level I (ppm)  | 50  | 50  | 50  | 5  | 5  | 5  | 5  |
| Level II (ppm) | 100 | 100 | 100 | 10 | 10 | 10 | 10 |

Table 4-8 Standard concentrations of elements for ICP measurement

# The analysis of solid phase

The chemical structure of the ash was determined *via* XRD spectra (DMAX-III Xrays rotating anode diffractometer, Rigaku, Japan). A 100mg ash was placed in the target cell of X-ray diffractometer.  $K_{\alpha}$  X-rays (wavelength  $\lambda = 1.54$ Å) irradiated from metal Cu were used to shoot samples and the diffraction was started at an incident angle of 5 degree and was completed at 120 degree. The morphology and chemical analysis of the solid residues were determined using a JEOL 840A Scan Electron Microscope (SEM) with Electron Derived X-rays (EDX) (SEM-EDX; JEOL LTD., Japan). Magnifications of SEM from 500x to 50000x were used. Chemical analysis using EDX was qualitative for both the compositions of surface area and the compositions of particles.
Sikun Xu, Ph.D. Thesis

# 5 PHYSICAL EQUATIONS IN SUPERCRITICAL WATER OXIDATION

# 5.1 Adoption of Equations of State to Supercritical Water and Its Mixtures

In supercritical water, chains of water molecules dissociate to form monomers and dimers [Ikushima et al. 1997], which is accompanied by breaking of more than 80% hydrogen bonding [Kohl et al. 1991]. As a consequence of the structural change, organics and gases are attracted and dissolved to form homogeneous mixtures with supercritical water. The behavior of mixing systems has been studied for H2O-inert gas (Ar, Xe) [Lentz and Franck 1969; Welsh et al. 1975], H<sub>2</sub>O-low reactive gas (N<sub>2</sub>, CO<sub>2</sub>, ) [Japas and Franck 1985a, Prokhorov 1970; Todheide and Franck 1963], H<sub>2</sub>O-gaseous alkane (CH<sub>4</sub>,  $C_{2}H_{6}$  [Christoforakos and Franck 1986; Danneil et al. 1967], and H<sub>2</sub>O-aromatic hydrocarbon (benzene, butane, pentane, heptane) [Alwani and Schneider 1967; Danneil et al. 1967; de Loos et al. 1983]. Equations of state (EOS) have been used to determine the behavior of supercritical water mixtures. However, most EOS were proposed to describe mixing systems containing similar molecules; hence, their prediction of the PVT behavior of the supercritical water mixtures results in significant errors because both polar molecules and non-polar molecules are present. Attempts have been made to eliminate the difference between experimental data and calculations [Christoforakos and Franck 1986].

# 5.1.1 CF equation

Christoforakos and Franck [Christoforakos and Franck 1986] proposed a Critical Fluid equation (called the CF equation) to describe the phase equilibria of the above aqueous systems at high temperature and pressure. The CF equation is given below:

$$p = \frac{RT}{v} - \frac{v^3 + \beta v^2 + \beta^2 v - \beta^3}{(v - \beta)^3} - \frac{4\beta RT}{v^2} (\lambda^3 - 1) \left[ exp\left(\frac{\varepsilon}{kT}\right) - 1 \right]$$
(5-1)

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where T = temperature in K; v = molar volume in cm<sup>3</sup>/mole;  $\beta$  = pure component parameter related to molecular size;  $\lambda$  = pure component parameter, square well width;  $\epsilon$  = pure component parameter, square well depth.

The parameters  $\beta$ ,  $\lambda$ , and  $\epsilon$  come from the Carnahan-Starling term concerning temperature-dependent particle diameters with molecular repulsion and attraction [Carnahan and Starling 1969]. For a binary system, both a mixing rule and a combination rule are required. Parameter  $\beta$  for a binary system is described as:

$$\beta = \sum_{i} x_{i} x_{j} \beta_{ij}$$
(5-2)

where

$$\beta_{ij} = \zeta^3 \left[ \frac{\beta_1^{1/3} + \beta_2^{1/3}}{2} \right]^3$$
(5-3)

and

$$\beta_{i} = \beta_{c,i} \left[ \frac{T_{c}}{T} \right]^{3/m}$$
(5-5)

The value of  $\beta_{c,i}$  can be calculated by setting the boundary conditions:  $(\partial P/\partial V)_T=0$  and  $(\partial^2 P/\partial^2 V)_T=0$  at the critical point of a pure substance or can be determined from data regression. The value of  $\varepsilon$  is determined from  $\lambda$  by:

$$\frac{\varepsilon}{k} = T_c \cdot \ln\left[1 + \frac{2.6503}{(\lambda^3 - 1)}\right]$$
(5-5)

The values of  $\varepsilon$  and  $\lambda$  of the mixture are determined as:

 $\varepsilon = \xi \sqrt{\varepsilon_i \varepsilon_j} \tag{5-6}$ 

$$\lambda = \max(\lambda_i \lambda_j) \tag{5-7}$$

For an oxygen-water system, four parameters ( $\lambda$ ,  $\varepsilon$ ,  $\beta$ , m) are required for each component and two interaction parameters ( $\xi$ ,  $\zeta$ ) are needed. It is difficult to acquire so many parameters by the regression of phase equilibrium data using the CF equation. Therefore, some parameters are usually fixed. The pure component PVT data for water and gas can be used to determine  $\lambda$ ,  $\beta$  of pure mass with invariant m = 10, and  $\varepsilon$ calculated from critical properties and  $\lambda$ . The values of  $\lambda$  and  $\beta_c$  were obtained by regression of the CF equation to the PVT properties of supercritical water over 500°C to 700°C [Haar et al. 1985].

The parameters of pure oxygen were obtained *via* PVT data regression [Sychev et al. 1987] in the range from 500°C to 700°C at pressures from 230 to 260 bar (23 to 26 MPa). The parameters  $\xi$  and  $\zeta$  of the mixtures were obtained through PVT data regression of the mixtures using the CF equation. For a water-oxygen system, PVT data are available at 500°C for oxygen contents ranging from 0.1 to 0.95 mole fraction at pressures up to 250 bar (25 MPa) [Japas and Franck 1985b]. The agreement between the CF equation and literature data is shown in Figure 5-1. This figure gives a large negative partial molar volume of oxygen in the supercritical water at infinite dilution at 500°C. This phenomenon was also observed by other authors [Paulaitis, 1983].

The CF equation can be used to calculate fugacity coefficient  $\varphi_i$  of specie-i *via* thermodynamic relationships [Prausnitz et al. 1986]:

$$RT\ln(\varphi_{i}) = \int_{v}^{\infty} \left[ \left[ \frac{\partial p}{\partial n_{i}} \right]_{T,v,n_{j}} - \frac{RT}{v} \right] dv - RT\ln Z$$
(5-8)

where Z is the compression factor of a mixture. However, the extrapolation of the CF equation to higher levels of oxygen dilution may therefore result in errors in the

calculations of fugacity coefficients near water's critical point (375°C, 22 MPa). These errors will be much smaller at higher temperature. The values of parameters  $\zeta$ ,  $\xi$  for other systems can be found in the simulated water-CO<sub>2</sub> system [Franck 1983].



Figure 5-1 Molar volume of O<sub>2</sub>-water system at 500°C [Webley, 1989b]

| Table 5-1 Gas-su       | percritical water parameters for the CF equation of state:   |     |
|------------------------|--|-----|
| 500~700 °C, 230~260bar | [Christoforakos and Franck 1985], 1 bar = 0.9868 atm = 0.10M | 1Pa |

| Compounds        | $\beta_{c}(T_{c})$ | λ      | ξ    | ζ    | $\lambda_{12}$ | m  |
|------------------|--------------------|--------|------|------|----------------|----|
| H <sub>2</sub> O | 12.0569            | 1.7255 |      |      |                | 10 |
| O <sub>2</sub>   | 15.882             | 2.5    | 0.55 | 1.0  | 2.5            | 10 |
| CH5              | 17.569             | 2.5    | 0.75 | 1.0  | 2.5            | 10 |
| CO <sub>2</sub>  | 19.98              | 2.5    | 0.95 | 0.99 | 1.5            | 10 |

Note:  $\lambda_{12}$ ,  $\xi$ , and  $\zeta$  refer to mixtures of gas –supercritical water.  $\beta_c(T_c)$ ,  $\lambda$  refers to pure compounds.

Table 5-1 shows the parameters in the CF equation for oxygen,  $CO_2$ ,  $CH_4$ -water systems for the temperature range of 500~700°C, and the pressure range of 230~260 bar (23~26 MPa). Those parameters can be used to obtain the fugacity coefficients in supercritical water [Webley 1989b]. These parameters suggested by Franck [Franck

1983] have a narrow pressure range. Therefore, the known temperature and pressure range for the applicable parameters ( $\lambda$ ,  $\varepsilon$ ,  $\beta$ , m,  $\xi$ ,  $\zeta$ ) is not enough for the practical application of this equation to supercritical water oxidation. (details of the CF equation refer to [Webley 1989b])

In our research, a mixture of supercritical water and oxygen is used to destroy organic wastes (less than 5%wt or 0.6%mol for 10-CB, cellulose, naphthalene). Since the organic amounts are relatively small, the system can be simplified as a binary system of the supercritical water and oxygen in order to calculate pressures. The experimental data of pressure and temperature are obtained *via* a batch reactor and a high-pressure transducer with a thermocouple (see Section 4.2). There are six parameters needed to

evaluate these calculations.  $\beta_{c,i}$  can be obtained from  $\left(\frac{\partial p}{\partial v}\right)_{T=Tc} = 0$  and  $\left(\frac{\partial^2 p}{\partial v^2}\right)_{T=Tc} = 0$ 

with the PVT data of pure water and pure oxygen. The values of the other parameters are estimated [Christoforakos and Franck 1985]. The parameters in Table 5-2 were used to calculate PVT of the supercritical water-oxygen system using the CF equation. The calculations and the experimental data are plotted in Figure 5-2 (a, b, c, d). Figure 5-2 (a) shows that the CF equation fails after molar volume decreases to 100cm<sup>3</sup>/mol. Figure 5-2 (b, c, d) shows that the errors between the experimental data and the calculations increase up to 20% with increasing molar volume and oxygen concentration. It should be concluded that the calculations with the CF equation do not well fit the experimental data. Possible reasons for the difference are too low temperatures and oxygen concentrations. The CF equation works properly only for high oxygen concentrations and high temperatures (>500°C).

| Compounds | $\beta_{c,i}$ | λ      | ξ    | ζ | $\lambda_{mix}$ | m  | T <sub>c</sub> in K |
|-----------|---------------|--------|------|---|-----------------|----|---------------------|
| H2O       | 12.0569       | 1.7255 |      |   |                 | 10 | 657.35              |
| O2        | 15.882        | 2.5    |      |   |                 | 10 | 155.6               |
| Mixture   |               |        | 0.55 | 1 | 2.5             | 10 |                     |

Table 5-2 Parameters used in PVT calculations using the CF equation



**Figure 5-2 Comparison of the CF calculations and the experimental data** Note: CF- calculations using the CF equation; Exp.- experimental data. 1 bar = 0.1 MPa

## 5.1.2 Peng-Robinson equation

Peng-Robinson equation (PR equation) was proposed for non-polar solvent/solute systems. It gives the least PVT errors in calculations of non-polar systems among the available EOS [Peng and Robinson, 1976]. Recently, different mixing rules for polysystems have been proposed in order to adopt the Peng-Robinson equation in mixtures of large molecular-weight compounds [Stryjek and Vera, 1986a, 1986b].

Following is the formula of the Peng-Robinson equation [Peng and Robinson, 1976]:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2vb - b^2}$$
(5-9)

Where

v: mol volume

$$b = b(T_c) = 0.07780 \frac{RT_c}{P_c}$$
(5-10)

$$a = a(T_c) * \alpha(T_r, \omega)$$
(5-11)

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c}$$
(5-12)

$$\alpha(T_{\rm r},\omega) = \left[1 + \kappa (1 - T_{\rm r})^{0.5}\right]^2$$
(5-13)

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5-14}$$

$$\omega = -\log \left( P_r^{\text{sat}} \right) - 1.00 \tag{5-15}$$

where  $P_r^{sat}$  is the value of saturated pressure at  $T_r = 0.7$ 

Mixing rules are represented by the following formulas:

(a) 
$$b_{mix} = \sum_{i} x_{i} b_{i}$$
, (b)  $a_{mix} = \sum_{i} \sum_{j} x_{i} x_{j} a_{ij}$ , (c)  $a_{ij} = (a_{i} a_{j})^{0.5} (1 - k_{ij})$  (5-16)

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In calculations,  $k_{ij}$  is a binary parameter considered as a constant for a certain binary system [Stryjek and Vera 1986a]. The comparison of the PR calculations and the experimental data is shown in Figure 5-3 (a, b, c, d), in which  $k_{ij}$  is assumed as zero. Generally the PR calculations give higher results than the experimental data. Similarly to the difference between the CF calculations and the experimental data, the difference between the PR data and the experimental data increases up to 15% with increasing temperature, increasing molar fraction of oxygen and decreasing molar volumes of mixtures.

If a constant  $k_{ij}$  is introduced, the profiles of PR calculations in Figure 5-3 will move up or down in a parallel way, depending on the sign and values of  $k_{ij}$ . Therefore, introducing a constant  $k_{ij}$  does not really improve the fit (figures are not presented since they are similar to Figure 5-3).

The PR equation gives higher values than the experimental data while the CF equation gives lower values. For the PR equation, the higher values are given because assuming  $k_{ij} = 0$  (the interacting parameter) ignores attraction and repulsion forces between water molecules and oxygen molecules. In the case of the CF equation, attraction and repulsion forces are overestimated since the CF calculations give much lower values than the experimental data. Therefore, direct adoption of the PR equation and the CF equation is not supported by the above calculations. However, the calculations with the PR equation fit the experimental data better than those with the CF equation. Therefore, the PR equation was selected for further investigations.



Figure 5-3 Comparison of the PR calculations and the experimental data Note: PR: calculations using Peng-Robinson equation without the interaction parameter  $k_{ij}$ ; Exp.: experimental data. 1 bar = 0.1 MPa

## 5.2 Modified Mixing Rule for Peng-Robinson Equation

## 5.2.1 Conceptually new mixing rule (or theoretically correct mixing rule)

Assuming that pure compounds in the mixtures obey the virial equation with the only second virial coefficient, which takes a form:

$$z = \frac{pv}{RT} = 1 + \frac{B}{V}$$
(5-17)

A new mixing rule was proposed for a mixture close to an ideal one [Zabaloy 1999, Wong 1992]:

$$\mathbf{B}_{\mathrm{mix}} = \sum_{i} \sum_{j} \mathbf{x}_{i} \mathbf{x}_{j} \mathbf{B}_{ij}$$
(5-18)

where B<sub>ij</sub> is the second virial coefficient of the i-j pair. For the PR equation:

$$B_i = b_i - \frac{a_i}{RT}$$
(5-19)

In the new mixing rule:

$$B_{ij} = \frac{B_i + B_j}{2} + A_{ij}(B_i - B_j) = B_{ji}, \text{ where } A_{ij} = -A_{ji}$$
(5-20)

Using the above mixing rule, we have to find  $A_{ij}$ , which is assumed to be a function of temperature. The virial equation with the second coefficient is not generally better than the PR equation. In the system of supercritical water and oxygen, calculations produce even worse results using the above mixing rule than the mixing rule in Section 5.1.2 (these data are not presented in the thesis due to significant discrepancy as compared to the experimental data). This is because supercritical water cannot be assumed as an ideal fluid in any sense. However, the suggestion of  $A_{ij}$  (similar to the interaction parameter  $k_{ij}$ ) being a function of temperature will be applied in the mixing rule of the PR equation in section 5.2.2.

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## 5.2.2 An approach to mixing rules

In the PR equation (see section 5.1.2), the parameters "a" and "b" are obtained from water and oxygen data below their critical conditions (see equations (5-10)  $\sim$  (5-15)). Errors obtained using "a" and "b" are higher than 1% at most conditions for pure water(see Table 5-3). The parameter "a" represents interaction forces between molecules. It is temperature-dependent. In order to obtain the accurate "a" in the mixing rule, we optimize the parameter "a" for supercritical water and supercritical oxygen in the PR equation. The parameter "b" represents sizes of molecules in compounds. It is constant vs. temperature and is not changed in the whole approach. The steam table [Haar 1985] is used for this pupose and the calculations are made using a computer program [Wagner 1997]. Oxygen is computed using a different commercial program [Senese 2001].

Initially, we optimize parameter " $\alpha$ " (equation (5-15)) for supercritical water as a function of temperature. By minimizing errors between the PR calculations and the steam data [Haar 1985], a formula for " $\alpha$ " above the critical point of water is obtained:

$$\alpha^{\text{scw}} = 1.8092T_r^2 - 4.5375T_r + 3.7344 \tag{5-21}$$

which is very close to the classical " $\alpha$ " discussed in section 5.1.2 (it is called " $\alpha^{scw}$ " in order to distinguish it from the classical " $\alpha$ "). Relative errors for " $\alpha^{SCW}$ " obtained by our calculations and the classical " $\alpha$ " in the P-R equation are given in Table 5-3. The absolute values of the errors for " $\alpha^{scw}$ " are lower at higher density, but slightly higher at lower density than that for " $\alpha$ ". Except at 56.37kg.m<sup>-3</sup>, the absolute values of the errors decrease with increasing temperature. The errors are within the range of ±1% using the " $\alpha^{scw}$ " function except at the critical point. Generally " $\alpha^{scw}$ " improves the calculations when the

PR equation is used for pure water. Hence, following is the formula for the parameter "a"

for water:

$$a = a_{c} * (1.8092T_{r}^{2} - 4.5375T_{r} + 3.7344)$$
(5-22)

| d(kg/m <sup>3</sup> ) | 193.20   | 155.56 | 115.92 | 77.28  | 56.37  |              | 193.20   | 155.56      | 115.92 | 77.28  | 56.37  |
|-----------------------|--|--------|--------|--------|--------|--------------|----------|-------------|--------|--------|--------|
| T(K)                  | $T(K)$ Relative errors for " $\alpha^{SCW}$ " obtained in this paper |        |        |        | Relati | ve errors fo | r"α" fon | n in PR sec | ction  |        |        |
| 657.3                 | -0.30%   | 0.53%  | 0.32%  | -0.55% | -1.01% |              | 1.11%    | 1.53%       | 0.97%  | -0.08% | -0.81% |
| 658.3                 | -0.27%   |        |        |        |        |              | 1.12%    |             |        |        |        |
| 659.3                 | -0.25%   | 0.38%  | 0.23%  | -0.52% | -1.05% |              | 1.13%    | 1.35%       | 0.86%  | -0.16% | -0.85% |
| 650.3                 | -0.20%   |        |        |        |        |              | 1.15%    |             |        |        |        |
| 651.3                 | -0.17%   | 0.35%  | 0.15%  | -0.59% | -1.08% |              | 1.15%    | 1.26%       | 0.76%  | -0.25% | -0.89% |
| 652.3                 | -0.15%   |        |        |        |        |              | 1.16%    |             |        |        |        |
| 653.3                 | -0.10%   | 0.29%  | 0.06%  | -0.66% | -1.12% |              | 1.18%    | 1.20%       | 0.66%  | -0.32% | -0.93% |
| 655.3                 | -0.07%   |        |        |        |        |              | 1.19%    |             |        |        |        |
| 655.3                 | -0.05%   | 0.25%  | -0.02% | -0.73% | -1.15% |              | 1.21%    | 1.13%       | 0.57%  | -0.39% | -0.97% |
| 656.3                 | 0.00%  |        |        |        |        |              | 1.23%    |             |        |        |        |
| 657.3                 | 0.03%  | 0.21%  | -0.09% | -0.79% | -1.19% |              | 1.25%    | 1.08%       | 0.58%  | -0.56% | -1.01% |
| 658.3                 | 0.06%  |        |        |        |        |              | 1.27%    |             |        |        |        |
| 659.3                 | 0.09%  | 0.17%  | -0.17% | -0.85% | -1.22% |              | 1.29%    | 1.03%       | 0.50%  | -0.52% | -1.05% |
| 661.3                 | 0.15%  | 0.13%  | -0.25% | -0.91% | -1.25% |              | 1.35%    | 0.98%       | 0.32%  | -0.58% | -1.07% |
| 663.3                 | 0.20%  | 0.09%  | -0.27% | -0.97% | -1.26% |              | 1.39%    | 0.95%       | 0.30%  | -0.65% | -1.08% |
| 665.3                 | 0.25%  | 0.05%  | -0.38% | -1.03% | -1.32% |              | 1.55%    | 0.90%       | 0.18%  | -0.70% | -1.13% |
| 667.3                 | 0.30%  | 0.02%  | -0.55% | -1.09% | -1.35% |              | 1.59%    | 0.87%       | 0.12%  | -0.75% | -1.16% |

#### Table 5-3 Relative errors for different " $\alpha$ "

The optimized parameter " $\alpha^{sc-o_2}$ " for supercritical oxygen from oxygen data does not reveal significant difference from the classical " $\alpha$ ". Therefore, the classical " $\alpha$ " in the parameter "a" will be used for oxygen in the calculations of PVT of the mixture.

After determining " $\alpha$ " in the parameter "a", we optimize " $a_{12}$ " (" $a_{12} = a_{21}$ ", assuming the interaction parameter  $k_{12} = k_{21}$  in the binary system of the supercritical water and oxygen in equation (5-16)). Initially,  $k_{12}$  is optimized. Plots of " $k_{12}$ " vs. molar volume show that " $k_{12}$ " is a function of molar volume at different temperatures. All plots show the same shape with different intercepts as seen in Figure 5-4. Therefore, " $k_{12}$ " is indeed a function of temperature and molar volume, and " $k_{12}$ " is represented by "-F(T)\*F(v)".



Figure 5-4 Interaction parameter k<sub>12</sub> versus molar volume

Therefore, " $a_{12}$ " in equation (5-16) can be written as:

$$a_{12} = a_{21} = (a_1 * a_2)^{0.5} (1 + F(v) * F(T))$$
(5-23)

By minimizing errors between the PR calculations and the experimental data of the wateroxygen system, F(T) and F(v) are found as:

$$F(v) = 8.9963619 \times 10^{-5} v^{2} + 6.3639198 \times 10^{-5} v - 0.90289783$$
 (5-25)

$$F(T) = 1.6815136 \times 10^{-3} T^2 - 2.155757T + 681.59002$$
 (5-25)

where v is mol volume of mixture in cm<sup>3</sup>/mol, T is temperature in Kelvin

Therefore, the mixing rule for parameter "a" is following:

$$a_{mix} = x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 (a_1 * a_2)^{0.5} (1 + F(v) * F(T))$$
(5-26)

The classical mixing rule for "b" (Equation (5-10)) is used for the supercritical wateroxygen mixture. Equation (5-26) and Equation (5-10) are used to calculate " $a_{mix}$ " and " $b_{mix}$ " for the mixtures of supercritical water and oxygen. The experimental data (exp.), the calculations of PR with " $a_{mix}$ " (cal.) and the calculations of PR with the classical mixing rules (PR) are illustrated in Figure 5-5 (a, b, c, d). Generally PR gives better

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results after introducing F(T)\*F(v) into the mixing rule between 657.3 and 665.3K. The maximum error decreases from more than 15% to less than 8%.

In this approach, it is found that direct adoption of the CF equation and the PR equation is not suggested for calculating properties of mixtures of supercritical water and oxygen. Therefore, " $\alpha$ " in the mixing rule has been modified to resolve the difference between the experimental data and the calculations. First, the parameter " $\alpha^{scw}$ " in the parameter "a" has been calculated for pure water above its critical point (see equations (5-21) and (5-22)). Figure 5-5 (a, b, c, d) shows that introducing F(T)\*F(v) in the mixing rule improves the prediction of PVT of the supercritical water-oxygen system using the PR equation (see Figure 5-5). However, about 8% error between our calculations and the experimental data also indicates that additional experimental data are required in order to obtain more accurate functions for F(T) and F(v).

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Figure 5-5 Comparison of the classical calculations (PR), this work (cal.) and the experimental data (exp.). Note:  $O_2$  in mol% in (c) and (d); 1 bar = 0.1 MPa

# 5.3 Calculation of Thermodynamic Properties

Thermodynamic quantities of water-oxygen mixtures can be calculated using the PR equation with mixing rules. Partial volume v<sub>i</sub>, the derivative of the total volume with respect to the mol number of component i, can be obtained through the standard relationship [Astarita 1989]. A partial molar volume for component "1" in a binary system is:

$$\mathbf{v}_{1} = \left(\frac{\partial \mathbf{V}}{\partial \mathbf{n}_{1}}\right)_{\mathrm{T},\mathrm{p}} = \mathbf{v} - (1 - \mathbf{x}_{2}) \left(\frac{\partial \mathbf{v}}{\partial \mathbf{p}}\right)_{\mathrm{T},\mathrm{x}} \left(\frac{\partial \mathbf{p}}{\partial \mathbf{x}_{1}}\right)_{\mathrm{T},\mathrm{v}}$$
(5-27)

where V is total volume, v is equal to V/n, n is the total mol number, T is temperature,  $n_i$  and  $x_i$  are molar number and molar fraction of component i, respectively.

The partial derivatives in Equation (5-27) are obtaining, by substituting Equations (5-25) to (5-26) into Equation (5-9) and differentiating the PR equation. For a binary system, following are the partial derivatives:

$$\left(\frac{\partial \mathbf{v}}{\partial \mathbf{p}}\right)_{\mathrm{T,x}} = \left(\frac{-\mathrm{RT}}{(\mathbf{v}-\mathbf{b})^2} - \frac{2^*\mathrm{F}(\mathrm{T})\sqrt{a_1^*a_2}}{(\mathbf{v}^2 + 2\mathbf{v}\mathbf{b} - \mathbf{b}^2)^*} * \frac{\partial\mathrm{F}(\mathbf{v})}{\partial\mathbf{v}} + \frac{(\mathbf{x}_1^2a_1 + \mathbf{x}_2^2a_2 + 2\mathbf{x}_1\mathbf{x}_2\sqrt{a_1a_2} * (1 + \mathrm{F}(\mathrm{T})^*\mathrm{F}(\mathbf{v})) * (2\mathbf{v} + 2\mathbf{b})}{(\mathbf{v}^2 + 2\mathbf{v}\mathbf{b} - \mathbf{b}^2)^2}}\right)^{-1}$$
(5-28)

$$\left(\frac{\partial p}{\partial x_{1}}\right)_{T,v} = \left(\frac{RTb_{1}}{(v-b)^{2}} - \frac{2a_{1}x_{1} + 2x_{2}\sqrt{a_{1}*a_{2}}*(1+F(T)*F(v))}{(v^{2}+2vb-b^{2})} + \frac{(x_{1}^{2}a_{1} + x_{2}^{2}a_{2} + 2x_{1}x_{2}\sqrt{a_{1}a_{2}}*(1+F(T)*F(v))*(2vb_{1}-2bb_{1})}{(v^{2}+2vb-b^{2})^{2}}\right)$$
(5-29)

$$\left(\frac{\partial p}{\partial x_{2}}\right)_{T,v} = \left(\frac{RTb_{2}}{(v-b)^{2}} - \frac{2a_{2}x_{2} + 2x_{1}\sqrt{a_{1}*a_{2}}*(1+F(T)*F(v))}{(v^{2}+2vb-b^{2})} + \frac{(x_{1}^{2}a_{1} + x_{2}^{2}a_{2} + 2x_{1}x_{2}\sqrt{a_{1}a_{2}}*(1+F(T)*F(v))*(2vb_{2}-2bb_{2})}{(v^{2}+2vb-b^{2})^{2}}\right)$$
(5-30)

where  $b = x_1b_1 + x_2b_2$  (see Equation (5-16)).

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Important quantities in equilibria are fugacity  $f_i$  and fugacity coefficients  $\phi_i$ ;  $f_i$  is defined to equate  $p^*x_i$  and  $\phi_i = 1$  at pressure near zero. The derivative of the chemical potential with respect to pressure at constant temperature and composition is equal to the

partial volume, 
$$\mu_i = RT \ln \left(\frac{f_i}{p^{\phi}}\right)$$
 and  $\left(\frac{\partial \mu_i}{\partial p}\right)_{T,x} = v_i$ .

For component 2:

$$\ln\left(\frac{f_2}{p^{\phi}}\right) = \frac{1}{RT} \int v_2 dp + \cos \tan t$$
(5-31)

Substituting  $v_2$  from Equation (5-27) and replacing "dp" by "dv" using the derivatives

$$\left(\frac{\partial p}{\partial v}\right)_{T,x} \text{ gives:}$$

$$\ln\left(\frac{f_2}{p^{\phi}}\right) = \frac{1}{RT} \int \left[v\left(\frac{\partial p}{\partial v}\right)_{T,x} - (1 - x_1)\left(\frac{\partial p}{\partial x_2}\right)_{T,v}\right] dv + \text{cons tan t}$$
(5-32)

The fugacity coefficient, defined by  $\varphi_i = f_i/(p^*x_i)$ , is given by:

$$\ln \phi_{2} = \frac{1}{RT} \int \left[ v \left( \frac{\partial p}{\partial v} \right)_{T,x} - (1 - x_{1}) \left( \frac{\partial p}{\partial x_{2}} \right)_{T,v} \right] dv + \ln (p^{\phi}) - \ln (x_{2} * p) + \text{constant}$$
(5-33)

Equilibrium constants and conversions of reactants can be calculated through the calculations of fugacity and fugacity coefficients. If  $a_{12}$  in equation (5-16) is only function of temperature, complete formulas are available in literature for calculating fugacity and fugacity coefficients *via* Peng-Robinson equation [Clifford 1999]. Since  $a_{12}$  is found dependent on molar volume in this work, those formulas should be re-developed in order to calculate fugacity and fugacity coefficients in water-oxygen systems. For ternary systems containing organics at dilute conditions (molar fraction  $x_3 \rightarrow 0$ ), the fugacity (f<sub>3</sub>) of organics is equal to  $x_3$ \*p because the fugacity coefficient  $\varphi_3$  is close to one

at  $x_3 \rightarrow 0$ . Hence, the ternary systems are simplified to the binary systems. Equations (5-27) to (5-33) are applied to calculate fugacity of oxygen and supercritical water.

### 5.4 Formulation of Pressure Effect on Kinetics

The calculations of partial volumes of oxygen and water are given as Eq. (5-27). The partial derivative terms of Eq. (5-27) are given as Eq. (3-28) ~ Eq. (3-30) using the Peng-Robinson equation with the mixing rule containing F(v)\*F(T). In Chapter 2, the integration part of Eq. (2-11) has been given as (the other part is Arrhenius equation):

$$k_{p} = \exp(\int_{p_{*}}^{p} (\frac{\bar{\nu}_{A} + \bar{\nu}_{B} - RT * k_{T}}{RT}) dp)$$
(5-34)

where  $k_p$  is defined as a reaction rate constant countering pressure effect and  $k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$  (V is the bulk volume of a system). Thus, it is possible to obtain a

complete formula of  $k_p$  by substituting  $v_A$  and  $v_B$  with Eq. (5-27) ~ Eq.(5-30). Integrating  $k_p$  from  $p_{\phi}$  to p allows to predict the pressure effect on the reaction rate constants in supercritical fluids (standard pressure  $p_{\phi}$  is normally assumed as 0.1MPa).

# **6** THE BEHAVIOR AND REACTIONS OF NAPHTHALENE IN SCW

. It is the most Naphthalene is composed of two fused benzene rings: important single constituent of coal-tar and the first of polycyclic aromatic hydrocarbons having fused rings. Naphthalene is less aromatic, more reactive than benzene because neither of two rings attains perfect benzenoid character that is the most aromatic and stable. Naphthalene has been known to cause exfoliative dermatitis, neurotic troubles and asthma [Florin et al. 1980, Kulka et al. 1988]. Large quantities of naphthalene have been used in manufacturing resins, insecticides, pharmaceuticals, leather-tanning agents, dyes and paint. About 238 metric tons waste naphthalene per year is disposed of on land in mixtures with other wastes, and 229 metric tons waste naphthalene per year is discharged to publicly owned treatment works in USA [Sciences International, Inc. 1995]. Directly disposed naphthalene poses a risk to human health. Environmental Protection Agency (EPA) [Sciences International, Inc. 1995] recommends incineration of naphthalene wastes in order to reduce naphthalene pollutants. However, the incineration may cause secondary emissions. For example, transformation to other PAHs may incur severe toxins [Sciences International, Inc. 1995]. It is of great interest to look for alternative technologies. In this work, naphthalene reactions, including destruction, in supercritical water are studied. Based on the results obtained, including data for intermediates, a reaction-pathway pattern and basic kinetics for naphthalene hydrolysis, oxidation and pyrolysis are all proposed.

# 6.1 Phase Behavior of Naphthalene in Supercritical Water

Visual observations of naphthalene's phase behavior were carried out in the hydrothermal diamond anvil cell (DAC) [Bassett 1993 and 1996, Xu 2001a], in which fluids are formed at pressure up to 2.5 GPa and temperature up to 1200°C (detailed experimental procedures are given in Chapter 4).

Table 6-1 summarizes the conditions and results. Density of water in the DAC ranges from 813 kg.m<sup>-3</sup> to 944 kg.m<sup>-3</sup>. The dielectric constant of supercritical water around 400°C is about 22~25. It rises to 65 with temperature decreasing to 250°C [Clifford 1999]. The density of naphthalene (Nap) in the DAC is around 28 kg.m<sup>-3</sup>. The dielectric constant of naphthalene vapor above 250°C is estimated to be about 3. The dielectric constant decreases with rising temperature [Fröhlich 1958]; hence, increasing temperature reduces the difference between the dielectric constants of water and naphthalene. Theoretically, naphthalene solubility in water above 250°C increases with increasing temperature and decreasing water density (or pressure).

## 6.1.1 Naphthalene and pure water

In run 1, when  $43wt\%Nap+H_2O$  with an air bubble (introduced to determine homogeneity temperature T<sub>h</sub>) (Figure 6-2 a) was heated at a rate of  $1.1^{\circ}C/s$  to  $424^{\circ}C$  and 315 MPa (Figure 6-1; temperature profile #1), air bubble disappeared at  $218^{\circ}C$  (T<sub>h</sub>) (Figure 6-2 b), at which the density of water was calculated as  $841 \text{ kg/m}^3$ . The system was isochorely heated, and pressure was calculated by knowing temperature and the density of water. At  $354^{\circ}C$ , naphthalene particle (or drop) became yellow (Figure 6-2 c) and changed to transparent at  $388^{\circ}C$  (Figure 6-2 d). The particle dispersed to tiny drops and started to dissolve at  $406^{\circ}C$  and  $417^{\circ}C$  (Figure 6-2 e, f). At the maximum temperature of  $424^{\circ}C$ , all naphthalene was dissolved in water (Figure 6-2 g). After cooling, many particles precipitated along with a gas bubble (Fig. 6-2 h). The residues in Figure 6-2 h were analyzed by IR. IR spectra (Figure 6-3) showed that little reaction occurred as compared with the spectra of run 1 and standard naphthalene.

In run 2, a sample was rapidly heated to 400°C and kept for 300s (Figure 6-1; temperature profile #2). As the time was increased, gas bubbles were produced. No homogenous phase was formed after 300s. Most of naphthalene was also obtained in the residues as confirmed by IR (Fig. 6-3).

In the experimental conditions (see Table 6-1 and Figure 6-1), the dielectric constant of water (22-25) is much higher than that of naphthalene (~3). The solubility of naphthalene in water is inhibited up to 400°C, where several naphthalene particles (or drops) are still observed and excluded from supercritical water (see Figure 6-2 e). Complete dissolution of naphthalene in supercritical water is observed when temperature reaches 424°C at water density of 841 kg.m<sup>-3</sup> (Figure 6-2 g) [Xu et al. 2001b]. At water density 918 kg.m<sup>-3</sup>, naphthalene particle (or drop) was observed at 400°C for 300s. It is confirmed that naphthalene has a high solubility of 43wt% in supercritical water (density of 841 kg.m<sup>-3</sup>) at 424°C.

## 6.1.2 Naphthalene and hydrogen peroxide solution

In runs 3-4, samples were kept at 400°C for 300s (Figure 6-4). However, 10wt% and 25wt%  $H_2O_2$  solution were applied in run 3 and run 4, respectively. Similarly to run 2, no complete dissolution was observed for both runs even though the amount of naphthalene is reduced as a result of partial oxidation of naphthalene. Dispersed particles are secondary phases due to the partial oxidation (Figure 6-4 b). The spectra in Figure 6-3 indicated that the residue in run 3 was decomposed due to numerous peaks absent

between 400 to 2000 cm<sup>-1</sup>. The sample in run 4 was decomposed further because an additional characteristic peak at 3052 cm<sup>-1</sup> disappeared.

In run 5, 7wt%Nap + 49wt%H<sub>2</sub>O<sub>2</sub> with air bubbles (Figure 6-5 a) was rapidly heated to 296°C. The air bubbles disappeared at 59°C (T<sub>h</sub>) (Figure 6-5 b). At 107°C, H<sub>2</sub>O<sub>2</sub> started to decompose as judged by the appearance of numerous tiny bubbles inside the chamber (Figure 6-5 c). A liquid globule (liquid naphthalene) was formed at 129°C (Figure 6-5 d). At 264°C, the chamber was covered with dissolved sample and became opaque. Several secondary liquid-phase particles were formed (Figure 6-5 e), which resulted from the partial oxidation. The sample was homogenously oxidized and the DAC became completely "clear" at 296°C and 82 MPa; the secondary phases disappeared (Figure 6-5 g). After cooling, no solid products were observed (Figure 6-5 h). It indicated that naphthalene was almost completely oxidized in the high-pressure aqueous phase.

The homogeneity in the system of  $7wt\%Nap + 49wt\%H_2O_2$  was due to both chemical reactions and physical dissolution. Higher concentration of hydrogen peroxide (hence, higher oxygen concentration) enhances dissolution processes. For example, 49wt% H<sub>2</sub>O<sub>2</sub> completely converted naphthalene; the homogeneous phase was formed even at 296°C while 10wt% and 25wt% H<sub>2</sub>O<sub>2</sub> could not oxidize naphthalene at 400°C in the heterogeneous phases. The opaque images in Figure 6-5 e and f, and the secondary phases in Figure 6-4 indicate that the partially oxidized products are formed.

The visual observations obtained with the DAC and FTIR prove that naphthalene and supercritical water (density 841 kg.m<sup>-3</sup>) form a homogeneous phase at 424°C. The dissolution confirms that supercritical water is a strong non-polar solvent at 424°C and 315MPa. FTIR spectra do not show that naphthalene reacts with pure supercritical water. Once an oxidant, e.g.  $H_2O_2$  (or  $O_2$ ), is introduced, naphthalene is oxidized. The heterogeneity is observed, which probably results from the formation of intermediates from the partial oxidation with deficient oxygen. Those intermediates are destroyed when excess oxygen (49wt%H<sub>2</sub>O<sub>2</sub>) is applied, which is accompanied by the appearance of homogeneity. We suggest that water acts as a medium, promoting the formation of radicals such as HO<sub>2</sub>, OH during oxidation [Xu 2001b]. Since water molecules have strong polarity, the reactant ion–dipole or dipole-dipole interaction would orient collisions of molecules to favor radical formation. For example, when H<sub>2</sub>O collides with C<sup>+</sup>, the reactant ion–dipole interaction orient H<sub>2</sub>O with O toward C<sup>+</sup>, forming extremely active H atoms through the reaction: C<sup>+</sup> + H<sub>2</sub>O  $\longrightarrow$  HOC<sup>+</sup>, HCO<sup>+</sup> + H [Ishikawa et al. 2001, 2003]; those active atoms, generated from water-oriented collisions, would speed up chemical reactions by lowering activation energy. Hence, water behaves like a catalyst.

| Experiments:                               | Decompo              | sition               | 0                                      |  |  |
|--|----------------------|----------------------|--|--|--|
|  | Run 1                | Run 2                | Run 3                                  | Run 4                                  | Run 5                                  |
| Systems:                                   | Nap+H <sub>2</sub> O | Nap+H <sub>2</sub> O | Nap+10wt%H <sub>2</sub> O <sub>2</sub> | Nap+25wt%H <sub>2</sub> O <sub>2</sub> | Nap+49wt%H <sub>2</sub> O <sub>2</sub> |
| Nap concentration (wt%)                    | 43                   | 44                   | 7                                      | 5                                      | 7                                      |
| Excess oxygen (mol%)                       | n.a.                 | n.a.                 | -79                                    | -17                                    | 2.2                                    |
| Max. T (T <sub>max</sub> , <sup>o</sup> C) | 424                  | 400                  | 400                                    | 400                                    | 296                                    |
| Density of water (kg/m <sup>3</sup> )      | 841                  | 918                  | 944                                    | 923                                    | 813                                    |
| Max. pressure at T <sub>max</sub> (MPa)    | 315                  | 456                  | 534                                    | 471                                    | 82                                     |
| Average heating rate (°C/s)                | 1.1                  | 1.2                  | 1.2                                    | 1                                      | 1.3                                    |
| Run time <sup>a</sup> (s)                  | 347.5                | 300                  | 300                                    | 300                                    | 208.5                                  |

# Table 6-1 DAC Experimental Summary of Conditions and Results

<sup>a</sup> Heating time to T<sub>max</sub> for short -time runs 1 and 5 or Holding time at 400°C for long-time runs 2-4.



Figure 6-1 Reaction temperature profiles



Figure 6-2 Visual observations of 43wt%Nap +  $H_2O$  heated to 424°C and 315 MPa



Figure 6-3 IR spectra of the residues for runs 1-4







Figure 6-5 Visual observations of 7wt%Nap + 49wt%H2O2 heated to 296°C and 82 MPa (run 5)

# 6.2 Hydrolysis and Pyrolysis of Naphthalene in Supercritical Water

The hydrolysis of naphthalene in water was conducted in the batch reactor. Temperature and pressure profiles in the batch reactor are recorded as shown in Figure 6-6. About 5.0%~10% naphthalene reacted with water up to 400°C and 30MPa during 1800s. More than 90% of naphthalene remained un-reacted. Naphthalene hydrolysis slightly increased from 25s to 1800s-residence time. It indicated that the reactions were achieving equilibria at different temperatures (see Figure 6-6). GC-MS (GCQ, Thermo Quest/Finnigan) was used to characterize the products of hydrolysis. A number of intermediates have been identified (see Figure 6-7). However, only 1,1'-Binaphthalene, 4,5-Dihydrobenzo(e)pyrene and 2,2'-Binaphthalene revealed considerably higher concentrations than the other intermediates. Naphthols (1-naphthol and 2-naphthol) were also found as intermediates; but were detected at almost 30 times lower concentrations than the above three main hydrocarbon intermediates.



Nap and pure water in batch reactor up to 400°C

Figure 6-6 Naphthalene versus residence time in the batch reactor (1 atm = 0.101325 MPa)





It is suggested that the following reactions are responsible for the hydrolysis (Figure 6-8) and pyrolysis (Figure 6-9) of naphthalene in supercritical water:



Figure 6-8 Hydrolysis of naphthalene (Note: \*  $\Delta_r$ H is estimated using data at 25°C)



## Figure 6-9 Pyrolysis of naphthalene

The hydrolysis of naphthalene initially produced naphthols (1-naphthol, 2naphthol) *via* ionic mechanisms. The naphthols might form naphthol radicals through reacting with OH<sup>\*</sup> in supercritical water. These radicals reacted with naphthalene, forming 1,1'-Binaphthalene and 2,2'-Binaphthalene (see Figure 6-8). In the pyrolysis process, one ring of naphthalene was initially broken, forming benzene derivatives and radicals. 4,5-dihydrobenzo(e)pyrene was subsequently formed *via* radical polymerization (see Figure 6-9). These three intermediates are heavy PAHs (heavier than naphthalene). The results suggest that deficient oxygen in supercritical water oxidation of naphthalene would form a hydrolysis-like environment, stimulating naphthalene transformation to other PAHs. Therefore, applying excess oxygen in SCWO of naphthalene is necessary to avoid formation of heavier PAHs.

## 6.3 Supercritical Water Oxidation of Naphthalene

#### 6.3.1 Decomposition of hydrogen peroxide in a batch reactor

In this work, hydrogen peroxide  $(H_2O_2)$  was used to introduce oxygen in order to achieve high oxygen contents.  $H_2O_2$  decomposes in the batch reactor, releasing oxygen according to the following reaction:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{6-1}$$

Figure 6-10 and 6-11 show time-dependent temperature and pressure profiles in the batch reactor. The temperature tended to be stable after 240s when the temperature of the fluidized sand bath was set to  $300^{\circ}$ C and  $400^{\circ}$ C. The loading of 1 ml H<sub>2</sub>O<sub>2</sub> did not affect the temperature profiles. During the first two minutes the temperature was increased to  $327^{\circ}$ C (the fluidized bath temperature was set to  $400^{\circ}$ C). The pressure started increasing above  $100^{\circ}$ C. It increased sharply between  $100^{\circ}$ C and  $200^{\circ}$ C, but this rate slowed down above  $200^{\circ}$ C.

The decomposition of hydrogen peroxide was documented elsewhere [Croiset et al. 1997]. The decomposition rates were independent of pressure below the critical temperature of water. The activation energy of  $H_2O_2$  decomposition changed with pressure above the critical pressure, and the conversions of hydrogen peroxide were about 2% at 150°C and 60s reaction time, 2% at 200°C and 15s, 75% at 250°C and 20 s, 98.5% at 300°C and 20s, and 99% at 374°C and 1s.  $H_2O_2$  conversion, as a function of the reaction time, was calculated as  $(1 - \exp(-k_g t))$  where  $k_g$  was the rate constant, and t was time (the surface of the reactor had a significant effect on the decomposition rate [Croiset et al. 1997]).



Figure 6-10 Temperature profiles inside the batch reactor at different Fluidized Bath temperatures (FBT) with 8.55mol/L and 1.44mol/L O<sub>2</sub> (1ml 49%wt H<sub>2</sub>O<sub>2</sub> in reactor), and without H<sub>2</sub>O<sub>2</sub> Note: FBT=300C: Fluidized Bath Temperature = 300°C, all the same in the context.



Figure 6-11 Pressure profiles inside the batch reactor at different Fluidized Bath temperature (FBT) with 8.55mol/L and 1.44mol/L O<sub>2</sub> (1ml 49%wt H<sub>2</sub>O<sub>2</sub> in reactor), and without H<sub>2</sub>O<sub>2</sub> (S-P1 at FBT=300C: saturated pressure at FBT=300°C; S-P2 at FBT=400C: saturated pressure at FBT=400°C) (1 atm = 0.101325 MPa)

Figure 6-10 and 6-11 show that the temperature rose to 150°C at 37 seconds, 200°C at 49 seconds, 250°C at 67 seconds, and to 300°C at 97 seconds. The pressure started rising after 25s at the fluidized bath temperature (FBT) of 400°C, and after 33s at FBT=300°C. These points were considered as the beginning of the reactions. The inflexions of the pressure profiles consistently appeared at 200°C in all tests with different contents of  $H_2O_2$  and different temperatures of fluidized bath (300°C and 400°C). An increase in pressure was significant on the left side of the inflexion due to fast  $H_2O_2$ decomposition rates. Thus, the flexion at 200°C (54s at FBT=400°C, 82s at FBT=300°C) indicated that most of  $H_2O_2$  had decomposed, and was defined as *the end point of the*  $H_2O_2$  decomposition [Xu et al. 2003a]. Not identical with data given in the literature [Croiset et al. 1997], the decomposition of  $H_2O_2$  proceeded fast enough below 200°C of a temperature indicator, thus being able to supply enough oxygen for the oxidation of naphthalene. We believe that it was related to the fact that the reactor wall was in direct contact with the hot sand in the fluidized bath; thus, the actual wall temperature of the reactor was higher than 200°C read by the thermocouple (contacting with the fluids inside the reactor). Therefore,  $H_2O_2$  was actually decomposing at a higher temperature than 200°C. A significant H<sub>2</sub>O<sub>2</sub> decomposition was observed at 129°C in a Diamond Anvil Cell [Fang and Kozinski 2000a], which was in agreement with the pressure profile from Figure 6-11. To confirm the above analysis, a heat transfer equation [Zhang and Zhou 2001] was used to calculate the temperatures of internal reactor wall. The temperatures, 229°C at 25s and 260°C at 54s, were obtained. Since the decomposition of  $H_2O_2$  was catalyzed by the internal surface of reactor, our result was not actually contradictory with the result given by Croiset [1997] after considering the estimated temperature of the internal reactor wall.

### 6.3.2 CO<sub>2</sub> yield and naphthalene conversion

## Effect of $H_2O_2$ decomposition on supercritical water oxidation

The conversion of naphthalene obtained in our experiments was 56% when the sample was quenched after 120s residence time at FBT=400°C (FBT= Fluidized Bath Temperature, real reaction time was 95s since the first 25s was used to heat up the reactor and the decomposition of H<sub>2</sub>O<sub>2</sub> started at 25s thereafter). The conversion reached 99% after 300s and FBT=400°C (the real reaction time was 275s). When H<sub>2</sub>O<sub>2</sub> decomposed at high temperature, it produced more active reactants, forming radicals more easily than a mixture of O<sub>2</sub> and H<sub>2</sub>O. It was suggested that a significant difference in the data between oxidation in the SCW+O<sub>2</sub> system and in the SCW+H<sub>2</sub>O<sub>2</sub> system might come from radicals' production in the oxidation reaction [NIST 1997]. An enhanced oxidation of organics by H<sub>2</sub>O<sub>2</sub> in supercritical water was also observed by other researchers [Bourhis et al. 1995]. The combustion model of cellulose showed that radicals involved in the oxidation and combustion include OH, HO<sub>2</sub> and O<sub>3</sub> etc [Liang and Kozinski 2000]. Free radicals from H<sub>2</sub>O<sub>2</sub> decomposition should stimulate the oxidation since supercritical fluid was a gas-like phase and the decomposition of H<sub>2</sub>O<sub>2</sub> proceeded simultaneously with the oxidation [Fang and Kozinski 2001].

## *Effect of Residence Time and* $H_2O_2$ *on* $CO_2$ *yield*

Hydrocarbon oxidation in SCW produces gases such as  $CO_2$ , CO, and  $H_2$  [Webley 1989]. CO comes from incomplete oxidation. Hydrogen is produced through the following reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$
 (6-2)

The hydrogen production was higher during the SCWO of carbon monoxide than the predicted by a gaseous combustion model [Helling 1988]. It was suggested that loosely bonded water molecules formed a cavity, which would work like a cage. CO molecules inside the cage would react with  $H_2O$  to produce  $H_2$ , CO<sub>2</sub>. CO and  $H_2$  were oxidized through the diffusion to the outside of the cage. Thus, hydrogen showed higher concentration than that predicted by the combustion models [Webley and Tester 1991, Webley 1989].

In the experiments of SCW oxidation of naphthalene conducted by the author, in some samples hydrogen and CO were present only in the ranges of GC sensitivity [Xu et al. 2003a]. Thus, it seems that SCWO did not promote the formation of CO and H<sub>2</sub> in our system at 400°C. In the SCW oxidation of benzene, DiNaro's [2000b] results showed that the formation of CO started at 505°C, reached maximum at 540°C, disappeared at 575°C, which supported our results.

Our GC results showed that  $CO_2$  yield considerably increased with increasing  $H_2O_2$  or oxygen concentration. Such behavior is expected since an increase in the reactant amounts must improve the reacting probability in terms of the collisional theory of chemical kinetics. In Figure 6-12, carbon in  $CO_2$  constituted 80~97% (±5%) of the total carbon. At the same conditions, the conversion of naphthalene reached 90~99.9%.  $CO_2$  yield reached 97% (±5%) when reacting time was extended to 1800s (naphthalene conversion was about 99.99%) (see Figure 6-12).



Figure 6-12 CO<sub>2</sub> yield during naphthalene (Nap) oxidation at FBT=400°C

Table 6-2 shows the effect of oxygen on yields of  $CO_2$  and acetic acid.  $CO_2$  yield considerably decreased with decreasing excess oxygen while the yield of acetic acid increased with less oxygen. Table 6-2 shows 6% yield of acetic acid after 300s. Thus, acetic acid would be one of the dominant intermediates in the naphthalene oxidation process, as compared to data in Table 6-3. The oxidation of acetic acid might be a ratecontrol step in the naphthalene oxidation as in the SCW oxidation of cellulose [Li et al. 1993a].

| Feeding Material   | Acetate yield | $\cdot$ CO <sub>2</sub> yield | Total  |
|--|---------------|-------------------------------|--------|
| 0.065mol/L Nap + $8.5$ mol/L H <sub>2</sub> O with 88% excess O <sub>2</sub>   | 2.36%         | 80.56%                        | 82.92% |
| 0.065mol/L Nap + 6.37mol/L H <sub>2</sub> O with 41%<br>excess O <sub>2</sub>  | 5.80%         | 74.40%                        | 80.20% |
| 0.065mol/L Nap +4.25mol/L H <sub>2</sub> O with (-6%)<br>excess O <sub>2</sub> | 6.47%         | 69.13%                        | 75.60% |

| Fable 6-2 Naphthalene (Nap) oxidation | n in SCW within 300s at FBT=420°C |
|---------------------------------------|-----------------------------------|
|---------------------------------------|-----------------------------------|

Table 6-3 Intermediates <sup>a</sup> identified in naphthalene oxidation at FBT=400°C

| Subject                 | Carbon percent <sup>b</sup> |        |        |        |        |  |  |  |
|-------------------------|-----------------------------|--------|--------|--------|--------|--|--|--|
| Time (s)                | 15                          | 25     | 45     | 150    | 300    |  |  |  |
| Temperature (°C)        | 55.7                        | 90.6   | 168    | 358    | 394    |  |  |  |
| Pressure (atm)          | 1                           | 1      | 95     | 210    | 276    |  |  |  |
| Salicylaldehyde         | 0                           | 0.019% | 0.047% | 0.211% | 0.035% |  |  |  |
| Naphthalene             | 99.98%                      | 89.80% | 46.85% | 38.16% | 0.338% |  |  |  |
| Salicylic acid          | 0                           | 0.001% | 0.076% | 0.080% | 0.029% |  |  |  |
| 1,4-naphthoquinone      | 0                           | 0.018% | 0.688% | 0.861% | 0.353% |  |  |  |
| 1-naphthol (2-naphthol) | 0                           | 0.042% | 0.161% | 0.085% | 0.024% |  |  |  |
| Fluorenone              | 0                           | 0      | 0      | 0.001% | 0.024% |  |  |  |
| Formic acid             | 0                           | 1.30%  | 2.42%  | 0.29%  | 0.06%  |  |  |  |
| Acetic acid             | 0                           | 0      | 0      | 0.47%  | 2.76%  |  |  |  |

Note: <sup>a</sup> the full spectra of intermediates will be seen in Section 6.3.3. <sup>b</sup> carbon percent = mole number of carbon in product / total mole number of feed carbon 1 atm = 1.01325 bar = 0.101325 MPa
#### 6.3.3 Oxidation profiles, kinetics, and intermediates

#### Naphthalene oxidation profiles of Nap with $H_2O_2$ (system A)

Naphthalene evolution up to 400°C and 297atm (30.1MPa) is shown in Figure 6-13. This figure also shows time-resolved temperature and pressure profiles. More detailed T-P profiles and the detailed decomposition of H<sub>2</sub>O<sub>2</sub> with temperature are presented in Section 6.3.1, 6.3.2 and reference [Croiset 1997]. As shown in Figure 6-13, the amount of unreacted naphthalene in the batch reactor decreases with time, and the conversion of naphthalene increases to about 100% at 230s. The disappearance of naphthalene occurs in three stages as shown in Figure 6-13 [Xu et al. 2001a, 2001b, 2003a]. Stage 1 corresponds to the T-P range of 100°C-1.0atm (0.101325MPa) and 200°C-120atm (12.1MPa) (where the decomposition of  $H_2O_2$  was completed); Stage 2 is in the range of T-P between 200°C-120atm (12.1MPa) and 360°C-225atm (22.8MPa); Stage 3 falls in the range of T-P between 360°C-225atm (22.8MPa) and the supercritical region of water. In Stage 1, the decomposition of hydrogen peroxide produces active free radicals, e.g. OH and HO<sub>2</sub>, and then causes naphthalene to react rapidly. In Stage 2, the decomposition of hydrogen peroxide ends releasing gaseous oxygen and the reaction rate slows down when naphthalene reacts with oxygen gas in the saturated water phase. In Stage 3, the temperature rises to 360°C and the pressure to 225atm (22.8MPa, as shown in the DAC results of Section 6.1), naphthalene starts dissolving and a homogeneous phase starts forming at these conditions. Therefore, the reaction rate of naphthalene increases with the dissolution of naphthalene in supercritical water.

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Figure 6-13 Naphthalene (Nap) evolution with 1ml 49% H<sub>2</sub>O<sub>2</sub> in the batch reactor (Nap sample of 50 mg) (1 atm = 0.101325 MPa)

In the DAC experiments, naphthalene was completely converted at about 296°C, 809atm (82MPa) and 208s, which was before Stage 3. In the batch reactor, more than 99% naphthalene was converted at about 360°C, 225atm (22.8MPa) and 220s. At almost the same reaction time, the same conversion of naphthalene was obtained in both reactors when the temperature increased from 296°C to 360°C and the pressure decreased from 809atm to 225atm. The effect of a small temperature change on the naphthalene conversion is offset by the effect of a large pressure change. *Our experimental results suggest that water pressure affects the reaction rates in SCW* (the effect of pressure on the reaction rates is often neglected in other SCW studies).

## Naphthalene oxidation profiles of Nap + $H_2O_2$ + $Cr(NO_3)_3 \circ 9H_2O_2 + Al_2Si_2O_5(OH)_4$ (system B) and Nap + $H_2O$ + $K_2CrO_4$ + $(SiO_2)_{1.37}(Al_2O_3)_{0.093}(Na_2O)_{0.127}$ (system C)

Kaolin  $(Al_2Si_2O_5(OH)_4)$  and amorphous aluminum silicate synthetic  $((SiO_2)_{1,37}(Al_2O_3)_{0.093}(Na_2O)_{0.127} = 82\% SiO_2 + 9.5\% Al_2O_3 + 8\% Na_2O$  in weight) were used to simulate inorganic ash in order to determine the effect of inorganics on organic oxidation. The two systems:  $Nap + H_2O_2 + Cr(NO_3)_3 \circ 9H_2O_2 + Al_2Si_2O_3(OH)_4$  and  $Nap + H_2O_2 + Cr(NO_3)_3 \circ 9H_2O_2 + Al_2Si_2O_3(OH)_4$  $H_2O + K_2CrO_4 + (SiO_2)_{1.37}(Al_2O_3)_{0.093}(Na_2O)_{0.127}$ , were labeled as Nap+H<sub>2</sub>O<sub>2</sub>+Cr(3+) and Nap+Cr(6+). The simulated ashes did not appear in the labels since they did not participate in the oxidation reactions (In Figure 6-14, they appear as legends "Nap+H2O2+Cr(3+)" and "Nap+Cr(6+)"). Nap +  $H_2O_2$  is presented for comparison in Figure 6-14. K<sub>2</sub>CrO<sub>4</sub> oxidized naphthalene with the presence of water and amorphous aluminum silicate synthetic. The unreacted naphthalene decreases up to 220°C, increases until 330°C, and decreases again after 330°C (see Figure 6-14 line Nap+Cr(6+)). The profile of Nap+Cr(6+) suggested that the oxidation of naphthalene produced unstable intermediates below 220°C. When temperature was increased above 220°C, metals (Cr, Fe, Ni) of the reactor walls might reduce the unstable intermediates; thus, the naphthalene concentration increased until the temperature reached 340°C. When the temperature was above 340°C, the naphthalene concentration decreased because the oxidation of naphthalene continued in sub/supercritical water and stable intermediates were formed. The oxidation rate of naphthalene by  $K_2CrO_4$  is much slower than by the other oxidants. However, the oxidation of naphthalene by  $Cr^{3+}$  plus H<sub>2</sub>O<sub>2</sub> is much faster than by K<sub>2</sub>CrO<sub>4</sub> and pure H<sub>2</sub>O<sub>2</sub> solution. The oxidation is fast even in saturated water phase between 200°C-120atm and 360°C-225atm (see Figure 6-14, line Nap+H2O2+Cr(3+)). The oxidation of naphthalene is completed in subcritical water region. It is believed that the

addition of kaolin and  $Cr^{3+}$  enhances the oxidation of naphthalene because  $Cr^{3+}$  cation would help electron transfer similarly, which is like the role of  $UO_2^{2+}$  cation in a system of naphthalene+ $UO_2^{2+}/O_2$  [Mao 1997].



Figure 6-14 Oxidation profiles of naphthalene (Nap) in the batch reactor (1 atm = 0.101325 MPa)

Note: M=mol/L

Nap+H2O2 = system A: 50 mg Nap + 1ml 49%  $H_2O_2$  (or 0.065M Nap+ 6.37M  $H_2O$  + 1.441M  $O_2$  or with 41% excess  $O_2$ );

Nap+H2O2+Cr(+3) = system B: 50 mg Nap + 1.0 ml 49%  $H_2O_2$  + 20 mg Cr(NO<sub>3</sub>)<sub>3</sub>.9 $H_2O$  + 100 mg Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> (or 0.065M Nap +1.441M O<sub>2</sub> + 0.008M Cr(NO<sub>3</sub>)<sub>3</sub> + 0.065M Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>.(OH)<sub>4</sub> + 8.624M H<sub>2</sub>O);

Nap+Cr(6+) = system C: 50 mg Nap + 10 mg K<sub>2</sub>CrO<sub>4</sub> +0.92 ml H<sub>2</sub>O+50mg (SiO<sub>2</sub>)<sub>1.37</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.093</sub>(Na<sub>2</sub>O)<sub>0.127</sub> (or 0.065M Nap + 0.0086M K<sub>2</sub>CrO<sub>4</sub> + 8.549M H<sub>2</sub>O + 0.130M (SiO<sub>2</sub>)<sub>1.37</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.093</sub>(Na<sub>2</sub>O)<sub>0.127</sub>).

#### **Reaction rates**

Phase behavior of system of 14.4mol% oxygen and 85.6mol% water with 0.06mol% naphthalene

The phase evolution is clarified in the batch reactor using equations of state.

According to Peng-Robinson equation, at the critical point of the mixture, a series of

equations are obtained [Peng and Robinson 1976]:

$$\frac{\partial^2 p}{\partial v^2} = 0, \ \frac{\partial p}{\partial v} = 0, \ p_c^m = \frac{RT_c^m}{(v_c^m - b^m)} - \frac{a_c^m * \alpha}{(v_c^{m^2} + 2b^m v_c^m - b^{m^2})}, \ \alpha = 1 \text{ at } T = T_c^m,$$
$$a_c^m = 0.45724 \frac{(RT_c^m)^2}{P_c}, \ b^m = 0.07780 \frac{RT_c^m}{P_c^m}$$

where the superscript 'm' indicates the mixture and the subscript 'c' indicates the critical properties. Since the amount of naphthalene is negligible, the mixture of naphthalene-water-oxygen is assumed as a binary system of water-oxygen. By solving the above equations using an interaction parameter  $k_{ij} = -0.267$  for oxygen and water (obtained from the experimental data using F(v)\*F(T) in Chapter 5), the critical point of the mixture,  $307^{\circ}C$  and 194.5atm (19.7MPa), is obtained. Therefore, the homogeneous supercritical phase in the mixture would be formed above  $307^{\circ}C$  and 194.5atm (19.7MPa).

In the system of  $H_2O_2$  and naphthalene, the decomposition of  $H_2O_2$  started after 100°C and 1.0atm (0.1 MPa) in the batch reactor, releasing all oxygen at 200°C and 120atm (12.1MPa). It was confirmed that the chemical reactions were negligible below 100°C because 99.9% naphthalene remained. Hence chemical reactions were initiated once oxygen was released. Fast increasing temperature and pressure resulted in phase changes, accompanied by chemical reactions in the batch reactor. Naphthalene changed into liquid phase while water started vaporizing above 100°C (the melting point of naphthalene is 80.2°C). Up to 200°C and 120atm, the system was composed of liquid naphthalene, partial liquid water and partial water vapor, and oxygen gas. Between 100°C-1.0atm (0.1MPa) and 200°C-120atm (12.1MPa) (corresponding to Stage 1), the chemical reactions took place between liquid naphthalene, hydrogen peroxide and oxygen. It was believed that the intensive bubbling of H<sub>2</sub>O<sub>2</sub> decomposition and water broke up the naphthalene into small hydrophobic particles (like Nap drops in Fig. 6-2). A

pseudo-single phase is formed in Stage 1. The chemical reactions took place at boundaries between gas, water and liquid naphthalene particles. After the decomposition of hydrogen peroxide was completed, naphthalene evaporated at about 230°C (its boiling point shifts to 230°C from 217.9°C, as calculated using Claypeyron Equation [Astarita 1989]). A homogeneous phase would form in the mixture of 15% mol oxygen and 85% mol water at 307°C and 194.5 atm. Therefore, between 200°C-120atm (12.1MPa) and 360°C-225atm (22.8MPa) (corresponding to Stage 2), the chemical reactions mainly took place in the vapor phase containing naphthalene, oxygen and water, and then in a homogeneous phase above 307°C and 194.5 atm. In Stage 3, the formation of a homogeneous phase was completed; hence, all reactions were carried out in the homogeneous phase.

# Naphthalene oxidation rates in the system of 0.065M Nap+1.441M $O_2$ +8.549M $H_2O(System A)$

Many researchers have approached the kinetics of SCWO of organics by regressing data obtained in plug-flow reactors, where reaction time was limited to seconds since SCWO proceeded very fast. Temperature, pressure, and concentrations of reactants were kept constant to measure the kinetic parameters [Dagaut 1995, Dunford 1974, Antal 1985]. In the SCWO in a batch reactor, all materials are fed into the reactor at once while temperature and pressure increase. This process is very different from the batch reactor processes at 1.0atm, where reactants can be added when temperatures are maintained constant. Therefore, there are a number of reactions occurring in the batch reactor while the system proceeds from low temperature to the critical point of water (374.2°C). To determine the kinetics of SCWO in the batch reactor, possible reaction mechanisms must be clarified since they might lead to different rate equations.

Naphthalene oxidation profile in the system of  $0.065MNap+ 1.441MO_2+$ 8.549MH<sub>2</sub>O is shown as Nap.-A in Figure 6-15. Naphthalene oxidation is divided into three stages (discussed in the first two paragraphs of Section 6.3.3). In Stage 1, H<sub>2</sub>O<sub>2</sub> decomposes into H<sub>2</sub>O and O<sub>2</sub> while temperature ranging from 100 to 200°C and pressure from 1 to 120atm (12.1MPa). In Stage 2, the decomposition of H<sub>2</sub>O<sub>2</sub> has been completed; a saturated water phase dominates between 200°C-120atm (12.1MPa) and 307°C-19.4atm (19.7MPa), followed by the critical phase of the water-O<sub>2</sub> mixture between 307°C-19.4atm (19.7MPa) and 360°C-225atm (22.8MPa). In Stage 3, when the temperature inside the reactor is above 360°C, the formation of supercritical mixture is completed. Following the defined stages, naphthalene oxidation proceeded as a fast-slow-fast process. In Stage 1, the fast oxidation was caused by active free radicals generated by decomposing H<sub>2</sub>O<sub>2</sub> between 100°C-1.0atm (0.1MPa) and 200°C-120atm (12.1MPa). In Stage 2, a slow oxidation was found in saturated water phase between 200°C-120atm and 360°C-225atm. SCWO revealed a fast oxidation in Stage 3 above 360°C-225atm. The reaction mechanisms varied in different stages.

The reactions are assumed to be similar in a uniform phase in order to calculate the global kinetics in Stage 1 and Stage 2. The pressure and temperature profiles are seen in Figure 6-15. Reaction rates in different stages were obtained by regressing data from the different stages. The stoichiometric reaction of naphthalene oxidation is:

$$C_{10}H_8 + 12O_2 = 10CO_2 + 4H_2O$$
 (6-3)

In reality, reaction (6-3) has much more complicated pattern since naphthalene and  $H_2O_2$  were both fed into the reactor before heating. The following reaction rate equation was used:

$$\frac{d[\operatorname{Nap}]}{dt} = -\operatorname{A}\exp(\frac{-E_a}{RT})[\operatorname{Nap}]^a[O_2]^b[H_2O]^c$$
(6-4)

 $[Nap] = (1 - X)[Nap]_{o}, [O_{2}] = [O_{2}]_{o} - \phi * [Nap]_{o} * X, [H_{2}O] = [H_{2}O]_{o} + \phi * [Nap]_{o} * X,$ X represents naphthalene conversion. By substituting related terms, equation (6-4) takes a form:

$$-\frac{dX}{dt} = -A \exp(\frac{-E_a}{RT})(1-X)^a [Nap]_0^{a-1} ([O_2]_0 - \phi * [Nap]_0 * X)^b$$

$$[[H_2O]_0 + \phi * [Nap]_0 * X]^c$$
(6-5)

where  $\phi=12$  is the stoichiometric ratio of O<sub>2</sub>-to-Nap,  $\phi=4$  is the stoichiometric ratio of H<sub>2</sub>O-to-Nap in Equation 6-3, based on the assumption that all reacted naphthalene was completely oxidized to CO<sub>2</sub> and water. Although this assumption may not be accurate since partial oxidation products were detected, using the stoichiometric ratio as a correlating measure was reasonable since CO<sub>2</sub> yield was always much higher than the yields of other products.

Each stage ended at the beginning of the following stage. Naphthalene conversions, reaction time and initial concentrations of naphthalene and  $O_2$  have all been recalculated according to their starting time. A simple self-developed computer program was used to carry out non-linear regression. It began with obtaining spline functions of naphthalene conversion profiles vs. time. The spline functions were derived against time; hence, dX/dt was obtained as a function of time. Two sets of values of dX/dt were produced at experimental points using spline functions and equation (6-5) by assuming approximate values of a, b, c, Ea and A in equation (6-5). By minimizing the difference between two sets of values, a set of the optimum values of a, b, c, Ea and A was obtained.

Nonlinear regression of all experimental data of  $0.065MNap+ 1.441MO_2+$ 8.549MH<sub>2</sub>O was performed to obtain A, E<sub>a</sub>, a, b, and c for three stages (see Table 6-4):

Stage 1 of Nap-A: 
$$-\frac{dX}{dt} = -1.59E2 \exp(\frac{-28.76}{RT})(1-X)[O_2]$$
 (6-6)

Stage 2 of Nap-A: 
$$-\frac{dX}{dt} = -4.52E - 4\exp(\frac{6.52}{RT})(1 - X)[O_2]$$
 (6-7)

Stage 3 of Nap-A (SCWO):

$$-\frac{\mathrm{dX}}{\mathrm{dt}} = -1.00\mathrm{E8}\exp(\frac{-139.5}{\mathrm{RT}})(1-\mathrm{X})^{0.14}[\mathrm{NT}]_0^{-0.86}[\mathrm{O}_2]^1[\mathrm{H}_2\mathrm{O}]^{0.99}$$
(6-8)

In Stage 1, a low activation-energy about 28.76 KJ/mol was obtained for the global oxidation rate; only  $O_2$  and naphthalene attended oxidation reactions, and  $H_2O$  did not affect the oxidation rate since c=0. The low activation energy confirmed that radicals generated during the decomposition of  $H_2O_2$  stimulate the oxidation of naphthalene. In Stage 2, a negative activation-energy about -6.52 kJ/mol was obtained. This result was similar to the kinetics of hydrolysis of methylene chloride from 100 to 500°C [Salvatierra et al. 1999], which was affected by the solvation of water. But in the system B the solvation of water was not supported in Stage 2 since c=0. In Stage 3 a SCW phase was formed. Naphthalene oxidation proceeded faster than its oxidation at low temperature (below 100°C) [England et al. 1998, Sasaki et al. 1997, Boylan and Sims 1953]. High activation energy of 139.5 kJ/mol was obtained, which supported kinetic-controlled reactions in the SCWO. Oxygen and water both participated in the oxidation of naphthalene in sub/supercritical water since b is equal to 1 and c is equal to 0.99.

Naphthalene oxidation rates in the system of 0.065M Nap +1.441M O<sub>2</sub> + 0.008M Cr(NO<sub>3</sub>)<sub>3</sub> + 0.065M Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> + 8.624M H<sub>2</sub>O (System B)

Nap-B profile in Figure 6-15 shows naphthalene oxidation in the system of 0.065Mnap +1.441M O<sub>2</sub> + 0.008MCr(NO<sub>3</sub>)<sub>3</sub> + 0.065MAl<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>.(OH)<sub>4</sub> + 8.624MH<sub>2</sub>O. It is seen that naphthalene is completely converted before the critical point of water

(374.2°C) is reached. Reaction rate equations are obtained only for Stage 1 and 2 using the approach for Eq. (6-3) to (6-6):

Stage 1 of Nap-B

$$-\frac{\mathrm{dX}}{\mathrm{dt}} = -6\mathrm{E} - 2\exp(\frac{-8.72}{\mathrm{RT}})(1-\mathrm{X})^{0.22}[\mathrm{NT}]^{-0.78}[\mathrm{O}_2]^{0.2}$$
(6-9)

Stage 2 of Nap-B

$$-\frac{dX}{dt} = -7.27E - 1\exp(\frac{-17.11}{RT})(1-X)^{0.76} [NT]_0^{-0.24} [O_2]^{1.8} [H_2O]$$
(6-10)

The low activation-energy was obtained for both Stage 1 and Stage 2 of System B (see Table 6-4). Calculated conversions of naphthalene for System B are shown as "dashed lines" in Figure 6-15. Relatively low activation energy was obtained in both Stages of System B: 8.72 and 17.11 kJ/mol, respectively (see Eq.(6-9) and (6-10)). Since ash  $Al_2Si_2O_5$ .(OH)<sub>4</sub> and a heavy metal Cr(NO<sub>3</sub>)<sub>3</sub> were added to this system, it was expected that their catalytic effect should speed up naphthalene oxidation. Thus, the lower activation energy of 8.72kJ/mol was obtained for Stage 1 of System B than that for Stage 1 of System A.

Naphthalene oxidation behavior in the system of 0.065M Nap + 0.0086M K<sub>2</sub>CrO<sub>4</sub> + 8.549M H<sub>2</sub>O + 0.130M (SiO<sub>2</sub>)<sub>1.37</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.093</sub>(Na<sub>2</sub>O)<sub>0.127</sub> (System C)

Naphthalene oxidation profile by  $Cr^{6+}$  in water is shown as Nap-C in Fig. 6-15. Naphthalene conversion increases, then decreases until 340°C and increases again above 340°C. Such behavior of naphthalene is explained while describing Fig. 6-14.  $CrO_4^{2-}$  was consumed completely between 300s and 600s residence time, precipitating as  $Cr_2O_3$  (details of heavy metal behavior are described in Chapter 8). Naphthalene continuously reacted with some intermediates, and its conversion increased after  $CrO_4^{2-}$  was completely reacted. Different reactions in the whole process of System C were involved. The reaction rates could not be achieved in this complex process. Naphthalene oxidation with  $\text{CrO}_4^{2-}$  proceeded slower than that of naphthalene with oxygen-SCW and oxygen-inorganics-SCW. However, naphthalene oxidation by  $\text{CrO}_4^{2-}$  became faster with increasing temperature and pressure. Some intermediates other than those present in System A and B were detected in System C.

#### Reaction Rate Constants

Table 6-4 summarizes the reaction rates in System A and System B. Except the activation energy for Stage 3 (SCWO) of System A, all other activation energies are relatively low. A disagreement is found in values of parameters between our data and reaction rates for different organic wastes obtained previously [Thornton 1992, Krainc and Levec 1996, Gopalan an Savage 1992]. A simple reason might be different analytical methods adopted by different authors [Krajnc and Levec 1996]. We believe that variations in temperature and pressure may affect the reaction rate in the high pressure/temperature systems. According to the transition-state theory of reaction kinetics [Astarita 1989],  $k = A \exp(\Delta S / R) \exp(-E_a / (RT))$ , where  $\Delta S$  is activation entropy,  $E_a$  is activation energy.  $\Delta S$  can be a function of pressure and temperature as  $\Delta S = \int_{p_1}^{p_2} (\partial v / \partial T)_p dp \quad . \quad It$ is found that  $exp(\Delta S/RT)$ corresponds to

 $\exp(\int_{p_*}^{p} (\frac{v_A + v_B - RT * k_T}{RT}) dp$ ) in section 2.5.3. Therefore, including H<sub>2</sub>O concentration in

the reaction rates would not be sufficient to counter the effect of pressure on the reaction rates. A better solution would be embedding a proper "state equation" into  $\exp(\int_{p_4}^{p}(\frac{\bar{v}_A + \bar{v}_B - RT * k_T}{RT})dp$ ) in the reaction rates (discussed in section 5.4). This equation of countering pressure effect should be confirmed using a plug-flow reactor. Thus, the kinetic data presented in this dissertation are limited by the experimental conditions.

|                            |         | a    | b   | с    | Α                       | Ea(kJ/mol) |
|----------------------------|---------|------|-----|------|-------------------------|------------|
| System A                   | Stage 1 | 1.0  | 1.0 | 0    | 1.59 x 10 <sup>-2</sup> | 28.76      |
|                            | Stage 2 | 1.0  | 1.0 | 0    | 4.52 x 10 <sup>-2</sup> | -6.52      |
|                            | Stage 3 | 0.14 | 1.0 | 0.99 | 1.0 x 10 <sup>8</sup>   | 139.5      |
| Stratem D                  | Stage1  | 0.22 | 0.2 | 0    | 6 x 10 <sup>-2</sup>    | 8.72       |
| System D                   | Stage 2 | 0.76 | 1.8 | 1.0  | 7.27 x 10 <sup>-1</sup> | 17.11      |
| [Thornton and Savage 1992] | Phenol  | 1.0  | 0.5 | 0.7  | 303                     | 51.83      |

Table 6-4 Summary of reaction rates



Figure 6-15 Naphthalene conversion in System A, B and C versus residence time (solid lines "——" for system A and dash line "——" for system B are conversions predicted by reaction rates, respectively) (1 atm = 0.101325 MPa)

Note: Nap.-A = System A: 0.065M Nap+ 1.441M O<sub>2</sub>+ 8.549M H<sub>2</sub>O; Nap.-B = System B: 0.065M Nap +1.441M O<sub>2</sub> + 0.008M Cr(NO<sub>3</sub>)<sub>3</sub> + 0.065M Al<sub>2</sub>Si<sub>2</sub>O<sub>3</sub>(OH)<sub>4</sub> + 8.624M H<sub>2</sub>O; Nap.-C= System C: 0.065M Nap + 0.0086M K<sub>2</sub>CrO<sub>4</sub> + 8.549M H<sub>2</sub>O + 0.130M (SiO<sub>2</sub>)<sub>1.37</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.093</sub>(Na<sub>2</sub>O)<sub>0.127</sub>.

#### Identification of intermediates

Organic species in the benzene phase were first identified at above 60% confidence using GC-MS (GCQ, Thermo Quest/Finnigan). Acetic acid and formic acid in the aqueous phase were identified using Ion Chromatograph (Dionex 100). Pure chemical standards were subsequently used to confirm the results. Figure 6-16 shows a GC-MS profile of intermediates and naphthalene. Figure 6-17 shows IC spectra for organic intermediates in the aqueous phase. The structures and formulas of the main intermediates are given in Table 6-5.

The intermediates' spectra suggest that naphthalene rings break one after another, accompanied by polymerization of intermediates. Dibenzofuran, fluorenone and xanthone were probably formed due to polymerization of intermediates. 1-naphthol and 2-naphthol were identified as intermediates in the initial oxidation of naphthalene at ambient conditions [Tuhkanen 1995, Brussol et al. 1999]. In Figure 6-16, 1-naphtol and 2-naphthol have low concentrations in comparison with the concentration of naphthoquinone. It indicates that the initial oxidation of naphthalene in SCW first results in the formation of 1,4-naphthoquinone.

Two other intermediates identified in the aqueous solution are formic acid and acetic acid (in Figure 6-17 formic acid is not appearing due to its low concentration in samples obtained after 300s residence time in the batch reactor). The peak of formic acid was at 100.8s while the peak of acetic acid was seen at 91.5s. They would raise two separate peaks if both had low concentrations while the overlapping of two peaks cannot be easily analyzed since both had high concentrations (it is difficult to dissociate the overlapping if one compound is present in a considerable amount in the sample). In order to obtain the concentrations of the highly concentrated species, samples were diluted to

erase peaks associated with lowly-concentrated compounds. Acetic acid was suggested as an important intermediate in the SCW oxidation process of cellulose [Li 1993]. We have found that formic acid formed first once the oxidative reaction started in the batch reactor. The concentration of formic acid decreased with increasing reaction time, and the concentration of acetic acid increased with increasing reaction time. No evidence was obtained for the transformation of formic acid to acetic acid. Both acids were the direct products from oxidation reactions. The results in Table 6-3 show that formic acid is formed at lower temperatures than acetic acid. However, there are still five peaks not identified, in which the two peaks with higher intensity were named as Organic M1 and M2. Decreasing temperature could increase the formation of the organic acid at RT= 103s (M1) and an organic acid at RT= 260s (M2). According to Figure 6-17, M1 and M2 stayed longer in the IC column than acetic acid and formic acid. It indicates that M1 and M2 are more acidic or heavier than formic acid and acetic acid.

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Figure 6-16 Spectra of intermediates in organic phases

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**Figure 6-17 The spectra of intermediates in aqueous phases** Note: Samples obtained after 300s residence time; FBT = Fluidized Bath Temperature

| Name                       | Formula                                      | Structure                                | Name                        | Formula                                       | Structure      |  |
|----------------------------|--|--|-----------------------------|---|----------------|--|
| Formic acid                | CH <sub>2</sub> O <sub>2</sub>               | но <sub>с</sub> =0<br>Н                  | Phthalic acid               | C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>  | он<br>он<br>он |  |
| Acetic acid                | C <sub>2</sub> H <sub>4</sub> O              | он<br>Н <sub>3</sub> с о                 | 2-<br>carboxybenzaldehyde   | C <sub>8</sub> H <sub>6</sub> O <sub>3</sub>  | OH OH          |  |
| Phenol                     | C <sub>6</sub> H <sub>6</sub> O              | он                                       | Coumarin                    | C <sub>9</sub> H <sub>6</sub> O <sub>2</sub>  |                |  |
| Benzoic acid               | $C_7H_6O_2$                                  | Он                                       | Chromone                    | C <sub>9</sub> H <sub>6</sub> O <sub>2</sub>  |                |  |
| Salicylaldehyde            | C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> | но                                       | 1(2H)-naphthalenone         | C <sub>10</sub> H <sub>8</sub> O              |                |  |
| 2'-<br>hydroxyacetophenone | C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> | СН3                                      | 1,4-naphthoquinone          | C <sub>10</sub> H <sub>6</sub> O <sub>2</sub> | °              |  |
| Salicylic acid             | C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> | ноно                                     | 1-naphthol (2-<br>naphthol) | C <sub>8</sub> H <sub>10</sub> O              | OH<br>C        |  |
| Phthalic anhydride         | C <sub>8</sub> H <sub>4</sub> O <sub>3</sub> | €<br>↓<br>°                              | Dibenzofuran                | C <sub>12</sub> H <sub>8</sub> O              |                |  |
| Phthalide                  | C <sub>8</sub> H <sub>6</sub> O <sub>2</sub> |  | Fluorenone                  | C <sub>13</sub> H <sub>8</sub> O              |                |  |
| 2-acetylbenzoic acid       | C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> | он о | Xanthone                    | C <sub>13</sub> H <sub>8</sub> O <sub>2</sub> |                |  |

### Table 6-5 Structures and formulas of intermediates of naphthalene oxidation in the batch reactor

#### **Evolution of intermediates**

Complex intermediates were identified and quantified in the naphthalene oxidation process. Here we report only on the selected intermediates, according to the increasing molecular weight, which played important roles during the naphthalene oxidation [Xu and Kozinski 2003b] since they had significant yields. The other intermediates were present at relatively low levels. Therefore, it is hard to explain their behavior versus temperature and pressure profiles.

#### Formic acid and acetic acid

In System A, formic acid was formed in Stage 1 and Stage 2 and disappeared in Stage 3 (see Figure 6-18). Three reactions were possibly responsible for the production of formic acid when the oxidation started:



The disappearance of formic acid in Stage 3 of system A was related to its fast oxidation in SCW. Acetic acid was found as an intermediate in other research, its oxidation controlled the processes of organic destruction [Li et al. 1993a, Krajnc 1996]. Acetic acid was formed during the SCWO (Stage 3) because double C=C broke fast by reacting with OH, HO<sub>2</sub> free radicals; and hydrogen possibly shifted to next carbon atom

when free alkyl radicals were formed right after carbon atoms were breaking away. The possible precursor of acetic acid was tran, trans Muconic acid:

In System B, the yield of formic acid had the same trend as in System A. Acetic acid had significant yields in all stages of System B. Catalytic action of  $Cr^{3+}$  and  $Al_2Si_2O_5.(OH)_4$  likely stimulated the oxidation of naphthalene, forming tran, trans Muconic acid during Stage 1 and 2. Its further oxidation produced acetic acid during Stage 1 and 2 in System B.

Acetic acid was formed in considerably lower yields in System C of Nap+ $\text{CrO}_4^{2-}$ +H<sub>2</sub>O. In System C the formation of acetic acid may be associated with reactions involving free radicals. No formation of formic acid was detected in System C.



**B= System B:** 0.065M Nap +1.441M O<sub>2</sub> + 0.008M Cr(NO<sub>3</sub>)<sub>3</sub> + 0.065M Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>.(OH)<sub>4</sub> + 8.624M H<sub>2</sub>O; **C =System C:** 0.065M Nap + 0.0086M K<sub>2</sub>CrO<sub>4</sub> + 8.549M H<sub>2</sub>O + 0.130M (SiO<sub>2</sub>)<sub>1.37</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.093</sub>(Na<sub>2</sub>O)<sub>0.127</sub>.

#### Salicylaldehyde and phthalic anhydride

Salicylaldehyde and phthalic anhydride were the direct products of breaking rings during the SCWO of naphthalene. Figure 6-19 showed that they had considerable yields in both systems A and B. Generally they had higher yields above 200°C and 120atm than at the conditions of Stage 1. However, their concentrations were higher in System A than in System B. In System B, the low yields can be explained by fast-catalyzed reactions in which they participate themselves. A significant part of salicylaldehyde was formed through the following oxidative reaction in both systems:



(6-15)

(6-16)

It was possible that phthalic anhydride transformed to salicylaldehyde through a hydrolysis-like reaction:



Salicylaldehyde and phthalic anhydride were very active. Their further reactions proceeded into two directions: (1) breaking into open-ring products or (2) polymerizing to form heavy compounds (e.g. dibenzofuran). Salicylaldehyde was almost destroyed at 1800s residence time in both System A and B while phthalic anhydride still remained in trace amounts (yields< 0.03%). It was likely a result of inter-conversion of other intermediates, such as dibenzofuran and fluorenone (for example, dibenzofuran was oxidized forming phthalic anhydride). In System C, they both had considerably yields because the further oxidation of them was prevented due to the complete consumption of the oxidants.



 $+ 0.130M (SiO_2)_{1.37} (Al_2O_3)_{0.093} (Na_2O)_{0.127}.$ 

#### 1,4-naphthoquinone and chromone

1,4-naphthoquinone and chromone were formed during the initial oxidation of naphthalene with oxygen. Chromone and coumarin were mainly found during the SCWO (their structures are seen in Table 6-5). Coumarin was formed through the reaction similar to the formation of chromone. The only difference was that the formation of coumarin resulted from the oxidation taking place at positions 1 and 2 (see Reaction (6-17)) on the naphthalene rings while chromone was formed *via* oxidation at positions 1 and 4 (Coumarin data are not presented in Fig.6-20 since it is similar to chromone):



In both systems, the yields of 1,4-naphthoquinone were higher than that of chromone (0.5% to 2.0% vs. <0.02%; see Figure 6-20). Chromone was an open-ring-like intermediate since one carbon was taken out from one of the naphthalene rings while 1,4-naphthoquinone still had intact carbon rings. Thus, the formation of chromone was more difficult, but its decomposition was easier than that of 1,4-naphthoquinone. Thus, the yield of chromone was lower than that of 1,4-naphthoquinone. In System A, 1,4-naphthoquinone's profile in Figure 6-20 has similar trend to the conversion of naphthalene shown in Fig. 6-15. When the oxidation of naphthalene was fast in the Stage 1 and 3, the yields of 1,4-naphthoquinone were increasing. Its decreasing yield in Stage 2 corresponded to the slow oxidation of naphthalene. Chromone revealed the same trend (see low scale in Figure 6-20). In System B, the trends of 1,4-naphthoquinone and

chromone were similar and also followed the rate of naphthalene oxidation much like in System A (see Figure 6-20 both low and high scales).

The yields of 1,4-naphthoquinone and chromone were the indicators of the reaction rate of naphthalene oxidation in both systems. Although they have similar trends in SCWO, which meant that they were formed at the same time, 1,4-naphthoquinone was more easily stabilized than chromone and was the dominating intermediate during the initial oxidation process of naphthalene.



Figure 6-20 The yields of 1,4-naphthoquinone and chromone Note: A= System A: 0.065M Nap+ 1.441M  $O_2$ + 8.549M  $H_2O$ ; B= System B: 0.065M Nap +1.441M  $O_2$  + 0.008M  $Cr(NO_3)_3$ + 0.065M  $Al_2Si_2O_5.(OH)_4$  + 8.624M  $H_2O$ ; C =System C: 0.065M Nap + 0.0086M  $K_2CrO_4$  + 8.549M  $H_2O$ + 0.130M  $(SiO_2)_{1.37}(Al_2O_3)_{0.093}(Na_2O)_{0.127}$ .

#### Dibenzofuran and Fluorenone

The yields of dibenzofuran and fluorenone are shown in Figure 6-21. In System A, dibenzofuran had higher yields in Stage 1 and Stage 2 than in Stage 3 (0.27% vs. 0.03%, respectively). It suggests that SCW oxidation helps destroying dibenzofuran. Fluorenone was not detected in System A in the Stage 1 and 2. It was seen in Stage 3 only. Both dibenzofuran and fluorenone were destroyed in 1800-s reaction time.

In System B, dibenzofuran and fluorenone revealed similar trend. They reached the highest yields in Stage 2 when naphthalene oxidation was fast, and they were destroyed at SCWO conditions. In System C, they both appeared in high concentrations in Stage 3 because salicylaldehyde and phthalic anhydride were formed at the relatively high concentrations (see Fig 6-19). Their yields were determined by the oxidation rate of naphthalene and the temperature in Systems A and B. Dibenzofuran and fluorenone were formed *via* the polymerization and oxidation of salicylaldehyde through the following reactions:

$$2 \bigoplus_{\substack{C_7H_6O_2\\\text{salicylaldehyde}}} + 0.5O_2 \longrightarrow \bigoplus_{\substack{C_{13}H_6O\\\text{Fluorenone}}} + 2H_2O + CO_2$$

$$(6-19)$$

$$2 \bigoplus_{\substack{C_7H_6O_2\\\text{salicylaldehyde}}} + 1.5O_2 \longrightarrow \bigoplus_{\substack{C_{12}H_6O\\\text{Dibenzofuran}}} + 2H_2O + 2CO_2$$

$$(6-20)$$

Therefore, monitoring salicylaldehyde could also help to determine the existence of dibenzofuran and fluorenone. Dibenzofuran and fluorenone can be completely oxidized. However, their oxidation process takes longer than the oxidation of other intermediates (e.g., compare Figure 6-21 with Figure 6-20).



 $\begin{array}{l} \textbf{B= System B: } 0.065M \text{ Nap } + 1.441M \text{ O}_2 + 0.008M \text{ Cr(NO}_3)_3 \\ & + 0.065M \text{ Al}_2\text{Si}_2\text{O}_5.(\text{OH})_4 + 8.624M \text{ H}_2\text{O}; \\ \textbf{C=System C: } 0.065M \text{ Nap } + 0.0086M \text{ K}_2\text{CrO}_4 + 8.549M \text{ H}_2\text{O} \\ & + 0.130M (\text{SiO}_2)_{1.37}(\text{Al}_2\text{O}_3)_{0.093}(\text{Na}_2\text{O})_{0.127}. \end{array}$ 

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#### 6.3.4 Reaction pattern and mechanism

A reaction pattern is proposed for the naphthalene oxidation by oxygen in the batch reactor (Fig. 6-22). All intermediates listed in Figure 6-16 were detected, identified and quantified. The pattern is almost entirely based on the experimental data (some reactions, from Eq.6-11 to Eq.6-20, have already been discussed) [Xu and Kozinski 2003b].

There were five main ways (R01 to R05), for oxygen to "invade" naphthalene rings. When oxygen broke  $C_{10}H_8$  rings, released carbons would form, through R03, R04 and R05, formic acid and 1,4-naphthoquinone, 1-naphthol, phthalic anhydride, coumarin and chromone, which were stable at lower temperature (below 200°C). They would be oxidized to CO<sub>2</sub> and H<sub>2</sub>O at higher temperature (above 200°C). Once one of the naphthalene rings broke into chains, the remaining chains would be fast oxidized, forming salicylaldehyde *via* R07, R10 and R11. This intermediate could be easily oxidized to an open-ring trans, trans-Muconic acid (R12), which then decomposed to CO<sub>2</sub> and H<sub>2</sub>O. Salicylaldehyde was an incipient species from which heavier compounds such as fluorenone, dibenzofuran and xanthone (R14-R16) were formed. Xanthone was formed only in System A *via* a reaction similar to the formation of fluorenone and dibenzofuran (see Eq.6-19 and 6-20):

$$2 \bigcup_{\substack{C_7H_6O_2\\\text{saticylaidehyde}}}^{O} + O_2 \xrightarrow{R15} \bigcup_{\substack{C_{13}H_6O_2\\C_{13}H_6O_2}}^{O} + 2H_2O + CO_2$$
(6-21)

These compounds require long residence time to be destroyed. Their oxidation in SCW seems to be complex (R17 to R19) and it is not clear at the present state of analysis.

However, our results showed that SCWO could completely destroy or convert these unwanted species.

Trans, trans-Muconic acid, formed *via* R09 and R12, has six carbons with two C=C bonds. Acetic acid was formed when its chain was 'fast-shortened' (R13). During the whole oxidation process,  $CO_2$  and formic acid were formed every time when a single carbon was being cut off.

The production of free radicals can be inhibited in a polar solvent. For example, liquid water does not promote the existence of free radicals and it will deactivate free radicals when they are formed. Hence, most of the radical-involving reactions take place in gaseous phase, such as free radical reactions in a flame or plasma. However, it has been suggested that free radical reactions dominate oxidation in supercritical water [Thornton 1991, Yang 1988, Dagaut 1992] since the density of water is sufficiently low  $(0.2 \sim 0.3 \text{g/cm}^3)$ . When naphthalene reacts with oxygen during the decomposition of H<sub>2</sub>O<sub>2</sub> (Stage 1) and in SCW (Stage 3), the fast oxidation supports free radical reaction mechanism. Free radicals, such as OH<sup>\*</sup>, HO<sub>2</sub><sup>\*</sup> and H<sup>\*</sup>, are known to initiate oxidation reactions. Their formation has been documented elsewhere [Cobos 1985, Baulch 1992, Fulle 1996].  $HO_2^*$  can be formed from H<sup>\*</sup> and O<sub>2</sub> at a high pressure of 243 atm (24.6MPa) [Cobos 1985]. In our system the pressure was about 297 atm, which favored the formation of HO<sub>2</sub><sup>\*</sup>. We believe that there is similarity between the SCWO of benzene and naphthalene because of their chemical structures. In the reduced combustion mechanism of benzene, one of the routes of benzene decomposition has been explained (see Table 2-4) [DiNaro 2000a]. It suggests that OH<sup>\*</sup> extracts H from benzene ring to form phenyl  $(C_6H_5)$ ; then phenyl reacts with O<sub>2</sub> to form phenylperoxy  $(C_6H_5OO^*)$  radicals while pbenzoquinone can form from phenylperoxy (see Table 2-4). In the naphthalene+O<sub>2</sub> system, 1, 4-naphthoquinone seems to be exactly corresponding to p-benzoquinone in the benzene+ $O_2$  system. By comparisons, simple radical reactions are proposed for initiating the SCWO of naphthalene:

(a) 
$$H_2O_2 \longrightarrow 2OH^*$$
 (b)  $O_2 + OH^* \longrightarrow O_2H^* + O$  (c)  $O + OH^* \longrightarrow O_2 + H^*$  (6-22)

These reactions illustrate the production of free radicals (the deactivation of the radicals is ignored) (also see Table 2-4) [DiNaro 2000a]. It is suggested that radicals from the reaction (a) promotes naphthalene oxidation in Stage 1 of System A and B, while all reactions, (a), (b) and (c), take place in Stages 2 and 3 of both Systems.

The products of initial oxidation of naphthalene such as 1,4-naphthoquinone, chromone and coumarin are formed in the reactions shown below. At first,  $C_{10}H_7^*$  is formed *via* OH<sup>\*</sup> extracting hydrogen from naphthalene:

$$C_{10}H_8 + OH^* \longrightarrow C_{10}H_7^* + H_2O$$
 (6-23)

Then,  $O_2$  reacts with radical  $C_{10}H_7^*$  to form  $C_{10}H_7OO^*$ :

$$C_{10}H_7^* + O_2 \longrightarrow C_{10}H_7OO^*$$
 (6-24)

 $C_{10}H_7OO^*$  decomposes into two directions: (1) forming 1,4-naphthoquinone:

$$C_{10}H_7OO^* \longrightarrow C_{10}H_6O_2 (1,4-naphthoquinone) + H^*$$
 (6-25)

and (2) forming  $C_9H_7^*$  via a reaction:

$$C_{10}H_7OO^* \longrightarrow C_9H_7^* + CO_2$$
 (6-26)

At this step, chromone and coumarin are formed by the decomposition of C<sub>9</sub>H<sub>7</sub>OO<sup>\*</sup>:

$$C_{9}H_{7}^{*} + O_{2} \longrightarrow C_{9}H_{7}OO^{*}$$
 (6-27)

$$C_9H_7OO^* \longrightarrow C_9H_6O_2$$
 (chromone + H\*  
or coumarin) + (6-28)

Reactions (22) to (28) show that the radical-involving processes proceed in the steps R01, R04 and R05 in Fig. 6-22. However, each step in Fig. 22 may contain complex reactions besides elementary reactions.

The free radical mechanisms discussed above also dominated oxidation in the System B (Nap+O<sub>2</sub>+Cr<sup>3+</sup>+H<sub>2</sub>O). However, it is likely that Cr<sup>3+</sup> helps to transfer electrons during the free radical oxidation of naphthalene (free-radical + ionic mechanisms) as seen in the oxidation process of naphthalene with  $UO_2^{2+}/O_2$  at room temperature [Mao 1997]. The addition of inorganic salts resulted in the visible difference between System A and System B.

Although the subtleties of some steps involved in the reaction pattern are still unanswered at the present state of analysis, the observations and arguments presented here offer a key to understand a number of phenomena connected with the behavior of naphthalene in SCW.

It was shown that, in general, the oxidation process of naphthalene can be divided into three stages characterized by  $H_2O_2$  decomposition to  $H_2O$  and  $O_2$  (Stage 1), oxidation in saturated/subcritical water up to 360 °C and 225 atm (Stage 2), and fast oxidation in supercritical region of water (Stage 3). The oxidation process revealed different reaction rates depending on the systems studied (A: Nap+O<sub>2</sub>+H<sub>2</sub>O and B: Nap+O<sub>2</sub>+H<sub>2</sub>O+Cr<sup>3+</sup>). The catalytic effect of Cr<sup>3+</sup>/ash led to low activation energy in System B.

The observed behavior of naphthalene may have significance in designing practical SCW reactors, tailoring their geometry and conditions according to different stages of the oxidation process. It seems that the presence of heavy metals and aluminosilicates stimulates SCWO reactions of hydrocarbons. Since possible industrial wastes contain more complex organics and would be oxidized in an uninterrupted manner, a similar study performed in a continuous-flow reactor including higher-than-naphthalene hydrocarbons would be the next logical step.



Figure 6-22 Reaction pattern proposed based on the experimental data

#### 7 DECACHLOROBIPHENYL IN SUPERCRITICL WATER-O2 SYSTEM

The conventional flame-based incineration is ineffective for PCBs destruction in the environmental point of view because the incineration of PCBs resulted in more fatal emission, such as chlorinated dioxins and furans [Schecter 1991]. Supercritical water oxidation (SCWO) was found to be an effective technique for the destruction of highly stable hazardous organics, such as polycyclic aromatic hydrocarbons (PAHs) [Kronholm 2002, Fang and Kozinski 2000a, 2001], dinitrotoluene [Kronholm 2002], 2-chlorophenol [Li et al. 1993b], dioxin [Modell 1992, Lin 2000], dichlorobenzene [Blaney 1995] and selected PCBs [Lin 2000, Jin 1992, Oe 1998, Hatakeda 1999]. It was found that 90% of PCBs in pulp and paper mill sludge [Blaney 1995], 99.99999% of selected 2-PCBs [Oe 1998], 99.999% of 3-PCB [Hatakeda 1999] and 99.95% of Aroclor 1248 (a mixture of ~76 PCB congeners) [Anitescu 2000] were decomposed using the SCWO process. However, the corrosion of the process reactor was severe when chloride-containing wastes were destroyed due to the formation of hydrochloric acid [Kriksunov 1995, Kim 2000, Kritzer 1998, Wagner 1999, Mitton 2000]. One of the methods to reduce corrosion is to neutralize the acid by adding NaOH and Na<sub>2</sub>CO<sub>3</sub>. Several authors reported that Na<sub>2</sub>CO<sub>3</sub> enhanced the oxidation of 2chlorophnol significantly while the corrosion was greatly reduced [Muthukumaran and Gupta 2000].

The phase behavior of 10-CB was previously studied in a diamond anvil cell (DAC) [Fang, Xu and Kozinski 2000b, 2000c]. The homogeneous phase of 10-CB in supercritical water was not observed due to decomposition and hydroxylation at temperatures up to 616°C. When 93% excess oxygen was applied, 100% 10-CB was converted at 450°C and 357MPa. It has been observed in the DAC that the addition of Na<sub>2</sub>CO<sub>3</sub> facilitated 10-CB oxidation in supercritical water, and 100% 10-CB was dissolved using 69.5% stoichiometric oxygen at 434°C and 125MPa.

In this dissertation, decachlorobiphenyl (10-CB;  $C_{12}Cl_{10}$ , molecular weight of 499, particle sizes < 500 µm) was studied with or without Na<sub>2</sub>CO<sub>3</sub>. A batch reactor (6 cm<sup>3</sup>) was used for the study of 10-CB destruction rate and the corrosion behavior of the reactor.

#### 7.1 Destruction Rate of 10-CB in a Batch Reactor

#### 7.1.1 Oxidation with less than stoichiometric O<sub>2</sub>

Six series of batch experiments were performed in the 6 ml batch reactors at  $450^{\circ}$ C and about 30 MPa without NaCO<sub>3</sub>, which are summarized in Table 7-1. The stoichiometric O<sub>2</sub> (mol%) is defined as the oxygen in mol% necessary for the complete oxidation of 10-CB according to the following reaction [Anitescu 2000]:

$$C_{12}Cl_{10} + 5 H_2O + 19/2 O_2 \rightarrow 12 CO_2 + 10 HCl$$
 (7-1)

Equation (7-1) summarizes more complex reactions other than it shows. It is clear that hydrogen necessary to form HCl is extracted from water molecules. In addition to  $O_2$ , water also supplies 5mol oxygen atoms to form  $CO_2$ . Thus, water acts as a reactant in Eq. (7-1).

Experimental data of Test 1 and 2 in Table 7-1, were collected at -36% excess  $O_2$  or 64% of the stoichiometric  $O_2$  required. As the reaction time was increased from 600 to 1200s, 10-CB conversion rate increased from 54.7 to 76.4%. However, only 26~29% Cl dissociated from 10-CB molecules. The dissociation of chlorine seemed to be stable from 600s to 1200s reaction time. The stabilization of chlorine concentrations indicated that the oxidation of 10-CB switched to the hydrolysis/transformation of 10-CB after 600s at -36% excess  $O_2$ . The analysis of the reaction products in the benzene sampling phases by GC-MS (GCQ. Thermo Quest/Finnigan) showed that there were twelve other products consisting

PCBs with low number of chlorine chlorobenzenes mainly of atoms, and chlorodibenzofurans (see Fig. 7-4). The analysis of ions in the aqueous phase gave 9.8 ppm and 7.2 ppm for HCOO<sup>-</sup>, 0.3 ppm and 0.9 ppm for CH<sub>3</sub>COO<sup>-</sup>, and 187.3 ppm and 168.2 ppm for CI according to the reaction times of 600s and 1200s, respectively. EDX spectrum (Fig. 7-1, Test 1) shows that the solid phases contain O, Fe, Cl, Si, and the traces of Cr. No Cr peak was detected in Test 2. EDX mapping demonstrates the presence of O and Fe in all areas of the sample, Cl and Si in abated parts of the sample and Cr in several small spots (Fig. 7-2), which suggests that one of the main components in the solid phase is  $Fe_xO_y$ . This is supported by comparing O and Fe distributions (Fig. 7-2, b and c). Silicon is in the form of  $SiO_2$  (Fig. 7-2, b and e).

|                         | Experiments Partial Oxidation in<br>SCW<br>Test 1 Test 2 |                                | Test 3 | Oxidatio<br>Test 4 | n in SCV<br>Test 5 | V<br>Test 6 |                                |
|-------------------------|--|--------------------------------|--------|--------------------|--------------------|-------------|--------------------------------|
| Conditions              | H <sub>2</sub> O <sub>2</sub> concentration              |                                |        |                    |                    |             |                                |
|                         | (wt%), 1mL   | 0.8                            | 0.8    | 2.5                | 2.5                | 3.3         | 4.2                            |
|                         | Excess $O_2$ (mol%)                                      | -36.0                          | -36.0  | 93.1               | 93.1               | 159.5       | 225.0                          |
|                         | Reaction time (s)  | 600                            | 1200   | 600                | 1200               | 1200        | 1200                           |
| Analysis<br>and Results | Benzene phase (10ml)                                     |                                |        |                    |                    |             |                                |
|                         | 10-CB conversion rate                                    | 54.7                           | 76.4   | 60.5               | 86.5               | 95.9        | 99.2                           |
|                         | (wt%)  |                                |        |                    |                    |             |                                |
|                         | Aqueous phase (11ml)                                     |                                |        |                    |                    |             |                                |
|                         | (HCOO) <sup>1-</sup> (ppm)                               | 9.8                            | 7.2    | 7.6                | 8.6                | 16.0        | 13.0                           |
|                         | (CH <sub>3</sub> OO) <sup>1-</sup> (ppm)                 | 0.3                            | 0.9    | 0.9                | 2.0                | 3.4         | 0.5                            |
|                         | Cl <sup>1-</sup> (ppm)                                   | 187.3                          | 168.2  | 323.6              | 426.6              | 570.0       | 620.4                          |
|                         | <sup>a</sup> Cl conversion (wt%)                         | 29.0                           | 26.0   | 50.0               | 66.0               | 88.1        | 95.9                           |
|                         | Solid phase  | O, Fe                          | O, Fe  | O, Fe              | O, Fe              | -           | O, Fe                          |
|                         | compositions by EDX                                      | Cl, Si                         | Cl, Fe | Si                 | Si                 | -           | Cr                             |
|                         | Mapping by EDX   | Fe <sub>x</sub> O <sub>y</sub> | -      | -                  | -                  | -           | Fe <sub>x</sub> O <sub>y</sub> |

Table 7-1 Experimental conditions and results in the batch reactor at 450°C and about 30 MPa

Note: <sup>a</sup> Cl conversion = (amount of  $Cl^{1-}$  in aqueous solution)/(total amount of Cl in feed 10-CB) x 100%



Figure 7-1 EDX Spectra of corrosive precipitates [Fang, Xu and Kozinski 2002c]



Figure 7-2 Energy dispersive X-ray spectrometric maps of solid phase from Test 1 [Fang, Xu and Kozinski 2002c]

#### 7.1.2 Oxidation with excess $O_2$

Oxidation of 10-CB was performed at 93% excess  $O_2$ . This concentration of  $O_2$  was selected because a complete dissolution of 10-CB was observed in the DAC at 450°C and less than 600s [Fang, Xu and Kozinski 2002b, 2002c]. The 10-CB conversion rate increased from 54.7% at -36% excess  $O_2$  to 60.5% at 93% excess  $O_2$  at 600s, and from 76.4% at -36% excess  $O_2$  to 86.5% at 93% excess  $O_2$  at 1200s, respectively (listed in Table 7-1). Cl conversion rate, defined as the Cl in 10-CB that is converted to water soluble Cl<sup>-</sup>, increased from 29% at -36% excess  $O_2$  to 50% at 93% excess  $O_2$  at 600s, and from 26% at -36% excess  $O_2$  to 66% at 93% excess  $O_2$  at 1200s, as seen in Table 7-1. In the solid phase, strong O and Fe peaks, very weak Si peaks and no Cl peak were detected with EDX (Fig. 7-1, Tests 3 and 4).

Solid phases obtained in the different tests were observed under a magnification of  $4000 \times$  with SEM. Needle-like crystals (Fig. 7-3a) were found, containing mainly Si, O and Fe, while hexagonal crystals were found mainly containing Fe and O after 600s reaction time (Test 3) (see Fig. 7-1). Cubic crystals (Fig. 7-3b) were obtained after 1200s reaction (Test 4), containing mainly O, Fe and trace amounts of Si (see Fig. 7-1). All crystals had strong Fe and O peaks, while little Cl and Cr were detected (Fig. 7-1). The needle-like crystals contained some Si that was most likely in the form of SiO<sub>2</sub>.

160% excess  $O_2$  was used to oxidize 10-CB for 1200s (Table 7-1), which gave 95.9% destruction rate of 10-CB. The Cl conversion rate increased from 66% in test 4 to 88.1% in test 5. A GC-MS spectrum (Fig. 7-4) of benzene phase showed that dinaphtho-furans, octaand nona-chlorobiphenyls, pentachlorobenzene and hexachlorodibenzofurans were still present. The spectra of intermediates indicated that a wide variety of PCBs was produced;
chlorinated benzenes were formed also after 10-CB was decomposed. However, chlorines still remain on most H positions of intermediates, which indicates that the dissociation of chlorine in 10-CB is extremely difficult at the experimental conditions. Hence, the dissociation of chlorine in PCBs actually determines the destruction rate of PCBs.

To completely destroy 10-CB, high excess  $O_2$  concentrations are likely required. Experiments were performed with 225% excess  $O_2$ , which is the same  $O_2$  concentration as that used in the DAC experiments [Fang, Xu and Kozinski 2002b, 2002c]. Reaction time was 1200s (Table 7-1, Test 6). A 99.2% of 10-CB was destroyed at these conditions. The Cl conversion rate reached its highest value among all experiments and was determined as 95.9%. The main components of the solid residues were Fe and O with sporadic inclusions of Cr as shown in Fig. 7-1. Cr appearing in residues indicated the intensified corrosion of the batch reactor.



Figure 7-3 SEM images (a): hexagonal and needle-like crystals (test 3); (b): cubic crystals (test 4) [Fang,

Xu and Kozinski 2002c]



Figure 7-4 Intermediate products identified by GC-MS from the Test 5 with 159.5% excess oxygen (Their structures are seen in Table 7-3)

# 7.1.3 Oxidation of 10-CB with Na<sub>2</sub>CO<sub>3</sub>

Na<sub>2</sub>CO<sub>3</sub> was added in order to neutralize HCl forming during the complete oxidation of 10-CB according to the following reaction:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$
(7-2)

#### Partial oxidation with -36.0 % excess $O_2$ (Test $1_c$ and $2_c$ )

In Table 7-2, data are listed from experiments performed at the same conditions (64% stoichiometric oxygen) when Na<sub>2</sub>CO<sub>3</sub> was used (Tests  $1_c$  and  $2_c$ ). This concentration is the same as the  $O_2$  concentration used in Test 1 and 2 (see Table 7-1). As the reaction time was increased from 600s to 1200s, the conversion rate of 10-CB rose from 95.6 to 98.3% (Test 1c vs. T<sub>c</sub>). The respective conversion rate without  $Na_2CO_3$  was 54.7 and 76.4% (Test 1 vs. 2). Thus, the addition of Na<sub>2</sub>CO<sub>3</sub> greatly enhanced the destruction rate. The yields of ion products in the 11.0 ml aqueous phase were 4.0 and 5.4 ppm of (CH<sub>3</sub>COO)<sup>-1</sup>, and 590.1 and 627.6 ppm of Cl<sup>-1</sup> for 600s and 1200s reaction time, respectively. No (HCOO)<sup>-1</sup> was detected. Most of the chlorine present in 10-CB was changed to Cl<sup>-1</sup> in the aqueous phase with conversion rates of 91.2% and 97.0% at 600s and 1200s time, respectively (the rates were 29.0% and 26.0% in the non-catalytic tests in Table 7-1). The conversions of chlorine and 10-CB were synchronous while the chlorine conversion without Na<sub>2</sub>CO<sub>3</sub> was much smaller than 10-CB's. It is clear that high destruction rates are due to Na<sub>2</sub>CO<sub>3</sub> addition, where NaCl precipitation from supercritical water reduced chlorine in the homogeneous phase, preventing reaction (7-10), (7-11), and (7-14) ~ (7-16) from left-forwarding. EDX data for Tests 1<sub>c</sub> and 2<sub>c</sub> indicated that the solid phase contained O, Fe, Si, Al and Na in Test 1<sub>c</sub>, while Al and Na peaks disappeared as the reaction time increased to 1200s (Test 2<sub>c</sub>). No Cl was present in the residue when Na<sub>2</sub>CO<sub>3</sub> was added [Fang, Xu and Kozinski 2002c]. It

indicated that chlorine was dissolved in water in the form of NaCl.

|             | View anima anta                             | Partial Oxida                    | tion in SCW         | Oxidation in SCW    |                     |                     |                                |  |  |
|-------------|---|----------------------------------|---------------------|---------------------|---------------------|---------------------|--------------------------------|--|--|
|             | Experiments                                 | <sup>b</sup> Test 1 <sub>c</sub> | Test 2 <sub>c</sub> | Test 3 <sub>c</sub> | Test 4 <sub>c</sub> | Test 5 <sub>c</sub> | Test 6 <sub>c</sub>            |  |  |
|             | H <sub>2</sub> O <sub>2</sub> concentration |                                  |                     |                     |                     |                     |                                |  |  |
| Conditions  | (wt%), 1mL                                  | 0.8                              | 0.8                 | 2.5                 | 2.5                 | 3.3                 | 4.2                            |  |  |
| Conditions  | Excess O <sub>2</sub> (mol%)                | -36.0                            | -36.0               | 93.1                | 93.1                | 159.5               | 225.0                          |  |  |
|             | Reaction time (s)                           | 600                              | 1200                | 600                 | 1200                | 1200                | 1200                           |  |  |
|             | Benzene phase (10ml)                        |                                  |                     |                     |                     |                     |                                |  |  |
|             | 10-CB conversion rate                       | 95.6                             | 98.3                | 97.6                | 99.7                | 100.0               | 100.0                          |  |  |
|             | (wt%)                                       |                                  |                     |                     |                     |                     |                                |  |  |
|             | Aqueous phase (11ml)                        |                                  |                     |                     |                     |                     |                                |  |  |
|             | (HCOO) <sup>1</sup> (ppm)                   | 0.0                              | 0.0                 | 0.0                 | 0.0                 | 0.0                 | 0.0                            |  |  |
|             | (CH <sub>3</sub> OO) <sup>1-</sup> (ppm)    | 4.0                              | 5.4                 | 2.5                 | 0.0                 | 0.0                 | 0.0                            |  |  |
| Analysis    | Cl <sup>1-</sup> (ppm)                      | 590.1                            | 627.6               | 601.5               | 645                 | 669.2               | 603.2                          |  |  |
| and Results | <sup>a</sup> Cl conversion (wt%)            | 91.2                             | 97.0                | 93.0                | 99.7                | 103.5               | 93.3                           |  |  |
|             | Solid phase                                 | O, Fe                            | O, Fe               | O, Fe               | O, Fe               | O, Fe               | O, Fe                          |  |  |
|             | Compositions by EDS                         | Al. Si                           | Si                  | Al. Cr              | Cr                  |                     | Cr                             |  |  |
|             |   | Na                               |                     | Si                  |                     |                     |                                |  |  |
|             | Mapping by EDX                              | -                                | -                   |                     | -                   | -                   | Fe <sub>x</sub> O <sub>y</sub> |  |  |

Note: <sup>a</sup> Cl conversion = ((amount of Cl<sup>1-</sup> in aqueous solution)/(total amount of Cl in feed 10-CB)) x 100% <sup>b</sup> Subscript 'c' indicates tests with Na<sub>2</sub>CO<sub>3</sub>; the order number of tests means the conditions were the same as the tests without Na<sub>2</sub>CO<sub>3</sub>. e.g. Test 1<sub>c</sub> has the same conditions as Test 1 in Table 7-1 except Na<sub>2</sub>CO<sub>3</sub>.

# Oxidation with 93.1, 159.5 and 225.0% excess $O_2$ plus $Na_2CO_3$ (Tests $3_c$ to $8_c$ )

In Tests 3<sub>c</sub> and 4<sub>c</sub>, 93.1% excess O<sub>2</sub> was used to decompose 10-CB in 600 and 1200s reaction time (see Table 7-2). The conversion rate of 10-CB increased to 97.6% in Test 3<sub>c</sub> (95.6% in Test 1<sub>c</sub>) and 99.7% in Test 4<sub>c</sub> (98.3% in Test 2<sub>c</sub>) at 600 and 1200s oxidation, respectively. The conversion rate of chlorine in 10-CB to Cl<sup>-1</sup> in the aqueous phase also increased to 93.0% (*vs.* 91.2%) and 99.7% (*vs.* 97%), respectively. As compared to the non-catalytic Tests 3 and 4 (see Table 7-1), the conversion rate of 10-CB increased by 61.3% (Test 3<sub>c</sub> *vs.* 3) and 15.3% (Test 4<sub>c</sub> *vs.* 4), while the conversion rate of Cl to Cl<sup>-1</sup> jumped by 86% and 51.1%, respectively. Si peak in Tests 4<sub>c</sub> disappeared while additional weak peaks of Cr in Tests 3<sub>c</sub> and 4<sub>c</sub> were detected with EDX.

In Tests 5<sub>c</sub> and 6<sub>c</sub>, more excess O<sub>2</sub> (159.5%, 225%) was used to oxidize 10-CB for 1200s (see Table 7-2). With 159.5% excess O<sub>2</sub>, 100% of 10-CB was converted in 1200s reaction time (95.9% for non-catalytic Test 5) without any detectable acetic and formic acid. Strong Fe and O peaks, weak Cr peak and very weak Si and Ni peaks were detected in the ash (Table 7-2). EDX mapping suggested the presence of  $FeO_x$  and an oxide form of Cr, Si and Ni.

In all catalytic tests only three isomers of octachloro-biphenyls (2,2', 3,3', 4, 5,5', 6,6'octachloro-1,1'-biphenyl, 2,2', 3,3', 4,4', 5, 6,6'-octachloro-1,1'-biphenyl, and 2, 3,3', 4,4', 5,5', 6,6'-octachloro-1,1'-biphenyl), in addition to 10-CB, were detected in the benzene phase *via* GC-MS (GCQ, Thermo Quest/Finnigan). However, twelve other products (mainly PCBs with low number of chlorine atoms, chlorobenzenes and chlorodibenzofurans) were found in the non-catalytic tests as seen in Fig. 7-4.

# 7.2 Phase Evolution, Hydrolysis and Oxidation in the Batch Reactor

The oxidation system in the batch reactor has much lower density (0.15~0.17g/cm<sup>3</sup>) than in the DAC (0.8~0.9g/cm<sup>3</sup>) [Fang, Xu, Kozinski 2002b, 2002c]. The phase evolution in the batch reactor is significantly different from that in the DAC. It was estimated using Peng-Robinson equation as used in "Reaction rates" of section 6.3.3 [Xu 2002b]. By solving those equations and using an interaction parameter  $\delta_{ij}$  = -1.85 for 1.11 mol% oxygen and 98.89 mol% water in 1.0 ml of 4.16 wt % H<sub>2</sub>O<sub>2</sub> solution (corresponding to 225% excess O<sub>2</sub> in Test 6 and 6<sub>c</sub>), the critical point of the water-oxygen system, 372°C and 22 MPa, was obtained. In the system of  $H_2O_2$ ,  $H_2O$  and 10-CB, the decomposition of  $H_2O_2$  started above 100°C and 1.0atm (0.101325MPa) in the reactor, and released all oxygen at 200°C and 120atm (12.1MPa) [Xu 2002a]. Since 10mg 10-CB was added in 1 ml 4.16% wt H<sub>2</sub>O<sub>2</sub> solution, 10-CB concentration in the reactor is less than 1 wt%, HCl concentrations is about 0.72 wt% (0.35 mol%) at the complete oxidation of 10-CB in the whole system. The critical point of HCl is at 51.4 °C, and 8.2 MPa. The mean critical temperature of HCl +  $(O_2 + H_2O)$  is estimated as 370°C since the properties of gaseous HCl molecule are similar to that of H<sub>2</sub>O and HCl is diluted. Pressure is calculated as 32.6 MPa at 450°C in the reactor using Peng-Robinson equation with the developed mixing rule (see section 5.2.2). The critical points of both HCl-H<sub>2</sub>O-O<sub>2</sub> and H<sub>2</sub>O-O<sub>2</sub> systems are much lower than 32.6 MPa at 450°C (CO<sub>2</sub> is not discussed since the molar number of CO<sub>2</sub>+O<sub>2</sub> is always equal to the initial molar number of O<sub>2</sub>, and CO<sub>2</sub> would not significantly alter the critical point in the discussed mixture [Mather and Franck 1992]). The homogenous conditions were obtained in the DAC at 434°C and 125 MPa with the addition of Na<sub>2</sub>CO<sub>3</sub> and 69.5% stoichiometric O<sub>2</sub> [Fang, Xu and Kozinski 2002b, 2002c]. The dielectric constant (ɛ) and hydrogen-bonding of water decreases with

decreasing pressure [Uematsu and Franck 1980, Hoffmann and Conradi 1997, Ikushima et al. 1998]. Therefore, supercritical water (SCW) in the batch reactor has a lower dielectric constant and weaker hydrogen-bonding at 32.6MPa and 450°C than at 434°C and 125 MPa in the DAC; it allows to dissolve organics more easily. Thus, the existence of supercritical fluid is confirmed at 32.6MPa and 450°C in either HCl-H<sub>2</sub>O-O<sub>2</sub> or H<sub>2</sub>O-O<sub>2</sub> system using the phase calculations. Lower dielectric constant and weaker hydrogen-bonding are expected in the batch reactor than that in the DAC [Fang, Xu and Kozinski 2002b, 2002c]. Similarly, the dissolution of 10-CB in the supercritical water-oxygen systems will be likely easier in the batch reactor. Hence, the oxidation of 10-CB is expected to take place in homogeneous phases.

Few reactions were observed when 10-CB underwent pyrolysis in 1200s at 450°C ('pyrolysis' refers to the case where no H<sub>2</sub>O and O<sub>2</sub> were presented) [Fang, Xu and Kozinski 2002b, 2002c]. This suggests that the destruction of 10-CB during SCWO was mainly *via* hydrolysis or homogeneous oxidation. In the non-catalytic partial oxidation, 10-CB was decomposed to compounds having C-H band at 3060 and O-H at 3451 and 3533 cm<sup>-1</sup>; the bands at 3060 and 3533 cm<sup>-1</sup> were due to hydrolysis while OH peak at 3451 cm<sup>-1</sup> was caused by oxidation. Therefore, simultaneous hydrolysis and oxidation reactions were occurring during the SCWO process [Fang, Xu and Kozinski 2002b, 2002c]. In the partial catalytic oxidation Test 2<sub>c</sub> (Table 7-2), using only 64% theoretical oxygen allowed destruction of 98.3% 10-CB (*vs.* 76.4% without Na<sub>2</sub>CO<sub>3</sub>). Some of 10-CB was decomposed *via* hydrolysis. Assuming that all O<sub>2</sub> was used to oxidize 10-CB according to Eq. (7-1), the destruction rate by hydrolysis rate by 177%. Thus, the homogenous hydrolysis of 10-CB was greatly

promoted by sodium carbonate. This is because the addition of  $Na_2CO_3$  promotes oxidation [Lee 2001] and hydrolysis [Jin 1992] of 10-CB to polar hydroxyl-containing compounds (e.g., acids, phenol), which subsequently dissolve in supercritical water due to their high affinity to  $H_2O_3$ .

The addition of  $Na_2CO_3$  was more effective for the destruction of 10-CB than increasing  $O_2$  concentration (Table 7-1 and 7-2). For example, the conversion rate increased to 98.3% by adding 100% theoretical amount of  $Na_2CO_3$  (Test 2<sub>c</sub>) from 76.4% in noncatalytic Test 2, as compared with an increase to only 86.5% when theoretical  $O_2$  rose to 93.1% excess  $O_2$  from -36% excess  $O_2$  (Test 4 *vs.* 2). In all catalytic tests only three isomers of octachloro-biphenyls (in addition to 10-CB), were detected while twelve other products were found in the non-catalytic tests. Addition of  $Na_2CO_3$  helped to precipitate Cl as NaCl from supercritical fluids. Hence, it inhibited the formation of intermediates. The enhancement of the reaction rate in the presence of  $NaCO_3$  was possibly by lowering the activation energy (e.g., from 11.5 kcal/mol without  $Na_2CO_3$  to 2.44 kcal/mol with  $Na_2CO_3$ for 2-chlorophenol) [Lee 2001, Muthukumaran 2000].

#### 7.3 The Corrosion of the Batch Reactor

Chlorine was found in the solid phase formed in non-catalytic Test 1 and 2 at inadequate amount of  $O_2$  (see Table 7-1). However, no chlorine was detected in all tests when Na<sub>2</sub>CO<sub>3</sub> was added, which indicates that chlorine was converted to the soluble chlorine (NaCl) even in the partial oxidation tests (Table 7-1 and 7-2: conversion rate to  $CI^{-1} = 91.2\%$  in Test 1<sub>c</sub> *vs.* 29% in Test 1). However, even in this case a small amount of metals was present in the solid phase (see Table 7-2). The presence of metals in the solid phase is due to the corrosion of the reactor (substantially larger corrosion was observed in the Na<sub>2</sub>CO<sub>3</sub>-free

tests).

Oxidation of chlorinated wastes in supercritical water could cause severe corrosion of the reactor because of acid-like SCW character [Muthukumaran 2000] and the formation of HCl. Addition of Na<sub>2</sub>CO<sub>3</sub> should neutralize the acidic solution. During the SCW incineration of 10-CB, the following overall reactions may occur:

$$\begin{array}{ll} \text{Me} + \text{yHCl} \rightarrow \text{MeCl}_{\text{y}} + \text{y/2 H}_2 & (7-3) [\text{Kriksunov 1995}] \\ \text{MeCl}_{\text{y}} + \text{H}_2\text{O} \rightarrow \text{Me}(\text{OH})_{\text{y}} + \text{y} \text{HCl} & (7-4) [\text{Smith 1997}] \\ \text{M}(\text{OH})_{\text{y}} \rightarrow \text{MO}_{\text{y/2}} + \text{y/2 H}_2\text{O} & (7-5) [\text{Smith 1997}] \\ \text{Me} + \text{x/2 O}_2 \rightarrow \text{MeOx} & (7-6) \end{array}$$

In reaction (7-3), metals (Me) are corroded to chloride MeCl<sub>y</sub> by HCl, which is the main product from the oxidation reaction (7-1). Metal hydroxides formed according to reaction (7-4) are dehydrated and form metal oxides according to reaction (7-5). Metal oxides could also be directly oxidized according to reaction (7-6). But this reaction was inhibited when a condense layer of oxides was formed on the reactor. If 100% stoichiometric Na<sub>2</sub>CO<sub>3</sub> was added, all the produced HCl in reaction (7-3) was neutralized and removed, according to reaction (7-2), to CO<sub>2</sub>, H<sub>2</sub>O, and NaCl (NaCl precipitated on the reactor's wall due to its low solubility in SCW). Thus, it enhanced the oxidation process. No corrosion is due to the formation of metallic compounds *via* reactions (7-4)-(7-5). However, reaction (7-3) would always take place due to the acid-like character of SCW and NaCl precipitation in SCW. Therefore, corrosion is unavoidable. However, the addition of excess Na<sub>2</sub>CO<sub>3</sub> helps to solve the problem by neutralizing the extra H<sup>+</sup> from SCW and providing a large surface area on the reactor's wall for the adsorption of the precipitated corrosive compounds since small Na<sub>2</sub>CO<sub>3</sub> particles (~1  $\mu$ m) were identified [Muthukumaran 2000].

# 7.4 Mechanisms of 10-CB Oxidation and Hydrolysis in SCW

In ambient solutions, solvents stabilize ions through the solvent solvation. Intermediates are formed *via* ionic dissociation while radicals are not stable. However, in gas phases, ionic intermediates are not stable. Instead, radicals are formed by evenly breaking chemical bonds. A threshold value of water density for completely disabling ionic dissociation is calculated as about 0.03~0.08 g/cm<sup>3</sup> using a model compound of t-BuCl (tertbutytl chloride) [Westacott 2001]. Above the threshold density, ionic and radical products may coexist. During PCBs oxidation in supercritical water, water density ranges from 0.2 to 0.7 g/cm<sup>3</sup>. The solvolysis of Cl<sup>-</sup> still stabilizes ionic intermediates like in ambient solutions. Therefore, it is believed that ionic and radical intermediates are both formed during PCBs decomposition in supercritical water. A number of PCBs and chlorinated alkanes were studied for their destruction in supercritical water [Yang 1988, Marrone 1995, Hatakeda 1997, Weber 2002, Lin 1998, 1999]. Ionic reactions were proposed in addition to possible radical reactions [Lin 1999]. Most of results showed a considerable hydroxylation of PCBs in supercritical water. A hydroxylation of 2,2', 4,4' 5,5'-hexa-CB follows a reaction containing Cl<sup>-</sup> abstraction [Weber 2002]:



Since nucleophilic substitution could proceed with either Cl<sup>-</sup> or OH<sup>-</sup>, Eq. (7-8) would be an equilibrium reaction. It is clear that Eq. (7-8) is an ionic reaction. However, the reaction for initial oxidation of 2,2', 4,4' 5,5'-hexa-CB was not given by Weber et al. [Weber et al.

2002]. Yang [Yang and Eckert 1988] proposed radical reactions to explain the initial oxidation of p-chlorophenol:



A radical Cl\* and a phenol radical are produced from Eq. (7-9). Subsequently p-chlorophenol is transformed to 1,4-benzoquinone by a series of radical reactions. Our SCWO results of 10-CB do not seem to support complete radical reactions because 5wt% 10-CB was slowly converted at more than 93% excess oxygen without Na<sub>2</sub>CO<sub>3</sub> (see Table 7-1). It is believed that radicals are partly inhibited in the system of 10-CB + O<sub>2</sub> + H<sub>2</sub>O because the hydrolyzed product HCl forms a strong ionic environment. Hence, the SCWO of 10-CB consists of both ionic and radical reactions. Intermediates in the SCWO of 10-CB without Na<sub>2</sub>CO<sub>3</sub> (shown in Table 7-3) come from both ionic and radical reactions. The mechanisms of 10-CB oxidation and hydrolysis in SCW are considered below. They are based on the analysis of the intermediate behavior in the SCWO of 10-CB.

In supercritical water, the hydroxylation of 10-CB is a single-molecule nucleophilic reaction ( $S_N1$ ) (which is confirmed by simulation using Hamiltonian equation and Molecular Dynamics (MD) [Westacott 2001], and explained in the SCWO of Hepta-CB [Weber 2002]).  $S_N1$  includes two reactions Eq. (7-10) and (7-11):



(7-10)

The reactive position is at one of position 2, 2', 6, 6' since they are affected by their neighbor ring. The dissociation of 10-CB produces Cl<sup>-</sup> and a cation of 9-CB. Cl<sup>-</sup> forms HCl by reacting with  $H^+$ . The 9-CB cation attracts OH<sup>-</sup> to form 2-hydroxyl-2', 3,3', 4,4', 5,5', 6, 6'-chloro-1,1'-biphenyl:



(7-11)

However, 2-hydroxyl-2', 3,3', 4,4', 5,5', 6, 6'-chloro-1,1'-biphenyl condenses to polychlorinated dibenzofuran (PCDF) (being found in relatively high amount as one of the intermediates):



When  $H_2O_2$  was used, both oxidation and hydroxylation were involved in the destruction of 10-CB. Several PCB isomers were identified in the products of 10-CB oxidation. The formation of 2,2',3,3',4,4',5',6,6'-nonachloro-1,1'-biphenyl was due to substituting Cl for H in 10-CB. Since  $H_2O$  is the only source of hydrogen, the substitution of Cl with H is believed to take place through radical reactions while the ionic hydroxylation results in phenol species (see Eq. (7-10) and (7-11)). First, the collision between molecules forms an activation complex:



The above complex decomposes to a 9-CB radical and a chlorine radical:

$$\begin{bmatrix} c_{i} & c_{i} & c_{i} \\ c_{i} & c_{i} & c_{i} \end{bmatrix}^{\#} \xrightarrow{c_{i}} c_{i} \xrightarrow{c_{i}} c_{i} \xrightarrow{c_{i}} c_{i} + c_{i} \xrightarrow{c_{i}} c_{i} \xrightarrow{$$

a HO<sub>2</sub> radical (HO<sub>2</sub> is a stable specie at high pressure) reacts with a 9-CB radical, forming 2,2',3,3',4,4',5',6,6'-nonachloro-1,1'-biphenyl (the detected intermediate):

$$\begin{array}{c} C_{1} \\ C_{2} \\ C_{1} \\$$

Cl\* finally combines with OH\* that is formed when HO<sub>2</sub>\* is formed:

$$Cl^* + HO^* \longrightarrow HClO \longrightarrow HCl + 0.5O_2$$
 (7-16)

Eq. (7-13) to Eq. (7-16) shows a way to substitute Cl for H and form HCl by extracting H atom from H<sub>2</sub>O. However, there are the reversible reactions of Eq. (7-14) to (7-16) if gaseous HCl is mixed with supercritical water and oxygen. They are responsible for the slow conversion rate in the SCWO of 10-CB without Na<sub>2</sub>CO<sub>3</sub>. The radical product of Eq. (7-14) may also react with O<sub>2</sub> forming quinone:

Further breaking and oxidation in Eq. (7-17) would produce chlorophenol. Besides the breaking reaction of (7-17), the hydroxylation products of 10-CB may break down according to the following reaction:



(7-18)



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Penrachlorobenzene is an intermediate with just half of 10-CB structure ( $\overset{()}{\circ}$  vs.  $\overset{()}{\circ} \overset{()}{\leftarrow} \overset{()}{\circ} \overset{()}{\leftarrow} \overset{()}{\circ}$  after breaking C-C bond connecting two rings as see in Table 7-3). Further oxidation of the product in Eq. (7-17) does not favor its formation. Hence, it is probably formed after the dissociation of C-C bond between two rings of 10-CB. Possible reactions are

proposed:



When Na<sub>2</sub>CO<sub>3</sub> is added to the SCWO system of 10-CB, Cl is precipitated as NaCl from the supercritical fluid phase, the reverse reactions of Eq. (7-10) to (7-11) and Eq. (7-13) to (7-16) are greatly disabled. Hence, the destruction rate of 10-CB is speeded up. Low number of intermediates (3 as compared to 12 without Na<sub>2</sub>CO<sub>3</sub>) and lower concentrations of intermediates (2,2', 3,3', 4, 5,5', 6,6'-octachloro-1,1'-biphenyl; 2,2', 3,3', 4,4', 5, 6,6'-octachloro-1,1'-biphenyl; 2,2', 3,3', 4,4', 5, 6,6'-octachloro-1,1'-biphenyl; and 2, 3,3', 4,4', 5,5', 6,6'-octachloro-1,1'-biphenyl) were identified; the formation of furans were greatly reduced since their concentrations were under the sensitivity of GC-MS. Hence, it is crucial to remove the chlorine from supercritical water phase during SCWO of PCBs in order to reduce secondary emissions.

| Compounds  | Structure | Molecular<br>weight                                     | Number |
|--|-----------|---|--------|
| S-tetrachlorobenzene                               | CI CI     | C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub><br>214    | fanna  |
| Penrachlorobenzene                                 |           | C <sub>6</sub> HCl <sub>5</sub><br>248                  | 2      |
| 2,3,4,5-tetrachlorophenol                          |           | C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub> O<br>230  | 3      |
| Dinaphtho[2,1-b:1',2'-d]furan                      |           | C <sub>20</sub> H <sub>12</sub> O<br>268                | 4      |
| Dinaphtho[1,2-b:1',2'-d]furan                      |           | C <sub>20</sub> H <sub>12</sub> O<br>268                | 5      |
| 2,2',3,3',4,5,5',6'-octachloro-<br>1,1'-biphenyl   |           | $\begin{array}{c} C_{12}H_2Cl_8\\ 426\end{array}$       | 6      |
| 2,2',3,4,4',5,6,6'-octachloro-<br>1,1'-biphenyl    |           | C <sub>12</sub> H <sub>2</sub> Cl <sub>8</sub><br>426   | 7      |
| 2,2',3,3',4,4',5,5'-octachloro-<br>1,1'-biphenyl   |           | $\begin{array}{c} C_{12}H_2Cl_8\\ 426\end{array}$       | 8      |
| 2,2',3,3',4,5',6,6'-octachloro-<br>1,1'-biphenyl   |           | C <sub>12</sub> H <sub>2</sub> Cl <sub>8</sub><br>426   | 9      |
| 2,2',3,3',4,4',5,6,6'-<br>nonachloro-1,1'-biphenyl |           | C <sub>12</sub> HCl9<br>460                             | 10     |
| 2,3,4,6,7,8-<br>Hexachlorodibenzofuran             |           | C <sub>12</sub> H <sub>2</sub> Cl <sub>6</sub> O<br>372 | 11     |
| 1,2,3,4,6,7,8-<br>hexachlorodibenzofuran           |           | C <sub>12</sub> HCl <sub>7</sub> O<br>406               | 12     |
| 2,3,3',4,4',5,5',6,6'-<br>nonachloro-1,1'-biphenyl |           | C <sub>12</sub> HCl <sub>9</sub><br>460                 | 13     |
| Octachlorodibenzofuran                             |           | C <sub>12</sub> Cl <sub>8</sub> O<br>440                | 14     |

# Table 7-3 Structures and formulas of intermediates in the SCWO of 10-CB without Na<sub>2</sub>CO<sub>3</sub>

# 8 SUPERCRITICAL WATER OXIDATION OF DE-INKING SLUDGE

# **RESIDURE (DISR)**

Previous research of supercritical water oxidation (SCWO) of de-inking sludge residue (DISR) showed that 99.2% of carbon, 99.86% of benzo(*a*)pyrene, and 100% of naphthalene in the DISR were converted within 300s [Fang and Kozinski 2000a]. The complete dissolution of cellulose (the main organic component of the DISR) in supercritical water was observed to a homogeneous phase of the mixture [Fang and Kozinski 2000a]. Therefore, the SCWO of cellulose-based sludge takes place in a supercritical fluid phase, where kinetic-controlled reactions dominate the SCWO process.

Cellulose is the main organic component in the DISR. It is polymerized glucoses. The supercritical water hydrolysis of cellulose mainly produces glucose and other light molecule compounds [Sasaki et al. 1998] through the following depolymerization:



In the previous experiments conducted in the diamond anvil cell (DAC), cellulose was fed with pure water. The DAC was subsequently heated up to 479.9°C and 636.3MPa. Cellulose was found to dissolve completely in supercritical water at 329.5°C and 435.1MPa, forming a homogeneous phase [Fang and Kozinski 2000a]. When the temperature was raised up to 479.9°C, and the pressure to 636.3MPa, precipitates (glucose and oligomers) occurred from the solution of water-cellulose. These precipitates were formed because of the hydrolysis of cellulose [Sasaki et al. 1998]. The precipitation

indicates that hydrolysis products, glucose and oligomers, likely have lower solubility in supercritical water than cellulose.

In this work, the de-inking sludge residue (the DISR), doped with heavy metals Cd, Pb and Cr, were oxidized in supercritical water (heavy metals were added in order to investigate easily their behavior at high concentrations, also enable to design concentrations of heavy metals in experimental matrix). Gases, aqueous phase and solid residues were analyzed, and results are presented. The evolution of metals and the interaction between components of the DISR are discussed. The feasibility of SCWO of sludge is confirmed.

#### 8.1 Gaseous Products of SCWO of De-inking Sludge Residue

A mixture of 2000ppm Cr, 2000ppm Cd, and 2000ppm Pb was doped into the DISR before their oxidation in supercritical water. The final concentration of lead was 2080 ppm, cadmium 2030 ppm, and chromium 2080 ppm. Experiments were carried out in the batch reactor. Gaseous samples were collected and analyzed by GC-TCD (HP4890). GC spectra of gaseous samples indicated that the main products were  $CO_2$ ,  $N_2$ , and excess  $O_2$  (>99.0%). Trace amounts of CO, CH<sub>4</sub> and H<sub>2</sub> were also detected (each <0.3% yield). More than 99% of organic carbon was converted to  $CO_2$  in the experiments.

Heterogeneous atoms in the DISR are chlorine, sulfur, nitrogen and silicon. During the SCWO of the DISR, chlorine is transformed to chloride, sulfur to sulfate, nitrogen to nitrogen gas and silicon is present in the form of silica [Modell 1982]. Recently, the formation of NO<sub>x</sub> and NH<sub>3</sub> was reported during the supercritical water oxidation of Ncontaining organics (e.g. pyridine) if heterogeneous catalysts (MnO<sub>2</sub>/CeO<sub>2</sub>, Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and  $MnO_2//\gamma$ -Al<sub>2</sub>O<sub>3</sub>) were used [Aki and Abraham 1999, Ding et al. 1998]. However,  $NO_x$  and  $NH_3$  were not detected though heavy metal oxides and salts, which might be catalysts for the SCWO of the DISR, were present in our experiments (heavy metal cations would help electrons transfer [Mao 1997]. Instead, nitrate, which was introduced with the doped heavy metals, mainly remained in aqueous phases during the SCWO of the DISR.

#### 8.2 TOC and Anions Level in SCWO of DISR

During the SCWO of the DISR, aqueous phases and acetone phases were collected and analyzed using GC-MS, ICP, TOC and IC (instrumental details are seen in Chapter 4). Results are seen in Table 8-1 [Fang, Xu and Kozinski 2000c]. GC-MS spectra of the acetone phase samples revealed that 0.07% (in yield) of  $C_{10}$ - $C_{50}$  aliphatic hydrocarbons was released [Fang and Kozinski 2000a]. No PAHs and no monocyclic aromatic hydrocarbons were detected. TOC level in aqueous phases is shown in Table 8-1 and its trend is shown in Figure 8-1. After 300s residence time, less than 2% organic carbon stayed in aqueous phases, more than 98% of carbon in the DISR was converted into CO<sub>2</sub>. Acetate was identified as an intermediate, the oxidation of which is a rate-controlled step. Acetate concentrations reached as low as 0.5% at 525°C, 30.6MPa after 1800s (see Table 8-1). However, its trend is not clear vs. residence like the trend of the TOC level (see Figure 8-2).

Concentrations of anions and pH values are shown in Table 8-1. The effluents from the SCWO of the DISR were acidic (pH ranging from 3 to 6) even after 1800s residence time in the batch reactor (see Table 8-1). Chloride levels in aqueous phases ranged from 0 to 0.2wt% (see Table 8-1). They correspond to chloride composition in the

DISR. Sulfate concentrations were from 0.16 to 0.40 wt% (see Table 8-1), at the same level of sulfur in the DISR (see Table 8-1 and Table 3-1). Both the levels and forms of chloride and sulfate were stabilized with temperature and residence time. The results indicated that all chlorine and sulfur were converted to chloride and sulfate in about 300s residence time. Up to 50wt% nitrate was determined in aqueous phases (the majority of it was from the nitrate doping). After 1800s residence time, nitrate was still in the aqueous phase.



**TOC vesus Residence time** 





Figure 8-2 Acetate in aqueous phases during the SCWO of the DISR Note: excess O<sub>2</sub> in mol percent, all the same in Chapter 8

|   |                       |       |      | a     | Prod | ucts i  | n aque  | eous     | phase    | (% wt. r | netals  | in starti | ng materia | al)    |       | lea<br>(%v | Ash<br>chabi<br>vt me | lity<br>tal) |
|---|-----------------------|-------|------|-------|------|---------|---------|----------|----------|----------|---------|-----------|------------|--------|-------|------------|-----------------------|--------------|
| Experiments Cd Pb Cr Al Ca Na Si          |                       |       |      |       | тос  | acetate | pН      | chloride | sulphate | chromate | nitrate | Cd        | Pb         | Cr     |       |            |                       |              |
| 30.6MPa<br>450°C<br>O <sub>2</sub> =17.1% | run<br>time<br>(min.) |       |      |       |      |         |         |          |          |          |         |           |            |        |       |            |                       | :            |
| Run 1                                     | 5                     | 7.82  | 0.03 | 4.07  | 0.04 | 14.40   | 20.36   | 0.46     | 0.34     | 0.25     | 5.66    | 0.13      | 0.39       | 12.44  | 10.04 | 6.78       | 7.27                  | 0.37         |
| Run 2                                     | 10                    | 10.64 | 0.81 | 1.96  | 0.35 | 19.04   | 15.26   | 1.15     | 2.01     | 6.26     | 3.74    | 0.06      | 0.30       | 4.54   | 14.76 | 2.52       | 1.55                  | 0.40         |
| Run 3                                     | 15                    | 4.10  | 0.03 | 12.06 | 0.06 | 12.27   | 8.60    | 0.82     | 1.22     | 0.36     | 4.74    | 0.06      | 0.22       | 30.84  | 6.70  | 2.83       | 2.08                  | 0.86         |
| Run 4                                     | 20                    | 9.68  | 0.00 | 18.14 | 0.13 | 13.76   | 9.03    | 1.38     | 0.18     | 0.12     | 5.82    | 0.09      | 0.33       | 51.80  | 1.41  | 4.14       | 1.59                  | 0.79         |
| Run 5                                     | 30                    | 10.69 | 0.00 | 19.24 | 0.14 | 13.83   | 12.78   | 0.94     | 0.15     | 0.12     | 5.44    | 0.08      | 0.31       | 60.71  | 16.08 | 4.70       | 0.59                  | 0.72         |
| 30.6MPa<br>450°C<br>O <sub>2</sub> =65.7% | run<br>time<br>(min.) |       |      |       |      |         |         |          |          |          |         |           |            |        |       |            |                       |              |
| Run 6                                     | 5                     | 7.60  | 0.24 | 15.03 | 0.26 | 18.80   | 19.00   | 1.31     | 24.87    | 2.78     | 4.21    | 0.10      | 0.30       | 80.30  | 24.99 | 2.81       | 2.71                  | 1.08         |
| Run 7                                     | 10                    | 7.64  | 0.00 | 15.24 | 0.02 | 15.83   | 15.00   | 0.18     | 0.18     | 0.11     | 5.70    | 0.09      | 0.32       | 51.15  | 15.76 | 4.03       | 1.62                  | 0.73         |
| Run 8                                     | 15                    | 14.49 | 0.00 | 37.53 | 0.26 | 18.99   | 17.04   | 1.72     | 0.45     | 0.06     | 4.70    | 0.10      | 0.34       | 105.26 | 38.92 | 3.09       | 1.20                  | 1.01         |
| Run 9                                     | 20                    | 10.00 | 0.00 | 32.00 | 0.16 | 16.00   | 10.13   | 1.76     | 0.65     | 0.12     | 5.03    | 0.09      | 0.32       | 89.13  | 13.63 | 1.82       | 0.90                  | 0.64         |
| Run 10                                    | 25                    | 8.79  | 0.00 | 21.71 | 0.27 | 18.68   | 16.11   | 1.84     | 0.38     | 0.10     | 4.25    | 0.10      | 0.32       | 60.25  | 47.98 | 1.54       | 0.88                  | 0.78         |
| Run 11                                    | 30                    | 9.25  | 0.57 | 12.58 | 0.25 | 23.27   | 18.89   | 0.95     | 1.63     | 4.83     | 4.96    | 0.09      | 0.30       | 0.00   | 25.72 | 2.68       | 2.55                  | 1.29         |
| 30.6MPa<br>525°C<br>O <sub>2</sub> =65.7% | run<br>time<br>(min.) |       |      |       |      |         |         |          |          |          |         |           |            |        |       |            |                       |              |
| Run 12                                    | 5                     | 4.74  | 0.00 | 26.13 | 0.22 | 20.55   | 21.97   | 1.23     | 0.48     | 0.43     | 4.97    | 0.15      | 0.32       | 81.56  | 34.00 | 2.98       | 1.42                  | 1.12         |
| Run 13                                    | 10                    | 4.78  | 0.00 | 33.39 | 0.22 | 22.44   | 14.54   | 1.26     | 0.63     | 0.08     | 4.88    | 0.10      | 0.31       | 100.67 | 42.22 | 0.86       | 0.67                  | 0.52         |
| Run 14                                    | 15                    | 3.73  | 0.00 | 27.70 | 0.19 | 18.96   | 12.66   | 1.09     | 0.33     | 0.04     | 4.70    | 0.08      | 0.29       | 73.24  | 34.59 | 0.97       | 1.11                  | 0.85         |
| Run 15                                    | 20                    | 2.76  | 0.00 | 33.05 | 0.16 | 18.70   | 20.41   | 1.06     | 0.68     | 0.37     | 5.17    | 0.20      | 0.34       | 92.46  | 20.74 | 1.24       | 1.21                  | 1.43         |
| Run 16                                    | 30                    | 2.44  | 0.00 | 12.73 | 0.12 | 14.00   | ) 11.14 | 0.85     | 0.51     | 0.27     | 5.00    | 0.13      | 0.30       | 33.51  | 20.83 | 0.60       | 0.47                  | 0.76         |
| Run 17                                    | 30                    | 81.99 | 0.03 | 79.4  | 0.59 | 28.4    | 13.6    | 1.63     | 0.31     | 0.00     | 3.1     | 0.06      | 0.16       | 133.43 | 39.79 | -          | -                     | -            |

| Table 8-1 Summary of results obtained during the supercritical water oxidation of the DISR doped | 1 |
|--|---|
| with a mixture of Cd, Pb and Cr  |   |

Note: <sup>a</sup>  $O_2$  is the excess oxygen to organics; No Cd, Pb, Cr were detected in acetone phase; Data for TOC, acetate, chloride and sulphate are based on the weight of the DISR; Chromate is determined based on Cr weight base; Run 17: 20,000 mg/kg heavy metals (9 times higher concentration of Cd, Pb and Cr than in other runs).

The SEM image in Figure 4-2 shows that some cellulose fibers are bound inside inorganic residues (organics inside inorganic lumps – called "inside organics"). During the SCWO oxidation, oxygen would have to diffuse into inorganic barriers in order to oxidize "inside organics". Hence, the destruction rates of "inside organics" were slowed and controlled by the diffusion rates through the inorganic barriers, which resulted in unclear trends of acetate concentrations and TOC levels (*vs.* residence time and temperature) (see Figure 8-1 and 8-2).

### 8.3 Behavior of Heavy Metal and Inorganic Ashes

Heavy metals are important hazardous components of the DISR. Their behavior affects oxidation of organics in the DISR, and determines the quality of effluents from supercritical water oxidation (SCWO) processes. A set of experiments (in addition to the experiments in Table 8-1) was carried out to determine their behavior during SCWO.

#### 8.3.1 Heavy metals in DISR

Tests, where the DISR was oxidized without adding heavy metals, were conducted at 17%-excess-O<sub>2</sub>-450°C and 65%-excess-O<sub>2</sub>-525°C for 300s and 1800s. The analysis of aqueous samples and ash indicated that about 97 ppm Cr, 343 ppm Cd and 493 ppm Pb were present in the DISR (see Table 8-2) [Xu et al. 2002]. Variations in the concentrations of heavy metals in different the DISR samples are probably due to heterogeneity of distribution of inorganic compounds in the DISR. At 450°C, 0.10 ppm Cr in the DISR was detected in the aqueous phase while more than 1 ppm Cr was present at 525°C. It seems that higher temperature promotes Cr presence in the aqueous phase. Pb and Cd data show that the effect of temperature on Pb and Cd distribution is almost negligible at low concentrations of heavy metals when no heavy metals are added to the DISR.

|             |   |        |                               |                           | Aqueous Phase (ppm)<br>ased on DISR weight) |      |       | Ashes (ppm ) (based on<br>DISR weight) |        |        |  |  |
|-------------|---|--------|-------------------------------|---------------------------|---|------|-------|--|--------|--------|--|--|
| Time (s)    | Metals  | T( °C) | <sup>a</sup> Excess<br>O2 (%) | <sup>b</sup> TOC<br>(wt%) | Cd  | Pb   | Cr    | Cd                                     | Pb     | Cr     |  |  |
| 300         | Not added   | 450    | 17.00                         | 1.40                      | 41.91                                       | 1.09 | 0.09  | 306.44                                 | 455.70 | 82.73  |  |  |
| 1800        | Not added   | 450    | 17.00                         | 0.40                      | 8.40  | 1.43 | 0.08  | 386.83                                 | 470.42 | 71.23  |  |  |
| 300         | Not added   | 525    | 65.00                         | 0.42                      | 13.04                                       | 2.20 | 28.34 | 339.29                                 | 518.08 | 69.45  |  |  |
| 1800        | Not added   | 525    | 65.00                         | 0.38                      | 11.89                                       | 2.70 | 1.15  | 264.17                                 | 521.47 | 136.59 |  |  |
| Average     |   |        |                               |                           | 18.81                                       | 1.86 | 7.42  | 324.18                                 | 491.42 | 90.00  |  |  |
| Metals in 1 | Metals in DISR: 343 ppm Cd, 493 ppm Pb, 97 ppm Cr |        |                               |                           |   |      |       |  |        |        |  |  |

Table 8-2 Heavy metals determined in the DISR (no metals added)

Note:  ${}^{a}O_{2}$  is the excess oxygen to organics (calculated excess oxygen based on the DISR in reference [Fang, Xu and Kozinski 2000c]. It is the same in other tables.  ${}^{b}$  TOC was based on the weight of the DISR

# 8.3.2 SCWO of DISR doped with a single heavy metal

Oxidation tests of the DISR in supercritical water were conducted after a single heavy metal (Pb, Cr, or Cd respectively; each at 2000ppm concentration) was added to the DISR. After doping, the concentration of Cr, Cd and Pb was 2097ppm, 2343ppm, 2493ppm, respectively. Compared to the SCWO results of the mixture of three heavy metals with the DISR, where only up to 10 % Cd, 0.3% Pb and 37.5 % Cr were retained in aqueous phases (see Table 8-1) [Fang, Xu and Kozinski 2000c], higher percentage of Cd & Pb (up to 59.4% Cd, 31.2% Pb) and similar concentration of Cr (30.5%) were present in aqueous phases (see Table 8-3). This comparison suggests that interaction between Cd, Pb and Cr helps to precipitate Cd and Pb. For example, Pb reacted with CrO<sub>4</sub><sup>2-</sup> to form PbCrO<sub>4</sub> precipitate [Fang, Xu and Kozinski 2000c]; without the presence of CrO42<sup>2-</sup> to precipitate Pb as PbCrO4, it stayed in an aqueous solution. Cd was precipitated as CdO and CdCl<sub>2</sub>•4Cd(OH)<sub>2</sub> during SCWO of the DISR. In the SCWO of the DISR doped with Cd only, chloride was easily oxidized to ClO4 without the competition of Cr oxidation by O<sub>2</sub> at 450°C (the competitive oxidation between Cr and Cl appeared during the SCWO of the DISR mixed with a mixture of Pb, Cd, and Cr) (see Figure 8-7) [Lees 1979]. Thus, a part of Cd reacted with ClO<sub>4</sub><sup>-</sup> forming soluble  $Cd(ClO_4)_2$ , present in aqueous phase [Aylett 1973].

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|              |                |           | -                | Prod                     | ucts in | aqueous | phases     | Products in solid phases |         |         |       |                        |
|--------------|----------------|-----------|------------------|--------------------------|---------|---------|------------|--------------------------|---------|---------|-------|------------------------|
|              |                |           |                  | (wt%)                    | (based) | on weig | ht of feed | (wt%                     | ) (base |         |       |                        |
|              |                |           |                  | materials <sup>a</sup> ) |         |         |            |                          | feed n  |         |       |                        |
| Time<br>(s). | Metal<br>added | Т<br>(°С) | Excess<br>O2 (%) | TOC<br>(wt%)             | Cd      | Pb      | Cr         | Cd                       | Pb      | Ni (mg) | Cr    | Mass balance<br>in wt% |
| 300          | Cr             | 450       | 17               | 5.43                     |         |         | 3.44       |                          |         | 5E-03   | 81.90 |                        |
| 1800         | Cr             | 450       | 17               | 0.51                     |         |         | 9.60       |                          |         | 1E-02   | 78.83 | 88.43                  |
| 300          | Cr             | 450       | 65               | 2.16                     |         |         | 3.76       |                          |         | 1E-02   | 63.98 | 67.75                  |
| 1800         | Cr             | 450       | 65               | 0.40                     |         |         | 21.86      |                          |         | 2E-03   | 74.34 | 96.20                  |
| 300          | Cr             | 525       | 65               | N.A.                     |         |         | 5.90       |                          |         | 6E-03   | 66.64 | 72.54                  |
| 1800         | Cr             | 525       | 65               | 3.59                     |         |         | 30.51      |                          |         | 6E-03   | 49.49 | 80.00                  |
| 300          | Pb             | 450       | 17               | 0.29                     |         | 1.79    |            |                          | 76.06   | 1E-02   |       | 77.85                  |
| 1800         | Pb             | 450       | 17               | 0.33                     |         | 0.04    |            |                          | 84.33   | 3E-03   |       | 84.37                  |
| 300          | Pb             | 450       | 65               | 1.19                     |         | 15.36   |            |                          | 85.95   | 5E-03   |       | 101.32                 |
| 1800         | Pb             | 450       | 65               | 0.22                     |         | 9.90    |            |                          | 86.88   | 2E-02   |       | 96.78                  |
| 300          | Pb             | 525       | 65               | 0.23                     |         | 31.17   |            |                          | 75.57   | 1E-02   |       | 106.74                 |
| 1800         | Pb             | 525       | 65               | 0.16                     |         | 18.50   |            |                          | 89.88   | 4E-02   |       | 108.38                 |
| 300          | Cd             | 450       | 17               | 1.06                     | 20.76   |         |            | 94.48                    |         | 7E-03   |       | 115.24                 |
| 1800         | Cd             | 450       | 17               | 0.16                     | 35.60   |         |            | 82.35                    |         | 1E-02   |       | 117.95                 |
| 300          | Cd             | 450       | 65               | 0.19                     | 59.44   |         |            | 31.25                    |         | 9E-03   |       | 90.69                  |
| 1800         | Cd             | 450       | 65               | 0.76                     | 49.96   |         |            | N.A.                     |         | 6E-03   |       | N.A.                   |
| 300          | Cđ             | 525       | 65               | 0.21                     | 50.14   |         |            | 46.61                    |         | 6E-03   |       | 96.75                  |
| 1800         | Cd             | 525       | 65               | 0.17                     | 25.60   |         |            | 91.89                    |         | 1E-02   |       | 117.48                 |

# Table 8-3 Metals in aqueous and solid phases during the SCWO of the DISRmixed with a single metal

Note: <sup>a</sup> feed materials were calculated as a sum of 2000 ppm doped plus the initial concentration of the heavy metal in DISR.

### 8.3.3 Chromium, ash and nitrate in SCWO of naphthalene

A mixture of 50 mg naphthalene and 20 mg Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O (about 1940 ppm Cr in total feed materials) with 100 mg Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> representing ash, plus 1 ml 49% hydrogen peroxide was experimented in the batch reactor. Cr and nitrate were quickly removed between 20°C and 350°C. Both 99.95% of Cr and 99.67% of nitrate were removed simultaneously from aqueous phases at 358.8°C and 233.5 atm (23.7MPa) (see Fig. 8-3). Decomposition of chromium nitrate was documented when the reaction was catalyzed by organics [Field 1964]:

$$4Cr(NO_3)_3 \rightarrow 2Cr_2O_3 + 2N_2 + 15O_2$$
 (8-1)

According to Eq. (8-1), most of nitrogen in the system was probably converted to nitrogen gas since it was not found in both solid and aqueous phases after 1800s residence time. NO<sub>x</sub> was not formed probably because the temperature ( $\leq 450^{\circ}$ C) was not high enough (NO<sub>x</sub> is normally formed above 1100°C). The removal of Cr<sup>3+</sup> from the aqueous phase was due to precipitation of Cr<sub>2</sub>O<sub>3</sub> (see Equation (8-1). Since organics, such as naphthalene and its intermediates, catalyzed reaction (8-1) [Field 1964], the decomposition of nitrate salt started below 100°C and Cr started precipitating out (see Figure 8-3).



Figure 8-3 Nitrate and  $Cr^{3+}$  profiles during the SCWO of 50mg Nap + 20mg Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O+100mg Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> + 1 ml 49wt% H<sub>2</sub>O<sub>2</sub>

Comparing the behavior of Cr and nitrate in the SCWO of the DISR with that in the SCWO of naphthalene, it was found that the removal of Cr and nitrate from the aqueous phase was reduced during the SCWO of the DISR. It was likely because a more acidic solution was formed during the DISR oxidation in supercritical water (pH= 3~6 for the SCWO of the DISR vs. pH =5~7 for the SCWO of naphthalene).

# 8.3.4 XRD results and morphology of ash

Ash samples were collected from the SCWO of the DISR and naphthalene, and were then analyzed by X-ray diffractometer after drying the samples at room temperature (DMAX III Rigaku rotating anode diffractometer, Japan). Their XRD spectra are seen in Figure 8.4 [Xu et al. 2002]. Profile "I" in Fig.8.4 shows several peaks of  $Cr_2O_3$  and  $CrO_2$ in the ash from the SCWO of 50 mg naphthalene + 1.0ml 49wt% H<sub>2</sub>O<sub>2</sub> + 20mg  $Cr(NO_3)_3 \bullet 9H_2O$ . This profile confirms the formation of  $Cr_2O_3$  and  $CrO_2$  due to decomposition of  $Cr(NO_3)_3$ .

Green-colored Cr<sub>2</sub>O<sub>3</sub> was also found when CrO<sub>4</sub><sup>2-</sup> reacted with naphthalene at  $394^{\circ}$ C & 297 atm (30.4MPa) during the supercritical water oxidation of 50 mg Nap + 10 mg K<sub>2</sub>CrO<sub>4</sub> + 0.92 ml H<sub>2</sub>O + 50 mg (SiO<sub>2</sub>)<sub>1.37</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.093</sub>(Na<sub>2</sub>O)<sub>0.127</sub> (Aluminum Silicate Synthetic: ASS). Amorphous ASS did not reveal any crystallization after 1800s of SCWO; Cr<sub>2</sub>O<sub>3</sub> did not raise peaks due to its low concentration as seen in the profile "IV" of Fig.8.4. The same phenomenon was observed in the SCWO of 50 mg naphthalene + 1.0ml 49wt% H<sub>2</sub>O<sub>2</sub> + 20mg Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O +100mg Kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) and the system of 50 mg naphthalene + 1.0ml 49wt% H<sub>2</sub>O<sub>2</sub> + 20mg Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O +100mg kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), in which no change was observed in the XRD spectra of kaolin.

It is clear that supercritical water and supercritical water oxidation have no effect on simulated ash of crystalline kaolin and amorphous aluminum silicate synthetic because these two compounds do not participate in SCWO reactions.

The solid residue obtained from the SCWO of the DISR has the same morphology as kaolin (see Fig.8.5 and 8.6). Chemical analysis of particle "a" shows the presence of O, Al and Si, which is in agreement with the chemical analysis of particle "b" of kaolin. Therefore, it is further confirmed that the ash formed in the SCWO of the DISR is dominated by Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> (kaolin) (first identified in [Fang, Xu, and Kozinski 2000c]). Most of kaolin in Nap+kaolin+O<sub>2</sub>+water system has 2  $\mu$ m crystal sizes, smaller than the kaolin obtained from the SCWO of the DISR (see Figure 8-5). This is because kaolin forms aggregate due to the binding of cellulose fibers in the DISR [Xu et al. 2002]. It was observed that Cr<sub>2</sub>O<sub>3</sub> and CrO<sub>2</sub> precipitate as fine particles with sizes up to 8  $\mu$ m in Cr(NO<sub>3</sub>)<sub>3</sub>+Nap+O<sub>2</sub>+H<sub>2</sub>O system. Chemical analysis of particle "c" shows the presence of only O and Cr (Al and Si come from impurities during sample collection), which is in agreement with the composition of Cr<sub>2</sub>O<sub>3</sub> and CrO<sub>2</sub>. This result was supported by the XRD profile "I" in Fig.8.4.



#### Figure 8-4 XRD spectra of ashes

Note: I: ash was collected after SCWO of a system: 50 mg naphthalene + 1.0ml 49wt% H<sub>2</sub>O<sub>2</sub> + 20mg Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O, 1500s residence time II: ash was collected after SCWO of a system: 50 mg naphthalene + 1.0ml 49wt% H<sub>2</sub>O<sub>2</sub> + 20mg Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O + 100mg Kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), 1800s residence time

- III: ash was collected after SCWO of a system: 50 mg naphthalene + 1.0ml 49wt% H<sub>2</sub>O<sub>2</sub>
   +100mg Kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), 1800s residence time
- IV: ash was collected after SCWO of a system: 50 mg Nap + 10 mg  $K_2CrO_4$  + 0.92 ml  $H_2O$  + 50 mg  $(SiO_2)_{1.37}(Al_2O_3)_{0.093}(Na_2O)_{0.127}$  (Aluminum Silicate Synthetic), 0s residence time



Figure 8-5 Chemical analysis and morphology of ashes of the SCWO of the DISR



Figure 8-6 Morphology and chemical analysis of kaolin (particle "b") and chromium oxides (particle "c") (Kaolin in the system of 50 mg naphthalene + 1.0ml 49wt% H<sub>2</sub>O<sub>2</sub> +100mg Kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) (Nap+kaolin+O<sub>2</sub>+water); chromium oxides in the system of 50 mg naphthalene + 1.0ml 49wt% H<sub>2</sub>O<sub>2</sub> + 20mg Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O (Cr(NO<sub>3</sub>)<sub>3</sub>+Nap+O<sub>2</sub>+H<sub>2</sub>O))

# 8.3.5 Reactions during the evolution of heavy metals

It was found that  $CrO_4^{2-}$ ,  $Cr_2O_3$  and  $CrO_2$  appeared in different SCWO systems. In order to understand their inter-transformation, a set of reactions is proposed based on our own data and literature. After  $Cr(NO_3)_3$  decomposed to form  $Cr_2O_3$  via organic catalytic reaction (see equation (8-1),  $Cr_2O_3$  was oxidized to  $H_2CrO_4$  by reacting with  $H_2O_2$  or  $O_2$ when temperature was above  $100^{\circ}C$  [Rollinson 1973]:

$$Cr_2O_3 + 3H_2O_2 \rightarrow 2H_2CrO_4 + H_2O \text{ or } 2Cr_2O_3 + 3O_2 + 4H_2O \rightarrow 4H_2CrO_4$$
 (8-2)

Above 197°C (the dehydration point of CrO<sub>3</sub>), H<sub>2</sub>CrO<sub>4</sub> decomposed [Rollinson 1973]:

$$3H_2CrO_4 \leftrightarrow CrO_2 + Cr_2O_3 + 2O_2 + 3H_2O$$
 (8-3)

in which  $CrO_2$  further decomposed to  $Cr_2O_3$ :

$$4CrO_2 \leftrightarrow 2Cr_2O_3 + O_2 \tag{8-4}$$

 $Cr_2O_3$  and  $CrO_2$  were the final products in ashes during supercritical water oxidation of naphthalene and the DISR.

The formation of  $Pb(OAc)_4$  (Ac stands for acetate) was responsible for Pb presence in the aqueous phase during the SCWO at high oxygen concentrations [Butler 1977]:

$$Pb_{3}O_{4} + 12Ac^{-} + 4O_{2} \rightarrow 3Pb(OAc)_{4}$$

$$(8-5)$$

 $CdCl_2$  and  $Cd(ClO_4)_2$  were Cd-containing compounds present in the aqueous phase while the precipitation of  $CdCl_2 \cdot 4Cd(OH)_2$  and CdO removed Cd from the aqueous phase [Aylett 1973]. CdO was formed during the decomposition of  $Cd(NO_3)_2$ . The formation of  $Cd(ClO_4)_2$  took place according to a reaction:

$$CdCl_2 + 2O_2 \rightarrow Cd(ClO_4)_2 \tag{8-6}$$

CdCl<sub>2</sub>•Cd(OH)<sub>2</sub> was formed *via* the hydrolysis of CdCl<sub>2</sub>:

 $5CdCl_2 + 8H_2O \rightarrow CdCl_2 \bullet 4Cd(OH)_2 + 8 H^+$ (8-7)

Reactions of Cr, Cd and Pb are concluded in Figure 8-7. The effect of heavy metals on chemical reactions is indicated using a mark "interaction".



Figure 8-7 Evolution of cadmium, lead and chromium in SCWO

#### 9 Conclusions and Recommendations

#### 9.1 Conclusions

- Peng-Robinson equation was improved to calculate phase behavior of supercritical water by introducing a new parameter called " $\alpha^{scw}$ ". This parameter is a function of temperature:  $\alpha^{scw} = 1.8092T_r^2 4.5375T_r + 3.7344$ . It has been obtained for pure water above its critical point.
- In the binary system of supercritical water and oxygen, the interaction parameter "k<sub>12</sub> or k<sub>21</sub>" is found to be a function of temperature and molar volume F(T)\*F(v). Applying F(T)\*F(v) considerably improves Peng-Robinson equation in predicting PVT of supercritical water-oxygen system. However, additional experimental data of supercritical water-oxygen systems are necessary to improve the accuracy of the F(T)\*F(v) function.

• A reaction rate constant,  $k = A * \exp(\frac{-E_a}{RT}) * \exp(\int_{P_a}^{P} (\frac{\overline{v_A} + \overline{v_B} - RT * k_T}{RT}) dp)$ , was proposed to incorporate the pressure effect by approximating the theoretical differential equation:  $RT\left(\frac{\partial \ln k}{\partial p}\right)_T = -\Delta v^{\#} - RT * k_T$ . This rate equation can be calculated using Peng-Robinson equation with the developed mixing rule.

• Naphthalene can completely dissolve in supercritical water at 424°C and 315 MPa without detectable decomposition, which confirms that SCW is a good solvent for organics. However, no homogenous phase was observed at 400°C and 5 minutes residence time due to the formation of intermediates during the deficient oxidation when  $H_2O_2$  concentration changed from 0 to 25wt%. Naphthalene and those

intermediates could be completely oxidized in a homogenous phase when 49wt%  $H_2O_2$  was used in the diamond anvil cell (DAC).

- Hydrolysis of naphthalene (up to 400°C and 30 MPa) indicates that oxygen deficiency in supercritical water oxidation of naphthalene promotes naphthalene transformation to other polycyclic aromatic hydrocarbons (PAHs). 1,1'-Binaphthalene, 2,2'-Binaphthalene, and 4,5-Dihydrobenzo(e)pyrene were identified as the main products of naphthalene hydrolysis.
- Naphthalene oxidation *via* hydrogen peroxide in the batch reactor occurred in three stages. Decomposition of hydrogen peroxide (Stage 1) took place between 100°C-0.1 MPa and 200°C-12.1MPa. A slow reaction rate was found between 200°C-12.1MPa and 360°C-22.8MPa (Stage 2), in which a saturated water-vapor-oxygen phase dominated. Stage 3 was characterized by fast reactions above 360°C-22.8MPa, where a supercritical fluid of water-oxygen mixture was formed.
- Naphthalene oxidation up to 400°C and 30MPa shows different reaction mechanisms depending on temperature. Low activation energy of 28.76 kJ/mol was obtained between 100°C and 200°C. Negative activation energy of -6.52 kJ/mol was obtained between 200°C and 360°C. High activation energy of 139.5 kJ/mol was obtained above 360°C. Addition of Cr catalyzed naphthalene oxidation by lowering the activation energy to 8.72 kJ/mol between 100°C and 200°C and 17.11 kJ/mol between 200°C and 360°C.
- Complex intermediates, including hazardous species, were formed during naphthalene oxidation. However, they are completely destroyed after 1800s residence time in the batch reactor (400°C and 30MPa).

- A first attempt was undertaken to determine the nature of naphthalene oxidation in subcritical/supercritical water. New data are presented on the conversion of naphthalene and the behavior of intermediates. The proposed reaction pattern describes the evolution of intermediates as a sequence of reactions comprising the transformations of the main compounds and their inter-conversion. A significant part of this radical-involving reaction mechanism is based on the detection, identification and quantification of intermediates in this work.
  - Decachlorobiphenyl was completely oxidized in supercritical water using 225% excess oxygen at 450°C and 32.6MPa. Addition of Na<sub>2</sub>CO<sub>3</sub> improved the destruction rate of 10-CB in the batch reactor and reduced the number of intermediates. A 100% of 10-CB was converted at 450°C and 1200s with 100% Cl dissociation from 10-CB when the stoichiometric amount of Na<sub>2</sub>CO<sub>3</sub> was applied to neutralize HCl. A radical reaction mechanism was used to explain the replacement of chloride in PCBs by hydrogen of water molecules. Both ionic reactions and radical reactions contributed the reaction mechanism. Reaction analysis reveals both hydrolysis and oxidation reactions in the SCWO of 10-CB.
  - A 99% of organic carbon was converted to CO<sub>2</sub> in the supercritical water oxidation of DISR. Less than 1.0% organic carbon appeared in effluents, in which 60% was in form of acetate. Heavy metals, almost 100% of Pb, 90% of Cd and more than 60% of Cr, were effectively removed from the effluents during the SCWO. The evolution of metals involved oxidation, hydrolysis and precipitation. Chlorine and sulphur were converted to Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, appearing in the effluents. Hazardous NO<sub>x</sub> and SO<sub>x</sub> were avoided in the exhaust gas, which consisted of CO2, O<sub>2</sub>, and N<sub>2</sub> with traces of CO and H<sub>2</sub>.

# 9.2 Recommendations

- Real wastes such as sewage sludge, food and backyard wastes contain more complex organics, and would be oxidized in an uninterrupted manner. Therefore, a continuous-flow reactor would be useful to perform a similar study including higher-than-naphthalene hydrocarbons.
- Batch processes span a wide temperature range. This brings difficulties to distinguish the reactions in order to determine kinetics at a certain temperature. A continuous reactor, which enables to carry out experiments at constant temperatures, would allow for better understanding of kinetics of naphthalene and polycyclic aromatic hydrocarbons.
- Pressures were estimated in the diamond anvil cell (DAC) experiments using water equation of state. The presence of air bubbles and oxygen may cause a significant difference between the real pressure and a pressure obtained by water equation of state. Thus, a laser-ruby based DAC device, capable of monitoring pressure online, should be used to determine pressures and temperatures in the phase behavior study.
- Although combustion mechanisms could be adapted to supercritical water oxidation (SCWO) because of the similarity of radical reactions, an experimental study of ionic and radical reactions in supercritical water is necessary to understand SCWO mechanisms. An infrared-rays-transparent diamond (diamond type II) or a tunable diode laser (TDL) will enable to detect radical species in the DAC. Thus, applying these techniques would be required to complete the existing models of SCWO mechanisms.

# **10 CONTRIBUTIONS TO KNOWLEDGE**

- A new function for an interaction parameter  $k_{12}$  was obtained to calculate the PVT of supercritical water-oxygen system for the first time:  $F(v)*F(T) = (8.9963619 \text{ x} 10^{-5} \text{ v}^2 + 6.3639198 \text{ x} 10^{-4} \text{ v} 0.90289783)*(1.6815136 \text{ x} 10^{-3} \text{ T}^2 2.144757\text{ T} + 681.59002)$ , where T in K, v in cm<sup>3</sup>/mol.
- The proposed equation of the reaction rate constant was approximated to account for the pressure effect:  $k = A * \exp(\frac{-E_a}{RT}) * \exp(\int_{*}^{P} (\frac{v_A + v_B - RT * k_T}{RT})_T dP)$ , in which parameters can be calculated using Peng-Robinson Equation with the mixing rule containing F(v)\*F(T).
- New data were obtained for the kinetics of naphthalene oxidation from 100°C to 400°C in sub/supercritical water. High activation energy of 139 kJ/mol was determined for the first time during the supercritical water oxidation of naphthalene.
- Intermediates of naphthalene oxidation in supercritical water were identified and quantified for the first time. The reaction pathways were proposed based on radical reaction mechanisms and quantitative data of naphthalene and its intermediates in this work.
- The destruction rates of decachlorobiphenyl (10-CB) in supercritical water oxidation and the mechanisms of 10-CB hydrolysis and oxidation are both new.

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