

Engineering Kinetics for Hydrothermal Oxidation of Hazardous Organic Substances

Frédéric Vogel, Kenneth A. Smith, Jefferson W. Tester, and William A. Peters

Dept. of Chemical Engineering and Energy Laboratory, Massachusetts Institute of Technology,
Cambridge, MA 02139

Supercritical water oxidation (SCWO) can decontaminate hazardous organic wastes, including mixtures whose constituents vary widely in their susceptibility to oxidation. The SCWO kinetics of complex organic wastes are analyzed using a mathematical model that eliminates the substantial input requirements and computationally demanding mathematics of multistep, component-specific rate expressions. The approach assumes that SCWO occurs by an infinite set of independent, parallel, first-order chemical reactions, with a continuous distribution of activation energies. The resulting model, distributed activation energies model (DAEM), was applied by earlier workers to other kinetics problems of comparable complexity, inter alia, decay of molecular defects in solids, and coal pyrolysis. A three-parameter DAEM is shown to correlate the SCWO kinetics of eight organic wastes, including several complex mixtures. These wastes are: JP-5 aviation fuel, Velsicol H537 hydraulic fluid, aqueous methanol solutions, NaOH and NH_4OH hydrolysates of solid rocket propellants, an orange military dye marker, municipal sewage sludge, and alcohol distillery waste water. The model was separately parameterized for each waste by best fitting its predictions of conversion as affected by residence time and/or temperature to experimental data from various investigators. A satisfying correlation resulted for each case. Illustrative reactor engineering calculations demonstrate DAEM's superiority to a single reaction model in sizing a PFR for SCWO of a complex organic mixture. The times required to achieve 99.99% destruction of different wastes depend strongly on the nature of the waste and differ by about three orders of magnitude from the most labile waste to the most refractory waste.

Introduction

Supercritical water oxidation (SCWO) shows substantial promise for clean and efficient decontamination of many aqueous organic wastes (Modell, 1989; Shaw et al., 1991; Barner et al., 1992; Tester et al., 1993; Peters et al., 1994; Smith et al., 1995; Peters, 1996a,b). SCWO is oxidation in an aqueous medium above the critical temperature and pressure of pure water, that is, 374°C (647 K) and 221 bar (22.1 MPa). SCW at typical process conditions of 500°C to 600°C and 250 bar, has appreciably lower density ($< 100 \text{ kg/m}^3$), dielectric constant (< 2), and dissociation constant ($K_w = [\text{H}^+][\text{OH}^-] < 10^{-22} \text{ (mol/kg)}^2$) than water at STP. Consequently, SCW behaves as a low-polarity, largely unassociated solvent in

which molecular oxygen and many organic compounds are totally miscible. SCWO can rapidly and efficiently destroy diverse organic substances, even when very dilute, in a self-contained process with very clean byproduct streams (little or no NO_x , SO_x , soot). The elevated temperature and the absence of mass-transfer resistances across a phase boundary lead to almost complete mineralization in short residence times (that is, 99% to 99.99% at 500 to 650°C in 1 s to 100 s).

Quantitative studies of SCWO kinetics have largely focused on single compounds reacting under near isothermal conditions in batch cells (Hirth and Franck, 1993) or in tubular flow reactors (Helling and Tester, 1987; Yang and Eckert, 1988; Thornton and Savage, 1990; LaJeunesse et al., 1992; Crain et al., 1993; Tester et al., 1993). Marrone (1998) has performed experiments on the SCWO of methanol in a con-

Correspondence concerning this article should be addressed to W. A. Peters.

tinuously fed stirred-tank reactor (CSTR). Kinetics modeling has utilized single-reaction Arrhenius rate expressions or multistep elementary reaction models. The latter often build upon related combustion studies at lower densities (but higher temperatures) and, to reduce computational and data demands, typically are implemented in “reduced” form, that is, with a smaller number of individual chemical steps chosen to reflect major kinetic bottlenecks. Many wastes that are good candidates for SCWO are complex organic mixtures that oxidize nonuniformly because their components react with oxygen at different rates. This article suggests a method to reliably model the SCWO kinetics of these and related complex starting materials without elaborate mathematics or oppressive data requirements. To illustrate the essentials of the method we focus on SCWO at constant temperature and fluid density, but we recognize that this idealization is seldom attained in practice.

The oxidation kinetics of complex mixtures, including substances that oxidize at nonuniform rates, are sometimes modeled by “lumped” or global kinetics expressions that simplify calculations of heat release rates and conversion, that is, extent of oxidation, by eliminating the appreciable data requirements and elaborate mathematics of multiple, component-specific rate expressions. There is an extensive literature on the theory and applications of lumped kinetics, for example, Wei and Prater (1962), Aris and Gavalas (1966), Luss and Hutchinson (1971), Bailey (1972), Weekman (1979), Shinnar and Feng (1985), Astarita and Ocone (1988), Astarita (1989), Astarita and Sandler (1991), Lakshmanan et al. (1991), Quann and Jaffe (1992), and Li et al. (1996). Reviews include those of Weekman (1979), Bischoff and Coxson (1987), and of Burnham and Braun (1999) on global methods for kinetic analysis of complex substances. Here we describe and test a continuum model for lumping the SCWO kinetics of complex organic substances. Description of a mixture as a continuum dates at least to DeDonder (1931). Our analysis assumes that SCWO of complex reactants occurs by an infinite set of independent, parallel first-order chemical reactions, with a continuous distribution of activation energies. This model, the *distributed activation energies model* (DAEM), has been applied to the relaxation kinetics of molecular defects in solids, that is, to batch systems at constant fluid density. Examples are Marie Curie’s (1939) analysis of the decay of phosphorescence in solids and Vand’s (1943) study of the annealing of lattice distortions in evaporated metal films. Primak (1955) and Astarita and Ocone (1988) discuss generalization of the DAEM to systems with kinetics that are nonlinear in concentration. Pitt (1962), Rennhack (1964), Hanbaba et al. (1968), Anthony et al. (1975) (see the review by Howard, 1981), and Howard et al. (1987) apply the DAEM to coal pyrolysis kinetics. Lakshmanan et al. (1991) use the DAEM together with appropriate thermal histories over geological time scales to estimate the timing of petroleum generation and the quantity of hydrocarbons generated from sedimentary organic matter.

The essence of the DAEM is its use of a continuous probability density function (PDF) for activation energies to quantify nonuniform kinetics in a reactant. Various closed-form PDFs are plausible but, as shown below, a simple Gaussian often suffices, in which case just two degrees of freedom, the mean E_0 , and the standard deviation σ , of the PDF, are

required to model an appreciable spread in chemical reactivity. These two parameters are recovered by best fitting predictions of the model to experimental data on conversion, as affected by known variations in reaction conditions, typically residence time and/or temperature. In some cases it may be feasible to infer the PDF from chemical or thermal analysis of the feedstock, here the waste. This article shows that using three waste-specific parameters (E_0 , σ , and A , an Arrhenius preexponential factor), the DAEM is sufficiently robust to satisfyingly correlate the SCWO kinetics of eight organic substances: JP-5 aviation fuel, Velsicol H537 hydraulic fluid, aqueous methanol solutions, NaOH and NH_4OH hydrolysates of solid rocket propellants, an orange military dye marker, municipal sewage sludge, and alcohol distillery wastewater, all under conditions approximating ideal plug flow. The article begins by outlining how classic DAEM theory for batch systems must be extended to treat the two limiting cases of ideal, isothermal chemically reacting flows: plug flow and perfect back-mixing. By design or owing to poor mixing or heat transfer, pilot scale and larger SCWO reactors often exhibit appreciable temporal and spatial variations in temperature, and thus involve nonisochoric flows. A related article (Vogel et al., 2002) describes extension of DAEM theory to nonisothermal tubular flow reactors, where effects of variable density on residence time and kinetics must be accounted for.

Generalized Equation of Change for Transport and Reaction of a Complex Mixture

We model a complex mixture as an ensemble of n virtual components. Each component, i , has a concentration, c_i , and chemically reacts by one independent, first-order reaction proceeding in parallel with the reactions of all the other components. The governing equation for transport and reaction for each component in an assumed to be constant density flow is

$$\frac{\partial c_i}{\partial t} + \mathbf{v} \cdot \nabla c_i = \nabla \cdot (D_i \nabla c_i) - k_i c_i. \quad (1)$$

The quantity \mathbf{v} is the velocity vector, D is the molecular diffusion coefficient, and k is the first-order kinetic rate constant. Let the unique chemical reactivity of each component, i , be indexed by a variable, ξ_i , that, as will be seen, is completely specified by a particular value of the activation energy, E_i . The contribution of component i to the total concentration of all virtual components, that is, to the concentration of the mixture, is given by the frequency of occurrence of ξ_i , $f_i(\xi_i, t)$. The index i denotes discrete quantities and is an appropriate formalism for a mixture of a finite number of components, n . In the limit as n approaches infinity, the frequency becomes a continuous PDF, $f(\xi, t)$ for the quantity ξ , and each c_i becomes a differential part of the total concentration, $c(t)$. Thus at any time t , the concentration of a mixture component, $c_i(\xi, t)$, $[=dc(\xi, t)]$ characterized by a value of ξ between ξ and $\xi + d\xi$ is given by

$$c_i = c_0 f(\xi, t) d\xi. \quad (2)$$

At $t = 0$ the distribution function, $f(\xi, t = 0) = f_0(\xi)$ is normalized so that

$$\int_0^\infty f(\xi, t = 0) d\xi = \int_0^\infty f_0(\xi) d\xi = 1, \quad (3)$$

where the subscript 0 denotes conditions at time = 0. The total concentration $c(t)$ of the reacting mixture at any time t , is obtained by integrating Eq. 2 over all ξ

$$c(t) = \int_0^\infty c_0 f(\xi, t) d\xi. \quad (4)$$

Note that the total concentration changes with time because of chemical reaction and physical transport. When applying the DAEM to engineering calculations, it is convenient to let the time-independent quantity, c_0 , define the initial distribution over ξ , and to capture the time dependence in c entirely in $f(\xi, t)$, which depends explicitly on time.

In the DAEM, the distributed variable, ξ , is the activation energy, E . Substitution of Eq. 2 into Eq. 1 gives

$$\frac{\partial f(E, t)}{\partial t} + \mathbf{v} \cdot \nabla f(E, t) = \nabla \cdot (D \nabla f(E, t)) - k f(E, t). \quad (5)$$

In the DAEM E is a proxy for the physicochemical individuality of the mixture components. Although, in general, different species will have different diffusion coefficients, the present analysis ignores any E dependence of D for simplicity. Further, we assume a simple Arrhenius rate constant, $k(E)$, for each component, where the E dependence is confined to the exponential term, that is,

$$k(E) = A \exp\left(-\frac{E}{RT}\right). \quad (6)$$

The two boundary conditions needed to solve Eq. 5 for $f(t, x, y, z, E)$ will be set by the reactor geometry and, in numerical simulations, by how that geometry is discretized into individual cells for computation. It is convenient to describe the initial condition by a known analytical PDF. For this study an initial Gaussian PDF was assumed, where the activation energies, E , are symmetrically distributed about a mean activation energy, E_0 , with a standard deviation, σ , where

$$f(t = 0) = f_0(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E - E_0)^2}{2\sigma^2}\right]. \quad (7)$$

Because more reactive fractions of a mixture will react faster than less reactive fractions, $f(E)$ will evolve with time becoming non-Gaussian for $t > 0$ (Figure 1). Because SCWO depletes the concentration of mixture, the PDF will be normalized only at $t = 0$, that is,

$$\int_0^\infty f(E, t) dE < 1; \quad t > 0. \quad (8)$$

For a constant density flow, the cumulative conversion $X_M(t)$ of feed material up to time t can be defined in terms of reac-

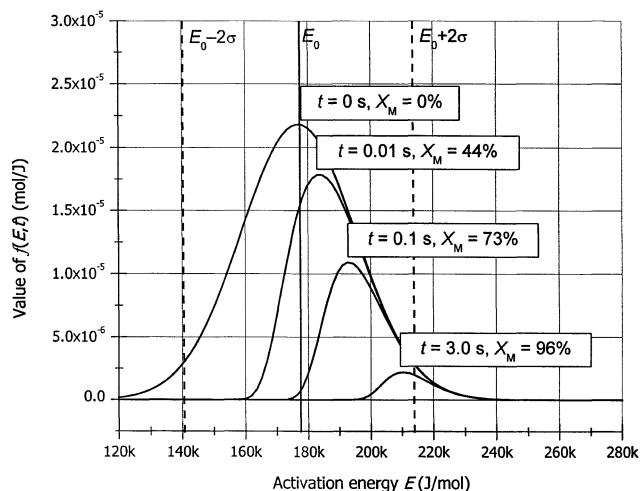


Figure 1. Time-evolving PDF $f(E, t)$, defined by Eq. 11 plotted for $T = 773.15$ K as a function of the activation energy E for the JP-5 best-fit parameters $A = 3.3925 \times 10^{13} \text{ s}^{-1}$, $E_0 = 177.0$ kJ/mol, $\sigma = 18.3$ kJ/mol, and at different reaction times t .

Vertical lines have been drawn at $E = E_0$, and $E = E_0 \pm 2\sigma$.

tant concentrations, that is,

$$X_M(t) = 1 - \frac{c(t)}{c_0} = 1 - \frac{\int_0^\infty c_0 f(E, t) dE}{\int_0^\infty c_0 f_0(E) dE} = 1 - \int_0^\infty f(E, t) dE. \quad (9)$$

In some applications of the DAEM, total organic carbon (TOC), or chemical oxygen demand (COD), both of which can be experimentally measured, can be reliable proxies for $c(t)$ and c_0 (however, see discussion below for limitations on this assumption).

Integration of the Transport/Reaction Equation for Two Limiting Cases of Fluid Mechanical Mixing

Isothermal isochoric plug-flow reactor with irreversible first-order reaction chemistry

For isothermal, plug flow, that is, uniform fluid velocity in the direction of flow and no diffusive or other dispersion of mass in any direction, Eq. 5 reduces to the expression for a uniform batch reactor at constant density

$$\frac{df}{dt} = -kf, \quad (10)$$

for which the solution is simply

$$f(E, t) = f_0 \exp(-kt). \quad (11)$$

Total conversion $X_{M,\text{PFR}}$ is obtained by substitution of Eq. 11 for $f(E, t)$ into Eq. 9

$$X_{M,\text{PFR}}(t) = 1 - \int_0^\infty f_0(E) \exp[-k(E)t] dE. \quad (12)$$

Equation 12 is the isothermal equivalent of a more general result obtained by Anthony et al. (1975) for nonisothermal pyrolysis of coal in a batch reactor where variations in fluid density were unimportant. Substituting Eqs. 6 and 7 for $k(E)$ and $f_0(E)$ in Eq. 12 gives

$$X_{M,\text{PFR}}(t) = 1 - \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \exp \left[-A \exp \left(-\frac{E}{RT} \right) t - \frac{(E - E_0)^2}{2\sigma^2} \right] dE. \quad (13)$$

This 3-parameter (A , E_0 , σ) DAEM can be best fitted to experimental data $X_M(t, T)$ on isothermal conversion-vs.-residence time, by evaluating the integral numerically while minimizing the residual sum of the squares (SSQ)

$$\text{SSQ} = \sum_i [X_{M,i}(\text{observed}) - X_{M,i}(\text{calculated})]^2. \quad (14)$$

The standard error of the estimate (SEE), is one statistic of the uncertainty of the DAEM prediction

$$\text{SEE} = \sqrt{\frac{\sum_i [X_{M,i}(\text{observed}) - X_{M,i}(\text{calculated})]^2}{n - p}} = \sqrt{\frac{\text{SSQ}}{n - p}}, \quad (15)$$

where n is the number of data points used for the fit, and p is the number of adjustable parameters.

Isothermal, isochoric continuously fed stirred-tank reactor with irreversible first-order reaction chemistry

For kinetics that are first order in concentration, the conversion $X_{M,\text{CSTR}}(\tau)$ of a complex mixture in a perfect CSTR with constant fluid density can be predicted by weighting the corresponding DAEM conversion for a plug-flow reactor, $X_{M,\text{PFR}}(t)$, Eq. 13, by the CSTR residence time distribution $E_{\text{CSTR}}(t)$

$$X_{M,\text{CSTR}}(\tau) = \int_0^\infty X_{M,\text{PFR}}(t) E_{\text{CSTR}}(t) dt. \quad (16)$$

Using a mean residence time, τ , $E_{\text{CSTR}}(t)$ is given by

$$E_{\text{CSTR}}(t) = \frac{1}{\tau} e^{-t/\tau}. \quad (17)$$

After substituting Eqs. 13 and 17 for $X_{M,\text{PFR}}(t)$ and $E_{\text{CSTR}}(t)$, respectively, in Eq. 16 we obtain

$$X_{M,\text{CSTR}}(\tau) = 1 - \frac{1}{\tau\sigma\sqrt{2\pi}} \int_0^\infty \int_0^\infty \exp \left[-A \exp \left(-\frac{E}{RT} \right) t - \frac{(E - E_0)^2}{2\sigma^2} - \frac{t}{\tau} \right] dE dt. \quad (18)$$

Equation 18 shows that for this idealized case, the time domain and the reactivity domain described by the activation energy PDF are separable. The time integration then yields

$$X_{M,\text{CSTR}}(\tau) = 1 - \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \frac{1}{A \exp \left(-\frac{E}{RT} \right) \tau + 1} \exp \left[-\frac{(E - E_0)^2}{2\sigma^2} \right] dE. \quad (19)$$

If the normalization condition of the Gaussian PDF is used, Eq. 19 can also be written as

$$X_{M,\text{CSTR}}(\tau) = \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \left(1 - \frac{1}{k(E)\tau + 1} \right) \exp \left[-\frac{(E - E_0)^2}{2\sigma^2} \right] dE. \quad (20)$$

As expected, this is equivalent to

$$X_{M,\text{CSTR}}(\tau) = \int_0^\infty X_{\text{CSTR}}(E, \tau) f_0(E) dE, \quad (21)$$

where

$$X_{\text{CSTR}}(E, \tau) = \frac{k(E)\tau}{k(E)\tau + 1} = \left(1 - \frac{1}{k(E)\tau + 1} \right) \quad (22)$$

is the conversion associated with a single first-order reaction in a perfect (isothermal) CSTR with constant fluid density (Levenspiel, 1972). Thus, Eq. 21 shows that, for an infinite set of independent parallel first-order reactions, the conversion in a perfect CSTR with average residence time τ and constant fluid density is merely the corresponding expression for conversion in a CSTR by a single first-order reaction of activation energy E , convolved with the time stationary PDF for the activation energy, $f_0(E)$.

Results

Conversion data from various investigators (Table 1) on the SCWO of eight different substances were best fitted to the PFR version of the DAEM, Eq. 13, by minimizing the quantity SSQ in Eq. 14. Practical calculations seek computational economy without sacrificing accuracy by confining the integration to a finite range of E . Moreover, as shown in Figure 1 for SCWO of jet fuel (see below), the PDF evolves in time according to Eq. 11, destroying the symmetry of the initial Gaussian about E_0 . Consequently the limits for numerical integration of Eq. 13 were taken as $E_0 - 3\sigma$ and $E_0 + 5\sigma$, that is, substantially broader than the 95.5% of a Gaussian captured within the domain $E_0 \pm 2\sigma$.

SCWO of JP-5 fuel

SCWO is of interest to the U.S. Navy for shipboard destruction of excess hazardous materials (EHMs), which include wastes from ships operations, for example, fuels, lubricants, and hydraulic fluids. To support development of suit-

Table 1. Sources of Experimental SCWO Data, and Isothermal, Best-Fit DAEM Parameter Values

Waste	Temp. (°C)	Pres. (bar)	Conversion	A (s ⁻¹)	E_0 (kJ/mol)	σ (kJ/mol)	SEE	Reference
JP-5 (TOC)	388–558	245	0.54–0.999	3.3925×10^{13}	177.0	18.3	0.0281	Rice et al., 1997
Velsicol H537 (TOC)	405–550	245	0.738–0.998	1.4590×10^{21}	262.6	29.7	0.0146	Rice et al., 1997
Methanol (GC)	423–485	269	0.322–0.997	8.7755×10^{11}	178.3	0	0.0623	Phenix, 1998
Methanol (TOC)	442–574	276	0.81–0.9991	3.3068×10^7	113.0	6.0	0.0129	Rice and Steeper, 1998
Methanol (TOC)	442–574	276	0.81–0.9991	8.7755×10^{11}	170.0	10.7	0.0166	Rice and Steeper, 1998
Hydrol. propellant, NH ₄ OH (TOC)	424–550	250(?)	0.583–0.999	8.2757×10^5	93.8	0	0.3907	Hazlebeck et al., 1995
Hydrol. propellant, NaOH (TOC)	395–498	250(?)	0.868–0.997	1.1228×10^8	111.8	7.2	0.2516	Hazlebeck et al., 1995
Orange dye (TOC)	484–556	246	0.769–0.9969	1.1227×10^7	114.1	0	0.0402	Rice et al., 1994
Municipal sewage sludge (TOC)	400–500	300	0.823–0.998	40.07	28.5	10.9	0.0176	Goto et al., 1998
Distillery waste water (TOC)	400–500	300	0.8751–0.9948	169.2	35.4	13.0	0.0127	Goto et al., 1998

able SCWO reactors, Rice et al. (1997) studied SCWO of JP-5 jet fuel, Velsicol H537 hydraulic fluid, and Delo 400 motor oil at throughputs of about 30 g/h. Wastes were treated individually in an isobaric and nearly isothermal tubular plug-flow reactor. Oxygen was generated by thermal decomposition of hydrogen peroxide just upstream of the reactor. Destruction efficiencies were measured by comparing the measured TOC of the reactor effluent to the TOC calculated for the waste feed. In the present study the DAEM was fitted to Rice et al.'s SCWO data for JP-5 and Velsicol H537.

JP-5 jet fuel, specific gravity 0.788–0.845, is a kerosene-based fuel used by military aircraft. JP-5 consists of hydro-treated light petroleum distillates (average molecular weight 185 amu) and is virtually insoluble (< 0.1 wt. %) in water at standard conditions (25°C, 1 atm) (Rice et al., 1997). As a base case we best fitted 36 data points on TOC conversion (0.543 to 0.999) as affected by temperature or residence time, to obtain parameters (A and E_a) for a single first-order reaction kinetic model. A data table in Rice et al. (1997) inadvertently reversed the TOC values for two runs (S. F. Rice, personal communication, 1999); the corrected values have been

used here. Figure 2 shows as individual points the temperature dependence of the first-order Arrhenius rate constant k calculated for each run. Note that the nonlinear abscissa has been scaled to be linear in $1/T$, where T is the absolute temperature in K. A clear difference is evident between the short (●) and long residence time (■) data. Fitting one single first-order reaction to the entire data set results in a poor correlation (dashed line, Figure 2). A much better fit for $\ln(k)$ vs. $1/T$ (dotted and solid lines, Figure 2) was obtained if distinct first-order reaction models were separately fit to the short and the long residence time data. The corresponding predictions of this model, which consists of two independent correlations with a total of four adjustable parameters, lie within $\pm 11\%$ of the measurements. Using a Simplex algorithm in MatLab, the DAEM for an isothermal plug-flow reactor, Eq. 13, was best fitted to all the data of Figure 2 by minimizing the residual sum of squares, Eq. 14, between the model predictions and the measurements. A parity plot (Figure 3), using the resulting DAEM parameters (Table 1) compares the measured conversions with those predicted from Eq. 13. The fit is satisfactory for the entire range of short and long residence observations, with the predictions and measurements agreeing to within +4% and -7%.

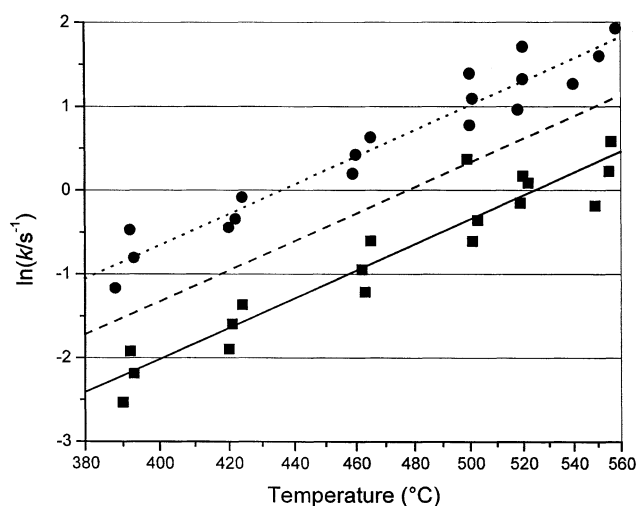


Figure 2. Fitting Rice et al.'s (1997) data on SCWO of JP-5 fuel to a single-reaction, first-order Arrhenius rate constant k .

(●) Short and (■) longer residence-times data. Dotted line, solid line, dashed line: linear least-square fit of $\ln(k)$ to the short, longer, and shorter + longer residence-times data. The abscissa has been scaled to be linear in $1/T$, the absolute temperature in K.

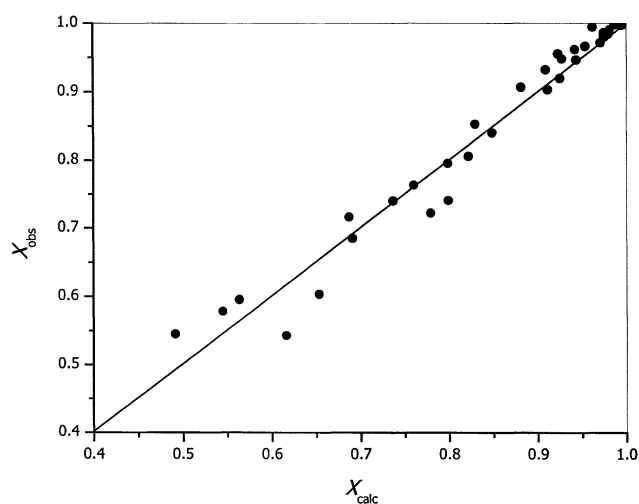


Figure 3. Parity plot for the DAEM fitted to data on the SCWO of JP-5; X_{obs} experimental data; X_{calc} predictions of DAEM using parameters from Table 1.

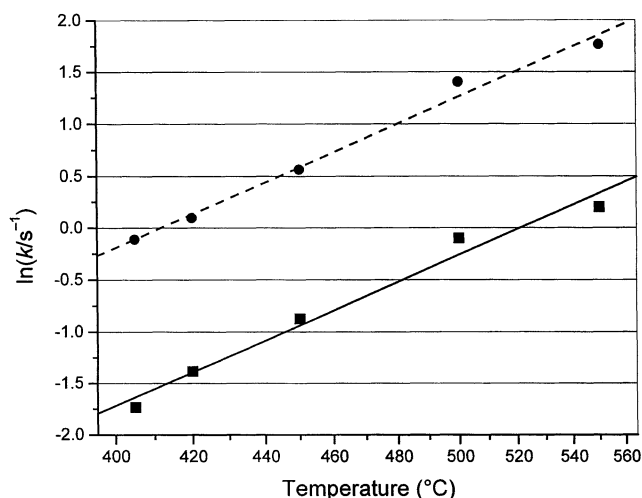


Figure 4. Fitting Rice et al.'s (1997) data on SCWO of Velsicol H537 hydraulic fluid to a single-reaction, first-order Arrhenius rate constant k .

(●) Short and (■) longer residence-times data. Dashed line, solid line: linear least-squares fit of $\ln(k)$ to the short and longer residence-times data, respectively. The abscissa has been scaled to be linear in $1/T$, the absolute temperature in K.

SCWO of Velsicol H537 hydraulic fluid

We lack detailed composition data for this clear red synthetic hydrocarbon liquid, which is almost completely insoluble in water. Ten data points from Rice et al. (1997) on TOC conversion as affected by temperature or residence time, spanning TOC conversions from 0.738 to 0.998 were used to obtain best-fit parameter values (A and E_a) for a single first-order reaction kinetic model. Figure 4 shows as data points the temperature dependence of the rate constant k calculated for each run. A clear difference exists between the short (●) and long residence time (■) data. A best fit of the combined data set to a single-reaction first-order rate model results in a poor correlation (not shown). Separately best fitting the short and long residence time data to a single-reaction first-order kinetic model gives a much better fit for $\ln(k)$ vs. $1/T$ (Figure 4, dashed and solid lines). Here this 4-parameter model predicts conversions within $\pm 3\%$ to 1.5% of the measurements. Using the same procedure as for JP-5, best-fitted DAEM parameter values (Table 1) and a parity plot of conversions (Figure 5) were obtained using the entire data set. An excellent fit over the whole range of conditions (short and long residence times) resulted, where predicted conversions were within $\pm 2\%$ of the measurements.

SCWO of methanol (conversion based on methanol concentration data)

Data from the MIT Supercritical Fluids Group [see Phenix (1998); Phenix et al. (2002)] spanning methanol conversions from 0.322 to 0.997 were fitted to test the DAEM for an individual model organic compound. Phenix determined methanol conversion by measuring methanol concentrations at the reactor inlet and outlet using gas chromatography. Figure 6 shows as data points the temperature dependence of a single-reaction first-order Arrhenius rate constant k calcu-

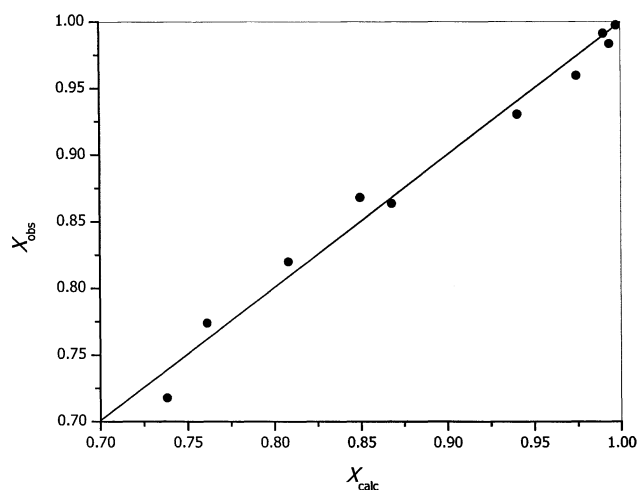


Figure 5. Parity plot for the DAEM fitted to data on the SCWO of Velsicol H537; X_{obs} experimental data; X_{calc} predictions of DAEM using parameters from Table 1.

lated for each run. Some of the data scatter may arise from the different feed concentrations, different oxidant sources (O_2 from H_2O_2 and pure O_2) (Phenix, 1998; Phenix et al., 2002), and departure from perfect first-order kinetic behavior. Figure 6 also compares the Arrhenius rate constant deduced by best fitting a single-reaction first-order kinetic model to these data, with a pseudo-Arrhenius rate constant. The latter was synthesized using the values of A and E_0 obtained by best fitting the DAEM to these data (Table 1). This approximation is justified because the accompanying best-fitted

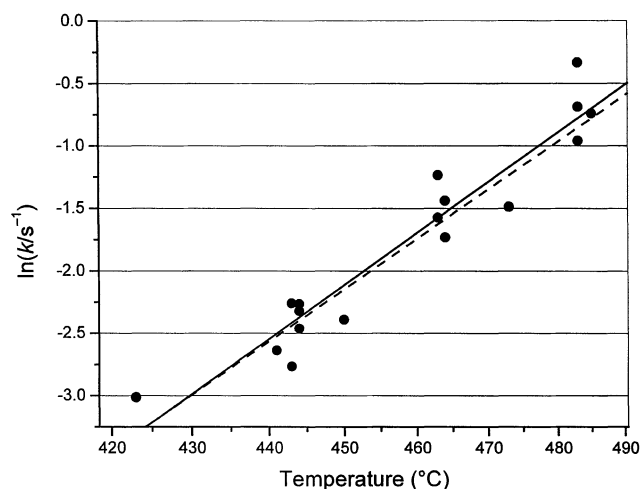


Figure 6. Results of fitting Phenix's (1998) data on SCWO of methanol to two different kinetic models.

Solid line: linear least-squares fit of a single-reaction, first-order Arrhenius rate constant k $\ln(k)$ vs. $1/T$; best-fitted parameters: $E_a = 184$ kJ/mol, $A = 2.393 \times 10^{12} \text{ s}^{-1}$. Dashed line: DAEM $\ln(k)$ equated to $A \exp[-E_0/(RT)]$ with $\sigma = 0$; best-fitted parameters: $E_0 = 178.3$ kJ/mol, $A = 8.7755 \cdot 10^{11} \text{ s}^{-1}$, $\sigma = 0$, obtained by nonlinear least-squares fit of X vs. T using Eq. 13. The abscissa has been scaled to be linear in $1/T$, the absolute temperature in K.

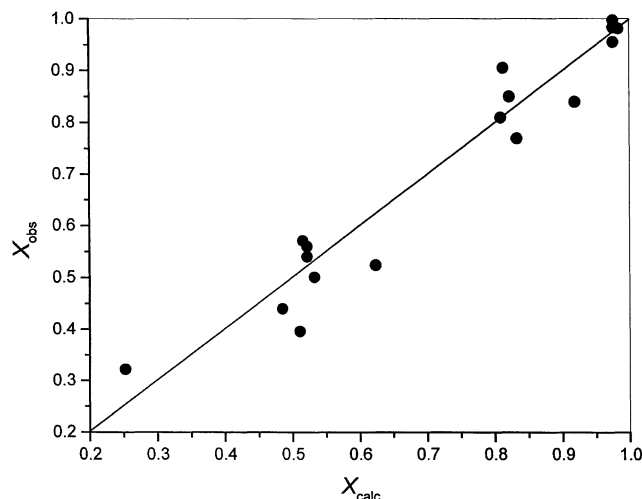


Figure 7. Parity plot for methanol SCWO: X_{obs} experimental data; X_{calc} conversion predicted from single-reaction first-order Arrhenius rate model best fitted to the data of Phenix (1998).

σ for the DAEM was zero (Table 1). A near-zero σ is consistent with the expectation that a single compound will exhibit more narrow chemical reactivity than a mixture of chemically different compounds (however, see the discussion of methanol TOC data below). Parity plots for the observed conversions and those predicted by the single-reaction (regular) Arrhenius rate constant and by the 3-parameter DAEM of Table 1 are shown in Figures 7 and 8, respectively. The nearly perfect agreement between these two figures shows that for this compound the DAEM matches, but does not exceed the performance of the single first-order reaction model in correlating the conversion data. Introduction of a PDF in the kinetic modeling does little to “smooth” the experimental data on conversion, as would be expected in light of the very small value of σ .

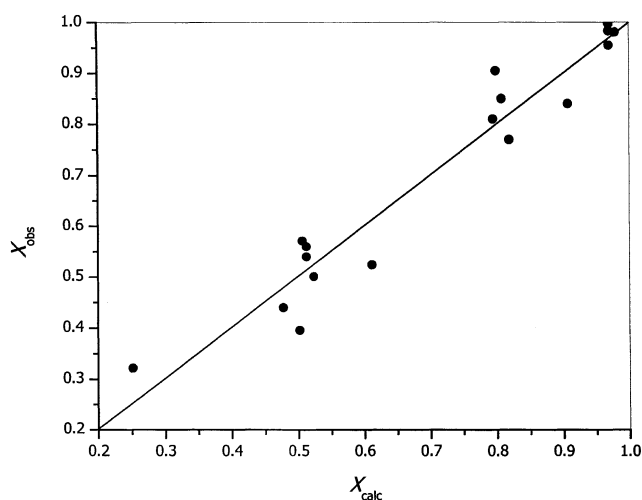


Figure 8. Parity plot for methanol SCWO: X_{obs} experimental data; X_{calc} conversion predicted from DAEM best fitted to the data of Phenix (1998); DAEM parameters from Table 1.

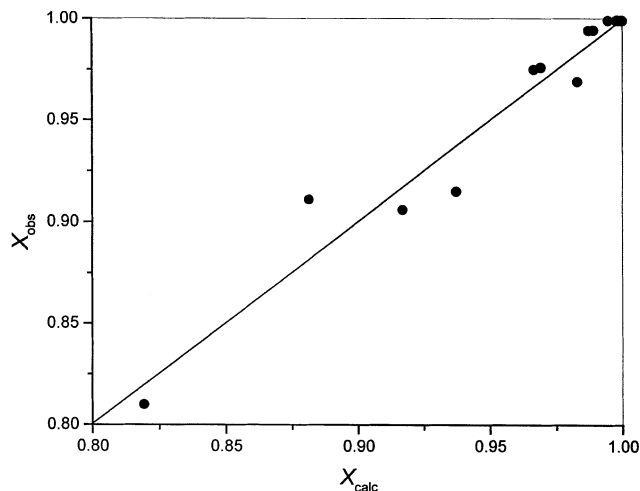


Figure 9. Parity plot for SCWO of methanol using data based on TOC: X_{obs} experimental data; X_{calc} predictions of DAEM using parameters from Table 1.

SCWO of methanol (conversion based on TOC data)

We also fitted the DAEM to Rice and Steeper's (1998) data on methanol SCWO, where methanol conversion was taken as the difference in the TOC of the reactor feed and effluent solutions. Table 1 and Figure 9, respectively, display the DAEM best-fitted parameters and corresponding parity plot for methanol conversion. In contrast to the DAEM results fitted to methanol concentration data, the PDF from TOC data has considerable breadth ($\sigma = 6.0$ kJ/mol vs. 0 kJ/mol, Table 1). Fitted values of the activation energy and preexponential factor are typically correlated. Thus to compare DAEM kinetics for these two data sets on a more consistent basis, the TOC data of Figure 9 were fitted to a two-adjustable-parameter DAEM, in which A was preset at the A value obtained from best-fitting the DAEM to the methanol concentration data (Table 1). The resulting best-fit value for E_0 is close to the value obtained from the concentration data (170.0 vs. 178.3 kJ/mol, Table 1). However, the corresponding fitted σ of almost 11 kJ/mol is substantially greater than the zero value from the concentration data (Table 1).

Because TOC measures all organic carbon in the SCW, not just carbon in methanol, a kinetic model fitted to TOC data describes the cumulative disappearance of feed and feed-derived organic intermediates. It is tempting to rationalize the different σ 's from the methanol concentration and TOC data by hypothesizing that methanol SCWO generates organic compounds that temporarily accumulate in SCW before further oxidation to H_2O and CO_2 , which are TOC transparent. If these organic intermediates mineralize by independent parallel reactions with an activation energy PDF wider than the PDF for methanol decomposition, a larger σ for TOC data would seem reasonable. It can be shown that if the overall kinetics of two sequential first-order reactions (e.g., $A \rightarrow B \rightarrow C$) with unequal rate constants k_{AB} and k_{BC} for the A to B and B to C reactions, respectively, are forced to fit one single first-order reaction rate model, the resulting apparent rate constant, k_a , must always be $< k_{AB}$ regardless of the value of k_{AB}/k_{BC} . Here A corresponds to methanol,

and $A + B$ to methanol plus organic intermediates, that is, the quantities tracked by TOC. The concentration (GC) data track A and their kinetic analysis provides the rate constant k_{AB} . For the preceding explanation to be true, most (ideally all) of the rate constants in the DAEM set from the TOC data should be $< k_{AB}$. Yet, using the TOC DAEM parameters in Table 1, we found that, at 450°C, only 23% of these reactions had rate constants $< k_{AB}$. This inconsistency forces us to conclude that the present GC and TOC data sets are mutually incompatible.

SCWO of hydrolyzed rocket-motor propellants

In the U.S. Air Force rocket-motor demilitarization program, an aqueous slurry of solid propellant is hydrolyzed with sodium hydroxide (NaOH) or ammonium hydroxide (NH₄OH). SCWO is then used to mineralize the hydrolysate to CO₂, H₂O, and inorganic salts. We deduced kinetic parameters by separately best fitting the DAEM to Hazlebeck et al.'s (1995) bench-scale TOC data on SCWO of NaOH and NH₄OH hydrolysates of rocket propellants. Our analysis assumed an isothermal, isochoric, tubular, plug-flow reactor. We calculated average residence times from the reported input flow rates and an estimated reactor volume of 6 mL. One run exhibited $> 99.9\%$ conversion at a temperature (450°C) and residence time (5.3 s) well below those giving comparable conversions in other runs. This run was suspected of being influenced by some artifact and was omitted from the analysis. The best-fit DAEM parameters (Table 1) imply appreciably different SCWO reactivity for these two hydrolysates. The activation energy PDF for the NH₄OH hydrolysate is very narrow ($\sigma = 0$, Table 1), suggesting that one or a few chemical pathways of similar activation energy dominate conversion. The larger value of σ of 7.2 kJ/mol given in Table 1 implies that SCWO of the NaOH hydrolysate occurs by multiple parallel chemical steps with dissimilar activation energies. Consequently, the DAEM analysis also predicts that, at

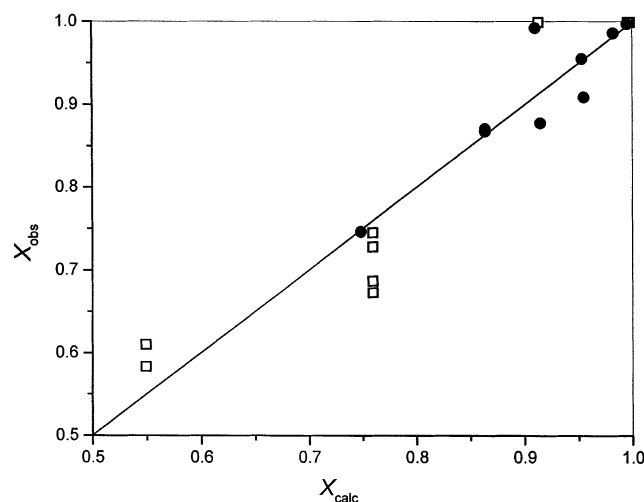


Figure 10. Parity plot for SCWO of NH₄OH hydrolysate (□) and NaOH hydrolysate (●) of rocket motor propellant: X_{obs} experimental data; X_{calc} predictions of DAEM using parameters from Table 1.

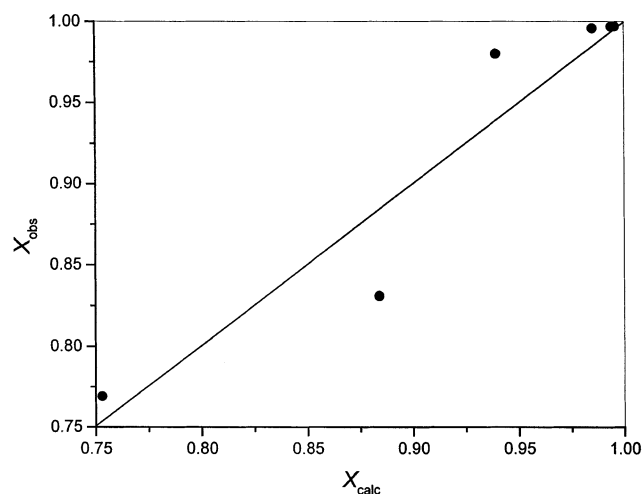


Figure 11. Parity plot for SCWO of orange dye: X_{obs} experimental data; X_{calc} predictions of DAEM using parameters from Table 1.

a fixed temperature, the NH₄OH hydrolysate will react over a narrower range of residence times than will the NaOH hydrolysate. A parity plot (Figure 10) shows good agreement between the DAEM-predicted and measured conversions.

SCWO of orange dye

As part of a U.S. Army demilitarization program, destruction of pyrotechnics and colored smokes and dyes by SCWO has been studied at Sandia National Laboratories (Rice et al., 1994). Using oxygen produced by thermal decomposition of hydrogen peroxide feed, orange dye was oxidized in a tubular, nearly isobaric and nearly isothermal reactor assumed to be plug flow. Destruction efficiencies were measured by comparing TOC analysis of the effluent and feed. Table 1 presents the parameters obtained by best fitting the DAEM to these data. The width of the distribution function is zero within the numerical accuracy of the Simplex algorithm. This suggests that TOC is consumed by one or a few kinetic pathways with identical activation energy. A parity plot (Figure 11) shows generally satisfying agreement between the DAEM-predicted and measured conversions.

SCWO of municipal sewage sludge and alcohol distillery wastewater

Goto et al. (1998; M. Goto, personal communication, 1999) investigated SCWO of municipal sewage sludge and alcohol distillery wastewater, the latter presumably from fermentation of grain or molasses. These studies provide useful quantitative data on overall destruction efficiencies attainable by SCWO. For reasons elaborated upon below, we infer that the experimental technique was not intended to probe waste destruction kinetics in detail. Nevertheless, because of the importance of sewage sludge as a potential target for commercialization of SCWO technologies (M. Modell, personal communication, ca. 1998), we elected to fit the DAEM to these data. In Goto et al.'s experiments a batch reactor (about 4 mL in volume) was filled with sludge (3.5 wt. % solids) or distillery wastewater (34 wt. % solids), hydrogen peroxide

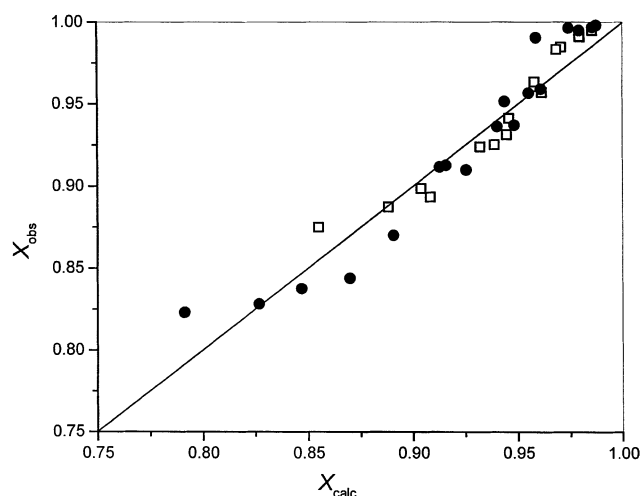


Figure 12. Parity plot for SCWO of municipal excess sewage sludge (●) and alcohol distillery wastewater (□): X_{obs} experimental data; X_{calc} predictions of DAEM using parameters from Table 1.

(H_2O_2 , the O_2 source), and water, and placed in a preheated electric furnace. Destruction of the organic contaminant was indexed by the corresponding reduction in TOC of the sludge or wastewater. Because the waste was premixed with H_2O_2 before heatup, oxidation by OH radicals from H_2O_2 decomposition may have preceded or complemented oxidation by H_2O_2 -derived O_2 . Further, if heavy metal ions were present in the sewage sludge (which seems quite probable), they may have catalyzed low-temperature decomposition of H_2O_2 to OH radicals during heat-up, increasing the probability that OH radicals were available to accelerate oxidation of the waste. The DAEM described earlier cannot properly simulate SCWO kinetics strongly impacted by these processes.

Table 1 presents, separately, the best-fit DAEM parameter values for the sewage sludge and the distillery wastewater. A parity plot (Figure 12) shows that, despite the possible experimental complexities and the limitations of the DAEM, there is generally satisfactory agreement between the DAEM-predicted and -measured conversions for both wastes. The low values obtained for E_0 (Table 1) are consistent with the minimal sensitivity of waste conversion to temperature observed by Goto et al. (1998; personal communication, 1999). However, this modest temperature dependence contrasts with a much higher E_0 (162 kJ/mol) obtained by fitting the DAEM to pilot-plant data on SCWO of a pharmaceutical sludge (Vogel et al., 2002). The low E_0 values deduced here for the sewage sludge and distillery waste may reflect our approximation of these nonisothermal experiments as isothermal. It appears that considerable time was needed to heat the reactants to the desired reaction temperature. A significant amount of reaction probably occurred during the nonisothermal heat-up period. This contribution to conversion is not accounted for in the present analysis (although it could be if the temperature-time history were known; see Vogel et al., 2002). We could not discern from the Goto et al. publications whether the heat-up time was subtracted from the reported reaction time. The low preexponential factors (A in Table 1)

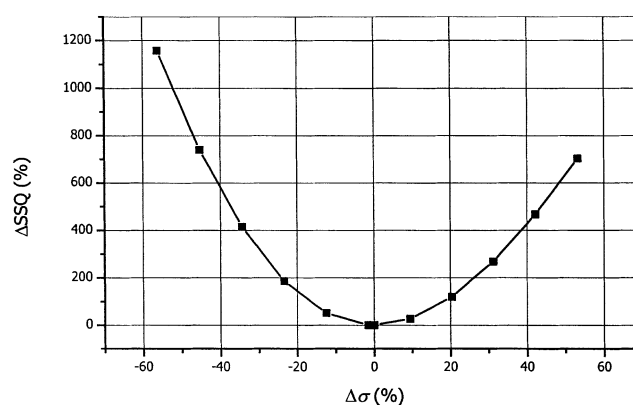


Figure 13. Sensitivity of the DAEM prediction to σ using best-fit parameter values for A and E_0 determined from the JP-5 SCWO data (Table 1).

are consistent with the low E_0 values and the strong correlation between A and activation energy typically encountered when fitting global kinetic models to conversion data. In light of these findings, we conclude that considerably more experimental information and modeling would be needed to deduce reliable kinetics parameters for waste destruction from these data.

Sensitivity analysis

The DAEM requires three parameters, A , E_0 , σ . The sensitivity of the model to the σ parameter compared to a single activation energy Arrhenius rate expression, that is, Eq. 6, was evaluated for the JP-5 DAEM predictions. The residual SSQ for the DAEM using the best-fitted values for A and E_0 (Table 1) and σ values from 8 kJ/mol to 28 kJ/mol is plotted vs. σ in Figure 13. The deviation ΔSSQ is the relative percent difference of the sum of squares calculated with σ values from 8 kJ/mol to 28 kJ/mol and the best-fit σ value of 18.3 kJ/mol. The quantity $\Delta\sigma$ is the relative percent difference of σ from the best-fit value of 18.3 kJ/mol. Other than at small values of $\Delta\sigma$, the quality of the DAEM fit shows considerable sensitivity to the width of the PDF (Figure 13). For example, decreasing σ by 12% and 50%, respectively, increases the SSQ by 50% and about 10-fold.

Discussion

The DAEM was successfully fit to nine data sets (Table 1) on the SCWO of eight different substances (two distinct methanol data sets based on methanol concentration and on TOC were analyzed). Many candidates for SCWO are mixtures whose components or decomposition products exhibit different oxidation rates at the same temperature. The DAEM is able to simulate this “chemical diversity” without the extensive data requirements or complicated mathematics of kinetic models that assign individual rate constants to multiple, component-specific reaction channels. The DAEM assumes that SCWO occurs by an infinite set of independent parallel first-order reactions and that differences in SCWO reactivity can be mathematically described by a continuous PDF for the activation energies of these reactions. With just

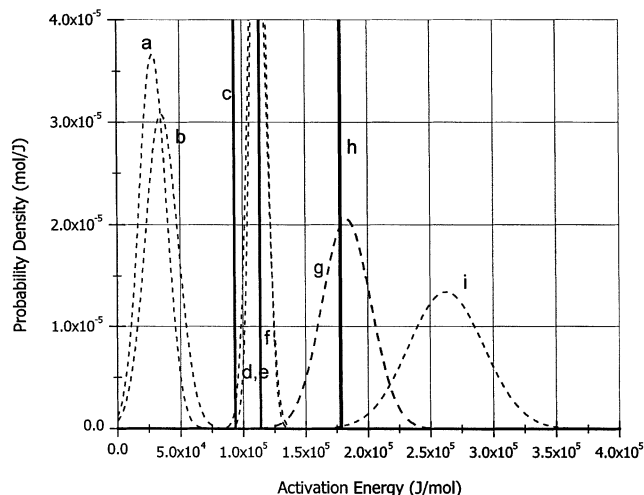


Figure 14. Initial probability density functions $f_0(E)$ for SCWO of (a) municipal sewage sludge, (b) alcohol distillery wastewater, (c) NH_4OH hydrolyzed rocket-motor propellant, (d) NaOH hydrolyzed rocket-motor propellant, (e) methanol TOC, (f) orange dye, (g) JP-5 fuel, (h) methanol, (i) Velsicol H537 hydraulic fluid, obtained by best fitting Eq. 13 to experimental data on reactant conversion.

two adjustable parameters, a Gaussian-based DAEM effectively aggregates substantial differences in chemical reactivity associated with a particular starting material. However, compared to multistep kinetics models, the DAEM provides little or no mechanistic information. The DAEM trades chemical detail for appreciable computational simplicity. It is best suited for computations of overall conversion and related quantities such as rates and cumulative extents of heat release.

Figure 14 shows that the nine cases of Table 1 called for a range of Gaussian PDFs. At one extreme, the hydraulic fluid (i) and JP-5 (g) exhibited broad activation energy distributions and large mean activation energies E_0 . In sharp contrast, the PDFs best fitted to the NH_4OH hydrolyzed rocket-motor propellant (c), the orange dye (f), and methanol (using methanol concentration data) (h) were all Gaussian PDFs of essentially zero breadth, that is, Dirac delta functions $\delta(E - E_0)$. Four of the substances exhibit intermediate behavior. The municipal sewage sludge (a) and alcohol distillery wastewater (b) have lower E_0 , but σ 's exceeding 10 kJ/mol (Table 1). However, for reasons already elaborated upon, we conclude that the DAEM parameters deduced for these two substances are far more uncertain than those for the other substances studied here. The NaOH hydrolysate of rocket-motor propellant (d), and methanol (using TOC data) (e), have somewhat higher values of E_0 , but σ 's of roughly 7 and 6 kJ/mol, respectively (Table 1). Table 1 and the parity plots of Figures 3, 5, and 7–12, illustrate the ability of the DAEM to simulate diverse reactivity within a single starting material and to model the SCWO kinetics of a wide range of substances. For kinetics governed by multiple independent parallel first-order reactions, σ is a measure of the range of activation energies for reactions that contribute significantly to

conversion of the waste. For a Gaussian PDF, the domain $E_0 - 2\sigma \leq E \leq E_0 + 2\sigma$ contains 95.5% of the reaction population at $t = 0$. In the limit of zero σ , only one reaction is present. Thus the large σ for aviation fuel and the small σ for NH_4OH hydrolysate of solid propellants for rockets suggest a large and a small number of reactions contributing appreciably to the SCWO of these substances. However, if the SCWO kinetics become sufficiently complicated, this simplistic interpretation of σ , and indeed use of the DAEM as well, becomes more and more approximate.

Because the DAEM parameters are specific to the starting material, and direct kinetic measurements based on feed-stock conversion are expensive and time-consuming, there is need for alternative means to generate reliable E_0 and σ values for SCWO of any substance. Plausible approaches are chemical or thermal analysis of the substance, *a priori* molecular computations, or correlation with some readily available characteristic. For example, in DAEM modeling of the kinetics of tar release by pyrolysis of different coal types, Ko (1988) correlated E_0 and σ with the elemental carbon content of the coals. Effects of random scatter in the conversion data on the DAEM fits are expressed in the value of the standard error of the estimate [the SEE of Eq. (15); see values in Table 1]. The DAEM inherently provides no information regarding systematic errors in the observed conversions or flaws in experimental design. The focus of this article is not to critique data on the SCWO of organic substances, but rather to use data for several wastes from several independent studies, to illustrate the broad applicability of the DAEM.

Care must be exercised in selecting and interpreting SCWO data for parameterization of the DAEM (or any kinetics model). In SCWO, TOC data monitor the concentration of all organic compounds in the aqueous medium, and therefore include unconverted organic feed and organic products of feed conversion. Thus TOC data illuminate rates of feed carbon conversion all the way to CO_2 (rigorously to high-volatility carbon-containing products, because TOC data cannot distinguish between volatile carbonaceous substances, such as CO from CO_2 .) The time dependence of the TOC inventory during SCWO may well be governed by the kinetics of consecutive reactions, that is, for feed disappearance and further conversion of feed-derived intermediates to TOC-transparent products. The DAEM can still provide a useful correlation for the rate of disappearance of the TOC signal, but it should be recognized that considerable underlying detail may be camouflaged in the DAEM parameters, and in particular that the TOC-based kinetics do not necessarily represent feed disappearance alone. To assure reliable kinetic tracking of feed conversion, the DAEM should be fitted to data that unequivocally differentiate feed concentration. Portela et al. (2001) determined kinetics for SCWO of cutting oil wastes. They used a model that allowed for waste disappearance by two parallel pathways, direct conversion to final products, and conversion to an intermediate, which is in turn converted to final products. They fitted this three-step model to composition data for two different intermediates, acetic acid and CO. They found reasonable agreement between waste conversions predicted from both of these fits and observed conversions deduced from TOC measurements.

Hazardous wastes may require destruction and removal efficiencies (DREs) of 99.99% up to 99.9999% (i.e., from four

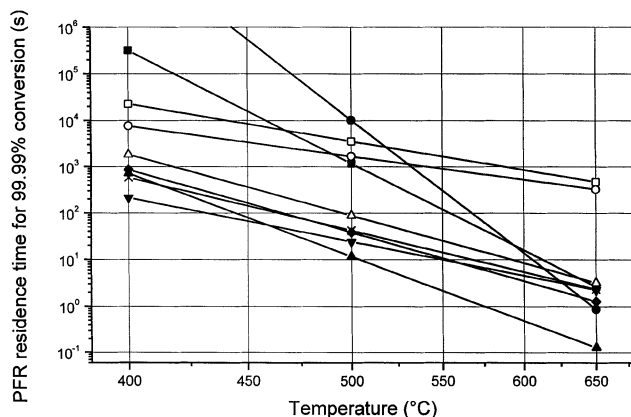


Figure 15. DAEM predictions of isothermal, isobaric SCWO plug-flow reactor residence time to achieve 99.99% abatement of TOC at various temperatures.

DAEM parameters from Table 1. The abscissa has been scaled to be linear in $1/T$. ■ JP-5, ● Velsicol H537, ▲ methanol (GC), ▼ NH_4OH hydrolysate, ◆ NaOH hydrolysate, △ methanol (TOC), × orange dye, ○ municipal sewage sludge, □ distillery wastewater.

nines to six nines) depending on their danger to humans and the environment. SCWO kinetics models must reliably predict operating conditions that provide ultrahigh levels of waste conversion. Mistakes that result in undersizing clearly pose unacceptable occupational and public health risks. Overdesign can be tolerable to some degree, but this increases capital and operating costs and is especially unwelcome in space-restricted applications of SCWO, for example, shipboard and trailer-borne units. The utility of the DAEM in predicting operating conditions that give rise to high waste destruction efficiencies is illustrated for an ideal plug-flow reactor in Figure 15. For the nine cases of Table 1, this figure plots the DAEM-predicted residence time needed to achieve 99.99% carbon destruction for a range of practically relevant temperatures. This time was computed by solving Eq. 13 for t , with $X_M = 0.9999$ and using the best-fit DAEM parameters from Table 1. Note that the abscissa is linear in $1/T$, the absolute temperature in K. Figure 15 predicts that, below 420°C, 99.99% destruction cannot be achieved in reasonable times, that is, < 100 s, for any of the wastes. The figure also shows that from 400°C to 650°C individual wastes vary widely in their vulnerability to destruction by SCWO. The JP-5 and Velsicol hydraulic fluid are predicted to be 99.99% destroyed in < 100 s at temperatures of 575°C or higher, whereas 99.99% destruction of the methanol (TOC or GC data), the orange dye, and the NH_4OH and NaOH hydrolysates of the rocket-motor propellant is achieved in < 100 s at temperatures modestly to substantially below 500°C. Figure 15 implies that even at temperatures of 650°C, the municipal sewage sludge and the alcohol distillery wastewater require ≥ 300 s to achieve 99.99% DRE. However, as elaborated upon earlier, our DAEM kinetics parameters for these two substances have appreciable uncertainty, and consequently the Figure 15 predictions for these two materials are unreliable.

Figure 16 illustrates how use of a single first-order kinetic model (SRM) rather than a DAEM could cause a SCWO

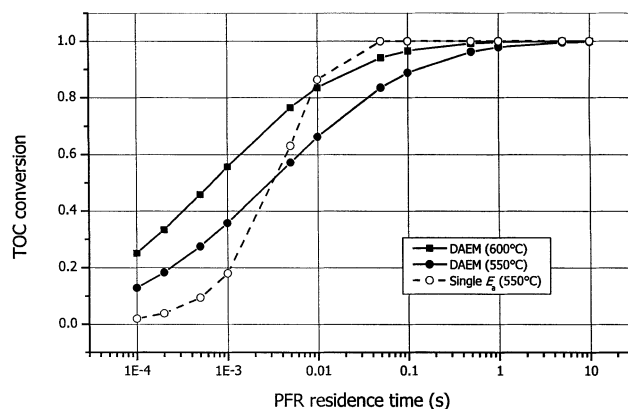


Figure 16. TOC conversion of JP-5 in an isothermal, isobaric SCWO plug-flow reactor calculated with the DAEM for 550°C and 600°C, and with a single activation energy model with $E_a = 177.0$ kJ/mol, as affected by residence time.

reactor to be undersized. The figure plots DAEM (550°C and 600°C) and SRM (550°C) predictions of TOC conversion for a complex organic mixture (JP-5 jet fuel) as affected by residence time in an ideal PFR. The SRM parameters were synthesized from the corresponding DAEM parameters (Table 1) by using identical values for the preexponential factor, A , and by taking $E_a = E_0$ for the DAEM, that is, 177.0 kJ/mol. The DAEM predicts that, at 550°C, almost 90% of the TOC is converted in the first 0.1 s, but that, even after 1 s, conversion (97.8%) falls short of “four nines,” or 99.99%. In contrast, the SRM predicts strong increases in conversion between 0.001 and 0.01 s, with conversion rising to 99.995% after 0.05 s and being virtually complete at 0.1 s. This should be compared with Rice et al.’s (1997) measurement of 99.81% conversion of JP-5 at 555°C only after 4.96 s, using a reactor that reasonably approximated plug flow. Thus for this example the SRM does not describe the high conversion behavior of the JP-5, and would badly underpredict the residence time (0.1 s vs. > 5 s) needed to achieve 99.99% DRE. The DAEM prediction for 600°C shows that, for JP-5, even a 50°C increase in temperature gives only 96.6% conversion at 0.1 s, that is, still substantially below the goal of four nines. The present analysis assumes that the DAEM is valid over the entire range of conversion from 0% to 100%, that is, that changes in the SCWO reaction mechanism as conversion proceeds are inconsequential.

Summary and Conclusions

The distributed activation energy model (DAEM) is a robust continuum model for kinetic lumping that provides satisfying correlations and predictions of the SCWO kinetics of a wide range of organic wastes, including complex organic mixtures poorly suited to kinetic modeling by a single first-order reaction model. Especially appealing is the ability of the DAEM with just three fitted parameters to model the overall SCWO kinetics of substances whose constituents or decomposition products exhibit substantial variations in their susceptibility to oxidation. The DAEM thus avoids the appreciable requirements for input data and the computational dis-

economy of models based upon multistep, component-specific kinetics models. On the other hand, the DAEM provides little or none of the mechanistic detail attainable from such multistep models. Thus the DAEM is best suited for applications that require overall conversion and related quantities such as rates and cumulative extents of heat release.

In this work, the DAEM was parameterized for nine cases of scientific and practical interest, by best fitting its predictions of conversion as affected by residence time and/or temperature to experimental data. Because the DAEM parameters are substance-specific and direct experimental measurements of conversion kinetics are expensive and time-consuming, there is need for alternative means to generate reliable values for the crucial DAEM parameters, that is, the quantities that specify the probability density function (PDF) for the activation energies. For a Gaussian PDF these parameters are the mean E_0 and the standard deviation, σ , of the PDF. Plausible approaches are chemical or thermal analysis of the reactant, *a priori* molecular computations, or correlation with some readily available characteristic of the reactant.

The DAEM appears to have been originally developed for batch systems with constant fluid density. This article describes the application of classic DAEM theory to the two limiting cases of fluid mechanical mixing in chemical reactors, that is, isothermal (constant density) plug flow, and perfectly back-mixed (CSTR). The DAEM can be applied to nonisothermal flows by accounting for effects of temperature on reaction kinetics and on density, which in turn influences residence time. For example, Vogel et al. (2002) use DAEM-predicted rates of heat release from waste oxidation to compute axial temperature profiles for SCWO of pharmaceutical waste in a nonisothermal, pilot-scale tubular flow reactor. Applications of the DAEM or other lumped kinetics models to reacting flows of greater fluid mechanical or chemical complexity, including rate phenomena nonlinear in conversion are challenging, for example, see Astarita and Ocone (1988), Astarita (1989), and Astarita and Sandler (1991).

It is important to select SCWO data appropriate to the objectives of the kinetics analysis. Kinetics parameters for feed conversion require data that clearly distinguish changes in feed concentration, for example, GC data. In SCWO, TOC data monitor the concentration of all organic substances in the aqueous medium, that is, unconverted feed plus non-volatilized organic products of feed conversion. Thus TOC data are useful for modeling the kinetics of feed carbon conversion all the way to CO_2 .

Simple applications of the DAEM to SCWO reactor engineering calculations illustrate the power and versatility of this model, for example, to predict residence times needed for "four nines" destruction of a diverse range of wastes in an ideal PFR. By comparing DAEM and single-reaction kinetic model (SRM) predictions of SCWO conversion of JP-5 jet fuel at the same temperature, our analysis also shows that oversimplification of SCWO kinetics for a complex mixture can cause a reactor to be seriously undersized.

Acknowledgments

We gratefully acknowledge financial support of this research by the U.S. Army Research Office by a subcontract to MIT from CFD Research Corporation; STTR Contract DAAG5-97-C-0047, and by Contract DAAD19-99-1-0211 to MIT. We thank Dr. Robert Shaw of

the ARO for his interest in this research, and Dr. Ning Zhou, of CFD Research Corp., Mr. Kai Lieball, Mr. Simon Stauffer, and other members of the MIT supercritical fluids research group for collaborations. We also thank Dr. M. Goto of Kumamoto University for information on his SCWO data, Dr. Steven Rice of Sandia National Laboratories for sharing his TOC data on methanol SCWO, and Prof. Marco Mazzotti of the Swiss Federal Institute of Technology (ETH) for drawing the work of Astarita and Ocone (1988) to our attention.

Literature Cited

- Anthony, D. B., J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization of Pulverized Coal," *Proc. Symp. (Int.) on Combustion*, The Combustion Institute, Pittsburgh, p. 1303 (1975).
- Aris, R., and G. R. Gavalas, "On the Theory of Reactions in Continuous Mixtures," *Philos. Trans. Roy. Soc. London*, **A-260**, 351 (1966).
- Astarita, G., and R. Ocone, "Lumping Nonlinear Kinetics," *AIChE J.*, **34**(8), 1299 (1988).
- Astarita, G., "Lumping Nonlinear Kinetics In A CSTR," *AIChE J.*, **35**, 1927 (1989).
- Astarita, G., and S. I. Sandler, eds., *Kinetic and Thermodynamic Lumping Multicomponent Mixtures*, Amer. Chem. Soc., Washington, DC (1991).
- Bailey, J. E. "Lumping Analysis of Reactions in Continuous Mixtures," *Chem. Eng. J.*, **3**, 52 (1972).
- Barner, H. E., C. Y. Huang, T. Johnson, G. Jacobs, M. A. Martch, and W. R. Killilea, "Supercritical Water Oxidation: An Emerging Technology," *J. Hazard. Mater.*, **31**, 1 (1992).
- Bischoff, K. B., and P. G. Coxson, "Mathematical Aspects of Kinetic Lumping Analysis," *Proc. ICREC Meet.*, Pune, India (1987).
- Burnham, A. K., and R. L. Braun, "Global Kinetic Analysis of Complex Materials," *Energy Fuels*, **13**, 1 (1999).
- Crain, N., S. Tebbal, L. Li, and E. F. Gloyna, "Kinetics and Reaction Pathways of Pyridine Oxidation in Supercritical Water," *Ind. Eng. Chem. Res.*, **32**, 2259 (1993).
- Curie, M., *Trans. Faraday Soc.*, **35**, 114 (1939).
- DeDonder, Th., *L'Affinité—Seconde Partie*, Chap. III, Gauthier-Villars, Paris (1931).
- Goto, M., T. Nada, A. Ogata, A. Kodama, and T. Hirose, "Supercritical Water Oxidation for the Destruction of Municipal Excess Sludge and Alcohol Distillery Wastewater of Molasses," *J. Supercrit. Fluids*, **13**, 277 (1998).
- Hanbaba, P., H. Juntgen, and W. Peters, "Nicht-isotherme Reaktionskinetik der Kohlenpyrolyse, Teil II. Erweiterung der Theorie der Gasabspaltung und experimentelle Bestätigung an Steinkohlen," *Brennstoff-Chemie*, **49**, 368 (1968).
- Hazlebeck, D. A., M. H. Spritzer, and K. W. Downey, "Supercritical Water Oxidation of Chemical Agents, Solid Propellants and Other DOD Hazardous Wastes," *Proc. Workshop on Advances in Alternative Demilitarization Technologies*, Science Applications International Corporation, McLean, VA (1995).
- Helling, R. K., and J. W. Tester, "Oxidation Kinetics of Carbon Monoxide in Supercritical Water," *Energy Fuels*, **1**, 417 (1987).
- Hirth, T., and E. U. Franck, "Oxidation and Hydrothermolysis of Hydrocarbons in Supercritical Water at High Pressures," *Ber. Bunsen-Ges. Phys. Chem.*, **97**, 1091 (1993).
- Howard, J. B., "Fundamentals of Coal Pyrolysis and Hydropyrolysis," *Chemistry of Coal Utilization Second Supplementary Volume*, Chap. 12, M. A. Elliott, ed., J. Wiley, New York, p. 665 (1981).
- Howard, J. B., W. S. Fong, and W. A. Peters, "Kinetics of Devolatilization," *Fundamentals of the Physical Chemistry of Pulverized Coal Combustion*, J. Lahaye and G. Prado, eds., Martinus Nijhoff Publishers, Dordrecht, p. 77 (1987).
- Ko, G. H., *Pyrolysis of Different Coal Types*, PhD Thesis, Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge (1988).
- LaJeunesse, C. A., S. F. Rice, J. J. Bartel, M. Kelley, C. A. Seibel, L. G. Hoffa, T. F. Eklund, and B. C. Odegard, "A Supercritical Water Oxidation Reactor: The Materials Evaluation Reactor (Mer)," Sandia National Laboratories, Livermore, CA, Tech. Rep. SAND91-8623 (1992).
- Lakshmanan, C. C., M. L. Bennett, and N. White, "Implications of Multiplicity in Kinetic Parameters to Petroleum Exploration: Dis-

- tributed Activation Energy Models," *Energy & Fuels*, **5**(1), 110 (1991).
- Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed., Wiley, New York (1972).
- Li, L., N. Crain, and E. F. Gloyna, "Kinetic Lumping Applied to Wastewater Treatment," *Water Environ. Res.*, **68**(5), 841 (1996).
- Luss, D., and P. Hutchinson, "Lumping of Mixtures with Many Parallel Nth-Order Reactions," *Chem. Eng. J.*, **2**, 172 (1971).
- Marrone, P. A., *Hydrolysis and Oxidation of Model Organic Compounds in Sub- and Supercritical Water: Reactor Design, Kinetics Measurements, and Modeling*, PhD Thesis, Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge (1998).
- Modell, M., "Supercritical Water Oxidation," *Standard Handbook of Hazardous Waste Treatment and Disposal*, H. M. Freeman, ed., McGraw-Hill, New York, p. 8.153 (1989).
- Peters, W. A., "Supercritical Water Technology: Process Systems Research for New Applications," *Proc. Int. Conf. on Solvothermal Reactions*, Shikoku National Industrial Research Institute, Kagawa, Japan, p. 35 (1996a).
- Peters, W. A., ed., "Data Needs to Support Modeling of Supercritical Water Oxidation Reactors and Processes for Chem Demil Applications," Report No. MIT-EL 96-002, Endicott House, MIT, Dedham, MA (1996b). (Report available from MIT Laboratory for Energy and the Environment, Publications, Room E40-473, MIT, Cambridge.)
- Peters, W. A., P. Griffith, J. G. Harris, H. J. Herzog, J. B. Howard, R. M. Latanision, K. A. Smith, and J. W. Tester, "Supercritical Water Oxidation for Wastes Cleanup: Enabling Research for Practical Application," *Proc. Int. Conf. on Solvothermal Reactions*, Takamatsu, Japan, p. 1 (1994).
- Phenix, B. D., *Hydrothermal Oxidation of Simple Organic Compounds*, PhD Thesis, Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge (1998).
- Phenix, B. D., J. L. DiNaro, J. W. Tester, J. B. Howard, and K. A. Smith, "The Effects of Mixing and Oxidant Choice on Laboratory-Scale Measurements of Supercritical Water Oxidation Kinetics," *Ind. Eng. Chem. Res.*, **41**(2), (2002).
- Pitt, G. J., "The Kinetics of the Evolution of Volatile Products From Coal," *Fuel*, **41**, 267 (1962).
- Portela, J. R., E. Nebot, and E. Martinez de la Ossa, "Generalized Kinetic Models for Supercritical Water Oxidation of Cutting Oil Wastes," *J. Supercrit. Fluids*, **21**, 135 (2001).
- Primak, W., "Kinetics of Processes Distributed in Activation Energy," *Phys. Rev.*, **100**, 1677 (1955).
- Quann, R. J., and S. B. Jaffe, "Structure-Oriented Lumping: Describing the Chemistry of Complex Hydrocarbon Mixtures," *Ind. Eng. Chem. Res.*, **31**, 2483 (1992).
- Rennhack, R., "Zur Kinetik der Entgasung von Schmelzkoks," *Brennstoff-Chemie*, **45**, 300 (1964).
- Rice, S. F., C. A. LaJeunesse, R. G. Hanush, J. D. Aiken, and S. C. Johnston, "Supercritical Water Oxidation of Colored Smoke, Dye, and Pyrotechnic Compositions," Sandia National Laboratories, Tech. Rep. SAND94-8209 (1994).
- Rice, S. F., R. G. Hanush, T. B. Hunter, R. R. Steeper, J. D. Aiken, E. Croiset, and C. A. LaJeunesse, "Kinetic Investigation of the Oxidation of Naval Excess Hazardous Materials in Supercritical Water for the Design of a Transpiration-Wall Reactor," Sandia National Laboratories, Tech. Rep. SAND97-8219 (1997).
- Rice, S. F., and R. R. Steeper, "Oxidation Rates of Common Organic Compounds in Supercritical Water," *J. Hazard. Mater.*, **59**, 261 (1998).
- Shaw, R. W., T. R. Brill, A. A. Clifford, C. A. Eckert, and E. U. Franck, "Supercritical Water: A Medium for Chemistry," *Chem. Eng. News*, **69**, 26 (1991).
- Shinnar, R., and C. A. Feng, "Structure of Complex Catalytic Reactions: Thermodynamic Constraints in Kinetic Modeling and Catalytic Evaluation," *Ind. Eng. Chem. Fundam.*, **24**, 153 (1985).
- Smith, K. A., P. Griffith, J. G. Harris, H. J. Herzog, J. B. Howard, R. M. Latanision, W. A. Peters, and J. W. Tester, "Supercritical Water Oxidation: Principles and Prospects," *Proc. Ann. Int. Water Conf.*, Pittsburgh (1995).
- Tester, J. W., H. R. Holgate, F. J. Armellini, P. A. Webley, W. R. Killilea, G. T. Hong, and H. E. Barner, "Supercritical Water Oxidation Technology—Process Development and Fundamental Research," *Emerging Technologies in Hazardous Waste Management III*, Chap. 3, D. W. Tedder and F. G. Pohland, eds., ACS Symposium Series 518, American Chemical Society, Washington, DC, p. 35 (1993).
- Thornton, T. D., and P. E. Savage, "Phenol Oxidation in Supercritical Water," *J. Supercrit. Fluids*, **3**, 240 (1990).
- Vand, V., "A Theory of the Irreversible Electrical Resistance Changes of Metallic Films Evaporated in Vacuum," *Proc. Phys. Soc. London*, **A55**, 222 (1943).
- Vogel, F., K. A. Smith, J. W. Tester, and W. A. Peters, "Distributed Activation Energy Kinetics Model for Supercritical Water Oxidation of Complex Organic Wastes," *Chem. Eng. Sci.*, to be submitted (2002).
- Weekman, V. W., "Lumps, Models, and Kinetics in Practice," *Chem. Eng. Prog. Monogr. Ser.*, **75**(11), 3 (1979).
- Wei, J., and C. D. Prater, "The Structure and Analysis of Complex Reaction Systems," *Adv. Catal.*, **13**, 203 (1962).
- Yang, H. H., and C. A. Eckert, "Homogeneous Catalysis in the Oxidation of *p*-Chlorophenol in Supercritical Water," *Ind. Eng. Chem. Res.*, **27**, 2009 (1988).

Manuscript received May 4, 2001, and revision received Feb. 7, 2002.