Oxidation rates of common organic compounds in supercritical water

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Abstract

Supercritical water oxidation is a rapidly emerging thermal waste-processing technology with potential as a hazardous-waste-treatment method for a variety of industrial chemicals ranging from common organic solvents to complex industrial formulations. An important design consideration in the development of supercritical water oxidation is the optimization of reactor operating temperature and feed preheat temperatures. In this paper, the temperature dependence of the oxidation in supercritical water of seven common organic compounds is examined over a temperature range of 430–585°C and reaction times ranging from 7 to 30 s at 27.6 MPa (4000 psi). The reactants are examined at approximate concentrations of 0.4 wt.% at conversion efficiencies from 50% to > 99.9%. The materials examined were methanol, phenol, methyl ethyl ketone, ethylene glycol, acetic acid, methylene chloride, and 1,1,1-trichloroethane. The conversion of these compounds was monitored using total organic carbon and gas chromatography on liquid effluent samples. The results indicate that for most compounds, temperatures over 550°C and residence times near 20 s afford conversion efficiencies of greater than 99.95% based on total organic carbon. © 1998 Elsevier Science B.V.

Keywords: Oxidation; Kinetics; Supercritical water; Waste treatment; High pressure

1. Introduction

Supercritical water oxidation (SCWO) is a developing hazardous-waste-treatment method that has attracted the interest of both industry and government agencies. Possible applications include the treatment of ordinary industrial solvent wastes, equipment

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changeout fluids, paints, herbicides, energetic munitions, chemical warfare agents, and chemical/radiological mixed waste. The SCWO process is conceptually simple [1–3]. Organic waste in aqueous solution, typically ranging from 1–10 wt.% oxidizable material, is pressurized and heated to conditions above the critical point of water (374°C, 22.1 MPa). At these conditions, the organic material can function as a fuel in an oxidation reaction. An oxidizer is added to this mixture, and given adequate reaction time, the waste (fuel) is converted to less hazardous materials. Organic carbon emerges as CO_2, nitrogen is primarily converted to N_2, and other heteroatoms and halides appear in the effluent as inorganic acid anions.

The development of SCWO technology depends on solving several materials issues such as corrosion and inorganic salt deposition. Engineering solutions to many of these issues are strongly dependent on the operating temperature of the reactor. Higher temperatures result in more rapid oxidation chemistry, but can also contribute to more rapid corrosion and other system operation difficulties. Existing pilot scale systems have adopted differing approaches to implementing SCWO to afford high conversion and minimize corrosion and scaling. Some systems use lower temperatures and longer reaction times and catalysis, others take advantage of higher processing temperature and innovative designs to prevent material problems. It is important to determine the optimal balance between sufficiently high temperature for satisfactory waste conversion, and sufficiently mild conditions for inexpensive and durable construction. Unfortunately, much of the information in the literature on existing pilot systems focuses on conversion without supplying adequate information to relate conversion efficiency to reaction time and system temperature.

This paper describes experiments performed to determine appropriate temperature ranges for supercritical water oxidation applied to a variety of test organic compounds. The chemicals selected for examination were methanol, phenol, methyl ethyl ketone, ethylene glycol, acetic acid, methylene chloride, and 1,1,1-trichloroethane. These compounds were chosen to represent common industrial wastes, as well as intermediate molecules in hydrolysis or partial oxidation reactions.

Measurements of total organic carbon (TOC) and gas chromatography (GC) conversion efficiencies were used to compare the different materials. The experiments evaluated the effect of reaction time and temperature on the oxidation of these test materials at high conversion. In order to facilitate the use of our results for process scale-up, the experiments were conducted at feed concentrations as high as possible while holding temperature constant. The primary goals of this work are: (1) to identify the range of temperatures at which a variety of organic chemicals oxidize with reasonable efficiency; (2) to identify the most difficult chemicals to oxidize; (3) and to quantitatively evaluate time–temperature tradeoffs. The results provide a guide to the design of SCWO equipment by presenting the tradeoff between conversion efficiency, residence time, and reaction temperature for a variety of different chemicals.

We note that the experimental results do not constitute complete oxidation kinetic data for any of these materials. Most of the experiments were conducted with a conversion efficiency of greater than 99% (less than 1% of the initial feed remains). Because the reactions were run to near completion, kinetics over the early stages of the reaction cannot be separated from the reaction behavior at late stages. In addition, the

oxidizer concentration was not varied so that oxidizer reaction order is not determined. Nonetheless, we can still reduce each compound's data to effective first-order rate constants for comparison with experimental results obtained by others.

2. Experimental apparatus and methods

2.1. Apparatus

All of the oxidation experiments were conducted using our supercritical flow reactor (SFR). This equipment is designed to mix two separate flows at a known temperature and fixed flow rate, and to permit this mixture to react at isothermal conditions. A complete description of the reactor is given elsewhere [4,5], and only a brief description of the design and operation features is included here.

A schematic of the SFR is shown in Fig. 1. The reactor has a maximum operating temperature of 650°C and a maximum operating pressure of 50 MPa (approx. 7300 psi). Flow rates can be varied from approximately 1.5 ml/s (nominal ambient-condition feed water, 25°C) to 0.1 ml/s. Two parallel lines preheat the feed and oxidizer streams using a series of Marshall tube furnaces with a combined power of 4500 W per line. These
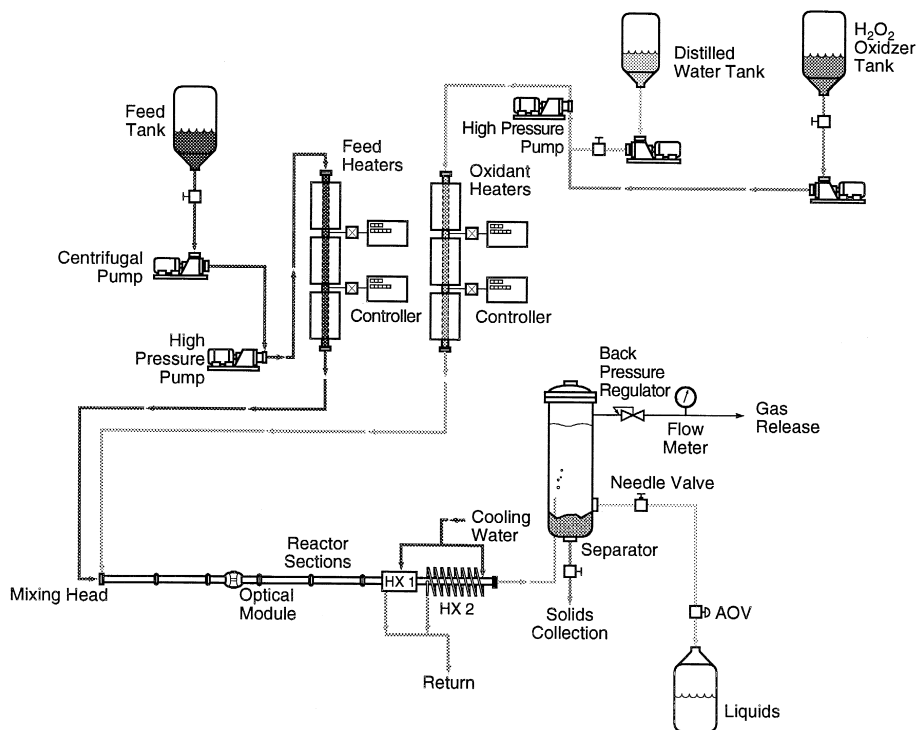

Fig. 1. Schematic diagram of Sandia's supercritical flow reactor.

furnaces are individually controlled with Omega process controllers. The 400 cm long reactor section is heated by six Watlow 375-W cable heaters that maintain isothermal conditions along the reactor by compensating for imperfect insulation, which affords a loss of about 200 W/m at 550°C.

The high-temperature portions of the system are made of 1.43 cm o.d. (9/16 in.), 0.48 cm i.d. (3/16 in.) Inconel 625 tubing with Autoclave Engineers Inconel 625 high-pressure fittings as unions. The temperatures of the feed, oxidizer, and reacting fluid are measured with Inconel 600 sheathed Type K thermocouples located directly in the fluid at tee unions. The reaction is quenched with a counterflow heat exchanger that drops fluid temperature from above 500°C to below 400°C in about 0.3 s.

2.2. Methods

A typical experiment begins by preparing a solution of the organic compound and water at about 0.8 wt.%. The solution is then pressurized and brought to reaction temperature in the feed preheater. In parallel, a solution of oxygen in water is prepared by pressurizing and preheating a 5 wt.% solution of hydrogen peroxide. These two solutions are mixed at equal temperatures and flow rates at the head of the reactor. The mixture reacts through the length of the reactor and then is cooled, depressurized, and sampled. Samples of the feed and effluent are analyzed using automatic total organic carbon (TOC) equipment and gas chromatography.

Preparation of the oxygen–water solution from a water–hydrogen peroxide mixture depends on a sufficient residence time at temperature. We have directly measured the thermal decomposition rate of H_2O_2 in supercritical water and found a first-order rate constant of 7.8 s^{-1} at 450°C [6]. At the maximum flow rate in our oxidizer preheater of 0.4 g/s, the residence time is at least 5 s at or above 450°C. These operating conditions result in 40 lifetimes of the disproportionation reaction in the preheater. We have sampled the effluent from the oxidizer preheat line and detected no residual H_2O_2 in solution above our detection limit of 0.02 ppm. The 5.0 wt.% H_2O_2 oxidizer solution produces a 2.35 wt.% solution of O_2. The initial fuel concentration in the high-temperature reacting mixture, C_r, is a function of both the fuel concentration in the feed and the two flow rates:

$$C_r = C_f F_f / (F_f + F_o)$$

(1)

where C_f is the fuel concentration in the feed and F_f and F_o are the volumetric flow rates of the feed and the oxidizer at the reaction temperature and pressure. Most runs were conducted with approximately equal oxidizer and fuel ambient volumetric flow rates. For any given sample, there was some variation in the ambient-condition volumetric flow rates for each pump and the results presented in the tables below reflect corrections for these mismatches.

2.3. Analytical procedures and error analysis

There are two types of errors affecting the overall accuracy of the experimental results presented in this paper. One is associated with control of experimental conditions

including temperature, flow rates, mixing rate, and sample collection techniques. The other is associated with the accuracy of the analytical methods.

Operation of the SFR is simple and routine, but there are design limitations governing the precision of its control. Because a finite number of heating elements (six) is used to control temperature along the length of the 'isothermal' reactor, the reactor is only approximately isothermal during an experiment. Typically, temperature is held constant to $\pm 8°C$ over the length of the reactor. The flow rates of the oxidizer and fuel streams are accurate to 1% at the higher flow rates (0.3–0.8 ml/s in each line, 6–20 s residence time). At lower flow rates, reduced reproducibility in the pumping speed of the pneumatic pumps is responsible for error in the calculated flow rates. As a result, the calculated feed fuel concentration and residence time have greater error associated with them, especially at the longer reaction times. Thus, the estimated error in reaction time for the samples with greater than 20 s residence time is $\pm 10\%$.

Accurately describing the concentration of reactants in the reactor requires a reliable equation of state for a mixture of several percent oxygen in supercritical water, which is not available. Identical volumetric flow rates of the feed and oxidizer streams at ambient temperature (liquids) will not necessarily produce identical volumetric flow rates at the mixing point, since the equations of state for the two streams are different. However, at these concentrations, this difference is small. As an approximation, we use the equation of state of water to calculate thermodynamic properties for both streams, and at the high conversion percentages examined in this work, this small error in residence time will not seriously affect the interpretation of the results.

The effect of a finite oxidizer and fuel mixing time on observed conversion efficiencies cannot be quantified accurately. The severity of this effect varies with the flow rate and reaction temperature, and may become important at the lowest flow rates and temperatures. Although the SFR generally operates under turbulent flow conditions, at low flow rates, the flow may be in the transition regime, which could lead to increased mixing times. For example, the Reynolds number at 27.6 MPa, 580°C, and 0.8 g/s is 6300. However, at 27.6 MPa, 580°C, and 0.3 g/s, it is reduced to 2350. As a result, effective residence time for some of the material could be different than the time calculated from the average mass flow rate, reactor dimensions, and fluid density. SFR experiments with more rapidly reacting feeds at residence times below 0.5 s indicate that the mixing time is less than 0.2 s in this system, and will not affect significantly the results from these experiments [7].

The chemical analysis methods also have an effect on the accuracy of our experimental results. Total organic carbon was measured with an Astro 2001 TOC analyzer. This unit was not equipped for the accurate detection of organic compounds that are easily sparged from water and, as a result, TOC readings for methylene chloride, TCA, and methyl ethyl ketone are not reported. The TOC analyzer has a total organic carbon accuracy of $\pm 2\%$ of full scale on scales > 10 ppm, and $\pm 5\%$ of the 10 ppm full scale for measurements < 10 ppm. Thus, many of the high-conversion efficiency results with TOC in the 1–3 ppm range have large percentage errors associated with them. TOC analysis is capable of detecting 0.1 ppm, but only with ideal samples under special conditions. The practical lower limit during our use of the analyzer was approximately 1.3 ppm.

The gas chromatographic results are from an HP 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a 10-m DB-5 0.530-mm capillary column. Although gas chromatography does not work optimally with water as the solvent, acceptable chromatograms were obtained on all the materials except ethylene glycol, which showed evidence of reaction on the column and in the injection port. Integrated intensities varied by as much as a factor of two on same-sample GC scans for ethylene glycol. The analyses for other materials were reproducible within $\pm 10\%$ of an average of same-sample scans.

3. Results

Tables 1–7 report reactor temperature, residence time, GC results, and TOC results. Fraction TOC is the ratio of TOC measured in the effluent and the TOC measured in the input feed, corrected for the dilution of the effluent according to Eq. (1). Similarly, Fraction GC is the ratio of the total integrated GC signals, again corrected using Eq. (1). Although the experiments were conducted with the same initial oxygen concentration in the reactor, 1.175 wt.%, and comparable organic reactant wt. fractions, the amount of excess oxygen supplied to the reactions varied significantly due the stoichiometry. In the tables, the fuel equivalence ratio is identified as Φ, where $\Phi = [O_2]_s/[O_2]_o$, with $[O_2]_s$ representing the concentration of oxygen required to fully oxidize the organic material to CO_2 and water determined by the stoichiometry of the reaction, and $[O_2]_o$ is the oxygen concentration initially in the reactor.

Table 1
Conversion of methanol

Sample no.	Temperature (°C)	Time (s)	TOC (ppm)	Fraction TOC	Fraction GC[a]
1	571	6.9	1.47	0.93×10^{-3}	n.d.
2	574	12.8	1.46	0.92×10^{-3}	n.d.
3	574	22.6	1.44	0.91×10^{-3}	n.d.
4	537	7.0	8.54	5.7×10^{-3}	6.7×10^{-3}
5	538	12.8	1.48	0.97×10^{-3}	0.99×10^{-3}
6	533	22.1	1.44	1.0×10^{-3}	n.d.
7	508	8.0	37.8	0.025	0.026
8	504	14.2	8.94	5.9×10^{-3}	6.1×10^{-3}
9	495	25.8	1.45	1.0×10^{-3}	n.d.
10	480	9.05	138	0.094	0.080
11	481	16.3	34.9	0.024	0.024
12	475	26.0	43.6	0.031	0.027
13	447	11.4	288	0.19	0.17
14	442	18.9	132	0.089	0.070
15	442	30.2	119	0.085	0.070

[a] n.d.: none detected.
$\Phi = 0.5$.

Table 2
Conversion of ethylene glycol

Sample no.	Temperature (°C)	Time (s)	TOC (ppm)	Fraction TOC	Fraction GC[a,b]
1	556	7.3	3.2	2.1×10^{-3}	n.d.
2	552	11.7	2.9	1.6×10^{-3}	n.d.
3	552	17.8	2.7	1.8×10^{-3}	n.d.
4	531	8.8	18.7	0.012	n.d.
5	524	13.3	25.2	0.015	n.d.
6	517	16.3	12.4	9.0×10^{-3}	n.d.
7	506	8.7	86.2	0.055	1.7×10^{-3}
8	502	15.1	25.0	0.015	0.24×10^{-3}
9	505	28.0	9.0	5.5×10^{-3}	n.d.
10	480	9.9	372	0.247	0.094
11	478	21.3	19.4	0.014	1.7×10^{-3}
12	456	12.8	678	0.47	0.22
13	449	22.4	393	0.28	0.16

[a] n.d.: none detected.
[b] Large error margins: see text.
$\Phi = 0.43$.

3.1. Methanol

Table 1 presents GC and TOC analyses of the methanol experiment samples with an initial reactor concentration, C_r, of 0.12 mol/l (0.39 wt.%). At temperatures above 570°C, the measured residual methanol is below the detection limit of the GC (about 2 ppm). Note that the TOC and GC results for the fraction remaining generally agree, especially at high conversion when data using both detection methods is available. This shows that the remaining organic carbon in the effluent is predominantly unreacted

Table 3
Conversion of phenol

Sample no.	Temperature (°C)	Time (s)	TOC (ppm)	Fraction TOC	Fraction GC[a]
1	585	6.9	22.3	9.3×10^{-3}	2.5×10^{-3}
2	575	12.8	1.57	0.67×10^{-3}	n.d.
3	578	22.8	1.68	0.72×10^{-3}	n.d.
4	575	7.1	25.3	0.010	2.8×10^{-3}
5	575	10.3	18.2	7.2×10^{-3}	1.7×10^{-3}
6	575	19.1	5.11	2.6×10^{-3}	0.45×10^{-3}
7	545	8.2	245	0.11	0.038
8	539	14.2	82.6	0.034	7.6×10^{-3}
9	533	24.7	44.3	0.018	3.9×10^{-3}
10	508	8.7	246	0.11	0.15
11	504	16.3	321	0.14	0.042
12	507	24.8	382	0.17	0.065

[a] n.d.: none detected.
$\Phi = 0.65$.

Table 4
Conversion of acetic acid

Sample no.	Temperature (°C)	Time (s)	TOC (ppm)	Fraction TOC	Fraction GC[a]
1	532	8.7	7.7	4.9×10^{-3}	0.61×10^{-3}
2	532	11.8	5.2	3.2×10^{-3}	0.096×10^{-3}
3	533	20.5	8.8	5.9×10^{-3}	n.d.
4	507	9.2	10.8	6.8×10^{-3}	0.40×10^{-3}
5	507	14.9	8.1	4.6×10^{-3}	0.11×10^{-3}
6	507	23.2	20.2	0.014	n.d.
7	484	10.2	192	0.12	0.11
8	480	16.3	93	0.055	0.045
9	480	25.2	18	0.013	6.1×10^{-3}
10	460	10.9	520	0.33	0.23
11	457	17.8	924	0.58	0.41
12	460	24.6	131	0.097	0.11
13	441	11.9	1360	0.89	0.86
14	441	18.6	1367	0.87	0.74

[a] n.d.: none detected.
$\Phi = 0.33$.

methanol. At the lower conversion temperatures, less than 480°C, the TOC results indicate that there is some additional organic carbon in the effluent that does not appear as methanol in the GC analysis. This is due to partial oxidation products that have a reaction rate comparable to, or slower than, that of methanol at lower temperatures. As a result, once they form, they do not rapidly disappear. Our recent work using in situ spectroscopic methods [7] has shown that the low-temperature partial oxidation product is formaldehyde.

Table 5
Conversion of methyl ethyl ketone

Sample no.	Temperature (°C)	Time (s)	Fraction GC[a]
1	568	7.7	n.d.
2	564	12.4	n.d.
3	563	21.8	n.d.
4	520	8.4	7.3×10^{-3}
5	517	15.5	5.5×10^{-3}
6	517	24.3	n.d.
7	483	9.9	0.11
8	482	18.1	0.053
9	477	27.8	0.054
10	456	11.2	0.85
11	454	20.0	0.70
12	450	34.8	0.37
13	445	11.9	0.81

[a] n.d.: none detected.
$\Phi = 0.96$.

Table 6
Conversion of methylene chloride

Sample no.	Temperature (°C)	Time (s)	Fraction GC[a]
1	577	8.1	n.d.
2	568	11.5	n.d.
3	570	18.9	n.d.
4	548	8.0	n.d.
5	539	13.0	n.d
6	539	19.8	0.25×10^{-3}
7	516	8.8	0.85×10^{-3}
8	512	14.2	n.d.
9	510	23.8	n.d.
10	477	9.9	0.024
11	471	17.7	2.6×10^{-3}
12	469	27.2	1.3×10^{-3}
13	450	12.6	0.033
14	446	19.9	2.4×10^{-3}
15	447	31.5	2.0×10^{-3}

[a] n.d.: none detected.
$\Phi = 0.06$.

3.2. Ethylene glycol

Ethylene glycol results are presented in Table 2 for a feed of 0.39 wt.%. There are major differences between the TOC and GC results. The GC results uniformly show a much higher conversion of the parent feed molecule than the TOC results. As in the case of methanol, but to a greater extent, this additional organic carbon is due to partial oxidation products of the glycol that react slower than the original feed material. Although the GC results are suspect because of the poor quality of the chromatography (see Section 2.3), it seems clear that significant amounts of intermediate oxidation products are present in the effluent. We have shown in the case of *i*-propanol oxidation that acetone can be formed as an intermediate at a concentration as high as 60% of the initial feed [8].

Table 7
Conversion of 1,1,1-trichloroethane

Sample no.	Temperature (°C)	Time (s)	Fraction GC
1	474	10.0	0.006
2	462	10.6	0.13
3	460	10.7	0.21
4	442	11.8	0.71
5	432	12.7	0.76
6	409	16.4	0.90

$\Phi = 0.07$.

3.3. Phenol

Table 3 shows the results from the oxidation of phenol at 0.32 wt.%. Phenol appears to be the most difficult to destroy among the different materials tested. However, at 2.35 wt.% O_2 in the oxidizer line (1.175 wt.% in the reactor), the fuel equivalence ratio of $\Phi = 0.65$ is nearly the highest of any of the materials we have examined. Again, the TOC results show an appreciable amount of oxidizable carbon present in the reaction products that does not appear as phenol in the GC traces. The GC traces exhibit a number of small features indicating the presence of lower and higher molecular weight partial oxidation products that varied as a function of temperature. Other examinations of phenol oxidation under hydrothermal conditions at low conversion have shown the production of a variety of condensation products with high molecular weight [9–11].

Note that at the lowest temperature (about 505°C), additional reaction time does not appreciably change the TOC in the effluent. This suggests that initially the phenol reacts, although not as rapidly as other species, but then the reaction of the partial oxidation products slows down as the fuel drops to lower concentration.

3.4. Acetic acid

Results for acetic acid are presented in Table 4, obtained from runs using initial acetic acid feed at 0.37 wt.%. Acetic acid is well behaved in the GC and in the TOC analyzer. It appears that at low conversion percentages and at lower temperatures, most of the residual organic carbon exists as acetic acid. At higher temperatures, a trace amount of oxidizable carbon remains, but it is about a factor of 10 more concentrated than the remaining acetic acid. Thus, high TOC conversion of acetic acid at high temperature depends on the oxidation rate of this trace side product, and not on the high-conversion oxidation rate of acetic acid.

3.5. Methyl ethyl ketone

Methyl ethyl ketone (MEK) has a boiling point of 79.6°C. Since the TOC reactor cell is heated above 50°C, the MEK has a significant vapor pressure in the TOC reactor cell. The TOC analyzer cannot produce reliable data for this volatile organic compound. For example, the 0.5 wt.% reference calibration measured only 210 ppm when it should have registered nearly 3300 ppm. When the reference sample was diluted by a factor of 10, the TOC registered 98 ppm. On the other hand, GC analysis of the reference feed sample yielded reproducible peaks with intensities in good agreement with calibration samples. This is clear evidence that the MEK is being sparged from the TOC analyzer before it is fully oxidized to CO_2. As a result, the TOC analysis does not represent all oxidizable carbon that is present in the original sample. In fact, the readings are probably about a factor of 10 too low and are therefore omitted from the table. Table 5 presents the GC results for MEK at an initial concentration of 0.46 wt.%.

Many of the lower temperature effluent TOC readings were higher than the 210 ppm recorded for the unreacted reference sample. This observation can be explained by recognizing that MEK oxidizes to form organic molecules that are not as easily sparged,

such as light alcohols. The GC traces for samples 7–13 exhibit several strong, well-defined, short-retention-time peaks that are not MEK. Note that the equivalence ratio here is 0.96 such that there is little excess oxygen for complete oxidation. It is likely that the difficulty in oxidizing this remaining organic material stems from the lowered O_2 concentration as the reaction proceeds.

3.6. Methylene chloride and 1,1,1 trichloroethane (TCA)

The same volatility problems existed with these species as with MEK, and the TOC measurements were not reproducible for same-sample measurements. The GC results for methylene chloride are listed in Table 6. Initial feed concentration for methylene chloride and TCA was 0.5 wt.%. TCA was examined in less detail than the other materials because of concern for the reactor vulnerability to corrosion with halogenated species. Table 7 lists the results.

4. Discussion

4.1. Rate analysis

To facilitate comparisons, the results from all of the runs can be consolidated by assuming that (1) the oxidation kinetics are first-order in fuel, and that (2) there is enough of an excess of oxidizer that the change in oxidizer concentration throughout the reaction is insignificant, regardless of the order of reaction with respect to the oxidizer. These assumptions permit the reduction of the data to an effective first order rate constant, k_{eff}, represented by

$$d[C]/dt = -k_{eff}[C].\tag{2}$$

Integration over time yields

$$-\ln[C/C_r]/t = k_{eff}(T),\tag{3}$$

where C is the effluent fuel concentration, C_r is the initial fuel concentration in the reactor, t is residence time, and $k_{eff}(T)$ is the temperature-dependent effective first-order rate constant.

Note that there is no fundamental reason to assume the oxidation rates of these compounds follow first-order kinetics. In fact, our experiments and modeling examining the feed concentration dependence over several orders of magnitude suggest more complex behavior is to be expected for methanol [12]. This work shows that for high initial concentrations (> 0.001 mol fraction), three oxidation regimes occur: (1) an induction period with little loss of the fuel ($< 20\%$); (2) a rapid oxidation period of comparable length to the induction period, but with a much faster reaction rate; and (3) a final period with a rate intermediate between the first two. Thus, the effective rate constant can appear to be simultaneously a function of conversion and reaction time. Nonetheless, the values obtained for k_{eff} at high conversion are useful as a guide for engineering applications.
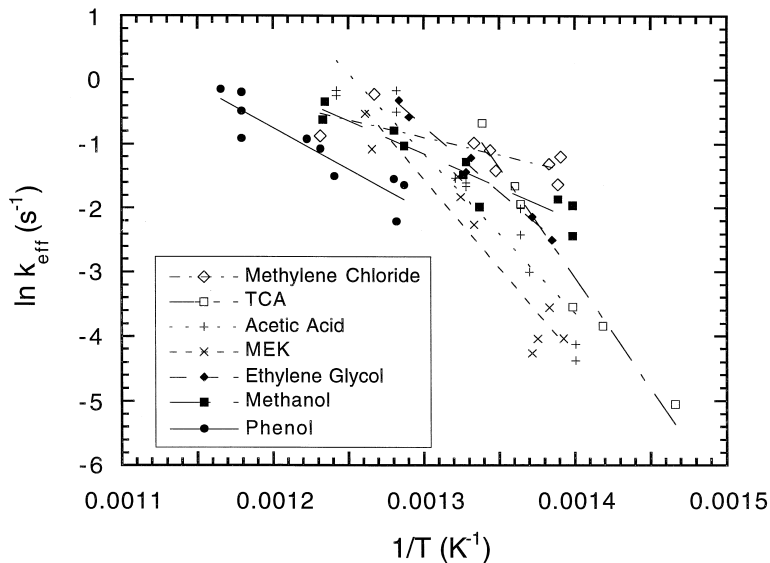
Fig. 2. Arrhenius plot of the seven compounds examined in this paper. The lines through each set are a best fit to an Arrhenius expression for the rate constant $k_{eff} = A \exp(-E_a/RT)$ and are tabulated in Table 8.

Fig. 2 displays the results of this analysis for all seven compounds using the GC data for C and C_r. From the $\ln(k_{eff})$ vs. $1/T$ plot, we obtain global Arrhenius parameters for the oxidation rates:

$$k_{eff}(T) = A \exp(-E_a/RT). \tag{4}$$

These values are presented in Table 8. The calculated activation energies cover a wide range and indicate a significant variation in the reactivity temperature dependence of our different feeds. Further analysis of these calculated parameters is not warranted because our small data sets yield large standard deviations, and because present understanding of reaction mechanisms in supercritical water is rudimentary.

Table 8
Arrhenius parameters from first-order analysis

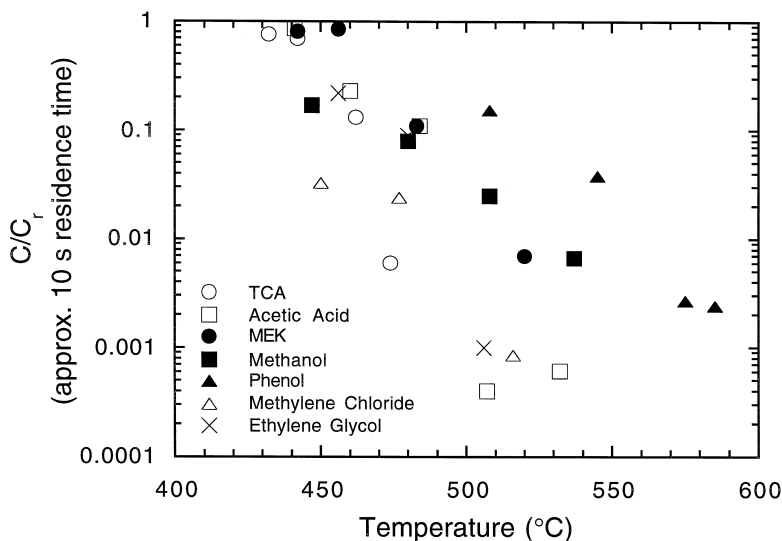| Compound	E_a (kJ/mol K)	$\log_{10} A$ (s^{-1})
Methanol	85.9 (10.5)	5.33 (0.73)
Ethylene glycol	171 (10.7)	11.2 (0.74)
Phenol	108 (16.4)	6.42 (1.05)
Acetic acid	208 (21.9)	13.6 (1.52)
MEK	230 (29.3)	14.9 (2.05)
Methylene chloride	45.6 (16.2)	2.71 (1.1)
1,1,1-Trichloroethane	286 (27.3)	19.6 (1.98)

95% error in parentheses.

Fig. 3. Summary plot of C/C_r from GC analysis for residence times of about 10 s. Note that the high-temperature points correspond to residence times of about 8 s, and the low-temperature points correspond to residence times of about 12 s. Results from reaction conditions that produce no detectable parent compound in the effluent (e.g., the 570°C and 540°C points for methylene chloride) are not included in the figure.

To provide a practical comparison for the seven organic compounds, Fig. 3 presents conversion efficiencies for individual experiments with similar residence times (about 10 s). This figure illustrates the most important general observation to be made from the measurements in this paper: conversion rates for different simple organic molecules differ by several orders of magnitude at a given temperature and reaction time. Note, in particular, that apparent conversion rates of ethylene glycol and acetic acid are significantly faster than those of methanol and phenol, especially at high temperature.

This figure represents a rough comparison only since the *similar residence times* vary from about 8 to 12 s as temperature decreases for a given compound (see tables). This is due to the fact that our experimental method maintained constant ambient volumetric flows while reaction temperatures varied. The resulting density variation produced different residence times. However, at any given temperature, the residence times for each compound are nearly identical.

A second important observation is that feed species disappearance rates tell only part of the story. Many of the compounds that have high disappearance rates at modest temperatures produce more robust and still incompletely oxidized products. This conclusion is best illustrated by our results for acetic acid. The TOC values at 532°C (Samples 1, 2, and 3, Table 4) and again at 507°C (Samples 4, 5, and 6) vary minimally, regardless of residence time. At the same time, the GC results show that acetic acid rapidly disappears with increased residence time within each temperature group (see Table 4). Acetic acid is being converted to more robust molecules that contribute to the TOC in the acetic acid effluent. The GC traces include unidentified peaks indicating the presence of such compounds; likely candidates include species such as methanol,

methane, formaldehyde, and formic acid. Contrary to previous reports, there is nothing especially refractory about acetic acid at sufficiently high temperatures in supercritical water. Li et al. [13] have suggested that acetic acid is a key stable intermediate in SCWO mechanistic schemes by analogy to lower pressure wet-air oxidation studies. In contrast, we find that at SCWO conditions, especially above 480°C, the general mechanism changes, and methanol, and perhaps formal-dehyde, are the most stable intermediates present.

Similar results were obtained for ethylene glycol, methylene chloride, phenol, and MEK, where the TOC fraction remaining is higher than that for the feed material determined from GC. If high TOC conversion efficiencies are needed in a particular waste treatment application, the controlling oxidation chemistry is not necessarily that of the starting material, but may best be represented by that of simple stable organics formed as intermediates during oxidation of the parent species. This suggests that high TOC conversion efficiencies will require high temperatures or longer residence times regardless of the nature of the feed pollutant.

4.2. Comparison to other work

There is a rapidly evolving body of data concerning reaction of simple organic compounds in supercritical water. A review of the literature has been published [1], although some newer kinetics measurements are available in more recent studies of methanol, phenol, and acetic acid as noted below.

Fig. 4 shows a plot of k_{eff} for our methanol results, and compares these results to those of Tester et al. [14] and Brock et al. [15]. Although there is little overlap in temperature, the results from Brock et al. appear to extrapolate well from the data of Tester et al. The data from all three sets have about the same amount of scatter and
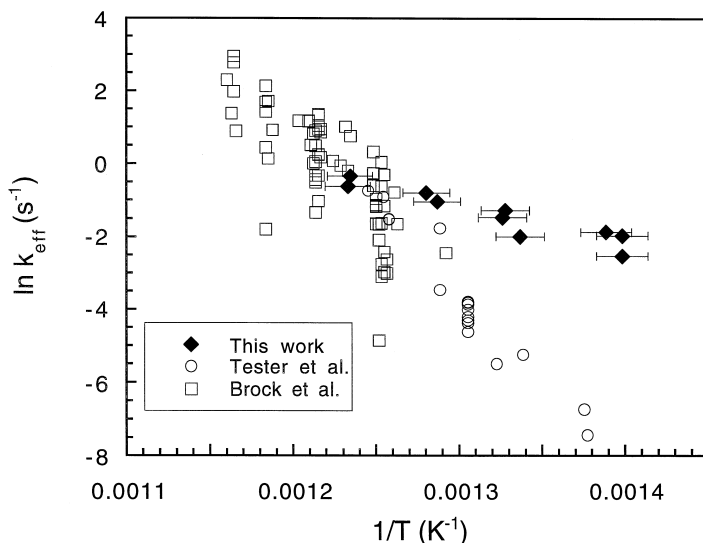

Fig. 4. Arrhenius plot comparing the effective first-order rate constants for methanol oxidation. Data presented are from Refs. [14,15] and those calculated from the results presented in this paper.

compare well at 520°C, but the temperature dependence of our results is much weaker, such that at lower temperatures, our conversion rates are significantly higher. The key to this discrepancy derives from an important distinction between the three studies. Our initial concentrations were 5 to 10 times greater than the experiments in these other studies, and the conversions are much higher at low temperature. At higher concentration, induction periods are shorter, and therefore affect our values of k_{eff} far less, resulting in substantially higher calculated rate constants at lower temperature. Note however, at higher temperatures, it appears that our data would extrapolate to a smaller effective rate constant. This may be due to the fact that the conversion at higher temperature for our data is very high and may represent a slowing of the overall rate at high conversion.

We can compare our phenol results to those of a number of other studies [9–11], omitting recent results by Koo et al. [16] because most of those data, as presented, cannot be converted to a first-order rate constant in a simple way. Fig. 5 displays our data along with a plot of the global expression for the 380–480°C temperature range presented in Ref. [11]. Our results appear to extrapolate well to those obtained at lower temperatures, although there appears to be a different temperature dependence of the Refs. [9,10] data at lower temperatures.

Krajnc and Levec [11] have also examined the oxidation of phenol in supercritical water at lean to very lean conditions in the range of 380–450°C, and observe the formation of multi-ring condensation products. As in this paper and our previous report
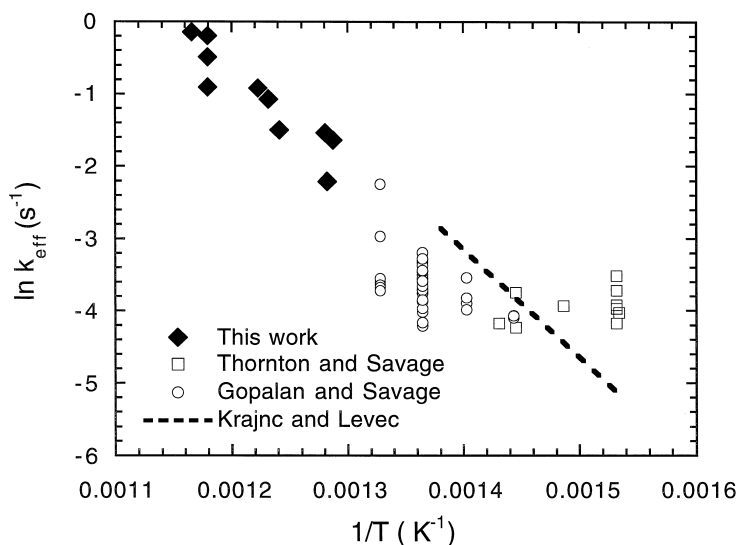

Fig. 5. Arrhenius plot comparing the effective first-order rate constants, k_{eff}, presented in Refs. [9,10] on phenol and those calculated from the results presented in this paper. Also included is the plot of the first-order rate constant calculated from Ref. [11]. The results from this work appear to extrapolate well to lower temperatures. Only the points in Ref. [9] for runs at 27.8 MPa and equivalence ratios of 0.5–1.0 are used for comparison.

[4,5], they employed a combination of chromatography and TOC to monitor both phenol and the presence of intermediates. The data in Ref. [11] show a considerable amount of TOC present that is not phenol and is less reactive than phenol. The global rate expression they present, when adjusted for zero-order oxygen concentration at a molar ratio of 7:1, produces the curve shown in Fig. 5. This extrapolates well to our data. They propose a reaction pathway similar to Ref. [10] that is consistent with much of the low-temperature data, in which a primary path for phenol oxidation is the formation of more robust polycyclic species including furans and dioxins.

The phenol data are indicative of a complicated multistep path to complete oxidation, with individual reactions that have different temperature dependencies. We suspect that as temperature is raised, the condensation reactions, typically with low activation energies, become less important, and that the higher activation energy ring-opening reactions begin to dominate.

Fig. 6 compares our results for acetic acid with those reported by Lee and Gloyna [17] using hydrogen peroxide, and Wightman [18] and Meyer et al. [19] using oxygen as the oxidizer. There are other studies on acetic acid in the literature [20,21], but similar to phenol, the data in these papers, as presented, could not be converted to an effective first-order rate constant or differed too much in reaction conditions to make a good comparison. Our data, with the exception of the lowest temperature point, agree well with Wightman's results and to a lesser degree with the other reports. Again, the high concentration in our experiments may be the source of differences in the comparison.
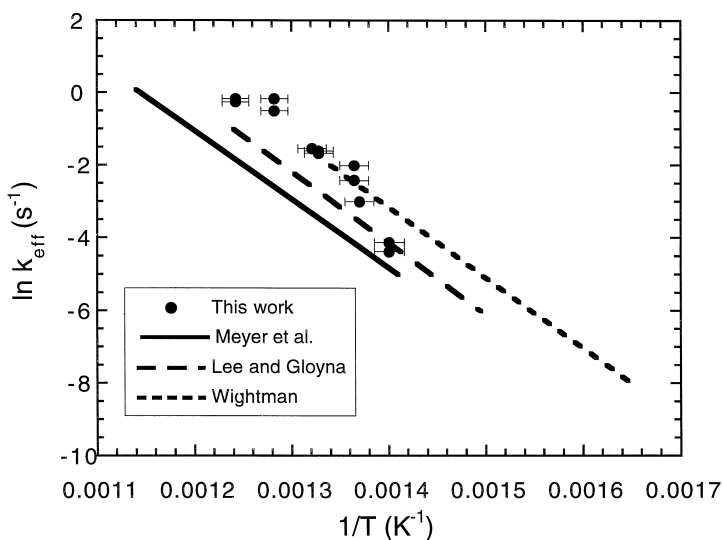

Fig. 6. Plot of the k_{eff} calculated for the oxidation of acetic acid taken from the short residence time runs. These results are compared with three lines that are the best fit to the work presented by Lee and Gloyna [17], Wightman [18], and Meyer et al. [19].

5. Conclusion

This paper focuses on an important aspect of SCWO technology development, namely, the need to quantify the trade-off between operating temperature and conversion efficiency for simple chemical systems. The results show that high conversion efficiency for nearly all the organic materials examined can be obtained with residence times well under 30 s if temperatures are maintained in excess of 550°C. In the range of 500-550°C, many materials can be destroyed, possibly leaving trace products of incomplete oxidation. However, some molecules that are less labile to oxidation, such as phenol, will require residence times longer than 30 s to obtain conversion efficiencies of 99.99%. Operation below 500°C, where materials of construction requirements can be relaxed, may require residence times of greater than 1 min for many organic solvents.

An important exception to these general observations is the behavior of the two chlorinated organics, TCA and methylene chloride. Although the TOC data are not valid, the gas chromatography data show that these materials react very rapidly. They may not be oxidized completely, but the original compound is destroyed. This may be due to rapid hydrolysis reactions that most likely form acetic acid from TCA and formaldehyde from methylene chloride.

The results of this investigation permit engineering estimates of residence times required for complete conversion of organic compounds at high volumetric flow rates in larger scale systems. It will be useful to compare the present results with measurements at higher initial concentrations to determine how well the rates can be extrapolated to processing systems designed for 5–10 wt.% organic loading in the inlet feed stream.

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