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ABSTRACT

Supercritical water oxidation (SCWO) is an innovative technology proposed for the destruction of hazardous organic wastes. Above its critical point (374°C, 221 bar), water behaves more like a nonpolar rather than polar solvent due to a significant drop in hydrogen bonding and density. The result is complete solubility of organic compounds and oxygen in a single phase, high temperature environment, which in turn results in a rapid and complete reaction to CO₂ and water. The present research work has involved the investigation of the reaction kinetics of several model compounds in both sub- and supercritical water, using tubular and stirred tank reactors. The overall goal has been to develop both a theoretical characterization of these reactions through modeling and mechanistic studies, and also a more engineering-oriented description through the generation of global kinetic rate expressions. This basic research is necessary for enhanced understanding of the SCWO process, which can lead to better and more efficient reactor designs for commercial waste treatment systems.

The model compounds chosen for study in this work were acetic acid, methylene chloride, and methanol. Oxidation and hydrolysis/pyrolysis (i.e. reaction in the absence of O₂) of acetic acid was carried out in a tubular plug flow reactor system over a range of 425-600°C, 160 - 263 bar, and 4 - 10 s reactor residence times. The oxidation reaction was found to be 0.72±0.15 order in acetic acid and 0.27±0.15 order in O₂, with an activation energy of 168±21 kJ/mol. Although it has a refractory nature below 500°C, acetic acid was completely destroyed by 550°C at a reactor residence time of 8 s. Major products observed were CO₂, CO, CH₄, and H₂. Hydrolysis/pyrolysis conversion was always much less than that under oxidation conditions, with a maximum of 35% at 600°C and 8 s reactor residence time.

Hydrolysis and oxidation of methylene chloride (CH₂Cl₂) was also carried out in the plug flow reactor system, over a range of 25 - 600°C and 13 - 23 s total residence time at 246 bar. Unlike that seen with acetic acid, CH₂Cl₂ hydrolysis was substantial. In addition, evidence clearly showed that most of the hydrolysis occurred under subcritical temperatures in the preheater tubing while very little conversion occurred in the supercritical main reactor. The explanation of these counterintuitive observations required a detailed study of solvation effects on the rate of reaction in a changing solvent dielectric environment. As water is heated through its critical point, the reaction rate is reduced because of the decreasing stability of the polar transition state complex in the increasingly less polar water solvent. This behavior was quantitatively captured in the rate expression through the use of a correction factor to the rate constant derived from a combination of Kirkwood and transition state theories.

Use of the correction factor required knowledge of the complete thermal history of the feed, along with the structure, dipole moment, and radius of the two reactants and their transition state. Temperature-time profiles in the preheater were determined for each experimen:... through heat trans-
fer calculations using a differential heat balance approach. Physical property values for the transition state and reactants were determined via *ab initio* quantum mechanical calculations. These *ab initio* calculations predicted the correct reaction stereochemistry of the transition state and an increasing activation energy associated with its formation with increasing temperature, thus providing theoretical verification for the observed slowing of the reaction rate. When the *ab initio* predicted physical property values were incorporated into the correction factor, the result was a substantial decrease in the reaction rate by a factor of > 1000 at 550°C, compared to that at ambient temperature. The hydrolysis reaction was found to be first-order in water density and 1.52±0.67 order in CH₂Cl₂, with an activation energy of 210±40 kJ/mol. A first-order model with respect to both reactants was also determined, yielding an activation energy of 180±14 kJ/mol.

Oxygen had a noticeable effect on CH₂Cl₂ conversion only above 525°C. The oxidation reaction was found to have an activation energy of 673±25 kJ/mol. Complete conversion was achieved at 600°C and 23 s total residence time. O₂ had a more significant effect on the product distribution at all temperatures. Major products from CH₂Cl₂ hydrolysis and oxidation were formaldehyde, HCl, H₂, CO, CO₂ and CH₃OH. A reaction network for CH₂Cl₂ hydrolysis and oxidation was developed. Major steps include reaction of CH₂Cl₂ and H₂O to form HCl and HCHO; HCHO decomposition to H₂ and CO; and CO conversion to CO₂ and more H₂ via the water gas shift reaction. In the presence of O₂, direct oxidation of HCHO and CO to CO₂ and H₂O also occurs, and becomes increasingly dominant at higher temperatures.

To address limitations of the plug flow reactor system and to improve and expand operating capabilities, two new reactor systems - a stirred tank reactor and large-scale tubular reactor - were designed and constructed for SCWO experiments. The 637 ml stirred tank reactor can be run in either continuous (CSTR) or batch mode, and can operate up to 650°C and 345 bar at a maximum flow rate of 200 mL/min. The 7.6 cm inner diameter is large enough to handle solids such as soils or precipitated salts without plugging. This reactor system has also been designed for direct injection of organic liquid feed into the reactor to avoid decomposition from preheating, and has three different methods of oxidant delivery. The large-scale tubular reactor has an inner diameter of 5.1 cm and is 46 cm in length. Its two unique features are: 1) a sampling probe that can move while under pressure to take fluid samples and temperature measurements at any point along the centerline of the reactor, and 2) sapphire windows for optical access. Both systems were specifically designed to accommodate not only current needs but also that of future experiments including contaminated soils studies, mixing and heat transfer studies under supercritical conditions, and *in situ* concentration measurements of stable and unstable species.

Hydrolysis/pyrolysis and oxidation experiments in sub- and supercritical water were conducted with methanol in order to evaluate performance of the CSTR system. The operating conditions explored ranged from 25 - 443°C, 238 - 286 bar, 2.5 - 20 min average residence times, and stirring speeds of 500 - 1000 rpm. No methanol decomposition was observed under hydrolysis/pyrolysis conditions at any temperature, or at subcritical temperatures in the presence of O₂. Oxidation at supercritical temperatures up to 443°C was significant. A first-order global rate expression was developed from the data, yielding an activation energy of 230 kJ/mol. Products detected were CO, CO₂, and formaldehyde. The overall results were in good agreement with a recent SCWO study of methanol performed on the plug flow reactor system, verifying acceptable system performance and the likely existence of well-mixed conditions.
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One of the greatest experiences that I have gained from my time at MIT has been the privilege and good fortune of being able to interact with a number of outstanding people. Many have had a direct impact on my education and on the research work which is part of this thesis. At the risk of omitting a few, I would like to especially recognize the following people.

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“The important thing is not to stop questioning. Curiosity has its own reason for existing.”

- Albert Einstein
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Chapter 1

Introduction and Background

1.1 Supercritical Fluids It has been known for over one hundred years that supercritical fluids possess a unique set of properties which allow them to function as remarkably good solvents (Haney and Hogarth, 1879; Villard, 1896). A "supercritical" substance is simply one which is above its critical pressure and temperature, as signified by the shaded region on the generic P-T diagram in Figure 1-1. Above the critical point, the substance is considered neither a liquid nor a gas, but a dense fluid. Since there is no phase change, the physical properties of a supercritical fluid vary continuously with temperature and pressure, achieving values intermediate between those typical of liquids and gases in the usual region of interest. Critical constants of some of the more popular compounds that have been used as supercritical fluids are given in Table 1-1.

Since the dissolution process involves the surrounding of a solute molecule completely by solvent molecules, density is the most important physical property governing a substance's solvent power. Because of their higher density, liquids are generally much better solvents than gases. Supercritical fluids have a density between that of a liquid and gas, but typically closer to that of a liquid (Paulaitis et al., 1982). Near the critical point, it is possible to achieve a dramatic change in density (and thus solvent power) with only a relatively small change in pressure. In contrast to liquid-like densities, supercritical fluids have mass transfer properties of viscosity and diffusivity closer to that of a gas. Typical values for these physical properties of a supercritical fluid as compared to gases and liquids are given in Table 1-2 (Squires et al., 1983).
Figure 1-1  Pressure-Temperature Diagram for a Pure Component, Indicating the Supercritical Region.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Critical Temperature (°C)</th>
<th>Critical Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>31.1</td>
<td>73.9</td>
</tr>
<tr>
<td>ethane</td>
<td>32.3</td>
<td>49.4</td>
</tr>
<tr>
<td>ethylene</td>
<td>9.3</td>
<td>51.2</td>
</tr>
<tr>
<td>propane</td>
<td>96.7</td>
<td>42.5</td>
</tr>
<tr>
<td>water</td>
<td>374.2</td>
<td>221.2</td>
</tr>
</tbody>
</table>

Table 1-1  Critical Constants for Commonly Used Supercritical Fluids
<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>PHASE</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>SCF</td>
<td>Liquid</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>$10^{-3}$</td>
<td>$10^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity (Pa s)</td>
<td>$10^{-5}$</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Diffusivity (cm²/s)</td>
<td>$10^{-1}$</td>
<td>$10^{-4}$</td>
<td>$10^{-5}$</td>
</tr>
</tbody>
</table>

Table 1-2  Comparison of Typical Values for Selected Physical Properties of Liquids, Gases, and Supercritical Fluids (SCF)

The combination of liquid-like solvent power, gas-like mass transfer properties, and the ability to affect substantial changes in these properties by changing pressure alone make supercritical fluids very effective as extractants in separation processes (McHugh and Krukonis, 1986). Many of the compounds used as solvents in supercritical fluid extraction (such as CO₂) have relatively low critical temperatures and are gases at ambient conditions. This has the further advantage of allowing complete separation of solvent from a solid or liquid solute by decreasing pressure below the critical point after extraction has been achieved. Another more recent application of supercritical CO₂ that has been attracting much attention has been its use as a more environmentally benign replacement solvent in organic synthesis reactions (DeSimone et al., 1992; Weinstein et al., 1996).

1.2 Properties of Supercritical Water  Water has a relatively high critical temperature and pressure of 374°C and 221 bar. Figure 1-2 shows graphs of density, dielectric constant, and self-dissociation constant vs. temperature for water at 250 bar. Above 450°C, water has a density on the order of $10^{-1}$ g/ml, which like most supercritical fluids, is between that of the liquid state (1 g/ml) and gaseous state ($10^{-3}$ g/ml) but closer to that of the liquid state. Although water in its
Figure 1-2 Solvation Properties of Pure Water As a Function of Temperature at 250 Bar
supercritical state has the same general characteristics of liquid-like density and gas-like viscosity and diffusivity that all supercritical fluids have, the high temperature needed to achieve supercritical conditions for water has additional and substantial effects on its solvent nature and general behavior above the critical point.

Water is a polar molecule that at room temperature exhibits a high degree of hydrogen bonding (which is the main reason water is a liquid at room temperature and not a gas like H₂S). It is commonly known and easily observed that water at room temperature will dissolve other polar substances such as inorganic salts readily, while most nonpolar substances such as hydrocarbons are insoluble. As temperature increases near the critical point, the density decreases enough so that water loses its ability to hydrogen bond with other water molecules (but not enough to lose its solvent ability), since hydrogen bonding forces are strong only when molecules are in close proximity. Also under these conditions, the water molecules are separated enough from each other (large enough void volume) that their dipole-dipole interactions are greatly diminished. With no hydrogen bonding and weakened interactions between molecules, water in the supercritical state starts to behave as if it were a nonpolar rather than polar solvent. Thus nonpolar organic compounds and inorganic diatomic gases such as O₂, N₂, and H₂ exhibit high solubility in supercritical water, while inorganic salts exhibit very low solubility in supercritical water - a complete reversal of water's behavior at room temperature.

This change in the solvent nature and structure of water with increasing temperature is best indicated by the changes in some of its solvation properties. As shown in Figure 1-2, water has a dielectric constant (ε) of 80 at room temperature, which decreases fairly rapidly to a value of about 5 at the critical point and a value of 1 or 2 above 450°C (Uematsu and Franck, 1980). Similarly, the dissociation constant of water (Kₐ) decreases from its usual room temperature value near 10⁻¹⁴ (mol/kg)² down to less than 10⁻²⁰ (mol/kg)² under supercritical conditions (Marshall and Franck,
1981). These low values for $\varepsilon$ and $K_w$ under supercritical conditions are consistent with those of a nonpolar substance and account for the poor ability of supercritical water to dissociate and dissolve ionic salts. As an example of a typical organic species, benzene solubility increases from about 0.07 wt. % at room temperature, to 7 - 8 wt% at 260°C, to complete miscibility above 300°C and 250 bar. As a typical inorganic salt, NaCl solubility changes from 37 wt% even up to 300°C, down to only about 120 ppm by 550°C and 250 bar.

Although supercritical water acts as an excellent solvent for nonpolar organic compounds, the high temperature needed to achieve its supercritical state makes it impractical to be used effectively for extractive purposes, since many organic compounds would break down at temperatures above 374°C. Instead, the combination of high temperature and ability of water in the supercritical state to bring organic species and oxygen together in one homogeneous, dense phase provides all the right conditions necessary for combustion to take place. Thus unlike most other commonly used supercritical fluids, the physical properties and solvent characteristics of supercritical water make it a much better medium for destruction of organic compounds rather than extraction.

1.3 Supercritical Water Oxidation In supercritical water oxidation (SCWO), organic compounds and oxygen or air are brought together in the presence of water under a temperature and pressure above the critical point of water. Under typical operating conditions of 550 - 650°C, 250 bar, and residence times of one minute or less. most organic compounds can be rapidly oxidized to just CO$_2$ and water (the standard products of complete combustion) with a destruction efficiency $> 99.99\%$ and no toxic by-products (Tester et al., 1993a). The complete miscibility of nonpolar organic compounds and oxygen in supercritical water in a single phase ensures good species contact and precludes any problems from mass transfer limitations. Unlike typical combustion processes, no NO$_x$ compounds are produced (Killilea et al., 1992), due to the relatively low operating temperatures (compared to a conventional incinerator or car engine for instance). Instead, nitrogen in
nitrogen-containing organic compounds is converted to \( \text{N}_2 \) or possibly some \( \text{N}_2\text{O} \). For organic compounds that contain other heteroatoms, such as halogens, sulfur, or phosphorus, the heteroatoms are converted to their corresponding acids or oxyacids, which can be neutralized with base pre-added to the organic feed. The resulting polar salts precipitate out in the supercritical water environment. In the case of large and/or labile organic compounds, appreciable destruction can also be achieved under subcritical temperatures (known as wet oxidation (Dietrich et al., 1985)), and even without oxygen present (hydrolysis or pyrolysis conditions). Although one may benefit from lower operating and equipment costs under these less extreme conditions, reaction times can be much longer compared to SCWO for comparable levels of conversion, and the presence of products of incomplete combustion must be expected and acceptable.

1.3.1 Applications The most useful and promising application for the SCWO process is in destruction of organic hazardous wastes. As traditional means of waste disposal options such as landfills have become less abundant and more expensive, and as governmental regulations on waste disposal have increased (and are expected to continue to do so), the use of SCWO for hazardous waste disposal has become more and more favorable. For this reason, much work has been done over the past two decades on exploring, characterizing, and documenting the oxidation of a number of toxic organic compounds in supercritical water, both in academia and industry. Examples of wastes that have been demonstrated to be successfully destroyed by the SCWO process include PCB's (Staszak et al., 1987), pesticides such as DDT (Modell et al., 1982), bacteria, dioxins (Thomason et al., 1990), urea (Timberlake et al., 1982) and human waste (Hong et al., 1987; Hong et al., 1988), paper mill effluent (Modell et al., 1992; Modell, 1985), pharmaceutical waste (Johnston et al., 1988), wastewater sludge (Shanableh and Gloyna, 1991; Tongdhamachart and Gloyna, 1991), and explosives (Harradine et al., 1993; Spritzer et al., 1995).
In addition to treating industrial wastes, SCWO has also been proposed as a means of remediation of contaminated soils and groundwater. This could be done by either feeding the contaminated material directly into a portable SCWO unit, or by a two step process involving extraction of the contaminant from the soil or water matrix using supercritical CO$_2$ (Yu et al., 1995) followed by destruction of the extractant via SCWO. In the absence of oxygen, supercritical water has been shown to effectively remediate clay soil from a paint factory (contaminated with a mixture of alkane, aromatic, and polyaromatic hydrocarbons) through a combination of extraction and thermal decomposition (Firus and Brunner, 1996).

1.3.2 The Process A typical process flow chart is shown in Figure 1-3. Most feeds consist of an aqueous waste stream (solution or slurry) containing 1-20 wt% organic. Within this range of organic concentration, the process is designed to be most efficient and economical compared to other technologies such as activated carbon treatment and incineration (Thomason et al. (1990). This feed is pressurized and preheated before mixing with oxidant (e.g. O$_2$, air, or H$_2$O$_2$) in the reactor. Any salts contained in the initial feed or formed during reaction/neutralization will precipitate here under supercritical conditions. For energy recovery, the effluent leaving the reactor can be heat exchanged with the incoming feed or used to generate steam. After depressurization, the resulting gas and liquid phase streams (consisting of CO$_2$ and possibly N$_2$, and clean water, respectively) are separated. A final polishing step for the liquid effluent would be required only if trace unwanted metals were present.

1.3.3 Advantages As compared to any current waste disposal method (such as incineration), SCWO holds a number of clear advantages: 1) it achieves complete destruction of a broad spectrum of organic compounds (even those normally difficult to break down) with no scrubbing of effluent gases necessary; 2) it is ideal for destroying dilute aqueous organic wastes (unlike incineration) since water is the reaction medium; 3) the reaction takes place in a closed system (meets EPA
SCWO PROCESS STEPS
Aqueous Waste (~ 2-20 wt% organic)

FEED PREPARATION AND PRESSURIZATION

PREHEAT

Oxidant (Air, oxygen)

Reaction Zone

Salt Separation Zone

Concentrated brine

HEAT RECOVERY

DEPRESSURIZATION

GAS/ LIQUID SEPARATION

EFFLUENT POLISHING

Vapor phase effluent (CO₂, N₂, etc.)

Aqueous effluent

Figure 1-3  Typical SCWO Process Flow Diagram
regulations) in a single dense phase which results in better reaction control; 4) nonoxidizable inorganic compounds can be removed from the effluent and concentrated as they precipitate out of the supercritical water; 5) no NOx or other toxic by-products are formed (a problem which plagues incineration); and 6) the reaction can be made self-sustaining, with the heat of reaction used to preheat feed and/or generate steam. Drawbacks to the SCWO process are the high pressure needed, the highly corrosive environment generated when dealing with halogenated feeds and the added cost of more corrosion-resistant nickel alloys, and the system design challenges in effectively preventing accumulating layers of precipitated salts (when present) from impeding the main effluent flow.

1.3.4 Commercialization Ventures and Current Status Ever since the initial discovery more than two decades ago at MIT that complex organic compounds could be dissolved and broken down into simpler, low molecular weight compounds (Amin et al., 1975), several companies have attempted to commercialize the SCWO process. The first, MODAR, Inc., conducted extensive work in the 1980's and early 90's on measuring destruction efficiencies of organic compounds and corrosion of materials in supercritical water, with the goal of proving the viability of the SCWO process and developing a large-scale reactor system to treat a wide range of waste compounds. Another early company, MODEC, Inc., developed its own version of the SCWO process. Among the U.S. companies currently supplying SCWO technology systems are Eco Waste Technologies and General Atomics (who acquired MODAR in 1996). In 1994, Eco Waste Technologies built and started the first commercial SCWO facility for waste destruction at the Huntsman Petrochemical Corp. in Austin, Texas. The plant, which operates at 5 gal/min and 10-15 wt% organic (Oil & Gas Journal, 1994), has been running successfully since this time, although it has only handled non-aggressive feeds of hydrocarbons and amines (i.e., no halogens).
Recently, three branches of the U.S. armed forces have separately committed to building their own SCWO units. Although the U.S. Army has been interested in and has sponsored basic research on SCWO for use in chemical weapons disposal (see below), it is also constructing an SCWO facility for use in destroying non-stockpile obsolete smokes, dyes, and pyrotechnics at Pine Bluff Arsenal in Arkansas. The plant, being designed by Foster Wheeler Development Corp. in conjunction with Sandia National Laboratories and Gencorp Aerojet, will have a capacity of 80 lbs/hr and employ a uniquely designed transpiring wall reactor to mitigate corrosion (Haroldsen et al., 1996a,b). The U.S. Navy is also committed to developing compact SCWO units for processing shipboard wastes (Kirts, 1995). As of 1996, the U.S. Air Force had commissioned General Atomics to design a SCWO plant capable of destroying 25,000 lbs/day of solid rocket propellant (Hurley, 1996). A pilot plant also built by General Atomics has already achieved complete propellant destruction to > 99.99% at a sustained rate of > 800 lbs/day. Just recently in 1998, the U.S. Army has solicited bids for the construction of a SCWO plant at one tenth full scale (based on use of a vertical downflow tubular reactor), and the implementation of a test matrix program to destroy hydrolysate of VX nerve agent at its Indiana arsenal. The goal will be to obtain necessary information for the design and operation of a full scale plant. From a commercial perspective, it is hoped that construction of these SCWO units for the military, along with continued operation of the Huntsman plant, will allow generation of enough data on a wide enough variety of feed types and large enough scale for the SCWO process to prove itself as a viable means of waste destruction for industry.

A number of review articles have been written that contain more detailed information about the SCWO process, such as those by Modell (1989), Thomason et al. (1990), Barner et al. (1992), and Tester et al. (1993a). Shaw et al. (1991) have surveyed work done to better characterize the nature of supercritical water and its ability to support reactions. Savage et al. (1995) have reviewed the much broader field of supercritical fluids in general as media for chemical reac-
tions, focusing on their properties and some of their many varied applications. An earlier and complementary review by Subramaniam and McHugh (1986) covers this same topic prior to 1985.

1.4 Previous Basic Research in SCWO Despite the demonstrated overall success of the SCWO process in effectively treating a wide variety of organic wastes, there is still a need today for a more fundamental understanding of the many physicochemical phenomena involved in the process. This information is crucial for achieving more efficient and economically competitive SCWO process designs. To meet this need, basic research studies have been carried out in academia and the national laboratories over the years in a number of important areas relevant to various parts of the SCWO process.

Here at MIT, both experimental and computational work have been carried out under the broad categories of reaction kinetics, salt precipitation studies, corrosion, transport property determination, and process simulation. In the area of reaction kinetics, our program has been focused since 1983 on the study of hydrolysis, pyrolysis, and oxidation reactions of a number of carefully chosen model compounds in sub- and supercritical water. For each compound, the primary goal has been the development of global reaction rate expressions through experimental data gathered under well defined conditions of temperature, pressure, concentration, and residence time. An equally important goal in these studies has also been the discerning and modeling of the complete reaction network, both on a global and elemental reaction level.

The model compounds that have been studied thus far include carbon monoxide (Helling and Tester, 1987; Holgate et al., 1992; Holgate and Tester, 1994a,b), ethanol (Helling and Tester, 1988), ammonia (Webley et al., 1990; 1991), methane (Webley and Tester, 1991), methanol (Webley and Tester, 1989; Webley et al., 1990; 1991; Tester et al., 1993b), hydrogen (Holgate and Tester, 1993; 1994a,b), and glucose (Holgate et al., 1995). More recent compounds investi-
gated include acetic acid and methylene chloride (the subjects of this thesis), malathion and thiodiglycol (Lachance, 1995), and benzene. In addition, methanol kinetics have been recently reexamined in regards to mixing and heat transfer issue, (Phenix, 1998) and in testing a new stirred tank reactor (this thesis). These species have been chosen as model compounds because they (a) have been found to be the rate limiting steps in the overall oxidation of larger or more complex compounds (e.g. CO, NH₃, CH₄), (b) are simulants for hazardous waste compounds (e.g. glucose, for biological or pharmaceutical wastes; thiodiglycol, for the chemical warfare agent HD sulfur mustard), or (c) are themselves characteristic hazardous waste compounds (e.g. CH₂Cl₂, C₆H₆).

Global reaction rate expressions have typically been expressed with a power-law dependence, with the exception of ammonia which displayed a catalytic effect from the Inconel 625 reactor walls. Many of these model compounds studied (as well as others reported in the literature) have been found to exhibit overall first-order oxidation kinetics (first-order in organic and zero-order in oxygen) on a global basis. Figure 1-4 shows a first order Arrhenius plot for several of the model compounds that we have investigated. As is shown, larger compounds such as glucose tend to break down rapidly under SCWO conditions (even in the absence of oxidant) into smaller more refractory compounds.

A number of other researchers of note have also established programs to investigate the kinetic behavior of various organic compounds in supercritical water. Savage and coworkers at the University of Michigan have done an extensive amount of work studying oxidation reactions in supercritical water, determining global rate expressions, performing analyses of reaction intermediates, and discerning reaction networks. Model compounds studied have included phenol and related compounds (Thornton and Savage, 1992; Li et al., 1993; Gopalan and Savage, 1995; Martino and Savage, 1997), acetic acid (Savage and Smith, 1995), and methanol (Brock et al., 1996).
Figure 1-4  First-order Arrhenius Plot for SCWO of Some Typical Model Intermediate Organic Compounds, Relative to Typical Wastes. Data for model intermediates taken from Webley and Tester, 1991; Webley et al., 1991; Holgate et al., 1992; Holgate and Tester, 1993; Tester et al., 1993b; and Meyer et al., 1995. Benzene data are preliminary results from unpublished work in progress. Glucose data taken from Katzer (1975). The band denoted as $\tau_{\text{residence}}$ represents the approximate magnitude of residence times that can be observed with the MIT plug flow reactor system (see Section 3.2.1). Note that the ordinate is the base ten logarithm.
Gloyna and coworkers at the University of Texas have conducted research and written extensively on many different aspects and phenomena associated with supercritical water. They have studied the oxidation kinetics and/or destruction efficiencies of phenol (Li et al., 1997), n-octanol (Li et al., 1997), pyridine (Crain et al., 1995; 1993), dimethyl methylphosphonate (McKendry et al., 1994), dinitrotoluene (Li et al., 1993), acetamide (Lee and Gloyna, 1992), 2,4-dichlorophenol (Lee et al., 1990), and acetic acid (Chang et al., 1993; Frisch and Gloyna, 1992; Frisch et al., 1994). At Sandia National Laboratories, Rice has led research on the measurement of reaction rates, products, and pathways of methanol (Rice et al., 1996), isopropyl alcohol (Hunter et al., 1996), and methane (Steeper et al., 1996). Similar work by Buelow and colleagues at Los Alamos National Laboratories has been performed on a number of compounds including hydrazine (Masten et al., 1993) and chlorinated hydrocarbons (Foy et al., 1996), and on the use of nitrates and nitrites as oxidants (Proesmans et al., 1997). Abraham and coworkers have focused on catalytic oxidation reactions, most notably of phenol (Ding et al., 1995), methane (Aki and Abraham, 1994), and 1,4-dichlorobenzene (Jin et al., 1990). In addition to measuring and correlating properties of supercritical water, Franck and coworkers have looked at oxidation reactions of methane, ethane, and methanol at conditions extreme enough to produce hydrothermal flames (Hirth and Franck, 1993).

As mentioned earlier, some organic compounds react readily in supercritical water without oxidant via hydrolysis or pyrolysis reactions. Klein and coworkers at the University of Delaware have focused primarily on studying hydrolysis reactions, most recently on nitrogen-containing compounds such as 1-nitrobutane (Iyer et al., 1996), butyronitrile (Iyer and Klein, 1997) and nitroanilines (Wang et al., 1995). Also at the University of Delaware, Brill and coworkers have used spectroscopic techniques to probe decomposition reactions in supercritical water of urea (Kieke et al., 1996), hydroxylammonium nitrate and ammonium carbonate (Schoppelrei et al., 1996a), ethylenediammonium nitrate (Maiella and Brill, 1996a), guanidinium nitrate (Schoppelrei
et al., 1996b), and malonic acid (Maiella and Brill, 1996b). At Western Michigan University, Houser has measured decomposition rates of various aromatic compounds (Tsao et al., 1992), chlorinated compounds (Houser and Liu, 1996), and other nitrogen- and sulfur-containing compounds (Houser et al., 1996; 1993). Antal and coworkers at the University of Hawaii have concentrated on measuring the kinetics of reforming reactions in sub- and supercritical water, particularly dehydration reactions of various alcohols (Xu and Antal, 1994; Xu et al., 1991; 1990; Narayan and Antal, 1990). Katritzky and coworkers have studied the reactions of a large array of cyclic heteroatom containing compounds (Katritzky et al., 1997; 1995; 1994). Penninger has focused on the decomposition in sub- and supercritical water of representative compounds for coal such as di-n-butylphthalate (Penninger, 1988) and methoxynaphthalene (Penninger and Kolmenschate, 1989). Through experiments and computer modeling, Johnston and colleagues at the University of Texas have probed both the solvent environment in supercritical water (Johnston et al., 1995) and acid-base reactions (Xiang and Johnston, 1997).

1.5 Motivation for the Current Work Understanding of the oxidation kinetics of simple model compounds such as CO, H₂, CH₄, and NH₃ has been an important and necessary first step in SCWO research. This is because knowledge of their kinetics forms the basis of any efforts to characterize and understand the oxidation kinetics and mechanisms of larger molecules, and would need to be incorporated in any model attempting to describe the oxidation kinetics of larger molecules. The same can be said for the hydrolysis or pyrolysis behavior of these compounds in supercritical water. With this basis established, we have now begun to address the need to look at the hydrolysis and oxidation kinetics of larger compounds which are in themselves more typical of waste products or potential intermediates in their breakdown.

As an example, acetic acid is one compound that was chosen for study as part of this thesis work. It has been cited as a byproduct in SCWO of more complex molecules such as diethylene
glycol, diethyl ether, acetonitrile, acetamide (Lee and Gloyna, 1992), biological sludges (Shanableh and Gloyna, 1991), and glucose (Holgate et al., 1995). Acetic acid can also be a waste product in and of itself (not very toxic when dilute, but very common), which must be disposed of. The above mentioned studies reveal that in the 400°C range or higher the above wastes rapidly decompose, but that acetic acid is refractory (i.e. resistant to any oxidation). However, above 500°C, we have found that acetic acid is susceptible to SCWO, and is completely destroyed by 550°C and 8 s residence time (see Chapter 3). It breaks down into a group of smaller compounds that includes the even more refractory CH₄. Thus, to characterize the kinetics and the reaction pathways leading to complete destruction of a more complex feed like sludge or glucose and to build up a useful kinetic data base requires an understanding of the oxidation and hydrolysis kinetics of intermediate byproducts such as acetic acid (among many other), which in turn requires characterization of the oxidation and hydrolysis kinetics of the simple compounds CO, H₂, and CH₄.

The need to study the destruction kinetics of more typical waste compounds in supercritical water cannot fully be addressed without consideration of heteroatom-containing compounds, particularly chlorinated hydrocarbons. There are two particular proposed applications for SCWO which have motivated the expansion of our oxidation kinetics database to more complex feeds with heteroatoms in the present work - the destruction of chemical weapons and the remediation of contaminated groundwater and soils.

The U.S. Army has between 25,000 to 30,000 tons of chemical weapons stored at eight locations in the continental U.S. and on Johnston Island (Ember, 1990; Picardi, 1991). As of 1995, the U.S. Department of Defense is required by law to destroy all of these weapons by December 31, 2004 (Peters, 1996). Under the international treaty provisions of the Chemical Weapons Convention of 1993, the deadline is 2006 (Ember, 1996). Destruction of these weapons has
also been motivated by the fact that many of the weapons (which are of World War II and Cold War vintage) have been deteriorating with age and represent an increasing health and safety risk in storage over time. The originally chosen method of disposal back in 1982 was incineration, which would be conducted on site at each of the storage locations. Faced with the operational problems and mounting delays plaguing the only incinerator constructed at the time (on Johnston Island), the increasingly negative public perception of incineration over the years, and unanticipated stiff local public opposition to the building of incinerators at the storage bases in the continental U.S., the Army began to look into alternative methods of disposal in the early part of this decade (U.S Congress, Office of Technology Assessment, 1992). Supercritical water oxidation was one of four potential destruction methods chosen in 1992 as a promising technology for chemical weapons disposal. For this reason, the U.S Army Research Office has funded basic research on SCWO related issues at MIT and a number of other universities through its University Research Initiative (URI) program.

The chemical weapons stored by the Army can be divided into two types. Mustard blister (vesicant) agents are organic compounds which contain the heteroatoms sulfur and/or chlorine. Nerve agents are organophosphorus esters that also contain nitrogen and/or sulfur and/or fluorine atoms. Our work on developing SCWO kinetics has not involved hydrolysis or oxidation of these actual weapon agents, but on less hazardous surrogates which have similar heteroatoms and functional groups, molecular structure, and other physical and chemical properties. We have chosen methylene chloride (CH₂Cl₂) as the representative chlorine-containing surrogate compound. In addition to being a widely used and somewhat hazardous solvent, its simple structure allows the study of C-Cl chemistry in supercritical water without competing or complicating effects arising from larger size or additional functional groups. Representative sulfur- and phosphorus-containing compounds, thiodiglycol (the hydrolysis product of the agent HD sulfur mustard) and malathion, respectively, have been studied by Lachance (1995). Focusing on the effects of particular het-
eroatoms or functional groups on SCWO kinetics of a few simpler compounds provides insight and allows predictions to be made regarding the oxidation kinetics not only of weapon agents but other complex molecules containing many different combinations of these heteroatoms and functional groups.

The Aberjona Basin, located in Woburn, Massachusetts, is a heavily contaminated watershed resulting from three centuries of tanning, chemical manufacturing, and other industrial activity (Durant et al., 1990). It is now the location of two Superfund sites. Among the many toxic chemicals that have been found here are several organochlorine compounds; in particular, trichloroethylene and tetrachloroethylene (Kim et al., 1995). The first site involves a contaminated groundwater plume primarily of trichloroethylene, while the second is a hazardous waste disposal site (Industriplex) with contaminated soil. The National Institute of Environmental Health Sciences (NIEHS) has commissioned a study of the area that includes determination of health and genetic effects of human exposure to the toxic chemicals found in the Aberjona Basin, the fate and transport of these chemicals, and how to safely and effectively destroy these chemicals already contaminating the Basin. Research on supercritical water oxidation is one of four remediation technology proposals being funded. Due to the dilute aqueous solution nature of contaminated groundwater (owing to the relatively low solubility of most organic compounds under ambient conditions), SCWO is ideally suited for treating wastes in comparison to incineration, where the high water concentration presents significant processing problems. Our choice of CH₂Cl₂ as a model compound is also appropriate given the chlorinated hydrocarbon contaminants found at the two sites.

The Aberjona Basin Superfund site clean up (along with many other contaminated soil sites) further provides impetus for exploring the kinetics of SCWO reactions in the presence of solid particles - particularly in the destruction of organic compounds sorbed on soil particles, and the oxidation of chlorinated compounds with precipitating salt particles resulting from pre-
neutralization of the feed. These experiments, however, cannot be carried out in the small diameter, tubular reactor used for all previously mentioned kinetic studies in our group because of the likelihood of immediate plugging. This fact has in turn prompted us to examine critically the limitations in general of the older, existing reactor, and to consider the design and construction of new reactor systems in order to increase the flexibility of operating conditions and types of experiments that could be carried out.
Chapter 2

Objectives

The overall objective of this thesis work is to increase the collective knowledge and fundamental quantitative understanding of chemical reactions and related physico-chemical phenomena as they occur in supercritical water. Ultimately the information gained from the study of these issues may play a small but important part in the efficient design of future SCWO systems and in providing further documentation of the strengths and weaknesses associated with SCWO technology in general. Specific objectives are as follows:

1. Study the hydrolysis and oxidation reaction kinetics of the model compounds acetic acid and methylene chloride. This work consists of the following three subtasks:

   a) Through the use of experimental data gathered under well-defined conditions in the existing, small-scale, plug flow tubular reactor system, develop global rate expressions for the hydrolysis and oxidation reactions of both model compounds. The experiments are designed to consider the effects of temperature, pressure, residence times, organic concentration, and oxidant/organic stoichiometric feed ratios on the kinetic data gathered.

   b) Determine the spectrum of products produced from these reactions and their distribution over the range of operating conditions explored for the above experimental variables.

   c) Deduce the likely reaction pathways and resulting reaction network that accounts for the nature of the breakdown observed in the given reaction and the type and amount of all products observed.
2. **Propose and evaluate designs for a new, “next generation” SCWO reactor, and then design, construct, and test the complete reactor system chosen.** In the evaluation stage, the goal is not only to design a reactor system that avoids the limitations of the existing plug flow reactor system, but also to add features that will allow for greater overall flexibility in the types of experiments that can be run and the range of operating conditions accessible. Two different types of reactors are to be considered: a stirred tank reactor and large-scale tubular reactor with optical access connection. Once the complete system is constructed, it is to be tested by running hydrolysis/pyrolysis and oxidation experiments with methanol and the results compared to those obtained from earlier studies performed with the existing plug flow reactor by Webley and co-workers (Tester *et al.*, 1993b) and Phenix (1998).

As mentioned earlier in Section 1.5, the choice of acetic acid and methylene chloride as model compounds for this study represents a significant step forward in the generation of a SCWO kinetics database by our group beyond the simpler compounds studied earlier. They are examples of real wastes and are intermediate products in the breakdown of a number of larger and more complex species. Acetic acid has been typically observed as an intermediate in SCWO of sludges and other pharmaceutical and bio-related wastes. The results of the hydrolysis/pyrolysis and oxidation experiments of acetic acid conducted as part of this work are included in Chapter 3.

Methylene chloride is the first chlorinated compound to be studied by our group. Despite its simple chemical structure, a number of factors made it very difficult to work with, among them being its low ambient solubility in water, high volatility, the corrosive nature of the HCl-containing effluent, and its tendency to hydrolyze rapidly at subcritical temperatures during heatup of the feed. In order to properly meet the objectives stated, these issues and their consequences had to be addressed as part of this work. Chapter 4 presents the experimental and analytical techniques employed, data gathered, and observations made (some initially counterintuitive). Chapter 5 details
the characterization of heat transfer in the preheater tubing under sub- and supercritical conditions and its use in the development of temperature-time profiles. The nature of the changing water solvent environment with increasing temperature and its strong effect on the $\text{CH}_2\text{Cl}_2$ hydrolysis reaction is explored and quantified in Chapter 6, along with the eventual development of hydrolysis and oxidation global rate expressions. Finally, the product spectrum and distribution resulting from $\text{CH}_2\text{Cl}_2$ hydrolysis and oxidation reactions is presented in Chapter 7. Here the experimental data and applicable data from the literature is used to construct a reaction network consisting of a series of most likely pathways that account for all of the products observed.

Chapter 8 examines design issues, both theoretical and practical, related to the new stirred tank and large-scale tubular reactors. It also reviews and documents the limitations of the existing, small-scale, plug flow tubular reactor, and the features considered in the design of the new reactors and peripheral equipment to avoid these limitations, improve operation, and expand capabilities. Although both reactors have been designed, only the stirred tank reactor system was fully built and operated as part of this thesis work. Chapter 9 details the results of hydrolysis/pyrolysis and oxidation experiments of methanol carried out with this system operating in a continuous feed mode (CSTR). These results are then compared to theoretical predictions of CSTR operation, and to the global kinetics results for methanol previously generated by our group with the existing plug flow reactor.
Chapter 3

Hydrolysis and Oxidation of Acetic Acid

Experimental work on acetic acid hydrolysis/pyrolysis and oxidation in supercritical water was carried out collaboratively with Jerry Meyer. As used here, the term hydrolysis/pyrolysis refers to reaction in the absence of O₂. The following represents a summary of the experimental observations and analysis. Data tables and more detailed information are contained in Meyer (1993) and Meyer et al. (1995).

3.1 Literature Review  The fact that acetic acid (CH₃COOH) has been observed as a refractory intermediate in the breakdown of a number of higher molecular weight and more complex compounds (Skaates et al., 1981; Shanableh and Gloyna, 1991; Tongdhamachart and Gloyna, 1991; Lee and Gloyna, 1992; Holgate et al., 1995) has motivated many researchers to study its destruction kinetics in supercritical water. Table 3-1 contains a listing of previous studies on SCWO of acetic acid and the resulting kinetic parameters determined in each case.

Wightman (1981) was one of the first to study the oxidation kinetics of acetic acid in supercritical water. Only seven experiments were conducted in a plug flow reactor, two of which were performed under subcritical temperatures (or wet oxidation conditions). In the data analysis, the reaction was assumed to be first order in both acetic acid and oxygen, although no explanation for this assumption was given. Lee carried out a number of SCWO experiments on acetic acid in a batch (Lee et al., 1990) and continuous flow system (Lee and Gloyna, 1990; Lee, 1990), and with O₂ and H₂O₂ as oxidants. Lee et al. (1990) found H₂O₂ to be a much better oxidant than O₂, resulting in higher conversions of acetic acid in shorter residence times. Their results are somewhat
\[
\frac{d[\text{CH}_3\text{COOH}]}{dt} = -Ae^{-\frac{E_a}{RT}} [\text{CH}_3\text{COOH}]^a [\text{Oxidant}]^b [\text{H}_2\text{O}]^c
\]

Units: kJ, mol, L, s

<table>
<thead>
<tr>
<th>Source</th>
<th>In A</th>
<th>E_a</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Oxidant Used</th>
<th>Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wightman (1981)</td>
<td>41.1</td>
<td>231</td>
<td>1</td>
<td>1</td>
<td></td>
<td>O_2</td>
<td>338 - 445°C 400 - 445 bar Plug flow reactor</td>
</tr>
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<td>Lee, 1990</td>
<td>24.0±21.8</td>
<td>167±7</td>
<td>1</td>
<td>0</td>
<td></td>
<td>H_2O_2</td>
<td>Continuous flow reactor</td>
</tr>
<tr>
<td>Lee and Gloyna, 1990</td>
<td>26.5±26.5</td>
<td>180±15</td>
<td>1.01±0.09</td>
<td>0.16±0.08</td>
<td></td>
<td>H_2O_2</td>
<td>415 - 525°C 225 - 310 atm Continuous flow reactor</td>
</tr>
<tr>
<td>Lee et al., 1990'</td>
<td>11.3</td>
<td>106</td>
<td>1</td>
<td>0</td>
<td></td>
<td>O_2</td>
<td>400 - 500°C 240 - 350 bar Batch reactor</td>
</tr>
<tr>
<td>Wilmanns and Gloyna, 1990</td>
<td>13.7±13.2</td>
<td>314±62</td>
<td>2.36±0.48</td>
<td>1.04±0.35</td>
<td></td>
<td>H_2O_2</td>
<td>400 - 510°C 272 bar</td>
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<tr>
<td>Frisch, 1992</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O_2</td>
<td>375 - 472°C p = 0.3 g/mL Batch reactor (same as Lee et al., 1990)</td>
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<tr>
<td>noncatalytic, first order</td>
<td>22.6</td>
<td>165±40</td>
<td>1.01±0.24</td>
<td>0</td>
<td></td>
<td>O_2</td>
<td></td>
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<tr>
<td>noncatalytic, first order</td>
<td>22.4</td>
<td>165±40</td>
<td>1</td>
<td>0</td>
<td></td>
<td>O_2</td>
<td></td>
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<td>catalytic, first order</td>
<td>4.1</td>
<td>45±19</td>
<td>1.03±0.13</td>
<td>0</td>
<td></td>
<td>O_2</td>
<td></td>
</tr>
<tr>
<td>Boock and Klein, 1993'</td>
<td>3.7</td>
<td>44±17</td>
<td>1</td>
<td>0</td>
<td></td>
<td>O_2</td>
<td>350 - 500°C Batch reactor</td>
</tr>
<tr>
<td>Rice et al., 1993'</td>
<td>30.9</td>
<td>205</td>
<td>1</td>
<td>0</td>
<td></td>
<td>O_2 (from H_2O_2 decomposition)</td>
<td>441 - 532°C 269 - 276 bar Continuous flow reactor</td>
</tr>
<tr>
<td>Savage and Smith, 1995</td>
<td>45.6</td>
<td>308</td>
<td>1.0</td>
<td>0.6</td>
<td>2.0</td>
<td>O_2</td>
<td>380 - 440°C Batch reactor</td>
</tr>
</tbody>
</table>

* As reported by Frisch, 1992

* Values for pseudo-first-order rate expression

Table 3-1 Global Kinetic Parameters for SCWO of Acetic Acid by Other Researchers
suspect, however, for the following reasons: ammonium acetate rather than actual acetic acid was used as the feed without any mention of NH₃ or N₂ recovery (Lee and Gloyna, 1990); the oxidant was premixed with organic before heating; and the nonisothermal heatup time (up to 33% of total time) was not taken into account in their analysis. Using the same batch reactor, Frisch (1992) investigated SCWO kinetics of acetic acid with and without a CeO₂/MnO₂ catalyst. The catalyst was observed to have a noticeable effect on the oxidation rate, with 95% conversion achieved at 395°C in 5 min with the catalyst, and at 440°C in 10 min without the catalyst. In both cases, resulting kinetic parameters were determined by nonlinear regression to a power law rate expression with zero order in O₂ assumed. Again, no account of heatup time (about 100 s) was taken in the analysis, which in all cases was significant (17-83% of total residence time). Wilmanns and Gloyna (1990) also studied SCWO of acetic acid using H₂O₂ as the oxidant. They developed four possible rate expressions to explain their results, the best of which is shown in Table 3-1. In these studies, H₂O₂ was premixed with the acetic acid feed. About 70% of the feed was destroyed during pre-heating.

Boock and Klein (1993) investigated acetic oxidation under sub- and supercritical temperatures in a batch reactor. Although pseudo first-order is assumed in the calculation of rate constants and the activation energy, the fact that a variation in initial rate with starting concentration was observed at the lowest temperature (380°C) suggests that this assumption is tenuous. Experimental results by Rice et al. (1993) have also been correlated using pseudo-first order kinetics. Although H₂O₂ was used as the oxidant in these experiments, it was preheated separately before mixing with acetic acid, allowing sufficient time at temperatures above 400°C for the H₂O₂ to completely decompose to O₂ before reaching the feed. Savage and Smith (1995) determined kinetic parameters for SCWO of acetic acid from their batch reactor data using a global rate expression form that explicitly accounts for the concentration of water. The rate expression developed is first order in acetic acid, 0.6 order in O₂, and second order in H₂O.
3.2 Experimental Techniques

3.2.1 Apparatus and Operating Procedures Acetic acid experiments were carried out in the small-scale tubular reactor system that has been used in various modified form in our laboratory for all previous kinetic studies. A diagram of the system as used in the present experiments is shown in Figure 3-1.

Aqueous oxidant and organic feed solutions were prepared separately at ambient temperature in two, 3 L Hoke sampling or saturator cylinders (model 8HD3000; rated for 1800 psig). For oxidant solutions, approximately 2.5 L of deionized water was first added to the oxygen saturator. The saturator was then pressurized with O$_2$ gas and the contents were recirculated via a positive displacement pump (LDC Analytical, minipump model 2396) over a period of at least 12 hours until equilibrium was achieved. The pressure of O$_2$ needed was back-calculated from the desired aqueous concentration by Henry’s Law:

$$\phi_i P_i = x_i K(T, P)$$  \hspace{1cm} (3-1)

where $P_i$ is the partial pressure of oxygen in the vapor phase (assumed to be pure O$_2$), $\phi_i$ is the O$_2$ fugacity coefficient in the vapor phase, $x_i$ is the aqueous mole fraction of O$_2$, $T$ is temperature, $P$ is the total pressure, and $K(T,P)$ is the Henry’s Law constant for O$_2$ in H$_2$O. Values for $\phi$, which are not unity due to the high O$_2$ pressures required (between 200 - 1000 psi), were determined using the Peng-Robinson equation of state with parameters for O$_2$ taken from Reid et al. (1987). Values for $K$ at ambient temperature were calculated from the correlation of Benson et al. (1979). To correct for high pressure, the following relation was used:

$$\left( \frac{\partial \ln K(T, P)}{\partial P} \right)_T = \frac{\bar{V}^{\infty_i}}{RT}$$  \hspace{1cm} (3-2)

where $\bar{V}^{\infty_i}$ is the partial molar volume of O$_2$ at infinite dilution and $R$ is the gas constant.
Figure 3-1 Schematic of Small-Scale Plug Flow Reactor System
Integrating Eqn. 3-2 and referencing to ambient pressure $P_0$ yields the following equation for $K$:

$$K(T_0, P) = K(T_0, P_0) \cdot e^{\frac{-V_1^*}{RT} (P - P_0)}$$  \hspace{1cm} (3-3)

Values for $V_1^*$ for $O_2$ in $H_2O$ were determined from the correlation of Brevli and O’Connell (1972). The accuracy of Equations 3-1, 3-2, and 3-3 in describing dissolved $O_2$ concentrations in the oxidant feed has been verified through control experiments without organic feed in the same reactor system by Phenix (1998) and earlier by Holgate (1993). For hydrolysis/pyrolysis experiments (i.e. no $O_2$ present), the oxygen saturator was filled with pure deionized water only.

Acetic acid feed solutions were prepared in volumetric glassware under ambient conditions and loaded directly into the organic saturator. Feed samples were taken and analyzed to determine initial concentrations according to the analytical methods described in Section 3.2.2. A 10 psi backpressure of helium was always applied to the organic saturator, and applied to the oxygen saturator during hydrolysis/pyrolysis runs. Pressures in both saturators were measured by two Bourdon tube dial gauges (Heise; model CM, 0-3000psi).

Both oxidant and organic feeds were pumped separately up to operating pressure with a two-head, variable speed, positive displacement pump (LDC Analytical, minipump model 2396). System pressure was maintained by a back pressure regulator (Tescom; 26-3100 series) at the end of the system, and measured via a pressure gauge (Omega Engineering, model PGS-35B-7500-F) after the pump and pressure transducer (Dynisco; model µPR690) just before the back pressure regulator. Pressure drop in the system was negligible relative to the typical operating pressure of 246 bar. The two feeds then passed through 1.5 m (5 ft) of 0.159 cm (1/16") OD 316 stainless steel tubing contained in a preheater fluidized sandbath (Techne; model SBL-2). This preheater sandbath heated both feeds up to approximately 30% of the final desired operating temperature,
taking some of the heating load off of the main fluidized sandbath. Both sandbaths contained fine alumina sand which was heated by heating elements imbedded in the sand either around the circumference or at the bottom and fluidized by compressed air. This provided a medium of high thermal mass, good for rapid heatup and control of isothermal conditions once at the desired temperature. After leaving the preheater sandbath, the feeds were passed directly into the preheater tubing in the main sandbath (Techne; model FB-08). These 0.159 cm (1/16") OD coiled preheater tubes were 3 m (10 ft) long (2.8 m actually immersed in the sand) and constructed of Hastelloy C-276. Both feeds were heated further in their respective preheater tubing up to the final desired operating temperature (within a few degrees of that of the main sandbath) before finally mixing at the end in a Hastelloy C-276 high pressure cross fitting (High Pressure Equipment). The two feeds were mixed via cross injection into the cross fitting, where the mixing temperature was measured with an Inconel 600 sheathed type K thermocouple (Omega Engineering), and then entered the main reactor.

The main reactor was a coiled, thick-walled tube of Inconel 625 that was 4.71 m long with 0.635 cm (1/4") OD and 0.171 cm (0.067") ID. At the end of the reactor, fluid temperature was again measured in an exit tee fitting via thermocouple. The total volume of the main reactor (including entrance and exit fittings) was 11.11 cm³. Isothermal conditions were always maintained in the main reactor, as organic concentrations were dilute enough to avoid heat of reaction effects (see Section 3.2.3). Flow rates in the main reactor were maintained in the turbulent or transition regime (i.e. Reynolds number > 2100). At these flow rates, it was verified that the criteria compiled by Cutler et al. (1988) for ensuring plug flow conditions were satisfied. It is important to emphasize that oxidation conditions (during oxidation experiments) only existed in the main reactor, while hydrolysis or pyrolysis conditions always existed in the organic preheater tubing.
After exiting the main reactor and main fluidized sandbath, the effluent was immediately cooled back to ambient temperature in a shell and tube countercurrent heat exchanger with water used as the coolant. The effluent was then reduced to ambient pressure after passing through the back pressure regulator. The resulting two phase mixture was separated in a gas/liquid separator column, which consisted of a 1.27 cm (1/2”) OD tube filled with 4 mm glass beads. Gaseous effluent exited out the top of the separator into a bubble column, where the flow rate was measured. Liquid effluent exited out the bottom of the separator, where flow rate was measured by observing the time to accumulate a known volume in a volumetric flask. Effluent samples of both phases were taken at this location for product analysis.

3.2.2 Analytical Procedures Gaseous effluent compositions were determined by gas chromatography. A Hewlett Packard (HP) 5890 Series II gas chromatograph (GC) with a thermal conductivity detector (TCD) and helium carrier gas (20 mL/min flow) was used to detect, identify, and quantify O₂, N₂, CO₂, CH₄, and CO (eluting in that order). Two 1/8” OD packed columns, one 12 ft long and packed with 80/100 mesh Porapak T and the other 8 ft long and packed with 60/80 mesh molecular sieve 5A, were used together to provide reliable and clean separations of components. The columns were connected in series through an air actuated switching valve that allowed reversal of column order after O₂ and N₂ elution in order to minimize the elution time of CO₂. The GC oven temperature was initially set at 60°C for 7 min before ramping at 40°C/min up to 100°C. The oven was then held at 100°C for 6 min, resulting in a total program time of 14 min. A Perkin Elmer Sigma 1B GC also with a TCD detector and the same columns but nitrogen carrier gas was used to detect and quantify H₂ and He. The carrier gas flow rate was 40 mL/min and the oven was kept at a constant 60°C for a total program time of 7 min. The small amounts of helium observed resulted from its use as a means of loading the organic feed into its saturator and for providing back pressure to this feed during experiments.
Calibrations of both GC's were performed frequently by volumetric injection of pure gases. During an experiment, two 200 mL gas samples would be taken in succession for injection into the HP and Perkin Elmer GC. At the end of the HP GC program time, this sampling procedure would be repeated. Typically, six sets of gas samples would be taken during the course of an experiment. Gas compositions were determined from the measured volume fractions (i.e. volume of a particular gas species divided by total volume injected), which were then averaged for each species over at least the last three samples taken (depending on when the reactor system reached steady state operation).

Dissolved concentrations of gases in the liquid phase were calculated in the same way as aqueous O₂ feed concentrations through the use of Henry’s Law (Eqn. 3-1). Here it is assumed that the vapor and liquid phases in the gas/liquid separator were in equilibrium. Partial pressures of each component were calculated in the usual way as the product of the species’ vapor mole fraction (measured via GC) and total pressure (ambient in this case). Because the vapor phase was at ambient conditions, the fugacity coefficient in Eqn. 3-1 was set to unity. Values for the Henry’s Law constants near ambient temperatures for each species were taken from the following correlations: carbon monoxide from Rettich et al. (1982); hydrogen, helium, nitrogen, and carbon dioxide (with a correction for the dissociation of carbonic acid) from Wilhelm et al. (1977); and methane from Rettich et al. (1981).

Liquid effluent concentrations, as well as acetic acid feed concentrations, were determined by high-performance liquid chromatography (HPLC). A Rainin HPXL solvent delivery system with an Interaction ORH-801 analysis column and Interaction Ionguard guard column was used, along with a Rainin Dynamax UV-1 UV/visible detector set at 210 nm wavelength. A Timberline column heater maintained temperature at a constant 65°C. The mobile phase was 0.002 M H₂SO₄ delivered at 0.5 mL/min. Injection volumes were 100 μL. Peaks were identified by matching re-
tention times with that for injections of aqueous solutions of known compounds. Once identified, the HPLC was calibrated by preparing solutions of each compound at various relevant concentrations. Peak height rather than area was used for quantification purposes, since earlier work had shown that peak areas could be distorted from occasional peak overlap. Typically, at least three 17 mL liquid samples were taken during each experiment after the reactor system reached steady state operation. Final concentrations for each liquid effluent compound were determined by averaging over all individual sample concentrations of that compound.

3.2.3 Operating Conditions A total of 74 experiments with acetic acid in supercritical water were conducted - 64 under oxidation conditions and 10 under hydrolysis/pyrolysis (i.e. no added oxygen) conditions. A summary of the range of relevant variable values (temperature, pressure, residence time, flow rates, concentrations, and feed ratio) spanned in these experiments is displayed in Table 3-2. Tabulated data for each experimental run is included in Meyer et al. (1995).

The oxidation experiments can be divided into three groups. Fifteen temperature variation runs were carried out over the range of 425-600°C, all at 246 bar, 8 s main reactor residence time, and stoichiometric conditions (initial feed ratio = \([O_2]_0/[CH_3COOH]_0 = F = 2\) mM / 1 mM). Thirty eight concentration variation runs were conducted all at 525°C and 246 bar. In these experiments, both \(O_2\) and \(CH_3COOH\) initial concentrations were varied separately to achieve substoichiometric or fuel-rich (\(F = 1/1\)), stoichiometric (\(F = 2/1, 1/0.5, 3/1.5, 4/2\)), and superstoichiometric or fuel-lean (\(F = 4/1\)) conditions. During these concentration variation experiments, main reactor residence times were also varied from 4.4 to 9.8 s. In addition, one experiment each was performed under the more extreme feed ratios of \(F = 1/2\) and \(1/0.1\). Finally, eleven pressure/density variation experiments were carried out at 550°C and stoichiometric conditions (\(F = 2/1\)) over the range of 160-263 bar and 3.7 to 5.9 s main reactor residence times.
<table>
<thead>
<tr>
<th></th>
<th>Hydrolysis</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Experiments</td>
<td>10</td>
<td>64</td>
</tr>
<tr>
<td>Temperature</td>
<td>475 - 600°C</td>
<td>425 - 600°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>246 bar</td>
<td>160 - 263 bar</td>
</tr>
<tr>
<td>Main reactor residence time</td>
<td>7.6 - 8.8 s</td>
<td>3.7 - 9.8 s</td>
</tr>
<tr>
<td>CH\textsubscript{3}COOH solution mass flow rate</td>
<td>2.7 - 5.5 g/min</td>
<td>0.8 - 7.3 g/min</td>
</tr>
<tr>
<td>O\textsubscript{2} solution mass flow rate</td>
<td>1.8 - 5.0 g/min (pure water)</td>
<td>2.9 - 7.5 g/min</td>
</tr>
</tbody>
</table>

**Feed Conditions (at beginning of main reactor):**

- \([\text{CH}_3\text{COOH}]_0\) = (0.96 - 1.06) \times 10^{-3} \text{mol/L}
- \([\text{O}_2]_0\) = (0.019 - 0.024) \times 10^{-3} \text{mol/L}
- \([\text{O}_2]_0 / [\text{CH}_3\text{COOH}]_0\) ratio = 0.02

**Table 3-2 Acetic Acid Experimental Operating Conditions**

The ten hydrolysis/pyrolysis experiments were all performed at 246 bar and approximately 8 s main reactor residence times over a temperature range of 475-600°C. Initial acetic acid concentrations for hydrolysis/pyrolysis runs were 1 mM, while residual concentrations of O\textsubscript{2} in the water were calculated to be about 0.02 mM. Although not zero, these residual O\textsubscript{2} concentrations during hydrolysis/pyrolysis runs were at least two orders of magnitude smaller than those typically used in the oxidation runs.

Experimental errors for all measured quantities (e.g. temperature, pressure, ambient concentrations, etc.) cited in the sections below were based on the intrinsic error and limitations asso-
ciated with the measuring device and/or the variability observed in multiple measurements of the same quantity. Unless otherwise stated, all confidence intervals given for these quantities was 95%. Measurement uncertainties were propagated to uncertainties in calculated quantities (e.g. residence times, reactor concentrations, etc.) using standard propagation-of-error formulas (Aikens et al., 1984).

3.3 Hydrolysis/Pyrolysis Results The limited number of hydrolysis or pyrolysis experiments were performed in order to establish a base case against which oxidation results could be measured. In these hydrolysis/pyrolysis experiments, acetic acid conversions ranged from 5.9±3.5% (at 475°C) to as high as 35.2±2.7% (at 600°C). The very low conversion observed at 475°C (and up to 512°C) implies that acetic acid does have a refractory nature below 500°C, even without oxidant present. By 562°C (21.4±2.2%) and certainly by 600°C, however, acetic acid hydrolysis/pyrolysis conversion was statistically significant and appreciable. In fact, compared to earlier model compounds studied by our group such as methane (negligible hydrolysis conversion up to 652°C, 14.8 s residence time; Webley and Tester, 1991) and ammonia (1.1% hydrolysis conversion at 700°C, 10.5 s residence time; Webley et al., 1990, 1991), the 35% hydrolysis/pyrolysis conversion observed for acetic acid at 600°C and 8 s main reactor residence time was relatively high. This different behavior of acetic acid at the two temperature extremes studied is consistent with its role as an intermediate in the overall chain of breakdown of larger molecular weight compounds in supercritical water. It is refractory at relatively lower temperatures where larger, more typical wastes like glucose are destroyed, but can decompose into smaller, even more refractory compounds at higher temperatures.

According to these results, it is certainly possible that the hydrolysis or pyrolysis reaction occurred simultaneously with the oxidation reaction during oxidation experiments at temperatures of 525°C and above. This would be similar to that observed by Holgate et al. (1992) with CO
oxidation and the water gas shift reaction under oxidative conditions in supercritical water. Thus some of the conversion measured under oxidation conditions would actually be due to hydrolysis/pyrolysis. However, any contribution by the hydrolysis/pyrolysis reaction would likely be relatively small compared to that from oxidation at any temperature, as can be immediately discerned from Figure 3-2. Under oxidation conditions, the oxidation reaction was clearly the dominant means of acetic acid destruction (see the following sections). As an example, acetic acid hydrolysis/pyrolysis conversion at 550°C was about 16%, compared to about 98% conversion under the same conditions but with O₂ present (greater by more than a factor of six). Because practically no acetic acid conversion was observed below 512°C in these hydrolysis/pyrolysis experiments, it is unlikely that any significant breakdown occurred during heatup of the feed in the preheater tubing (where hydrolysis conditions always existed). Thus all kinetics calculations were based on residence times and volume in the supercritical main reactor only.

An assumed first-order regression of the acetic acid hydrolysis/pyrolysis data with an Arrhenius form for the rate constant resulted in the following global rate expression:

\[
R_{\text{hyd.CH₃COOH}} = \left(10^{4.4 \pm 1.1} \times e^{-\frac{94 \pm 17}{RT}}\right)[\text{CH₃COOH}]
\]  

(3-4)

where the units for the activation energy (\(E_a\)), pre-exponential factor (\(A\)), and concentration are kJ/mol, (L s)/mol, and mol/L, respectively. Uncertainties in Eqn. 3-4 reflect 95% confidence intervals. An Arrhenius plot (Figure 3-3) shows that the prediction of Eqn. 3-4 matches the data well, and that the assumption of first order for the hydrolysis or pyrolysis reaction of acetic acid appears reasonable. However, due to the limited number of data points and the fact that only temperature was varied, it is unclear how accurate Eqn. 3-4 truly is. Any model verification would require more experiments conducted over a wider range of operating conditions such as residence
Figure 3-2  Comparison of Acetic Acid Hydrolysis/Pyrolysis and Oxidation (Stoichiometric) Conversion at 246 Bar and 8 s Main Reactor Residence Time. For hydrolysis, $[\text{CH}_3\text{COOH}]_0 = 1$ mM. For oxidation, $F = 2/1$. Error bars represent 95% confidence intervals.
Figure 3-3 Comparison of Acetic Acid Hydrolysis/Pyrolysis and Oxidation (Stoichiometric) First-Order Arrhenius Plots at 246 Bar and 8 s Main Reactor Residence Time. For hydrolysis, [CH₃COOH]₀ = 1 mM. For oxidation, $F = 2/1$. Error bars represent 95% confidence intervals. Rate constant units are s⁻¹.
time, concentration, and pressure in addition to temperature. Figure 3-3 also compares hydrolysis/pyrolysis kinetics to assumed first-order oxidation kinetics (see Section 3.5).

The products detected from acetic acid hydrolysis/pyrolysis were methane (CH\textsubscript{4}), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}), and hydrogen (H\textsubscript{2}) in the vapor phase, and trace amounts of propenoic acid (about 10\textsuperscript{-7} M) in the liquid phase. Gases accounted for 76.0±16.6% of all reacted carbon at 512\textdegree C, which increased to 93.8±7.5% by 600\textdegree C. Below 550\textdegree C, effluent gas flow rates were below the lower limit of measurement in our reactor system (~ 0.3 mL/min). Because the vast majority of products were gaseous, the lack of an accurate gas flow rate below 550\textdegree C made carbon mass balances for runs at these temperatures unreliable. Mass balances on carbon were calculated based only on the amount of carbon in the acetic acid feed that reacted (as opposed to total effluent carbon) according to the following equation:

$$\text{product carbon balance} = \frac{\sum [\text{product } i] [\text{mol carbon/mol product } i]}{2([\text{CH}_3\text{COOH}]_0 - [\text{CH}_3\text{COOH}])} \times 100$$  \hspace{1cm} (3-5)

Carbon balances calculated via Eqn. 3-5 for runs at 562\textdegree C, 587\textdegree C, and 600\textdegree C were 75\%, 87\%, and 94\%. In general, mass balances improved with increasing temperature in both hydrolysis/pyrolysis and oxidation experiments because of the greater likelihood of breakdown of any intermediates to simpler compounds such as CH\textsubscript{4}, CO, CO\textsubscript{2}, and H\textsubscript{2}, which we were able to detect. Thus, one possibility for the lower carbon balances at 562\textdegree C and 587\textdegree C could have been the presence of one or more undetected compounds.

At temperatures above 512\textdegree C, CH\textsubscript{4} and CO\textsubscript{2} were the dominant products. Above 525\textdegree C, these two products accounted for > 91\% of gaseous products and were consistently observed in equal amounts. In contrast, H\textsubscript{2} and CO accounted for < 8\% and < 2\% of gaseous products, respectively. These findings suggest that the main reaction pathway of acetic acid occurring under
hydrolysis/pyrolysis conditions could have been a thermally-induced self-oxidation/reduction reaction, where a single acetic acid molecule decomposes into an oxidized product (CO₂) and a reduced product (CH₄) at the same time.

3.4 Oxidation Results The vast majority of experiments, and the more extensive investigation on the effects of changes in key operating variables on kinetics and product concentrations, were performed under oxidation conditions. Over the complete set of oxidation experiments conducted, acetic acid conversions ranged from as low as 7.9±3.7% up to complete destruction (99.9±0.1%). Values of the Reynolds number in the supercritical main reactor ranged from about 2100 to 5500. Under all conditions, the set of criteria assembled by Cutler et al. (1988) to ensure plug concentration and temperature profiles in the main reactor were satisfied.

The same gaseous products of CO, CO₂, CH₄, and H₂ seen in hydrolysis/pyrolysis experiments were seen in these oxidation experiments. The difference, however, was that in general there was much more CO and CO₂ and less CH₄ and H₂ from the oxidation experiments. In the liquid phase, propenoic acid was occasionally detected, but unreacted acetic acid was the only compound conclusively detected in all experiments via HPLC with UV detection. Two additional peaks were also observed in liquid phase analysis at approximately 5.0 and 17.7 min. Although reproducible, they could not be identified (i.e. retention times did not match) even after testing aqueous solutions of a number of different compounds thought to be the most likely possibilities. The compounds tested (Table 3-3) ranged over 1 to 6 carbon alcohols, aldehydes, ketones, esters, and acids, and included those such as maleic acid that could possibly result from additive combinations of acetic acid monomers. Even without identification of these unresolved peaks, product carbon balance closures for oxidation were reasonably good, particularly at the higher temperatures (90+% carbon accounted for in all but 3 runs above 500°C) where greater gasification, a disappearance in the 5.0 minute peak, and a reduction in the 17.7 minute peak occurred. Because of the
<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>15.9</td>
</tr>
<tr>
<td>Acetol (Hydroxyacetone)</td>
<td>10.4, 14.8</td>
</tr>
<tr>
<td>Acetone</td>
<td>18.3</td>
</tr>
<tr>
<td>Acetonylacetone (2,5-hexanediione)</td>
<td>19.75</td>
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<tr>
<td>Adipic acid</td>
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</tr>
<tr>
<td>n-Butanol</td>
<td>29.3</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>18.5</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>28.9</td>
</tr>
<tr>
<td>Crotonic acid</td>
<td>21.7</td>
</tr>
<tr>
<td>Dihydroxyacetone</td>
<td>11.9</td>
</tr>
<tr>
<td>3,3-Dimethylacrylic acid</td>
<td>27.4</td>
</tr>
<tr>
<td>Ethanol</td>
<td>18.2</td>
</tr>
<tr>
<td>Ethylacetate</td>
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</tr>
<tr>
<td>Ethylene Glycol</td>
<td>15.1, 15.6</td>
</tr>
<tr>
<td>Ethylmethacrylate</td>
<td>47.8</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>-</td>
</tr>
<tr>
<td>Formic acid</td>
<td>11.8</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>10.1, 11.0</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>10.6, 11.5</td>
</tr>
<tr>
<td>Glyceraldehyde</td>
<td>10.1</td>
</tr>
<tr>
<td>Hydroxyacetic (glycolic) acid</td>
<td>10.7</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>19.9</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>11.1</td>
</tr>
<tr>
<td>Levulinic acid</td>
<td>13.7</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>4.8, 5.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>16.1</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>5.2</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>21.7</td>
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<tr>
<td>Propenal (acrolein)</td>
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<td>Propenoic (acrylic) acid</td>
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<tr>
<td>Propionic acid</td>
<td>15.3</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>10.1</td>
</tr>
</tbody>
</table>

* Corresponds to detection at 290 nm wavelength

**Table 3-3  Compounds Tested As Possible Liquid Effluent Products from Oxidation of Acetic Acid.** Detection performed by HPLC with a UV detector. Retention times are for a wavelength of 210 nm except where indicated.
good carbon balance closure, the lack of a match in retention times with the known possible compounds tested, and more recent evidence of spurious peak detection by HPLC in the liquid effluent of methylene chloride oxidation, it is unlikely that the unidentified peaks at 5.0 and 17.7 minutes correspond to any new compounds present in a significant amount in the product stream above 500°C. Poor carbon balances (< 90%) below 500°C coincided with low acetic acid conversions and concentrations of gaseous products. Under these conditions it is possible that one or more products may have been present in the liquid effluent which were not sensitive to UV detection.

3.4.1 Temperature Variation Effects Temperature had the strongest effect on acetic acid conversion, with the maximum and minimum conversion values cited above occurring at the high and low end, respectively, of the temperature range investigated. A conversion of 98.0±0.3% was measured at 550°C (and 8 s residence time in the main reactor), with complete conversion (i.e., 99.9±0.1%) seen at all temperatures higher. At the other extreme, the three lowest temperatures of 425°C, 437°C, and 450°C all yielded similar very low conversion values of 9.2±8.9%, 7.9±3.7%, and 8.7±4.2%, respectively, implying a leveling off in conversion at these temperatures. Figure 3-2 shows experimental conversion values as a function of temperature for these temperature variation runs under oxidation conditions, along with the comparable runs under hydrolysis/pyrolysis conditions for comparison.

Below 500°C, these results confirm the refractory reputation repeatedly attributed to acetic acid in many earlier studies (such as those listed in Table 3-1). Our oxidation experiments show that even up to 487°C, acetic acid conversion was only about 25%. Since most of the earlier studies focused only on the 400-500°C operating regime, it is therefore not surprising that one would consider acetic acid to be a refractory compound. Our results also show, however, that acetic acid is destroyed quite readily above 500°C, and completely above 550°C. Thus, whether acetic acid is considered refractory or not really depends on the thermal intensity to which it is subjected. As
with the hydrolysis/pyrolysis results, this reactivity behavior of acetic acid is again consistent with it being an intermediate compound in the breakdown of higher molecular weight compounds.

3.4.2 Concentration, Feed Ratio, and Residence Time Variation Effects All of the concentration, feed ratio, and residence time variation experiments were performed at the same temperature of 525°C. This temperature was chosen because it was the value at which approximately 50% conversion of acetic acid was observed during the temperature variation experiments at 8 s residence time and a stoichiometric feed. Thus, use of this temperature as a base case would allow for the maximum possible changes in conversion to be observed resulting from variations in concentrations, feed ratios, and residence times above and below their base case values.

Acetic acid conversion values for the highest and lowest main reactor residence times at each of the six different sets of initial concentrations and feed ratios are listed in Table 3-4. In general, conversions showed a slight tendency to increase with increasing concentrations. For example, conversion values from 5 to 10 s residence time for the two stoichiometric feed cases of $F = 1/0.5$ and $2/1$ ranged roughly from 34 to 63%. At the higher stoichiometric concentrations of $F = 3/1.5$, conversions over the same residence time range were higher at 42 to 70%. The highest conversions for this residence time range of 46 to 77% occurred for the highest stoichiometric concentrations of $F = 4/2$. In line with this trend, substoichiometric ($F = 1/1$) conversions ranged slightly below those values for low-concentration stoichiometric conditions, while superstoichiometric ($F = 4/1$) conversions were similar to those at the higher stoichiometric concentrations. The data also show that varying $O_2$ concentrations ($F = 1/1, 2/1, 4/1$) has a larger effect on conversion than varying the acetic acid concentration ($F = 1/1, 1/0.5$). Although the magnitude of these effects of concentrations on conversions is not huge, this behavior is not consistent with true first-order kinetics. It should be noted that substoichiometric or fuel-rich runs were never oxygen
<table>
<thead>
<tr>
<th>$F ([O_2]_0 / [CH_3COOH]_0)$, (All concentrations in mmol/L)</th>
<th>$\tau$ (s)</th>
<th>$x$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stoichiometric feed</strong></td>
<td></td>
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</tr>
<tr>
<td>1 / 0.5</td>
<td>4.9 ± 0.2</td>
<td>34.2 ± 2.2</td>
</tr>
<tr>
<td></td>
<td>9.7 ± 0.5</td>
<td>63.5 ± 1.5</td>
</tr>
<tr>
<td>2 / 1</td>
<td>4.6 ± 0.3</td>
<td>31.0 ± 4.7</td>
</tr>
<tr>
<td></td>
<td>9.8 ± 0.5</td>
<td>62.2 ± 1.7</td>
</tr>
<tr>
<td>3 / 1.5</td>
<td>5.0 ± 0.2</td>
<td>42.2 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>9.7 ± 0.5</td>
<td>69.6 ± 1.1</td>
</tr>
<tr>
<td>4 / 2</td>
<td>4.9 ± 0.2</td>
<td>45.5 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>9.7 ± 0.5</td>
<td>76.7 ± 0.9</td>
</tr>
<tr>
<td><strong>Substoichiometric feed</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 / 1</td>
<td>4.4 ± 0.2</td>
<td>27.7 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>9.7 ± 0.5</td>
<td>55.1 ± 2.4</td>
</tr>
<tr>
<td><strong>Superstoichiometric feed</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 / 1</td>
<td>4.4 ± 0.2</td>
<td>41.6 ± 1.8</td>
</tr>
<tr>
<td></td>
<td>9.7 ± 0.5</td>
<td>76.5 ± 0.7</td>
</tr>
</tbody>
</table>

Table 3-4  Acetic Acid Conversion Values ($x$) for the Highest and Lowest Main Reactor Residence Times ($\tau$) at Each of the Six Different Sets of Initial Concentrations and Feed Ratios ($F$)

limited because there was always residual $O_2$ detected in the effluent, and acetic acid conversion at the longest residence time was only 55%.

The effect of concentration on acetic acid conversion can be better seen in Figures 3-4 and 3-5. Both figures show a plot of the logarithmically normalized acetic acid concentration versus main reactor residence time. Figure 3-4 shows data from the four sets of stoichiometric runs, while Figure 3-5 shows data from the substoichiometric, superstoichiometric, and stoichiometric
Figure 3-4  Normalized Decay Profiles for Stoichiometric Oxidation of Acetic Acid in Supercritical Water at 525°C and 246 Bar. Lines are linear fits to data. Error bars represent 95% confidence intervals. Concentration units are mM.
Figure 3-5  Normalized Decay Profiles for Sub- to Superstoichiometric Oxidation of Acetic Acid in Supercritical Water at 525°C, 246 Bar, and Constant Initial Acetic Acid Concentration. Lines are linear fits to data. Error bars represent 95% confidence intervals. Concentration units are mM.
(F = 2/1) runs all at the same initial acetic acid concentration (1 mM). For a first-order reaction in acetic acid, all the data points on each graph should be fit by the same straight line (since temperature was constant) which should also pass through the origin. Figure 3-4 shows that each group of data can be fit well by a straight line, but not all by the same line (except for the two sets of lowest concentrations). The same can be seen in Figure 3-5, although the separation of different sets of data is more pronounced. Again, these graphs indicate that conversion increases with increasing feed concentrations. Figure 3-5 in particular suggests that there must be some oxygen dependence in the reaction rate.

Another important point to note in Figures 3-4 and 3-5 is that none of the lines pass through the origin. Instead, they intersect at times ranging from 0.8 to 1.7 s. This behavior has been observed in previous SCWO studies on CO (Holgate and Tester, 1994a) and has previously been attributed to an apparent induction time (τ_{ind}). This induction time, or ignition delay after mixing, is frequently seen in free radical based combustion reactions, due to the finite time needed to build up a free radical pool of sufficient size to begin and propagate the reaction. While this may certainly be the case here since most SCWO reactions have free radical mechanisms, later work by Phenix (1998) since the time of these acetic acid experiments has shown that poor feed mixing might also be part of the cause for this observed induction time. In studies of methanol oxidation in supercritical water with the same apparatus, Phenix (1998) initially determined induction times of about 3 s from extrapolation of conversion versus time curves back to the x-axis. However, he noticed that if the inlet diameters for organic and oxidant feed in the mixing cross before the beginning of the main reactor were restricted, induction times were reduced down to 0.5 - 1 s. The reason for this decrease has been attributed to the higher inlet velocities and Reynolds numbers, and hence better mixing, resulting from the smaller feed diameters. The fact that the new methanol conversion data still could not be extrapolated back to the time axis through the origin indicates that there may still be a true kinetic induction time component associated with SCWO reactions in this
system. However, it is clear from these results that what was previously thought to be purely a kinetics phenomenon was affected to some extent by the geometry of the mixing cross and the resulting quality of feed mixing within it. Thus, apparent induction times from the acetic acid data may have also been due in part to less than ideal mixing conditions in the mixing cross. The magnitude of this effect may not have been as great as with methanol, though, because the observed acetic acid induction times were already lower than those seen with methanol.

Gaseous product concentrations, in general, increased with increasing main reactor residence times. Over residence times ranging from 4.6 to 9.8 s for a typical set of stoichiometric feed runs (i.e., 525°C, 246 bar, F = 2/1), CO₂ concentrations increased the most from 3×10⁻⁴ M up to 8×10⁻⁴ M, representing an increase in the product carbon balance from 45% to 62%. CO and CH₄ concentrations increased only slightly from about 1×10⁻⁴ M to 2×10⁻⁴ M under the same conditions. H₂ concentrations were about an order of magnitude lower from 1×10⁻⁵ M to 2×10⁻⁵ M. Based on earlier SCWO studies of H₂ (Holgate and Tester, 1993) and CH₄ (Webley and Tester, 1991), however, the lower concentrations of H₂ likely reflect some loss due to its own oxidation under these conditions. The observed CH₄ concentrations, on the other hand, are probably a good indicator of all that was formed from acetic acid breakdown since minimal CH₄ oxidation would be expected at 525°C.

Figure 3-6 compares product concentrations from the most concentrated and least concentrated stoichiometric feed runs (i.e., F = 1/0.5 and 4/2). As acetic acid and O₂ concentrations were increased by a factor of four, CO₂ concentrations were affected the most, increasing by about an order of magnitude. CO and CH₄ concentrations both increased by a comparable factor of four. H₂ concentrations showed minimal effect from increasing feed concentrations. As expected, product concentration profiles for the stoichiometric runs of F = 3/1.5 and 2/1 lie in between the limits defined by the F= 4/2 and F = 1/0.5 runs.
Figure 3-6 Major Products Profiles for Stoichiometric \( F = 1/0.5, 4/2 \) Acetic Acid Oxidation in Supercritical Water at 525°C and 246 Bar: (a) CO and CO\(_2\); (b) CH\(_4\) and H\(_2\). Lower profile for each species represents \( F = 1/0.5 \); higher profile represents \( F = 4/2 \). Error bars represent 95% confidence intervals.
The effects on the product distribution of varying O$_2$ feed concentration by a factor of four while keeping acetic acid feed concentration constant can be seen in Figure 3-7. Here, product and residual feed concentrations from the superstoichiometric ($F = 4/1$) and substoichiometric ($F = 1/1$) runs are displayed as a function of main reactor residence time. Note that the O$_2$ concentration profile for the superstoichiometric runs has been omitted to enhance the detail of the other lower concentration profiles. The shift in the residual acetic acid profile with increasing O$_2$ feed concentrations again shows evidence of the oxygen dependence of the rate of acetic acid oxidation. As before, CO$_2$ concentrations showed the largest effect from increasing O$_2$ feed concentrations, while CH$_4$ and CO were less affected and H$_2$ showed little effect. This behavior for H$_2$ is consistent with the first order kinetics for H$_2$ oxidation in supercritical water determined by Holgate and Tester (1993).

3.4.3 Pressure Variation Effects  The pressure variation experiments spanned from subcritical to supercritical values of 159.6±4.8 to 263.0±6.2 bar. Experiments were carried out at either 4 s or 6 s residence time in the main reactor. All of the experiments were conducted at a constant temperature of 550°C and stoichiometric feed concentrations of O$_2$ and acetic acid ($F = 2/1$). As with the concentration variation runs, these conditions were chosen in order to allow for the maximum possible change in the acetic acid oxidation rate and conversion due to effects associated with the changing pressure. Note that the conditions at the lowest pressure correspond to a high density vapor phase.

Acetic acid conversions from the 4 s runs ranged from 63.9±2.0% to 85.6±1.3%, while conversions from the 6 s runs ranged from 80.1±3.6% to 92.5±0.3%. At a given residence time, conversions generally increased with increasing pressure. If one assumes a first-order reaction rate, the apparent first-order rate constant $k'$ can be calculated from the well-known integrated form of the rate expression:
Figure 3-7  Major Product Profiles for Substoichiometric (Oxygen-Lean; $F = 1/1$) and Superstoichiometric (Oxygen-Rich; $F = 4/1$) Acetic Acid Oxidation in Supercritical Water at 525°C and 246 Bar. Lower profile for each species except acetic acid represents $F = 1/1$; higher profile for each species except acetic acid represents $F = 4/1$. Note that $O_2$ profile for $F = 4/1$ is not shown. Error bars represent 95% confidence intervals.
\[ k^* = \frac{-\ln(1-x)}{\tau} \]  

(3-6)

where \( x \) is the acetic acid conversion and \( \tau \) is the residence time. Figure 3-8 displays the calculated values of \( k^* \) for these experiments as a function of pressure and water density. At both residence times, \( k^* \) shows a slight increase in value with increasing pressure and density. This effect of pressure on \( k^* \) is much smaller than that observed in \( \text{H}_2 \) oxidation (Holgate and Tester, 1994a), where values of \( k^* \) increased by almost an order of magnitude over a comparable pressure range.

Although already small, the observed effect of pressure on \( k^* \) is still somewhat exaggerated in Figure 3-8 for two reasons. First, the natural variation in fluid volumetric flow and density with pressure, restrictions imposed by our feed pump, and the desire to maintain Reynolds numbers above 2100 (to avoid the laminar flow region) resulted in an unavoidable small variation of residence time with pressure. At low pressures, the maximum residence time was constrained by the desire to maintain turbulent flow conditions. At high pressures, the minimum residence time was constrained by maximum flow rate of the pump. The result was that lower pressures tended to correspond to slightly shorter residence times, while higher pressures tended to correspond to slightly longer residence times (and more time to react). The difference in actual residence time between the lowest and highest pressures was as much as 0.5 s. Second, the complicating effect of induction times (which cannot be accounted for in the simple form of Eqn. 3-6) may have affected the calculation of \( k^* \). Regardless of whether the source of the measured induction time is due to the true kinetic phenomenon or less than ideal mixing, small increases in the residence time could result in a noticeable increase in \( k^* \) when the induction time is of similar magnitude to the residence time. This may explain why the apparent effect of pressure on \( k^* \) for the 4 s residence time runs was greater than for the 6 s residence time runs.
Figure 3-8  Effect of Operating Pressure on the Apparent First-Order Rate Constant, $k^*$, for Stoichiometric ($F = 2/1$) Acetic Acid Oxidation in Supercritical Water at 550°C. Error bars represent 95% confidence intervals.
In terms of product concentrations, CO₂ production was slightly enhanced at the expense of CO while H₂ concentrations showed a small decrease with increasing pressure. CH₄ concentrations remained virtually the same over the same range. In general, pressure seems to have had less of an effect on acetic acid oxidation kinetics and products than the other variables investigated.

3.5 Development of Oxidation Global Kinetics Rate Expression  In principle, the global oxidation reaction rate of acetic acid in supercritical water can be expressed as follows:

\[ R_{\text{ox,CH}_3\text{COOH}} = -k[\text{CH}_3\text{COOH}]^a[\text{O}_2]^b[\text{H}_2\text{O}]^c \] (3-7)

where \( k \) is the rate constant and \( a, b, \) and \( c \) are the reaction orders with respect to acetic acid, oxygen, and water, respectively. Eqn. 3-7 is of a power law rate form, which assumes that there are no complicating catalytic effects present from the reactor walls. The rate constant \( k \) is assumed to be of Arrhenius form:

\[ k = A e^{\left(\frac{E_a}{RT}\right)} \] (3-8)

where \( E_a \) is the activation energy, \( A \) is the pre-exponential factor, and \( R \) is the universal gas constant.

Because water was present in vast excess (mole fraction > 0.999) with the dilute feeds used in our experiments, and because temperature and pressure were constant in the supercritical main reactor where most of the reaction of acetic acid occurred (see Section 3.3), the water density or concentration was virtually constant in the area of interest of the reactor system. The temperature difference between the entrance and exit of the main reactor was never more than 3°C, while the pressure variations in the isobaric runs were typically only ± 6 bar at 246 bar in these experiments. Thus, the water concentration term in Eqn. 3-7 could be absorbed into the rate constant, resulting in the following form of the rate expression:
\[ R_{\text{ox,CH}_3\text{COOH}} = -k' [\text{CH}_3\text{COOH}]^a [\text{O}_2]^b \] (3-9)

where

\[ k' = k [\text{H}_2\text{O}]^c \] (3-10)

In order to relate the kinetic parameters of activation energy, pre-exponential factor, and reaction orders to the measurable experimental data, the plug flow reactor design equation must be used:

\[ \frac{\tau}{C_{i,0}} = \int_0^1 \frac{dx_i}{R_i} \] (3-11)

where \( \tau \) is the space time, \( C_{i,0} \) is the initial concentration of species \( i \), \( x_i \) is the conversion of species \( i \), and \( R_i \) is the rate of reaction for species \( i \). Another consequence of water being in such excess is that the effect of the change in volume due to reaction stoichiometry on the overall solution density should be negligible. Thus \( \tau \) is also the residence time. By combining Eqn. 3-11 with Eqns. 3-9 and 3-8, and relating oxygen concentration to acetic acid concentration via the extent of reaction, the following form of the plug flow reactor design equation for isothermal acetic acid oxidation is derived:

\[ [\text{CH}_3\text{COOH}]_{i,0}^a (k \tau)^{-1} = \int_0^1 \frac{dx}{(1-x)^a (F - S x)^b} \] (3-12)

where \([\text{CH}_3\text{COOH}]_{i,0}\) is the initial acetic acid concentration, \( x \) is the acetic acid conversion, \( F \) is the feed ratio of initial concentrations ([O\(_2\)]/[CH\(_3\)COOH]\(_{i,0}\)) as defined earlier, and \( S \) is the \text{O}_2/\text{CH}_3\text{COOH} stoichiometric ratio for the oxidation reaction. Integration of Eqn. 3-12 gives acetic acid conversion as a function of the experimental variables of temperature, residence time, and initial concentrations.

Optimal values of the kinetics parameters \((E_a, A, a, \text{ and } b)\) for use in Eqn. 3-12 were determined by nonlinear regression of the experimental data. The objective of the nonlinear regression was to find values for the unknown kinetics parameters (regarded as the independent vari-
ables) that predict a chosen experimental (or dependent) variable as close as possible to that observed experimentally (i.e. by minimizing the sum of squares differences between the predicted and observed values). Results from fifty of the fifty three constant pressure experimental runs (i.e., temperature variation and concentration, feed ratio, and residence time variation runs) were used as the input data for the regression routine (runs with conversions > 99% were excluded).

The procedure is a two-step, iterative process. First, for a given choice of \( A, E_a, a \) and \( b \), one must compute values for the dependent parameter by numerically integrating Eqn. 3-12 for each experimental data set. Second, one adjusts the independent parameters based on the difference between the computed and measured values for the dependent parameter. This step was performed using the multivariable Powell SSQMIN algorithm (Kuester and Mize, 1973) as the nonlinear optimization routine. This program requires as input a subroutine containing a model to compute the dependent parameter in terms of the independent parameters, which in this case is provided by the isothermal plug flow reactor design equation (Eqn. 3-12). After generating new values for the kinetic parameters, values for the dependent parameter are recalculated by returning to step one. The process repeats in this fashion until a set of kinetic parameter values that provides a best-fit to the dependent parameter values is obtained.

Although the choice of dependent variable for the regression routine is arbitrary in principle, there are practical constraints which clearly rank some variables as a better choice than others. In the present case, neither \( x \) nor \( F \) can be chosen since the integral in Eqn. 3-12 cannot be evaluated without knowledge of these values. Of the remaining experimental variables (\( T, [\text{CH}_3\text{COOH}]_0 \) and \( \tau \)), the one chosen as the dependent variable must have all values known to good precision and of the same order of magnitude to avoid skewed results that arise when considering the percentage difference between predicted and observed values for values of different orders of magnitude. As elaborated on further by Holgate (1993), \( T \) is the best choice in this case since it is known not only to high precision (unlike \( \tau \)) but also varies by only a factor of 1.4 over a
relatively narrow range from 425°C to 600°C (unlike [CH₃COOH]₀, which varies more than 4 fold). To solve for T as the dependent variable in the nonlinear regression routine, Eqn 3-12 is first solved via numerical integration for \( k' \), from which T in turn can be calculated through the Arrhenius expression (Eqn. 3-8).

One final point to note in the integration of Eqn. 3-12 is the appropriate value to use for the stoichiometric ratio, \( S \). Based on the stoichiometry for the complete oxidation reaction of acetic acid:

\[
\text{CH}_3\text{COOH} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}
\]  

(3-13)

one would expect a value of 2 to be used for \( S \). Although this choice would be unequivocally correct if \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) were the only products observed experimentally, the other carbon-based products detected (such as CO and \( \text{CH}_4 \)) indicate that not all of the acetic acid reacting was converted to \( \text{CO}_2 \). Because \( \text{CO}_2 \) was always the dominant product in the oxidation experiments, however, it is still reasonable to start by using a value of \( S = 2 \).

With temperature chosen as the dependent variable and a value of two chosen for \( S \), the best-fit kinetic parameters and resulting global rate expression for acetic acid oxidation in supercritical water is:

\[
R_{\text{ox.CH}_3\text{COOH}} = \left( 10^{9.9 \pm 1.7} \cdot e^{-(168 \pm 2)/R_T} \right) [\text{CH}_3\text{COOH}]^{0.72 \pm 0.15} [\text{O}_2]^{0.27 \pm 0.15}
\]  

(3-14)

where the rate is in units of mol/(L s), concentrations are in mol/L, and the assumed constant activation energy is in kJ/mol. All parameter uncertainties are at the 95% confidence interval and were determined by an inverted curvature matrix (Press et al., 1986). This nonlinear regression gives a significance level of 100%, with an F-statistic of 110 and a 0.85 R-squared value (adjusted for degrees of freedom). Note that Eqn. 3-14 includes the contribution of the relatively small hydroly-
sis/pyrolysis reaction occurring simultaneously. In regards to the presence of the incomplete oxidation products, the regression was rerun with a value for $S$ of 1.5. The results for the best-fit kinetic parameters in this case were: $A = 10^{9.6 \pm 1.6}$, $E_a = 160 \pm 18$ kJ/mol, $a = 0.70 \pm 0.14$, and $b = 0.38 \pm 0.16$. The fact that these values are not statistically different from the values determined for $S = 2$ indicates that the regression results are not sensitive to the value chosen for $S$.

The two most noticeable features of Eqn. 3-14 are the small but statistically significant $O_2$ dependence and the close but still non-first-order dependence of acetic acid. This $O_2$ dependence in the rate expression confirms and explains the lack of first-order behavior already pointed out in the data shown in Figures 3-4 and 3-5. In this regard, acetic acid oxidation is different from other simpler model compounds studied by our group such as methanol, ethanol, and hydrogen, which all displayed global oxidation kinetics in supercritical water independent of $O_2$ and first-order in organic species.

Because many other researchers have correlated acetic acid oxidation kinetics in terms of first-order behavior, and because our values for $a$ and $b$ in Eqn. 3-14 are not too far removed from 1 and 0 respectively, the regression routine was rerun with $a$ and $b$ forced to these values. In this case, Eqn. 3-12 simplifies to the following form:

$$k^* = \frac{-\ln(1-x)}{\tau} \quad (3-15)$$

The resulting first-order global rate expression determined is:

$$R_{ox,CH_3COOH} = \left(10^{1.1 \pm 1.6} e^{-\frac{[183 \pm 24]}{RT}}\right)[CH_3COOH] \quad (3-16)$$

with parameter 95% confidence intervals shown. Figure 3-9 shows an assumed first-order Arrhenius plot of data from the temperature variation runs and the concentration, feed ratio, and
residence time variation runs (which appear as a stack of data points at 525°C). Values of the apparent first-order rate constant corresponding to the data points were calculated via Eqn. 3-15. The straight line is the predicted behavior from the regressed first-order kinetic parameters given in Eqn. 3-16. Overall, the linear fit to the data is reasonably good, indicating that first-order behavior is not a bad approximation. Nevertheless, the slight curvature of the data relative to the straight line shows again that first-order is still just an approximation of the experimentally determined behavior, in accordance with Eqn. 3-14. The fact that the data points at 525°C don’t all fall on top of each other further shows the non-first-order dependence on concentrations.

Finally, our data is compared to those of other researchers (listed in Table 3-1) in the assumed first-order Arrhenius plot of Figure 3-10. The results from the other studies shown are for those that used O₂ as the oxidant under reaction conditions. This plot shows that our results are comparable to these other studies, at least in terms of activation energy.
Figure 3-9 Assumed First-Order Arrhenius Plot for Acetic Acid Oxidation in Supercritical Water at 246 Bar Based on Data from Present Study. Error bars represent 95% confidence intervals.
Figure 3-10 Assumed First-Order Arrhenius Plot for Acetic Acid Oxidation in Supercritical Water - Comparison of Data from Present Study with Those of Other Investigators Who Used $O_2$ as the Oxidant under Reaction Conditions. Error bars represent 95% confidence intervals.
Chapter 4

Hydrolysis and Oxidation of Methylene Chloride - Experimental Data and Observations

4.1 Introduction and Literature Review  In recent years, there has been much interest in the use, disposal, and environmental fate of chlorinated organic compounds. The past popularity of many of these compounds can be traced to their many useful roles in industrial and commercial processes, most notably as solvents, pesticides, and chemical intermediates. With increasing use, however, has come a mounting concern over their increasing presence in the environment and the relatively high toxicity that is characteristic of many of these halocarbon compounds. For example, polychlorinated alkanes now account for a significant fraction of organic chemicals on the US EPA designated priority pollutant list (Roberts et al., 1993).

Chlorinated organic compounds have also been one of the most difficult groups of compounds to destroy by conventional processes such as incineration due to their high stability and/or the often more toxic by-products such as dioxins that can form under some conditions. SCWO is one technology, however, that has been shown to be very effective in destroying many types of chemically stable compounds including these troublesome chlorinated species. In numerous tests before 1996, MODAR, Inc. demonstrated greater than 99.99% destruction for many chlorinated aromatics and hydrocarbons such as polychlorinated biphenyls (PCBs), DDT, chlorinated dioxins, chlorobenzenes, trichloroethylene, and chlorinated methanes, to name a few, under temperatures in the range of 550-650°C and residence times of about 1 minute or less (Tester et al., 1993; Thoma-
son et al., 1990; Staszak et al., 1987). In a similar process but under subcritical conditions known as wet oxidation, Dietrich et al. (1985) reported destruction efficiencies in excess of 99% for 2-chlorophenol, chloroform, carbon tetrachloride, 1,2-dichloroethane, hexachloropentadiene, 1-chloronaphthalene, and 2,4-dichloroaniline, all at temperatures between 275 and 320°C and residence times of 60 minutes.

Although destruction efficiency studies are useful, they do not give any quantitative information about the rate of organic destruction or any mechanistic information. Kinetic studies under well defined conditions of temperature, pressure, and composition provide data and mathematical models necessary for design and optimization of effective commercial scale SCWO processes. Kinetic studies on the oxidation of chlorinated organic species in supercritical water thus far, however, have focused mostly on aromatic compounds. Yang and Eckert (1988) studied oxidation kinetics of p-chlorophenol in a flow reactor under conditions of 310 - 400°C and 5 - 60 s residence time. Jin et al. (1990) studied catalytic oxidation of 1,4-dichlorobenzene with a V₂O₅ catalyst in a batch reactor under conditions of 343 - 412°C and up to 60 min residence times. Lee et al. (1990) studied oxidation of 2,4-dichlorophenol with both O₂ and H₂O₂ as oxidants. Li et al. (1993) used a plug flow reactor to determine the global kinetics of 2-chlorophenol oxidation for the conditions of 300 - 420°C and 4 - 70 s residence times. More recently, Houser and Liu (1996) have studied the pyrolysis and hydrolysis reactions of 1-chloro-3-phenylpropane, 2-chlorotoluene, and 4-chlorophenol between 400 - 500°C and from 30 - 260 min residence times. The reactions were carried out in metal and glass ampoule batch reactors to explore catalytic effects. Foy et al. (1996) have explored hydrolysis and oxidation reactions of trichloroacetic acid, trichloroethylene, and 1,1,1-trichloroethane in water from 250 - 500°C and 30 - 100 s residence times near 650 bar.

As mentioned earlier in Chapter 1, methylene chloride (CH₂Cl₂) was selected as a model chlorinated compound for this present study. Because of its nonflammable nature, low boiling
Hydrolysis and Oxidation of Methylene Chloride - Experimental Data and Observations

point, and excellent solvent power for nonpolar compounds, methylene chloride has been widely used commercially in the past, such as in metal cleaning and degreasing, liquid extraction, manufacture of paint strippers and adhesives, as a foaming or aerosol agent, and as a process solvent in the manufacture of pharmaceuticals and fine organic chemicals (Edwards et al., 1982). Although its use today is becoming increasingly restricted because of concern over its health effects, it remains a good choice for study as a representative chlorinated waste because its earlier widespread use has made it a common environmental contaminant (Page, 1981). Study of CH₂Cl₂ also allows the details of C-Cl chemistry in sub- and supercritical water to be investigated using a comparatively simple substrate.

The literature does not appear to show evidence of any prior kinetic studies of CH₂Cl₂ in supercritical water. While MODAR, Inc. (Thomason et al., 1990) and Sandia National Laboratories (Rice et al., 1993) have experimentally studied SCWO of CH₂Cl₂ (as well as a number of other chemicals), their focus was on obtaining high destruction and removal efficiencies, not kinetic data. There have been, however, several kinetic studies on subcritical liquid and vapor hydrolysis of CH₂Cl₂ and a number of other chlorinated alkanes and alkenes. Fells and Moelwyn-Hughes (1958) investigated the kinetics of CH₂Cl₂ hydrolysis in water under acidic and alkaline conditions over a temperature range of 80 to 150°C (see Chapter 6 for more details on their results). Moelwyn-Hughes also conducted similar kinetic studies on the other members of the chlorinated methane series: chloromethane (Moelwyn-Hughes, 1949; 1953), and chloroform and carbon tetrachloride (Fells and Moelwyn-Hughes, 1959). In similar studies, Chuang and Bozzelli (1986) investigated the vapor phase hydrolysis of chloroform at 611 to 1050°C and 1 atm, while Gaisinovich and Ketov (1969) investigated the hydrolysis kinetics of carbon tetrachloride at 350 - 550°C. More recently, Jeffers and coworkers (Jeffers et al., 1989; Jeffers and Wolfe, 1996; Jeffers et al., 1996) have examined and correlated the hydrolysis kinetics of a number of chlorinated methanes, ethanes, ethenes, and propanes over the range of 0 - 180°C and pH values of 3 - 14.
There are a number of review articles (Mabey and Mill, 1978; Vogel et al., 1987; Washington, 1995) that have tabulated hydrolysis kinetic data in the literature for a number of halogenated species including CH₂Cl₂.

Recent specific work on reactions of CH₂Cl₂ range from combustion to surface reaction studies. Catalytic combustion of methylene chloride in air was carried out by a number of researchers using a variety of different catalysts (Young, 1982; Liepa, 1988; Hung and Pfefferle, 1989; and Shaw et al., 1993). All compared conversions and product distributions achieved with the different catalysts tested. Taylor et al. (1991) have investigated the oxidative pyrolysis of CH₂Cl₂ (i.e. combustion under fuel rich conditions) in a laminar flow, fused silica tubular reactor between 300 - 1000°C and atmospheric pressure at a gas phase residence time of 2.0 s. They looked at the oxidative pyrolysis of CHCl₃ and CCl₄ as well. Bond and Calzadilla (1996) examined the catalytic hydrolysis of CH₂Cl₂ (along with CHCl₃ and CCl₄) over γ-Al₂O₃ and TiO₂ catalysts at 340 - 435°C, and determined kinetic parameters for a Langmuir-Hinshelwood type rate expression. Papenmeier and Rossin (1994) also developed a catalytic rate expression for CH₂Cl₂ (as well as for CHCl₃ and CH₂Cl₂/CHCl₃ mixtures), but under oxidation conditions between 300 - 400°C with a Pt/κ-δ Al₂O₃ catalyst in the presence of both dry and humid air. Gillham and O'Hannesin (1994) and Matheson and Tratnyek (1994) studied the effect of iron on the reduction of a number of chlorinated methanes (including CH₂Cl₂), ethanes, and ethenes in aqueous solution (see Section 7.3.6.2 for more details on their results).

Earlier MIT work on SCWO of CH₂Cl₂ was reported by Meyer (1993). Because of various experimental difficulties encountered, this early study led to significant improvements in sampling techniques and analytical capabilities, which were used in the gathering of the data reported in the present study (and described below). These developments have in turn led to an enhanced overall understanding of the reaction of CH₂Cl₂ in sub- and supercritical water.
4.2 Experimental Apparatus and Operating Procedures The experimental system used for this study of CH$_2$Cl$_2$ was the same small-scale, plug flow, tubular reactor system used in the study of acetic acid (and described fully in Section 3.2.1). Methylene chloride feed solutions were prepared under ambient conditions by adding pure CH$_2$Cl$_2$ by syringe to a 2 L volumetric flask of deionized water. Following vigorous mixing to solubilize the CH$_2$Cl$_2$ (the amount added was always an order of magnitude below its solubility limit in water at STP), the resulting single phase, dilute solution was then loaded into the organic saturator (see Figure 3-1) and pressurized with 10 psi of helium. Because of the relatively high volatility and low solubility of CH$_2$Cl$_2$ in water, a low pressure valve was installed on the organic feed line just before the feed pump. This added valve (which was the only physical change to the system compared to that described earlier for acetic acid) allowed us to sample the aqueous CH$_2$Cl$_2$ feed as close to the reactor as possible for accurate determination of CH$_2$Cl$_2$ feed concentrations.

The preheater fluidized sandbath was not turned on for these experiments to help minimize the time spent by the CH$_2$Cl$_2$ at high temperature before entering the reactor. Thus both organic and oxygen aqueous feeds entered their respective preheater coils in the main fluidized sandbath at ambient temperature. The main reactor was again kept isothermal; the measured temperature difference between reactor inlet and exit was usually $\leq$ 3°C and never $>$ 6°C. Flow conditions were always turbulent (Re $>$ 2100) in the main reactor while laminar conditions did exist in sections of the preheater tubing during some experiments. As will become evident shortly, it is important to again emphasize that regardless of the type of experiment conducted (hydrolysis or oxidation), hydrolysis conditions always existed in the preheater tubing containing the CH$_2$Cl$_2$ aqueous feed. By its very nature, much of the time spent in the preheater tubing by the feed was under subcritical or near-critical temperatures. In oxidation experiments, oxygen was not introduced to the CH$_2$Cl$_2$ feed until the end of the preheater tubing, where both CH$_2$Cl$_2$ and O$_2$ feeds (now at supercritical
temperatures) were joined in the mixing cross at the entrance to the main reactor. Oxidation, therefore, always took place under supercritical conditions only.

### 4.3 Operating Conditions

A total of 66 experiments with CH₂Cl₂ were conducted - 43 under oxidation conditions and 23 under hydrolysis (i.e. no oxygen added) conditions. Complete data tables which include all measured and calculated run conditions for each experiment are included in Tables 12-1 and 12-2 in the Appendix. Table 4-1 summarizes the range of values for the major operating variables (temperature, pressure, residence time, flow rates, concentrations, and feed ratio) over all these experiments in both the preheater tubing and the main reactor.

In both Table 4-1 and the data tables in the Appendix, feed concentrations ([CH₂Cl₂]₀ and [O₂]₀) cited at the beginning of the preheater are values at ambient temperature. Feed concentrations cited at the entrance to the isothermal main reactor correspond to the reactor operating temperature after adjusting for dilution due to the mixing of the two feed solutions at the end of their respective preheater coils. The CH₂Cl₂ feed concentrations at the beginning of the main reactor also reflect the effect of subcritical hydrolysis in the preheater tubing in addition to density changes and dilution, and were calculated using the temperature profile models developed in Chapter 5 and the global rate expression determined in Chapter 6. Preheater residence times were also determined from the temperature profiles. In all calculations, the concentrations of the CH₂Cl₂ and O₂ feed solutions were considered sufficiently dilute to permit the use of density values for pure water at the given temperature and pressure. In Tables 12-1 and 12-2, values of conversion were calculated from measured CH₂Cl₂ concentrations from samples taken at the end of the experimental system (i.e. after the gas/liquid separator under ambient conditions). These conversion values thus reflect net reaction in the preheater tubing and main reactor for any given run. Note also that all experiments were isobaric at approximately 246 bar.
Number of pure hydrolysis experiments performed: 23 (two with the main reactor removed)

Number of oxidation experiments performed: 43

<table>
<thead>
<tr>
<th>Environmental Conditions</th>
<th>Preheater Tubing</th>
<th>Isothermal Main Reactor</th>
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<tbody>
<tr>
<td>Environment of CH₂Cl₂ feed</td>
<td>hydrolysis only</td>
<td>hydrolysis, oxidation</td>
</tr>
<tr>
<td>Temperature</td>
<td>ambient - 600°C</td>
<td>450°C ≤ T ≤ 600°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>246 bar</td>
<td>246 bar</td>
</tr>
<tr>
<td>Residence time</td>
<td>7 - 17 s</td>
<td>4 - 9 s</td>
</tr>
</tbody>
</table>

**Feed Conditions:**

- [CH₂Cl₂]₀: 6 - 38 × 10⁻³ mol/L
- [O₂]₀: 14 - 52 × 10⁻³ mol/L
- [O₂]₀ / [CH₂Cl₂]₀ feed ratio: 0
- CH₂Cl₂ solution mass flow rate: 2.4 - 6.4 g/min
- O₂ solution mass flow rate: 2.9 - 6.7 g/min
- 0.2 - 0.6 × 10⁻³ mol/L
- 0.56 - 2.08 × 10⁻³ mol/L
- (0.02 - 0.03 × 10⁻³ mol/L)
- 1.0 - 4.9
- (0.04 - 0.1)

| Table 4-1 Summary of Experimental Operating Conditions for CH₂Cl₂. Initial concentrations listed correspond to conditions at the entrance to the appropriate tubing. Values in parenthesis are for hydrolysis runs. |

All twenty three of the pure hydrolysis experiments were carried out over a main reactor or sandbath temperature range of 450 - 600°C at a constant main reactor residence time of 6 s. Preheater residence times, however, were not constant for these runs, and tended to increase with increasing sandbath temperature. The reason for this is that in order to maintain constant main reactor residence times with increasing sandbath temperature, feed mass flow rates were decreased to...
compensate for the increasing volumetric flow rates at higher temperatures. Methylene chloride feed concentrations at the entrance to the main reactor (i.e. under supercritical temperatures) were generally between 0.2 - 0.6 mM. Oxygen concentrations, representing residual O₂ in the water used, were at least an order of magnitude smaller under the same conditions. Most of these hydrolysis experiments were originally conducted primarily to serve as a base case for a corresponding oxidation experiment under the same conditions. In order to gain a measure on the amount of CH₂Cl₂ breakdown occurring in the preheater tubing, two hydrolysis runs, one at 450°C (#467) and the other at 575°C (#468), were performed with the main reactor removed from the sandbath and replaced by a 40 cm length of stainless steel tubing. All other run operating conditions were kept the same as that for the corresponding hydrolysis run with the reactor in place.

The oxidation experiments can be divided into two groups: sandbath or main reactor temperature variation runs, and concentration, feed ratio, and residence time variation runs. The twenty sandbath temperature variation runs were carried out at a fixed main reactor residence time of 6 s and superstoichiometric feed ratios \( F = [O_2]_0/[[CH_2Cl_2]_0 = 1.9 \text{ to } 5.5 \), based on the complete oxidation reaction:

\[
CH_2Cl_2 + O_2 \rightarrow CO_2 + 2HCl
\]  

(4-1)

For these runs, O₂ feed concentrations at the entrance to the main reactor were kept constant at 1.1 mM, while CH₂Cl₂ feed concentrations varied slightly from 0.2 - 0.6 mM. As with the corresponding hydrolysis runs, preheater residence times were not constant and increased with increasing sandbath temperatures. The twenty three concentration, feed ratio, and residence time variation runs were conducted at a constant sandbath temperature of 550°C. Main reactor residence times ranged from 4 - 9 s, while total residence times (preheater + main reactor) ranged from 11 - 23 s. CH₂Cl₂ and O₂ feed concentrations were varied both proportionally (to maintain a constant feed ratio) and independently in these runs to explore effects of relative and absolute amounts of each.
reactant on the reaction rate. As displayed in Table 4-2, six experiments were performed at stoichiometric, or slightly above stoichiometric, conditions \((F = 1.0 \text{ to } 1.4)\). The remaining experiments were performed at superstoichiometric conditions \((F = 1.9 \text{ to } 4.9)\).

4.4 Products, Mass Balances, and Analytical Procedures As with acetic acid experiments, liquid and vapor effluent samples were taken after cooling and decompression back to ambient conditions. The products that were conclusively detected and identified from both hydrolysis and oxidation experiments of \(\text{CH}_2\text{Cl}_2\) included formaldehyde (HCHO), hydrochloric acid (HCl), carbon monoxide (CO), carbon dioxide (CO\(_2\)), hydrogen (H\(_2\)), and methanol (CH\(_3\)OH). Small amounts of methane (CH\(_4\)) \((\leq 1.4\% \text{ of the carbon mass balance})\) were detected during runs at higher sandbath temperatures \((\geq 562^\circ\text{C})\) and residence times. In addition, trace amounts of the following chlorinated hydrocarbons were detected in the vapor phase: chloromethane (CH\(_3\)Cl), chloroform (CHCl\(_3\)), trichloroethylene (C\(_2\)H\(_3\)Cl\(_3\)), and isomers of dichloroethylene \((1,1-C_2H_2Cl_2, \text{ cis-}1,2-C_2H_2Cl_2, \text{ and trans-}1,2-C_2H_2Cl_2)\). Of these, only CH\(_3\)Cl was present in quantities large enough to have a statistically significant effect on the carbon and chlorine mass balances. CH\(_3\)Cl accounted for \(< 3\% \text{ of the carbon mass balance, and the next most abundant chlorocarbon, C}_2\text{HCl}_3, \text{ accounted for } < 0.7\%\). The other chlorinated hydrocarbons, combined, accounted for \(< 0.1\% \text{ of the carbon balance. Their presence is noted, however, because of their importance in identifying all possible reaction pathways and because they may be toxic trace products of interest. Atomic absorption tests on liquid effluent samples indicated ppm levels of soluble nickel ions (presumably from corrosion of Hastelloy C-276 preheater tubing; see Section 4.5.2). Equilibrium calculations indicated that the formation of NiCl\(_x\) soluble complexes was unlikely at the concentrations of soluble nickel observed in effluent samples. No presence of Cl\(_2\), C\(_2\)H\(_6\), C\(_2\)H\(_4\), or C\(_2\)H\(_2\) was detected.}
<table>
<thead>
<tr>
<th>Group #</th>
<th>Experimental Run Numbers</th>
<th>$[O_2]_o$ $^a$ (mmol/L)</th>
<th>$[\text{CH}_2\text{Cl}_2]_o$ $^b$ (mmol/L)</th>
<th>Feed Ratio$^c$</th>
<th>Feed Conditions</th>
<th>Residence Time$^d$ (s): Main Reactor; (Total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>418 - 423</td>
<td>1.08</td>
<td>0.43 - 0.58</td>
<td>1.9 - 2.5</td>
<td>superstoichiometric</td>
<td>4 - 9 (11 - 20)</td>
</tr>
<tr>
<td>2</td>
<td>424 - 429</td>
<td>0.58</td>
<td>0.27 - 0.36</td>
<td>1.6 - 2.1</td>
<td>superstoichiometric</td>
<td>4 - 9 (11 - 22)</td>
</tr>
<tr>
<td>3</td>
<td>434 - 436; 456 - 458</td>
<td>0.56</td>
<td>0.40 - 0.55</td>
<td>1.0 - 1.4</td>
<td>stoichiometric</td>
<td>4 - 9 (11 - 23)</td>
</tr>
<tr>
<td>4</td>
<td>437 - 439</td>
<td>0.56</td>
<td>0.16 - 0.19</td>
<td>2.9 - 3.4</td>
<td>superstoichiometric</td>
<td>4, 6, 8 (7, 15, 21)</td>
</tr>
<tr>
<td>5</td>
<td>440 - 442</td>
<td>2.08</td>
<td>0.43 - 0.54</td>
<td>3.9 - 4.9</td>
<td>superstoichiometric</td>
<td>4, 6, 8 (7, 15, 21)</td>
</tr>
</tbody>
</table>

$^a$ Average inlet $O_2$ concentration at entrance to main reactor (supercritical conditions)

$^b$ Inlet $\text{CH}_2\text{Cl}_2$ concentration (calculated) at entrance to main reactor (supercritical conditions)

$^c$ Feed ratio $= F = [O_2]_o/[\text{CH}_2\text{Cl}_2]_o$

$^d$ Total residence time (in parenthesis) = preheater + main reactor

Table 4-2  Conditions for Concentration, Feed Ratio, and Residence Time Variation Experiments. All runs performed at 550°C and 246 bar.
Carbon and chlorine mass balance results for each run, along with values for the percentage of effluent carbon contained in gaseous products (% gasification), are listed in the CH₂Cl₂ experimental data tables (12-1 and 12-2) in the Appendix. These mass balances were based on the total amount of CH₂Cl₂ fed into the reactor system (not just what reacted), and thus include unreacted CH₂Cl₂ in the calculations:

\[
\text{carbon balance} = \frac{\left( \sum_i \left[ \text{mol carbon/mol product } i \right] \right) + [\text{CH}_2\text{Cl}_2]}{[\text{CH}_2\text{Cl}_2]_0} \times 100 \quad (4-2)
\]

\[
\text{chlorine balance} = \frac{\left( \sum_i \left[ \text{mol chlorine/mol product } i \right] \right) + 2 [\text{CH}_2\text{Cl}_2]}{2 [\text{CH}_2\text{Cl}_2]_0} \times 100 \quad (4-3)
\]

There was ≥ 87% closure on carbon and on chlorine mass balances for all runs, with all but 3 out of the 66 total runs having ≥ 90% closure. The mean carbon mass balance over all runs was 99.9%, with a standard deviation of 6.6%. The mean chlorine mass balance over all runs was 100.0%, with a standard deviation of 5.7%. Values of % gasification increased with increasing temperature for hydrolysis and oxidation runs primarily because of the greater amounts of CO, H₂, and CO₂ that formed as more CH₂Cl₂ and its intermediate products decomposed at the higher temperatures.

Gaseous effluent compositions were determined primarily by gas chromatography (GC). The gases O₂, N₂, CO, CO₂, CH₄, H₂, and He were detected and quantified via TCD detector using the same GC’s (Hewlett Packard 5890 Series II and Perkin Elmer Sigma 1B), columns, and methods as employed for the acetic acid experiments (see Section 3.2.2). Chlorinated hydrocarbons in the vapor phase, including CH₂Cl₂, were analyzed using a second Hewlett Packard GC with an electron capture detector (ECD) and a DB-624 capillary column (J&W Scientific Inc.).
The carrier gas was helium, with nitrogen used as makeup gas to the detector. The presence of any HCHO, CH₃OH, or Cl₂ in the vapor phase was checked by allowing the gaseous effluent to flow through a glass impinger into a vial of water of known volume for a fixed period of time. The water solution was then analyzed for HCHO and CH₃OH as detailed below. Cl₂ was analyzed for by using the o-toluidine colorimetric test.

A variety of analytical techniques were employed for analysis of liquid phase products. Methylene chloride concentrations in feed and effluent samples were determined by GC using either an electrolytic conductivity (Hall) detector (ELCD) in a Tracer 585 GC, or by a flame ionization detector (FID) in one of the Hewlett Packard GCs (both HP GCs were also equipped with FID detectors). The fuel used for both detectors was hydrogen. A DB-624 capillary column with helium carrier gas was used in the Tracer GC, while a DB-1 capillary column (also from J&W Scientific) and helium carrier gas with nitrogen makeup was used in the Hewlett Packard GC. Methanol was also analyzed by FID detection in the other Hewlett Packard GC using an SPB-1 capillary column (Supelco, Inc.) with helium carrier gas and nitrogen makeup. A colorimetric test known as the chromotropic acid method (Bricker and Vail, 1950; West and Buddhadev, 1956; Altshuller et al., 1961) was used to detect formaldehyde. Addition of a 1% solution of chromotropic acid in concentrated sulfuric acid to aqueous formaldehyde, in the presence of excess sulfuric acid, gives a violet color. The intensity of color is proportional to the original formaldehyde concentration, which can be quantified by a calibrated spectrophotometer. A Shimadzu UV160U spectrophotometer was used for this purpose at a wavelength of 580 nm. HCl concentrations were determined with a chloride specific ion electrode (Orion Research, Inc.). No ions that would be expected to interfere with the electrode’s operation were present in effluent samples.

All GCs and other analytical equipment were calibrated regularly using appropriate gaseous or liquid solution standards. During the course of an experiment, six sets of two gas samples were
taken for analysis by the two GC's with TCD detectors, while three gas samples were typically taken for GC analysis by ECD detector. As described for the acetic acid experiments (Section 3.2.2), gas compositions were determined from the measured volume fractions and then averaged for each species over at least the last three samples taken. Dissolved concentrations of gases in the liquid phase were calculated via Henry's Law also as described in Section 3.2.2. At least three sets of two liquid samples (one 120 mL bottle and one 17 mL bottle) were typically taken during each experiment for the numerous liquid product analysis tests. Final concentrations for each liquid effluent compound were determined by averaging over all individual sample concentrations determined for that compound.

4.5 Initial Results and Observations

4.5.1 Kinetics Over the range of sandbath temperatures explored (450 to 600°C), CH₂Cl₂ conversions varied from 26±9% to 91±1% for pure hydrolysis experiments, and from 30±9% to 99.9±0.1% (complete conversion) for oxidation experiments. Complete conversion under oxidation conditions occurred by 563°C. Conversion data as a function of sandbath temperature for all hydrolysis runs and the temperature variation oxidation runs is plotted in Figure 4-1.

The most striking feature to note in Figure 4-1 is the similarity between hydrolysis and oxidation conversions at the same sandbath temperatures. For temperatures ≤ 525°C, hydrolysis conversions were not statistically different from the corresponding oxidation conversions, and were virtually indistinguishable from oxidation conversions below 500°C. Even at sandbath temperatures higher than 525°C, hydrolysis conversions were never far below their corresponding oxidation conversions. This behavior is unusual compared to that observed for most other model compounds studied by our group such as H₂, CO, CH₃OH, and CH₃COOH (compare Figure 4-1 to Figure 3-2), where the presence of oxygen resulted in much greater conversions than that observed in its absence. These results imply two points - that CH₂Cl₂ hydrolysis is significant, and that O₂
Figure 4-1  Graph of Experimental CH₂Cl₂ Conversion Versus Sandbath Temperature for Hydrolysis and Oxidation Runs. Total pressure = 246 bar. Error bars indicate 95% confidence intervals.
does not appear to have as much of an effect on CH₂Cl₂ decomposition under these conditions studied relative to that seen with earlier compounds.

Another unusual feature that can be observed in Figure 4-1 is an apparent leveling off of conversion (hydrolysis and oxidation) at sandbath temperatures \( \leq 500^\circ C \), and a somewhat abrupt jump in conversion values between 550°C and 562°C. Both effects are artifacts of the way this graph has been plotted in that the increasing total residence times that occurred with increasing sandbath temperatures have not been accounted for in this plot. To correct this requires knowledge of the temperature/time history of the CH₂Cl₂ feed in the preheater tubing, which will be developed and discussed in Chapter 5.

Further evidence of the lack of O₂ influence on the mechanism of CH₂Cl₂ breakdown can be observed in Figure 4-2. Here, CH₂Cl₂ oxidation conversion data from the concentration, feed ratio, and residence time variation runs are plotted versus main reactor residence time for a constant sandbath temperature of 550°C. The data are from run groups 1, 3, and 5 in Table 4-2, where CH₂Cl₂ feed concentrations at the entrance to the main reactor were roughly constant while O₂ feed concentrations were varied from 0.6 - 2.1 mM, representing stoichiometric to superstoichiometric feed ratios. Almost all data points fall well within experimental error of each other for any given residence time regardless of the feed ratio value (and in no particular order), showing that varying the initial concentration of O₂ had no statistically significant effect on CH₂Cl₂ conversion. It should be noted, however, that the presence of O₂ did have a significant effect on the concentrations of products (both intermediate and final) resulting from CH₂Cl₂ breakdown, as is discussed in Chapter 7. Fixing the O₂ concentration and varying CH₂Cl₂ initial concentrations resulted in slightly lower conversions with increasing CH₂Cl₂ concentration.
Figure 4-2 Graph of CH₂Cl₂ Conversion Versus Main Reactor Residence Time; Effect of O₂ Feed Concentration Variation. All data at 246 bar and sand-bath temperature of 550°C. Error bars indicate 95% confidence intervals.
Values of CH₂Cl₂ conversion from the two hydrolysis runs performed with the main reactor removed are shown in Table 4-3 and compared to similar hydrolysis runs with the main reactor in place. At each temperature, the same conversion within experimental error was achieved both with and without the main reactor present. Although only two experiments without the main reactor were performed, the results clearly suggest that very little or no reaction occurred in the supercritical main reactor at both sandbath operating temperature extremes of 450°C and 575°C. This somewhat counterintuitive behavior is unusual compared to that exhibited by all previous model compounds studied, where most, if not all, conversion occurred only under supercritical temperatures in the main reactor.

4.5.2 Corrosion Severe corrosion was observed in the Hastelloy C-276 preheater tubing containing the CH₂Cl₂ feed solution over the course of the experiments. Failure of four separate preheater coils occurred after about 104, 44, 54, and 65 hours of operation with CH₂Cl₂ feed (Table 4-4). Each tube rupture occurred within a zone from 7 to 29 cm downstream of where the preheater tubing entered the sandbath. Values of pH measured in the ambient temperature liquid effluent from the experimental system typically ranged between 1.5 and 2.5, due primarily to HCl.

Analysis of the failed tubes by Dr. D.B. Mitton of the H.H. Uhlig Corrosion Laboratory at MIT has revealed that the cause of failure in each case was due to the formation of an axial, intergranular through-wall crack (Mitton et al., 1995; 1996). The analysis for each tube showed that corrosion occurred further upstream and downstream of where the crack formed, over a distance spanning at least 40 cm after the point where the tubing entered the sandbath (i.e. began heating). The cracks were likely the result of intergranular corrosion and/or stress corrosion cracking, since the stress (high pressure; bends in tubing) and hostile environment (elevated temperature; low pH) requirements for this form of corrosion were readily available.
<table>
<thead>
<tr>
<th>Sandbath Temperature (°C)</th>
<th>$\text{CH}_2\text{Cl}_2$ Conversion (no reactor)</th>
<th>$\text{CH}_2\text{Cl}_2$ Conversion (with reactor; no O$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>36±10 % $^a$</td>
<td>40±13 % $^b$</td>
</tr>
<tr>
<td>575</td>
<td>82±2 % $^c$</td>
<td>85±4 % $^d$</td>
</tr>
</tbody>
</table>

$^a$ Run # 467  
$^b$ Average of Runs 381, 445, 454, and 461  
$^c$ Run # 468  
$^d$ Run # 450

Table 4-3 Comparison of $\text{CH}_2\text{Cl}_2$ Conversions Measured in Experiments with and without the Supercritical Main Reactor

<table>
<thead>
<tr>
<th>Preheater Tube #</th>
<th>Total Time of Exposure to $\text{CH}_2\text{Cl}_2$ Feed* (hr)</th>
<th>Position of Tube Failure Relative to the Beginning of the Tube (cm)</th>
<th>Position of Tube Failure Relative to the Point Where Heating Begins (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>104</td>
<td>41</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>59</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>56</td>
<td>37</td>
<td>7</td>
</tr>
</tbody>
</table>

* at operating temperatures

Table 4-4 Corrosive Failure Data for Preheater Tubing
Dealloying was another form of corrosion, however, that was clearly evident. Elemental analysis of the corroded layer of the tubing revealed a substantial depletion of nickel by more than a factor of 10 (compared to the standard alloy composition) and enrichment of chromium by almost a factor of four. Depletion of iron and molybdenum and enrichment of tungsten was observed as well. These results are supported by separate atomic absorption tests that were performed on liquid effluent samples which showed elevated levels of soluble nickel present in the effluent. Concentrations of soluble nickel were found on the order of 3 to 16 ppm in samples tested, with the higher concentrations found for experiments performed near the time of failure of a preheater coil. Similar atomic absorption tests to determine concentrations of chromium in the effluent samples indicated levels near the detection limit (≤ 0.6 ppm). Rice et al. (1993) report similar problems with corrosion observed during SCWO of CH₂Cl₂ and other chlorinated organics. Concentrations of nickel and chromium in their effluent were comparable to those found in this study, at values of 30.7 ppm and 0.02 ppm respectively. This dealloying behavior observed is consistent with that predicted from Pourbaix diagrams for nickel and chromium at a hot, subcritical temperature of 300°C for pH values near 2 (Mittone et al., 1995).

Not surprisingly, the highest corrosion, as measured by the amount of intergranular corrosion and dealloying, occurred in the region where the through-wall crack developed. No evidence of corrosion was observed at both the entrance (ambient temperature) and exit (always at supercritical temperatures) of the preheater tubing. Altogether, the above data suggests that the most severe corrosion occurred in a region that was higher in temperature than ambient, but below the critical point, which is where it is predicted to be most aggressive (Huang et al., 1989). See Chapter 5 for a further discussion of these corrosion related phenomena in light of calculated temperature profiles in the preheater tubing.
Evidence for Subcritical Hydrolysis of CH₂Cl₂

Taken all together, the initial experimental observations on kinetics and corrosion cited above strongly indicate that most of the conversion of the initial CH₂Cl₂ feed occurred via hydrolysis in the subcritical temperature zone of the preheater tubing. The appreciable and closely similar conversions for hydrolysis and oxidation experiments (Figure 4-1) certainly show that breakdown of CH₂Cl₂ under hydrolysis conditions is important.

More specifically, however, the corrosive failures of the CH₂Cl₂ feed preheater tubing provide solid evidence that a considerable amount of this hydrolysis occurred at lower temperatures, well upstream in the preheater tubing. This point is consistent with the following facts. Significant concentrations of Cl⁻, one of the most aggressive agents of corrosion, were measured in the cold effluent. Agreement of these concentrations with pH measurements showed that Cl⁻ was largely present as HCl, which accounted for all of the acidity and the majority of the chlorine balance in all experiments. Because the only source of Cl⁻ was CH₂Cl₂, HCl must have formed from CH₂Cl₂ breakdown sufficiently early in the preheater tubing to cause the corrosion to occur where it was observed near the beginning of the heated section (Table 4-4). This proposition is also supported by the fact that HCl is a known product of low temperature (subcritical) hydrolysis of CH₂Cl₂ in liquid water (Fells and Moelwyn-Hughes, 1958) - conditions similar to those near the beginning of the preheater tubing.

Finally, the results obtained from experiments performed with the main reactor tubing removed show that subcritical hydrolysis of CH₂Cl₂ was not only considerable, but most likely the major source of CH₂Cl₂ hydrolysis (Table 4-3). Comparison to similar experiments performed with the main reactor section in place shows that only a very limited amount of hydrolysis conversion occurred under supercritical conditions in the main reactor. Thus most of the observed CH₂Cl₂ hydrolysis, which occurred in the preheater tubing, must have taken place in the subcritical
temperature zone. This is because the existence of a subcritical region was the only significant and relevant difference between the preheater tubing and main reactor tube in the pure hydrolysis experiments.

Overall, these results imply a rapid, subcritical hydrolysis reaction of CH₂Cl₂ that decreases in rate significantly as temperature increases into the supercritical regime. This further implies that the organic feed that contacted the O₂ at the beginning of the main reactor during oxidation experiments was not pure CH₂Cl₂, but a mixture of remaining unhydrolyzed CH₂Cl₂ and its products. Thus, before the global oxidation kinetics of CH₂Cl₂ can be properly characterized, the hydrolysis component and its kinetics must first be determined. Determining the full hydrolysis kinetics, in turn, requires a complete knowledge of the thermal history and residence time of the CH₂Cl₂ feed in the preheater tubing. This task is the topic of Chapter 5.
Chapter 5

Hydrolysis of Methylene Chloride - Heat Transfer and Temperature Profile Modeling

5.1 Motivation As presented in Chapter 4, the data gathered and observations noted from the CH₂Cl₂ hydrolysis and oxidation experiments performed indicate that substantial hydrolysis of CH₂Cl₂ occurred under subcritical, non-oxidative, and (by definition) nonisothermal conditions in the preheater tubing. Because of this, a detailed knowledge of the changing thermal conditions in the preheater tubing as a function of position and time for each experimental run is required if one is to properly infer hydrolysis kinetic parameters. Because the density of water (and thus the volumetric flow rate) varies by at least an order of magnitude over the temperature range encountered in the preheater tubing by the CH₂Cl₂ feed solution, the preheater residence time itself is coupled strongly to the thermal history of fluid passing through the tubing. Calculation of an axial temperature-time profile, in turn, requires an understanding of the rate of heat transfer as a function of the many relevant variables describing the physical configuration, internal flow conditions, and external sandbath environment of the tubing.

This chapter describes the development of temperature-time profile models for the CH₂Cl₂ feed preheater tubing. It also explores the nature of heat transfer in sub- and supercritical water in order to determine appropriate values of heat transfer coefficients for use in the model. This is done through the evaluation of various heat transfer correlations that incorporate the effects of a number of different phenomena that apply to conditions in different sections of the preheater tubing.
5.2 Modeling procedure In order to develop the necessary temperature-time profiles in the preheater tubing for each experimental run, the basic modeling approach of Holgate et al. (1992) was used. The variation of bulk fluid temperature $T$ with the axial distance $z$ along the preheater tubing was obtained from a differential heat balance on the feed solution flowing through the tubing:

$$\frac{dT}{dz} = \frac{2\pi r_i U_i (T_{fsb} - T)}{\dot{m} C_p(T)} \quad (5-1)$$

where $r_i$ is the internal radius of the tube, $T_{fsb}$ is the sandbath temperature, $\dot{m}$ is the mass flow rate of the feed solution, $C_p$ is the heat capacity of the feed solution, and $U_i$ is the overall heat transfer coefficient (based on inner surface area of the tube). Note that, because of the dilute feed solutions used, the heat of reaction was negligible and not included in Eqn. 5-1. Starting from the point at which the tubing first enters the sandbath, Eqn. 5-1 was integrated over a small segment $dz$ of the tubing using a Runge-Kutta technique to yield $T$ at the end of that segment. The residence time increase, $\Delta \tau$, over any segment was calculated from $T$ according to the following equation:

$$\Delta \tau = \frac{\rho(T) \pi r_i^2 \Delta z}{\dot{m}} \quad (5-2)$$

where $\rho$ is the density of the feed solution at temperature $T$. This value of $T$ was then used as the new starting point for the next stepwise integration of Eqn. 5-1 over a new length segment $dz$ and to evaluate all physical properties over that segment. This process was repeated until the end of the tubing was reached. Initially the step size $dz$ was chosen to be 0.1% of the heated length of the tubing, but this was modified as the calculation progressed down the length of the tubing depending on the value of $T$ calculated from the previous segment. All physical properties were calculated using the NBS/NRC steam tables (Harr et al., 1984). For these calculations, $U_i$ was considered to be a function of $z$ and was calculated for each segment using the usual sum of resistances formula:
\[ \frac{1}{U_i} = \frac{1}{h_i} + \frac{t_w d_i}{\lambda_w d_{LM}} + \frac{d_i}{d_o h_o} \]  \hspace{1cm} (5-3)

where \( h_i \) and \( h_o \) are the internal and external heat transfer coefficients, respectively; \( d_i, d_o, \) and \( d_{LM} \) are the inner, outer, and log mean tube diameter, respectively; \( t_w \) is the wall thickness; and \( \lambda_w \) is the wall thermal conductivity.

5.3 Calculation of the Internal Heat Transfer Coefficient

5.3.1 Important Variables A description of heat transfer in the preheater tubing necessitates consideration of a number of important factors and phenomena including changing physical properties, geometric and flow effects, and the proper coupling of forced and natural convection. This required us to carefully review and evaluate over 30 years of research conducted on heat transfer effects in near-critical and supercritical fluids.

5.3.1.1 Critical Point Phenomena Heat transfer near the critical point is complicated because of the large variations in physical property values that occur with small changes in temperature or pressure (Hall and Jackson, 1978). These variations can lead to appreciable enhancement or impairment of heat transfer. Enhancement is mainly correlated to increases in the heat capacity, \( C_p \), which rises to infinity at the critical point and to a large but finite value at the pseudocritical temperature, \( T_{pc} \) (Jackson and Hall, 1979a). The pseudocritical temperature is defined as the temperature at which \( C_p \) reaches a maximum at a specified supercritical pressure (e.g. 383°C at 246 bar). In most formulations, \( h_i \) is proportional to some fractional power of \( C_p \) (as contained in the Prandtl number (Pr)), and thus \( h_i \) increases with temperature as it approaches \( T_{pc} \), although not by as much as \( C_p \). Above \( T_{pc} \), \( C_p \) decreases with increasing temperature, leading to a diminished enhancement of the heat transfer to the bulk fluid (\( C_p \) values would be lowest in the boundary layer near the hot wall where heat transfer resistance is greatest), and consequently lower \( h_i \) values.
(Mayinger and Scheidt, 1984). Because standard constant property heat transfer correlations do not always capture this behavior effectively, correction factors consisting of functions of $C_p$ and/or density $\rho$ at the wall and bulk temperature are often added.

5.3.1.2 High Heat Flux  At a high heat flux relative to the mass flow rate of fluid, the heat transfer enhancement normally seen near the pseudocritical point is diminished, and can even be completely eliminated at high enough values. To explain this effect, Jackson and Hall (1979a) argue that as heat flux increases, the band of fluid in the thermal boundary layer that experiences temperatures nearest to $T_{p_c}$, and therefore the highest $C_p$ values, is increasingly narrowed. The result is that the $C_p$-related enhancement on heat transfer is reduced. Yamagata et al. (1972) observed this heat transfer deterioration at high heat fluxes experimentally and developed an empirical equation to predict the limiting value of heat flux as a function of mass flux before deterioration begins. Empirical heat transfer correlations with $C_p$ and $\rho$ correction factors are able to predict some, but not all, of the effects associated with increasing heat flux, and work best at low to moderate heat fluxes.

5.3.1.3 Mixed Convection  Natural convection can either augment or attenuate the heat transfer effects associated with passing through the critical or pseudocritical point. The dimensionless parameter that characterizes the magnitude of natural convection relative to that of forced convection is $Gr/Re^m$, where $Gr$ is the dimensionless Grashof number and $Re$ is the Reynolds number (Gebhart et al., 1988). Thus if $Gr/Re^m$ is very large, natural convection dominates. When both modes of heat transfer are of comparable magnitude, neither can be ignored and a condition of mixed convection is said to exist. The appropriate value of $m$ to use depends on a number of criteria including geometry and the thermal boundary condition.
Although conditions for forced convection in our experiments clearly existed, further analysis was required to quantify the importance of natural convection. The large density differences and low viscosities of stratified near-critical and supercritical fluids in particular provide excellent conditions for natural convection. A number of researchers have proposed criteria based on the $Gr/Re^m$ parameter to determine when natural convection can be neglected for flow in a tube (Table 5-1). The criteria of Hall and Jackson (1978) and Jackson and Hall (1979a) were derived theoretically, while those of Protopopov (1977) and Watts and Chou (1982) are based on experimental data. For the conditions in our experiments, all these criteria suggest that natural convection could not be ignored in the preheater tubing. As an example, values of $Gr$ ranged from 80 to 530,000 over the length of the preheater. Values of $Gr/Re^2$ ranged from $2 \times 10^5$ to $4 \times 10^1$, with typical values throughout most of the tubing lying between $10^{-2}$ and $10^{-1}$. Not surprisingly, the highest values of $Gr$ and $Gr/Re^2$ were found near the pseudocritical point, where the density difference between the bulk fluid and fluid near the tube wall was greatest, generating the largest buoyant forces. Mixed convection can result in either enhanced or impaired heat transfer relative to forced convection, depending on the magnitude of natural convection and the physical operating conditions (see below).

5.3.1.4 Flow Regime The magnitude of the internal heat transfer coefficient also clearly depends on the fluid flow regime, since the very mechanism of heat transfer differs depending on whether laminar or turbulent flow exists. Flow at the entrance of the $\text{CH}_2\text{Cl}_2$ feed preheater tubing was always laminar in all experiments, as determined from calculated values of $Re$. The volumetric flow increase with increasing temperature along the preheater caused the flow to became turbulent at some point for many, but not all, experiments. Those experiments with the smallest mass flow feed rates remained laminar throughout the preheater tubing. Overall, values of $Re$ ranged from 50 to 4500, depending on experimental conditions. The presence of mixed convection can lower the point of transition from laminar to turbulent conditions. This effect has been correlated
### Table 5-1 Criteria for Negligible Natural Convection for Flow in Tubes

in terms of the Rayleigh number ($Ra = Gr Pr$) multiplied by a tube diameter to length ratio ($d / L$). Metais and Eckert (1964) have developed a set of graphs of $Re$ vs. $Ra d / L$, one each for horizontal and vertical tubes, that show the various regimes and limits of convective heat transfer (forced, mixed, and free) and fluid flow (laminar and turbulent) based on experimental data. These graphs show that, for horizontal tubes, the criterion for the onset of turbulence drops to $Re = 800$ (from the usual $Re = 2100$) for values of $(Ra d / L) > 20,000$. For vertical tubes, the situation is slightly
more complicated, with the transition to turbulence occurring at as low as \( Re = 200 \) when \( Ra \, d_i / L \) > 10,000.

5.3.1.5 **Geometric and Coiling Effects** Other variables of importance that had to be considered for heat transfer analysis in our experimental apparatus were tube orientation (vertical or horizontal), flow direction (up or down) for vertical sections of tubing, and the effects of coiling for the horizontal sections of tubing. The primary reason for considering tube orientation and direction of flow is because of the effects of natural convection. Buoyant forces can significantly affect the nature of heat transfer depending on which direction the forces act relative to that of the bulk flow and gravity, as will be pointed out shortly.

Coiled tubing adds another complexity to heat transfer analysis in that a secondary flow due to centrifugal forces is established. This flow, which is perpendicular to the primary axial flow, can cause stratification according to density (highest density at the outer bend) and distortion of the velocity field (maximum velocities at the outer bend). This secondary flow generally results in increased heat and mass transfer rates. To account for the effects of coiling in tubing on \( h_i \), correlations for the corresponding Nusselt number \( (Nu = h_d \lambda) \) were developed by Dravid et al. (1971) for laminar flow, and by Miroplonkis and Pikus (1968) for supercritical water undergoing turbulent flow. In both cases, the key parameter governing whether the effects of coiling are significant or not is the ratio of the tube radius, \( r_i \), to the radius of coil curvature, \( R \). As \( r_i / R \) tends to zero, the effects of coiling become negligible. This is also expressed in the simple empirical equation cited by Williams and Smith (1987) for turbulent flow of water in a coiled pipe:

\[
h_i = h_{i,sp} (1 + 3.5 r_i / R)
\]

(5-4)

where \( h_{i,sp} \) is the heat transfer coefficient calculated for a straight pipe and \( h_i \) is the heat transfer coefficient adjusted for the effects of curvature. For the preheater tubing used in our experiments, \( r_i \)
was 0.054 cm while $R$ was about 6.7 cm, yielding a very small value for the parameter $r_i/R$ of 0.008. When inserted into Eqn. 5-4, this leads to a difference of less than 3\% between $h_i$ and $h_{i,sp}$.

Similarly, the correlations of Dravid et al. (1971) and Miropolskiy and Pikus (1968) also show that the effects of curvature are small for a value of $r_i/R$ of 0.008. Thus corrections for the effects of curvature have been ignored here.

5.3.2 Correlations used The period from 1950 to 1980 was an active one for research on heat transfer to supercritical water. This interest was motivated in part by expanding development of supercritical pressure steam generators and nuclear reactors with supercritical water coolants (Jackson and Hall, 1979a; Bishop et al., 1965). Supercritical CO$_2$ is also a popular fluid for which there exists abundant experimental data because it achieves its supercritical state under relatively mild conditions. These studies on heat transfer to supercritical water and CO$_2$ can be divided roughly into two groups: (1) those that set up and give specific numerical solutions to the transport equations for a particular geometry and set of conditions, and (2) those that develop more general but empirical correlations for $Nu$ from experimental data. Although the latter group is of greater interest to the current work, no one correlation covers the full range of operating conditions and other factors pertinent to every part of the preheater tubing.

For heat transfer analysis, the preheater tubing can be divided into three sections after entering the sandbath (refer to Figure 3-1): (1) the first 25 cm section once the tubing is immersed in the fluidized sand is vertically oriented with fluid flowing down; (2) the next 2.3 m section (the longest) is horizontal and coiled; and (3) the last 20 cm section is vertical again with fluid flowing up before entering the mixing cross. In each of the three sections, either laminar or turbulent flow could exist, depending on the particular experimental conditions. Thus six correlations, taken from the literature (and listed in Table 5-2), were needed for determining the internal heat transfer coefficient at any point in the preheater tubing to account for either flow regime in each of the three
Table 5-2  Heat Transfer Correlations Used for Sub- and Supercritical Water Flow in Tubes

Horizontal Tube; Laminar Flow (Morcos and Bergles, 1975):

\[ Nu = \left\{ (4.36)^2 + \left[ 0.055 \left( \frac{GrPr^{1.35}}{Pr_w^{0.25}} \right)^{0.40} \right]^2 \right\}^{1/2} \]  

(1)

where \( P_w = \left( \frac{h_d}{\dot{m}_w} \right) \left( \frac{d_i}{t_w} \right) \)  

(2)

Horizontal Tube; Turbulent Flow (Robakidze et al., 1983):

\[ K = \left( 1 - \frac{\rho_w}{\rho} \right) \frac{Gr}{Re^2} \]  

(3)

For \( K < 0.01 \):

\[ Nu = Nu_c \]  

(4)

where \( Nu_c = Nu_o \left( \frac{\rho_w}{\rho} \right)^{0.3} \left( \frac{C_p}{C_p} \right)^n \)  

(5)

\[ Nu_o = \frac{0.125RePr}{\left( 1.82 \log Re - 1.64 \right)^2 \left[ 1.07 + \frac{4.25 \left( Pr^{2/3} - 1 \right)}{1.82 \log Re - 1.64} \right]} \]  

(6)

\[ \overline{C_p} = \frac{h_v - h_b}{T_w - T_b} \quad (h = \text{specific enthalpy}) \]  

(7)

\[ n = 0.4 \quad \text{for} \quad T_b < T_w < T_{pc} \quad \text{and} \quad 1.2T_{pc} < T_b < T_w \]  

(8)
Table 5-2 (continued)

\[ n = 0.4 + 0.2 \left( \frac{T_w}{T_{pc}} - 1 \right) \quad \text{for} \quad T_b < T_{pc} < T_w \quad (9) \]

\[ n = 0.4 + 0.2 \left( \frac{T_w}{T_{pc}} - 1 \right) \left( 1 - 5 \left( \frac{T_b}{T_{pc}} - 1 \right) \right) \quad \text{for} \quad T_{pc} < T_b < 1.2T_{pc} \quad (10) \]

For \( K > 0.01 \): \( Nu = Nu_c \varphi(K) \) (11)

where \( \varphi(K) = 0.587 + 0.5K + 1.333K^2 \) \quad \text{for} \quad 0.01 < K < 0.4 \quad (12)

\[ \varphi(K) = 1.40K^{0.082} \] \quad \text{for} \quad K > 0.4 \quad (13)

Vertical Tube; Laminar Flow; Upflow (Churchill, 1984):

\[ Nu = \left\{ (4.36)^6 + \left[ 0.846 \left( Ra^* \right)^{0.25} \right]^6 \right\}^{1/6} \quad (14) \]

Vertical Tube; Laminar Flow; Downflow (Churchill, 1984):

\[ Nu = \left( (4.36)^3 - \left[ 0.846 \left( Ra^* \right)^{0.25} \right]^3 \right)^{1/3} \quad (15) \]

Vertical Tube; Turbulent Flow; Upflow (Watts and Chou, 1982):

For \( \frac{Gr}{Re^{2.7}Pr^{0.5}} < 10^{-5} \):

\[ Nu = Nu_{varp} \quad (16) \]
where $Nu_{varp} = 0.021Re^{0.8}Pr^{-0.55}\left(\frac{\rho_w}{\rho}\right)^{0.35}$ \hfill (17)

For $10^{-5} < \frac{Gr}{Re^{2.7}Pr^{0.5}} < 10^{-4}$:

$$Nu = Nu_{varp}\left(1 - 3000\frac{Gr}{Re^{2.7}Pr^{0.5}}\right)^{0.295}$$ \hfill (18)

For $\frac{Gr}{Re^{2.7}Pr^{0.5}} > 10^{-4}$:

$$Nu = Nu_{varp}\left(7000\frac{Gr}{Re^{2.7}Pr^{0.5}}\right)^{0.295}$$ \hfill (19)

**Vertical Tube; Turbulent Flow; Downflow** (Watts and Chou, 1982):

$$Nu = Nu_{varp}\left(1 + 30000\frac{Gr}{Re^{2.7}Pr^{0.5}}\right)^{0.295}$$ \hfill (20)

\textsuperscript{a} Note: Unless otherwise indicated, all physical properties in equations are evaluated at bulk temperature. $Gr$ and $Pr$ are as defined in Table 5-1. The following subscripts indicate the temperature at which the associated property is evaluated: $w = \text{wall}; b = \text{bulk}; f = \text{film (average between bulk and wall)}; pc = \text{pseudocritical}$. All dimensionless numbers are defined at the end of this chapter.

sections. Each of the correlations takes into account natural convection and its effect on the transition to turbulence. The correlations for turbulent flow also include terms to treat effects associated with passing through the pseudocritical point.

### 5.3.2.1 Horizontal Tube; Laminar Flow

For these conditions, we used a correlation (Eqn. 1 in Table 5-2) developed by Morcos and Bergles (1975) from experiments with water and with ethylene glycol in glass and stainless steel tubes. The second term in the correlation accounts
for natural convection with its $Gr_f$ dependence and for wall conductivity effects via the tube wall parameter, $P_w$. When mixed convection exists in a horizontal tube, buoyant forces resulting from the warmer wall temperatures act perpendicular to the forced flow and result in a secondary cross-flow circular motion of fluid. The warm, lighter fluid near the wall rises while the colder, heavier fluid in the center sinks. Over the length of the tube, superposition of this buoyancy effect on to the axial bulk flow creates a helical flow pattern which enhances heat transfer relative to the pure forced convection case. This enhancement can be diminished, however, by a low wall thermal conductivity or thickness (Eqn. 2, Table 5-2). As required, Eqn. 1 in Table 5-2 reduces to a constant $Nu$ value of 4.36 for fully-developed laminar flow conditions with constant heat flux when $Gr_f$ is very small.

One drawback of Eqn. 1 in Table 5-2 is that it does not explicitly account for critical point phenomena. Most of the available heat transfer correlations for flow of supercritical water in tubes were developed under the more industrially relevant conditions of turbulent flow. Although there are some studies of supercritical water under laminar conditions (e.g. Popov and Yan'kov (1982)), they either do not treat flow in tubes, do not consider both forced and natural convection, or do not develop a specific correlation for $Nu$. The turbulent correlations typically include a factor, consisting of some function of heat capacities and densities, to account for critical point effects (see below). However, because of the empirical nature of all these correlations, we have not transplanted specific features from one correlation into another in an effort to expand its applicability. Such action could actually make the “corrected” correlation less reliable. Thus the correlation of Morcos and Bergles was used without modifications because it was the one that most closely matches all the other conditions and criteria relevant to our analysis of the preheater tubing.

5.3.2.2 Horizontal Tube; Turbulent Flow The correlations recommended by Robakidze et al. (1983) were used under these conditions (Eqns. 3 through 13 in Table 5-2). Their approach
was to use a core forced convection term represented by $Nu_a$ (Eqn. 6 in Table 5-2), which is multiplied by additional terms to include the effects of natural convection and critical point phenomena. $(\rho_a/\rho)^{0.3}(C_p/C_p)^n$ are the terms that account for passing through the pseudocritical point, with $C_p$ and $n$ defined in Eqns. 7 - 10 in Table 5-2. The form of the natural convection term to use depends on the value of a modified version of the $Gr/Re^2$ parameter that includes a density-dependent term, which is denoted as $K$ in Eqn. 3 of Table 5-2.

These correlations were developed using published data from many studies of supercritical water and CO$_2$. The form for the supercritical forced convection term, $Nu_c$ (Eqn. 5 in Table 5-2), is exactly the same as that proposed earlier by Krasnoschekov and Protopopov (1966). In their survey of a number of correlations dealing only with supercritical forced convection, Jackson and Hall (1979a) concluded that this correlation for $Nu_c$ was by far the most effective at fitting data from approximately 2000 experiments, about 75% of which were with water and the rest with CO$_2$. This correlation predicted 79% of the water data to within $\pm$ 15%. Although the form for $Nu_c$ is mathematically cumbersome, Jackson and Hall (1979a) have shown that the $Nu_a$ expression can be reduced to a simpler Dittus-Boelter form with little loss of accuracy. Jackson and Hall (1979a) and Hall (1971) emphasize that many of the early experimental studies overlooked the importance of certain variables or phenomena such as natural convection, which could explain the poor agreement among early correlations. This problem should not affect Eqn. 5 in Table 5-2 because Jackson and Hall (1979a) reportedly screened the data set carefully to remove any points contaminated by buoyancy effects.

Robakidze et al. (1983) concluded that the correlation for $Nu_c$ was sufficient for matching the experimental data up to a value of $K$ of 0.01. For higher values of $K$, the experimentally determined values of $Nu$ differed from those predicted by $Nu_c$, which was attributed to the increasing importance of natural convection. For values of $K$ between 0.01 and 0.4, Robakidze and cowork-
ers recommend that $Nu$ can be calculated by multiplying $Nu_c$ by an empirical correction factor $\varphi(K)$ originally proposed by Protopopov (1977) (Eqn. 11, Table 5-2). Eqn. 12 in Table 5-2 is an empirical curve fitted to Protopopov’s data that estimates the appropriate value of $\varphi$ to use for a given value of $K$. For values of $K > 0.4$, Robakidze and coworkers recommend $\varphi(K) = 1.40 K^{0.082}$ (Eqn. 13, Table 5-2).

5.3.2.3 Vertical Tube; Upflow; Laminar Flow In vertical tubes, natural convection effects are more substantial and more variable. They can result in either enhancement or impairment of heat transfer relative to the effects of forced convection, depending on the direction of flow, the flow regime, and the intensity of the natural convection present. For example, the behavior of a fluid with mixed convection under laminar flow is opposite to that which occurs under turbulent flow. Under laminar upflow, the buoyant forces always enhance heat transfer. Warmer, lower density fluid near the walls results in an increased velocity gradient near the walls, enhancing the rate of heat transfer. In his review of mixed convection in channels, Churchill (1984) suggests that Eqn. 14 in Table 5-2 be used to calculate $Nu$ under these conditions. This correlation consists of two terms; one for pure forced convection effects and one for pure natural convection effects. The forced convection term is again the familiar constant value of 4.36 for $Nu$ under fully-developed laminar conditions and constant heat flux. The natural convection term depends on a modified Rayleigh number, $Ra^*$. The main drawback to this correlation (similar to that for laminar flow in horizontal tubes) is that it was not specifically created for supercritical water. Churchill’s correlation, however, does account for most of the factors relevant to conditions found in our preheater tubing.

5.3.2.4 Vertical Tube; Downflow; Laminar Flow For downward laminar flow, the buoyant forces act in an opposite direction to the forced flow and hinder heat transfer. The appropriate correlation recommended by Churchill (1984) (Eqn. 15 in Table 5-2) is similar to that for
vertical upflow, except that the natural convection term is now subtracted from the forced convection term. Although it is seen experimentally that $Nu$ decreases initially as natural convection increases, it clearly does not become negative. When natural convection becomes more important than forced convection, heat transfer rates start to increase again. This effect is captured in the correlation (and the artifact of negative numbers is avoided) by the absolute value sign. Churchill notes that this correlation predicts $Nu$ values which are too low if the forced and natural convection terms are of comparable value, and these predictions can therefore be considered to be a lower bound. The correlation performs better at either extreme when forced or natural convection is dominant, but again it does not explicitly account for supercritical water effects.

5.3.2.5 Vertical Tube; Upflow; Turbulent Flow Unlike with laminar flow, heat transfer can either be impaired or enhanced for upward flow under turbulent conditions, depending on the magnitude of the natural convection component. When the temperature difference between the fluid near the wall and that in the bulk becomes significant, buoyant forces are generated from the resulting density difference. These buoyant forces serve to decrease the shear stress as distance from the wall increases (Jackson and Hall, 1979b). Since the energy that drives the turbulence in the bulk flow is supplied by the product of the shear stress and the gradient of the mean velocity, a reduction in the shear stress by buoyancy results in a drop in turbulence. This in turn reduces the turbulent thermal diffusivity that is primarily responsible for heat transfer under turbulent conditions. The consequent result is a lower effective rate of heat transfer, compared to that for forced convection alone. Eventually if the density differences and buoyant forces become large enough, Hall (1971) claims that the value of the shear stress in the bulk could become negative. The low density fluid layer near the wall will now exert an upwards force on the higher density bulk layer, which will help restore the production of turbulence. The net effect is that heat transfer eventually begins to improve again when the intensity of natural convection becomes large enough, and ultimately exceeds the heat transfer rates achieved under pure forced convection conditions. These
effects (and those associated with turbulent downflow also) can be observed with any gas or li-
uid, not just fluids near their critical point (Jackson and Hall, 1979b).

Watts and Chou (1982) propose three separate correlations for $Nu$ to cover the regimes of
negligible natural convection, reduced heat transfer, and restored and improved heat transfer. To
distinguish between the zones, a specific buoyancy parameter, $\frac{Gr}{(Re^{2.7} Pr^{0.5})}$, is used. When
$\frac{Gr}{(Re^{2.7} Pr^{0.5})} < 10^5$, natural convection effects are negligible and a Dittus-Boelter form for the
forced convection Nusselt number, $Nu_{varp}$ ("variable property"), is suggested (Eqns. 16 and 17 in
Table 5-2). This equation is actually similar in predictive capability to Eqn. 5 in Table 5-2, except
that Eqn. 17 uses only a density term (instead of also including a heat capacity term) to account for
critical point effects. For $10^{-5} < \frac{Gr}{(Re^{2.7} Pr^{0.5})} < 10^{-4}$, heat transfer is impaired, and $Nu_{varp}$ is
multiplied by a two term correction factor that is dependent on the buoyancy parameter to give the
correct value of $Nu$ (Eqn. 18 in Table 5-2). For $\frac{Gr}{(Re^{2.7} Pr^{0.5})} > 10^{-4}$, heat transfer is enhanced,
and $Nu_{varp}$ is multiplied by a different correction factor to give $Nu$ (Eqn. 19 in Table 5-2).

5.3.2.6 Vertical Tube; Downflow; Turbulent Flow For downflow, buoyancy forces
always act in the same direction as the shear stress. Thus turbulence and heat transfer are always
enhanced as natural convection becomes important. Watts and Chou (1982) developed a single
correlation that applies for all turbulent downflow conditions (Eqn. 20 in Table 5-2). This correla-
tion is similar in form to those for turbulent upflow, with an enhancement factor dependent on the
buoyancy parameter multiplied by the same $Nu_{varp}$ to give the correct value of $Nu$.

5.4 Wall Conductivity and External Heat Transfer Coefficient Calculation Values
for the tube wall conductivity, $\lambda_w$, were calculated from a temperature-dependent empirical equa-
tion fit to thermal conductivity data for Hastelloy C-276 (Alloy Digest, 1985).
The external heat transfer coefficient, $h_o$, was assumed constant over the tubing length for a given sandbath temperature. Values for $h_o$ were chosen for each experiment so that the model predicted the measured value of the mixing cross temperature at the end of the preheater tubing. For the entire range of operating conditions, the necessary values of $h_o$ ranged from 69 to 316 W/m²K, varying by less than a factor of 5. Uncertainty in the measured mixing cross temperature had only a modest effect on calculated $h_o$ values; a ± 1°C change in the mixing cross temperature resulted in only a 3% change in $h_o$. The assumption that $h_o$ was constant is reasonable, given the uniform thermal conditions that existed in the fluidized sandbath in which the preheater tubing and main reactor were immersed. The experimentally fitted values of $h_o$ agree reasonably well with values of about 260-450 W/m²K predicted for the current range of operating conditions using the following correlation from Vreedenberg (1958) for a horizontal tube in a fluidized sandbath:

$$Nu = \frac{h_o d_o}{\lambda_g} = 0.66 Pr^{0.3} \left[ Re \left( \frac{D_o}{\rho_g} \right) \left( \frac{1 - \varepsilon_f}{\varepsilon_f} \right) \right]^{0.44}$$

(5-5)

Here all physical properties in both $Pr$ and $Re$ are those for the fluidizing medium (air in this case), $Re$ depends on the outer tube diameter $d_o$, $\lambda_g$ and $\rho_g$ are the thermal conductivity and density of the fluidizing medium respectively, $\rho_s$ is the density of the sand particles (alumina in this case), and $\varepsilon_f$ is the void fraction of the solids bed when fluidized. This rough agreement between model-fitted $h_o$ values and those calculated from Eqn. 5-5 shows that the fitted values are consistent with what would be expected.

5.5 Predicted Results

5.5.1 Heat Transfer Characteristics Most of the heat transfer resistance was found to occur external to the preheater tubing, with $h_i$ typically being about an order of magnitude larger than $h_o$. Although Holgate et al. (1992) reached a comparable conclusion, the fact that they used a single heat transfer correlation that only accounted for critical point phenomena made it difficult to
predict *a priori* that similar results would be achieved with the more detailed correlations used in the present study. In fact, internal and wall resistances were sometimes found to be non-negligible in our case. Holgate and coworkers also used constant values for \( U_i \) averaged over the preheater tubing length in their heat transfer analysis. Their focus was on CO hydrolysis, however, which was found to be virtually negligible in the preheater profiles and in deriving global rate expressions. Because of the rapid and substantial hydrolysis of \( \text{CH}_2\text{Cl}_2 \) that occurred in the preheater tubing in the present work, even small errors in the temperature profiles could significantly affect the calculation of concentration profile estimates and kinetics. Therefore, the use of variable, position-dependent values of \( U_i \) (Eqn. 5-3) rather than a constant, averaged value was in fact required in our case.

Estimated values for the internal heat transfer coefficient versus bulk temperature along the length of the preheater tubing are shown in Figure 5-1 for two experiments representing the two extremes in sandbath temperature (450°C and 600°C) and flow rate (6.4 g/min and 2.4 g/min). Note that the curves end at the temperature of the mixing cross, which approaches the sandbath temperature. Both curves exhibit the expected peak in \( h_i \) near the pseudocritical point. Discontinuities in the curves represent either the point where tube orientation changed or a transition occurred in the flow regime (laminar to turbulent or vice versa). On the low sandbath temperature \( (T_{fb}) \) high flow (\( \dot{m} \)) curve, the first discontinuity (*i.e.*, at 258°C) represents the location where the preheater tubing becomes horizontal (refer to Figure 3-1) and the last discontinuity (*i.e.*, at 442°C) is where the preheater tubing becomes vertical again. The small "shoulder" near 375°C as the curve rises to the pseudocritical point is the first point where the fluid passes from laminar to turbulent flow. This is not observed on the high \( T_{fb} \) low \( \dot{m} \) curve because fluid flow was laminar throughout the entire tubing. The persistence of laminar flow probably accounts for the generally lower \( h_i \) values for the high \( T_{fb} \) low \( \dot{m} \) runs.
Figure 5.1 Values of the Internal Heat Transfer Coefficient As a Function of Bulk Fluid Temperature for Two Experimental Runs, Calculated Using the Correlations in Table 5.2.
The behavior of the overall heat transfer coefficient $U_i$ with temperature for these same two experimental runs differs considerably, as shown in Figure 5-2. This is primarily due to the magnitude of the external heat transfer coefficient. For the low $T_{fb}/\text{high } \dot{m}$ case, $h_o$ equaled 313 W/m$^2$K and $h_o d_o/d_i$ was 460 W/m$^2$K, which was high enough to cause $U_i$ to be affected by changes in $h_i$ and $\lambda_w$. For the high $T_{fb}/\text{low } \dot{m}$ case, $h_o$ was only 73 W/m$^2$K and $h_o d_o/d_i$ was 107 W/m$^2$K, so that the external resistance dominated the heat transfer in most of the tubing. Thus in this case the behavior of $U_i$ largely mimics that of the constant $h_o$ except near the end of the tubing. The results in Figures 5-1 and 5-2 are typical of the present data set.

According to the criteria in Table 5-1, the variation of the parameter $Gr/Re^2$ with temperature (Figure 5-3) shows that natural convection was generally non-negligible in our experiments and probably appreciable in some cases. Not surprisingly, the runs at high $T_{fb}/\text{low } \dot{m}$ like that shown had the highest values of $Gr/Re^2$, because these runs had laminar flow conditions throughout the preheater tubing and thus smaller values of $Re$. Also as expected, the highest values of $Gr/Re^2$ occurred near the pseudocritical point, where density differences between wall and bulk fluid were the greatest.

5.5.2 Temperature-Time Profiles Using the heat transfer model already described and incorporating all of the effects discussed above, predicted temperature-time and temperature-length histories in the preheater tubing are displayed for several experiments in Figures 5-4 and 5-5, respectively. Each curve represents a different sandbath temperature and mass flow rate ranging from 450°C and 6.4 g/min to 600°C and 2.4 g/min. In general, $\dot{m}$ was decreased as $T_{fb}$ was increased in the experiments performed in order to maintain the same constant residence time of 6 s in the supercritical main reactor. This is primarily why preheater residence times increase rather than decrease with increasing $T_{fb}$. Each curve in Figures 5-4 and 5-5 ends at the time the fluid exits the preheater tubing. For all experiments, calculated residence times in the preheater tubing
Figure 5-2  Calculated Values of the Overall Heat Transfer Coefficient As a Function of Bulk Fluid Temperature for Two Experimental Runs. The value used for the external heat transfer coefficient ($h_o$) is listed for each run; internal heat transfer coefficients were those calculated for Figure 5-1.
Figure 5-3 Calculated Values of the Natural Convection Parameter $Gr/Re^2$ As a Function of Bulk Fluid Temperature for Two Experimental Runs.
Figure 5-4  Calculated Temperature-Time Profiles in the Preheater Tubing for Various Experimental Runs at Different Sandbath Temperatures and Flow Rates. The end of the curve corresponds to the point where fluid exits the preheater tubing. The origin corresponds to the point where the tubing enters the sandbath.
Figure 5-5  Calculated Temperature-Length Profiles in the Preheater Tubing for Various Experimental Runs at Different Sandbath Temperatures and Flow Rates. The end of the curve corresponds to the point where fluid exits the preheater tubing. The origin corresponds to the point where the tubing enters the sandbath.
ranged from 7 to 17 s. In all cases, these were greater than the corresponding residence times in the supercritical isothermal main reactor.

The temperature-time profiles in Figure 5-4 convey much information about the subtleties of heat transfer in this system and its effect on reaction of CH₂Cl₂. One can see in Figure 5-4 that the spacing between the temperature-time profiles below $T_{pc}$ increases with increasing $T_{fsh}$ and/or decreasing $\dot{m}$. Most of the low temperature and high flow runs below sandbath temperatures of 550°C have very similar profiles below $T_{pc}$, with the total time required to attain $T_{pc}$ for the 450 and 550°C profiles differing by only about 2 s. All temperature-time profiles level off near $T_{pc}$, but remain below 390°C for about 70-80% of the total residence time of fluid in the preheater tubing. It is only above the pseudocritical region that all the profiles differ from one another. Since the majority of CH₂Cl₂ breakdown occurred under subcritical conditions, however, the most relevant part of the temperature profile for modeling CH₂Cl₂ conversion kinetics is that below the pseudocritical region. Thus, the low $T_{fsh}$/high $\dot{m}$ runs with similar subcritical profiles (450°C to ~550°C) should therefore be expected to have similar conversions, despite $T_{fsh}$ differences of up to 100°C. For higher $T_{fsh}$/lower $\dot{m}$ runs where the temperature-time histories are more distinct, more substantial differences in conversion should be expected.

5.6 Comparison of Results to Experimental Data The behavior of CH₂Cl₂ conversion predicted by the calculated temperature-time profiles in Figure 5-4 is consistent with the experimental conversion data and helps to explain the unusual shape shown in Figure 4-1. There is little or no increase in observed conversion as $T_{fsh}$ is increased from 450 to 500°C, a small gradual increase in conversion between 500 and 550°C, and a strong increase in conversion above 550°C. Based on the fact that most of the conversion was subcritical, however, one can see that $T_{fsh}$ is not the most relevant variable to use, and thus a plot of conversion versus total residence time is shown in Figure 5-6. Note that the main reactor component of the total residence time was a constant 6 s
Figure 5-6 Experimental CH₂Cl₂ hydrolysis conversion as a function of sandbath temperature and calculated total residence time in the preheater tubing and main reactor. Total pressure = 246 bar. Error bars indicate 95% confidence intervals.
<table>
<thead>
<tr>
<th>Preheater Tube #</th>
<th>Position of Tube Failure Relative to the Point Where Heating Begins (cm)</th>
<th>Bulk Fluid Temperature (°C) (^a)</th>
<th>Inner Wall Temperature (°C) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>130 - 190</td>
<td>150 - 200</td>
</tr>
<tr>
<td>2</td>
<td>29</td>
<td>250 - 330</td>
<td>270 - 350</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>100 - 140</td>
<td>110 - 150</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from heat transfer model; see text

**Table 5-3**  **Bulk and Wall Temperatures Predicted at Points of Corrosive Failure in Preheater Tubing**

for each data point; it was the preheater component that varied in each experiment as already described. With the possible exception of the data points at 14 s (corresponding to a \(T_{ib}\) of 450°C), Figure 5-6 exhibits the more usual trend of continuously increasing conversion with increasing residence time.

The heat transfer analysis also elucidates corrosion effects in the organic feed preheater tubes used during the course of the experiments. As described in Section 4.5.2, post-failure analysis revealed that each tube ruptured at one location after undergoing various extents of corrosion over an extended region beginning at the point where the tube first entered the fluidized sand-bath. The rupture location and the calculated temperature range over all experiments at the failure site for the bulk fluid and the inner wall of the tube are presented in Table 5-3. Note that these temperatures never exceed the pseudo-critical point. The highest wall temperature for any experiment that is predicted by the model at the end of the 40 cm region where all corrosion evidence ends is 380°C (see Figure 5-5). Corrosion was insignificant in the region of the preheater calculated to always be supercritical, such as where the end of the preheater tubing enters the mixing
cross (Figure 3-1). These findings confirm that the corrosion was confined to a region of hot, but subcritical, temperatures, which is precisely the regime in which ionic reactions are favorable and corrosion should be particularly rapid and most damaging.

**Dimensionless Number Notation for Chapter 5:**

\[ Gr = \frac{g \rho_b (\rho_b - \rho_w) d_i^3}{\mu^2} \]

\[ \overline{Gr} = \frac{g \rho_b (\rho_b - \overline{\rho}) d_i^3}{\mu^2} \]

\[ Nu = \frac{h_d i}{\lambda} \]

\[ Pr = \frac{C_p \mu}{\lambda} \]

\[ \overline{Pr} = \frac{\overline{C_p} \mu}{\lambda} \]

\[ Ra = Gr Pr = \frac{g \rho_b (\rho_b - \rho_w) d_i^4 C_p}{\mu \lambda} \]

\[ Ra^* = \frac{g \rho_b (\rho_b - \rho_w) d_i^4 C_p}{\mu \lambda} \frac{dT_h}{dz} \]

\[ Re = \frac{d v \rho}{\mu} \]

- \( C_p \) heat capacity
- \( d_i, z \) tube inner diameter, axial position
- \( g \) acceleration due to gravity
- \( h_i \) internal heat transfer coefficient
- \( v \) velocity
- \( \lambda \) thermal conductivity
- \( \mu \) viscosity
- \( \rho \) density

**Subscripts:**

- \( b \) property evaluated at bulk temperature
- \( w \) property evaluated at wall temperature
Chapter 6

Hydrolysis and Oxidation of Methylene Chloride - Kinetics and Solvent Effects

6.1 Introduction With the complete temperature-time history of the CH$_2$Cl$_2$ feed in the preheater tubing now established for each experiment according to the techniques discussed in Chapter 5, determining the hydrolysis kinetics of CH$_2$Cl$_2$ can now be attempted. Recall that in Chapter 4, however, it was noted that the collective experimental data and observations suggest that considerable destruction of CH$_2$Cl$_2$ occurred under subcritical temperatures in the preheater tubing while very little additional reaction occurred under the generally more highly reactive supercritical conditions in the main reactor. Thus any kinetic rate expression proposed must account for this somewhat unusual and counterintuitive behavior.

Toward this end, the objectives of the first part of this chapter are four-fold. The first is to review the nature of the CH$_2$Cl$_2$ hydrolysis reaction in liquid water, and to demonstrate that a simple Arrhenius form for the rate constant does not alone capture the behavior observed experimentally at higher temperatures. The second is to establish that it is the influence of the changing dielectric properties of the solvent which dramatically slows the reaction at higher temperatures. It will be shown that because of the rapidly changing dielectric constant, the transition state complex itself of the hydrolysis reaction is highly sensitive to the solvent environment in this case. The third objective is to develop a quantitative theory of the kinetics of such a reaction. This will be accomplished by the use of a unique combination of Kirkwood theory, transition state theory, and ab initio quantum mechanical calculations. The final objective is to then use these results, along
with experimental temperature-time profiles, to generate engineering-oriented global kinetic rate expressions for the hydrolysis reaction of CH₂Cl₂.

It was also noted in Chapter 4 that very little additional CH₂Cl₂ conversion occurred under oxidation conditions compared to that observed from the corresponding hydrolysis experiment until temperatures of about 525°C and above were reached. The last part of this chapter will address this issue of the effect of O₂ on CH₂Cl₂ destruction, both qualitatively and quantitatively as a function of temperature, initial feed concentrations and ratios, and total residence time. A global oxidation rate expression for CH₂Cl₂ will also be generated from the oxidation data while accounting for the parallel occurrence of hydrolysis via the hydrolysis rate expression and temperature-time profiles already developed.

6.2 General Nature of the CH₂Cl₂ Hydrolysis Reaction In an earlier investigation, Fells and Moelwyn-Hughes (1958) studied the hydrolysis kinetics of CH₂Cl₂ in liquid water from 80 to 150°C in a series of batch experiments conducted in Pyrex ampoules, under both neutral and basic conditions. Despite the lower temperatures and different experimental system, their kinetics results support the proposition that much of the CH₂Cl₂ breakdown observed in our apparatus occurred at subcritical temperatures.

The hydrolysis of CH₂Cl₂ can generally be classified as a nucleophilic substitution reaction. As is usually the case with methyl and methylene halides, the substitution reaction mechanism is most likely of the single-step, bimolecular type (Sₐ2) rather than the two-step, unimolecular type (Sₐ1) (Hine and Lee, 1951; Hine et al., 1955). The products observed and intermediates postulated by Fells and Moelwyn-Hughes are consistent with this type of reaction. Under neutral conditions, water adds an OH group to the central carbon displacing one Cl, which combines with the extra H⁺ to form HCl:
\begin{equation}
\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{ClOH} + \text{HCl}
\end{equation}

This first reaction is the actual nucleophilic substitution. The resulting unstable species CH₂ClOH formed then undergoes a much faster internal rearrangement, expelling another H⁺ and Cl⁻ to form HCHO:

\begin{equation}
\text{CH}_2\text{ClOH} \rightarrow \text{HCHO} + \text{HCl}
\end{equation}

The overall rate of reaction is dictated by the slower first substitution step in Eqn. 6-1 (Fells and Moelwyn-Hughes, 1958). Nucleophilic substitution reactions usually involve one or more charged or polar species (reactants or intermediates) and proceed via a polar mechanism. This probably accounts, in part, for why hydrolysis of CH₂Cl₂ occurred readily under subcritical temperatures, since the polar water solvent under these conditions could clearly support this type of reaction.

Although H₂O and OH⁻ are both possible nucleophiles for a hydrolysis reaction, H₂O was more important under our operating conditions. While the OH⁻ ion is a stronger nucleophile than H₂O by about four orders of magnitude (Swain and Scott, 1953), the concentration of OH⁻ (formed only from dissociation of water in our experiments) was much less than that of the solvent water. At the most favorable conditions for [OH⁻], we have estimated the rate of neutral hydrolysis to still be greater than that of basic hydrolysis by at least a factor of 10³ (typically much higher) under the full range of experimental conditions employed. The presence of H₂O as the dominant nucleophile is further supported by Schwarzenbach et al. (1993), who state that reactions of aliphatic halides in aqueous solution with OH⁻ are unimportant at pH values less than about 10, which was well above the acidic pH of the present experiments.

### 6.3 Failure of the Arrhenius-Form Rate Expression for High Temperature CH₂Cl₂ Hydrolysis

Fells and Moelwyn-Hughes (1958) proposed the following empirical, Arrhenius type correlation for the first order rate constant for neutral/acidic hydrolysis of CH₂Cl₂:
\[ \log k_{FMH} = 98.4408 - 29.66 \log T - 10597.3/T \]  

where \( T \) is in Kelvins and \( k_{FMH} \) in s\(^{-1}\). Note that \( k_{FMH} \) is essentially of simple Arrhenius form, but includes an explicit temperature dependence in the pre-exponential factor via the \( \log T \) term. We explored the suitability of Eqn. 6-3 to predict the \( CH_2Cl_2 \) hydrolysis conversion in our experimental system. Note that this required extrapolation far outside the 80 to 150\(^\circ\)C range for which the correlation was developed.

### 6.3.1 Concentration Profile Modeling Procedure

As was the case with the temperature profiles, the approach adopted for calculating the concentration profiles in the experimental system was similar to that of Holgate et al. (1992). In the preheater tubing, a differential transient analysis of coupled heat transfer and kinetics was used which involved solving the following equations:

\[
\frac{dT}{dz} = \frac{2\pi r_i U_i (T_{fb} - T)}{m C_p(T)} \tag{5-1}
\]

\[
\frac{d[CH_2Cl_2]}{dz} = -\frac{R_{hyd} \pi r_i^2 \rho(T)}{m} + \frac{[CH_2Cl_2]}{\rho(T)} \frac{d\rho(T)}{dT} \frac{dT}{dz} \tag{6-4}
\]

where the hydrolysis reaction rate \( R_{hyd} \) (using Eqn. 6-3 for \( k_{FMH} \)) is given as:

\[
R_{hyd} = \frac{d[CH_2Cl_2]}{dt} = -k_{FMH}(T)[CH_2Cl_2] \tag{6-5}
\]

In the mass balance of Eqn. 6-4, the first term accounts for chemical reaction, while the second term accounts for the effect of decreasing density that occurs as the feed is heated. The term \( dT/dz \) is obtained directly from the differential heat balance (Eqn. 5-1), which is exactly the same as that used in the heat transfer model to generate temperature profiles. In the isothermal main reactor, the concentration was determined directly from Eqn. 6-5, which is what Eqn. 6-4 reduces to under
constant temperature after employing the differential form of Eqn. 5-2 relating residence time $\tau$ to axial length $z$. Here the rate constant was evaluated at the constant, measured main reactor temperature.

Because of the dilute feed solutions used, heat of reaction effects were negligible, and values for fluid properties such as density were again taken as that of pure water from the NBS/NRC steam tables (Harr et al., 1984). Eqns. 6-4, 6-5, 5-1, and 5-2 form a non-linear, coupled set that were solved simultaneously via a Runge-Kutta numerical integration technique applied over the entire length of the preheater tubing and main reactor (similar to that described in Section 5.2) to ultimately yield values of $[\text{CH}_2\text{Cl}_2]$ as a function of residence time and axial distance for each experimental run. Thus values of $\text{CH}_2\text{Cl}_2$ concentration could be calculated at any axial location in the experimental system, and in particular, at the end of the preheater and main reactor.

Eqn. 6-4 assumes the existence of plug flow conditions. Although this was nearly true in the main reactor which always was in turbulent flow, it could not necessarily be assumed to be true in the preheater tubing where fluid in some or all sections was in laminar flow. Nevertheless, plug flow can be a sufficiently reliable approximation for kinetic analysis even when laminar fluid flow conditions exist provided that there is minimal axial diffusion of heat or mass and that radial diffusion is very fast. Cutler et al. (1988) provide a series of criteria to determine if such an approximation is appropriate. Based on the present experimental apparatus dimensions and operating conditions, all of the stated criteria are met, justifying use of the plug flow assumptions in Eqn. 6-4 for both preheater and main reactor sections.

6.3.2 Arrhenius Model Results  Calculated $\text{CH}_2\text{Cl}_2$ concentration profiles using predicted temperature profiles and the Fells and Moelwyn-Hughes rate constant (Eqn. 6-3) are shown for our hydrolysis runs in Figure 6-1. Three sets of results are presented in Figure 6-1: the experi-
Figure 6-1  Experimental and Predicted CH$_2$Cl$_2$ Hydrolysis Conversion As a Function of Sandbath Temperature and Residence Time. Total pressure = 246 bar; error bars indicate 95% confidence intervals. Model values generated using the first order rate constant correlation of Fells and Moelwyn-Hughes (Eqn. 6-3). Note that residence time does not scale linearly with sandbath temperature.
mentally measured CH₂Cl₂ conversions at the end of the reactor system (also shown in Figure 4-1), values predicted from the model at the end of the preheater tubing, and values predicted from the model at the end of the isothermal main reactor. The data are plotted versus sandbath temperature, and calculated values of residence time in both the preheater and complete system (preheater and main reactor) are also shown to facilitate interpretation. Note that residence time does not scale linearly with sandbath temperature because of the decrease in experimental mass flow rates made with increasing sandbath temperature in the experiments to compensate for the increasing volumetric flow rates at higher temperatures. In all cases, the main reactor (supercritical) residence time was 6 s, which was always less than the calculated preheater residence time (~ 75% of which was at subcritical temperatures).

Figure 6-1 shows that the simple Arrhenius-type model of Fells and Moelwyn-Hughes has major shortcomings. Although the calculated values of conversion are of the same order of magnitude as the experimental values, the shape of the curves formed by the set of calculated conversion values (both at the end of the preheater tubing and at the end of the main reactor) clearly do not match the experimental trends. Note also that, in each case, almost half of the total conversion is predicted to occur in the supercritical main reactor, which contradicts the experimental observations. These results are not necessarily unexpected, since the magnitude of the Fells and Moelwyn-Hughes rate constant (and indeed of any rate constant of Arrhenius form) should increase monotonically with increasing temperature. Thus, considering only temperature effects, one would in fact predict that the amount of total conversion would be very high in the supercritical main reactor, as opposed to the lower temperature preheater tubing, for a rate constant of this form. This model, however, is unable to capture the behavior shown by the experimental data and observations over our extended sub- and supercritical temperature range.
These discrepancies between experimental results and the Fells and Moelwyn-Hughes model suggest that the simple Arrhenius-type rate expression is failing to account for some important effect. Specifically, an additional temperature-dependent phenomenon must be offsetting the strong positive temperature effect of the Arrhenius term at high temperatures. Apart from the temperature, the one factor which varied significantly during the course of each experiment was the nature of the water solvent itself. Below we investigate the impact of solvation effects on the CH$_2$Cl$_2$ hydrolysis reaction rate.

6.4 The Influence of the Solvent on Reaction Rates in Solution When water is heated from ambient to supercritical conditions, it transforms from being a dense, strongly polar, hydrogen bonded liquid to a lower density, nonpolar fluid with gas-like diffusivity and viscosity (Modell, 1989; Tester et al., 1993a; Franck, 1987). Two quantities which are likely to affect reaction rates in supercritical water are thus the density and dielectric nature of the solvent. The polar mechanism of the subcritical hydrolysis reaction of CH$_2$Cl$_2$ makes it reasonable to suspect that the changing dielectric nature plays a key role. Below, it will be shown from *ab initio*-based evidence that, in this case, the dielectric effect is two to three orders of magnitude more important than the density effect.

6.4.1 Literature Review on Solvent Effects For those relatively few reactions that take place in the gas phase as well as liquid solution, it is commonly observed that the solvent does not play a significant role in affecting the reaction rate (Laidler, 1965). For those reactions that only occur in solution and not in the gas phase, however, the effect of the solvent can often be found to be very important.

The literature provides strong precedent for noticeable solvent effects on reaction rates, particularly in the vicinity of the critical point of water. For example, the computer simulations of
Gao and Xia (1994) show that the rate of two reactions, the Claisen rearrangement of allyl vinyl ether and the \( S_{\text{N}2} \) reaction of \( \text{NH}_3 \) and \( \text{CH}_3\text{Cl} \) increase when conducted in aqueous solution as opposed to the gas phase. Researchers at the University of Texas at Austin have explored the solvation effects of supercritical water on a number of reactions via simulation and spectroscopy, including proton transfer reactions (Xiang and Johnston, 1994; Ryan et al., 1996) and the \( S_{\text{N}2} \) reaction between \( \text{Cl}^- \) and \( \text{CH}_3\text{Cl} \) (Balbuena et al., 1995). Townsend et al. (1988) observed parallel pyrolysis and hydrolysis mechanisms for the reaction of a number of coal model compounds in sub- and supercritical water, and found the product selectivity to be dependent upon the solvent. These trends were also seen in a similar study of nitroaniline explosive simulants (Wang et al., 1995). In addition, Townsend et al. (1988) found that the value of the rate constant for a few compounds was highly correlated to the dielectric constant of the water solvent. In a follow-up study, Huppert et al. (1989) showed that the hydrolysis rate constant of guaiacol could be manipulated by changes in the solvent water density near the critical point (at a temperature of 383°C) by pressure variation and by adding salts. Similarly, in a study of 1-propanol dehydration in supercritical water, Narayan and Antal (1990) observed a decrease in the acid-catalyzed rate constant by a factor of three when the water dielectric constant was increased by a proportional amount by an increase in pressure. Iyer and Klein (1997) incorporated a dielectric constant dependent term in their correlation for the rate constant for butyronitrile hydrolysis to account for changes in the electrostatic nature of the solvent resulting from pressure variation. Finally, Habenicht et al. (1995) observed improved fits in their reaction model when accounting for the influence of the solvent dielectric constant on the synthesis of ethyl tert-butyl ether from tert-butyl alcohol in liquid ethanol.

### 6.4.2 Qualitative Description of Solvent Effects

In general, solvents that help stabilize the transition state complex of a reaction (relative to the reactants) result in faster reaction rates. One way to characterize the electrical nature of a solvent is by its polarity, which is best represented quantitatively by its dielectric constant, \( \varepsilon \). So for those reactions where the transition state has a
stronger electric field than the reactants (due to a higher net charge or stronger dipole moment, for example), a more polar (or high dielectric constant) solvent will lower the energy of the transition state more than that of the reactants, resulting in a lower activation energy and thus a faster reaction (Lowry and Richardson, 1981). Conversely, for those reactions where the reactants have stronger electric fields than the transition state, a more polar solvent will lower the total energy of the reactants more than that of the transition state, resulting in a higher activation energy and a slower reaction. The reverse is true for a more nonpolar (or low dielectric constant) solvent, where the above arguments apply to raising instead of lowering the energy of the transition state and reactants. In the present case, the dielectric response of H₂O decreases dramatically with increasing temperature near the critical point. One would thus in principle expect the rate of an aqueous reaction with a highly polar transition state to slow down as the water is heated from subcritical (polar) to supercritical (nonpolar) conditions, and for the reaction to accelerate if the reactants are more polar than the transition state.

To qualitatively determine how the solvent can affect the rate of a nucleophilic substitution reaction, Lowry and Richardson (1981) have divided this family of reactions into four main categories. The categories are based on the electrical nature of both the nucleophile and the leaving group, as shown in Table 6-1. Based on this classification system, only the Type 2 category of reactions has a transition state with a stronger electric field than the reactants. In the other three categories, the transition state charge is more highly dispersed than that of the reactants, resulting in a relatively weaker electric field for the transition state. Thus one would expect Type 2 reactions to proceed faster in polar solvents than nonpolar solvents, and slow down as the polarity or dielectric constant of the same solvent medium decreases.

Note that the neutral hydrolysis of CH₂Cl₂ would be classified as a Type 2 reaction (nucleophile = H₂O, leaving group = Cl⁻), while the basic hydrolysis of CH₂Cl₂ would be classified as a
\[
\text{Nu}^+ + \begin{array}{c}
\text{R}_1 \\
\text{R}_2 \end{array} \begin{array}{c}
\text{C} \\
\text{LG} \\
\text{R}_3
\end{array} \rightarrow \begin{array}{c}
\text{Nu}^- \\
\text{R}_1 \end{array} \begin{array}{c}
\text{C} \\
\text{R}_2 \end{array} \begin{array}{c}
\text{R}_3 \\
\text{LG}^-
\end{array}
\]

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Nucleophile (Nu)</th>
<th>Leaving Group (LG)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Negative charge</td>
<td>Negative charge</td>
<td>( \text{OH}^- + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{OH} + \text{Cl}^- )</td>
</tr>
<tr>
<td>2</td>
<td>Neutral</td>
<td>Negative charge</td>
<td>( \text{H}_2\text{O} + \text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{ClOH}_2 + \text{Cl}^- )</td>
</tr>
<tr>
<td>3</td>
<td>Negative charge</td>
<td>Neutral</td>
<td>( \text{I}^- + \text{CH}_3\text{NH}_3 \rightarrow \text{CH}_3\text{I} + \text{NH}_3 )</td>
</tr>
<tr>
<td>4</td>
<td>Neutral</td>
<td>Neutral</td>
<td>( \text{N(CH}_3)^+ + \text{S(CH}_3)_2 \rightarrow \text{N(CH}_3)_4 + \text{S(CH}_3)_2 )</td>
</tr>
</tbody>
</table>

Table 6-1  Mechanism and Classification of Bimolecular Nucleophilic Substitution (S_n2) Reactions (Based on Lowry and Richardson, 1981)

Type 1 reaction (nucleophile = OH\(^-\), leaving group = Cl\(^-\)). The two different hydrolysis mechanisms should therefore exhibit opposite behaviors as the polarity of the solvent changes. As water goes through the critical point with increasing temperature, the rate of the neutral hydrolysis reaction is expected to be retarded due to the changing nature of the solvent. Although one in principle would expect the rate of basic hydrolysis to accelerate under the same conditions, the greatly reduced water dissociation constant and low ion solubilities typical in supercritical water would likely result in a low OH\(^-\) concentration available and prevent basic hydrolysis from becoming significant. The experimentally observed fast hydrolysis of CH\(_2\)Cl\(_2\) under subcritical conditions but much slower reaction under supercritical conditions is thus consistent with the neutral hydrolysis mechanism.

6.5 Theoretical Development

6.5.1 Kirkwood Theory  To account quantitatively for this solvent-related slowing of the CH\(_2\)Cl\(_2\) hydrolysis reaction rate as conditions go from sub- to supercritical, one needs to first de-
termine the energy associated with solvation of the reacting species in water at a given temperature and then incorporate this result into the reaction rate constant form. The method for doing this which will be used here involves a unique combination of transition state theory, electrostatics and \textit{ab initio} quantum mechanical calculations.

The theory originally developed by Kirkwood (1934) is a reasonable starting point for calculating the solvation energy of a molecule. Kirkwood formulated this theory to calculate the change in the Gibbs free energy of a molecule or ion as it is transferred from a medium of a dielectric constant of unity (vacuum) to a medium having a dielectric constant $\varepsilon$. According to the theory, the solute molecule is modeled as a sphere of radius $r$, in which is embedded a number of discrete point charges $q_k$, and in which a separate internal molecular dielectric constant, $\varepsilon_i$, accounts for internal screening effects, as depicted in Figure 6-2. The solvent is modeled as a dielectric continuum that exerts a potential $\phi_{\text{solute}}(r, \theta, \phi)$ on the charges in the solute molecule, where $r$, $\theta$, and $\phi$ are the usual spherical coordinates. It is also assumed that only electrostatic forces are important between the solute and solvent; van der Waals and other short range forces are only coarsely included in this development. This assumption is certainly reasonable for reactions between ions and for reactions with highly polar neutral molecules or those that form a polar transition state complex (Laidler, 1965). The validity of this assumption decreases as the polarity of the reactants and their transition state complex decreases.

The total electrostatic potential at any point within the solute molecule has two contributions, one from the charges within the molecule and one from the effect of the solvent:

$$
\phi = \sum_{k=1}^{M} \frac{q_k}{\varepsilon_i |\vec{r} - \vec{r}_k|} + \phi_{\text{solute}} \tag{6-6}
$$
where $|\vec{r} - \vec{r}_k|$ is the distance from the charge $q_k$ to the point $(r, \theta, \varphi)$ and $M$ is the total number of charges in the solute molecule. In a vacuum, only the first term in Eqn. 6-6 survives, as $\varphi_{solvant}$ would be 0. The change in the Gibbs free energy for charging a molecule $i$ in solution versus charging the molecule in a vacuum is equal to one-half of the sum of the products of each charge $q_k$ and the total potential in solution (Eqn. 6-6) subtracted from the sum of the products of each charge $q_k$ and the total potential in vacuum, which reduces simply to:
\[ \Delta G_{\text{solv},i} = \frac{1}{2} \sum_{k=1}^{M} q_k \phi_{\text{solv}} \]  \hspace{1cm} (6-7)

The factor of one-half is included to avoid overcounting. The functional form for \( \phi_{\text{solv}} \) is found by solving Laplace's equation in spherical coordinates along with the standard separation of variables technique (Jackson, 1962) to yield the following:

\[ \phi_{\text{solv}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} B_{nm} P_n^m(\cos \theta) e^{im\phi} \]  \hspace{1cm} (6-8)

where \( P_n^m(\cos \theta) \) are the associated Legendre polynomials, \( B_{nm} \) are constants, and \( i \) here represents \( \sqrt{-1} \).

By applying the appropriate boundary conditions at the solute-solvent interface to solve for the \( B_{nm} \) constants (Kirkwood, 1934) and substituting Eqn. 6-8 into Eqn. 6-7, the following form for Eqn. 6-7 is achieved:

\[ \Delta G_{\text{solv},i} = \frac{1}{2} \sum_{n=0}^{\infty} \frac{(n+1)Q_n(\varepsilon_i - \varepsilon)}{4\pi \varepsilon_\infty \varepsilon_i r^{2n+1} [(n+1)\varepsilon + n\varepsilon_i]} \]  \hspace{1cm} (6-9)

where \( \varepsilon_\infty \) is the vacuum permittivity and

\[ Q_n = \sum_{k=1}^{M} \sum_{l=1}^{M} q_k q_l r_k^n r_l^n P_n(\cos \theta_{kl}) \]  \hspace{1cm} (6-10)

In Eqn. 6-10, \( P_n(\cos \theta_{kl}) \) represents the ordinary Legendre polynomials and \( \theta_{kl} \) is the angle formed between the position vectors \( \vec{r}_k \) and \( \vec{r}_l \) to their respective charges \( q_k \) and \( q_l \). Eqn. 6-9 is in fact nothing other than a multipole expansion for the energy associated with the solvent potential, with the \( Q_n \) terms containing the individual multipoles. When \( n = 0 \), \( Q_0 = \sum_k \sum_l q_k q_l = (Ze)^2 \), which is
just the square of the total charge or monopole of the solute (which is nonzero if the solute is an ion). When \( n = 1 \), \( Q_i = \sum_k \sum_l q_k q_l \eta_k \eta_l \cos \theta_{kl} = (q_i)^2 = \vec{\mu}^2 \), which is the square of the dipole moment of the solute. In the same way, higher values of \( n \) correspond to higher multipoles such as the quadrupole, octapole, etc.

The appropriate value of \( \varepsilon_i \) to use depends on the strength of screening within the molecule. A value of unity corresponds to zero, or negligible screening. Kirkwood himself set \( \varepsilon_i \) equal to unity, as do Moore and Pearson (1981). In his presentation, Laidler (1965) uses a somewhat larger value of two, resulting in a slightly different form of equation. Here we set \( \varepsilon_i \) equal to unity. Our final form for the solvation energy of a molecule or ion of species \( i \) is as follows:

\[
\Delta G_{solv,i} = \frac{Z^2 e^2}{8 \pi \varepsilon_o r} \frac{1 - \varepsilon}{\varepsilon} + \frac{\mu^2}{4 \pi \varepsilon_o r^3} \frac{1 - \varepsilon}{2 \varepsilon + 1} + \ldots \tag{6-11}
\]

Note that the first term is the same as what would be derived if the solute consisted of a point charge. If the solute is an ion, only this first term is important and the rest can usually be neglected. For a neutral molecule, the first term drops out and the second term (the dipole term) becomes the most important. In either case, the series solution form of Eqn. 6-11 converges rapidly for nearly spherical molecules, and it is usually acceptable to cut the series after the second term: without serious numerical error for molecules such as \( \text{H}_2\text{O} \) or \( \text{CH}_2\text{Cl}_2 \) which have significant dipole moments. Below, we shall always truncate Eqn. 6-11 to these two terms. A final point to note is that all of the above arguments hold equally well for a more realistic solute molecule or ion model where the charge is continuously distributed rather than existing as discrete point charges. The only difference is that the charge density \( \rho(r,\theta,\phi) \) replaces the point charges \( q_k \) and all summations are replaced by integrals. The same form for Eqn. 6-11, however, is achieved.
The subtle effects missed in this simple description of a solute molecule can in principle be treated correctly in a series of ever more demanding calculations (described in Section 6.9). Eqn. 6-11, however, is a reasonable approximation of at least semiquantitative reliability which we apply in this initial attempt to understand and characterize the reaction.

6.5.2 Application to Transition State Theory In order to couple the solvent energy effects to the reaction rate constant, one must now invoke Transition state theory. For a reaction between two neutral molecules A and B (such as that between CH₂Cl₂ and H₂O) in solution, the rate constant can be written as follows:

\[
k = \frac{k_b T}{h} e^{-\Delta G^f / RT}
\]  \hspace{1cm} (6-12)

where \( T \) is the temperature, \( k_b \) is Boltzmann's constant, \( h \) is Planck's constant, and \( R \) is the universal gas constant. The term \( \Delta G^f \) is the standard Gibbs free energy of activation for the reaction of A and B to form the transition state complex AB₄. In this case, the \( \Delta G^f \) can be divided into two separate terms for each species \( i \) (reactant or product):

\[
\Delta G^f = \sum_i v_i \left( G''_i + \Delta G_{solv,i} \right)
\]  \hspace{1cm} (6-13)

Here \( v_i \) is the stoichiometric coefficient for species \( i \) according to the reaction, \( G''_i \) is the standard Gibbs free energy for pure species \( i \) in vacuum, and \( \Delta G_{solv,i} \) is the solvation energy for species \( i \) from vacuum given in Eqn. 6-11. (We use the vacuum reference in this development as it is most convenient for making contact with \textit{ab initio} calculations.) Note that the term \( \sum_i v_i G''_i \) is equivalent to the \( \Delta G_{ran} \) for reaction in a vacuum. With the expression for \( \Delta G^f \) in Eqn. 6-13, Eqn. 6-12 can now be written in natural log form as:
\[
\ln k = \ln \left( \frac{k_o T}{h} \right) - \frac{\Delta G_{\text{sm}}}{RT} - \frac{\sum \nu_i \Delta G_{\text{solv},i}}{RT} \quad (6-14)
\]

The first two terms on the right hand side of Eqn. 6-14 together represent the value of the rate constant \(k_o\) for reaction in a vacuum and account for all of the usual effects except for that due to the solvent, which is contained in the last term. Inserting the form for \(\Delta G_{\text{solv},i}\) developed in Eqn. 6-11 for neutral species and putting this on a molar basis yields the following:

\[
\ln k = \ln k_o - \frac{N_A(1 - \varepsilon)}{4\pi\varepsilon_o RT(2\varepsilon + 1)} \left[ \frac{\mu_i^2}{r_i^3} - \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3} \right] \quad (6-15)
\]

where \(N_A\) is Avogadro’s number, \(\mu_i\) is the dipole moment of species \(i\) and \(r_i\) is the radius of species \(i\). Written this way, the term containing \(k_o\) can be thought of as a reference, reflecting the rate of the reaction in vacuum. The second term on the right containing the Kirkwood expression then becomes the factor that “corrects” the magnitude of the rate constant due to the influence of the solvent. The value of this term is positive, representing an increase in the reaction rate as \(\varepsilon\) (and the polarity of the solvent) increases, provided that the term \(\mu_i^2/r_i^3\) for the transition state is greater than the sum of the same terms for the reactants.

In the present analysis of hydrolysis reactions, it is more useful to reference Eqn. 6-15 to conditions of ambient water density (\(\varepsilon_a \approx 80\)) rather than a vacuum (\(\varepsilon = 1\)). To do this, we first compare the prediction of Eqn. 6-15 for such ambient conditions with the observable behavior near ambient temperature characterized by an Arrhenius form with pre-exponential factor \(A\) and activation energy \(E_a\):

\[
\ln k = \ln k_o - \frac{N_A(\varepsilon_a - 1)}{4\pi\varepsilon_o RT(2\varepsilon_a + 1)} \left[ \frac{\mu_i^2}{r_i^3} - \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3} \right] \\
= \ln A - \frac{E_a}{RT} \quad (6-16)
\]
Using the above equations to solve for the unknown $k_o$ and substituting the result into Eqn. 6-15 yields the following expression for the rate constant now referenced to ambient water conditions:

$$
\ln k = \ln A - \frac{1}{RT} \left( E_a + \frac{N_A}{4\pi\varepsilon_o} \left( \frac{(\varepsilon_a - 1)}{(2\varepsilon_a + 1)} \right) \left( \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3} \right) \right) \left( \frac{\varepsilon - 1}{2\varepsilon + 1} \right) \left( \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3} \right) \right) \right)
$$

(6-17)

This shift in the reference not only makes the form of the equation consistent with how the CH$_2$Cl$_2$ hydrolysis experiments were performed (going from ambient starting conditions up to supercritical), but also allows one to separate out the activation energy at conditions of ambient water density, which are the conditions most comparable to those cited in the literature for hydrolysis experiments at ambient or low subcritical temperatures. Thus it allows comparison of activation energy values on a more equal basis. In the form of Eqn. 6-17, the entire quantity in the outermost brackets represents the actual activation energy for the reaction, which consists of the activation energy under ambient conditions ($E_a$) and the Kirkwood-derived second term which acts as the correction factor. The Kirkwood term works to increase the total activation energy (or slow the reaction rate) as $\varepsilon$ decreases, provided that the transition state is more polar than the reactants.

Eqn. 6-17 implicitly assumes that the form of the transition state, and thus the corresponding values of $\mu$ and $r$, do not vary with the solvent dielectric constant. When the transition state itself depends sensitively on the dielectric behavior of the solvent, the explicit form to use for $\ln k$ is slightly more complicated for two reasons. First, the value of the $\mu^2/r^3$ term for the transition state in the Kirkwood expression (Eqn. 6-11) will now depend implicitly on the value of $\varepsilon$. Similarly, the energy of the transition state in vacuum will also vary with $\varepsilon$ as its nature changes. Accounting for these two facts while following the same development as for Eqn. 6-17 yields the following expression:

$$
\ln k = \ln A - \frac{1}{RT} \left( E_a + (\Delta G^\text{vac}_T - \Delta G^\text{vac}_T) + \frac{N_A}{4\pi\varepsilon_o} \left( \frac{(\varepsilon_a - 1)}{(2\varepsilon_a + 1)} \right) \left( \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3} \right) \right) \left( \frac{\varepsilon - 1}{2\varepsilon + 1} \right) \left( \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3} \right) \right) \right)
$$

(6-18)
In this expression, the terms $\Delta G_j^{\text{vac}}$ correspond to the energy in vacuum of the transition state species relative to the reactants for the transition state held with the structure it has in a medium of dielectric constant $j$. Similarly, the $\mu_{x,j}^2/r_{L,j}^3$ terms represent the appropriate value when the transition state species is in a medium of dielectric constant $j$. $E_a$ remains the activation energy for the reaction as it occurs in a medium of $\epsilon_a = 80$ at 298 K (ambient conditions). In Eqn. 6-18, it is assumed that the structure of the neutral molecule reactants A and B do not change significantly as the medium dielectric constant changes. Note that if the transition state structure does not vary with $\epsilon$, then the vacuum energy at any value of $\epsilon$ is the same, as is the case with $\mu_{x,j}^2/r_{L,j}^3$, and Eqn. 6-18 reduces back to the form of Eqn. 6-17. Eqn. 6-18 should thus be viewed as the more general equation to use. As in Eqn. 6-17, the effective activation energy represented by the quantity in brackets consists of: (a) the activation energy under ambient conditions, and (b) remaining terms that collectively can be viewed as the correction factor arising from interaction with the solvent dielectric medium.

To calculate a value for the correction factor in Eqn. 6-18 requires knowledge of a number of variables. The value of $\epsilon$ for water (used in this case because experimental concentrations of CH$_2$Cl$_2$ were very dilute) is a function of temperature and pressure, and can be determined from the correlation of Uematsu and Franck (1980). The dipole moment and size of the reactants and their transition state, along with the vacuum energy and structure of the transition state complex must still be determined.

6.5.3 Ab Initio Techniques For Determination Of Dipole Moments, Molecular Sizes, And Transition State Structure

6.5.3.1 Motivation and Overview For stable molecules, a number of sources exist that contain tabulated experimental values for the dipole moment, such as that by McClellan (1963). This is especially true for relatively common molecules such as water or CH$_2$Cl$_2$. Unstable species such as a reaction transition state complex create problems, however, in that there is very little in-
formation available in general on their physical properties. In this case, one can resort to vector group contribution methods for estimating the dipole moment (Minkin et al., 1970; Smyth, 1955), but these methods are fairly complex and require considerable effort for all but the most simple and symmetric molecules (Reid et al., 1987). Since using these methods requires a detailed knowledge of the structure of the molecule including bond lengths and angles, one is at a further disadvantage with a transition state complex because this information is not always known accurately, if at all. In addition, such semiempirical rules, even when all of the relevant bond lengths and angles are known, cannot be relied upon to capture the subtle effects in the molecular charge distribution which arise as bonds are in the process of forming and breaking in the transition state.

In trying to determine the radius of a molecule, one has the added difficulty that very few polyatomic molecules, both stable and unstable, are spherical and none have rigid boundaries. Recall that Kirkwood formulated his theory based on the assumption of spherical species and a solvent which presents a uniform dielectric continuum all the way up to the boundary of the solute. Although these assumptions greatly simplify the problem and allow one to develop a tractable analytical solution for the solvation energy in functional form, this treatment begs the question of what is meant by the radius of a species, especially for those which are not spheres at all such as the bent planar water molecule, the tetrahedral CH$_2$Cl$_2$ molecule, and their reaction transition state complex. The assumption of species sphericity and rigid boundaries are just two of several critical assumptions contained in Kirkwood's original formulation that may limit its overall effectiveness and accuracy in results predicted. This is an issue which will be examined more closely in Section 6.9.

For now, though, to be consistent with Kirkwood's formulation, there are a few options available. One could use the van der Waals radius, which is the nonbonded contact radius of an implicitly spherical atom or molecule. Bondi (1968) contains tables that allow one to calculate the van der Waals radius of carbon-based molecules by a group contribution technique. If one knows
the volume of the molecule, an "equivalent" radius (or the radius of a sphere of equal volume to that of the molecule) can be calculated from the equation for the volume of a sphere. To estimate the molecular volume, one could use the van der Waals volume, which can be calculated from the van der Waals radius or by its own group contribution method (Bondi, 1968). Another rough way to estimate volume is through the volume parameter $b$ for a given pure species from the van der Waals equation of state. This $b$ parameter is roughly equivalent to $1/4$ of the molar volume, and it can be determined from the species critical constants through the principle of Corresponding States. All of these methods for calculating either radii or volume are fairly crude, however, and suffer from not having a way to take into account important second order effects and from limited species data available to make the necessary calculations. As with dipole moment calculations, these facts make calculation of the radius or volume of an unstable transition state species much more difficult and questionable than that for stable molecule reactant species. Furthermore, the van der Waals radius may not be the best value to use since it is inconsistent with the Kirkwood model, which requires the solvent dielectric constant to be at its full bulk value beyond the solute molecule boundary.

A technique free of many of these uncertainties is to calculate molecular properties directly from first principles many-body quantum mechanics. This \textit{ab initio} approach has the advantage of not only circumventing the problems associated with a lack of data for unstable species but also allowing one to in fact discern the structure and stereochemistry of unstable species such as transition state complexes. This approach gives unambiguous results for a variety of fundamental molecular properties and thus limits the uncertainties in the calculations. We used the \textit{ab initio} approach to identify the formation of the transition state in the hydrolysis of $\text{CH}_2\text{Cl}_2$ and to calculate its dipole moment, radius, and vacuum energy along with that for the two reactants. In addition to providing the necessary physical property values for use in calculating the rate constant correction factor, following the \textit{ab initio} approach has provided valuable insight, both qualitative and quan-
titative, into the nature of the CH₂Cl₂ hydrolysis reaction as the solvent environment changes from sub- to supercritical conditions. A brief overview of the ab initio modeling technique utilized for the current work is given below, while a more detailed description can be found in the review by Payne et al. (1992).

6.5.3.2 Ab Initio Theory As its name implies, ab initio calculations determine the equilibrium position and properties of a collection of atoms from a knowledge only of the initial spatial position, nuclear charge, and number of valence electrons for each atom. The procedure is the same regardless of whether the collection of atoms forms a stable molecule or short lived intermediate, and so in principle should work equally well at predicting the proper atomic configuration and related properties of the transition state complex of the reactants without any further prior knowledge.

Since finding the many-body wave function in a multi-atom system is an immense task in terms of computational power and time, a few carefully chosen simplifying assumptions are made in the algorithm. First, the Born-Oppenheimer Approximation is used to represent the atomic nuclei as stationary point charges. Since the nuclei are much more massive than the electrons and as a result move much more slowly, we assume that the nuclei remain adiabatically in their instantaneous ground state at all times. Next, density functional theory is used to reduce the complexities of the interactions among all of the electrons exactly to the equivalent, much simpler problem of non-interacting electrons moving in an effective potential. The principal objective of the calculations then becomes to determine the total energy for the system of atoms and the electronic charge density ρ as a function of space. This is done by effectively solving Schrodinger’s equation (called the energy functional in this form):

\[
E \left( \{ \psi_n \}_{n=1}^N \right) = \sum_{\alpha=1}^{N} -\frac{\hbar^2}{2m_e} \int \psi_\alpha^* \nabla^2 \psi_\alpha dV + \int \left[ \phi_{\text{core}}(\mathbf{r}) + \frac{1}{2} \phi_c(\mathbf{r}) + \phi_n(\mathbf{r}) \right] \rho(\mathbf{r}) dV \tag{6-19}
\]
by determining the wave functions which minimize the Kohn-Sham energy of the system (Kohn and Sham, 1965). In Eqn. 6-19, $E$ represents the total energy of the system, $N$ is the number of electrons, $\psi$ is the wave function, $V$ is volume, $m_e$ is the mass of the electron, and $\vec{r}$ is the position vector. The first term on the right represents the kinetic energy of the electrons and the second term collectively accounts for the potential energy (individual $\phi$ terms explained below). The wave functions are represented in the computations by a set of different coefficients $c_{\alpha}(\vec{G})$ for each wavefunction $\psi_{\alpha}(\vec{r})$ in a plane wave basis set expansion:

$$\psi_{\alpha}(\vec{r}) = \sum c_{\alpha} e^{i\vec{G} \cdot \vec{r}}$$  \hspace{1cm} (6-20)

The $\vec{G}$ in Eqn. 6-20 are the wave vectors of the various plane waves in the expansion.

In Kohn-Sham theory, the potential energy term in the energy functional is split into three contributions, each depending only on the *total* electronic density. The first term, $\phi_{\text{core}}$, accounts for the combined electrostatic potential of the nuclei and inner core (nonvalence) electrons by means of a known pseudopotential function. This representation of each nucleus and core electrons by a single unchanging pseudopotential is justified because the effects of atomic interactions usually do not penetrate any deeper than the valence electrons. The pseudopotential differs for each atomic element and is determined also from first principles in another set of calculations performed once for each element. The second term in the potential energy, $\phi_{\epsilon}$, accounts for the electrostatic potential due to the valence electrons themselves. It is found from Poisson’s equation:

$$\nabla^2 \phi_{\epsilon} = -\frac{\rho(\vec{r})}{\varepsilon_o}$$ \hspace{1cm} (6-21)

and is known as the Hartree potential. The factor of 1/2 in the Hartree term in Eqn. 6-19 is to avoid overcounting. The final term is called the exchange correlation potential, $\phi_{xc}$, which accounts
for all effects of correlation among the electrons. In general, the form of this term is too complex to be known. In this work, we approximated this term using the Local Density Approximation.

6.5.3.3 Details of the Present Calculations In this work, the electronic wave functions are expanded in a plane wave basis up to a kinetic energy cutoff of 40 Rydberg, for a total of 35,000 coefficients for each wave function. The plane wave basis has the advantage of allowing the use of fast Fourier transform techniques; however, because plane waves are periodic, the calculations must be performed with periodic boundary conditions. Using the supercell approach (Payne et al., 1992), each molecular system in our calculations is surrounded with a large volume cell of vacuum and then repeated periodically throughout space. In all of the calculations reported here for either of the two reactants, a cubic cell of side length 10 Å is used. For the transition state, the molecules are separated from each other by 9 Å in the y and z directions and, to allow for the fact that the transition state is elongated, 15 Å along the x direction. With these cells, the closest distance between atoms from different molecules is about 7 Å. We have verified that the electron density decays essentially to zero between the molecules. This amount of separation ensures that there is minimal interaction among the periodic images of our molecules.

As discussed above, the interaction between the ionic cores (nuclei plus core electrons) is represented using the pseudopotential approximation. The particular pseudopotentials which we use are optimized according to the procedure of Rappe et al. (1990) with operators of the Kleinmann--Bylander nonlocal form (Kleinmann and Bylander, 1982) for the s channel for carbon and the p channel for oxygen and chlorine. For hydrogen, we use the bare Coulomb potential of the proton.

The exchange-correlation energy is approximated within the local density approximation using the Perdew-Zunger parametrization (Perdew and Zunger, 1981) of the Ceperly-Alder results
for the homogeneous electron gas (Ceperly and Alder, 1980). Finally, the minimization of the energy with respect to the plane wave coefficients was carried out using a parallel fortran code based upon the conjugate gradient technique of Teter et al. (1989), on the experimental Xolas SUN supercomputing cluster at the MIT Laboratory of Computer Science.

### 6.5.3.4 Generation of Equilibrium Structures

Once the wavefunctions and their coefficients are determined, the electron density at every position in space can be found in the usual way from the sum of squares of the wavefunctions:

$$\rho(\vec{r}) = \sum_{\sigma} (-e) (\psi_\sigma^* \psi_\sigma)$$  \hspace{1cm} (6-22)

where $e$ is the electron charge. In addition to generating the electron density and total energy of the system as output, the method used also determines the forces on each of the atomic nuclei. This allows one to move each nucleus in the direction of the net force acting on it to a new position and iterate the process. The stable equilibrium configuration of the atoms is then found when all the forces on all the atoms are minimized, in this work to a value on the order of 0.01 eV/Å.

When the combination of atoms represents a known stable molecule, the equilibrium atomic positions where the forces are found to be minimized should be such that the calculated distances between neighboring atoms, angles formed by any three atoms, and the overall geometry correspond to the bond lengths, bond angles, and stereochemistry of the molecule. When trying to identify the transition state complex, however, simply finding the atomic positions where forces are minimized is not sufficient. Because the transition state complex coincides with the position of maximum energy along the reaction coordinate, only the maximum of the minimized total energy arrangements of atoms can be identified as the transition state. This can be found by calculating the equilibrium atomic positions for the two reactants held at various separations along the axis of ap-
proach, forming a collection of configuration "snapshots" of minimized energy. Of these snapshots, the one with the highest total energy value (but clearly before the reactants are close enough for the full product to form) corresponds to the transition state. Because these calculations include only the reacting molecules ignoring other solvent molecules, the reaction occurs in vacuum. To account for the presence of a dielectric medium as a solvent, the change in energy due to solvation must be added to the total energy determined in vacuum. As will be shown in Section 6.6.2, a simple way to do this is by using the equation developed from Kirkwood Theory for the solvation energy $\Delta G_{\text{solv},i}$ (Eqn. 6-11) and adding this result to the total energy predicted by the \textit{ab initio} calculations.

6.5.3.5 Determination of Dipole Moment and Molecular Size from the Results of \textit{Ab Initio} Calculations Regardless of whether the configuration of atoms corresponds to a stable molecule or an unstable intermediate species, the physical properties of the dipole moment and volume for that collection of atoms can be determined once the electron density is known. The calculation of the dipole moment is straightforward. One uses its definition as the first moment of charge:

$$\vec{\mu} = \sum_n (Ze_n) \vec{r}_n + \int \vec{r} \rho(\vec{r}) d\vec{r}$$

(6-23)

where $Z$ is the charge number. The first term in Eqn. 6-23 represents the contribution to the dipole moment of the atomic nuclei, while the second integral term represents that due to the electrons.

In general, the determination of the volume occupied by a molecule is a much more subtle task because the concept of a finite volume in which the electrons of a molecule are confined does not exist in quantum mechanics - electrons may be found at all distances from a molecule but with decreasing probability as one moves away. One must therefore draw some sort of cutoff taking into account what the molecular volume is supposed to represent in a given situation. The first
boundary we consider is the concept of a van der Waals surface, which we define such that under experimental conditions two molecules are unlikely to be found with their van der Waals surfaces overlapping. In the case where the van der Waals surface is spherical, its radius represents the van der Waals radius. Because no solvent molecule can penetrate the van der Waals surface, the dielectric constant must be unity at the surface. As one moves outward from the van der Waals surface, the value of the dielectric constant approaches its full value in the bulk solvent over a finite distance rather than by a step-change. The question, then, is whether to consider this van der Waals surface as the boundary of the molecule, or to take the boundary further out where the solvent dielectric constant truly reaches its full bulk value. As a compromise, we have decided to base the volume calculation on a surface which is halfway between these two boundaries. We define this surface as the “dielectric surface”. As depicted in Figure 6-3, this choice of the dielectric surface as the solute molecule boundary should minimize the error associated with modeling the dielectric environment immediately surrounding the solute molecule, at least within the constraints of Kirkwood theory.

In the present work, the van der Waals radius of H₂O and CH₂Cl₂ were determined using ab initio calculations. For H₂O, two molecules were simulated with their oxygen atoms facing each other and one moved closer and closer to the other, starting from an initial separation distance of 7.5 Å between the oxygen nuclei. The energy of the two molecule system was then calculated at each point. The results are shown as a plot of energy vs separation distance in Figure 6-4. Not surprisingly, the total energy shows no change at first and then begins to increase sharply as the two molecules get closer to each other. This data was used to generate Boltzmann probabilities to determine the likelihood of the two molecules existing at any given separation distance. The distance at which the probability was < 0.001 at 600°C (the maximum temperature in our experiments) was designated as the point where the van der Waals surfaces overlapped, since it was unlikely that another H₂O molecule would approach any closer. This distance was determined to be 2.5 Å, giv-
Figure 6-3  Schematic View of the Variation of the Solvent Dielectric Constant with Distance Away from the Solute Molecule. The “model” curve corresponds to that used to approximate the behavior of the dielectric constant in the present study to be consistent with the Kirkwood model.
Figure 6-4  Energy of Two Water Molecules in Vacuum As a Function of Their Separation Distance. Energy values determined via \textit{ab initio} simulation with the two oxygen atoms facing each other. Separation distance corresponds to that between the two oxygen atoms.
ing a distance out from the oxygen nucleus to the van der Waals surface of 1.25 Å. To the extent that H₂O is spherical, this represents our calculated value for its van der Waals radius.

To determine the van der Waals surface for CH₂Cl₂, the same procedure was followed, except that the two molecules consisted of H₂O and CH₂Cl₂. The H₂O molecule was made to approach the CH₂Cl₂ from the backside opposite the Cl atom in the same manner as in the Sₘ₂ hydrolysis reaction mechanism. The data is shown in Figure 6-5. Using the same criteria as before, the distance of closest likely approach between the H₂O and CH₂Cl₂ molecules was again 2.5 Å. Subtracting the H₂O van der Waals radius leaves the location of the van der Waals surface of CH₂Cl₂ 1.25 Å outward from the carbon nucleus opposite one chlorine atom. This is not a uniform representative “radius” of CH₂Cl₂ because of the asymmetric nature of the molecule.

To determine the location of the dielectric surface for CH₂Cl₂, information on how ε changes with distance away from the van der Waals boundary was needed. We approximated this behavior through simulation. A simulation was conducted where a 6 Å box was filled with 10,000 randomly distributed and oriented H₂O molecules. After discarding all molecules where the oxygen atom was within 1.25 Å of either side of the box (representing the van der Waals surface that cannot be penetrated), an arbitrary but typical molecular electric field value of 1 eV/Å electronic charge was imposed and Boltzmann probabilities calculated. This section of the box was then divided up into 40 segments, and the total charge was determined in each section by summing up each nuclei or portion of electron cloud contained in each segment, weighting by their probability, and then multiplying by the appropriate atomic or electron charge. Since it is this distribution of charge which is responsible for the observed dielectric constant, the distribution of charge plotted as a function of distance from the box end should be proportional to and a good indicator of the variation of ε with distance. It was observed that the accumulated charge increased from 0 at the end of the box up to a steady value of about 1.5 Å away from the box end. The point at which the
Figure 6-5  Energy of a H₂O and CH₂Cl₂ Molecule Pair in Vacuum As a Function of Their Separation Distance. Energy values determined via *ab initio* simulation with the H₂O molecule approaching the CH₂Cl₂ molecule in the same manner as the *S₉₂* hydrolysis mechanism. Separation distance corresponds to that between the carbon and oxygen atoms.
total charge reached half its steady value was at approximately 0.9 Å away from the box end. Moving this distance outward from the van der Waals surface of CH₂Cl₂ gives a distance to the dielectric surface of 2.15 Å for CH₂Cl₂ outward from the carbon nucleus. In the ab initio calculations for CH₂Cl₂, the electron density at this distance away from the central C atom is 0.003 electrons/Å³.

To locate the entire dielectric surface through this procedure of the previous three paragraphs would be prohibitive. As an approximation to the dielectric surface, we take another surface which also follows the contours of the molecule and contains the point already identified on the dielectric surface; namely, we take the surface of constant charge density = 0.003 electrons/Å³. Thus our final definition of the volume occupied by molecules in our calculations is wherever in space the electron density was above this cutoff value. From the charge density contour, a value for the radius to use in Eqn. 6-18 can subsequently be calculated as that for a sphere containing the same volume. This equivalent spherical radius is our means of achieving consistency with both the actual volume (contained within the dielectric surface) and the requirements of the Kirkwood model for having a spherical molecular shape.

6.6 Results And Implications Of Ab Initio Calculations

6.6.1 Reactants To explore and verify its accuracy, particularly the choice of planewave cutoff and pseudopotentials construction, the ab initio technique described above was first used to see how well it could predict the structure and dipole moment of the H₂O and CH₂Cl₂ molecules, which could be compared to known, well established experimental values. The structure of these molecules, as summarized in Table 6-2, is well reproduced. For both, all bond lengths were within ± 0.03 Å of their tabulated values. The correct bent and tetrahedral geometries were observed for the stable equilibrium structure calculated for H₂O and CH₂Cl₂ respectively. The calculated H-C-H and Cl-C-Cl bond angles for CH₂Cl₂ differed from their accepted values by only 0.5°
<table>
<thead>
<tr>
<th>Species</th>
<th>Dipole Moment (Debye)</th>
<th>Radius (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Experimental</td>
</tr>
<tr>
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<td>1.85</td>
</tr>
<tr>
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<td>1.79</td>
<td>1.6</td>
</tr>
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</table>

Table 6-2  Calculated and Experimental Values of Bond Lengths and Angles, Dipole Moments, and Radii for H\(_2\)O and CH\(_2\)Cl\(_2\). Experimental values of bond lengths and angles are taken from Lide (1996). Experimental values of dipole moments are taken from McClellan (1963). Calculated values of all above physical properties were generated via \textit{ab initio} simulation.
and 0.2° respectively, while the H-O-H angle in the water molecule was within 1.6° of the established value of 104.5°.

Figure 6-6 shows a view of the *ab initio* determined valence electron density for CH$_2$Cl$_2$ in the plane defined by the carbon and two chlorine atoms, and also in the orthogonal plane defined by the carbon and two hydrogen atoms. A three-dimensional representation of the CH$_2$Cl$_2$ molecule in terms of its full electron density is shown in Figure 6-7. The inner spheres have been artificially inserted to represent the location of the atomic nuclei and have been roughly scaled to size. The boundaries of the molecule as shown include 99.5% of the total charge density of the molecule. In this figure, the largest lobes in the plane of the paper represent the chlorine atoms while the smaller lobes going into and coming out of the paper represent the hydrogen atoms.

The predicted dipole moment values also compare favorably to the experimental values. The value of 1.89 Debye calculated for H$_2$O differs from the tabulated value by just 2%, while that of 1.79 Debye for CH$_2$Cl$_2$ differed slightly more from the tabulated value by about only 12% (Table 6-2).

The van der Waals radius for H$_2$O of 1.25 Å (determined from the *ab initio* charge density and the closest likely approach procedure described above) is in fairly good agreement with the value of 1.4 Å determined from the van der Waals equation of state $b$ parameter (Table 6-2). The equivalent spherical radius of the volume enclosed by the dielectric surface for water (as determined from the charge density contour chosen from the CH$_2$Cl$_2$ molecule) is 2.14 Å. As expected, this is larger, since it is based on a volume that extends beyond the van der Waals radius. The fact that this is very nearly the same as the sum of our 1.25 Å van der Waals radius for H$_2$O and the 0.9 Å width of our dielectric buffer zone supports our notion of using a fixed charge density contour, and suggests that the appropriate value is reasonably transferable between species.
Figure 6-6 Valence Electron Charge Density for the CH₂Cl₂ Molecule Determined by Ab Initio Calculations. (a) View of the plane containing the carbon and both hydrogen atoms. (b) View of the plane (orthogonal to the plane in (a)) containing the carbon and both chlorine atoms. Crosses indicate location of atomic nuclei.
Figure 6-7 Three-Dimensional Representation of the CH₂Cl₂ Molecule in Terms of Charge Density Determined from Ab Initio Calculations. Boundary of molecule shown includes 99.5% of charge density. Center spheres indicate locations of atomic nuclei.
For CH₂Cl₂, the predicted value of 2.98 Å for the equivalent spherical radius matches a rough value of about 3 Å given by Bondi (1968) for the van der Waals radius of the -CHCl₂ fragment. This closeness in values is not that surprising in this case of an asymmetric molecule because the calculated equivalent spherical radius is effectively an average of the small H side and much larger Cl side “radius”, whereas the Bondi fragment value mostly considers the Cl side. Overall, the results confirm that our pseudopotentials are well suited for the atomic species involved in the reactions, and that our energy cutoff in the plane wave expansion is sufficient to describe the electronic wave functions of the system. These values of dipole moments and equivalent spherical radii for H₂O and CH₂Cl₂ appear therefore to be reasonable choices to use in Eqn. 6-18.

6.6.2 Transition State With a validated ab initio approach based on the successful modeling of the stable reactants, it is possible to now look at the transition state. Because of the demanding nature of the ab initio calculations, a complete search for all possible transition states would be prohibitive. Fortunately, the chemistry of the present reaction is sufficiently well-understood that the pathway to search for the transition state is already known. The SN₂ reaction mechanism occurs via a very specific stereochemistry, with the nucleophile attacking from the “back side”; the side directly opposite from the leaving group. Thus to locate the transition state, we positioned a water molecule (as specified by the coordinates of its atomic nuclei) on the opposite side of the leaving Cl atom in a CH₂Cl₂ molecule, as depicted in Figure 6-8. The carbon atom was held fixed at the origin (i.e. the center of the supercell of the calculation) as the oxygen atom was forced to approach the carbon atom along the long axis of the supercell. At each C-O separation distance λ (describing the reaction coordinate for this reaction), the remaining degrees of freedom of the complex were relaxed without constraint, so that the other nuclei could change orientations at will according to the magnitude and direction of the forces calculated on them, until the equilibrium configuration and minimum energy were obtained. Rotational symmetry of the system ensures that this choice of reaction coordinate results in no loss of generality.
Figure 6-8 Stereochemistry of Species in CH₂Cl₂ Hydrolysis Determined from Ab Initio Calculations. (a) reactants (b) transition state complex.
To ensure that the molecules did not lock into false local minima during the approach, we explored the two most likely pathways for H₂O-CH₂Cl₂ approach. In the first, (a), the two hydrogen atoms from H₂O began in the same plane as the carbon and leaving chlorine atoms. This approach minimizes the energy by positioning the hydrogen atoms from the H₂O as far as possible from the two hydrogen atoms from CH₂Cl₂ (see Figure 6-8). In the second approach, (b), the H₂O molecule was rotated 90° so that its hydrogen atoms now began in the plane orthogonal to that containing the H₂O molecule in (a). In this alignment, one proton from the H₂O molecule approaches the non-leaving Cl and the other approaches the two hydrogen atoms of the CH₂Cl₂ molecule. For the case explored, at a typical value of λ where the transition state complex was found to occur, the results from orientation (b) showed a significantly greater energy than from orientation (a) by about 20 kJ/mol. We thus focused our effort on pathway (a).

In our cell of length 15 Å, the largest possible value of the generalized coordinate, λ = 7.5 Å, corresponds to two separate, stable H₂O and CH₂Cl₂ molecules. We confirmed that the resulting equilibrium structures at λ = 7.5 Å match our results for the two isolated species. As λ decreases, the two reactants begin to feel the effects of their proximity, as reflected in significant changes calculated in the energy and physical property values relative to the two separate molecules. The most critical region occurs over the range 2.0 Å < λ < 1.4 Å. As λ decreases through this range, the dipole moment μ increases by more than a factor of two (Figure 6-9), and the total energy (in vacuum) of the system relative to the isolated reactants at λ = 7.5 Å increases by almost a factor of three (Figure 6-10a). This dramatic variation in the dipole moment over such a small range of the reaction coordinate has profound consequences for the reaction as the nature of its dielectric environment changes, as will be discussed below. However, because there is not much change in the physical size of the transition state over such a limited range of reaction coordinate, variations in the volume of the activated complex are minimal (e.g. ± 0.1 Å in the equivalent spherical radius over the same range in λ).
Figure 6-9  Plot of Dipole Moment $\mu$ of the H$_2$O - CH$_2$Cl$_2$ Pair As a Function of the Carbon - Oxygen Separation Distance $\lambda$. All values of $\mu$ were determined from charge densities calculated via $ab$ initio simulation.
**Figure 6-10a** Energy of the H₂O - CH₂Cl₂ Pair in Vacuum As a Function of Their Carbon - Oxygen Atom Separation Distance $\lambda$. All energy values are determined directly from *ab initio* calculations and are referenced to the sum of energies for the individual H₂O and CH₂Cl₂ molecules.
Although the total energy of the $\text{H}_2\text{O}$ and $\text{CH}_2\text{Cl}_2$ pair clearly changes as the two molecules are brought closer together, it does not show the usual profile one would expect for two reacting species. Note in Figure 6-10a that the reaction profile, or energy relative to isolated reactants as a function of the reaction coordinate, increases continuously with decreasing $\lambda$. This implies that there is always repulsion and never attraction between the species, and thus no tendency for reaction to occur. Recall, however, that this data represents the behavior of these two species in vacuum.

To represent the behavior of $\text{H}_2\text{O}$ and $\text{CH}_2\text{Cl}_2$ in a solvent of dielectric constant $\varepsilon$, the energy of solvation must be added to the vacuum energy. Using the relation for $\Delta G_{\text{solv}}$ derived from Kirkwood theory (Eqn. 6-11) along with the appropriate $ab\ initio$ values of $\mu(\lambda)$ and $r(\lambda)$ already correlated, the total energy for the $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ pair can be calculated in a solvent of arbitrary dielectric constant $\varepsilon$ at any separation distance $\lambda$. The results (Figure 6-10b) show a dramatically different behavior for $\text{H}_2\text{O}$ and $\text{CH}_2\text{Cl}_2$ when surrounded by a water solvent. Figure 6-10b shows the reaction profiles for a variety of different dielectric strengths $\varepsilon$ of water (which itself is a function of temperature and pressure), including the base case of vacuum ($\varepsilon = 1$) from Figure 6-10a. For values of $\varepsilon > 3.6$, the reaction profiles exhibit the local maximum and minimum characteristic of two reacting species and the formation of a product. Recall that because the $ab\ initio$ technique used results in the minimum configuration energy at any position $\lambda$, the profiles in Figure 6-10b represent the lowest energy pathway for reaction at any given $\varepsilon$. Along any profile, therefore, we identify the value of $\lambda$ where the local maximum in energy occurs as the location of the transition state complex. The location of the local minimum likewise corresponds to the product. This maximum and minimum in the profiles become more pronounced as $\varepsilon$, or the polarity of the water solvent, increases. Thus, the influence of the solvent on the $\text{CH}_2\text{Cl}_2$-$\text{H}_2\text{O}$ transition state, and therefore on the nature of the reaction itself, is substantial.
Figure 6-10b  Energy of the H$_2$O - CH$_2$Cl$_2$ Pair in Solution As a Function of Their Carbon - Oxygen Atom Separation Distance $\lambda$ and Dielectric Constant $\varepsilon$. All energy values are determined from *ab initio* calculations and Eqn. 6-11, and are referenced to the sum of energies for the individual H$_2$O and CH$_2$Cl$_2$ molecules.
Close examination of the reaction profiles in Figure 6-10b reveals that the local maximum energy points do not all occur at the same value of $\lambda$, but happen at slightly smaller values of $\lambda$ as $\varepsilon$ decreases. Thus for every $\varepsilon$, there is a particular, slightly different, value of $\lambda$ at which the transition state occurs. As a result, the structure and physical properties of the transition state, already functions of $\lambda$, are ultimately functions of $\varepsilon$ (or $T$ at fixed pressure, from the correlation of Uematsu and Franck (1980)), and can be traced and correlated as such.

Over the full range of values for $\varepsilon$ appearing in our experiments, the structural transformations predicted along the reaction pathway are consistent with the known sterochemistry of the $S_N2$ reaction and with empirical rules for intermolecular transition states. As $\varepsilon$ varies from 80 (22°C) to 1.3 (600°C), our predicted location of the transition state occurs at values of $\lambda$ of 1.72 Å to 1.63 Å respectively (Figure 6-11). Values of the other predicted bond lengths for the transition state corresponding to both limiting values of $\lambda$ are displayed in Table 6-3, along with the accepted bond lengths for stable molecules. The calculations show that as the $H_2O$ molecule approaches the carbon atom of the $CH_2Cl_2$ molecule (i.e. as $\lambda$, or C-O bond length, decreases), the Cl atom opposite the approaching $H_2O$ begins to move further away from the carbon atom (i.e. C-Cl bond length increases), as expected for this reaction. Note that the C-O bond length calculated for the transition state is about 0.2 - 0.3 Å greater than the normal C-O bond length of 1.41 Å. Likewise, the C-Cl bond length (for the leaving Cl) calculated for the transition state is about 0.5 - 0.7 Å greater than the normal C-Cl bond length of 1.77 Å. These variations in bond length are consistent with the empirical rule cited by Benson (1976) that bonds in the process of being formed or broken in intermolecular transition states for molecule-molecule reactions should be 0.3 - 0.5 Å greater than their nominal length in stable molecules.

Although the lengths of bonds not participating in the reaction do not deviate far from their values in the isolated reactants (Table 6-3), the orientations of these bonds change significantly
Figure 6-11  Graph of the Carbon-Oxygen Separation Distance Corresponding to the CH₂Cl₂ Hydrolysis Transition State ($\lambda_{TS}$) As a Function of Temperature.
<table>
<thead>
<tr>
<th>Bond lengths (Angstroms)</th>
<th>Calculated&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Expected&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Value in Stable Molecule</th>
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<td>C-O</td>
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<td>1.02</td>
<td></td>
<td>0.96</td>
</tr>
</tbody>
</table>

Dipole Moment (Debye) 8.21 - 9.95

Equivalent Spherical Radius (Angstroms) 3.25 - 3.27

<sup>a</sup> For property values with a range listed, the first value corresponds to that at $\varepsilon = 80$ while the second value corresponds to that at $\varepsilon = 1.3$.

Table 6-3 Calculated and Expected Values of Bond Lengths, Dipole Moment, and Equivalent Spherical Radius for the CH₂Cl₂ Hydrolysis Transition State Complex. All calculated values were generated via ab initio simulation. Expected bond length values are determined via the criteria of Benson (1976) for a "tight" transition state species. Stable molecule bond lengths represent accepted single bond length values between the listed atoms found in unreacting molecules, and are taken from Lide (1996).
along the reaction pathway. Specifically, the two C-H bonds and the C-Cl bond with the non-leaving Cl fold over from their tetrahedral geometry to a planar arrangement perpendicular to the direction of the incoming water molecule, as shown in Figure 6-8. This planar configuration for the transition state corresponds precisely to the stereochemistry expected for an $S_N^2$ reaction.

Although the reaction coordinate $\lambda$ at which the transition state occurs varies by only 0.1 Å over the range of $\epsilon$ sampled in our experiments, the calculated value of the dipole moment for the transition state varies by almost 2 Debye units (or about 25%) (Table 6-3). This is because the value of $\mu$ for the CH$_2$Cl$_2$-H$_2$O pair is particularly sensitive to the value of $\lambda$ in the region where the transition state was found to occur (i.e., the steep portion of the curve in Figure 6-9). One should also note that the magnitude of $\mu$ for the transition state in this active region is predicted to be more than four times larger than that for either of the reactants, which again is consistent with expectations for an $S_N^2$-type reaction between neutral reactants resulting in a charged leaving group. Both trends observed for $\mu$ will be shown to have a profound effect on the hydrolysis rate. In contrast, the equivalent spherical radius varies by only 0.02 Å over the relevant range of $\lambda$ and therefore is not the determining factor in the behavior of the rate constant.

6.6.3 Implications of Solvent Effects on Reaction Rate Figure 6-10b exhibits three major trends in the behavior of the transition state as the dielectric nature of the solvent varies. The detailed information which the $ab$ $initio$ calculations provide allow one to understand these trends in terms of the behavior of the reacting molecular complex, summarized as follows:

(1) As already mentioned earlier, the transition state occurs at smaller values of $\lambda$ as $\epsilon$ decreases. The reason for this is that as $\epsilon$ decreases, the dielectric solvent environment becomes less effective in its role in stabilizing the reactants. To compensate, the transition state moves to smaller
values of $\lambda$ (i.e. smaller intermolecular distances), where the dipole moment of the complex is stronger.

(2) As $\varepsilon$ decreases, the energy associated with the transition state (local maximum) increases. Since the difference in energy between that of the transition state and that of the two reactants (which is what is plotted in Figure 6-10b) is defined as the activation energy for the reaction, the calculations predict an increasing activation energy with decreasing solvent polarity. Between 25°C and 600°C, the activation energy is predicted to increase by more than 50 kJ/mol. This increase in energy can be traced to the fact that despite the increase in $\mu$ described in item 1, the vacuum energy of the transition state complex (Figure 6-10a) rises so quickly as $\lambda$ decreases that the net effect is for energy to increase with decreasing $\varepsilon$. The resulting trend is consistent with a decreasing reaction rate, as observed experimentally.

(3) The local maximum and minimum in energy become less pronounced and move closer together (i.e. occur at the same value of $\lambda$) as $\varepsilon$ decreases and vacuum conditions are approached. By the point where $\varepsilon = 3.6$ (corresponding to 386°C), the maximum and minimum become indistinguishable and are replaced by a small plateau (inflection point). This decreasing energetic separation between the maximum and minimum points as $\varepsilon$ decreases indicates a reaction whose product is becoming less stable and more likely to recross the transition state barrier and return to the original reactants. This too would lead to a reduced rate of reaction.

Item (2) above provides the theoretical explanation for the experimental observation of slower hydrolysis kinetics of CH$_2$Cl$_2$ upon heating from sub- to supercritical conditions. Table 6-4 lists values of the activation energy for CH$_2$Cl$_2$ hydrolysis calculated from our ab initio results at various temperatures and corresponding values of $\varepsilon$. A value of 130 kJ/mol is predicted for the ambient activation energy $E_a$ at 25°C. The accuracy of the local density approximation used in our
Table 6-4  **Values of Activation Energy for CH$_2$Cl$_2$ Hydrolysis at Various Temperatures.** Values listed from the present study were determined from the difference in energy between the transition state species and two reactants at the given temperature. Energy values were determined via *ab initio* simulation in vacuum and adjusted for the effects of solvation via Eqn. 6-11. The activation energy value cited from Fells and Moelwyn-Hughes was taken from Fells and Moelwyn-Hughes (1958).

Calculations for an absolute reaction barrier is generally to be considered to be on the order of 10 to 20 kJ/mol because of the large difference in the variation in the molecular electron density in going from the isolated reactants to the transition state. Our determination of the reaction barrier in ambient water also depends upon several approximations inherent in the Kirkwood approach. More detailed calculations (Ismail-Beigi *et al.*, 1998) place the error associated with these approximations also at around 10 kJ/mole when comparing isolated reactants and the transition state. Given these uncertainties, our *ab initio* result for $E_a$ compares quite well with the value of 107 kJ/mol found experimentally by Fells and Moelwyn-Hughes (1958) at 115°C.

Finally, item (3) raises the issue as to the nature of the reaction when $e < 3.6$ (*i.e.* above 386°C at 246 bar). Within simple transition state theory, the disappearance of the maxima and minima in the reaction profile for $T \geq 386$°C would imply that without sufficient dielectric screening, there is no stable product and that the reaction comes to a halt. However, because we have not studied the subsequent phase of the hydrolysis reaction (where the $S_N^2$ product CH$_2$ClOH rearranges to form the final products HCHO and another HCl), it is difficult to give a definitive inter-
pretation of the significance of the inflection point. It would also therefore be precipitous to construct a model where the reaction rate is taken to be strictly zero above 386°C, which would be equivalent to setting the reaction barrier to infinity above this temperature. Instead, we have taken a more conservative approach. To allow for the possibility that the reaction does not shut off entirely, we have tracked the inflection point (which persists for $\epsilon < 3.6$) as indicating some feature on the reaction surface relevant to the subsequent progress of the reaction. Using the energy corresponding to the location of the inflection point as an energy barrier for $\epsilon < 3.6$ gives a continuous extrapolation to ever decreasing reaction rates. Passing from the last true maximum to the first inflection point at 386°C occurs smoothly and with no abrupt changes in any calculated physical properties of the transition state, and the inflection point continues to occur at higher energies and small values of $\lambda$ with decreasing $\epsilon$. The results will show (see below) that the reaction rate has slowed enough by 386°C that even with this extrapolation, not much conversion occurs above this temperature.

6.7 Generation of the Kirkwood Rate Constant Correction Factor With the critical parameters of the CH$_2$Cl$_2$-H$_2$O transition state and the isolated reactants (*i.e.* vacuum energy, dipole moment, and equivalent spherical radius) known as functions of the solvent dielectric constant $\epsilon$ (and therefore as functions of temperature $T$), values for the correction term to the activation energy identified in Eqn. 6-18 can now be determined. Note that the more complex form of the correction term from Eqn. 6-18 must be used rather than Eqn. 6-17 in this case for CH$_2$Cl$_2$ hydrolysis because the position and structure of the transition state were found to vary with $\epsilon$. To determine correction term values, we first rewrite Eqn. 6-18 as:

$$\ln k = \ln A - \frac{E_a}{RT} + \Phi,$$  

(6-24)
\[ \Phi = -\frac{1}{RT} \left( \Delta G_{\text{voc}} - \Delta G_{\text{voc}}^0 \right) + \frac{N_A}{4\pi\varepsilon_0} \left( \frac{(\varepsilon_a - 1)}{(2\varepsilon_a + 1)} \left[ \frac{\mu^2_{\text{t},\varepsilon_a}}{r_{\text{t},\varepsilon_a}^3} - \frac{\mu^2_{\text{t}}}{r_{\text{t}}^3} - \frac{\mu^2_{\text{v}}}{r_{\text{v}}^3} \right] + \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} \left[ \frac{\mu^2_{\text{t},\varepsilon}}{r_{\text{t},\varepsilon}^3} - \frac{\mu^2_{\text{t}}}{r_{\text{t}}^3} - \frac{\mu^2_{\text{v}}}{r_{\text{v}}^3} \right] \right) \]

(6-25)

We formally define \( \Phi \) in Eqn. 6-25 as the Kirkwood correction factor to the rate constant. Here, the reactants A and B represent \( \text{CH}_2\text{Cl}_2 \) and \( \text{H}_2\text{O} \).

Breaking up the expression for the reaction rate constant in this way into an Arrhenius form and a correction term increases the reliability of our prediction by collecting into a single term the major sources of error involved in the local density approximation employed in our \textit{ab initio} calculations and the simple dipole - sphere model from Kirkwood theory. The local density approximation reproduces the energy differences among configurations with similar electron densities (such as two transition states at slightly different \( \lambda \)) much better than between configurations with far different densities (such as the transition state and the isolated reactants). Preliminary results indicate similar trends for the approximations in Kirkwood theory (Ismail-Beigi \textit{et al.}, 1998). Thus, while the overall reaction barriers (\( E_a - RT\Phi \)) are reliable to only 20 kJ/mol, the differences among barriers for different \( \lambda \) (contained in the \( \Phi \) term) are much more reliable. Most of the uncertainty is contained in \( E_a \), which may be determined from experimental data. Note also that \( \Phi \) contains no fitted or adjustable parameters.

A plot of the magnitude of the Kirkwood correction factor \( \Phi \) as a function of the dielectric constant and temperature is shown in Figure 6-12. Each value of \( \Phi \) was calculated by first finding \( \lambda \) for the transition state for a given \( \varepsilon \) (from Figure 6-10b as detailed earlier), and then using this value of \( \lambda \) to calculate all the remaining transition state physical properties needed from the \textit{ab initio} determined correlations (Figures 6-9, 6-10a; Table 6-3). Required reactant physical properties were taken from Table 6-2. Selected calculated values of \( \Phi \) at different \( \varepsilon \) and \( T \) are also given in Table 6-5.
Figure 6-12  Kirkwood Correction Factor $\Phi$ and Water Dielectric Constant $\varepsilon$ As a Function of Temperature. The curve for $\Phi$ is determined from \textit{ab initio} data in Figures 6-9 and 6-10b and Table 6-2. Polynomial correlations for this curve are given in Table 6-6. Values of $\varepsilon$ determined from the correlation of Uematsu and Franck (1980) at 246 bar.
<table>
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<th>550</th>
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<td>1.4</td>
</tr>
<tr>
<td>(\Phi)</td>
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<td>-1.00</td>
<td>-7.48</td>
</tr>
<tr>
<td>(k_{FMH} / k') (rate decrease factor)</td>
<td>1.04</td>
<td>2.72</td>
<td>1765</td>
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</tbody>
</table>

| Table 6-5 | Values of the Kirkwood Correction Factor (\(\Phi\)), and the Hydrolysis Rate Decrease Relative to that Predicted by Fells and Moelwyn-Hughes (1958), at Various Values of \(T\) and \(\varepsilon\). \(\varepsilon\) is calculated from \(T\) at 246 bar from the correlation for water by Uematsu and Franck (1980). \(\Phi\) is calculated according to Eqn. 6-25, using data from Figures 6-9 and 6-10b and Table 6-2. \(k'\) and \(k_{FMH}\) are calculated as defined in Eqns. 6-26 and 6-3 respectively. |

These calculated results in Figure 6-12 and Table 6-5 indicate that \(\Phi \leq 0\) over the entire temperature range of interest (25-600°C), consistent with the expected tendency to retard the reaction as the water solvent becomes less polar. In the subcritical region where water is still quite polar, \(\Phi\) is very small or negligible, and only decreases the rate constant by less than one natural log unit. The magnitude of \(\Phi\) increases dramatically, however, in the range of temperatures just beyond the critical point, where \(\varepsilon\) drops by an order of magnitude. By 550°C, well into the supercritical regime, we predict the Kirkwood correction factor to decrease the rate constant by 7.5 natural log units (three orders of magnitude) relative to that predicted by simple Arrhenius behavior. Because the density of the solvent drops by only a single order of magnitude over the same range of conditions, our results demonstrate that for this reaction, the rate is much more strongly correlated to the dielectric constant than to the density.

For ease of use in calculations, the results for \(\Phi\) (\(T\)) in Figure 6-12 have been fit to four polynomial functions which cover the temperature ranges 25-374°C, 374-386°C, 386-525°C, and
\[ \Phi = \alpha_0 + \alpha_1 T + \alpha_2 T^2 + \alpha_3 T^3 + \alpha_4 T^4 + \alpha_5 T^5 + \alpha_6 T^6 + \alpha_7 T^7 + \alpha_8 T^8 + \alpha_9 T^9 \]

<table>
<thead>
<tr>
<th>Temperature range (^{\circ}C)</th>
<th>(25 \leq T &lt; 374)</th>
<th>(374 \leq T \leq 386)</th>
<th>(386 &lt; T \leq 525)</th>
<th>(525 &lt; T \leq 600)</th>
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</thead>
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<tr>
<td>(\alpha_0)</td>
<td>(1.3658 \times 10^{-1})</td>
<td>(7.2641851 \times 10^{4})</td>
<td>(1.2294119 \times 10^{5})</td>
<td>(-2.6826 \times 10^{1})</td>
</tr>
<tr>
<td>(\alpha_1)</td>
<td>(-1.1319 \times 10^{-2})</td>
<td>(-5.8225257 \times 10^{2})</td>
<td>(-1.4212424 \times 10^{3})</td>
<td>(1.1691 \times 10^{1})</td>
</tr>
<tr>
<td>(\alpha_2)</td>
<td>(3.8850 \times 10^{-4})</td>
<td>(1.5556709 \times 10^{0})</td>
<td>(6.3373575 \times 10^{0})</td>
<td>(-2.3416 \times 10^{4})</td>
</tr>
<tr>
<td>(\alpha_3)</td>
<td>(-7.9558 \times 10^{-6})</td>
<td>(-1.3855168 \times 10^{3})</td>
<td>(-1.2385424 \times 10^{2})</td>
<td>(1.5557 \times 10^{-7})</td>
</tr>
<tr>
<td>(\alpha_4)</td>
<td>(9.4188 \times 10^{-8})</td>
<td>(4.1293324 \times 10^{6})</td>
<td>(2.3961584 \times 10^{8})</td>
<td>(-3.8255570 \times 10^{11})</td>
</tr>
<tr>
<td>(\alpha_5)</td>
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<td>(1.8223581 \times 10^{-14})</td>
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<td>(\alpha_6)</td>
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<td>(\alpha_7)</td>
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<td>(-6.8988 \times 10^{-21})</td>
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</tr>
</tbody>
</table>

Table 6-6 Correlations for Kirkwood Correction Factor \(\Phi\) Determined from Data in Figure 6-12. Appropriate values of coefficients to use are chosen based on the temperature range of interest.

525-600\(^{\circ}C\) at 246 bar (see Table 6-6). It is important to note that each correlation implicitly contains all the relevant information of solvent dielectric strength and transition state location and properties found in the original correlations used to generate \(\Phi\) from Eqn. 6-25.

To illustrate the effect that the Kirkwood correction factor \(\Phi\) can have on \(\text{CH}_2\text{Cl}_2\) hydrolysis kinetics, we have used it to modify the empirical correlation for the rate constant, \(k_{FMH}\), proposed by Fells and Moelwyn-Hughes (1958) (see Eqn. 6-3):

\[ \ln k' = \ln k_{FMH} + \Phi \]  
(6-26)
Figure 6-13 compares the value of \( \ln k_{FMH} \) to its corrected value \( \ln k' \) over the much wider temperature range of 25 to 600°C (compared to the 80-150°C range originally studied by Fells and Moelwyn-Hughes). Note that in the limited temperature range of Fells and Moelwyn-Hughes’ experimental data, both \( k' \) and \( k_{FMH} \) are essentially the same, verifying that solvent effects are negligible in this regime. As temperature increases, the two rate constant values begin to diverge from each other due to the increasing magnitude of \( \Phi \). In the supercritical region at \( T > 400°C \), \( k' \) is substantially lowered to a value comparable to that seen around 165°C, where the rate is relatively slow. Solvent effects decrease the uncorrected hydrolysis rate by more than a factor of 1700 at 550°C (Table 6-5). Thus inclusion of the Kirkwood correction factor in the form of the rate constant yields rate behavior consistent with our experimental observation of a slowing reaction with increasing temperature.

6.8 Determination Of Hydrolysis Global Kinetic Rate Expressions

As mentioned earlier, the neutral/acidic hydrolysis reaction of \( \text{CH}_2\text{Cl}_2 \) occurs in a two stage process. Because the substitution reaction is the slow step in the sequence, the overall rate of reaction incorporating the Kirkwood correction factor \( \Phi \) is:

\[
R_{\text{hyd}} = \frac{d[\text{CH}_2\text{Cl}_2]}{dt} = -\left(A e^{-(E_a/RT)+\Phi}\right)[\text{CH}_2\text{Cl}_2]^a[H_2O]^b
\]

(6-27)

where \( A \) and \( E_a \) represent the pre-exponential factor and activation energy under ambient conditions, and \( a \) and \( b \) are the reaction orders with respect to \( \text{CH}_2\text{Cl}_2 \) and \( H_2O \), respectively. The explicit dependence on \( H_2O \) concentration reflects the order of magnitude variation of solvent density (over the subcritical section of the preheater) in our experiments. As a result, despite being always in excess relative to \( \text{CH}_2\text{Cl}_2 \), the \( H_2O \) concentration was not constant, and therefore cannot be lumped \textit{a priori} into the rate constant.
Figure 6-13  Plot of the Natural Logarithm of the Fells and Moelwyn-Hughes Rate Constant with and without the Kirkwood Correction Factor ($k'$ and $k'_{FMH}$ Respectively) As a Function of Temperature. Values of $k'$ and $k'_{FMH}$ are calculated as defined in Eqns. 6-26 and 6-3. The temperature range of the Fells and Moelwyn-Hughes (1958) experiments on neutral CH$_2$Cl$_2$ hydrolysis (80-150°C) is indicated.
Optimal values of the kinetic parameters $A$, $E_a$, $a$ and $b$ were determined by nonlinear regression of our experimental data. This allows us to combine the results of the *ab initio* calculations describing the strong variations in the energy and dipole moment of the transition state which are embodied in $\Phi$, with the experimental results, to yield a quantitatively reliable rate expression. The regression procedure was the same iterative two-step process as used for the regression of acetic acid kinetic parameters (and described in Section 3.5), except for the following differences. Because temperature had to be calculated at every point in the preheater tubing and was not known ahead of time, it could not be used as the dependent parameter for the regression program in this case. Also, since temperature varied continually in the preheater, the differential form of the rate expression rather than an integrated form (as in Eqn. 3-12) had to be used. As a result, CH$_2$Cl$_2$ conversion was chosen as the dependent parameter. The unknown parameters were therefore optimized to match as closely as possible the experimentally determined CH$_2$Cl$_2$ conversions (at the end of the main reactor).

Experimental data from all 23 hydrolysis runs were used as input to the regression program. For a given set of kinetic parameters at any point in the regression process, the model used to compute values of conversion was the same set of coupled differential heat and mass balance equations for temperature and CH$_2$Cl$_2$ concentration described earlier (Eqns. 5-1 and 6-4). In this case, however, Eqn. 6-27 was used for the hydrolysis rate expression $R_{hyd}$ instead of Eqn. 6-5 or 6-26. These equations were solved using the same Runge-Kutta routine described in Section 5.2. The same nonlinear optimization routine as was used in the acetic acid regressions (*i.e.* the multivariable Powell SSQMIN algorithm (Kuester and Mize, 1973)) was used here for the adjustment of the kinetic parameters based on the sum of squares differences between model predicted and experimental values of conversion.
6.8.1 Three Parameter Data Regression  The full four-parameter regression to the hydrolysis experimental data showed the best-fit values of \( b, A \) and \( E_a \) to be highly correlated, making it difficult to extract meaningful values. Similar behavior was noticed by Holgate et al. (1992) in performing a four-parameter regression for the water gas shift reaction between CO and H\(_2\)O. As the expected reaction order for H\(_2\)O (given the nature of the S\(_\text{N}2\) reaction) is first order, \( b \) was set to unity in all further regression attempts.

With \( b = 1 \), the three-parameter regression for \( A, E_a, \) and \( a \) yielded the following global rate expression for CH\(_2\)Cl\(_2\) hydrolysis:

\[
R_{\text{hyd}} = \frac{d[\text{CH}_2\text{Cl}_2]}{dt} = -\left(10^{16.5\pm0.36} e^{-(210\pm40/RT)+\Phi}\right)[\text{CH}_2\text{Cl}_2]^{1.52\pm0.67}[\text{H}_2\text{O}]
\]  

(6-28)

where \( R_{\text{hyd}} \) is in units of mol/(L s), activation energy is measured in kJ/mol, and the concentrations are in mol/L. All parameter uncertainties are quoted at the 95% confidence level, and \( \Phi \) is as given by Eqn.: 6-25, with values determined through the polynomial correlations given in Table 6-6. A statistical analysis yielded a significance level of 100%, an \( r \)-squared value of 0.72 (adjusted for degrees of freedom), and an F-statistic value of 31 for Eqn. 6-28. The regressed value of 210\( \pm \)40 kJ/mol for the ambient activation energy (\( E_a \)) includes all experimental uncertainties, modeling uncertainties, and variability due to the number of parameters in the regression. Therefore this value is not unreasonable when compared to the parameter-free Kirkwood-\textit{ab initio} determined value of 130 kJ/mol (Table 6-4).

Figure 6-14 compares total CH\(_2\)Cl\(_2\) conversion calculated using the rate expression of Eqn. 6-28 with both the experimental hydrolysis data and the results using the simple first-order model of Fells and Moelwyn-Hughes (1958) (Eqn. 6-3). All conversion values in Figure 6-14 are plotted as a function of experimental residence time and sandbath or final reactor temperature. Figure 6-14
Figure 6-14  Experimental and Predicted CH\textsubscript{2}Cl\textsubscript{2} Hydrolysis Conversion As a Function of Sandbath Temperature and Residence Time at 246 Bar (3 Parameter Model). FMH predicted conversion is from the first order model of Fells and Moelwyn-Hughes (1958) with the rate constant as given in Eqn. 6-3. MIT + Kirkwood predicted conversion uses the three parameter global rate expression of Eqn. 6-28 developed in the present work. Error bars for experimental data represent 95% confidence intervals.
shows predicted CH$_2$Cl$_2$ conversion both at the end of the preheater and after the main reactor for our model of Eqn. 6-28 and that of Fells and Moelwyn-Hughes.

Figure 6-14 demonstrates that accounting for solvent dielectric and density effects improves significantly the prediction of conversion both qualitatively and quantitatively over simply extrapolating the experimental Arrhenius correlation of Fells and Moelwyn-Hughes. Of equal importance, use of the Kirkwood correction factor Φ in Eqn. 6-28 also leads to a much reduced further conversion of CH$_2$Cl$_2$ in the supercritical main reactor itself, in agreement with the unusual trend observed experimentally. For sandbath temperatures below 525°C (total residence times < 16.5 s), predicted conversions at the end of the preheater and main reactor were within the experimental error of the data, and were essentially identical at 450°C (14 s), exactly as observed. The ability of Eqn. 6-28 to capture this behavior, not predicted by extrapolation of the single Arrhenius rate expression of the Fells and Moelwyn-Hughes model, underscores the importance of the Kirkwood correction factor on the kinetics of polar reactions occurring in solvent media undergoing appreciable changes in dielectric constant.

At higher temperatures and longer residence times, the fit of predicted conversion at the end of the reactor from Eqn. 6-28 still matches the data well, but is increasingly higher than that predicted at the end of the preheater. Although the maximum difference between predicted preheater and main reactor conversions was only 16%, it is higher than the 3% difference observed experimentally at a sandbath temperature of 575°C (20 s) (Table 4-3). One hypothesis to explain this discrepancy in incremental conversion in the main reactor is that perhaps the disappearance of the local maximum and minimum points in the reaction profile at higher temperatures does indeed signal a dramatic decrease in the reaction rate.
6.8.2 Two Parameter (First-Order) Data Regression The three-parameter regression of Eqn. 6-28 contains the theoretical value of $a = 1$ within experimental uncertainty. Accordingly, the regression was rerun with $a$ and $b$ fixed at unity. This two parameter regression yielded the following second-order overall rate expression:

$$R_{\text{hid}} = \frac{d\text{[CH}_2\text{Cl}_2\text{]}}{dt} = -\left(10^{12.9\pm1.0} e^{-(180\pm14/RT)\Phi}\right)\text{[CH}_2\text{Cl}_2\text{][H}_2\text{O]} \quad (6-29)$$

where units and confidence levels for uncertainties are the same as for Eqn. 6-28. Statistical analysis yielded a significance level of 100%, an r-squared value of 0.73 (adjusted for degrees of freedom), and an F-statistic value of 59 for Eqn. 6-29. In Figure 6-15, calculated values of total CH$_2$Cl$_2$ conversion using Eqn. 6-29 are compared to the experimental data and Fells and Moelwyn-Hughes model in a similar plot as that of Figure 6-14. The results are similar to those seen in Figure 6-14, with the fit of predicted conversion at the end of the reactor to the experimental data being equally as good (similar $\chi^2$), as expected. The only exception is that the increasing difference between preheater and reactor predicted conversions at higher sandbath temperatures/longer residence times is greater than that generated from use of Eqn. 6-28 in Figure 6-14. The ambient activation energy of 180 kJ/mol is, however, in somewhat better agreement with the Kirkwood-\textit{ab initio} value of 130 kJ/mol.

6.9 Discussion And Critique of CH$_2$Cl$_2$ Hydrolysis Results Using the Kirkwood Model Given the simplistic nature of the Kirkwood model and its many assumptions, the parameter-free correction factor $\Phi$ captures the essential form and magnitude of the diminishing effects of the solvent on the CH$_2$Cl$_2$ hydrolysis rate remarkably well. Our results establish that the dielectric coupling between the reacting species and the solvent is the major factor leading to the non-Arrhenius behavior of the reaction rate under supercritical conditions.
Figure 6-15  Experimental and Predicted CH₂Cl₂ Hydrolysis Conversion As a Function of Sandbath Temperature and Residence Time at 246 Bar (2 Parameter Model). FMH predicted conversion is from the first order model of Fells and Moelwyn-Hughes (1958) with the rate constant as given in Eqn. 6-3. MIT + Kirkwood predicted conversion uses the two parameter global rate expression of Eqn. 6-29 developed in the present work for $a$ and $b$ forced to 1. Error bars for experimental data represent 95% confidence intervals.
The modest discrepancies between our prediction of preheater and main reactor conversions at higher sandbath temperatures, however, suggest that our physical model is still incomplete. There are three possible explanations for this behavior: (1) more than one reaction mechanism occurred over the extended temperature range covered in the experiments, confounding our attempts to model the conversion as proceeding by a single reaction; (2) our conservative continuation of the reaction rate beyond the disappearance of the local energy maximum along the reaction profile for $\varepsilon < 3.6$ ($T > 386^\circ$C) is unrealistic, as the reaction rate might become negligible beyond this temperature; (3) our picture is essentially correct and the discrepancies which we observe are purely due to quantitative errors associated with the simplifying assumptions in the Kirkwood model itself.

A more detailed view of the first possibility is that the reaction may be proceeding via different pathways at different temperatures (i.e. subcritical polar vs. supercritical free radical pathways), or that one or more additional reactions involving CH$_2$Cl$_2$ become important at higher temperatures. The detection of CHCl$_3$, C$_2$HCl$_3$, and C$_2$H$_2$Cl$_2$ isomers in the vapor effluent (see Section 4.4) does prove that some additional reaction of CH$_2$Cl$_2$ must have occurred by free radical mechanism under supercritical conditions. However, because the concentrations of these chlorinated hydrocarbons were extremely small (in total accounting for < 1% of either carbon or chlorine mass balances), their formation reactions could not have been a major sink for CH$_2$Cl$_2$. As will further be shown in Chapter 7, there is no direct evidence either in the literature or the experimental product distribution from our studies that suggests that any other significant secondary reactions involving CH$_2$Cl$_2$ could have occurred.

With the second possibility, the precise nature of the change in the reaction signaled by the disappearance of the local energy maximum and minimum at $T = 386^\circ$C ($\varepsilon = 3.6$) is uncertain. Without further exploration of the reaction phase space, we chose the more conservative route of
allowing for a finite reaction rate above this temperature. Even with this approach of extrapolating the decreasing reaction rate near \( T = 386^\circ C \), most of the \( \text{CH}_2\text{Cl}_2 \) hydrolysis is still predicted to occur in the subcritical region. It does appear, however, that the magnitude of the correction factor at higher temperatures (i.e. \( > 550^\circ C \)) is not large enough to counteract the increasing magnitude of the Arrhenius component of the rate expression. This may signify that the disappearance of the maxima and minima should be taken to mean that the reaction stops completely above \( 386^\circ C \). One interesting direction for future work is therefore to explore the hydrolysis reaction phase space more fully.

With regards to the third possibility, the shortcomings of the Kirkwood model are readily apparent. First are the structural idealizations: (a) molecules are not spherical, so that one cannot properly characterize the size of a molecule like \( \text{CH}_2\text{Cl}_2 \) or its hydrolysis transition state complex by a single radius; and (b) the charge distribution of a molecular complex is distributed in space and not concentrated at a point so that in the vicinity of such a complex, where the coupling to the solvent is the strongest, the charge distribution cannot be captured by the first few terms in a multipolar expansion. Second, is the manner in which the dielectric response of the solvent is treated on the molecular level: (c) by using a local dielectric function \( \epsilon \) outside of the molecule, Kirkwood theory ignores molecular correlations which are needed to describe such effects as hydrogen bonding; and (d) the theory also assumes an unrealistically sharp transition of the solvent dielectric as one approaches the interior of the molecule. Minor flaws include an uncertainty as to how to define the interior and exterior regions of the molecule and the value of the dielectric constant which one should use in the interior solute region. Our \textit{ab initio} work described above, however, mitigates the uncertainties as to the boundary of the molecule, and it is clear that in self-consistent \textit{ab initio} calculations, the dielectric constant inside of the molecule should be taken to be that of vacuum.
Both continuum and molecular-level studies are underway to evaluate the importance of the above simplifications and to find ways to correct for these deficiencies. Preliminary results show that the impact of using a more realistic shape for the molecular cavity and the complete \textit{ab initio} charge distribution as opposed to a spherical cavity containing only the dipole moment of the distribution is relatively mild, changing the correction factor by less than 10\% (Ismail-Beigi et al., 1998). Thus, while future improved results may refine some of the quantitative details of our regression, they will preserve the overall picture. Finally, molecular dynamics (MD) simulations of large numbers of water molecules interacting with the potential field of the solute as determined by \textit{ab initio} are underway to evaluate the impact of more realistic microscopic treatment of the dielectric response of the solvent.

6.10 CH$_2$Cl$_2$ Oxidation Kinetics Although CH$_2$Cl$_2$ is susceptible to direct oxidation, the experimental results indicate that the reaction appears to become important only at higher temperatures. As already noted in Section 4.5.1, exposure of CH$_2$Cl$_2$ feed solution to O$_2$ in the supercritical main reactor after preheating resulted in little or no further conversion of CH$_2$Cl$_2$ beyond that obtained from otherwise similar hydrolysis runs for sandbath temperatures below 525$^\circ$C. Below 500$^\circ$C, conversions were virtually the same. Evidence of a distinct oxidation reaction above the always present background hydrolysis can be seen above 525$^\circ$C, however, as it is here that oxidation conversions started to become statistically significant. By 563$^\circ$C, complete conversion was observed from oxidation experiments, compared to about 80\% conversion from the corresponding hydrolysis experiments. Oxidation and hydrolysis conversions of CH$_2$Cl$_2$ were still closer at these higher sandbath temperatures than that observed for many other compounds previously studied. However, unlike at lower temperatures, this closeness in conversion at higher temperatures is more likely due to the substantial hydrolysis that CH$_2$Cl$_2$ experienced with the longer residence times in the preheater tubing rather than a slow oxidation reaction. This transition from essentially zero to
complete conversion under oxidation conditions over such a relatively small temperature range suggests that the oxidation reaction has a high activation energy.

A slow oxidation reaction, or increased resistance to oxidation by CH₂Cl₂ at lower temperatures, would not be that surprising given the fact that chlorinated hydrocarbons are known to be combustion inhibitors (Hung and Pfefferle, 1989). Andelman (1978) has also reported that chlorinated compounds had the greatest half lives for reaction with alkoxy radicals compared to several other organic compounds including alkanes, olefins, ethers, and ketones. As will be discussed in Chapter 7, a similar persistance in gaseous chlorinated hydrocarbon products was seen under oxidation conditions up to 550°C, which suggests high activation energies for oxidation of these compounds as well. Nevertheless, the fact that complete conversion of CH₂Cl₂ was observed by 563°C and that only CO₂ and HCl were detected in the effluent by 600°C and 23 s total residence time (6 s in the presence of O₂) is important. From a practical perspective, it suggests that dilute concentrations of CH₂Cl₂ (and several other C₁ and C₂ chlorinated hydrocarbons) can be efficiently destroyed by oxidation in supercritical water at still reasonable temperatures and residence times (600°C, < 10 s).

6.10.1 Determination Of Oxidation Global Kinetic Rate Expressions Based on the net reaction for complete oxidation of CH₂Cl₂ to CO₂ and HCl given in Eqn. 4-1, the following global rate expression forms can be written for the two reactants:

\[
\frac{d[CH₂Cl₂]}{dt} = R_{ox} + R_{hyd}
\]  \hspace{1cm} (6-30)

where

\[
R_{ox} = -\left(A_{ox}e^{-\left(E_{a,ox}/RT\right)}\right)[CH₂Cl₂]^a[O₂]^b,
\]  \hspace{1cm} (6-31)

and

\[
\frac{d[O₂]}{dt} = R_{ox}
\]  \hspace{1cm} (6-32)
where \( R_{\text{hvd}} \) is the component due to \( \text{CH}_2\text{Cl}_2 \) hydrolysis already determined (Eqn. 6-28 or 6-29). The oxidation kinetic parameters in the above equations were determined by nonlinear regression of the oxidation data by exactly the same procedure as for \( \text{CH}_2\text{Cl}_2 \) hydrolysis (Section 6.8). In this case, however, Eqn. 6-28 was used for \( R_{\text{hvd}} \) in order to calculate \( \text{CH}_2\text{Cl}_2 \) preheater concentrations in the model. Eqns. 6-30, 6-31, and 6-32 were used to describe concentrations of \( \text{CH}_2\text{Cl}_2 \) and \( \text{O}_2 \) in the isothermal main reactor, with Eqn. 6-28 again used for \( R_{\text{hvd}} \) in Eqn. 6-30. All experimental oxidation data points except those four corresponding to complete conversion (99.9%) were used as input in the regression program.

Before proceeding, it is important to note two points regarding the reliability of the regression results. First, as with other previous SCWO studies on model compounds, \( \text{CH}_2\text{Cl}_2 \) oxidation in the supercritical main reactor most likely consisted of a series of free radical elementary reactions. This is unlike the simple, two step, polar mechanism of the subcritical hydrolysis reaction. Thus, although it can be argued that the hydrolysis rate expression form of Eqn. 6-27 does represent how the subcritical reaction occurs and that the reactant orders \( a \) and \( b \) are theoretically significant, the same cannot be said for the oxidation rate expression of Eqn. 6-31. Since it is unlikely that there is any elementary reaction in the oxidation sequence involving the species \( \text{CH}_2\text{Cl}_2 \) and \( \text{O}_2 \) together, the reactant orders \( c \) and \( d \) in Eqn. 6-31 have no theoretical meaning. Eqn. 6-31, therefore, is truly a global rate expression. Second, one must remember that due to the significant \( \text{CH}_2\text{Cl}_2 \) hydrolysis that occurred in the preheater, the feed that was exposed to \( \text{O}_2 \) at the beginning of the main reactor was not pure \( \text{CH}_2\text{Cl}_2 \) but a mixture of unreacted \( \text{CH}_2\text{Cl}_2 \) and its hydrolysis products. The effects, if any, on \( \text{CH}_2\text{Cl}_2 \) oxidation kinetics due to the presence of these products (which were also competing for \( \text{O}_2 \) for their own oxidation) are unknown.

The full four parameter oxidation regression resulted in the following best-fit values for kinetic parameters contained in the global rate expression below:
\[ R_{\text{ox}} = -(10^{38.3 \pm 1.0} e^{-(673 \pm 20/RT)} [\text{CH}_2\text{Cl}_2]^{0.29 \pm 0.30} [\text{O}_2]^{-0.28 \pm 0.30} \] (6-33)

\( R_{\text{ox}} \) is in units of mol/(L s), activation energy is measured in kJ/mol, and the concentrations are in mol/L, and all parameter uncertainties are quoted at the 95% confidence level. A statistical analysis yielded a significance level of 100%, an r-squared value of 0.95 (adjusted for degrees of freedom), and an F-statistic value of 85 for Eqn. 6-33. As anticipated from the qualitative experimental evidence discussed above, the \( \text{CH}_2\text{Cl}_2 \) oxidation reaction was found to be best characterized by a relatively high activation energy of 673 kJ/mol. The \( \text{O}_2 \) and \( \text{CH}_2\text{Cl}_2 \) reaction orders indicate only a weak dependence on both reactant concentrations. Although it is difficult to explain the negative order with respect to \( \text{O}_2 \) as representing anything other than the best mathematical fit to the data, a value of zero is within the uncertainty of this parameter. With this parameter set to zero, the regression was rerun and resulted in the following three parameter version of the global rate expression:

\[ R_{\text{ox}} = -(10^{38.8 \pm 1.5} e^{-(673 \pm 25/RT)} [\text{CH}_2\text{Cl}_2]^{0.14 \pm 0.30} \] (6-34)

where units and uncertainty levels are the same as for Eqn.6-33. Statistical analysis gave a significance level of 100%, an r-squared value of 0.97 (adjusted for degrees of freedom), and an F-statistic value of 129 for Eqn. 6-34. Here the dependence on \( \text{CH}_2\text{Cl}_2 \) concentration is even weaker than in Eqn. 6-33, and includes a value of zero well within the uncertainty. Setting the \( \text{CH}_2\text{Cl}_2 \) order to zero and again rerunning the regression routine resulted in the following two parameter expression:

\[ R_{\text{ox}} = -10^{43.1 \pm 1.7} e^{-(75 \pm 30/RT)} \] (6-35)

where units and uncertainty levels are the same as before. Statistical analysis yielded a significance level of 100%, an r-squared value of 0.97 (adjusted for degrees of freedom), and an F-statistic value of 258 for Eqn. 6-35. This zero-order expression has an even higher activation energy than that of either Eqn. 6-33 or 6-34.
6.10.2 Comparison of Global Rate Expression Predictions to Oxidation Experimental Data All of the above rate expressions (Eqns. 6-33, 6-34, and 6-35) give results that are in close agreement with each other and in good agreement with the experimental data. Figure 6-16 shows a graph of experimental and calculated values of conversion from the temperature variation runs of the CH₂Cl₂ oxidation experiments as a function of sandbath temperature and residence times (this figure is the oxidation experiment analog of Figure 6-14). The graph shows three groups of data points: experimentally measured conversion, calculated conversion at the end of the preheater (hydrolysis only, using Eqn. 6-28), and calculated conversion at the end of the main reactor (oxidation and hydrolysis, using Eqns. 6-34 and 6-28). Almost all calculated conversion values at the end of the main reactor are within the uncertainty of the corresponding experimental values. The results demonstrate that the combination of hydrolysis (with the Kirkwood correction factor) and oxidation rate expressions used can predict the data very well, both qualitatively (i.e. shape of curve) and quantitatively.

Experimental and calculated results for concentration, feed ratio, and residence time variation experiments are displayed in Figures 6-17 and 6-18. Figure 6-17 shows the effect of varying O₂ concentration (at three different superstoichiometric values) for an approximately constant CH₂Cl₂ concentration at a constant sandbath temperature of 550°C. All concentrations cited are at the beginning of the main reactor. Calculated values are again from Eqns. 6-34 and/or 6-28. The experimental data corresponds to those in listed in groups 1, 3, and 5 in Table 4-2. The experimental data shown is the same as that in Figure 4-2, except here it is plotted versus total residence time rather than just main reactor residence time. This is more appropriate since the experimental data includes the conversion due to hydrolysis in the preheater. Again, the data is well reproduced by the developed global rate expressions and shows that varying O₂ concentration clearly has little effect on conversion at these concentrations. As discussed earlier, however, comparison to the few corresponding hydrolysis experiments does show lower conversions at 550°C in the absence
Figure 6-16  Experimental and Predicted CH₂Cl₂ Oxidation Conversion As a Function of Sandbath Temperature and Residence Time at 246 Bar. Predicted conversion at the end of the preheater represents only hydrolysis conversion (with Kirkwood correction), calculated using Eqn. 6-28. Predicted conversion at the end of the main reactor is calculated using the three parameter global oxidation rate expression of Eqn. 6-34 for $R_\text{ox}$ in Eqn. 6-30, with Eqn. 6-28 used for $R_\text{hyd}$. Error bars for experimental data represent 95% confidence intervals.
Figure 6-17  Experimental and Predicted CH\textsubscript{2}Cl\textsubscript{2} Oxidation Conversion As a Function of Total Residence Time at 550°C and 246 Bar: Effect of [O\textsubscript{2}]\textsubscript{0} Variation. Experimental data corresponds to groups 1, 3, and 5 in Table 4-2. Error bars represent 95% confidence intervals. All cited feed concentrations are at the entrance to the main reactor. Calculated conversions are from the three parameter global oxidation rate expression of Eqn. 6-34 for \( R_{ax} \) in Eqn. 6-30, with Eqn. 6-28 used for \( R_{hyd} \). All conversions are at the end of the main reactor.
Figure 6-18 Experimental and Predicted CH₂Cl₂ Oxidation Conversion As a Function of Total Residence Time at 550°C and 246 Bar: Effect of [CH₂Cl₂]₀ Variation. Experimental data corresponds to groups 2, 3, and 4 in Table 4-2. Error bars represent 95% confidence intervals. All cited feed concentrations are at the entrance to the main reactor. Calculated conversions are from the three parameter global oxidation rate expression of Eqn. 6-34 for $R_{ox}$ in Eqn. 6-30, with Eqn. 6-28 used for $R_{hyd}$. All conversions are at the end of the main reactor.
of added O\textsubscript{2}. This implies, then, that there must be some limiting concentration of O\textsubscript{2} (specifically, between 0.02 and 0.6 mM) that is needed for oxidation to take place but above which results in no further increase in conversion.

Figure 6-18 is the counterpart to Figure 6-17, showing the effects on conversion of varying CH\textsubscript{2}Cl\textsubscript{2} concentration at a fixed O\textsubscript{2} concentration of 0.6 mM and sandbath temperature of 550°C. The experimental data corresponds to those in listed in groups 2, 3, and 4 in Table 4-2. Again, calculated values are from Eqns. 6-34 and/or 6-28 and predict the data well. Although experimental data points from the two highest CH\textsubscript{2}Cl\textsubscript{2} concentration groupings (0.4 - 0.6 mM and 0.3 - 0.4 mM) are indistinguishable, the lowest concentration (0.2 mM) does seem to consistently result in somewhat lower conversions. This weak [CH\textsubscript{2}Cl\textsubscript{2}] dependence exhibited by the data is consistent with the small reaction orders determined for CH\textsubscript{2}Cl\textsubscript{2} in Eqns. 6-33 and 6-34.
Chapter 7

Hydrolysis and Oxidation of Methylene Chloride - Product Distribution and Reaction Network/Pathways

7.1 Introduction Of equal importance with knowing that one can destroy a toxic compound effectively by a given process is knowing what products it is transformed into under a given set of operating conditions. Although some methods of waste disposal may be very effective at breaking down the original starting compound, the resulting products may in some instances be worse than the starting material, as in the case of dioxin formation from incineration of chlorinated compounds. In addition, some organic species are sufficiently reactive to undergo substantial conversion under hydrolysis (i.e. oxygen-free) conditions at subcritical temperatures, as has already been demonstrated to be the case with CH₂Cl₂ in the present work. These less severe operating conditions have attracted interest because they may result in simpler, less expensive equipment. Again, however, a major concern is that some intermediate or end products may be more toxic than the starting material and require further processing. Thus it is important to characterize the complete product spectrum and distribution in order to understand what products form under different operating conditions and to provide information for optimizing system performance for specific applications. Of no less importance, this information is also useful in deducing the reaction mechanism(s).

The present chapter focuses on the products identified from the hydrolysis and oxidation of CH₂Cl₂, and their subsequent reactions. The objective is to deduce a reaction network for CH₂Cl₂ destruction that includes the most likely pathways of formation and further breakdown of these
products using a combination of evidence from the current experimental data and from the literature.

7.2 Experimental Product Data and Trends As mentioned in Section 4.4, the following major products from both hydrolysis and oxidation experiments of CH₂Cl₂ were conclusively detected: CO, CO₂, HCHO, CH₃OH, H₂, and HCl. In addition to these products, trace amounts of CH₄ and the following chlorinated hydrocarbons were detected in the vapor phase: chloromethane (CH₃Cl), chloroform (CHCl₃), 1,1-dichloroethylene (C₂H₂Cl₂), cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and trichloroethylene (C₂HCl₃).

Although the presence of O₂ did not have a major effect on CH₂Cl₂ breakdown, it did have a significant impact on the number of product species observed and their concentrations compared to those seen under pure hydrolysis conditions. Sandbath temperature also was important in influencing the relative abundance of each product in all experiments. No new or additional product species, however, were generated under oxidation conditions, compared to those detected from hydrolysis experiments.

Figures 7-1a and 7-1b illustrate the relative amounts of carbon-based products formed at the two sandbath (and main reactor) temperature extremes for hydrolysis and oxidation experiments. The percentages of each product shown represent the fraction of total carbon in the CH₂Cl₂ feed recovered in that product. Thus the percentages of all products shown add up to the total carbon balance for that run. A similar illustration for chlorine-based species would consistently show HCl as the only major product, and is therefore not included. Figure 7-1a shows product carbon percentages for hydrolysis experiments at 451°C and 14 s total residence time (i.e. preheater + main reactor), and 600°C and 22 s total residence time (6 s in the main reactor in each case). Figure 7-1b shows the same for oxidation experiments at 451°C and 14 s total residence time, and
Figure 7-1a  Distribution of Carbon-Containing Products from Hydrolysis Experiments at Sandbath Temperatures of 451°C and 600°C. Data are from Run #454 (451°C) and Run #415 (600°C). Percentages shown are based on total amount of carbon fed that was recovered as product. All percentages sum to total carbon balance. All data at 246 bar and 6 s main reactor residence time. Total residence times are 14 s at 451°C and 22 s at 600°C.
Figure 7-1b  Distribution of Carbon-Containing Products from Oxidation Experiments at Sandbath Temperatures of 451°C and 550°C. Data are from Run #455 (451°C) and Run #418 (550°C). Percentages shown are based on total amount of carbon fed that was recovered as product. All percentages sum to total carbon balance. All data at 246 bar and 6 s main reactor residence time. Total residence times are 14 s at 451°C and 16 s at 550°C.
550°C and 16 s total residence time (again, 6 s exposed to O₂ in the main reactor in each case). At 451°C, the dominant product was formaldehyde for both hydrolysis and oxidation. At 600°C under hydrolysis conditions, the product spectrum was more diverse. Here, the dominant product was CO₂, followed by significant amounts of CO₂ and CH₃OH, but much less HCHO. At 600°C under oxidation conditions, where complete conversion was achieved, practically all of the carbon was in the form of CO₂. Thus 550°C (at which all of the subsequent concentration, feed ratio, and reactor residence time variation runs were conducted) was selected to illustrate the high temperature oxidation spectrum. At this temperature, the dominant product was CO, with a significant amount of CO₂ but little HCHO and hardly any CH₃OH. As one can see, the percentage of gaseous products and the variety of total products increased with increasing temperature.

The graphs in Figures 7-2 and 7-3 show how major product distributions varied over the complete temperature and residence time ranges explored in these experiments for hydrolysis and oxidation (temperature variation) runs. All graphs plot molar yield of product versus sandbath temperature and total residence time. Each point plotted is for a 6 s residence time in the main reactor at a constant supercritical temperature equal to that of the sandbath (± 2 to 3°C). As used here, molar yield is defined as the moles of product formed divided by the moles of CH₂Cl₂ feed that reacted. Thus the total molar yield for the carbon products at any given temperature should sum to 1, while the molar yield for chlorinated products should sum to 2. CO, CO₂, and HCHO are shown in Figures 7-2a and 7-3a, while H₂, CH₃OH, and HCl are shown in Figures 7-2b and 7-3b.

The total residence time is included along with temperature in these figures because it is possible that reaction of some of the products (in addition to CH₂Cl₂) occurred in the subcritical region of the preheater tubing. As noted earlier (Section 5.5.2), a significant amount of the residence time of the fluid in the preheater tubing (about 70-80%) was spent at temperatures < 390°C.
Figure 7-2 Molar Yield of Major Products from Hydrolysis (Oxygen-Free) Runs As a Function of Sandbath Temperature and Total Residence Time: a) CO, CO₂, and HCHO; b) H₂, CH₃OH, and HCl. All data are at 246 bar. Total residence time includes the preheater residence time + the isothermal main reactor residence time of 6 s for all runs.
Figure 7-3 Molar Yield of Major Products from Oxidation Runs As a Function of Sandbath Temperature and Total Residence Time: a) CO, CO₂, and HCHO; b) H₂, CH₃OH, and HCl. All data are at 246 bar. Total residence time consists of the preheater residence time + the isothermal main reactor residence time of 6 s for all runs.
Thus in principle, the subcritical residence time and preheater temperature profile, as well as supercritical residence time and final fluid (or sandbath) temperature, could all influence the net concentration and distribution of products by affecting the rates of all subcritical (e.g. polar) and supercritical (e.g. free radical) reactions governing product formation and disappearance.

Altogether, these figures show that the molar yield or relative amount formed of HCHO always decreased with increasing temperature under hydrolysis and oxidation conditions. The molar yield of all other products (except HCl) increased with increasing temperature under purely hydrolysis conditions. In oxidation experiments, however, CO₂ was the only product that continually increased with increasing temperature. As the major chlorinated product, HCl remained near 2 in both hydrolysis and oxidation effluents. Note that by 600°C and 23 s total residence time, CO₂ and HCl were the only products detected in oxidation experiments.

A comparison of Figures 7-2a and 7-3a shows that the amount of HCHO present under oxidation conditions was always less than that under hydrolysis conditions at any given temperature. The amount of CO (up to 550°C) and CO₂ from oxidation experiments, however, was always more than that from hydrolysis experiments. CO exhibited a maximum concentration during oxidation experiments at 550°C, above which its molar yield decreased essentially to zero by 600°C. Comparing Figures 7-2b and 7-3b shows that the amount of H₂ and CH₃OH increased with temperature during hydrolysis experiments, but remained close to or at zero for all temperatures during oxidation experiments. In summary, the presence of O₂ increased the amount of CO and CO₂ formed while reducing the yield of HCHO and also suppressing the buildup of CH₃OH and H₂.

The concentration of trace chlorinated hydrocarbons in the vapor phase increased with increasing temperature during hydrolysis experiments. Higher amounts were observed from oxida-
tion experiments up to a maximum at 550°C, above which concentrations quickly dropped to < 0.2% of the total mass fed on a carbon basis by 600°C. Highest concentrations were noted at 550°C for the runs with the highest O₂ feed concentrations. Although these chlorinated hydrocarbons in general accounted for only a very small amount of the total feed, their presence and increase or decrease with temperature does give information about possible mechanisms and side reactions that could be occurring.

Product distributions overall did not change much in oxidation experiments when main reactor residence times (or exposure time to O₂) were varied at constant reactor temperature. The only effect was a relatively greater amount of CO₂ and HCl, and smaller amount of CO produced as residence time increased. Variations in reactant feed concentrations and feed ratios also had a weak effect on product distributions compared to temperature effects.

7.3 Reaction Pathways for Product Formation and Destruction

7.3.1 Formaldehyde  Figures 7-2 and 7-3 show that HCHO was the only product species whose yield decreased continuously with increasing temperature and residence time. At a sandbath temperature of 451°C and total residence time of 14 s under hydrolysis conditions, HCHO accounted for most of the carbon (~ 94%) in the products. For sandbath temperatures ≥ 562°C and total residence times ≥ 18 s, very little HCHO was detected for hydrolysis runs (< 10%), and none was found for oxidation runs. These facts suggest that HCHO was a primary intermediate formed from CH₂Cl₂ breakdown. This hypothesis is consistent with the two-stage, polar mechanism for subcritical, neutral hydrolysis of CH₂Cl₂ proposed by Fells and Moelwyn-Hughes (1958) (and discussed more fully in Section 6.2):

\[
CH₂Cl₂ + H₂O \rightarrow CH₂ClOH + HCl \quad (6-1)
\]

\[
CH₂ClOH \rightarrow HCHO + HCl \quad (6-2)
\]

The net reaction stoichiometry is obtained by combining the two reactions:
\[ \text{CH}_2\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCHO} + 2\text{HCl} \]  
(4-1)

Based on the considerable evidence of significant \( \text{CH}_2\text{Cl}_2 \) preheater hydrolysis (Section 4.6), \text{HCHO} must have also formed early on in the preheater tubing, according to reaction (4-1). This would allow ample time for the \text{HCHO} to react further to form other products, conceivably by both polar mechanisms under subcritical conditions in the preheater and free radical mechanisms under supercritical conditions. Because relatively few other products were observed in the effluent, the number of possible \text{HCHO} reactions is relatively small. Several are known to occur under conditions reasonably similar to those in our experiments.

In the gas phase, \text{HCHO} thermally decomposes to \text{CO} and \text{H}_2 at high temperatures:

\[ \text{HCHO} \rightarrow \text{CO} + \text{H}_2 \]  
(7-1)

Although the kinetics are extremely slow below 300°C, several investigators cite reaction (7-1) as the dominant reaction for \text{HCHO} above 300°C (Bone and Smith, 1905; Fletcher, 1934; Walker, 1964). Klein et al. (1956) determined that reaction (7-1) occurs by a free radical chain mechanism with second-order kinetics in \text{HCHO}.

By observing rising \text{CO}/\text{H}_2 ratios as temperature decreased below 300°C, Fletcher (1934) suggested the occurrence of a second surface catalyzed \text{HCHO} decomposition reaction:

\[ 2\text{HCHO} \rightarrow \text{CH}_3\text{OH} + \text{CO} \]  
(7-2)

Calvert and Steacie (1951) confirmed this reaction by detecting both \( \text{CH}_3\text{OH} \) and \text{CO} as the major products of a slow, heterogeneous, nonphotolytic \text{HCHO} decomposition over the temperature range of 150-350°C. Longfield and Walters (1955) observed the same reaction for temperatures up to 415°C in Pyrex reactors, but saw no significant surface effects on the reaction rate. They also
developed an Arrhenius expression for the second-order, gas phase rate constant for reaction (7-2). It predicts a reaction time on the order of seconds to generate a concentration of CH₃OH similar to that seen in our experiments, although only at the highest operating temperatures (i.e. near 600°C).

The situation is very different when HCHO is in aqueous solution. In this case, the above decomposition reactions do not occur, as evidenced by the lack of formation of any CO or H₂ (Walker, 1964). Instead, HCHO under these conditions reacts primarily by means of a Cannizzaro reaction, where one molecule of HCHO is oxidized to formic acid and another is reduced to methanol by means of a hydride transfer (McMurray, 1988). This highly polar mechanism has been verified by Fry et al. (1931) under basic conditions, although they claim that H₂ is the reductant intermediate rather than the hydride ion. The Cannizzaro reaction is unusual not only in mechanism but also in that more than one study claims it to be either a third or fourth order reaction or the sum of a third and fourth order reaction, according to Martin (1954). Although the reaction is normally initiated by nucleophilic addition of OH⁻, several researchers have cited that the reaction can also occur when HCHO is heated in the presence of acids (Walker, 1964; Soboleva et al., 1980; Staudinger et al., 1929). Under acidic conditions, the nucleophile would likely be H₂O, resulting in the following net reaction:

$$2\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{CH}_3\text{OH}$$ (7-3)

In the absence of O₂, particularly if H₂ has been formed via reaction (7-1), HCHO can be directly reduced to methanol (Walker, 1964):

$$\text{HCHO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH}$$ (7-4)

With O₂ present, the primary reaction of HCHO is direct oxidation to either CO or CO₂:

$$\text{HCHO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$$ (7-5)
\[ \text{HCHO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (7-6) \]

In HCHO oxidation studies conducted between 287 and 337°C, Fort and Hinshelwood (1930) found evidence that these reactions occurred through a free radical chain mechanism; namely, the existence of induction times, a strong dependence of the reaction rate on HCHO concentration, and a relatively small influence of O\(_2\) on the reaction rate. The studies of Axford and Norrish (1948) at 337°C further showed that although both reactions (7-5) and (7-6) occur together, reaction (7-5) predominates. They also showed that as the O\(_2\) concentration decreases, the normally suppressed pyrolytic reaction (7-1) becomes more prominent. Their proposed mechanism is similar to those postulated for gaseous oxidation of H\(_2\) and CO, and that employed by Holgate and Tester (1994b) in modeling H\(_2\) oxidation in supercritical water, where the OH and HO\(_2\) radicals play a crucial role.

In the present experiments, aqueous CH\(_2\)Cl\(_2\) feed solutions were heated from liquid water conditions at the beginning of the preheater tubing (25°C) to more gas-like supercritical conditions in the main reactor (up to 600°C). Thus our reaction conditions overlap all of those encountered in the experiments in the literature cited above. Consequently, all of reactions (7-1) through (7-6) may have contributed at some point and to some extent to the observed product spectra over the course of the changing reaction environment. The data in Figures 7-2 and 7-3 allow the importance of each reaction to be assessed. Under hydrolysis conditions, the data clearly show that considerable amounts of CO and H\(_2\) were produced, while much less CH\(_3\)OH and no HCOOH were detected. In fact, CO and H\(_2\) were the most abundant products after HCl and HCHO on a molar basis. The increasing CO and H\(_2\) yields with increasing temperature and residence time correlated well with the corresponding decrease in HCHO. For all hydrolysis runs, the combined amount of HCHO, HCl, CO, and H\(_2\) accounted for 90-99.9% of the total mass of products. In addition, after correcting for further CO loss and H\(_2\) production by the water gas shift reaction (see Section 7.3.3 on CO reactions), the CO to H\(_2\) ratio was always close to one (Table 7-1). These observations
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<th>Sandbath Temperature (°C)</th>
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<th>([\text{CO}]_{\text{wgs}}/\text{[H}<em>2\text{]}</em>{\text{wgs}}) (^b)</th>
<th>Water Gas Shift Conversion (%) (^c)</th>
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\(^a\) Total residence time shown includes time in preheater tubing plus 6 s in isothermal main reactor

\(^b\) \([\text{CO}]_{\text{wgs}} = [\text{CO}] + [\text{CO}_2]\) = concentration of CO prior to water gas shift reaction assuming no other reactions involving CO.

\([\text{H}_2\text{]}_{\text{wgs}} = [\text{H}_2] - [\text{CO}_2]\) = concentration of H\(_2\) prior to water gas shift reaction assuming no other reactions involving H\(_2\).

\(^c\) water gas shift conversion = \(\frac{[\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} \times 100\)

**Table 7-1** Ratio of CO to H\(_2\) before the Water Gas Shift Reaction (Reaction (7-9)), and CO Conversions Assuming the Water Gas Shift Reaction Was the Only CO Depletion Reaction. All data are from hydrolysis (oxygen-free) runs only (see also Table 12.1 in Appendix). Pre-water gas shift concentrations of CO and H\(_2\) are calculated from the measured values according to the stoichiometry of reaction (7-9).
clearly indicate that reaction (7-1) was the dominant HCHO decomposition reaction in the hydrolysis runs.

In contrast, none of the experimental evidence suggests that any of reactions (7-2), (7-3), or (7-4) alone were dominant. The small measured concentrations of CH$_3$OH compared to CO indicate that reaction (7-2) had to be much slower than reaction (7-1). The low CH$_3$OH concentrations combined with CO/H$_2$ ratios near unity indicate that H$_2$-mediated reduction of HCHO (reaction (7-4)) could not have been a major reaction. Formic acid was not detected in the present experiments by HPLC with a UV detector. Although this would appear to rule out the Cannizzaro reaction (reaction (7-3)), it is also possible that some of the HCOOH formed could have reacted further to either CO$_2$ and H$_2$, or CO and H$_2$O, particularly under the highly acidic conditions that existed at subcritical temperatures (Gibson, 1969; Waring, 1952; Branch, 1915). Extrapolation of data by Van Buren et al. (1982) assuming a first order decomposition to CO$_2$ and H$_2$ suggests that significant reaction of HCOOH could occur between 450-600°C for residence times on the order of seconds, but that complete conversion of HCOOH would only be expected near 600°C. Even without further reaction, any HCOOH formed from reaction (7-3) may still have gone unnoticed because of a relatively high detection limit for HCOOH (probably near 0.001 M) by the UV detector used. If HCOOH were there at all, however, its concentration (and therefore the importance of reaction (7-3) for HCHO decomposition) would have been very small, since it could not be greater than the already small concentrations of CH$_3$OH observed (according to the reaction stoichiometry). The good closure on the carbon balances further implies that there were no missing major products.

Although not individually dominant, reactions (7-2), (7-3), and (7-4) are not necessarily insignificant. Exactly how important each of these reactions is, however, is still somewhat difficult to determine conclusively. In general, the fact that the CO/H$_2$ ratio is always close to one sug-
gests that there should be no further significant sources or sinks for these products under hydrolysis conditions. At the same time, the amount of CH₃OH produced, though small (<10%), was not negligible, particularly at higher temperatures and longer residence times. Although one of these reactions may have been the sole source of the CH₃OH formed, it is also possible that all three of these reactions for CH₃OH production (along with CH₃Cl hydrolysis) could have proceeded separately to some small extent - enough to collectively account for the total amount of CH₃OH observed, while at the same time not resulting in a significant or detectable change in other products used up or generated (i.e. CO, H₂, and HCOOH). Such a scheme would not be inconsistent with both the data and studies in the literature.

The noticeably decreased yields of HCHO at all temperatures and residence times in the oxidation runs compared to the hydrolysis runs (Figures 7-2a and 7-3a) show that, unlike with CH₂Cl₂ breakdown, O₂ has a very significant effect on HCHO breakdown. The lack of essentially all other carbon products besides HCHO, CO, and CO₂ for the oxidation runs is certainly consistent with reactions (7-5) and (7-6) being dominant. The higher amounts of CO at lower temperatures and residence times does appear to favor reaction (7-5) as the first step in the oxidation of HCHO however, with an increase of CO₂ at higher temperatures and residence times due to direct oxidation of the CO.

7.3.2 Methanol Most of the possible formation reactions for CH₃OH under the given experimental conditions have already been discussed. One additional pathway of formation is by hydrolysis of CH₃Cl, which is discussed in Section 7.3.6.1. Earlier work on CH₃OH hydrolysis and oxidation in supercritical water elucidates the potential for CH₃OH decomposition reactions here. In principle, CH₃OH could undergo thermal decomposition in the absence of O₂ to form CO and H₂ (Fletcher, 1934):
\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \\
(7-7)
\]

However, in experiments using virtually the same apparatus as that of the present study, Tester \textit{et al.} (1993b) observed a methanol conversion without \text{O}_2 of only 2.1\% at a sandbath temperature of 544°C and a main reactor residence time of 6.6 s (a likely total residence time of about 18 s) at 246 bar. This result implies that reaction (7-7) was probably negligible in the present study and that any \text{CH}_3\text{OH} measured in the effluent of hydrolysis runs was a true indicator of all that was formed in the course of reaction. This provides further evidence that reactions (7-2), (7-3), and (7-4) were probably of minor importance compared to reaction (7-1) for HCHO decomposition.

In contrast, methanol is highly susceptible to oxidation in supercritical water:

\[
\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
(7-8)
\]

Tester \textit{et al.} (1993b) reported a 96\% methanol conversion under oxidizing conditions at a sandbath temperature of 530°C, a main reactor residence time of 9.6 s, and 246 bar. Note that in the absence of \text{O}_2 in the present work, \text{CH}_3\text{OH} was conclusively detected only at or above this temperature (Figure 7-2b). Thus it is not surprising that \text{CH}_3\text{OH} was not observed in any of the present oxidation runs (Figure 7-3b), since complete conversion would be expected just at the point where it would start to form.

\subsection*{7.3.3 Carbon Monoxide}

As already discussed, the major CO formation pathway was by homogeneous thermal decomposition of HCHO (reaction (7-1)), with possibly a small contribution from the heterogeneous reaction that also produces \text{CH}_3\text{OH} (reaction (7-2)) and from any HCOOH decomposition. Under hydrolysis conditions, the water gas shift reaction is an important CO sink (Helling and Tester, 1987):

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \\
(7-9)
\]
Working on the same experimental apparatus and at similar temperatures as that used in the present study, Holgate et al. (1992) found that breakdown of CO in the absence of O₂ via the water gas shift reaction (reaction (7-9)) never resulted in more than a few percent conversion of CO in the preheater tubing. In the main reactor under isothermal, supercritical conditions without O₂, they reported CO conversions ranging from 1 to 16% at temperatures of 446 to 593°C respectively, 246 bar, and 7.5 s reactor residence time. If one assumes that reaction (7-9) was the only CO sink and only CO₂ source, then by stoichiometry the measured concentration of CO₂ divided by the sum of the measured CO and CO₂ concentrations should yield the CO conversion from the water gas shift reaction in the hydrolysis runs of the present set of CH₂Cl₂ experiments. Values of CO conversion estimated in this way (Table 7-1) vary from 0% up to 26% over the main reactor temperature range of 450-600°C and constant 6 s residence time. These values are in excellent agreement with those of Holgate et al. (1992), suggesting that the water gas shift reaction was the most likely pathway for CO loss and CO₂ production in the absence of O₂.

Holgate et al. (1992) also showed that direct oxidation of CO:

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\]  

(7-10)
is faster than the water gas shift reaction in the presence of O₂. This fact, coupled with its lack of occurrence in the preheater tubing, indicates that the water gas shift reaction was negligible in the oxidation runs. Over the range of oxidation runs carried out, the CO concentration exhibited a maximum at a temperature of 562°C and 12 s total residence time (Figure 7-3a). This behavior implies competing production and destruction reactions for CO. Since thermal decomposition of HCHO can in principle begin in the preheater tubing, it is likely that CO was present when the flow first encountered O₂ at the beginning of the main reactor. Data from Holgate et al. (1992) for CO oxidation in supercritical water show a low conversion of 5% at 445°C, 246 bar, and 7.5 s main reactor residence time. The direct oxidation reaction proceeds much faster at higher temperatures,
with 60% conversion at 560°C and 93% conversion at 571°C, both for a main reactor residence
time of 5 s. Holgate et al. (1992) observed this particularly large increase in CO conversion at the
same temperature range where the present oxidation experiments found CO yields to maximize and
then drop appreciably. Thus the observed behavior of increasing CO yields at lower temperatures
and residence times, followed by decreasing CO yields at higher temperatures and residence times,
is consistent with the known kinetics of CO oxidation in supercritical water. As expected, at high
temperatures and long enough residence times, direct oxidation of CO to CO₂ predominates.

7.3.4 Hydrogen  H₂ formation occurred by two major pathways under hydrolysis conditions;
thermal decomposition of HCHO (reaction (7-1)) being the primary pathway, followed by the wa-
ter gas shift reaction (reaction (7-9)) at supercritical temperatures. The importance of both of these
reactions is supported by the experimental data and studies in the literature, as pointed out above.
In terms of further reactions of H₂, Holgate and Tester (1993) concluded that there was no signifi-
cant net reaction (either pyrolytic or hydrolytic) between H₂ and water in the absence of O₂ under
conditions similar to those of the present study. The absence of O₂ together with the relatively high
concentrations of H₂ measured, especially at higher temperatures and longer residence times, imply
that reducing conditions existed throughout the preheater tubing and also in the main reactor during
hydrolysis runs (see Figure 7-2b). Note that the maximum molar yield of H₂ based on the stoichi-
ometry of reactions (4-1) and (7-1) is 1. Thus it is conceivable that several reduction reactions may
have occurred in these regions, explaining the presence of other observed products (e.g., reduction
of HCHO to CH₃OH, of CH₂Cl₂ to CH₃Cl, and of CH₃Cl to CH₄). The experimental data, how-
ever, suggest that none of these reactions should be major sinks for H₂ because: 1) reduction of
HCHO is only one of four possible reactions that collectively produced a relatively small amount of
CH₃OH (see above Section 7.3.1); 2) concentrations of CH₃Cl never exceeded 3% of the total car-
bon balance; and 3) only trace amounts of CH₄ were detected. The closeness of CO/H₂ ratios to
unity in the hydrolysis runs further suggests that, in general, only minimal consumption of H₂ by other reactions could have occurred.

The H₂ yields in the oxidation runs were much lower than those from the hydrolysis runs, with no H₂ detected above 562°C and 6 s exposure to O₂ (main reactor residence time) (Figures 7-2b and 7-3b). Comparison of the H₂ and CO yield data in Figures 7-2 and 7-3, imply that direct H₂ oxidation, i.e.,

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \]  

(7-11)
is much faster than CO oxidation, at least up to temperatures of 562°C where CO concentrations start to drop substantially with increasing temperature. Holgate and Tester (1993) found 98% conversion of H₂ by oxidation in supercritical water at a temperature of 571°C, main reactor residence time of 5 s, and pressure of 246 bar using double the stoichiometric amount of O₂ at the main reactor inlet. Almost all of the present experiments were fuel-lean relative to H₂. Under such conditions at 560°C and 246 bar, Holgate and Tester (1994a) showed that H₂ oxidation was faster than H₂ production via the water gas shift reaction over a main reactor residence time range of 3 - 8 s. They also determined that H₂ oxidation proceeds more rapidly than CO oxidation at 550°C, but that the rates become comparable at 560°C. Thus, H₂ concentrations measured in the present study are consistent with earlier data and conclusions.

7.3.5 Hydrochloric Acid and Carbon Dioxide Despite the number of different products observed in these experiments, HCl and CO₂ were the final and only products of CH₂Cl₂ destruction under oxidation conditions at high enough temperatures and long enough residence times (600°C and 23 s in the present experiments). This fact confirms that CH₂Cl₂ and the other trace chlorinated hydrocarbon products found at lower temperatures and residence times can be destroyed cleanly and completely by SCWO at still reasonable operating conditions. HCl was always the dominant chlorinated product in both hydrolysis and oxidation experiments, accounting for
> 97% of the chlorine from CH₂Cl₂ conversion. HCl molar yields were also roughly constant at 2 for both hydrolysis and oxidation experiments (Figures 7-2b and 7-3b). CO₂ concentrations were much less in hydrolysis runs compared to oxidation runs, because CO₂ could only be formed from the water gas shift reaction under hydrolysis conditions, whereas oxidation of all carbon-containing species could produce CO₂ under oxidation conditions.

7.3.6 Other Reactions of CH₂Cl₂

7.3.6.1 Formation of Chlorinated Hydrocarbons Although subcritical hydrolysis (reaction (4-1)) accounted for most of the breakdown of CH₂Cl₂ observed in the present experiments, there was evidence suggesting the occurrence of additional side reactions of CH₂Cl₂ to a small extent. This was the detection of the various chlorinated hydrocarbon compounds (e.g. CHCl₃, C₂HCl₃, C₂H₂Cl₂) in the vapor effluent during both hydrolysis and oxidation runs. Although most of these compounds were present at extremely low concentrations, their relative magnitudes over different sandbath temperatures and residence times could be tracked via gas chromatography with an electron capture detector by the size of their peaks. The maximum concentrations of these products (inferred from peak sizes and areas) occurred in hydrolysis runs at the highest sandbath temperatures and residence times (600°C, 23 s). For oxidation runs, slightly larger peaks were observed compared to hydrolysis runs up to a maximum at 550°C and 17 s. Above these conditions, all peak sizes rapidly decreased toward zero with increasing sandbath temperatures and residence times.

The presence of most of these compounds, including CHCl₃, C₂HCl₃, and all three isomers of C₂H₂Cl₂, cannot easily be explained by any polar mechanism. Thus they were likely formed via free radical mechanisms under supercritical conditions, possibly as recombinations of radical fragments from CH₂Cl₂ pyrolysis or oxidation. Taylor et al. (1991) observed exactly the same products (along with HCl) in the same order of abundance from the oxidative pyrolysis of CH₂Cl₂,
which they accounted for by a free radical, 28-reaction network. In the present experiments, the extremely low concentrations of these compounds are consistent with the relatively low CH₂Cl₂ conversions observed in the supercritical main reactor.

Of all the chlorinated hydrocarbons detected, CH₃Cl is unique in that it was present in the greatest amount (up to 2.9% of the total carbon balance), and could participate in non-free radical reactions. The most likely source of its formation was via reduction of CH₂Cl₂. With appreciable amounts of H₂ present in hydrolysis runs from HCHO thermal decomposition (as mentioned earlier in Section 7.3.1), H₂ clearly could have been the reducing agent:

\[
\text{CH}_2\text{Cl}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl} \quad (7-12)
\]

Other possibilities for the reducing agent include either iron or nickel in the tube wall functioning through a surface reaction (see Section 7.3.6.2 below). Once formed, CH₃Cl could either be reduced further to CH₄, or hydrolyzed to CH₃OH and HCl via a polar SN₂ mechanism:

\[
\text{CH}_3\text{Cl} + \text{H}_2 \rightarrow \text{CH}_4 + \text{HCl} \quad (7-13)
\]

\[
\text{CH}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCl} \quad (7-14)
\]

The fact that: 1) CH₄ was detected only in small quantities and only at higher sandbath temperatures and longer residence times (18 s at 562°C, 19 s at 550°C), 2) CH₃OH concentrations were much greater than those of CH₄, and 3) CH₃Cl hydrolyzes more rapidly than CH₂Cl₂ (Moelwyn-Hughes, 1953), implies that reaction (7-14) rather than reaction (7-13) likely was the more important reaction for CH₃Cl destruction under hydrolysis conditions. Because there are other possible CH₃OH sources (i.e. reactions (7-2), (7-3), and (7-4)), the CH₃OH concentrations cannot be used to determine the total amount of CH₃Cl produced. However, even if one assumes that all the CH₃OH detected formed from reaction (7-14), the total amount of CH₃OH, residual
CH₂Cl, and CH₄ typically accounted for < 12% of the total carbon in the effluent, implying that CH₂Cl formation was not a major sink for CH₂Cl₂.

This at best modest role for reactions (7-12), (7-13), and (7-14) may be due to the need for certain reactants to be formed before these reactions could begin. For example, with H₂ as the reducing agent, reaction (7-12) could not become important until after CH₂Cl₂ hydrolysis and HCHO decomposition had proceeded to build up enough H₂. Thus by the time there was enough H₂, there may have been insufficient time left under polar, subcritical conditions for reaction (7-14) to proceed to any significant extent (We are not aware of any evidence for CH₂Cl hydrolysis in a gas-like, free radical environment). Quantitative support for this hypothesis would require further measurements and detailed kinetic modeling computations. However, qualitatively this reasoning is supported by observations of increasing amounts of CH₂Cl, CH₃OH, and CH₄ at higher sandbath temperatures owing to longer residence times in the preheater tubing (see Section 5.5.2).

7.3.6.2 Surface Reactions There is further evidence, both in our work as well as in the literature, that additional CH₂Cl₂ reactions may have occurred under "hydrolysis" conditions, without further affecting the product spectrum. At all temperatures shown in Figure 6-1, experimentally measured values of CH₂Cl₂ hydrolysis conversion were consistently greater than the conversion predicted at the end of the mostly subcritical preheater tubing by the empirical correlation (Eqn. 6-1) of Fells and Moelwyn-Hughes (1958) by a factor of two. It is interesting to note that Fells and Moelwyn-Hughes conducted their experiments in Pyrex ampoules rather than a metal reactor. Even after accounting for solvent effects via the Kirkwood correction factor (Figures 6-14 and 6-15), discrepancies between calculated preheater conversion values and experimental values were a little larger than expected at sandbath temperatures above 550°C and total residence times longer than 17 s. The fact that higher conversions were observed in the high-nickel alloy tubing of the present experiments, compared to those in the Pyrex ampoules of Fells and Moelwyn-Hughes,
does hint that some of the discrepancy could be due to an additional metal-catalyzed surface reaction for CH$_2$Cl$_2$ breakdown.

Evidence in the literature does support the possibility of a surface reaction taking place. It has been known for some time that chlorinated organic compounds in water can undergo degradation when in the presence of metals (Wilson, 1995; Reynolds et al., 1990). The process is believed to be a redox reaction where the chlorinated organic compound is reduced and the metal is oxidized. Gillham and O'Hannesin (1994) studied the degradation of fourteen chlorinated methanes, ethanes, and ethenes (including CH$_2$Cl$_2$) in water by zero-valent iron under ambient conditions. For most compounds, they found that the presence of iron metal increased destruction rates, relative to those for iron-free hydrolysis, by 3 to 13 orders of magnitude. Also, they found that the rate was directly proportional to the metal surface area-to-volume ratio, and that the enhancement in rate increased with increasing number of Cl atoms. A subsequent similar study by Matheson and Tratnyek (1994) specifically focused on the sequential reduction of the chlorinated methanes with iron. They measured pseudo-first order reaction kinetics, with a decreasing reaction rate for each successive dehalogenation step. The data from both studies support a mechanism that requires direct contact between the organic compound and metal surface. Interestingly, however, CH$_2$Cl$_2$ was the only compound in both studies that showed no rate enhancement in the presence of iron, for which no explanation was given. Unlike that observed for the other compounds, Matheson and Tratnyek did not detect any measurable amount of CH$_2$Cl$_2$ degradation until only after several months. That conversion which was detected was much more likely to have occurred by homogeneous hydrolysis rather than surface reduction, based on the magnitude of the observed rate at ambient temperature and the fact that no CH$_3$Cl or CH$_4$ was found. Despite this result, they speculate that conditions may exist where CH$_2$Cl$_2$ does undergo significant destruction by surface reduction.
Catalytic reactions are also a possibility for chlorinated compounds. Houser and Liu (1996) observed a strong catalytic effect of Inconel 600 reactor walls in the decomposition of 1-chloro-3-phenylpropane and 4-chlorophenol in supercritical water, as compared to control experiments in Vycor ampoules. Specifically regarding CH₂Cl₂, Bond and Calzadilla (1996) found that CH₂Cl₂ hydrolysis with water vapor can be catalyzed by the acidic oxide catalysts γ-Al₂O₃ and TiO₂. They conducted their experiments in a fixed bed flow reactor over temperatures ranging from 259 to 500°C at atmospheric pressure. From their published activation energies, γ-Al₂O₃ appeared to be the stronger catalyst, with nearly complete conversion observed at 487°C. For either catalyst, the mechanism is hypothesized to involve chemisorption of both the organic compound and water to Lewis acid sites (i.e., Al or Ti), followed by attack of the resulting Cl-metal bonds by the water to form HCl and CO₂ and regenerate the surface. They also noted that HCl was detected long after the chlorinated feed was stopped, a trend also observed in our experiments. The authors did not provide an explanation for this persistence of HCl, but the implication is that it continues to form from reaction of the chlorinated organic compound already sorbed on to the catalyst surface.

CH₂Cl₂ oxidation is also subject to catalysis, as was found by Papenmeier and Rossin (1994) in experiments conducted with dry and humid air in the presence of a 3% Pt/κ-δ Al₂O₃ catalyst between 300 - 400°C at atmospheric pressure. Their data are consistent with a reaction mechanism involving adsorption and reaction of CH₂Cl₂ with oxygen sorbed on the Pt. The kinetics were found to be independent of both oxygen and water concentrations, although the presence of water favored the generation of HCl rather than Cl₂ in addition to CO₂ as the final products. HCl was found to inhibit the catalytic reaction.

The literature on surface reactions of CH₂Cl₂ and other chlorinated compounds is intriguing in the present context. On the one hand, earlier studies confirm the possibility that the chlorinated methanes can undergo surface reactions (both reduction and oxidation). On the other hand, not all
of the experimental conditions (temperatures, pressures/densities, and the metal/catalyst surfaces used) overlap those of our experiments. It is therefore difficult to unequivocally determine the importance of surface reactions in our system based on this information and the present data from our tubular flow reactor system. The high-nickel alloy tubing used in our experiments (Hastelloy C-276 and Inconel 625) contains only 5 wt.% of iron. Because the activity of nickel as a catalyst is greater than that of iron for reduction reactions such as hydrogenation (Satterfield, 1991), and because of the common use of nickel as a catalyst for many reactions in organic chemistry, it is tempting to propose that the walls of the Hastelloy C-276 and/or Inconel 625 tubing provided an equally active or even more active catalyst surface. The higher temperatures in our experiments would also likely promote faster reaction rates compared to that at ambient temperature. However, there are also equally compelling reasons to believe that surface reactions did not occur to any significant extent relative to the known homogeneous reactions discussed above (i.e. reactions (4-1), (7-1), and (7-9)). The small concentrations of reduced products (CH₃Cl and CH₄), along with the fact that no evidence for a reduction reaction with iron was seen for CH₂Cl₂ by Gillham and O'Hannesin (1994) and Matheson and Tratnyek (1994), oppose a surface reduction being important. The lack of any appreciable amount of CO₂ formation until higher temperatures and longer residence times does not support the purely catalytic reactions described above, although it is conceivable that partially oxidized products such as HCHO rather than CO₂ could form via catalysis.

To resolve this issue of surface effects on CH₂Cl₂ decomposition, we planned a series of controlled batch experiments to determine if Hastelloy C-276 had any influence on the rate of CH₂Cl₂ hydrolysis. These experiments were carried out by Dolors Salvatierra, a post-doctoral colleague. Quartz ampoules of approximately 6 mL in total volume were used as the reactor vessels. Each ampoule was filled with 5 mL of an aqueous CH₂Cl₂ solution of concentration 31.2 mM under ambient conditions. This concentration chosen was within the range used in the earlier plug flow reactor experiments (Section 4.3). A very fine powder of Hastelloy C-276 beads (-60
mesh size) was added to some ampoules. The amount of Hastelloy C-276 was determined based on achieving either a 1:1 or 10:1 molar ratio of Ni to CH₂Cl₂, accounting for the percentage of nickel in the alloy (approximately 60%). The mass of Hastelloy C-276 used to obtain these ratios was approximately 15 mg and 150 mg, respectively.

After loading the feed solution and metal (if used) into the ampoule, it was flame sealed immediately and placed in a 1.9 cm (3/4”) OD and 12 cm long 316 stainless steel tube. The tube was used as a container to hold the ampoule during heating. In order to avoid breakage of the ampoule due to pressure increase while heating, a calculated amount of water was added to the tube container along with the sealed ampoule to maintain a pressure balance on the ampoule. Temperature was measured by a thermocouple inserted through the top end of the tube container. A schematic of the ampoule and container are shown in Figure 7-4. The system of container and ampoule was heated either by insertion into a Techne SBL-2D fluidized sandbath (for short residence times) or a convection oven (for longer residence times). After the specified time in the sandbath or oven, the system was removed and cooled in an ice bath. The container was then opened, ampoule removed and cracked, and its contents analyzed for CH₂Cl₂ by GC using an FID detector (as described in Section 4.4).

Experiments were carried out at four different temperatures - 100°C, 150°C, 200°C, and 250°C. For each temperature, four to seven different residence times ranging from 10 min to 14 days were explored. Each experiment at any given temperature and residence time consisted of a set of three ampoules - one containing only CH₂Cl₂ solution, one containing CH₂Cl₂ solution and 15 mg of Hastelloy C-276, and one containing CH₂Cl₂ solution and 150 mg of Hastelloy C-276. Each ampoule had its own container. Because two of the temperatures chosen lie within the range of temperatures investigated by Fells and Moelwyn-Hughes (1958), these batch ampoule reactor experiments allow us to determine the accuracy of their results. Note that all four temperatures are
Figure 7-4 Diagram of Quartz Ampoule and Stainless Steel Container Tube Used for CH$_2$Cl$_2$ Hydrolysis Batch Experiments.

low enough so that values of the Kirkwood correction factor $\Phi$ (see Chapter 6; Figure 6-13) are negligible.

Results for three different temperatures are shown in Figure 7-5 as a plot of log normalized concentration versus time. At each temperature, the data points clearly show that the presence and amount of Hastelloy C-276 had no apparent effect on the rate of CH$_2$Cl$_2$ decomposition. Each set of like data points (i.e., 0, 15, or 150 mg of Hastelloy C 276) at a given temperature can be fit well by a straight line, indicating that the data exhibits first-order behavior. First-order rate constant values calculated from the slopes of these best-fit lines are included in Table 7-2, along with the r-squared values for the linear fit. Note that rate constant values for each data set at the same temper-
Figure 7-5  Normalized Decay Profiles for CH₂Cl₂ Hydrolysis Batch Experiments with Various Amounts of Hastelloy C-276 at 100°C, 150°C, and 200°C. Lines and first-order rate constants (k) cited represent linear fits to all data points at the same temperature. Error bars represent 95% confidence intervals.

Results are well within experimental uncertainty of each other, indicating that there is no evidence of any catalytic or other rate enhancing effect. Thus all data at the same temperature should be fit equally well by the same line. A linear fit to all data points at the same temperature is what is displayed for each temperature in Figure 7-5, with first-order rate constant values for the pooled data at each temperature listed in Table 7-2.

Corresponding values of the first-order rate constant predicted by the Fells and Moelwyn-Hughes correlation (Eqn. 6-1) at each operating temperature are also shown in Table 7-2. Note that for each temperature, the rate constant value from the present batch experiments (combined data fit) is about twice as much as that from the Fells and Moelwyn-Hughes correlation. This fact
<table>
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<th>Temperature (°C)</th>
<th>Data set</th>
<th>$k$ (s$^{-1}$)</th>
<th>$r^2$</th>
<th>$k_{FMH}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>No metal</td>
<td>$(8.76\pm0.75) \times 10^{-7}$</td>
<td>0.99</td>
<td>$5.66 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>15 mg Hastelloy C-276</td>
<td>$(6.89\pm0.58) \times 10^{-5}$</td>
<td>0.99</td>
<td>$3.10 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>150 mg Hastelloy C-276</td>
<td>$(7.60\pm0.56) \times 10^{-5}$</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>All data</strong></td>
<td>$(7.30\pm0.32) \times 10^{-5}$</td>
<td><strong>0.99</strong></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>No metal</td>
<td>$(10.20\pm1.72) \times 10^{-4}$</td>
<td>0.96</td>
<td>$5.01 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>15 mg Hastelloy C-276</td>
<td>$(8.21\pm1.10) \times 10^{-4}$</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150 mg Hastelloy C-276</td>
<td>$(8.94\pm3.06) \times 10^{-4}$</td>
<td>0.79</td>
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</tr>
<tr>
<td></td>
<td><strong>All data</strong></td>
<td>$(7.93\pm2.01) \times 10^{-4}$</td>
<td><strong>0.88</strong></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>No metal</td>
<td>$(6.51\pm1.47) \times 10^{-3}$</td>
<td>0.97</td>
<td>$3.53 \times 10^{-3}$</td>
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<tr>
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<td>15 mg Hastelloy C-276</td>
<td>$(6.55\pm1.87) \times 10^{-3}$</td>
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</tr>
<tr>
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<td>$(6.98\pm0.97) \times 10^{-3}$</td>
<td><strong>0.93</strong></td>
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**Table 7-2** Results from CH$_2$Cl$_2$ Hydrolysis Batch Experiments. Experimental first-order rate constants ($k$) determined from slope of linear fit to corresponding data set from a graph of ln ([CH$_2$Cl$_2$]/[CH$_2$Cl$_2$]$_0$) vs. time. Values of the correlation coefficient ($r^2$) correspond to linear, first-order fits to the experimental data. Values of $k_{FMH}$ are calculated from the correlation of Fells and Moelwyn-Hughes (1958) (Eqn. 6-1). Uncertainty values represent 95% confidence intervals.
is consistent with that seen in comparison of the plug flow reactor system data to the prediction of the Fells and Moelwyn-Hughes correlation at the end of the preheater (Figure 6-1).

In summary, the results of these batch experiments clearly show that (1) surface effects due to Hastelloy C-276 metal on CH₂Cl₂ hydrolysis are negligible, and (2) the Fells and Moelwyn-Hughes rate constant correlation (Eqn. 6-1) appears to predict slower CH₂Cl₂ hydrolysis kinetics, compared to all of our experimental results, by about a factor of two.

7.4 Proposed Reaction Network

Based on our experimental data, relevant studies in the literature, and the preceding discussion, we have proposed a reaction network for CH₂Cl₂ hydrolysis in sub- and supercritical water (Figure 7-6). This scheme accounts for all products detected experimentally by one or more reaction pathways. The most prominent reactions of CH₂Cl₂ hydrolysis, HCHO thermal decomposition, and the water gas shift reaction are shown at the top with larger arrows and font to indicate their importance. An analogous reaction network for post-hydrolysis oxidation of CH₂Cl₂ can be written by adding to Figure 7-6 pathways for oxidation to CO and CO₂ and/or H₂O for each species (except HCl). These oxidation pathways should be considered major reactions for all compounds except CH₂Cl₂ and the chlorinated hydrocarbons. Oxidation of these species does not become important until high temperatures and residence times (i.e. > 550°C, 17 s).
Figure 7-6  The Proposed Reaction Network for CH₂Cl₂ Breakdown under Hydrolysis Conditions in Sub- and Supercritical Water.
Chapter 8

Design and Construction of New SCWO Research-Scale Reactors

8.1 Limitations of the Existing Small-Scale Tubular Reactor System  All previous SCWO kinetic data, including that of acetic acid and methylene chloride described in this thesis, have been obtained using our small-scale, plug flow, tubular reactor system. This system is described fully in Section 3.2.1. Although some components and operating procedures have been modified slightly over time in order to accommodate the particular needs of the different model compounds studied, the overall system has remained largely the same since it was first constructed back in 1983 (Helling, 1986). It has worked well over this time period, providing reliable kinetic data from the hydrolysis and oxidation of a number of simple liquid and gaseous compounds in supercritical water.

The current reactor system has a number of advantages which have accounted for its continued use, both past and present. Because feed solutions of oxygen and the organic compound must be prepared in water at room temperature, their concentrations are generally very low, limited by their aqueous solubility. This avoids the potential hazards of dealing with large volumes of the pure materials, particularly that of oxygen. The relatively low flow rates (maximum combined feed flow is about 18 mL/min) and small size of the reactor make the system easier to contain and control for safe operation and yields low volumes of waste for disposal. The low organic concentration in the feed also results in only a small quantity of heat released during reaction, making it relatively easy to keep the reactor isothermal.
Nevertheless, the current reactor system has a number of inherent limitations that have restricted the range and type of experiments that can be carried out. They are enumerated below.

(1) **Concentration range** Although an advantage on the one hand, the low solubility of many organic compounds and oxygen in ambient temperature water is also a disadvantage in that it severely limits the concentration range accessible for conducting kinetic experiments. The maximum concentration of O\textsubscript{2} achievable in the oxygen saturator is about 0.1 M. This concentration is reduced further as density decreases with preheating, and with dilution from mixing with the organic feed before entering the main reactor. The maximum organic concentration varies with the particular compound, but is at least equally as low or lower for the nonpolar compounds previously studied (see Section 1.4). These solubility limitations have ultimately restricted typical feed concentrations under supercritical conditions to only a few millimolar. The organic feed solubility constraint will likely become even worse as we move on to study compounds that are more typical of real wastes such as benzene and halogenated species. The implications of these concentration restrictions can be significant, as they limit the overall concentration range used to develop an empirical rate expression. Depending on the severity of this restriction, inaccuracies may result when trying to apply these rate expressions in industrial applications, where feed concentrations tend to be much higher (i.e. several weight percent). Low organic solubility in liquid water also may lead to inhomogeneous feed solutions, due to the inherently poor mixing of immiscible components.

(2) **Residence time** In addition to concentration restrictions, the current system has a limited residence time range that can be explored as well. With a fixed reactor volume, the main reactor residence time is determined solely by the operating temperature and pump flow rate. The minimum residence time is set by the limited maximum speed of the pump cited above. The maximum residence time is fixed by the Reynolds number criteria to maintain turbulent plug flow conditions. The result for this system is that main reactor residence times range from only about 3 to
15 s. Thus one can only study compounds whose characteristic reaction time is of this order over temperatures of interest. Because of the relatively short residence times available, it is difficult to study reactions in the isothermal main reactor at low subcritical temperatures (such as wet oxidation below 250°C), where reaction times are typically orders of magnitude lower.

(3) Preheating  As has already been seen in the case of CH₂Cl₂, the method in the current system of gradually preheating the aqueous organic feed over a time period equal to or greater than that spent at operating temperature can lead to difficulty in interpreting the kinetic data. This is particularly true for those larger and/or labile compounds prone to reaction at low temperatures. Although subcritical hydrolysis or decomposition has not been an issue with the earlier and smaller compounds studied such as CO, NH₃, and H₂, the results of the CH₂Cl₂ experiments prove that this method of preheating may become increasingly more restrictive as we move to study larger and more typical waste compounds.

(4) Salts and solids  The small diameter of the preheater and main reactor tubing in the system prevents any experiments from being conducted in the presence of salts or solid particles. The limitation here is two-fold. First, it prevents the preneutralizing of the organic feed with base for the case of heteroatom-containing compounds. Base preneutralization helps avoid corrosive damage resulting from the mineral acids that would otherwise form from these compounds under SCWO conditions (as was well demonstrated in the CH₂Cl₂ experiments; see Section 4.5.2). The likelihood of immediate plugging of the tubing by the precipitating neutralized salt particles under supercritical conditions is why this approach could not be taken in this reactor system. Second, the small diameter tubing also prevents running experiments with real or simulated contaminated soils. Again, the fear of plugging by the solid particles if pumped as a slurry, and also the lack of any room to contain these particles in a fixed position for semi-batch operation, are the problems here.
(5) Reactor surface area to fluid volume ratio  The existing small diameter tubing has a relatively large surface area to volume ratio of about 24 cm⁻¹. The high surface area to volume may result in significant catalytic effects from the metal walls on the reaction of certain, susceptible organic compounds such as ammonia (Webley et al., 1991). It would also make it difficult to study the intrinsic destruction kinetics of these compounds in this system.

(6) Sampling  Finally, the fact that sampling can only be done at the end of the reactor means that one experiment yields only one “data point” (in terms of conversion achieved). This prevents any way of determining a concentration profile of reactant or products as a function of position (or time) within the reactor under the same operating conditions. It also prohibits the measuring of any unstable, short-lived intermediate compounds that would only exist under the supercritical conditions in the main reactor. Knowledge of the identity of these intermediates, however, would be of great benefit in elucidating reaction mechanisms in supercritical water.

In general, all of the limitations described above either constrain the range of operating conditions that can be explored in standard SCWO experiments with aqueous feeds or prevent new types of experiments from being conducted. A more flexible reactor system is needed to overcome these disadvantages for the next generation of SCWO experiments.

8.2 Design Requirements and Objectives for New SCWO Reactor Systems  Not surprisingly, the requirements for any new reactor system stem in large part from the drawbacks of the existing one. These requirements are listed below:

(1) Reproducibility of existing capabilities  Any new system should at least be able to duplicate the same experiments and operating condition ranges achievable in the existing system. Like the existing system, the new system must be capable of operating successfully under SCWO
conditions. That is, it must be able to accurately measure, control, and withstand temperatures up to 600°C and pressures up to 300 bar, and have the ability to sample fluids. In addition, one must be able to achieve well defined residence time and/or flow conditions in the reactor and have a well known degree of mixing (where necessary) to allow valid extraction of kinetic rate information from the data collected.

(2) Flexibility The new system should be flexible enough to expand the range of all key operating variables and allow for multiple methods of operation. For example, it should be able to accommodate a higher concentration of both organic and oxidant feeds, ideally up to 10 wt% for the organic. The method of introducing the organic feed into the reactor should be designed to minimize premature thermal breakdown. The new system should also be capable of employing more than one type of oxidant at any time, such as O₂ or H₂O₂, and more than one method of feed delivery. Higher flow rates, with a pulseless flow to diminish pressure oscillations from pump strokes, and longer residence times are necessary as well. The ability to take multiple samples as a function of reactor position and time would be useful in consolidating experiments and verifying reactor performance.

(3) Accommodation of solids The new system should be large enough to allow reactions to take place in the presence of solid particles without plugging or other complications. These solids can either be salts formed during the reaction from oxidation of compounds with heteroatoms, soil particles containing organic compounds, or even material specimens for corrosion resistance testing. The presence of these solids would allow one to study the effects of salt formation and precipitation, soil particles, and the products of corrosion of various materials on SCWO reaction kinetics. In the case of soils, experiments could be conducted in order to explore the mechanism and overall effectiveness of supercritical water on removal and destruction of organic
compounds initially sorbed to a solid matrix. Thus it would also require a means of containing the solid particles within the reactor.

(4) *New experiments* The new system should allow for an increased number and variety of experiment types that could be run. Although there are many possibilities here in addition to the soil experiments described above, some examples include the study of mixing phenomena, heat transfer, and physical property measurements in supercritical water. It could also include studying the effects of additional components on reaction kinetics, such as in running salt precipitation and kinetic experiments together. Having optical access would further allow for the use of spectroscopic measurements to study any of the above phenomena or for detecting unstable reaction intermediates.

As part of this thesis work, the two main types of chemical reactors - tubular and stirred tank - were considered to determine optimal designs which are best suited for meeting the above requirements. The rest of this chapter explores the theoretical and practical issues related to the design of these reactors. As part of its objectives, this thesis work also included construction of a complete reactor system based on one of these new reactor designs. For this purpose, the stirred tank reactor was chosen. This chapter therefore also includes a discussion of the choice and design of key peripheral equipment employed in the stirred tank reactor system.

8.3 The Continuous Stirred Tank Reactor (CSTR) In contrast to tubular reactors, very little has been reported on SCWO carried out in stirred tank reactors. A recent exception is that of Hirth and coworkers, who have used a stirred tank reactor (functioning in batch mode) for hydrolysis and oxidation experiments of hexachlorocyclohexane, polyvinylchloride, and tetrabromo-bisphenol A (a polymer additive) in supercritical water (Hirth *et al.*, 1997). One reason for the lack of popularity of stirred tank reactors and favoring of tubular reactors in SCWO is that in an
axially unmixed tubular reactor, all fluid elements must travel down the same length of reactor and thus have the same fixed residence time and conversion. Because of the nature of the CSTR, not all fluid elements remain in the reactor for the same amount of time, resulting in a residence time distribution and an average residence time. With the emphasis in industrial applications on achieving complete destruction, a single residence time in tubular reactors is more effective than having a distribution of residence times. Nonetheless, as a research instrument to characterize chemical kinetics, the CSTR has several significant advantages over the standard tubular reactor, as discussed below.

8.3.1 Theoretical Reactor Design Issues  A stirred tank reactor can be operated in one of three different modes - batch, semi-batch, or continuous (CSTR). In continuous mode, all reactants are continuously fed to the reactor while an effluent stream is constantly being drawn off. In order to obtain valid quantitative kinetic data with a CSTR, knowledge of its fluid mixing characteristics is required. In the ideal case, the fluid is perfectly mixed, so that temperature and composition within the reactor are uniform. Because of the well-mixed conditions, an instantaneous step change in composition and temperature occurs as the feed streams enter the reactor, while the reactor effluent has the same composition and temperature as the reactor contents. Under ideal, steady state conditions, the experimentally determined space time $\tau$ and conversion $x$ can be related to the rate of reaction $R$ by the relatively simple design equation for the CSTR:

$$\tau = \frac{C_0 x}{-R}$$  \hspace{1cm} (8-1)

where $C_0$ is the initial concentration of organic feed. For conditions of constant density, which is approximated with dilute organic feeds in supercritical water under isothermal conditions, the space time is equivalent to the average residence time. When the fluid is not well-mixed, Eqn. 8-1 no longer applies and the situation is more difficult. In this case, one needs to know the residence
time distribution function for the fluid under the given operating conditions in order to relate the kinetic parameters to the operating variables. Some causes of non-ideal mixing in a stirred tank reactor could be short circuiting of feed directly out the effluent line or the existence of pockets of stagnant fluid.

For a given set of operating conditions and reactor design parameters, there is an associated characteristic mixing time which represents the finite amount of time needed for all feed components to mix uniformly. To be assured of well-mixed conditions in the reactor, the average residence time must be proportionally greater than the mixing time by a certain amount, usually taken to be 5:1 (McCabe et al., 1985). Estimating the characteristic mixing time, however, is difficult since there are very few correlations available (all empirical) and most are for mixing of liquids as opposed to supercritical fluids. These correlations predict mixing time as an empirical function of the Reynolds number, Froude number, rotational speed of the stirring rod, and various geometric ratios involving reactor height, reactor diameter, and impeller diameter. (See Section 8.3.2 for further discussion of these methods of estimating mixing time.)

Compared to a tubular reactor, the inherently larger diameter of a tank reactor is much better suited for accommodating the presence of solid particles (e.g. soils or precipitating salts) without interfering with flow. The larger diameter also translates into a larger volume. Even a relatively small tank reactor of 100 mL is about ten times as large a volume as our existing tubular reactor. The larger volume in turn translates into a longer average residence time. Thus without any further improvement in pump flow capacity, one would expect in general to be able to conduct more kinetic experiments at lower temperatures in the CSTR due to the inherently longer residence times available. The larger volume also results in a much lower surface area to fluid volume ratio than could be achieved practically within a tubular reactor. This would be important in reducing any wall catalytic effects if the potential exists for the compound under study.
Because there is no minimum Reynolds number value for well-mixed operation of a CSTR, there is no minimum pump rate requirement for obtaining kinetic data as with a plug flow reactor. However, because the residence time must always be greater than the characteristic mixing time by a certain amount, a minimum practical residence time exists which specifies a maximum pump rate. The potential problem with this restriction is that at a high enough temperature, the oxidation kinetics of the particular organic compound being studied will be fast enough to prevent having less than complete conversion and well-mixed conditions at the same time. This is because the only way to lower conversion is by decreasing the residence time (and increasing the pump rate) for a reactor of fixed volume size. Therefore the temperature range over which SCWO kinetic experiments can be carried out may be limited on the high end, ultimately depending on the activation energy for oxidation of the particular organic.

Finally, as noted earlier, the same stirred tank reactor can be operated in either batch or semi-batch mode with minimal modification. Batch mode would be useful for experiments at particularly low temperatures such as reactions in ambient water, where characteristic reaction times may be too slow for exploring through continuous flow mode. Under these conditions, temperature and composition would still be uniform but would vary (uniformly) with time. Semi-batch operation would likely be the method of choice for soil experiments, due to the difficulty in pumping solids at high pressure. Here the contaminated soils would be loaded into the reactor before starting the experiment. The supercritical water and oxidant would then be allowed to flow through the reactor continuously during operation, with the effluent be sampled frequently to determine the organic concentration profile(s).

8.3.2 Mixing Time Determination  Because of the impact the characteristic mixing time has on the allowable residence times in a CSTR, it is important to have an accurate method for calculating this mixing time, in order to determine whether use of Eqn. 8-1 is valid for determining ki-
netic information from the data under a given set of operating conditions. Unfortunately, predicting the time necessary to achieve well-mixed conditions in a stirred vessel containing supercritical fluids is not that straightforward. There are few empirical correlations available and most are for mixing of liquids. With the density for supercritical water under expected normal operating conditions ranging down to as low as 0.07 g/mL (at 600°C, 246 bar), correlations developed for the mixing of pure liquids may not always be accurate or applicable. Nevertheless, they are still useful for providing at least a rough gauge for estimating the degree of mixing in the stirred tank reactor.

Most mixing time correlations found in the literature are expressed in terms of a dimensionless mixing time in the following functional form:

$$nt_{mix} = f(Re, Fr, \text{geometric factors})$$  \hspace{1cm} (8-2)

where $n$ is the rotational speed of the stirring rod (rev/s), $t_{mix}$ is the mixing time, $Re$ is the Reynolds number, and $Fr$ is the Froude number. As applied to a stirred tank, these dimensionless numbers are defined as follows:

$$Re = \frac{nd_a^2 \rho}{\mu}$$  \hspace{1cm} (8-3)

$$Fr = \frac{n^2 d_a}{g}$$  \hspace{1cm} (8-4)

where $d_a$ is the impeller diameter, $\rho$ and $\mu$ are the fluid density and viscosity, respectively, and $g$ is the acceleration due to gravity.

Empirical correlations found in the literature are often grouped according to the type of impeller. Most have been generated for either propellers or turbines. For mixing with a flat-blade turbine, Norwood and Metzner (1960) proposed the following mixing time correlation, which utilizes a mixing time factor $f_i$: 


\[ f_i = n t_{\text{mix}} \left( \frac{d_a}{d_i} \right)^2 \left( \frac{d_i}{h} \right)^{1/2} Fr^{-1/6} \] (8-5)

where \( d_i \) is the reactor tank diameter and \( h \) is the tank height. The value of \( f_i \) is determined as a function of the Reynolds number from a graph which the authors provide. The function \( f_i \) decreases with increasing \( Re \) beginning at a value of about 1000 at \( Re = 1 \) and leveling off at a value of about 5 for \( Re \geq 10^4 \). A constant value of \( f_i \) under turbulent conditions is common in many of these empirical mixing correlations. Once \( f_i \) is known, the mixing time \( t_{\text{mix}} \) can be determined. Another correlation for mixing with a turbine was determined by Moo-Young et al. (1972):

\[ f_i = n t_{\text{mix}} \left( \frac{d_a}{d_i} \right)^2 \left( \frac{d_i}{h} \right) \] (8-6)

The value of \( f_i \) determined from the Reynolds number, reaches a constant value of 4.3 under turbulent conditions (\( Re > 10^4 \)).

Fox and Gex (1956) proposed the following correlation for mixing liquids with a propeller:

\[ f_i = n t_{\text{mix}} \left( \frac{d_a}{d_i} \right)^{3/2} \left( \frac{d_i}{h} \right)^{1/2} Fr^{-1/6} \] (8-7)

The value of \( f_i \) is determined from the Reynolds number again by a similar (but slightly different) graph provided by the authors, from which in turn the mixing time is determined. Another correlation for mixing time in a baffled tank with a propeller under turbulent conditions (constant \( f_i \)) proposed by Landau and Procházka (1961) is:

\[ n t_{\text{mix}} = 5.6 \left( \frac{d_i}{d_a} \right)^2 \] (8-8)
A more detailed correlation is given by Van de Vusse (1955), who generated the following more complicated mixing time factor:

\[
 f_t = \left( \frac{nt_{mix} d_a^2 p}{V} \right) \left( \frac{\rho n^2 d_a^2}{\Delta \rho gh} \right)^y 
\]  

(8-9)

where \( p \) is the pitch of the impeller, \( V \) is the tank volume, and \( \Delta \rho \) is the density difference between the two mixing fluids. The value of the exponent \( y \) depends on the type of impeller: 0.25 for propellers, 0.35 for pitched blade paddles, and 0.30 for vertical blade paddles and curved-blade turbines. This mixing time factor is also a function of the Reynolds number, and can be determined from a graph provided by the author. For \( Re > 10^4 \), \( f_t \) approaches a constant value of 9.

Khang and Levenspiel (1976) have proposed a different correlation for the mixing of fluids in baffled tanks. They state that the concentration fluctuation or deviation about a final value after mixing, \( A \), caused by the introduction of one fluid to another should be related to the mixing time by an exponential decay process:

\[
 A = 2 e^{-K t_{mix}} 
\]  

(8-10)

The mixing time can be determined for any chosen minimum deviation \( A \) by knowing the decay constant \( K \). The value of \( K \) is determined from a dimensionless mixing rate number:

\[
 \frac{n \left( \frac{d_a}{d_i} \right)^z}{K} 
\]  

(8-11)

where \( z = 2/3 \) for turbine mixers and 2 for propeller mixers. The value of the dimensionless mixing rate number is in turn determined from the Reynolds number according to the appropriate graphs given by the authors. For \( Re > 10^4 \), the mixing rate number equals a constant value of 0.5 for turbine mixers and 0.9 for propeller mixers.
To get an estimate of the magnitude of the mixing time $t_{mix}$ to expect in a CSTR under typical SCWO operating conditions, Table 8-1 shows the results of each of the correlations mentioned above for two different volume reactors and two different rotational speeds. The table is organized vertically first with the results of the correlations for propellers, followed by those for turbines. All geometric and operating parameters have been chosen for these calculations to represent typical operating conditions. The two reactor volumes looked at were 500 mL and 1000 mL. As manufactured by vendors, the reactor diameter ($d_r$) is typically the same at 7.6 cm (3") for both volume sizes, with the length ($h$) varying in each case: 11.4 cm (4.5") for 500 mL, and 22.9 cm (9") for 1000 mL. This yields $d_r/h$ ratios of 2/3 for the 500 mL reactor, and 1/3 for the 1000 mL reactor. The impeller diameter was chosen to be 4.4 cm (1.75"), giving a $d_i/d_r$ ratio of 0.58 for all cases. The typical maximum rotational speed found for most commercially available stirred tank reactors is 2500 rpm. For the two rotational speeds, 2500 rpm was chosen to give "best case" results for the mixing time and 500 rpm was chosen as a typical minimum speed.

For the purpose of these calculations, the following physical property values were chosen: $ho = 0.1$ g/mL and $\mu = 2.9\times10^{-4}$ g/cm s, which correspond to water at 460°C and 246 bar. For the Van de Vusse correlation, the above value of $\rho$ was used for supercritical water, while the density of the organic fluid being mixed was taken to be that of a typical gas (as a worst case) of 0.001 g/mL, yielding a $\Delta\rho$ of 0.099 g/mL. Also the pitch $p$ was taken to be equal to the impeller diameter, as is usually done. For the Khang and Levenspiel correlation, the maximum concentration deviation was taken to be 0.1% ($A = 0.001$). The Reynolds number under these typical conditions is greater than $10^4$ at both rotational speeds used, indicating turbulent conditions, where the mixing time factors $f_i$ are constant.

Most of the correlations are in reasonably good agreement with each other. Not surprisingly, the mixing times predicted by all the correlations increase with increasing reactor volume.
At $\rho = 0.1$ g/mL, $P = 246$ bar:

<table>
<thead>
<tr>
<th>$n$ (rpm)</th>
<th>$Re$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>$5.7 \times 10^4$</td>
</tr>
<tr>
<td>2500</td>
<td>$2.8 \times 10^5$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Impeller type</th>
<th>Source</th>
<th>$n$ (rpm)</th>
<th>$d_r/h = 2/3$ (V = 500 mL)</th>
<th>$d_r/h = 1/3$ (V = 1000 mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propeller</td>
<td>Fox and Gex (1956)</td>
<td>500</td>
<td>6.3</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>1.8</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Landau and Prochazka (1961)</td>
<td>500</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Van de Vusse (1955)</td>
<td>500</td>
<td>3.7</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Khang and Levenspiel (1976)</td>
<td>500</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Turbine</td>
<td>Norwood and Metzner (1960)</td>
<td>500</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Moo-Young et al. (1972)</td>
<td>500</td>
<td>2.3</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Khang and Levenspiel (1976)</td>
<td>500</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Van de Vusse (1955)</td>
<td>500</td>
<td>3.0</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>1.8</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 8-1  Mixing Time Estimations in a Stirred Tank Vessel. Values of mixing time are calculated using the empirical correlations of Eqns. 8-5 to 8-11 under conditions of $\rho = 0.1$ g/mL and $P = 246$ bar. An impeller diameter $d_q$ of 4.4 cm (1.75") and tank diameter $d_r$ of 7.6 cm (3") is also used for these calculations. The indicated $d_r/h$ ratios of 2/3 and 1/3 correspond to typical vessel volumes of 500 mL and 1000 mL respectively.
size and decreasing rotational speed of the stirring rod. The trend with volume occurs because the volume size is increased in each case only by increasing the length (which decreases the $d_r / h$ ratio), making it harder to achieve well mixed conditions. The results also indicate that turbines produce shorter mixing times than propellers. Since the correlation by Khang and Levenspiel (1976) is only for $d_r / h = 1$, these mixing times are the shortest. Although it is highly unlikely that a reactor with an equal diameter and length would be practical for a volume of 500 mL or more, the Khang and Levenspiel (1976) correlation results were included as a "best case" example of the minimum probable mixing time under the indicated conditions. Although not stated, the lack of dependence on $d_r / h$ and the similar results numerically to those of Khang and Levenspiel (1976) suggest that the correlation of Landau and Procházka (1961) also is for a $d_r / h$ ratio of 1.

Over all, predicted mixing times ranged from as low as 0.1 s up to as much as 9 s. An estimate of the minimum residence time range for the assumption of well-mixed conditions to be valid would be obtained by multiplying the mixing time by 5. These results suggest that residence times in general should be no less than about a minute for the assumption to hold.

A final point to note is that, although not shown in Table 3.3, the diameter of the impeller ($d_o$) has a significant effect on the mixing time predictions of most of the correlations. If the impeller diameter value is cut in half, the mixing times predicted by the correlations increase by at least a factor of two and in many cases even more. This suggests that the impeller diameter should be as large as is allowable to help minimize the mixing time as much as possible.

### 8.3.3 Physical Reactor Design Issues and Specifications

After careful consideration of all of the issues discussed in the previous two subsections, it was decided to purchase a 500 cc AE Closure Stirred Reactor from Autoclave Engineers, Inc. of Erie, PA. Although the basic vessel is a standard item, the design had to be modified to accommodate both the harsh environment
(physical and chemical) characteristic of the SCWO process, and our own requirements for present and future experiments. A diagram of this reactor is shown in Figure 8-1.

Because of the potential for corrosion, the reactor itself is constructed of the high nickel alloy Inconel 625, along with all other parts exposed to process fluid. The reactor has been designed to operate up to 650°C and 345 bar (5000 psi). The vessel employs a modified Bridgman seal to withstand the high pressures. The internal diameter of the reactor chamber is 7.6 cm (3"”), and its height is 15.2 cm (6”). The walls have a thickness of 3.2 cm (1.25”). Although the vessel is officially listed as having a volume of 500 mL, our own measurements and the design drawings show that the reactor chamber (without accounting for any components such as baffles or the stirring rod) actually has a volume of about 637 mL.

The stirring mechanism is an AE MagneDrive unit, which is magnetically driven. An outer set of magnets is placed around an encapsulated inner set of magnets located at the top of the center rotating shaft and contained within the pressure sealed environment. As the outer magnets are rotated by a belt attached to a motor, the resulting magnetic coupling causes the inner magnets to turn at the same speed. Rotational speeds up to 2500 rpm can be safely reached, and are measured by a tachometer attached around the top of the stirring rod housing above the outer magnets. Based on the discussion in Section 8.3.2, this maximum speed should allow for well-mixed conditions to be achieved under most typical operating conditions. The inner magnets must be externally cooled with water (about 0.5 gpm) in order to keep their temperature below 150°C. The rotating shaft, also constructed of solid Inconel 625, penetrates into the reactor to a depth of about 12.7 cm (5”).

The shaft has a total of four guide bearings. Three of these bearings are located in the upper (and cooler) portion of the MagneDrive unit near the magnets, while the last is located just at the top of the reactor volume. This lower bearing is directly exposed to process fluid within the
Figure 8-1  Diagram of the Stirred Tank Reactor (CSTR). Access ports are shown configured for either fluid passage or thermocouples. Figure not drawn to scale.
reactor. Because of the reactivity of carbon in SCWO environments, the standard pure graphite (Purebon) type bearing could not be used in this design. Discussions with the personnel at MODAR, Inc. suggested zirconia (ZrO₂) as a material that would withstand the SCWO environment chemically. Its behavior as an appropriate bearing material, however, was unknown. Nevertheless, upon further inquiry with the manufacturer of the material (Coors Ceramics) by Autoclave Engineers, it was decided that (magnesium stabilized) zirconia appeared promising enough that it could be used as the material for the lower bearing. The understanding with Autoclave Engineers, however, is that this is a prototype bearing design which may need to be modified and/or replaced with another material if it is insufficient. Although contact of the upper bearings with process fluid is much lower, the possibility of graphite particles being generated from normal wearing of the bearings and getting into the reactor was feared if standard bearings were used here. Thus, the upper bearings are manufactured out of Rulon LR, which is a more rugged graphite-Teflon composite.

The impeller is secured to the shaft by two set screws, and one or more can be positioned at any point along the length of the shaft. Currently there are four different impellers available for use. Three are pitched blade (45°) in type. Of these, one has four blades pitched down, a diameter of 3.2 cm (1.25"), and construction of Inconel 625; one has four blades pitched up, a diameter of 3.2 cm, and construction of Hastelloy C-276; and one has four blades pitched up, a diameter of 4.4 cm (1.75"), and construction of Hastelloy C-276. The remaining impeller available is a flat, 6 blade type (turbine) of 3.2 cm diameter and Inconel 625 construction. In addition to the impellers, the rotating shaft is designed to allow mounting of a “basket” along its length, which will spin with the shaft. The current basket is about 3.8 cm (1.5") in diameter and 5.1 cm (2") long, and is constructed of Hastelloy C-276. Its center portion is porous (mesh 50 × 50 × 0.009 wire) to allow access of fluid to the contents inside (such as soil particles). The maximum rotational speed with this spinning basket mounted is 500 rpm.
The reactor is heated by three, 120 V ceramic band heaters manufactured by Industrial Heaters, Co. Two of the heaters are rated for 1400 W and one is rated for 700 W. The heaters are stacked vertically around the lower portion of the unit and surround the actual reactor chamber. There is a 0.3 cm (1/8") air gap between the heaters and the vessel walls, so that the heaters are never in direct contact with the metal. The reactor temperature is controlled through a feedback control loop which has its input signal from a thermocouple measuring the heater temperature. This thermocouple is connected to a controller (Omega Engineering, model CN9000A), which is in contact with a solid state relay (Omega Engineering, model SCR71Z-260). All three heaters are wired in parallel so as to receive the same power signal from the relay. All thermocouples used here and throughout the system are of Type K.

Most of the access ports to the reactor were custom designed according to our specifications, which were based on our objective of making the vessel as versatile as possible for carrying out present as well as future anticipated experiments. The vessel has a total of ten access ports which may be utilized for either fluid input or output, or thermocouple insertion. The diagram in Figure 8-1 shows a typical port configuration for fluid flow and thermocouples. Four ports allow access through the top cover portion of the reactor. The end of each port at the top of the reactor is threaded to allow for attachment of 0.64 cm (1/4") OD tube extensions or thermowells of the following lengths: 2.5 cm (1"), 5.1 cm (2"), 7.6 cm (3"), or 10.2 cm (4"). Of these four ports, one is exclusively designed to hold a 0.03 cm (1/32") thermocouple, and one is connected to a pressure gauge (0 - 7500 psi) and rupture disk. The remaining two, located 180° apart, are intended for fluid entry or exit. These two are each connected to two-way straight valves (Autoclave; model 30VM4071HTIN625) of Inconel 625 construction with extended stuffing boxes (to insulate valve packing material from high temperature fluid).
The two bottom ports can be used for either fluid access or thermocouples. The larger one is located at the center of the vessel and has a 0.95 cm (3/8"") external connection. A 0.64 cm (1/4"") tube is attached to this fitting and penetrates through the reactor block into the vessel about 1.3 cm (0.5"") up from the bottom of the reactor volume. This is 1.3 cm below the bottom of the rotating shaft. There is no dead space between the tubing and reactor bottom for fluid in the reactor to collect. The smaller port is a 0.2 cm (3/32"") diameter opening located approximately 1.7 cm (11/16"") away from the larger port (off-center). This smaller port is designed to accommodate either a 0.16 cm (1/16"") tube or thermocouple.

In addition to allowing fluid flow or thermocouple access, the four side ports were also designed for the possibility of conducting jet mixing studies. Thus they are all identical 0.2 cm (3/32"") diameter openings that have been drilled off-center so as to give any fluid entering through these ports a tangential velocity component necessary for jet mixing. The ports were drilled at an angle of 45° from vertical, and at a horizontal off-set angle from the radial line to the center of the reactor (in a plane slicing through the reactor) of 35°. Apart from this, these four ports are identical to the smaller bottom port.

All side and bottom ports had plugs with solid tube rod attachments for filling the port opening completely when the particular port is not being utilized, in order to minimize dead volume. Each plug is manufactured out of a continuous piece of Inconel 625, with the rod section being 0.16 cm (1/16"") in diameter. The length of each plug is such that its end is flush with the internal wall of the reactor when installed.

8.3.4 Design of Peripheral Equipment A schematic of the complete CSTR reactor system is given in Figure 8-2. The configuration shown represents the initial one in use at the time of the
Figure 8-2  Diagram of the Complete CSTR System.
first test runs and experiments with methanol (see Chapter 9). Details of all peripheral equipment shown are given below.

8.3.4.1 Upstream Feed Delivery and Preheating Section This CSTR reactor system has been designed for separate feed of organic and oxidant components by different methods. In all cases, the pure organic compound to be studied is fed directly into the reactor without preheating via a syringe pump (Isco, model 100DM). Thus it is only upon entering the reactor that the organic first contacts water and oxidant already at operating temperature. The required flow rate of the organic compound is calculated by a mass balance based on the water flow rate, operating temperature and pressure, and the desired reactor concentration (once in solution). The syringe pump has a reservoir of 103 mL and can deliver a pulseless flow from as high as 25 mL down to 0.01 μL/min. The maximum operating pressure is 690 bar (10,000 psi). It can operate in either constant pressure mode (where flow rate is continuously adjusted to keep pressure steady) or constant flow mode (where flow rate is kept constant while pressure is allowed to vary). In these experiments, the pump is run in constant flow mode to keep a steady feed to the reactor, while the pressure is dictated by that in the reactor. The organic feed line from the pump is 0.16 cm (1/16") OD and is attached to an o-ring type check valve (Autoclave, model SWO1100-TO) with a Teflon o-ring, to prevent back-flow from the reactor. As it is presently configured, the tubing continues after the check valve through one of the reactor side ports until the tubing end is flush with the inside reactor wall. This choice of side entry port (as opposed to top and bottom ports) provides the least amount of distance that the feed must travel through the hot metal walls before entering the reactor, minimizing any possible premature degradation.

For hydrolysis (i.e. no oxidant) experiments, the pure water feed is stored in two polyethylene tanks, one 50 L and the other 57 L. The 50 L tank has a screw cap top with three access ports to allow for water loading, helium sparging (to remove O₂) or pressurizing, and venting.
The 57 L tank also has a water loaded line through the top, but the cover cannot hold any pressure. The water feed lines to both tanks deliver 18 MΩ-cm deionized water from a Barnstead Nanopure-A water purification system (model D2797) (the same source of water for the small-scale plug flow reactor). This system employs an activated carbon cartridge, two ion exchange cartridges, and a 0.2 μm filter cartridge. For all experimental runs performed thus far (at flow rates ≤ 70 mL/min), only the 50 L tank has been needed. Higher flow rates, however, will likely require one tank for use during heatup and the other during the actual experiment when stable operating conditions have been reached.

Plastic tubing of 0.64 cm (1/4") OD from the bottom of each tank leads up to a three way valve, which allows one to switch water feed flow to the system as coming from one tank or the other. A second valve immediately after the first allows a choice between feed from the tanks or the O₂ saturator (for oxidation runs; described below). Because feeds from the saturator will be under high pressure, the tubing after this point is 316 stainless steel of 0.64 cm OD. After passing through a shutoff valve, the main water feed passes through a 7 μm line filter, a tee fitting with thermocouple for measuring feed temperature, and a Rheotherm thermal flow sensor (Intek, model 100CS). The flow sensor is set to detect if flow drops below 1 mL/min and will trigger a safety shutoff valve when the direct O₂ injection system (see below) is used. All thermocouples used in this reactor system are either 0.3 cm (1/8") or 0.16 cm (1/16") Type K thermocouples (Omega Engineering). Unless connected to a temperature controller or scanner, all thermocouples are wired to a twenty channel rotary selector switch (Omega Engineering, model OSW3-20), which allows the selected temperature to be displayed on a digital meter (Omega Engineering, model DP460-TC).

After passing through the flow sensor, the water feed reaches the main feed pump, which is a Rainin Dynamax (model SD-1) HPLC-type pump. It provides pulseless flow up to a maxi-
mum rate of 200 mL/min and maximum pressure of 414 bar (6000 psi). It also contains a digital pressure transducer and flow indicator. The normal inlet fittings for this pump have been modified in order for it to accept a pressurized feed input (from the O₂ saturator if used). After exiting the main feed pump, the water is at operating (supercritical) pressure. It then passes by an analog pressure gauge (Omega Engineering; model PGS-35B-7500-F; 0-7500psi) and a pressure relief valve (Nupro, R3A series) set to relieve at 330 bar (4800 psi). Following this, the water feed enters the preheating section.

The preheating section consists of four, 2000 W (at 208 V) Watlow Firerod cartridge heaters (model N6AX242A), contained in an insulated aluminum box. Each heater has a diameter of 1.9 cm (3/4”), is 15.2 cm (6”) long, and has an internal Type K thermocouple. Each heater is inserted into a bored out copper rod of equal length and 5.1 cm (2”) diameter. Around each copper rod, 6.1 m (20’) of 0.3 cm (1/8”) OD Hastelloy C-276 tubing is tightly wrapped, through which the water feed flows and is heated. These heaters are extremely efficient in transmitting heat to the water in this configuration. Separate tests in our lab generated heat absorption efficiencies greater than 90 %, based on a comparison of measured fluid temperatures and calculated temperatures assuming all energy absorbed by the water. After each heater, the 6.1 m sections of tubing are joined together with Hastelloy C-276 tee fittings (High Pressure Equipment, model 60-23HF2). Each tee fitting contains a thermocouple to monitor the fluid temperature increase after each heater. The final thermocouple after the last heater is connected to a temperature controller (Omega Engineering, model CN9000A), which provides feedback control through a solid state relay (Omega Engineering, model SCR71Z-260). All four heaters are wired in parallel. To prevent against overheating of the heaters, all internal heater thermocouples are connected in series to a temperature monitor (Omega Engineering, model CN101). The monitor scans each input and compares it to the alarm setpoint, which in this case is set at 800°C. Power is cut to all heaters when the alarm is
triggered until the system is manually reset. All heaters, tubing, and fittings are heavily insulated with Kaowool soft insulation (Lynn Products).

After the last tee fitting, the heated water feed passes through a Hastelloy C-276 cross fitting (High Pressure Equipment, model 60-24HF4) wrapped in insulation. This fitting contains a thermocouple, and is the point where pressurized, pure O₂ feed will mix with the water if the direct O₂ injection feed method is used during oxidation runs (see description below). Leaving the cross, the water is transported through insulated 0.64 cm (1/4") OD Hastelloy C-276 tubing into the reactor through one of the reactor access ports. It is currently configured to enter the reactor through the larger bottom port.

For oxidation experiments, there are three methods of oxidant feed which can be used: O₂/H₂O saturator, H₂O₂, or direct O₂ injection. The three different feed methods have been designed (with overlap among them) to allow for O₂ reactor concentrations from 0.0001 M up to 1 M over the full range of experimental operating conditions. The O₂/H₂O saturator method is similar to that feed procedure used in the small-scale plug flow reactor and can be used when dilute O₂ concentrations are desired (i.e. up to a few millimolar in the reactor). The aqueous O₂ solution is prepared at ambient temperature by adding a predetermined pressure of O₂ gas to pure deionized water in a saturator cylinder and recirculating the contents overnight until equilibrium is achieved, just as described in Section 3.2.1. The only differences in this case are that a 15 L (4 gal) saturator (Hoke, model 8HD4G) is used instead of a 3 L saturator, and about 12 L of water are used rather than 2.5 L. A similar Heise Bourdon tube dial gauge (model CM; 0-3000 psi) is connected to the saturator for monitoring pressure, and a three-way valve allows access of O₂ or helium gas. The recirculating pump used is an Eldex triple piston, positive displacement metering pump (model BBB-4), capable of delivering a maximum flow rate of 100 mL/min. When this method of oxidant feed is used, pure water from the water tanks is pumped through the reactor system while heating
until the reactor operating temperature is reached. Then the feed is switched to that from the saturator via the three way switching valve described earlier. The combined $O_2/H_2O$ feed passes through the main feed pump and preheater section, and finally into the reactor as described above for hydrolysis experiments.

Hydrogen peroxide can be used to generate higher concentrations of $O_2$ in the reactor than can be provided by the saturator. In this feed method, a solution of $H_2O_2$ is prepared in one of the water feed tanks by adding a predetermined amount of an aqueous 30 wt% $H_2O_2$ stock solution (Mallinckrodt; ACS grade) to a measured volume of water. The amount added is based on the desired reactor $O_2$ concentration and the stoichiometry of the $H_2O_2$ decomposition reaction:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (8-12)$$

This $H_2O_2$ solution is fed from the water tank to the main feed pump and preheater section exactly as described above for the pure water feed in hydrolysis experiments. During preheating, the $H_2O_2$ undergoes complete decomposition according to Eqn. 8-12. This was confirmed by testing the effluent at the end of the line for $H_2O_2$ using semi-quantitative test strips (see Section 9.2.3). The resulting $O_2/H_2O$ feed after the preheater then proceeds into the main reactor as before.

The third method of oxidant feed, direct $O_2$ injection, can generate the highest $O_2$ concentrations, but is potentially the most hazardous. It involves compressing pure $O_2$ gas up to operating pressure and mixing directly with supercritical water (in which $O_2$ is completely soluble) in the cross fitting after the preheater section. The lowest flow of pure $O_2$ that may still be regulated via this method is around 10 SCCM, which translates to a minimum $O_2$ reactor concentration of about $10^{-3}$ M. Because of the intrinsic dangers involved in compressing and heating pure $O_2$ to typical SCWO conditions, and because of the much safer, easier, and reliable other two methods, the direct $O_2$ injection section was not used in the initial experiments and has not been fully assembled as
of this writing. However, all components have been designed and purchased (except for the mass flow controller), and can readily be assembled. The description that follows and depiction in Figure 8-2 describe the expected operating procedure and order of components once assembly is complete. All components described below have been properly cleaned for oxygen service. All tubing is 0.64 cm (1/4") OD 316 stainless steel.

Oxygen gas is fed from a standard cylinder (BOC gases) to a two stage gas booster (Haskel, model 53742 (AGT 30/75)). The booster compresses the incoming O₂ from cylinder pressure up to 345 bar (5000 psi). It is powered by compressed air at 7 bar (100 psi) supplied by physical plant. The compressed gas then enters a 328 mL (20 in³) receiver chamber (Haskel, model 27826-10) to dampen pulsations from compression. From here, the O₂ passes through a forward pressure regulator (Go, model PR56), which regulates pressure from 345 bar down to the reactor operating pressure. The regulator is constructed of Monel 400, and can only perform effectively for O₂ flows > 10 SCCM. Two pneumatically actuated isolation valves, one after the forward pressure regulator and the other before the gas booster, are installed for safety purposes. The valves (Autoclave Engineers, model 10V4071-O1S) are piston-type, air-to-open models and have a fail-closed setting. The air flow to the valve after the forward pressure regulator is controlled by a solenoid valve, which receives an electrical signal from the flow sensor in the water feed line (described earlier). When water flow drops below 1 mL/min, air flow to the isolation valve is cut and the valve closes. Air flow to both isolation valves can also be shut manually at any time. Two metering valves, one 316 stainless steel (Autoclave Engineers, model 10V4071) and the other brass (Whitey, model B-1RS4), are also included before the second isolation valve for emergency gas venting.

A mass flow meter and controller follow the second isolation valve and forward pressure regulator. It has been difficult to find one mass flow control unit that will meet both conditions of
high \( O_2 \) pressure and relatively low flows such as 10 SCCM. In addition, no one unit can cover the full desired flow range of 10 - 30,000 SCCM (corresponding roughly to reactor \( O_2 \) concentra-
tions from 0.01 - 1 M). The best model that we have identified is manufactured by Brooks In-
struments. It consists of a thermal sensing mass flow meter (model 5860E) connected to a digital meter (model 5896), and separate control valve (model 5835P). The control valve has a 20:1 turn
down ratio (ratio of maximum to minimum flow), so it could, for example, be set to cover a flow rate range of 10 - 200 SCCM. Multiple flow controllers set for higher flow rate ranges can be in-
stalled in parallel and used when needed to allow for wider \( O_2 \) flow rate flexibility. Although all units can withstand a maximum pressure of 310 bar (4500 psi), the meter is only calibrated by the manufacturer up to a pressure of about 100 bar (1500 psi). Because there is no accurate way to extrapolate this low pressure calibration up to 246 bar, the user must calibrate the meter at this pressure on one’s own. Primarily for this reason, the meter and control valve remain the only items not yet purchased for this system as of this writing. After leaving the control valve, the \( O_2 \) gas will pass through a 316 stainless steel check valve (Haske\( i \), model 28201-10) just before mix-
ing with supercritical water at the Hastelloy C-276 cross fitting described earlier.

8.3.4.2 Downstream Section Effluent leaves the reactor through the top right access port of the reactor. After passing through the two way straight valve, the fluid enters a short length of shell and tube type heat exchanger where its temperature can quickly be lowered. This is to pre-
vent any further reaction from occurring in the fluid. The shell and tube heat exchanger is about 46 cm (18") long and is similar to that used in the small-scale plug flow reactor system, except for its shorter length. The fluid is contained in 0.64 cm (1/4") OD Hastelloy C-276 tubing, and is sur-
rounded by cooling water flowing in parallel in a 1.3 cm (1/2") OD copper tube shell. At the end, both Hastelloy tubing and cooling water exit directly into a 64 L (17 gal) rectangular, stainless steel tank filled with more cooling water. The tank which measures 46 cm \( \times \) 30 cm \( \times \) 46 cm (18” \( \times \) 12” \( \times \) 18”) provides a compact way to further increase exposure time of the fluid to a cooling medium
in order to reduce the fluid temperature fully down to ambient. Upon entering the tank, the Hastelloy tubing is reduced to 0.3 cm (1/8") OD in size. The effluent fluid then passes through 6.1 m (20') of the 0.3 cm OD tubing, which is coiled so as to fit in the tank below the water level. Excess cooling water empties out of the tank through three 1.3 cm (1/2") OD flexible tubing lines at the top of the tank, and one 0.64 cm (1/4") OD flexible tubing line (with brass metering valve) at the bottom of the tank. After the 6.1 m length, the effluent line exits the tank and its temperature is measured via thermocouple.

Once out of the tank, the effluent tubing changes to 0.64 cm (1/4") OD, 316 stainless steel. The fluid then passes through another relief valve and line filter (same as the upstream ones), and a pressure transducer (Dynisco, model G832-000-7.5M) of 0-7500 psig range connected to a digital meter (Dynisco, model µPR690). Following this, pressure reduction back to ambient occurs as the fluid passes through the back pressure regulator valve (Go, model BP66). This regulator valve, which has been modified by the manufacturer to have a \( C_v \) value of 0.025, allows manual pressure control throughout the entire CSTR system. The resulting two-phase flow then enters a gas/liquid separator column similar to that used in the small-scale plug flow reactor system. The column is approximately 23 cm (9") long, has a 1.3 cm (1/2") OD, and is filled with 4 mm beads of borosilicate glass to assist in vapor disengagement from the liquid. The temperature of the fluid in the column is measured via thermocouple. Gaseous components exit through the top of the column and travel past a syringe port, where samples may be taken, and into a 25 mL bubble column (Supelco, model 2-0431), where flow rates can be measured. The gas then is vented to a fume hood. Liquid effluent from the gas/liquid separator exits through the bottom of the column, where samples can be taken and flow rates measured by collection into a graduated cylinder. The liquid effluent then drains into a waste jug.
8.3.4.3 Safety Barrier Sizing and Design  The complete CSTR system with all peripheral equipment occupies approximately 5.4 m² (58 ft²) of floor space, which is much more space than the small, bench-scale, plug flow reactor takes up. Most of the tubing and equipment in the CSTR system is of a larger size or diameter than their counterparts in the plug flow reactor system. The CSTR vessel itself is 58 times larger in volume than the plug flow reactor, which makes it that much more serious a safety issue if there ever were a sudden release of fluid or a metal component under typical SCWO operating conditions. For all of these reasons, particular attention was devoted to the proper design of a containment barrier that would allow for ease of operation but yet keep all personnel safe in the unlikely event of a system failure. One side of the system was contained by the concrete basement wall of the building. A metal Unistrut frame was constructed around the other three sides of the system on to which barrier material in the form of panels or windows could be secured. The question, however, was what barrier material to use and how thick it should be, given the components of the system inside and their typical operating conditions.

There were two specific types of failures that were addressed: (1) catastrophic failure of the hot, pressurized stirred tank reactor, and (2) the possibility of stray particles such as a metal fitting coming loose under pressure and behaving as a projectile. Given the abundance of reactors of this type in industry, we were surprised (and disturbed) to find only limited information available regarding proper barrier design.

One source of helpful information was Appendix G ("Personnel and Equipment Shields") of the DOE Pressure Safety Manual, which was provided by Dr. Steve Buelow of the Los Alamos National Laboratories in New Mexico. This guide provides a collection of semi-theoretical or empirical correlations culled from various sources as a means of estimating barrier wall thicknesses of various substances to contain overpressure or projectiles under a given set of conditions. Another
less extensive source of correlations primarily for estimating the containment volume needed to protect against a catastrophic failure and the resulting overpressure is given by Fryer (1981). Personnel at Textron Specialty Materials in Lowell, MA were also helpful in providing advice and numerical data.

For catastrophic failures (which is a worst-case form of a sudden release of a pressure vessel), the general procedure is to first estimate the compressive energy contained by the fluid in the vessel. The velocity of the fluid on release and the overpressure generated can then be estimated assuming all of the stored internal energy is transformed into kinetic energy. For projectile calculations, most correlations have been developed from ballistics tests. They are therefore generally organized in terms of predicting a certain barrier thickness of a given material for which a given size and type of particle will have a 50% probability of penetrating when traveling at the given velocity. Because of the infinite possibilities and combinations of projectile shapes, sizes, speeds, and angles of approach, it is impossible to determine exactly what minimum barrier thickness will stop all possible projectiles. However, using reasonable estimations for sizes of projectiles and correlations for estimating projectile velocities given in the references, we estimated thicknesses for a few different types of steel under a variety of conditions. A wall thickness of 0.3 cm (1/8") was sufficient up to a safety factor of two, while a wall thickness of 0.64 cm (1/4") satisfied the correlations with a safety factor of three. Based on these results, panels of 0.3 cm thick carbon steel were selected as the primary barrier material. Panel sizes range from 0.4 - 1.1 m² (4 - 12 ft²). A few strategic panels were mounted on hinges or in such a way as to allow easy access to the interior when the system is not running.

Six Lexan® windows were installed in place of steel panels at various positions so as to have a clear view of all parts of the system from outside the barrier. Of these, four were mounted in a fixed Unistrut window frame, while two were attached to rollers in Unistrut tracks allowing
them to be rolled open or closed. To determine the appropriate grade and thickness of Lexan® to use, personnel at General Electric Co. in Mount Vernon, IN (where it is manufactured) were consulted. Based on the description of our system, they recommended use of MR5 grade Lexan® at a thickness of 1.3 cm (1/2").

The overall system has been designed so that all controls, valves, gauges, switches, etc. needed for operation are accessible from a control panel on the outside of the barrier. The only exceptions are the control panels of the three pumps (main feed, syringe, and saturator recirculation), which can all be reached behind one sliding Lexan® panel; and the speed control knob for the stirring rod of the reactor, which can be reached behind the other sliding Lexan® panel. Thus when running at operating temperatures and pressures, the reactor system remains completely enclosed, with no inside access required for proper monitoring and control.

**8.3.5 Intended Applications** Consistent with its multi-functional design, there are a variety of experiments that have been proposed for running in the new CSTR system in the near future. With liquid model compounds or aqueous organic feeds, the CSTR system is not meant to replace the small-scale, plug flow tubular reactor system, but rather to augment and work in parallel with it. Experiments can be run over extended operating conditions with the CSTR compared to the PFR in order to increase the reliability of the data set used for regression of global rate expressions. For example, the effects of higher organic concentrations (> 0.001 M) and subcritical temperatures (or longer residence times) on kinetics can be explored in the CSTR, expanding the core data gathered with the PFR. A better determination of the presence of catalytic wall effects can be made by comparing data gathered from the two systems with their different surface area / volume ratios. For halogenated compounds, the effects of feed preneutralization with resulting salt precipitation could be easily explored with the CSTR and compared to kinetic data under unneutralized acidic conditions from the PFR. Verification of reaction kinetic data for the same compound gath-
ered from the two fundamentally different reactor systems would also substantially increase its creditability.

The CSTR is also intended to be used for new experiments, however. Organic feeds in the solid phase or sorbed to solid matrices (such as contaminated soils) can now be employed in SCWO experiments. A number of experiments have been proposed to investigate the behavior of a few model organic compounds sorbed to well-characterized, common soil constituents of increasing complexity. In many ways, this situation would be very similar to that of a typical catalytic reaction study, but only in reverse (i.e., the goal would be to transport the organic molecules away from, not towards, the solid surface into the SCWO environment of the bulk fluid where reaction takes place). The ease with which the desorption process occurs in the low polarity fluid environment provided by supercritical water would also be of great interest, as well as intriguing to explore. Experiments with real contaminated solids from industrial or environmental sources are also planned.

Finally, a number of non-kinetics experiments will be able to be conducted in the CSTR system. Studies of mixing in supercritical water, of which none to our knowledge exists, can be explored. Because of the angled design of the four side ports to the reactor, jet mixing can also be studied and utilized. The threaded ports at the top of the reactor and large diameter of the vessel allow installation of closed loops of tubing for heat transfer studies. Mass transfer studies and material exposure studies (for corrosion information) in a supercritical fluid environment may also be investigated.

8.4 The Large-Scale Tubular Reactor The design of the CSTR system described in the preceding section meets most of the criteria posed in Section 8.2 for a new SCWO reactor system. There are two criteria, however, than cannot be met with this system: (1) There is no optical ac-
cess for in situ detection and measurement of chemical species, and (2) Samples can only be taken from one point in the reactor per experiment (i.e. where the entire effluent exits) and analyzed after restoring to ambient conditions at the end. Optical access, which requires a clear path across the diameter of the reactor perpendicular to flow, is blocked by definition in the CSTR due to the central position of the stirring rod. Although effluent can be drawn from a different vertical position in the reactor by changing the threaded tube extensions in the top ports, these clearly cannot be changed in the middle of an experiment while at operating temperature and pressure. Both of the above requirements can be met, however, with a large diameter tubular reactor, as will be described below.

8.4.1 Theoretical Reactor Design Issues Tubular reactors have been the reactor of choice for most continuous flow SCWO studies in the literature, and have the benefit of already proven viability for gathering SCWO kinetic data. The simplest mode of operation for a tubular reactor is plug flow. It is characterized by 1) no axial mixing, so that fluid elements move as discrete "plugs" or units of material down the length of the reactor, and 2) all fluid elements having the same fixed residence time. Unlike axial mixing, radial mixing is usually complete, resulting in uniform concentration and temperature profiles over each plug. These characteristics are most easily met when the velocity profile of the fluid is flat, which is achieved when the fluid flow is in the turbulent regime (Re > 2100 for a tube). Although it is possible to achieve plug flow for concentration profiles under laminar flow conditions, it is much more difficult and requires one to verify that the conditions of fast radial diffusion and negligible axial diffusion exist (Cutler et al., 1988). The design equation for a plug flow reactor is given in Eqn. 3-11.

One can incorporate optical access into a tubular reactor in a relatively simple manner by either boring directly through the tube diameter, or dividing the tube into two parts and joining them with a cross-type fitting. In each case, the fittings used must allow for the placement of ap-
appropriate light transmitting material in the form of windows that can withstand high pressure. One way to gather multiple samples for the measurement of axial concentration profiles is by means of a probe which would have the ability to move up and down the tube. This would allow one to sample the reactor contents at any point along the length of the reactor (corresponding to a certain residence time) rather than just what comes out the end. A movable sample probe would also allow one to measure a concentration profile of reactant and products along the axis of the reactor. At high temperatures where otherwise complete conversion would be seen in the reactor’s effluent stream, the movable probe could sample at a point where conversion is less than complete, increasing the effective temperature operating range for the reactor.

Implementing both ideas of optical access and a movable probe, however, requires a straight tube of a much larger diameter than that of the existing small-scale tubular reactor. A larger diameter would also make it easier for running experiments involving solids (though the nature of the tubular reactor makes it not as ideal for this application as the stirred tank reactor), and minimizing wall effects. Although the larger diameter is not in itself a problem, it does make it much more difficult to satisfy the criteria for plug flow operation. With a diameter of 2.5 cm (1”), a mass flow rate of 75 g/min would be required for the Reynolds number just to reach 2100 under typical SCWO operating conditions. With a diameter of 5.1 cm (2”), the minimum flow would be 150 g/min. Because this is reaching the high end capacity of most laboratory scale pumps, it is unlikely that a tubular reactor large enough in diameter to meet our design requirements could be run exclusively under turbulent flow conditions. If one considers the criteria compiled by Cutler et al. (1988), radial heat and mass conduction may not always be fast enough at flow rates > 10 g/min to ensure plug concentration profiles under laminar flow. Thus it is likely that the tubular reactor would have to be run fully under laminar flow conditions.
The difficulty of laminar flow operation in regards to interpreting kinetic data is that all fluid elements no longer have the same residence time. Because of the characteristic parabolic profiles for flow in a tube, the residence time $\tau$ now becomes a function of radial position $r$ as follows:

$$
\tau(r) = \frac{L}{v(r)}
$$  \hspace{1cm} (8-13)

where $L$ is the length of the tube and $v$ is the radially dependent velocity for Poiseuille flow:

$$
v(r) = \frac{\Delta P R^2}{4 \mu L} \left[ 1 - \left( \frac{r}{R} \right)^2 \right]
$$  \hspace{1cm} (8-14)

Here, $\Delta P$ is the pressure drop over the length of the tube, $R$ is the tube radius, and $\mu$ is the fluid viscosity. Use of Eqn. 8-14 assumes that fully developed flow has been achieved. This effective residence time distribution in a laminar flow reactor (LFR) must be accounted for in the reactor design equation when interpreting kinetic data. Following the development by Carberry (1976), the isothermal design equation for the LFR for power law kinetics of order $\alpha \neq 1$ is:

$$
x = 1 - \frac{\pi R^2 v_{\text{max}} C_o}{F_o} \int_0^1 \left( 1 + \frac{\beta}{W} \right)^{-\frac{1}{\alpha}} W \, dW
$$  \hspace{1cm} (8-15)

where

$$
v_{\text{max}} = \frac{\Delta P R^2}{4 \mu L}
$$  \hspace{1cm} (8-16)

$$
\beta = \frac{k(\alpha - 1)C_o^{\alpha - 1} L}{v_{\text{max}}}
$$  \hspace{1cm} (8-17)

$$
W = \left[ 1 - \left( \frac{r}{R} \right)^2 \right]
$$  \hspace{1cm} (8-18)

In the above equations, $C_o$ is the initial reactant concentration and $F_o$ is the initial reactant molar flow rate. For a first-order reaction, the isothermal LFR design equation is:
\[ x = 1 - 2 \int_0^1 e^{-\gamma W} W dW \quad (8-19) \]

where
\[ \gamma = \frac{k L}{v_{\text{max}}} \quad (8-20) \]

Although the design equations for the LFR are more complex than for the PFR, operation of the tubular reactor and analysis as an LFR has the advantage of not imposing any restriction on flow rate as does operation and analysis as a PFR.

If radial conduction is slow enough to make isothermal operation infeasible, it is also possible to run in an adiabatic mode. This would make the data analysis more difficult, however, by coupling an energy balance with the above LFR design equations.

8.4.2 Physical Reactor Design Issues and Specifications  Although the concept of a sample probe that can move up and down the reactor tube length against pressures of 250 bar is extremely useful, it was unclear when first proposed whether or not it could be practically designed and implemented. Because of the unique requirements of the probe and allowance for optical accessibility, it was clear that this reactor would have to be custom designed and built. To see if this design would be feasible, we contacted Harwood Engineering Co. of Walpole, MA, who specialize in the design of high pressure equipment. They were chosen because they previously custom designed an optically accessible cell currently used for studies of salt phase behavior and nucleation in supercritical water (Armellini and Tester, 1991; 1993). It was thought that the same slightly modified design could be incorporated into the design of the tubular reactor.

A successful design which includes the movable probe and optical access options was developed by Harwood, who then went on to construct the complete reactor. The unit is designed
for operation up to 650°C and 345 bar (5000 psi), and can be divided into the following parts: feed nozzle and entrance tube section, optical cell, primary or main reactor tube, and movable probe with associated equipment. A diagram of the reactor unit (not drawn to scale) is shown in Figure 8-3.

The feed nozzle is designed to send both organic feed (pure or in aqueous solution) and supercritical water coaxially into the reactor through the use of concentric tubes. The coaxial feed design is similar to that employed by Armellini and Tester (1991) in shock crystallization experiments of salts in supercritical water. In the present case, the organic feed (instead of salt solution) travels down the centermost tube, which is 0.3 cm (1/8") in OD and of Hastelloy C-276. A 0.03 cm (1/32") OD thermocouple (Type K) is also inserted down the 0.3 cm tube to measure the temperature of the organic feed at the end of the nozzle where it enters the reactor (the thermocouple extends about 0.3 cm beyond the nozzle tip). Concentric around the 0.3 cm OD organic feed tube is a 316 stainless steel tube of 0.64 cm (1/4") OD, and a Hastelloy C-276 tube of 0.95 cm (3/8") OD. The two annular spaces created by these three tubes allows for flow of cooling water to travel down the entire length of the nozzle and back. The outermost tube is of Hastelloy C-276 and 1.3 cm (1/2") OD, and contains the supercritical water and oxidant feed. The cooling water between the two feeds is necessary to minimize the temperature increase of the organic feed in the center tube from the surrounding supercritical water feed as much as possible. This is to prevent premature decomposition before the organic feed enters the reactor at the nozzle tip. In addition, the supercritical water tube begins just before the nozzle enters the reactor tube, to further minimize the time for thermal contact effects on the organic feed.

At the nozzle tip, the 0.95 cm tube is welded shut to the center 0.3 cm tube, causing the cooling water to reverse direction down the 0.64 cm tube. The remaining supercritical water and organic feeds then enter the reactor in parallel flow. The currently designed nozzle tip is flat, but it
Figure 8-3  Diagram of Large-Scale Tubular Reactor and Sample Probe. Figures not drawn to scale.
can be removed and replaced with a different design in the future to promote alternate means of introducing and/or mixing the water and organic feeds. The end of the feed nozzle penetrates into the reactor about 2.5 cm (1") in diameter. The reactor tube has an ID of 5.1 cm (2") and OD of 7.6 cm (3"), and is made of Inconel 625. The ID is dictated by the size and requirements of the movable sample probe (see below). This first part of the reactor tube is only 11.6 cm (4.6") long before it connects to the optical cell. In principle, any length of the same diameter tubing can be used here if one wants to increase the flow time before the fluid reaches the optical cell.

The optical cell was modeled after that used by Armellini and Tester (1991; 1993). It is a block of Inconel 625 measuring 11.4 cm × 14.9 cm × 14.9 cm (4.5" × 5.875" × 5.875"), with one threaded port drilled through each of the six faces. Two of the ports on opposite faces are large enough to accommodate the two sections of reactor tube. The other four ports are about 2.5 cm (1") in diameter and are meant to hold either windows or thermocouples. The windows are 0.95 cm (3/8") thick and made of optically clear synthetic sapphire (α-Al₂O₃). They are contained in a specially designed holder, which is sealed for high pressure use by a gland-like retainer fitting and metal gasket. When not being used for windows or thermocouples, the ports can be plugged.

After passing through the optical cell, the fluid enters the longer or primary section of reactor tube. It has the same properties of the entrance tube, except it is 46 cm (18") long. The end of the reactor tube is threaded into an 8.9 cm × 10.2 cm × 12.7 cm (3.5" × 4" × 5") connection block of Inconel 625. The fluid exits the reactor through a 0.3 cm (1/8") port in the bottom of this connection block. There is a similar port in the top of the block which may be used for insertion of a thermocouple or can be plugged.

The sample probe is designed to draw in and quench a fluid sample from the center line of the reactor at whatever axial position the tip is located. Like the feed nozzle, it consists of a series
of concentric tubes. The inner most is a 0.3 cm (1/8”) OD tube made of Hastelloy C-276, through which the effluent fluid sample is drawn. A 0.03 cm (1/32”) thermocouple (Type K) is contained within this tube and extends out past the probe tip by 0.3 cm (1/8”) to measure the temperature at the point where the sample is taken. Surrounding this inner tube is a 1.3 cm (1/2”) OD tube of 316 stainless steel, and a 2.5 cm (1”) OD tube of Hastelloy C-276 which forms the outer wall of the probe. The annular spaces between these tubes is where cooling water can flow down the complete length of the probe and back in order to cool the effluent sample quickly and prevent any further reaction from continuing inside the probe. The tip of the probe is conically shaped with no sharp edges in order to minimize any flow disturbances from the bulk fluid traveling around the probe from propagating upstream. At the opposite end of the probe are connections for cooling water input and output, and for transporting the cooled fluid sample to its own further downstream processing. The probe is moved by a 5.1 cm (2”) bore hydraulic cylinder (Sheffer, model 2HHSL18), attached to the end of the probe after the fluid connection points.

The entire probe assembly is 91 cm (3’) long, and it can travel a net axial distance of 46 cm (1.5’). At its maximum forward position, it reaches past the optical cell into the entrance tube section, coming within 1.9 cm (0.75”) of the feed nozzle tip. When fully withdrawn, the probe tip samples a position almost at the end of the primary reactor tube. This stroke distance over which the fluid may be sampled effectively defines the boundaries of the reactor. There are no spacers or supports in the reactor tube to guide the sample probe, due to the fact that these would interfere with the fluid flow profile upstream of the probe. The outer diameter of the unsupported probe must therefore be large enough to prevent buckling when it is moved forward against the maximum operating pressure. The minimum diameter is dependent on the length of the probe. For a length of 91 cm (3’), stress calculations have shown that the diameter of the probe should be 2.5 cm (1”) for safe operation. Thus, 2.5 cm was chosen as the OD of the probe. The reactor tube ID
of 5.1 cm (2") was in turn chosen to accommodate this size probe and allow a sufficiently large annular space around it for the bulk fluid to flow without backmixing effects.

The connection block at the end of the reactor tube is where one of two sets of seals are located that allow the probe to move into the reactor while maintaining pressure. This first set of c-seals are designed to work at operating temperature. As backup, a second set of viton o-ring seals are used at the end of a seal tube which surrounds the probe after the connection block. This Inconel 625 probe seal tube has the same OD as the reactor tube but an ID just large enough for the probe to pass through. It is 28.7 cm (11.3") long and has an external cooling water jacket. The purpose of the probe seal tube is to provide a cool buffer zone away from the reactor where the more standard o-ring seals can be used.

The complete reactor unit with all above components has a length of 2.5 m (8.2'). It is currently mounted horizontally on a machined flat, steel base, which is 20.3 cm (8") wide and supported by two leg stands at a height of about 1 m (40") above ground. Two studs are located at the center of the base for future possible trunnion mounting. The trunnion would allow the reactor unit to be rotated and operated in a vertical position. This option might be needed in the event that buoyancy effects become a problem when operating in the horizontal position.

As of this writing, the reactor unit has already been delivered to our lab and work is currently focused on assembling the peripheral equipment and safety barriers that will form the complete large-scale tubular reactor system. Many of the peripheral equipment components will be similar to those employed and described earlier for the CSTR system (e.g., Firerod preheaters, temperature controllers, tank-type heat exchanger).
8.4.3 Intended Applications The main applications of the large-scale tubular flow reactor all stem from the opportunities allowed by its two unique features of optical access and the movable sample probe. Most experiments will probably involve SCWO kinetics measurements of model organic compounds in the liquid phase or aqueous solution. The optical cell will permit the use of Raman spectroscopy in the identification of reacting species (stable and unstable). It may also be possible to use this technique to measure concentrations of species across the tube diameter. Through the use of the movable sample probe, centerline concentrations and temperatures can be measured along almost the entire length of the reactor. Thus thermal and kinetic data over a complete range of residence times can be gathered under exactly the same experimental operating conditions, minimizing the number of experiments needed to be performed. Further built-in options such as the removable feed nozzle, the ability to add a longer section of reactor tube before the optical cell, and the ability to position the reactor vertically will all enable a wider variety of experimental conditions for operation.
Chapter 9

Hydrolysis and Oxidation of Methanol Using the CSTR System

9.1 Introduction The first experiments performed with the new CSTR system were designed with several objectives in mind. The first was to test all system components to make sure that they all functioned properly and as intended under the appropriate operating conditions. The second was to become familiar with the behavior of the system (particularly the new preheating and pure organic feed designs), and how it responds to changes in various operating variables. This information is necessary for establishing standard operating procedures for the system. The third and final objective was to verify how well the complete system, and reactor in particular, would perform as a device for gathering kinetic data under well-defined conditions. For this purpose, the specific experimental goal was to reproduce data already obtained from the small-scale plug flow reactor under similar conditions. This last objective is especially important because it is vital to be sure that we can repeat the same experiments and achieve consistent kinetics results (which should be independent of the reactor used) before we can confidently move on to explore new types of experiments.

After initially testing the system with pure water, methanol was chosen as the model compound for the validation runs because it has been studied extensively by our group. Both Webley and coworkers (Webley, 1989; Webley and Tester, 1989; Webley et al., 1990; 1991; Tester et al., 1993b) and Phenix (1998) have previously explored hydrolysis/pyrolysis and oxidation kinetics of methanol in supercritical water using the small-scale plug flow reactor (described in Chapters 3 and 4). The original studies by Webley were carried out over a temperature range of 450 - 550°C
at 246 bar and main reactor residence times of 6 - 10 s. In these experiments, CH$_3$OH and O$_2$ concentrations ranged from 1 - 6 mM under sub- to superstoichiometric feed conditions. A thermocouple problem resulting in inaccurate temperature measurements was found to have occurred during some of these experiments, but was corrected for systematically (see Tester et al., 1993b for details). Nevertheless, a substantial difference in rate constants still remained between that obtained from this MIT data and measurements made by Rice and coworkers at the Combustion Research Facility of Sandia National Laboratory in Livermore, CA (Rice et al., 1996). Specifically, first-order rate constants generated from the Webley data were as much as three to five orders of magnitude lower than that determined from the Sandia data. This discrepancy motivated a reexamination of CH$_3$OH oxidation kinetics by Phenix (1998).

The experiments conducted by Phenix covered most of the same operating range as Webley, except for the use of pressures up to 269 bar and generally higher CH$_3$OH concentrations (0.011 - 0.39 wt%) in order to match the conditions of the Sandia data. During the course of this inter-laboratory study to determine the cause of the data discrepancy, an examination of feed mixing, preheating, and temperature measurement in the MIT plug flow reactor system led to the redesign of several system components and a new interpretation of induction times (as discussed in Section 3.4.2). As a result of these improvements, the new data of Phenix are not only much better characterized in terms of feed homogeneity and temperature, but also are in much better agreement with the Sandia data. In addition to this work at MIT and Sandia, a number of other researchers have studied SCWO of methanol through experiments and/or modeling (Alkam et al., 1996; Brock et al., 1996; Dagaut et al., 1996; Hirth and Franck, 1993; Schmitt et al., 1991; Butler et al., 1991a; 1991b).

Thus the use of methanol as a model compound for these first SCWO experiments in the CSTR system provides a good kinetic reference to which one can compare the CSTR data and
characterize the new system's behavior. The rest of this chapter will focus on describing the methanol experiments that were conducted and evaluating the results.

9.2 Experimental Operating Conditions and Overview

9.2.1 Reactor Configuration Over all of the water tests and methanol experiments performed, the ten access ports to the reactor (described in Section 8.3.3) were configured in the following format. For fluids, the water and oxidant feed entered the reactor through the large central bottom port. The pure organic feed entered through the back left side port (closest to the syringe pump). Effluent from the reactor was drawn up and out through the top right fluid port from a point in the reactor 2.5 cm (1") down from the top cover, using the 1" tube extension. The top left fluid port was not used and was plugged after the external two-way straight valve. The remaining ports (except for that to the pressure gauge) were used for insertion of thermocouples into the reactor to various depths and locations. All thermocouples were type K (Omega Engineering). A 0.03 cm (1/32") OD thermocouple was fed through the top thermocouple port until it was in contact with the bottom of the 2.5 cm (1") long thermowell, which was threaded into the top cover of the reactor. This thermocouple thus measured temperature at a point 2.5 cm (1") down from the top cover. Three 0.16 cm (1/16") OD thermocouples were inserted through the remaining side ports. One was inserted 2.9 cm (1.125") into the reactor chamber and 11.4 cm (4.5") up from the reactor bottom through the front left port; one 5.1 cm (2") in and 9.5 cm (3.75") up from the reactor bottom through the back right port; and one 7.3 cm (2.875") in and 8.9 cm (3.5") up from the reactor bottom through the front right port. The last 0.16 cm OD thermocouple was inserted through the remaining bottom port up 1.9 cm (0.75") into the reactor chamber.

In the reactor, a single impeller was mounted at the bottom of the shaft for all experiments. The impeller used was the 4.4 cm (1.75") in diameter pitched blade propeller, with blades pitched for upward flow direction. Accounting for the volume of the impeller, shaft, baffle, thermocou-
amples, thermowell, and fluid extension tubes used resulted in a total available reactor volume of approximately 610 mL for these experiments.

9.2.2 Operating Procedures During typical operation, the organic feed line was first removed from its side port, primed with methanol using the syringe pump, and reinstalled. Then, water (and oxidant during oxidation experiments) was pumped into the system at the desired feed rate until flow was observed at the exit point after the gas/liquid separator. At this point, the water feed pump was stopped, the reactor isolated by closing the top effluent valve, and a vacuum line was placed through the left top fluid port. The purpose of the vacuum was to ensure that there was no air gap or head space at the top of the reactor. After a few minutes under vacuum, the valve before the top left fluid port was closed and the line replugged. The water pump was then restarted to allow flow into the reactor. Once the reactor was filled, the top right (effluent) fluid port valve was reopened, sending flow through the entire system again. When the desired water/oxidant flow was established, system pressure was increased by tightening the back pressure regulator valve until the desired operating pressure was achieved. Mixing was also usually begun at this time by starting cooling water flow to the magnets and setting the rotational speed of the MagneDrive shaft (as measured by the tachometer) to the intended value.

The next procedure was to start the methanol flow. With the exit line from the pump closed, the syringe pump was loaded with pure methanol and purged of air. The methanol reservoir inside the pump was then pressurized to a value approximately 17 bar higher than that indicated by the reactor pressure gauge. After switching to constant flow mode and entering the desired flow rate, the pump was started and exit valve opened to allow flow to enter the reactor. The pressure of the methanol feed (as measured by a transducer in the syringe pump) usually dropped to a value below that of the reactor initially, but eventually increased until it matched that within the reactor. The lower the flow rate, the longer this process of pressure equilibration took.
After establishing a stable organic feed flow, the cooling water flow to the shell and tube heat exchanger was started, and the reactor heaters and Firerod preheaters were turned on. Regardless of the final desired operating temperature, the setpoints of the temperature controllers for both sets of heaters were initially set at 100°C. The setpoints were raised in increments of 100°C when the previous value was reached, up to a maximum of 600°C. Recall that the thermocouple inputs to the preheater and reactor temperature controllers were the fluid temperature after the last preheater, and the surface temperature of the reactor heaters, respectively (see Sections 8.3.4.1 and 8.3.3). Because of the large thermal mass of the reactor, there was a significant lag between the fluid temperature within the reactor and the temperature of the reactor heaters (and even with the fluid temperature after the preheaters) during heatup. This thermal lag prevented our direct control of fluid temperature within the reactor. When the reactor fluid temperature (as measured by the five thermocouples installed in the reactor) reached a value about 20 to 30°C away from the desired operating temperature, the setpoints on both temperature controllers were reduced to values much closer to the operating temperature. Both controllers were then further adjusted as needed to maintain the desired fluid temperature in the reactor at a constant value during the course of the experiment. See Section 8.3.4 for a more general description of all system components and the fluid flow path through the system during operation.

9.2.3 Analytical Techniques Concentrations of methanol and liquid products were measured by gas chromatography with an FID detector using one of the Hewlett Packard 5890 gas chromatographs (GC’s) described earlier (Sections 3.2.2 and 4.4). For these experiments, a 30 m × 530 μm × 5 μm film thickness DB-1 capillary column (J&W Scientific, model 123-1035) was used, with helium as the carrier gas and nitrogen as the make-up gas for the FID detector. The column was preceded by a 2.5 m × 530 μm polar Hydroguard retention gap (Restek, model 10081) for solvent focusing. The analysis method used, which employed a splitless sample injection by an automatic liquid sampler, was the same one developed by Phenix (1998) for his methanol experi-
ments. A new calibration was performed for the present experiments, however, covering the expected ambient CH\textsubscript{3}OH concentration range of 9 - 900 ppm by weight. Because of the importance in monitoring effluent concentrations of methanol for determining when steady state was achieved, frequent liquid samples were taken (generally every 10 - 15 min) in 2 mL sample vials. Periodically, larger size liquid samples were taken in 17 mL bottles. Formaldehyde in the liquid phase was detected using a Merck semi-quantitative formaldehyde test kit (EM Science, model 10036-1). Gaseous products were measured with a TCD detector using the same two GC’s, analysis methods, and sampling procedure as described for acetic acid and methylene chloride experiments (Sections 3.2.2 and 4.4). Concentrations of dissolved gaseous products in the liquid effluent were calculated via Henry’s law using the procedure described in Section 3.2.2.

Feed solutions of O\textsubscript{2} in the O\textsubscript{2}/H\textsubscript{2}O saturator or H\textsubscript{2}O\textsubscript{2} in the 50 L water feed tank were prepared according to the procedure described in Section 8.3.4.1. When using the O\textsubscript{2}/H\textsubscript{2}O saturator as the oxidant source, the O\textsubscript{2} concentration was determined by the same method given in Section 3.2.1. When H\textsubscript{2}O\textsubscript{2} was the oxidant source, the H\textsubscript{2}O\textsubscript{2} feed concentration was determined via a ceric ion titration method. This is performed by adding 30 mL of deionized water, 2 mL of 19.2 N H\textsubscript{2}SO\textsubscript{4}, one drop of orange colored ferroin indicator solution, and a specified amount of feed solution from 100 - 500 μL (depending on the anticipated H\textsubscript{2}O\textsubscript{2} concentration range) to a 50 mL Erlenmeyer flask. This mixture is then titrated with a 0.5 N ceric ion solution (Hach, model 22707-01) using a digital titrator (Hach, model 16900-01). When all the H\textsubscript{2}O\textsubscript{2} has been oxidized by the ceric ion solution, the ferroin indicator is oxidized, causing the color to change from orange to pale blue. The result from a blank using water as the feed solution is subtracted from that measured for the H\textsubscript{2}O\textsubscript{2} solution. Over a range of 2000 - 35000 ppm, the concentration of H\textsubscript{2}O\textsubscript{2} is linearly proportional to the amount of titrant used. During experiments, samples of the H\textsubscript{2}O\textsubscript{2} feed were taken at the beginning and end of the run to ensure that no change in concentration occurred. Each sample was analyzed by the above method multiple times and the results averaged to get the H\textsubscript{2}O\textsubscript{2} feed
concentration. For very dilute H₂O₂ feeds and for measuring the effluent to determine when all the H₂O₂ had decomposed, Merck Peroxide Test strips (EM Science, model 10011-1) were used. After exposure to solution for 1 s, the strip changes color in proportion to the amount of H₂O₂ present. The concentration is determined by comparing the color of the strip to the given color scale after 15 s. The concentration range of these test strips is from 0 - 25 ppm.

9.2.4 Experiments Performed The first tests to be performed on the CSTR system were with pure water. In these tests, all mechanical and electrical components were checked for viable operation up to the following variable values: temperature: 520°C; pressure: 298 bar; water pump rate: 80 mL/min (ambient); stirring rod speed: 2500 rpm.

After the water tests, the following experiments with methanol were performed: ambient hydrolysis/pyrolysis (2 runs); subcritical hydrolysis/pyrolysis at 330°C (2 runs); supercritical hydrolysis/pyrolysis at 443°C (1 run); subcritical oxidation at 330°C (1 run); and supercritical oxidation at 411 - 443°C (4 runs). All experiments were carried out at supercritical pressures between 238 - 286 bar, water flow rates of 30 - 50 mL/min, average residence times between 2.5 - 20 min, stirring speeds of 500 or 1000 rpm, initial O₂ concentrations of 0.00025 - 0.0053 M (under reactor conditions), and initial CH₃OH concentrations (after mixing in the reactor) of 0.001 - 0.0026 M. Note that concentrations were deliberately chosen to be of the same magnitude as is typically run in the small-scale plug flow reactor. Flow rates, however, were much faster and residence times much longer than those typical of the plug flow reactor (compare to values given in Sections 3.2.3 and 4.3). Even the longest mixing time at 500 rpm in a 500 mL vessel calculated from the different correlations listed in Table 8-1 yields a minimum residence time for well-mixed conditions of about 30 s (using the 5:1 ratio discussed in Section 8.3.1). The shortest experimental residence time was itself still five times more than this minimum value, thus suggesting that the slowest stirring speed used of 500 rpm should still be sufficient for generating well-mixed conditions. The complete data
set of operating conditions and results for each of the methanol experiments is listed in Tables 12.3 and 12.4 in the Appendix. A summary of the range of operating conditions employed is given in Table 9-1.

In addition to measuring methanol kinetics and product concentrations for data comparison with the plug flow reactor, there were a number of other critical issues which were explored during these first CSTR experiments. The degree of isothermality in the reactor under the different operating conditions, particularly stirring rate and flow rate, was clearly important to monitor. The quality of mixing as measured by concentration variations in the effluent over time was also important. Finally, because of this in situ mixing of the pure organic feed, the ability to achieve a concentration of feed in the system that was both steady and accurate (after the appropriate amount of time to reach steady-state conditions) was crucial to determine in order to ensure valid operation.

9.3 Hydrolysis/Pyrolysis Experiments A limited number of methanol hydrolysis/pyrolysis experiments (i.e. no O₂) were conducted by both Webley (Tester et al., 1993b; Webley, 1989) and Phenix (1998) on the plug flow reactor system. At 544°C and 6.6 s in the main reactor, Webley observed only 2.1% conversion of methanol. At a main reactor residence time of 8 s, Phenix measured 0.5± 2.6% conversion at 422°C and 3.8±3.2% conversion at 483°C. Both studies thus show that methanol is resistant to thermal decomposition in the absence of O₂, even up to supercritical temperatures. The purpose of the present CSTR-based hydrolysis experiments was: (1) to see if a longer residence time (on the order of minutes instead of seconds) resulted in any measurable conversion increase; and (2) to provide a baseline for the forthcoming oxidation experiments.

9.3.1 Ambient Temperature Two experiments were performed at 25°C, each at different average residence times and stirring speeds, in order to see if these variables had any noticeable ef-
<table>
<thead>
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<th></th>
<th>Hydrolysis</th>
<th>Oxidation</th>
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<tr>
<td>Number of Experiments</td>
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<td>5</td>
</tr>
<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Pressure</td>
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<td>238 - 280 bar</td>
</tr>
<tr>
<td>Average residence time</td>
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<td>2.5 - 13.3 min</td>
</tr>
<tr>
<td>Stirring speed</td>
<td>500, 1000 rpm</td>
<td>500, 1000 rpm</td>
</tr>
<tr>
<td>Pure CH₃OH feed flow rate</td>
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<td>1.75 - 23.0 μL/min</td>
</tr>
<tr>
<td>Water (and oxidant) feed flow rate</td>
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<td>30.8 - 38.6 mL/min</td>
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<td>[CH₃COOH]₀ a</td>
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<td>(1.0 - 2.6) x 10⁻³ mol/L</td>
</tr>
<tr>
<td>[O₂]₀ b</td>
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<td>(1.5 - 5.3) x 10⁻³ mol/L</td>
</tr>
<tr>
<td>[O₂]₀ / [CH₃COOH]₀ ratio</td>
<td>-</td>
<td>1.5 - 2.1</td>
</tr>
</tbody>
</table>

a  [CH₃OH]₀ = initial concentration of methanol in reactor
b  [O₂]₀ = initial concentration of oxygen in reactor

Table 9-1 Summary of Methanol Experimental Operating Conditions

fecteds on the results. One experiment (Run #2) was carried out with a water flow rate of 31 mL/min, average residence time of 19.7 min, and a stirring speed of 500 rpm, while the other (Run #5) was carried out with a water flow rate of 51 mL/min, average residence time of 12.0 min, and a stirring speed of 1000 rpm. The same initial CH₃OH concentration in the reactor of 0.001 M was targeted in both experiments, requiring a pure CH₃OH flow rate of 1.75 μL/min for Run #2 and a slightly faster flow rate of 3 μL/min for Run #5.

As shown in Table 9-2, the concentration of CH₃OH measured in the effluent during both runs matched that which would be expected if no reaction occurred. The fact that no vapor flow
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<td>2</td>
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<td>47.8</td>
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<td>4</td>
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<td>46.2</td>
<td>56 ± 3</td>
</tr>
<tr>
<td>6</td>
<td>443 ± 1</td>
<td>586</td>
<td>594 ± 20</td>
</tr>
</tbody>
</table>

Table 9-2 Steady State Values of Methanol Concentration in the Effluent for Hydrolysis/Pyrolysis Experiments. Predicted values are calculated from Eqn. 9-3 and assume no reaction. Measured values are averages of all experimental data points after the listed steady state temperature was achieved.

rate was observed and that no gaseous or liquid products were detected in their respective phases further confirms that there was no methanol decomposition under these conditions.

Because of the observed absence of any measurable hydrolysis reaction rate, methanol can be used as a tracer in ambient temperature water to examine the mixing behavior of the CSTR. An unsteady mass balance on the reactor for the methanol species yields the following equation:

$$\rho_m \dot{Q}_m = C_m M_m \frac{\rho_{\text{amb}}}{\rho_T} + M_m V \frac{dC_m}{d\tau}$$  \hspace{1cm} (9-1)

Here, $\rho_m$, $Q_m$, $M_m$, and $C_m$ are the density, pure volumetric flow rate (from the organic feed syringe pump), molecular weight, and effluent concentration of methanol, respectively; $Q$, $\rho_{\text{amb}}$, and $\rho_T$ are the volumetric flow rate, density at ambient temperature, and density at operating tempera-
ture of the effluent (essentially that of pure water in this case of dilute methanol concentrations), respectively; \( V \) is the reactor volume; and \( \tau \) is residence time. Values of \( \rho_{\text{amb}} \) and \( \rho_T \) in all calculations were obtained using the NBS/NRC steam tables (Harr et al., 1984). The first term on the left in Eqn. 9-1 represents the incoming mass of pure methanol feed, the second term represents the mass of methanol leaving the reactor in the effluent stream, and the third term represents transient accumulation of methanol in the reactor. Note that the form of Eqn. 9-1 assumes well-mixed behavior within the reactor.

Solving Eqn. 9-1 for \( C_m \) results in the usual exponential decay profile for unsteady conditions:

\[
C_m = C_{m,\infty} + \left(C_{m,0} - C_{m,\infty}\right)e^{-\frac{q\left(\frac{\rho_{\text{amb}}}{\rho_T}\right)}{V} \tau}
\]  

(9-2)

where \( C_{m,0} \) is the methanol concentration initially in the reactor \( (\tau = 0) \), and \( C_{m,\infty} \) is the methanol concentration reached at steady state \( (\tau = \infty) \):

\[
C_{m,\infty} = \frac{\rho_m Q_m}{M_m Q \frac{\rho_{\text{amb}}}{\rho_T}}
\]  

(9-3)

For the case where \( C_{m,0} \) is zero, Eqn. 9-2 reduces to

\[
C_m = C_{m,\infty} \left(1 - e^{-\frac{q\left(\frac{\rho_{\text{amb}}}{\rho_T}\right)}{V} \tau}\right)
\]  

(9-4)

Figure 9-1 compares experimental and predicted (Eqn. 9-4) methanol concentrations as a function of time for one of the ambient hydrolysis/pyrolysis runs (Run #5). The zero point for time on this graph corresponds to the point when the organic feed syringe pump was first turned on (in all experiments, the water flow was already established and the reactor filled with water.
Figure 9-1  Effluent Methanol Concentration Profiles As a Function of Experimental Run Time for Ambient Temperature Hydrolysis/Pyrolysis (Run #5). Error bars on measured values indicate 95% confidence intervals. Predicted values are calculated from Eqns. 9-3 and 9-4. All predicted values assume no reaction of methanol.
prior to starting the methanol feed). The predicted steady state concentration value from Eqns. 9-3 and 9-4 for this run was 47.8 ppm (see also Table 9-2). The time required to reach this steady state value was calculated to be about 80 min. The profile of measured values shows that concentration did not rise to a steady state value as sharply as would have been predicted. However, the measured concentration did appear to level off at a steady (though slightly lower) value of 43±1 ppm (Table 9-2) at about the same time as that for the predicted profile. The somewhat sluggish initial response of measured concentration and small steady state offset (~ 10%) compared to that predicted is probably due more to the behavior of the syringe pump at these low organic feed flow rates than to mixing deficiencies in the reactor (see Section 9.3.2). With this fact in mind, the results in Figure 9-1 indicate a reasonably good performance of the reactor with regards to mixing and expected behavior.

9.3.2 Subcritical Temperature Two experiments were performed under essentially the same operating conditions at a subcritical temperature of 331°C (Runs 3 and 4). The purpose of conducting these two identical experiments was to check reproducibility of operating conditions and results. Both experiments were carried out at an average ambient water flow rate of 30.8 mL/min, average residence time of 13.4 min, stirring speed of 500 rpm, and initial concentration of methanol in the reactor of 0.001 M. Although pressure differed slightly (246 bar for Run #3 and 258 bar) for Run #4), this was not an important factor.

Using the procedure described in Section 9.2.2, the heatup time of the reactor was relatively fast. Figure 9-2 shows the variation in fluid temperature in the reactor with time during Run #3, beginning at the point when the heaters were first turned on. Starting at ambient temperature, the final, steady state fluid operating temperature of 331°C was reached after approximately 2 hr. This heatup time is comparable to that normally observed for the fluidized sandbath in the small-scale plug flow reactor system. The profile in Figure 9-2 was typical for all of the present runs
Figure 9-2  Typical Profile of Fluid Temperature in the Reactor As a Function of Experimental Run Time. Data taken from Run #3. The origin of the time axis corresponds to the point when heating of the fluid began.
conducted (including supercritical). Once at steady state, temperature uniformity within the reactor was very good for these subcritical runs, as all five reactor thermocouples were consistently within 0.3°C of each other.

Methanol did not react under the operating conditions of these subcritical experiments. This was again evidenced by a lack of any vapor flow rate, no detection of any gaseous or liquid products in the effluent, and recovery of all of the methanol in the feed. Predicted steady state CH₃OH concentrations in the effluent based on the feed conditions for Runs 3 and 4 (calculated from Eqn. 9-3) are compared to average measured concentrations in Table 9-2. Both runs resulted in the same average effluent methanol concentration (to within statistical uncertainty), confirming the good reproducibility of data with this reactor system.

The primary reason for the higher than predicted methanol concentrations can be seen in Figure 9-3. Here, experimentally measured methanol concentrations from Run #3 are plotted as a function of time. The origin on the time axis in this figure corresponds to the point when heating began. The spike observed near 120 min was due to overpressurization of the syringe pump in an attempt to equilibrate methanol feed line and reactor pressures. This behavior is indicative of the difficulties had in trying to establish a steady methanol flow at feed rates of 1.75 μL/min (see below). After steady state temperature was reached, the change in methanol concentration with time was much smaller, but still consistently and slowly decreased towards the predicted value. Similar behavior was observed in Run #4. Because the drop in concentration over the 4.5 hr time period from where steady state temperature was reached until the end of the run was only 26 ppm, this period was assumed to define that of concentration steady state. The slow but continuous drift of concentration with time, however, suggests that the methanol feed flow may not have been truly constant.
Figure 9-3  Effluent Methanol Concentration Profile As a Function of Experimental Run Time for Subcritical Hydrolysis/Pyrolysis (Run #3). The origin of the time axis corresponds to the point when heating of the fluid began. The predicted steady state value was calculated from Eqn. 9-3 at the given operating conditions for no reaction of methanol. The average measured steady state value listed in Table 9-2 corresponds to all data points after steady state temperature was reached.
This behavior is more understandable when one compares the behavior of the feed line pressure (as measured by the syringe pump) to the reactor pressure over the course of the experiment. Ideally, as the pressure in the reactor undergoes fluctuations, the syringe pump operating in constant flow mode should instantly detect the pressure change and adjust the motion of the piston which provides flow to compensate for the change. If the reactor pressure drops, the syringe pump must decrease pressure in the reservoir to prevent an increase in flow. If reactor pressure increases, the syringe pump must increase reservoir pressure to reopen the check valve in the feed line and prevent a temporary stoppage of flow. At a flow rate of 1.75 μL/min, however, the piston movement is apparently so slow that the pump cannot respond as quickly as is needed to fluctuations in the reactor pressure. This is supported by the observation in Runs 3 and 4 that pressures measured by the syringe pump often took an appreciable amount of time to reequilibrate (e.g. on the order of minutes) when there was a change in reactor pressure. Such behavior would be enough to increase the time necessary to achieve a consistent steady state. This problem was probably exacerbated by the check valve, which provided an increased resistance in the detection and response to reactor pressure changes by the syringe pump. Furthermore, fear of disrupting the methanol flow prevented any attempts to adjust the reactor pressure through the back pressure regulator in order to dampen fluctuations or compensate for any drift over time as would normally otherwise be done.

9.3.3 Supercritical Temperature A single hydrolysis/pyrolysis experiment was performed under supercritical conditions of 443°C and 286 bar (Run #6). The temperature and reactor methanol concentration (0.0026 M) for this run were chosen specifically to match those used in an oxidation run conducted by Phenix (1998) in the small-scale plug flow reactor (Run #682). Other operating conditions for Run #6 included an ambient water flow rate of 31 mL/min, average residence time of 2.8 min, stirring speed of 1000 rpm, and pure methanol feed rate of 22.36 μL/min. Note that the methanol feed rate for this supercritical run was about an order of magnitude greater than
that used in the ambient and subcritical runs to achieve almost the same concentration in the reactor. The reason for this necessary increase in flow was to compensate for the significant drop in water density that occurs in passing through the critical point. From ambient temperature up to 330°C, water density decreases by only a factor of 1.5. From ambient temperature up to 443°C, however, water density decreases by almost a factor of 10, thus requiring the higher flow of methanol to reach the same concentration level. This also explains the higher ambient effluent concentrations of methanol.

Even at a temperature of 443°C and 2.8 min average residence time, no methanol conversion was observed. As in all of the present hydrolysis/pyrolysis runs, there was no vapor effluent flow, no gaseous or liquid products detected in the effluent, and full recovery of all methanol. Table 9-2 shows that the average measured concentration of methanol in the effluent for this run was well within the uncertainty limits of that which would be predicted without reaction (from Eqn. 9-3). These results are consistent with the conclusions of Webley (Tester et al., 1993b; Webley, 1989) and Phenix (1998) that methanol does not decompose in supercritical water in the absence of oxidant. This apparently is true even at the longer residence times of the present study.

Figure 9-4 shows the effluent methanol concentration profile over time in Run #6. The origin on the time axis again represents the point when heating began. The methanol feed was started only a few minutes prior to the start of heating. In contrast to its behavior in the ambient and subcritical temperature runs (Figures 9-1 and 9-3), the methanol concentration reached its expected steady state value much faster in this supercritical run. This first occurred after only about 1 hr. After this point, concentration oscillated randomly above and below the expected steady state value, in a manner more representative of a true steady state than the slow but overall directed change in concentration with time observed in the ambient and subcritical runs. (As an example of this difference, compare Figure 9-4 with Figure 9-3.) The average value of all concentration data
Figure 9-4 Effluent Methanol Concentration Profile As a Function of Experimental Run Time for Supercritical Hydrolysis/Pyrolysis (Run #6). The origin of the time axis corresponds to the point when heating of the fluid began. The predicted steady state value was calculated from Eqn. 9-3 at the given operating conditions for no reaction of methanol. Error bars on measured values indicate 95% confidence intervals. The average measured steady state value listed in Table 9-2 corresponds to all data points after steady state temperature was reached.
points after the time when steady state temperature was reached is the value cited in Table 9-2 as the measured average steady state concentration. This value of 594±22 ppm was very close to the expected value of 586 ppm.

This improvement in concentration response, accuracy, and consistency can be directly connected to the higher methanol feed rate used in this run. At a methanol flow rate of 22.36 μL/min, the syringe pump was able to compensate for reactor pressure fluctuations much faster than it did at a flow rate of 1.75 μL/min in Runs 3 and 4. It was observed during Run #6 that the pressure as measured by the syringe pump tracked the reactor pressure very closely throughout the experiment, with a response time to reactor pressure changes often of only a few seconds. The result was a much more stable methanol concentration in the reactor and effluent over the course of the run, as evidenced by the data in Figure 9-4.

9.4 Oxidation Experiments

9.4.1 Testing of the Oxidant Feed Delivery Methods Before doing any methanol oxidation experiments, a few runs were performed (Runs 7 and 8) to test the performance and reliability of O₂ delivery to the reactor via the O₂/H₂O saturator and H₂O₂ decomposition. Both methods of O₂ delivery were tested in each run and under the same operating conditions to verify reproducibility of results. Each run started with H₂O₂ feed and then switched to feed from the O₂/H₂O saturator. The temperature for these runs was about 330°C with pressure between 246 - 253 bar. A flow rate of 31 mL/min was maintained, to give an average residence time of 13 min. The stirring speed was 500 rpm.

In Run #7, the H₂O₂ feed concentration was 25 ppm, yielding an O₂ concentration of 0.00025 M in the reactor with complete H₂O₂ decomposition. In Run #8, the H₂O₂ feed concentration was increased to 150 ppm, to give an O₂ concentration of 0.0015 M in the reactor with
complete \( \text{H}_2\text{O}_2 \) decomposition. In both runs, an \( \text{O}_2 \) pressure of 40 bar was set for the saturator. This pressure was arbitrarily chosen to generate an \( \text{O}_2 \) concentration and vapor flow about an order of magnitude higher than that generated with the \( \text{H}_2\text{O}_2 \) feed. To see how much time would be needed to achieve equilibrium with this saturator (which is five times larger in volume than that used for the plug flow reactor system), the \( \text{O}_2 \) and \( \text{H}_2\text{O} \) mixture was allowed to recirculate for 15.5 hrs before Run #7 and for 23 hrs before Run #8. Over the course of the longer recirculation time before Run #8, the \( \text{O}_2 \) pressure actually varied between 37 - 41 bar. The \( \text{O}_2 \) saturator pressure in both runs was chosen to generate an aqueous \( \text{O}_2 \) concentration of 0.05 M at equilibrium, and a concentration of 0.03 M in the reactor. The complete tabulation of operating conditions and data for these runs is given in Table 12.4 in the Appendix.

With the \( \text{H}_2\text{O}_2 \) feed, complete decomposition was achieved by the time a fluid temperature of 500°C after the last preheater was reached. This was determined by the lack of detection of any \( \text{H}_2\text{O}_2 \) in the effluent at this point. In Run #7, no gas flow was observed in the bubble column during the \( \text{H}_2\text{O}_2 \) feed. The reason for this is likely that the flow was too low to form a bubble to measure it. Calculations (assuming ideal gas behavior) indicate that for the amount of \( \text{O}_2 \) generated from 25 ppm of \( \text{H}_2\text{O}_2 \) at the given feed flow, a flow rate of \( \text{O}_2 \) gas in the effluent of only 0.3 mL/min would be expected. From prior experience with the plug flow reactor system (which utilizes the same type of bubble column), 0.3 mL/min is right at the limit of detectability of gas flow. With the higher \( \text{H}_2\text{O}_2 \) feed concentration in Run #8, an average \( \text{O}_2 \) gas flow rate of 1.4±0.2 mL/min was measured, which is in good agreement with the expected value of 1.7 mL/min.

With the saturator feeds, the same average steady state gas flow rate of \( \text{O}_2 \) was measured in both runs, demonstrating good reproducibility. This measured flow rate (33±1 mL/min in Run #7 and 32.9±0.6 mL/min) also agreed well with the expected calculated value of 35.9 mL/min (from an \( \text{O}_2 \) saturator pressure of 40 bar). Figure 9-5 shows the measured \( \text{O}_2 \) gas flow rate profile over
Figure 9-5 Profile of the Vapor Effluent (O₂) Flow Rate As a Function of Time for One O₂/H₂O Saturator Test (Run #8). \( P_{sat} \) is the pressure of O₂ gas in the saturator. The dashed lines represent expected flow rate values for indicated value of \( P_{sat} \). Temperature was constant at 330°C for the entire duration of the test.
time for Run #8. The origin on the time axis corresponds to the point when the oxidant feed was switched from H₂O₂ to the saturator. Here one can see that the O₂ flow rate increased quickly and reached a steady state in about 40 min. From this time on until the end of the experiment, the flow rate was consistently in the range expected based on the saturator pressure values experienced during the earlier recirculation/equilibration period. From these results, we conclude that both O₂ feed delivery methods work well and can be relied on to deliver accurate concentrations of O₂ to the reactor.

9.4.2 Subcritical Oxidation Neither Webley (Tester et al., 1993b; Webley, 1989) nor Phenix (1998) conducted any methanol oxidation experiments under subcritical conditions. At the lowest temperature investigated, Webley observed only 0.5% conversion at 453°C and 8.7 s residence time in the main plug flow reactor. With the improvements made to the system (Section 9.1), Phenix observed approximately 30% conversion at his lowest temperature of 420°C and 7 s residence time in the main reactor. As a companion to the subcritical hydrolysis runs in the present study (Runs 3 and 4), and to see once again if the longer residence times capable of being achieved in the CSTR would result in some conversion at these temperatures, one oxidation experiment (Run #9) was performed at 331°C. All operating conditions were essentially the same as that for Runs 3 and 4. Hydrogen peroxide was used as the O₂ source for this experiment. A 150 ppm solution of H₂O₂ was used to generate an O₂ concentration of 0.0015 M of in the reactor after complete decomposition, corresponding to stoichiometric feed conditions relative to the initial CH₃OH concentration of 0.001 M (Eqn. 7-8).

Methanol did not react under the operating conditions of this run, as no carbon-containing products were detected in either the liquid or vapor effluent. Apart from a small amount of N₂, the vapor effluent consisted primarily of O₂ gas. No H₂O₂ was detected in the liquid effluent. Table 9-3 shows that the average measured CH₃OH concentration for this run (after reaching steady state
<table>
<thead>
<tr>
<th>Run #</th>
<th>$T$ ($^\circ$C)</th>
<th>$\tau$ (s)</th>
<th>$[\text{CH}<em>3\text{OH}]</em>{\text{predicted}}$ (ppm)</th>
<th>$[\text{CH}<em>3\text{OH}]</em>{\text{measured}}$ (ppm)</th>
<th>$x$ (%)</th>
<th>$k$ (s$^{-1}$)</th>
<th>Carbon balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>331.2 ± 0.2</td>
<td>800 ± 30</td>
<td>46.2</td>
<td>40 ± 2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>443 ± 2</td>
<td>152 ± 8</td>
<td>604</td>
<td>64 ± 6</td>
<td>89 ± 1</td>
<td>0.055 ± 0.003</td>
<td>106 ± 8</td>
</tr>
<tr>
<td>11</td>
<td>411.4 ± 0.7</td>
<td>158 ± 6</td>
<td>480</td>
<td>194 ± 9</td>
<td>60 ± 5</td>
<td>0.009 ± 0.001</td>
<td>102 ± 7</td>
</tr>
<tr>
<td>12</td>
<td>428 ± 1</td>
<td>158 ± 6</td>
<td>541</td>
<td>93 ± 4</td>
<td>83 ± 2</td>
<td>0.030 ± 0.002</td>
<td>101 ± 7</td>
</tr>
<tr>
<td>13</td>
<td>427.0 ± 0.6</td>
<td>163 ± 5</td>
<td>540</td>
<td>90 ± 3</td>
<td>83 ± 2</td>
<td>0.031 ± 0.001</td>
<td>99 ± 7</td>
</tr>
</tbody>
</table>

* for no reaction

**Table 9-3**  Steady State Values of Methanol Concentration in the Effluent and Kinetic Parameters for Oxidation Experiments. Predicted concentration values are calculated from Eqn. 9-3 and assume no reaction. Measured concentration values are averages of all experimental data points after the listed steady state temperature was achieved. Values of the first-order rate constant, $k$, are calculated from Eqn. 9-5.
temperature) was in fairly close agreement with that predicted by Eqn. 9-3, further verifying that no reaction occurred. The methanol concentration profile over the course of the experiment is shown in Figure 9-6, where the origin on the time axis corresponds to the point when heating began. As with the other subcritical runs, one can see that the low CH₃OH feed flow rate again resulted in a less than ideal steady state behavior.

9.4.3 Supercritical Oxidation Four SCWO experiments were performed at 411, 427, and 443°C (Runs 10 - 13). The temperature, pressure, and initial reactor concentrations in one run (Run #10) were deliberately chosen to duplicate Run #682 conducted by Phenix (1998) in the plug flow reactor system. This was done to explore how well the reactor could reproduce the intrinsic kinetics of methanol oxidation assuming ideal CSTR mixing. A temperature of 443°C, pressure of 270 bar, and initial reactor concentrations of CH₃OH and O₂ of 0.0024 M and 0.0051 M, respectively, were used in both Run #10 and PFR Run #682. Hydrogen peroxide was the O₂ source in both runs, also. These concentrations resulted in superstoichiometric conditions in the reactor, with a [O₂] /[CH₃OH]₀ ratio of 2.1. Run #10 differed from Run #682 only in the effluent flow rate and resulting reactor residence time, with values of 30.8 mL/min and 2.5 min in the CSTR as opposed to 8 s in the small-scale PFR. The operating conditions unique to the CSTR system in Run #10 were a pure methanol flow rate of 22.89 μL/min and a stirring speed of 500 rpm. Run #10 was the oxidation counterpart of the hydrolysis/pyrolysis Run #6.

Runs 11 and 12 were carried out under nominally the same conditions of concentration and average residence time as Run #10 by varying the water/oxidant feed flow rate. Thus, Runs 10 through 12 explored the effect of temperature only on methanol kinetics. Runs 12 and 13 were conducted consecutively on the same day under the same conditions, differing only in stirring speed. These two runs were designed to investigate the effect of mixing speed on kinetics (500 and 1000 rpm), and thus would allow some tentative conclusions to be drawn regarding the mix-
Figure 9-6 Effluent Methanol Concentration Profile As a Function of Experimental Run Time for Subcritical Oxidation (Run #9). The origin of the time axis corresponds to the point when heating of the fluid began. The predicted steady state value was calculated from Eqn. 9-3 at the given operating conditions for no reaction of methanol. Error bars on measured values indicate 95% confidence intervals. The average measured steady state value listed in Table 9-3 corresponds to all data points after steady state temperature was reached.
ing characteristics in the reactor. The complete data set of operating conditions and results from these SCWO experiments is included in Table 12.4 in the Appendix.

Unlike that observed under subcritical oxidation conditions, significant conversion of methanol occurred in all of these SCWO experiments. This is indicated by the fact that steady state methanol concentrations in the effluent were much lower than that which would be expected if no reaction took place (Table 9-3). It is also supported by detection of vapor and liquid effluent products (CO, CO₂, HCHO) consistent with methanol oxidation. All carbon balances were closed to within experimental uncertainty (Table 9-3), verifying not only the identification of all major products but also the accuracy of the pure methanol feed flow and initial concentration after mixing.

The methanol effluent concentration profile over time from Run #10 (Figure 9-7) provides a good indication of when oxidation of methanol begins to occur. With the origin of the time axis corresponding to the point where heating began, the steady state operating temperature of 443°C was reached after about 140 min. The first four data points in Figure 9-7 are labeled with the fluid temperature in the reactor at the time the corresponding liquid effluent samples were taken. With no reaction, a methanol effluent concentration of 604 ppm would have been expected at steady state (calculated from Eqn. 9-3). The data show that reaction begins only after passing the critical point (T > 385°C), where methanol concentrations were first observed to decrease. By 411°C, a methanol conversion of about 60% is indicated, which was verified as the steady state conversion at this operating temperature in Run #11. Upon reaching 443°C, methanol concentrations were consistent at 64±6 ppm, resulting in a conversion of 89%. As shown in Figure 9-7, the concentration behavior once at 443°C and the average concentration value were indicative of a true steady state. This again coincided with the higher methanol feed flow rates needed for achieving the desired reactor concentration at supercritical densities. The steady state behavior seen in all the SCWO runs was typical of that shown in Figure 9-7.
Figure 9-7  Effluent Methanol Concentration Profile As a Function of Experimental Run Time for Supercritical Oxidation (Run #10). The origin of the time axis corresponds to the point when heating of the fluid began. Error bars on measured values indicate 95% confidence intervals. The average measured steady state value (also listed in Table 9-3) corresponds to all data points after steady state temperature was reached. Temperatures indicated are those measured for the fluid in the reactor at the given time.
The methanol effluent concentration profile over time for the two runs which probed the effect of stirring speed (Runs 12 and 13) is displayed in Figure 9-8. Run #12 was conducted with a stirring speed of 500 rpm, while Run 13 had a stirring speed of 1000 rpm. All other operating conditions for the two runs were exactly the same or at least within experimental uncertainty of each other. The results show that doubling the stirring speed had no apparent effect on the methanol concentration and its oxidation kinetics. Note in Figure 9-8 that the steady state concentration behavior over both runs shows no clear response (above the normal background variance in the data points) due to the change in stirring speeds. Although the average steady state concentration for Run #13 (90±3 ppm) was slightly less than that of Run #12 (93±4), the difference was not statistically significant. The same can be said for the resulting conversion values (both 83±2%). The only difference to note between these two runs was that the maximum difference in temperature among the five reactor thermocouples was less at 1000 rpm than at 500 rpm. In Run #12, this \( \Delta T \) among the thermocouples was about 2.3°C, while for Run #13 the \( \Delta T \) was about 1.3°C, resulting in an average reactor temperature for Run #13 with slightly less uncertainty.

Assuming first-order kinetics for methanol oxidation, and that well-mixed conditions existed within the CSTR during these experiments, the design equation given in Eqn. 8-1 can be written as follows:

\[
k\tau = \frac{x}{1-x}
\]

(9-5)

where \( k \) is the first-order rate constant, \( \tau \) is the average residence time, and \( x \) is the conversion. A first-order global rate expression (first-order in \( \text{CH}_3\text{OH} \), zero-order in \( \text{O}_2 \)) was determined by Webley and coworkers (Tester et al., 1993b) from nonlinear regression of their SCWO methanol data taken with the plug flow reactor. The later data of Phenix (1998) is also consistent with first-order kinetics for SCWO of methanol. Thus, the use of first-order kinetics here is certainly reasonable. Eqn. 9-5 was used to determine values of the rate constant from the experimental CSTR data (see
Figure 9-8  Comparison of the Effect of Stirring Speed on Effluent Methanol Concentration over Time in Consecutive Supercritical Oxidation Experiments (Runs 12 & 13). Stirring speeds: Run#12 = 500 rpm; Run #13 = 1000 rpm. The origin of the time axis corresponds to the point when heating of the fluid began. Error bars on concentration data points indicate 95% confidence intervals. The average measured steady state values (also listed in Table 9-3) correspond to all data points for Run #13, and all data points after steady state temperature was reached for Run #12.
Table 9-3), and were used to formulate the Arrhenius plot of Figure 9-9. A linear fit approximates the data fairly well, and gives the following Arrhenius expression for the methanol first-order rate constant:

$$k = A e^{-\frac{E_a}{RT}} = \left(10^{15.6 \pm 0.7}\right) e^{-\frac{230 \pm 140}{RT}}$$

(9-6)

where the units of the activation energy, $E_a$, and the pre-exponential factor, $A$, are kJ/mol and s$^{-1}$, respectively. Uncertainty values cited for the kinetic parameters in Eqn. 9-6 represent 95% confidence intervals. The fact that these uncertainty values are somewhat high is primarily because the fitted parameter values are based on only four data points (i.e. two degrees of freedom for the linear fit).

The products of methanol oxidation detected in the vapor phase were CO and CO$_2$. The only product detected in the liquid phase was formaldehyde. CO and CO$_2$ were clearly the major products, with HCHO accounting for $\leq 7\%$ of the carbon balance. Both Webley and coworkers (Tester et al., 1993b) and Phenix (1998) detected CO and CO$_2$. Webley also detected small amounts of H$_2$ in the vapor phase, which were not detected by Phenix or in the present study. The kinetics of H$_2$ oxidation determined by Holgate and Tester (1993) suggest that some H$_2$ should have been detected at the temperatures employed in our study if it were present. Although Webley did not find any HCHO (to a detection limit of 5 ppm), Phenix did detect small concentrations of HCHO consistent with that of the present study. Product concentration data are shown in Figure 9-10 as a plot of molar yield versus temperature. The data clearly show that CO$_2$ increases with increasing temperature at the expense of CO and HCHO, as would be expected.

**9.4.4 Comparison of CSTR Results to Earlier PFR Data** Comparison of the present data gathered with the CSTR system to the earlier data of Webley and coworkers (Tester et al.,
Figure 9-9  Arrhenius Plot for Methanol Oxidation in Supercritical Water from CSTR Data. Rate constants are first-order, and calculated from Eqn. 9-5. Error bars indicate 95% confidence intervals.
Figure 9-10  Molar Yield of Methanol Oxidation Products As a Function of Temperature.
1993b; Webley, 1989) and Phenix (1998) allows us to assess the validity and accuracy of the latest methanol data in particular, and the CSTR system operation in general. As noted in the previous section, Run #10 had the same operating conditions as Run #682 performed by Phenix in the plug flow reactor, except for the difference in residence time. The 8 s residence time of Run #682 at 443°C and 269 bar resulted in a methanol conversion of 39.6%. In order to extrapolate up to the 2.5 min average residence time in the CSTR, an Arrhenius expression for the first-order rate constant had to first be fit to the data of Phenix.

The methanol data set of Phenix used to determine the Arrhenius expression consisted of the 17 data points gathered as part of the joint MIT/Sandia National Laboratory methanol study mentioned earlier (Section 9.1). This data set spanned a temperature range of 423 - 485°C, all at the same pressure and main reactor residence time of 269 bar and 8 s, respectively. All were conducted at superstoichiometric $[O_2]/[\text{CH}_3\text{OH}]_0$ feed ratios of 1.9 - 2.8. Hydrogen peroxide was the O$_2$ source for most of these experiments, but three utilized a feed from the O$_2$/H$_2$O saturator. Methanol feed concentrations ranged from 0.011 - 0.39 wt%. Values of the first-order rate constant were calculated from the data via Eqn. 3-15 and are displayed in the Arrhenius plot of Figure 9-11. The linear best-fit shown corresponds to the following Arrhenius expression:

$$k_{\text{PFR, Phenix}} = \left(10^{12.3 \pm 2.1}\right) e^{\left(\frac{183 \pm 30}{RT}\right)}$$  \hspace{1cm} (9-7)

where the activation energy has units of kJ/mol, $k$ has units of s$^{-1}$, and uncertainty values represent 95% confidence intervals. At 443°C, Eqn. 9-7 yields a rate constant value of 0.09 s$^{-1}$. Use of this PFR-derived value for the rate constant in the CSTR design equation (Eqn. 9-5) along with a value for $\tau$ of 2.5 min results in a predicted conversion in the CSTR of 93%. This is in remarkably good agreement with the experimentally determined CSTR conversion value for Run #10 of 89%. Note
Figure 9-11: Arrhenius Plot for Methanol Oxidation in Supercritical Water from PFR Data of Phenix (1998). Rate constants are first-order, and calculated from Eqn. 3-15. Solid best-fit line is given by Eqn. 9-7. Dotted lines represent 95% confidence intervals.
that the activation energy value derived from the CSTR data (Eqn. 9-6) is within experimental uncertainty of that derived from the PFR in Eqn. 9-7, differing by only 47 kJ/mol.

The first-order Arrhenius expression for the rate constant determined by Webley and co-workers from their data (Tester et al., 1993b) is:

\[ k_{PFR, Webley} = 10^{26.2 \pm 5.8} \exp\left(-\frac{408.8 \pm 85.4}{R_\tau}\right) \]  

(9-8)

where the activation energy again has units of kJ/mol, \( k \) has units of s\(^{-1}\), and uncertainty values represent 95% confidence intervals. Webley did not conduct any methanol experiments in the temperature range of 411 - 443°C. The lowest temperature at which oxidation experiments were conducted was 453°C. At this temperature, a main reactor residence time of 8.7 s, and CH\(_3\)OH and O\(_2\) feed concentrations of 2.76 mM and 2.47 mM, respectively, he observed a conversion of only 0.5%. Nevertheless, if Eqn. 9-8 is used to determine a value for the first-order rate constant at 443°C and then inserted into Eqn. 9-5 to predict a CSTR conversion for \( \tau = 2.5 \) min, values of 0.0002 s\(^{-1}\) and 3.6% result. These values are much lower than either that observed experimentally with the CSTR or predicted using the Arrhenius expression of Phenix (Eqn. 9-7), likely due to the higher activation energy in Webley’s expression (Eqn. 9-8).

Table 9-4 compares measured conversion and rate constant data from the CSTR (Runs 10 - 13) with that calculated for the CSTR using the PFR derived rate constant expressions of Eqns. 9-7 and 9-8 as described above. Although the experimental values for Runs 11 - 13 are not as close to those predicted using the Phenix expression as they are for Run #10, they are still in much better agreement overall with the predicted values from the Phenix expression than the Webley expression. This trend is further expressed in the Arrhenius plot shown in Figure 9-12. Here the CSTR experimental data from Figure 9-9 is replotted, along with the Phenix and Webley expressions of
Table 9-4  Comparison of Experimental and PFR-Derived Methanol Kinetics in the CSTR. All rate constants are first-order. For CSTR experimental data, $k$ is calculated from Eqn. 9-5 using the measured conversion. Calculated values of rate constants are from expressions determined from PFR experiments of Phenix (Eqn. 9-7) or Webley (Eqn. 9-8). All calculated values of conversion are from Eqn. 9-5 using the appropriate calculated rate constant.
Figure 9-12  Comparison of CSTR and PFR Arrhenius Plots for Oxidation of Methanol in Supercritical Water. CSTR data and linear best-fit is from the present study (also shown in Figure 9-9). Arrhenius expressions of Phenix (1998) and Webley (Tester et al., 1993b) were derived from earlier data taken in the MIT plug flow reactor system, and given in Eqn. 9-7 and 9-8, respectively. All rate constants are first-order.
Eqns. 9-7 and 9-8 for comparison. Figure 9-12 clearly shows that the CSTR data is in accord with that predicted by the data of Phenix, but not by that of Webley.

Based on the results of this comparison and the fact that the methanol data of Phenix is more recent and better characterized (as discussed in Section 9.1) than that of Webley, the overall close agreement between the methanol CSTR data of this study and the PFR data of Phenix suggests that the well-stirred assumption is valid and that the CSTR system as configured is capable of generating reliable kinetic data. In a complementary manner, the present CSTR data appear to validate the improvements made to the PFR system by Phenix. Despite these promising results, however, one must remember that definitive proof that the CSTR is truly functioning as a well-stirred reactor can only be obtained from a residence time distribution study.

9.5 Critical Analysis of Reactor Performance Issues The initial testing and methanol experiments performed with the CSTR provided many opportunities to explore some of the key reactor operating and design parameters which will be important for present and future experiments.

9.5.1 Isothermality As noted earlier, there were no problems noticed with heatup or temperature stability once reaching steady state in any of the testing or experiments performed. The fact that the reactor heater temperature was controlled rather than the reactor fluid temperature, however, made it difficult at times to pinpoint a precise fluid temperature quickly. Temperature uniformity within the reactor was generally good, but differed depending on whether the fluid temperature was above or below the critical point. At temperatures below the critical point, all five reactor thermocouples were in very good agreement, varying among each other by < 1°C. Above the critical point, the thermocouples appeared to show a slight thermal gradient, decreasing from the bottom of the reactor to the top. Table 9-5 compares average steady state temperatures from the
<table>
<thead>
<tr>
<th>Thermocouple (identified by reactor port)</th>
<th>Approximate distance from bottom of reactor (cm)</th>
<th>Temperature (°C) Run #9</th>
<th>Temperature (°C) Run #10</th>
</tr>
</thead>
<tbody>
<tr>
<td>top (thermowell)</td>
<td>12.7</td>
<td>331.4 ± 0.1</td>
<td>441.5 ± 0.2</td>
</tr>
<tr>
<td>side port; front left</td>
<td>11.4</td>
<td>331.0 ± 0.2</td>
<td>441.2 ± 0.2</td>
</tr>
<tr>
<td>side port; back right</td>
<td>9.5</td>
<td>331.4 ± 0.1</td>
<td>443.1 ± 0.2</td>
</tr>
<tr>
<td>side port; front right</td>
<td>8.9</td>
<td>331.0 ± 0.1</td>
<td>442.8 ± 0.3</td>
</tr>
<tr>
<td>bottom</td>
<td>1.9</td>
<td>331.2 ± 0.1</td>
<td>444.4 ± 0.3</td>
</tr>
</tbody>
</table>

Table 9-5  **Comparison of Reactor Thermocouple Measurements at Subcritical and Supercritical Temperatures.** See Section 9.2.1 for description of thermocouple placement.

five thermocouples for Runs 9 and 10. The thermocouples are listed in order of the height in the reactor at which the temperature is measured. Note that for the subcritical Run #9, temperatures differed by only 0.4°C, while the supercritical Run #10 temperatures differed by 2.9°C.

There are two possible explanations for this gradient formation. One has to do with the current reactor setup and constraints of operation. As described in Section 8.3.3, the magnets which rotate the stirring rod must always be kept below 150°C during operation. This is achieved by a constant flow of cooling water around the stirring rod housing just above the point where the top effluent fluid port exits. This cooling constraint clearly provides a continuous thermal sink at the top of the reactor increasing conductive heat loss. In the current setup, the hottest part of the reactor was at the bottom, because the feed water (usually preheated above the desired reactor temperature) entered there. Thus the present temperature data is consistent with a decreasing thermal gradient forming from the bottom to the top of the reactor. The second explanation for the observed temperature variance (which would explain the importance of the critical point) is a possible
decrease in fluid mixing efficiency that may occur with the sudden decrease in density above the critical point.

At the present time, it is not clear which one (or both) of the above explanations accounts for all of the temperature related facts observed. If the problem is purely a result of conductive heat loss imposed by the current reactor configuration, one would expect to resolve the problem by changing the entry port of the water feed, and/or providing additional heating near the top of the reactor chamber to counteract the effect of the magnet cooling water. One would also expect an increasing thermal gradient at higher reactor temperatures. Although there are indications that the gradient may indeed be a little higher near 500°C, heating tape placed around the top of the reactor but below the point of cooling failed to make any significant change, decreasing the gradient by at most 0.5°C. If the problem is purely due to mixing, one would expect higher stirring speeds or a different size or number of impellers to eliminate the gradient. Although higher speeds did result in a smaller observed temperature gradient, they did not eliminate it entirely, and speeds above 1500 rpm resulted in no further improvement. These results were obtained using the single, 4.4 cm, pitched blade (up) propeller. Use of the smaller, 3.2 cm, pitched blade (down) propeller resulted in no significant change. Multiple impeller use was not attempted, but may be helpful.

Because the observed gradient is not that severe and the overall thermal stability in the reactor is still very good, the thermocouple variance may not be as big a problem as it may first appear. However, it would be useful to conclusively identify and correct the source of the problem in case it does become an important issue under more extreme operating conditions.

9.5.2 Organic Feed Performance  As already noted earlier, methanol effluent concentrations in the supercritical runs reached steady state rapidly and were very stable on average over time. The good carbon balances and/or methanol recovery in the effluent of these runs indicate that the
correct amount of pure methanol feed was delivered to the reactor. The fact that steady state was not achieved as quickly and was not quite as stable in the subcritical runs as in the supercritical runs appears to be mostly due to the lower methanol flow rates used, and possibly compounded by the presence of the check valve (see Section 9.3.2). Therefore, the present configuration may best be used in future subcritical runs for reactor organic concentrations higher than 0.001 M. However, because the feed line is primed with methanol as part of the normal startup procedure, the presence of the check valve originally intended for preventing backflow of water to the syringe pump is probably not necessary. It could thus be easily removed for possibly better results at lower flow rates.

9.5.3 Stirring Mechanism and Lower Bearing For most of the testing and experiments, the MagneDrive unit ran smoothly and without any problems. After approximately 100 hr of use, however, a grinding noise was noticed, which suggested that something was out of tolerance. The noise rapidly became louder until the point where the unit could no longer be operated. Inspection after disassembly of the MagneDrive unit revealed significant erosion of the Inconel stirring rod shaft by the lower zirconia bearing. A gap of 0.041 cm (0.016") between the shaft and lower bearing was measured. This was much larger than the manufacturer’s maximum tolerance of 0.005 - 0.008 cm (0.002 - 0.003").

The MagneDrive was returned to the manufacturer (Autoclave Engineers, Inc.) for realignment of the shaft and replacement of all bearings. In the process, it was also discovered that the outer diameter of the zirconia bearing had apparently expanded during use and wedged itself against the wall of the cylindrical housing enclosing the bearings and shaft. Before installing the new zirconia bearing, an Inconel sleeve was machined to fit around the outer diameter to allow for future ease of removal. After discussion with Autoclave Engineers on how to best solve the erosion problem, it was agreed to chrome plate the section of the shaft in contact with the zirconia
bearing. The much harder chrome surface should provide increased resistance to erosion, but it is not known by how much more. These repairs returned the MagneDrive unit back to normal, and in followup runs (#11 - 13), no further noise or bearing problems were encountered. This experience suggests, however, that the unit will require regular maintenance in the future. If rapid shaft erosion occurs again, a different plating material or even an altogether different bearing material or design may be necessary.
1. **Hydrolysis and Oxidation of Acetic Acid** Hydrolysis/pyrolysis and oxidation kinetics of acetic acid in supercritical water have been investigated in the small-scale, plug flow tubular reactor system. Operating conditions ranged from 425 - 600°C, 160 - 263 bar, and 3.7 - 9.8 s residence time in the main reactor. Initial concentrations of acetic acid and oxygen ranged from 0.1 - 2 mM and 1 - 4 mM, respectively, and sub- to superstoichiometric feed ratios were explored. The refractory nature commonly attributed to acetic acid was confirmed under both hydrolysis/pyrolysis and oxidation conditions below 500°C. Above this temperature, however, acetic acid does undergo increasingly significant reaction, with complete conversion under oxidation conditions observed at 550°C, 246 bar, and 8 s residence time. Hydrolysis/pyrolysis conversions were always much less than the corresponding oxidation conversions, with a maximum hydrolysis/pyrolysis conversion of 35% observed at 600°C, 246 bar, and 8 s residence time.

Nonlinear regression of the oxidation data resulted in a global oxidation rate expression which is 0.72±0.15 order in CH₃COOH and 0.27±0.15 order in O₂, with an activation energy of 168±21 kJ/mol and pre-exponential factor of $10^{9.9±1.7}$ mol$^{0.01}$/L$^{0.01}$/s. Regression of the hydrolysis/pyrolysis data assuming a first-order reaction yielded a global hydrolysis/pyrolysis rate expression with an activation energy of 94±17 kJ/mol and pre-exponential factor of $10^{4.4±1.1}$ s$^{-1}$. The major products of acetic acid destruction under oxidation and hydrolysis/pyrolysis conditions were CO₂, CO, CH₄, and H₂. In general, more CO₂ and CO and less CH₄ and H₂ were observed in oxidation experiments as opposed to hydrolysis/pyrolysis experiments.
2. Hydrolysis and Oxidation of Methylene Chloride  Hydrolysis and oxidation kinetics of methylene chloride in sub- and supercritical water have been investigated in the plug flow tubular reactor system. Operating conditions over the preheater and main reactor tubing ranged from 25 - 600°C and 13 - 23 s total residence time, all at 246 bar. Stoichiometric and superstoichiometric \( \text{O}_2/\text{CH}_2\text{Cl}_2 \) feed ratios were explored. Measured \( \text{CH}_2\text{Cl}_2 \) conversion varied from 26 - 91% in pure hydrolysis experiments, and from 30 - 99.9% in oxidation experiments.

Unlike that observed in previous model compounds studied, hydrolysis conversion of \( \text{CH}_2\text{Cl}_2 \) was significant, and comparable to that observed in oxidation experiments at sandbath temperatures below 525°C. Severe corrosion was experienced in the preheater tubing due to HCl formation from subcritical hydrolysis, resulting in through-wall failure of four separate tubes over the course of the experiments. Failures occurred after a period of 45 - 104 hrs of use, at a location 7 - 29 cm downstream of the point where heating began. Experiments performed with the main reactor removed (i.e., with just the preheater) revealed essentially no change in conversion relative to that measured with the reactor in place. The bulk of the experimental evidence indicated that most \( \text{CH}_2\text{Cl}_2 \) hydrolysis occurred under subcritical temperatures in the preheater, with little or no further hydrolysis occurring in the supercritical main reactor.

Heat Transfer and Temperature Profile Modeling  Because of the significant hydrolysis in the nonisothermal preheater, a heat transfer model was used to calculate the temperature-time history of the feed in the preheater for each run. Several empirical heat transfer correlations for sub- and supercritical water from the literature were evaluated and used in the model. They account for a number of important phenomena including geometric and flow regime effects, the coupling of forced and free convection, and the unique behavior of water near its critical point. Calculated residence times in the preheater tubing ranged from 7 - 17 s. The results of the model agreed well with experimental findings, explaining the apparent insensitivity of \( \text{CH}_2\text{Cl}_2 \) degradation to sandbath tem-
perature from 450 to 500°C. The model also predicted high but subcritical temperatures in the region of the preheater tubing where corrosion was observed.

*Hydrolysis Kinetics and Solvent Effects*  The calculated temperature-time profiles were used to model CH₂Cl₂ hydrolysis kinetics. The observed substantial decrease in the apparent hydrolysis reaction rate upon heating from subcritical to supercritical temperatures could not be explained by normal Arrhenius behavior for a single reaction. A satisfying explanation was found by accounting for the changing nature of the water solvent environment as temperature increases. The significant decrease in solvent polarity near the critical point and beyond results in a reduced ability to stabilize the polar hydrolysis transition state complex, and consequently a slower reaction rate relative to that in subcritical liquid water.

A combination of Kirkwood theory and *ab initio* calculations provided an effective framework and the necessary microscopic parameters to successfully describe this behavior both qualitatively and quantitatively. *Ab initio* predicted stereochemistry and physical properties of the CH₂Cl₂ and H₂O reactants and their transition state were consistent with expectations. The results also showed that increases in the activation energy and a changing reaction profile with a decreasing dielectric constant of the medium provide a mechanism for reducing the reaction rate constant at higher temperatures by as much as three orders of magnitude. These solvent effects were captured quantitatively in a correction factor to the Arrhenius form of the rate constant. The *ab initio*-based correction factor was incorporated into a global hydrolysis rate expression, which provided good predictions of the experimental data over the entire range of sandbath temperatures explored. The rate expression is first-order in H₂O and 1.5±0.67 order in CH₂Cl₂, and has an ambient activation energy and pre-exponential factor of 210±40 kJ/mol and 10^{16.5±0.6} L^{1.5}/(mol^{1.5} s), respectively - all determined via nonlinear regression of the hydrolysis data against the corrected Arrhenius model.
An alternative rate expression first-order in both reactants has an activation energy and pre-exponential factor of $180\pm14$ kJ/mol and $10^{12.9\pm1.0}$ L/(mol s), respectively.

**Oxidation Kinetics** The presence of $O_2$ had no statistically significant effect on $CH_2Cl_2$ decomposition below sandbath temperatures of 525°C. $CH_2Cl_2$ oxidation did become important above this temperature, and resulted in complete conversion by 563°C. Variation of initial $O_2$ feed concentrations from 0.6 to 2.1 mM at 550°C, however, had no effect on the $CH_2Cl_2$ conversion. A global oxidation rate expression was determined from nonlinear regression of the data after subtracting contributions from hydrolysis. The most reliable global rate expression was zero-order in $O_2$ and 0.14±0.30 order in $CH_2Cl_2$, with an activation energy and pre-exponential factor of $673\pm25$ kJ/mol and $10^{18.8\pm1.5}$ mol$^{0.86}$/L$^{0.86}$/s, respectively. The overall accuracy is suspect, however, due to the fact that the main reactor feed during oxidation consisted of a mixture of unhydrolyzed $CH_2Cl_2$ and its products from the extensive subcritical hydrolysis in the preheater.

**Product Distribution and Reaction Network/Pathways** The product spectrum, yields, and distribution for $CH_2Cl_2$ hydrolysis and oxidation reactions have been measured and analyzed. This was done to identify and prioritize likely reaction pathways for formation and destruction of all species observed, and to assess their relative importance. The products detected were HCHO, HCl, CO, $H_2$, $CH_3OH$, and $CO_2$, with trace amounts of $CH_4$, $CH_3Cl$, and other one- and two-carbon chlorinated hydrocarbons in the vapor phase.

A complete reaction network for $CH_2Cl_2$ and its products under hydrolysis conditions was developed using the experimental data and evidence from the literature. The main route deduced for $CH_2Cl_2$ breakdown was via subcritical hydrolysis to formaldehyde and HCl, followed by decomposition of formaldehyde to CO and $H_2$, and subsequent CO conversion to $CO_2$ and $H_2$ by the water gas shift reaction. A combination of lesser reactions involving HCHO reduction, $CH_2Cl_2$
reduction, and CH₃Cl hydrolysis likely accounted for the formation of CH₃OH, CH₄, and the other trace compounds. Separate batch experiments confirmed that Hastelloy C-276 exhibited no surface effects on CH₂Cl₂ hydrolysis.

In the presence of O₂, oxidation of HCHO, CO, H₂, and CH₃OH was significant, while CH₂Cl₂ and the chlorinated hydrocarbons exhibited no oxidation conversion below 525 - 550°C. By 600°C and a 6 s residence time under oxidation conditions, however, CO₂ and HCl were the only products observed, signifying complete destruction of all other compounds (> 99.99% of total carbon) under these conditions.

3. Design and Construction of New SCWO Research-Scale Reactors Two new reactor systems were designed in order to: (1) improve on limitations associated with the existing plug flow reactor system, and (2) increase overall flexibility in the operating conditions accessible and the types of experiments that could be run. The vessels designed were a stirred tank reactor (CSTR) and a large-scale tubular reactor. The stirred tank reactor has a volume of 637 mL and an internal diameter of 7.6 cm. It can operate up to 650°C and 345 bar in batch or continuous feed mode, and has a magnetically driven stirring rod with a maximum rotational rate of 2500 rpm. It has several custom options included in the design, such as multiple access ports, the capability of jet mixing or accommodating a spinning basket for solids containment, and a lower stirring rod bearing made of zirconia.

The complete CSTR system, which was also constructed as part of this work, allows for direct injection of pure organic feed into the reactor, multiple means of oxidant delivery, and an increased flow capacity up to 200 mL/min. The system has been designed for a number of experimental applications, including SCWO in the presence of solids (contaminated soils or precipitating salts), exploring the effects of higher organic or oxidant concentrations, and studying physi-
cal phenomena such as fluid mechanical mixing as well as heat and mass transfer in supercritical water, to name a few.

The large-scale tubular reactor was entirely custom designed. The reactor tube has an ID of 5.1 cm and is 46 cm long. Its distinguishing features are a cell block which provides optical access, and a movable sample probe which can take multiple fluid samples at any axial position of the tube during operation under pressure (up to 300 bar). Because of the large diameter and practical limitations on mass flow rates, it is likely to be run as a laminar flow reactor. Intended experimental applications include *in situ* measurement of stable and unstable species via spectroscopy, and measurement of concentration profiles as a function of axial position (corresponding to residence time) using the movable probe under a uniform set of experimental operating conditions.

4. **Hydrolysis and Oxidation of Methanol Using the CSTR System** To test and verify the performance of the new CSTR system, hydrolysis/pyrolysis and oxidation experiments in sub- and supercritical water were conducted with the previously well studied compound, methanol. Operating conditions ranged from 25 - 443°C, 238 - 286 bar, water flow rates of 30 - 50 mL/min, pure methanol flow rates of 1.75 - 23 μL/min, average residence times of 2.5 - 20 min, and stirring speeds of 500 - 1000 rpm. Initial reactor concentrations of CH$_3$OH and O$_2$ after mixing were 1 - 2.6 mM and 1.5 - 5.3 mM, respectively, resulting in stoichiometric and superstoichiometric conditions. All system feed, heating, and stirring components functioned reasonably well. Steady state methanol concentrations were achieved faster and were more stable in the supercritical experiments, where larger methanol feed rates resulted in better syringe pump operation.

No CH$_3$OH decomposition was observed under hydrolysis/pyrolysis conditions at any temperature, or at subcritical temperatures in the presence of O$_2$. Oxidation of methanol readily occurred at all supercritical temperatures explored. A first-order global oxidation rate expression
with an activation energy of 230 kJ/mol and pre-exponential factor of $10^{15.6}$ s$^{-1}$ was developed from the data. Kinetic results were in good agreement with recent data gathered on our plug flow reactor system, suggesting that the assumption that the reactor volume was well-stirred was reasonable. Products detected (CO, CO$_2$, and HCHO) and their associated trends also were in agreement with the PFR data. Based on the overall results of these experiments, we conclude that after a residence time distribution study to properly assess/confirm mixing conditions, the system will be ready for general use in kinetics experiments and other proposed applications.
Chapter 11

Recommendations

The results of the work comprising this thesis have led to the following recommendations for future work, which are enumerated below:

1. **Refine modeling of solvation effects on CH$_2$Cl$_2$ hydrolysis kinetics.** As discussed in Section 6.9, the Kirkwood model used to calculate solvation energies and identify the transition state location contains a number of approximations. These include the treatment of all molecules as spheres, the unrealistically sharp transition in dielectric constant to the bulk value outside the molecular boundary, and the failure to account for the effects of higher order multipoles in regions near the solute boundary. Because the solvation energy strongly influences the reaction profile, these assumptions could have a significant impact on the calculation of the hydrolysis activation energy and resulting kinetics, and may account for some of the small remaining discrepancies with the experimental data noted.

Currently, work in our group and the Division of Condensed Matter in the Department of Physics has focused on relaxing these assumptions in Kirkwood theory. Specific work already underway includes using a more realistic geometric shape for each species and a smoothly varying function for the dielectric electric constant outside the solute boundary. Molecular dynamics simulations are also being conducted to determine the energetic effects of large numbers of individual water molecules interacting with the *ab initio* charge potential of CH$_2$Cl$_2$. These latter simulations will allow one to compute solvent-solute interaction effects directly without treating the solve.it as a dielectric continuum with a single bulk value everywhere. From such simulations, one would
hope to develop more accurate dielectric continuum models, which could be incorporated into the
*ab initio* code to calculate the species solvation energy directly. This approach should yield more
accurate results and eliminate the need for Kirkwood theory and its constraints altogether.

In addition, *ab initio* study of the second step (Eqn. 6-2) of the two stage hydrolysis reaction
mechanism would be helpful in elucidating the significance of the energy maxima and minima
disappearance in the reaction profiles above 386°C. By combining these results with those of the
present study, one will have a more complete picture of the reaction phase space, which should
allow one to determine whether the reaction rate indeed becomes zero near the critical point or
transforms to another mechanism or pathway. In either case, the answer to this question will en-
able one to better model the reaction in the supercritical region above 386°C.

2. **Conduct isothermal measurements of CH₂Cl₂ hydrolysis kinetics in the near
critical temperature region.** The present CH₂Cl₂ data gathered with the plug flow reactor
system indicated minimal or negligible hydrolysis at the supercritical temperatures in the main re-
actor. Batch experiments on CH₂Cl₂ hydrolysis from 100 - 250°C showed normal, first-order
Arrhenius behavior. The transition in the nature of the reaction must therefore occur over some
region between 250 - 450°C where no experimental data has been directly obtained yet. Kirkwood
theory and the *ab initio* calculations performed all predicted the most substantial changes in the
water solvent properties (and thus the hydrolysis reaction behavior), to occur roughly between 380
and 420°C (based on the magnitude of the dielectric constant and Kirkwood correction factor).
Isothermal batch data over the range of 250 - 450°C would be useful not only in verifying the *ab
initio* predicted behavior, but also in defining the maximum temperature range over which a simple
Arrhenius rate expression (such as that by Fells and Moelwyn-Hughes (1958)) would be applica-
ble.
In order to ensure true isothermal reaction conditions without the complications of preheating effects, it will be necessary to devise a means to accurately inject a known amount of CH$_2$Cl$_2$ feed into an already heated batch reactor. One possibility would be to use the CSTR system (described in Chapters 8 and 9) with its delivery method of pure, unheated organic feed to the reactor via syringe pump. Such a method could also be used to gather more accurate CH$_2$Cl$_2$ oxidation data as well, because the feed will not contain hydrolysis reaction products competing for O$_2$.

3. **Perform residence time distribution studies on the CSTR.** The evaluation of mixing time correlations for liquids and the good agreement of methanol oxidation results with that of previous studies both suggest that well-stirred conditions can be achieved in the new stirred tank reactor. However, the only way one can be sure of this fact is if the signature exponential decay profile associated with ideal mixing is observed in residence time distribution measurements. For this reason, residence time distribution studies should be the very next work performed with the CSTR system, so that kinetic data gathered in future experiments can be properly analyzed. For these tests, a compound that can function as an inert tracer under SCWO operating conditions would be required. As shown by the present experimental results, methanol in the absence of O$_2$ could fulfill this role and would be a good choice. Additional candidates include CO$_2$, a salt such as NaCl, or any other refractory organic compound under the conditions of interest. The choice of tracer will likely be guided by the availability of an appropriate analytical detector that can be installed online for constant monitoring of concentration profiles. Residence time distribution studies should be performed under a variety of likely operating temperatures and stirring speeds.

In addition to the residence time distribution studies, several other issues should be addressed to improve or further explore system performance. The cause of the slight thermal gradient observed at supercritical temperatures should be conclusively determined and eliminated or minimized as much as possible, especially if it is found to be significant at higher temperatures.
The check valve on the organic feed line should be removed to see if concentration profiles become more stable at low organic flow rates. The gas/liquid separator needs to be enlarged to prevent entrainment of liquid in the vapor effluent line at flow rates larger than 80 mL/min. Finally, the already purchased components for direct O₂ injection can be assembled, in the event that high feed concentrations of O₂ may be desired in the future.

4. **Finish construction, and begin testing and operation of the large-scale tubular reactor system.** At present, design and assembly of the necessary peripheral components is near completion. As was done with the CSTR system, tests with water should be performed first to verify proper operation of all components. SCWO experiments with a previously studied compound such as methanol should then be conducted, in order to evaluate the system's ability to produce reliable data and to determine standard operating procedures. Of particular interest will be the functioning of the movable sample probe for generating concentration profiles, and the optical cell for allowing *in situ* concentration measurements via Raman spectroscopy.

5. **Continue to explore the SCWO kinetics of new model compounds.** Further expansion of the SCWO kinetics data base should be carried out through the study of additional model compounds of interest. The information gained from these studies regarding reaction rates, mechanisms of destruction, product species formed, and the occurrence of any unique phenomena such as corrosion is critical in enhancing the overall understanding of the SCWO process. The accumulated knowledge can in turn lead to better and more efficient designs of large-scale systems for waste destruction.

At the present time, there are several good candidates for model compounds. Benzene, the first aromatic compound to be looked at by our group, is already being studied in the plug flow reactor system. Toluene, another common industrial waste and environmental contaminant, would
be one logical choice to follow benzene in the study of aromatic compounds of interest. Hydrolysis and oxidation experiments with formaldehyde would be useful for further clarification of the reaction network of CH₂Cl₂. For heteroatom-containing compounds, trichloroethylene has been proposed as another good representative of a chlorinated environmental contaminant. Of particular importance to the destruction of chemical weapon agents would be the further study of organophosphorus and organosulfur compounds. Complex organic mixtures should also be tested.

In addition to liquid or aqueous organic model compounds, experiments can now be conducted with solids or simulated contaminated soils in the CSTR. In choosing model soil components, it would probably be best to start with chemically simple materials before working up to more complex minerals. Candidate materials could also include EPA synthetic soil matrices.
12.1 Tabulated Methylene Chloride Experimental Data  The following tables contain numerical data from the present study of hydrolysis and oxidation of methylene chloride in sub- and supercritical water. All data were gathered using the plug flow reactor system described in Chapters 3 and 4. Calculated values for preheater residence time and CH₂Cl₂ concentration at the entrance to the main reactor are also included in the tables. Preheater residence times have been calculated from the heat transfer model (Eqns. 5-1, 5-2, and 5-3) of Chapter 5. CH₂Cl₂ concentrations at the entrance to the main reactor reflect the occurrence of hydrolysis in the preheater. These concentration values have been calculated from the developed rate expression of Eqn. 6-28, along with Eqns. 5-1, 5-3, 6-4, and 6-25.
Table 12-1  \( \text{CH}_2\text{Cl}_2 \) Data from Hydrolysis Experiments. All data at 246 bar.

<table>
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<tr>
<th>Run No.</th>
<th>Temperature ( ^\circ\text{C} ) (^{a})</th>
<th>Ambient ( \text{[CH}_2\text{Cl}_2 ) (_a ) (mmol/L)</th>
<th>Main Reactor ( \text{[CH}_2\text{Cl}_2 ) (_o ) (mmol/L)</th>
<th>Preheater Residence Time (s) (^d)</th>
<th>Reactor Residence Time (s)</th>
<th>Conversion (%) (^e)</th>
<th>% Gasification (carbon basis) (^f)</th>
<th>Carbon Balance Closure (%) (^g)</th>
<th>Chloride Balance Closure (%) (^h)</th>
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<td>Main Reactor [CH₂Cl₂]&lt;sub&gt;c&lt;/sub&gt; (mmol/L)</td>
<td>Preheater Residence Time (s)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Reactor Residence Time (s)</td>
<td>Conversion (%)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>% Gasification (carbon basis)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Carbon Balance Closure (%)&lt;sup&gt;g&lt;/sup&gt;</td>
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<sup>a</sup> Main reactor (sandbath) temperature

<sup>b</sup> Average inlet CH₂Cl₂ concentration at beginning of preheater tubing

<sup>c</sup> CH₂Cl₂ concentration at beginning of main reactor (under supercritical conditions); calculated from ambient concentration and Eqn. 6-28 in preheater

<sup>d</sup> Preheater residence time calculated from Eqns. 5-1, 5-2, and 5-3.

<sup>e</sup> Net conversion (preheater + main reactor) measured after main reactor.

<sup)f</sup> Percent gasification = fraction of all gaseous carbon-based products formed based on total amount of CH₂Cl₂ fed

<sup>g</sup> Calculated from Eqn. 4-2.

<sup>h</sup> Calculated from Eqn. 4-3.

<sup>i</sup> Run performed without main reactor (preheater only)
Table 12-2 CH$_2$Cl$_2$ Data from Oxidation Experiments. All data at 246 bar.

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<th>Run No.</th>
<th>Temperature ($^\circ$C)</th>
<th>Ambient [CH$_2$Cl$_2$]</th>
<th>Main Reactor [CH$_2$Cl$_2$]</th>
<th>Main Reactor [O$_2$]</th>
<th>Feed Ratio</th>
<th>Preheater Residence Time (s)</th>
<th>Reactor Residence Time (s)</th>
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<td>68±8</td>
<td>100±7</td>
<td>101±9</td>
</tr>
<tr>
<td>Run No.</td>
<td>Temperature (°C)</td>
<td>Ambient [CH\textsubscript{2}Cl\textsubscript{2}]\textsubscript{0} (mmol/L)</td>
<td>Main Reactor [CH\textsubscript{2}Cl\textsubscript{2}] \textsubscript{0} (mmol/L)</td>
<td>Main Reactor [O\textsubscript{2}] \textsubscript{0} (mmol/L)</td>
<td>Feed Ratio</td>
<td>Preheater Residence Time (s)</td>
<td>Reactor Residence Time (s)</td>
<td>Conversion (%)</td>
<td>% Gasification (carbon basis)</td>
<td>Carbon Balance Closure (%)</td>
<td>Chloride Balance Closure (%)</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>-----------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>437</td>
<td>550±1</td>
<td>7±1</td>
<td>0.24±0.03</td>
<td>0.56±0.04</td>
<td>2.31</td>
<td>7.0</td>
<td>4.0±0.3</td>
<td>71±4</td>
<td>64±8</td>
<td>95±7</td>
<td>100±10</td>
</tr>
<tr>
<td>438</td>
<td>550±1</td>
<td>7±1</td>
<td>0.24±0.03</td>
<td>0.56±0.04</td>
<td>2.31</td>
<td>9.4</td>
<td>5.9±0.4</td>
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<td>76±10</td>
<td>98±9</td>
<td>101±13</td>
</tr>
<tr>
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<td>550±1</td>
<td>7±1</td>
<td>0.24±0.03</td>
<td>0.56±0.04</td>
<td>2.36</td>
<td>12.2</td>
<td>7.9±0.5</td>
<td>95±3</td>
<td>89±18</td>
<td>96±17</td>
<td>101±13</td>
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<td>549±1</td>
<td>21±2</td>
<td>0.79±0.08</td>
<td>2.09±0.09</td>
<td>2.66</td>
<td>6.9</td>
<td>4.0±0.2</td>
<td>63±5</td>
<td>67±8</td>
<td>106±8</td>
<td>107±10</td>
</tr>
<tr>
<td>441</td>
<td>550±1</td>
<td>22±2</td>
<td>0.81±0.09</td>
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<td>6.0±0.3</td>
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<td>75±9</td>
<td>105±8</td>
<td>108±11</td>
</tr>
<tr>
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<td>550±1</td>
<td>22±2</td>
<td>0.81±0.08</td>
<td>2.07±0.06</td>
<td>2.56</td>
<td>11.7</td>
<td>8.0±0.4</td>
<td>86±2</td>
<td>89±10</td>
<td>106±7</td>
<td>108±10</td>
</tr>
<tr>
<td>444</td>
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<td>1.30</td>
<td>9.6</td>
<td>5.9±0.3</td>
<td>49±6</td>
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<td>99±8</td>
</tr>
<tr>
<td>446</td>
<td>451.5±1</td>
<td>15±2</td>
<td>0.87±0.09</td>
<td>1.10±0.05</td>
<td>1.26</td>
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<td>6.0±0.3</td>
<td>47±7</td>
<td>10±1</td>
<td>87±8</td>
<td>90±9</td>
</tr>
<tr>
<td>449</td>
<td>525±1</td>
<td>24±2</td>
<td>0.82±0.09</td>
<td>1.07±0.05</td>
<td>1.31</td>
<td>10.2</td>
<td>5.9±0.3</td>
<td>55±6</td>
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<td>99±9</td>
</tr>
<tr>
<td>451</td>
<td>575±1</td>
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<td>0.81±0.09</td>
<td>1.09±0.05</td>
<td>1.34</td>
<td>13.6</td>
<td>5.9±0.3</td>
<td>99.8±0.2</td>
<td>108±12</td>
<td>108±11</td>
<td>103±12</td>
</tr>
<tr>
<td>453</td>
<td>500±1</td>
<td>22±2</td>
<td>0.87±0.09</td>
<td>1.07±0.04</td>
<td>1.23</td>
<td>9.3</td>
<td>5.9±0.3</td>
<td>40±6</td>
<td>29±3</td>
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<td>97±8</td>
</tr>
<tr>
<td>455</td>
<td>451.5±1</td>
<td>15±2</td>
<td>0.86±0.09</td>
<td>1.07±0.04</td>
<td>1.24</td>
<td>7.7</td>
<td>6.0±0.3</td>
<td>37±7</td>
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<td>98±8</td>
</tr>
<tr>
<td>456</td>
<td>550±1</td>
<td>23±2</td>
<td>0.86±0.09</td>
<td>0.56±0.02</td>
<td>0.66</td>
<td>8.2</td>
<td>5.0±0.2</td>
<td>63±5</td>
<td>54±6</td>
<td>96±7</td>
<td>95±8</td>
</tr>
<tr>
<td>457</td>
<td>550±1</td>
<td>23±2</td>
<td>0.85±0.09</td>
<td>0.56±0.03</td>
<td>0.65</td>
<td>10.6</td>
<td>7.0±0.4</td>
<td>85±3</td>
<td>82±9</td>
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<td>99±10</td>
</tr>
<tr>
<td>458</td>
<td>550±1</td>
<td>23±2</td>
<td>0.86±0.09</td>
<td>0.56±0.03</td>
<td>0.65</td>
<td>14.5</td>
<td>9.1±0.5</td>
<td>96±2</td>
<td>98±11</td>
<td>107±8</td>
<td>103±11</td>
</tr>
<tr>
<td>460</td>
<td>563±1</td>
<td>29±3</td>
<td>0.78±0.08</td>
<td>1.07±0.04</td>
<td>1.38</td>
<td>12.2</td>
<td>5.9±0.3</td>
<td>99.6±0.3</td>
<td>116±14</td>
<td>117±12</td>
<td>110±12</td>
</tr>
<tr>
<td>462</td>
<td>451±1</td>
<td>15±2</td>
<td>0.84±0.09</td>
<td>1.11±0.04</td>
<td>1.31</td>
<td>8.0</td>
<td>6.0±0.3</td>
<td>30±7</td>
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<td>104±8</td>
</tr>
<tr>
<td>464</td>
<td>463±1</td>
<td>17±2</td>
<td>0.89±0.09</td>
<td>1.10±0.04</td>
<td>1.24</td>
<td>8.5</td>
<td>6.0±0.3</td>
<td>33±8</td>
<td>12±1</td>
<td>97±8</td>
<td>96±9</td>
</tr>
<tr>
<td>466</td>
<td>563±1</td>
<td>31±3</td>
<td>0.84±0.09</td>
<td>1.07±0.04</td>
<td>1.28</td>
<td>12.2</td>
<td>5.9±0.3</td>
<td>99±1</td>
<td>103±21</td>
<td>105±20</td>
<td>104±11</td>
</tr>
</tbody>
</table>

\( ^{a} \) Main reactor (sandbath) temperature

\( ^{b} \) Average inlet CH\textsubscript{2}Cl\textsubscript{2} concentration at beginning of preheater tubing

\( ^{c} \) CH\textsubscript{2}Cl\textsubscript{2} concentration at beginning of main reactor (under supercritical conditions); calculated from ambient concentration and Eqn. 6-28 in preheater

\( ^{d} \) O\textsubscript{2} concentration at beginning of main reactor

\( ^{e} \) Feed ratio = [O\textsubscript{2}]\textsubscript{0}/[CH\textsubscript{2}Cl\textsubscript{2}]\textsubscript{0} at beginning of main reactor

\( ^{f} \) Preheater residence time calculated from Eqns. 5-1, 5-2, and 5-3.

\( ^{g} \) Net conversion (preheater + main reactor) measured after main reactor.

\( ^{h} \) Percent gasification = fraction of all gaseous carbon-based products formed based on total amount of CH\textsubscript{2}Cl\textsubscript{2} fed

\( ^{i} \) Calculated from Eqn. 4-2.

\( ^{j} \) Calculated from Eqn. 4-3.
12.2 Tabulated Methanol Experimental Data The following tables contain numerical data from the present study of hydrolysis/pyrolysis and oxidation of methanol in sub- and supercritical water. All data were gathered using the CSTR system described in Chapters 8 and 9. The tables also contain data from the tests of the oxidant feed delivery systems ($\text{H}_2\text{O}_2$ and $\text{O}_2/\text{H}_2\text{O}$ saturator).
Table 12-3  \( \text{CH}_3\text{OH} \) Data from Hydrolysis/Pyrolysis Experiments  Note that no methanol conversion was measured for any of these hydrolysis/pyrolysis runs.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Run Description</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Stirring Speed (rpm)</th>
<th>Liquid Effluent Flow (mL/min)</th>
<th>Avg. Residence Time (min)</th>
<th>Pure CH(_3\text{OH}) Feed Flow (µL/min)</th>
<th>([\text{CH}_3\text{OH}]_0) in Reactor (mmol/L)</th>
<th>Ambient, Steady-State [CH(_3\text{OH})] if No Reaction (ppm)</th>
<th>Ambient, Steady-State [CH(_3\text{OH})] Measured in Effluent (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Ambient Hydrolysis</td>
<td>25±1</td>
<td>249±8</td>
<td>500</td>
<td>31.0±0.1</td>
<td>19.7</td>
<td>1.75</td>
<td>1.43</td>
<td>45.9</td>
<td>46±2</td>
</tr>
<tr>
<td>3</td>
<td>Subcritical Hydrolysis</td>
<td>330.9±0.2</td>
<td>246±3</td>
<td>500</td>
<td>30.8±0.3</td>
<td>13.3</td>
<td>1.75</td>
<td>0.97</td>
<td>46.2</td>
<td>58±4</td>
</tr>
<tr>
<td>4</td>
<td>Subcritical Hydrolysis</td>
<td>331.0±0.1</td>
<td>258±3</td>
<td>500</td>
<td>30.8±0.2</td>
<td>13.4</td>
<td>1.75</td>
<td>0.98</td>
<td>46.2</td>
<td>56±3</td>
</tr>
<tr>
<td>5</td>
<td>Ambient Hydrolysis</td>
<td>25±1</td>
<td>264±1</td>
<td>1000</td>
<td>51.0±0.1</td>
<td>12.0</td>
<td>3.00</td>
<td>1.49</td>
<td>47.8</td>
<td>43±1</td>
</tr>
<tr>
<td>6</td>
<td>Supercritical Hydrolysis</td>
<td>443±1</td>
<td>286±12</td>
<td>1000</td>
<td>31.0±0.2</td>
<td>2.8</td>
<td>22.36</td>
<td>2.58</td>
<td>586</td>
<td>594±20</td>
</tr>
</tbody>
</table>

\( ^{a} \) Data from Run #1 is not included because of a leaking seal in the \( \text{CH}_3\text{OH} \) feed syringe pump, replaced after this run.

\( ^{b} \) Temperature is average of all five thermocouple measurements in reactor.

\( ^{c} \) Flow set for syringe pump feed rate.

\( ^{d} \) \( \text{CH}_3\text{OH} \) concentration in reactor after mixing.

\( ^{e} \) Calculated from Eqn. 9-3.
## Table 12-4 Data from Oxidant Feed Delivery Tests, and CH\textsubscript{3}OH Oxidation Experiments

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Run Description</th>
<th>Temperature (°C) (^b)</th>
<th>Pressure (bar)</th>
<th>Stirring Speed (rpm)</th>
<th>Liquid Effluent Flow (mL/min)</th>
<th>Avg. Residence Time (min)</th>
<th>Pure CH\textsubscript{3}OH Feed Flow (µL/min) (^c)</th>
<th>[CH\textsubscript{3}OH] (_{in}) in Reactor (mmol/L) (^d)</th>
<th>Ambient, Steady-State [CH\textsubscript{3}OH] if No Reaction (ppm) (^e)</th>
<th>Ambient, Steady-State Measured in Effluent (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 (^*)</td>
<td>H\textsubscript{2}O\textsubscript{2} Test</td>
<td>333.8±0.1</td>
<td>248±2</td>
<td>500</td>
<td>30.8±0.7</td>
<td>13.2±0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{2} Sat. Test</td>
<td>330.5±0.2</td>
<td>252±3</td>
<td>500</td>
<td>30.6±0.4</td>
<td>13.5±0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8 (^*)</td>
<td>H\textsubscript{2}O\textsubscript{2} Test</td>
<td>331.3±0.2</td>
<td>246±4</td>
<td>500</td>
<td>31.1±0.8</td>
<td>13.2±0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{2} Sat. Test</td>
<td>330.2±0.1</td>
<td>248±5</td>
<td>500</td>
<td>30.8±0.4</td>
<td>13.3±0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Subcritical Oxidation</td>
<td>331.2±0.2</td>
<td>238±7</td>
<td>500</td>
<td>30.8±0.4</td>
<td>13.3±0.5</td>
<td>1.75</td>
<td>0.97±0.04</td>
<td>46.2</td>
<td>40±2</td>
</tr>
<tr>
<td>10</td>
<td>Supercritical Oxidation</td>
<td>443±2</td>
<td>270±3</td>
<td>500</td>
<td>30.8±0.2</td>
<td>2.5±0.1</td>
<td>22.89</td>
<td>2.4±0.1</td>
<td>604</td>
<td>64±6</td>
</tr>
<tr>
<td>11</td>
<td>Supercritical Oxidation</td>
<td>411.4±0.7</td>
<td>267±2</td>
<td>500</td>
<td>38.6±0.3</td>
<td>2.6±0.1</td>
<td>22.77</td>
<td>2.5±0.3</td>
<td>480</td>
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<tr>
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<td>428±1</td>
<td>276±4</td>
<td>500</td>
<td>34.6±0.3</td>
<td>2.6±0.1</td>
<td>23.03</td>
<td>2.5±0.3</td>
<td>541</td>
<td>93±4</td>
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<tr>
<td>13</td>
<td>Supercritical Oxidation</td>
<td>427.0±0.6</td>
<td>280±3</td>
<td>1000</td>
<td>34.7±0.2</td>
<td>2.7±0.1</td>
<td>23.03</td>
<td>2.6±0.3</td>
<td>540</td>
<td>90±3</td>
</tr>
</tbody>
</table>

\(^*\) H\textsubscript{2}O\textsubscript{2} Test = test of O\textsubscript{2} feed delivery from H\textsubscript{2}O\textsubscript{2} decomposition;  
O\textsubscript{2} Sat. Test = test of O\textsubscript{2} feed delivery from O\textsubscript{2}/H\textsubscript{2}O saturator (see Section 9.4.1)  
\(^b\) Temperature is average of all five thermocouple measurements in reactor.  
\(^c\) Flow set for syringe pump feed rate.  
\(^d\) CH\textsubscript{3}OH concentration in reactor after mixing (before reaction).  
\(^e\) Calculated from Eqn 9.3.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Run Description</th>
<th>Vapor Effluent Flow (mL/min)</th>
<th>Ambient $[\text{H}_2\text{O}_2]$ (ppm)</th>
<th>$\text{O}_2$ Pressure in Saturator (bar)</th>
<th>$[\text{O}<em>2]</em>{\text{in}}$ in Reactor (mmol/L)</th>
<th>Feed Ratio $^c$</th>
<th>CH$_3$OH Conversion (%)</th>
<th>First-order Rate Constant k (s$^{-1})^d$</th>
<th>Carbon Balance Closure (%) $^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 $^a$</td>
<td>$\text{H}_2\text{O}_2$ Test</td>
<td>$\leq 0.3$</td>
<td>25</td>
<td>-</td>
<td>0.25±0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>7 $^a$</td>
<td>$\text{O}_2$ Sat. Test</td>
<td>$33±1$</td>
<td>-</td>
<td>40</td>
<td>33±2</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>8 $^a$</td>
<td>$\text{H}_2\text{O}_2$ Test</td>
<td>1.4±0.2</td>
<td>150</td>
<td>-</td>
<td>1.5±01</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>8 $^a$</td>
<td>$\text{O}_2$ Sat. Test</td>
<td>32.9±0.6</td>
<td>-</td>
<td>40</td>
<td>33±2</td>
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</tr>
<tr>
<td>9</td>
<td>Subcritical Oxidation</td>
<td>0.92±0.07</td>
<td>150</td>
<td>-</td>
<td>1.5±0.1</td>
<td>1.5</td>
<td>0</td>
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<td>-</td>
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<td>Supercritical Oxidation</td>
<td>20.4±0.4</td>
<td>2710</td>
<td>-</td>
<td>5.1±0.3</td>
<td>2.1</td>
<td>89±1</td>
<td>0.055±0.003</td>
<td>106±8</td>
</tr>
<tr>
<td>11</td>
<td>Supercritical Oxidation</td>
<td>25.8±0.1</td>
<td>2073</td>
<td>-</td>
<td>5.0±0.2</td>
<td>2.0</td>
<td>60±5</td>
<td>0.009±0.001</td>
<td>102±7</td>
</tr>
<tr>
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<td>Supercritical Oxidation</td>
<td>21.7±0.3</td>
<td>2408</td>
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<td>5.3±0.2</td>
<td>2.1</td>
<td>83±2</td>
<td>0.030±0.002</td>
<td>101±7</td>
</tr>
<tr>
<td>13</td>
<td>Supercritical Oxidation</td>
<td>21.9±0.2</td>
<td>2408</td>
<td>-</td>
<td>5.4±0.2</td>
<td>2.1</td>
<td>83±2</td>
<td>0.031±0.001</td>
<td>99±7</td>
</tr>
</tbody>
</table>

$^a$ $\text{H}_2\text{O}_2$ Test = test of $\text{O}_2$ feed delivery from $\text{H}_2\text{O}_2$ decomposition;  
$\text{O}_2$ Sat. Test = test of $\text{O}_2$ feed delivery from $\text{O}_2$/$\text{H}_2\text{O}$ saturator (see Section 9.4.1)  
$^b$ $\text{O}_2$ concentration in reactor after mixing (before reaction).  
$^c$ Feed ratio = $[\text{O}_2]_{\text{in}}$/$[\text{CH}_4\text{Cl}_2]_{\text{in}}$ in reactor after mixing (before reaction).  
$^d$ Calculated from Eqn. 9-5 using experimental conversion.  
$^e$ Calculated from Eqn. 4-2.
Chapter 13

References


Frisch, M.A., "Supercritical Water Oxidation of Acetic Acid Catalyzed by CeO$_2$/MnO$_2$" Masters Thesis, The University of Texas at Austin, Austin, TX (1992).

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