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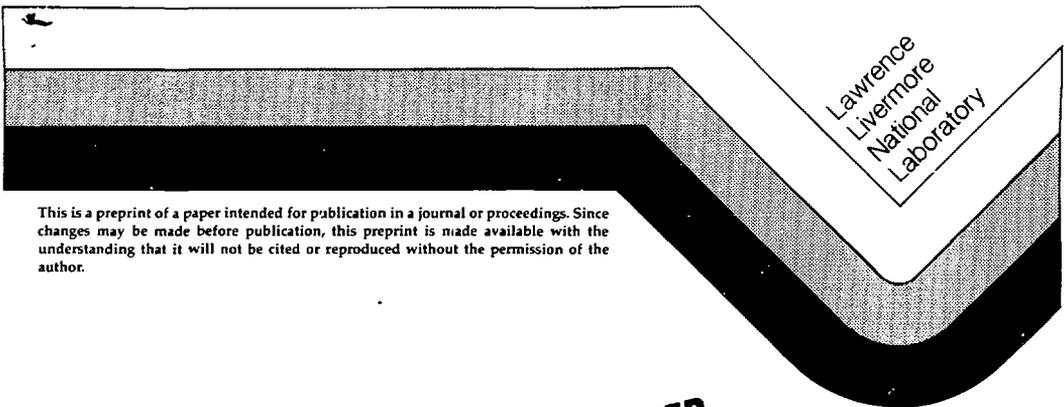
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Oxidation of Hazardous Waste in Supercritical Water: A Comparison of Modeling and Experimental Results for Methanol Destruction

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Abstract

Recent experiments at Sandia National Laboratories conducted in conjunction with MODEC Corporation have demonstrated successful clean-up of contaminated water in a supercritical water reactor. These experiments targeted wastes of interest to Department of Energy (DOE) production facilities. In this paper we present modeling and experimental results for a surrogate waste containing 98% water, 2% methanol, and parts per million of chlorinated hydrocarbons and laser dyes. Our initial modeling results consider only methanol and water. Experimental data are available for inlet and outlet conditions (composition, flow rate, and temperature), and axial temperature profiles along the outside reactor wall. The purpose of our model is to study the chemical and physical processes inside the reactor. We are particularly interested in the parameters that control the location of the reaction zone. The laboratory-scale reactor operates at 25 MPa., between 300 K and 900 K; it is modeled as a plug-flow reactor with a specified temperature profile. We use Chemkin Real-Gas to calculate mixture density, with the Peng-Robinson equation of state. The elementary reaction set for methanol oxidation and reactions of other C_1 and C_2 hydrocarbons is based on previous models for gas-phase kinetics. Results from our calculations show that the methanol is 99.9% destroyed at 1/3 the total reactor length. Although we were not able to measure composition of the fluid inside the experimental reactor, this prediction occurs near the location of the highest reactor temperature. This indicates that the chemical reaction is triggered by thermal effects, not kinetic rates. Results from ideal-gas calculations show nearly identical chemical profiles inside the reactor in dimensionless distance. However, reactor residence times are overpredicted by nearly 150% using an ideal-gas assumption. Our results indicate that this oxidation process can be successfully modeled using gas-phase chemical mechanisms. The oxidation process is characteristic of intermediate temperature chemistry dominated by the hydroxyl and hydrogen peroxy radical species and the hydrogen peroxide reaction intermediate.

INTRODUCTION

Oxidation of organics in supercritical water is a promising technology for the detoxification of contaminated groundwater and industrial waste streams. Recent experiments at Sandia National Laboratories conducted in conjunction with an industrial partner have demonstrated successful clean-up of contaminated water in a supercritical water reactor.[1] These experiments targeted wastes of interest to Department of Energy (DOE) production facilities and the electronics industry. Because current supercritical water reactor designs are based on global models and limited experimental data, scale-up and design optimization remain pressing issues hindering technology development. Detailed computational models can provide valuable information in these areas.

In supercritical water oxidation (SCWO), organics are oxidized in the presence of a high concentration of water, at temperatures and pressures above the critical point of water (374°C and 22.1 MPa). Above its critical point, water has properties that make it an ideal medium for the oxidation of organic compounds: nonpolar organic molecules are completely miscible; many inorganic salts become virtually insoluble and may be precipitated in a controlled manner; oxidation reactions occur at considerably lower temperatures than in conventional combustion systems; and gas-like transport properties and liquid-like densities lead to rapid fluid dynamic mixing and compact designs. These characteristics have been exploited for the destruction of a variety of compounds in several different SCWO configurations.[2-9] An historical review of both supercritical and subcritical water oxidation is given in Ref. 10, which also presents preliminary system design and economic analyses for several possible system configurations.

In practice, supercritical oxidation is usually conducted at 400 to 650°C and approximately 25 MPa. For treatment of aqueous wastes, SCWO is energetically more efficient than incineration. More importantly, however, SCWO technology has been shown[1] to be applicable to mixed wastes (wastes that contain chemically toxic organic, inorganic, and radiological components). These wastes constitute one of the most serious problems facing DOE production facilities. Cost estimates for long-term storage of one such mixed waste at Hanford are on the order of fifteen billion dollars. Currently, no commercial technology exists that will treat mixed waste.

Because of the extremely promising nature of SCWO technology as a technique for destroying hazardous wastes, a feasibility demonstration was conducted at Sandia National Laboratories, Livermore in collaboration with several DOE/DP production facilities and private industry. The objectives of the study were: (1) to determine the feasibility of

applying SCWO technology to DOE wastes, and (2) to identify areas requiring further investigation. The materials selected for demonstration were simulated wastes of specific interest to Hanford, Rocky Flats, and the electronics industry. Tests to determine the destruction efficiency of the supercritical process were conducted in a laboratory-scale supercritical water oxidation flow reactor developed by Modell Development Corporation (MODEC). Because of the anticipated corrosion potential of the Hanford waste, several reactor materials were also evaluated under supercritical conditions. Results from both series of tests, and recommendations for further work, are presented in detail in reference 1.

In this paper, modeling and experimental results are presented for a surrogate waste containing 98% water, 2% methanol, and parts per million of chlorinated hydrocarbons and laser dyes. The initial calculations presented here consider only the major constituents, methanol and water. Experimental data are available[1] for inlet and outlet conditions (composition, flow rate, and temperature), and axial temperature profiles along the outside reactor wall. The purpose of the present model is to study the chemical and physical processes inside the reactor. We are particularly interested in parameters that control the location of the reaction zone, and thus, the physical dimensions of the reactor. The experiments are modeled as a constant-pressure, plug-flow reactor with a specified temperature profile. Based on these thermodynamic constraints, the present model consists of mass conservation expressions written in terms of species production rates with finite-rate chemistry and real-gas thermodynamics. Chemkin Real-Gas[11] (Chemkin-RG) is used with the Peng-Robinson equation of state to calculate real-gas mixture thermodynamic properties. The elementary reaction set for methanol oxidation and reactions of other C_1 and C_2 hydrocarbons is based on previous models for gas-phase kinetics.[12-13] A principal goal of this modeling effort is to assess whether gas-phase kinetic rate expressions and mechanisms can be used for supercritical water oxidation.

EXPERIMENTAL APPARATUS

The MODEC supercritical water flow reactor used in this study is shown schematically in Figure 1. Details of the flow reactor internal geometry and the effluent separation system considered proprietary by MODEC are not shown. The material to be processed is pressurized to between 24.5 and 28.0 MPa by a high-pressure pump, after which it enters the Preheat Section of the flow reactor, which is electrically heated. Oxygen, pressurized to 1.4 MPa above the reactor pressure, is introduced either at the inlet to the Preheat Section

or at its midpoint. After exiting the insulated Reactor Section, the reaction products are cooled to ambient temperature in the Cooldown Section and then processed by the Separation Subsystem. Gaseous, liquid, and solid effluents can be collected for subsequent analyses. Process variables that are monitored include: mass flow rates, pressure, and external surface temperatures at selected locations. Fluid temperatures are not measured; however, theoretical calculations suggest that they lag (in the Preheater) or lead (in the Reactor) the surface temperature by approximately 30°C - 70°C, so that the surface temperatures are qualitative indicators of the fluid conditions. Composition of the fluid in the supercritical reactor is not sampled, however, mass flow rates and thermal profiles on the outside of the reactor suggest that most of the chemical reaction is over in the first 1/4 to 1/3 of the total reactor length.
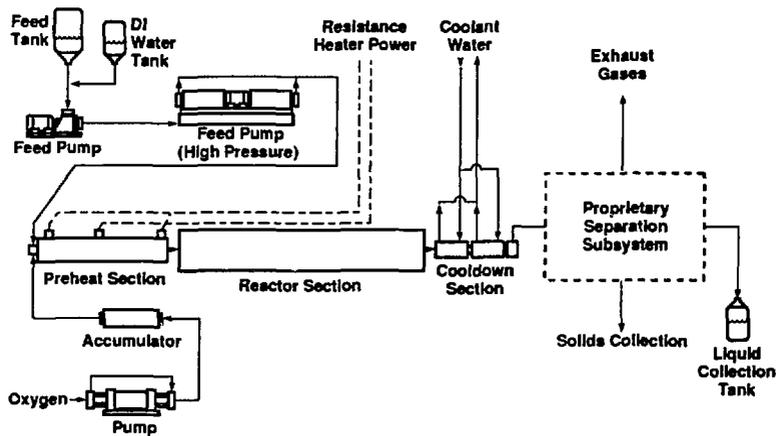
Figure 1. Schematic illustration of the MODEC supercritical water oxidation reactor .[1]

ANALYSIS

Conservation Equations

A one-dimensional, plug-flow reactor model was developed to simulate the experimental conditions discussed in the previous section. The model serves as a computational tool to study the influence of critical design parameters (e.g., preheat temperature profiles) on the extent of reaction that occurs in the flow direction. The plug-flow model assumes the fluid mixture is well-mixed in the reactor radial direction and axially isobaric. Diffusion of species in the axial direction is neglected.

Figure 2 shows a schematic of the three primary reactor components treated in the plug-flow model. Included in the figure are the preheater, reactor, and cooldown sections. The axial distance x is measured relative to the entrance of the preheater section ($x = 0$). The preheater/reactor interface is designated as x_1 and the reactor/cooldown interface is given as x_2.

In the present analysis the axial temperature profile, $T(x)$, is taken from experimental measurements of the outside surface, and thus eliminates the need for an independent energy conservation equation. The plug-flow model reduces to a set of governing equations that describe the species mass-fraction profiles in the reactor axial direction. The mass-fraction of the k-th chemical species is:

$$Y_k = m_k/\Sigma m_k , \qquad (k = 1,..KK) \qquad (1)$$

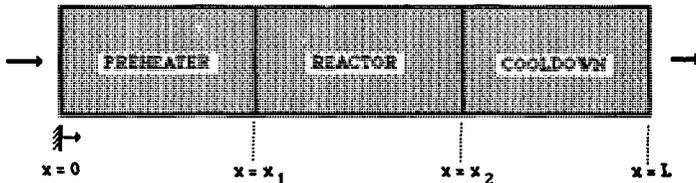where we have a total of KK species in the system. Based on conservation of total mass,

Figure 2. Preheater, reactor, and cooldown sections treated in plug-flow model.

the instantaneous rate of change of Y_k is:

$$\frac{dY_k}{dt} = v \, \dot{\omega}_k \, W_k \, . \qquad\qquad (k = 1,...,KK) \qquad (2)$$

In the previous equation, t represents time, v is the mixture specific volume, W_k is the molecular weight of species k, and $\dot{\omega}_k$ represents the net molar production rate of species k. The molar production rates are assembled in Chemkin-RG[11] by summing the contributions of each elementary reaction to the production or destruction of species k in the mixture.

The species equations form a system of dimensionless ordinary differential equations with X as the independent variable by introducing the dimensionless reactor distance $X = x/L$, the reactor cross-sectional area $A(x)$, and the inlet mass-flow rate $\dot{m}_o$. The resulting dimensionless species equations solved in the plug-flow model are,

$$\frac{dY_k}{dX} = \dot{\omega}_k \, W_k \, L \, A(x) \, \dot{m}_o^{-1} \qquad\qquad (k = 1,...,KK) \qquad (3)$$

The equations are solved using LSODE.[14]

Equation of State

In modeling supercritical oxidation, the influence of real-gas thermodynamics must be considered. An equation of state is required to calculate local fluid velocity (i.e., mass-flow constraint) and molar production rates, $\dot{\omega}_k$. Given the high operating pressure (25 MPa) of the SCWO reactor and the range of temperatures (293 K to 913 K), the thermodynamic states are in the real-gas regime. In this model, the Peng-Robinson real-gas equation of state[15] was used to calculate the specific volume. This equation of state was originally developed for applications in hydrocarbon processing as an improvement over the Soave-Redlich-Kwong equation of state to predict liquid densities more accurately. The form of the Peng-Robinson equation of state is that of a modified van der Waals-type cubic equation of state, and applies to pure species,

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + 2bV + wb^2} \quad , \qquad\qquad (4)$$

where P is pressure, T is temperature, R is the universal gas constant, and V is molar volume (cc/mole).

Consistent with van der Waals original hypothesis, real-gas effects are described by attractive terms, a, and repulsive terms, b. The attractive terms are temperature-dependent as demonstrated in the relationship to reduced temperature $T_r = T/T_c$,

$$a = \frac{0.45724 \, R^2 T_c^2}{P_c} \left(1 + f(\omega) \, (1 - T_r^{1/2}) \right)^2 , \qquad (5)$$

where $f(\omega)$ is a constant for each species

$$f(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 . \qquad (6)$$

Equation (6) has been correlated with accentric factors, ω, such that Equation (4) predicts vapor pressures over a wider range of temperatures than the Redlich-Kwong equation of state. The repulsive term in the Peng-Robinson equation of state is written in terms of critical temperature, T_c, and critical pressure, P_c, and takes the form,

$$b = \frac{0.07780 \, RT_c}{P_c} . \qquad (7)$$

Equation (4) can also be written in terms of the compressibility factor $Z = PV/RT$,

$$Z^3 - (1 - B^*)Z^2 + (A^* - 3B^{*2} - 2B^*)Z - A^*B^* + B^{*2} + B^{*3} = 0 \qquad (8)$$

where,

$$A^* = \frac{aP}{R^2 T^2} \qquad and \qquad B^* = \frac{bP}{RT} \qquad (9)$$

Note that this form is an approximation to Equation (4); higher order terms have been truncated.

Mixing Rules

Cubic equations of state were originally developed for pure species. To extend this model to mixtures of species, we must make some assumption about mixing rules, which are exact only for the virial equation of state. Peng and Robinson have demonstrated good agreement with pressure-volume-temperature *(PVT)* and vapor-liquid equilibrium (VLE) data using standard quadratic mixing rules: quadratic summations for the attractive and repulsive terms of all species weighted by mole fractions,[15]

$$a_m = \sum_{i=1}^{KK} \sum_{j=1}^{KK} X_i X_j \ (a_i a_j)^{1/2} \ (1 - k_{ij}) \tag{10}$$

$$b_m = \sum_{i=1}^{KK} X_i \ b_i^{1/2} \tag{11}$$

where the summations are over the number of species i and j (KK species total) and k_{ij} is a binary interaction coefficient specific to this equation of state. The database in Chemkin RG contains critical properties of species from Ref. 16 and binary interaction coefficients taken from Ref. 17. If data for k_{ij} are not available, they are set to zero. Peng and Robinson's VLE calculations show that the binary interaction coefficients can be neglected for mixtures with only moderate differences in molecular size (e.g., methane/ethane/propane mixtures), but these terms are important for mixtures with relatively large differences in molecular size.

Test Conditions

The plug-flow reactor model was used to simulate test data from a SCWO reactor which was tested at Sandia National Laboratories, Livermore.[1] The reactor was designed to oxid re dilute organics in water under supercritical conditions. The experimental results presented in this paper are for a waste stream containing water, methanol, and small amounts of contaminants (50 - 500 ppm). These contaminants were not considered in the model. The nominal SCWO reactor operating conditions for this case are listed below in Table 1.

Table 1. Reactor Operating Conditions[1]

Reactor Operating Pressure	24.8	MPa
Maximum Reactor Temperature	903	K
Oxygen Flow Rate	4247.5	scc/min
Process Stream Flow Rate	58	scc/min
Process Stream Composition	98% H_2O, 2% CH_3OH	

Detailed Chemical Kinetic Mechanism

The chemical kinetic mechanism used in this model is based on a mechanism developed previously for the oxidation of hydrocarbon fuels.[18] The mechanism includes reactions important to the low-, intermediate-, and high-temperature oxidation of hydrocarbons up to C_2 including methanol, methane, ethane and ethene. The mechanism was assembled from a submechanism for H_2/O_2 oxidation from Miller and Bowman[19], and a submechanism for high temperature oxidation of methanol from Norton and Dryer[13], Westbrook and Dryer[20] and Tsang[21]. The remainder of the mechanism is documented in Wilk et al.[12] and Kaiser et al.[22]

The oxidation of methanol under the present conditions is dominated by the radical species hydrogen peroxy, HO_2. In the early stages of oxidation, the HO_2 radical is formed by the initiation reaction,

$$CH_3OH + O_2 = CH_2OH + HO_2 . \qquad (R1)$$
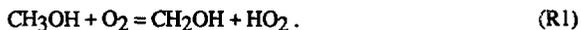
Very little initiation of the radical pool occurs by decomposition of methanol,

$$CH_3OH + M = CH_2OH + H + M , \qquad (R2)$$

(where M is a third body) because of the high activation energy (80 kcal/mole) of this reaction and the relatively low temperatures in the reactor.

After an initial level of radicals has been established, the methanol is consumed mainly by hydroxyl radicals, OH via the steps:

$$CH_3OH + OH = CH_2OH + H_2O \qquad (R3)$$

$$CH_3OH + OH = CH_3O + H_2O . \qquad (R4)$$

Three important intermediate species are produced in the reactor: formaldehyde, CH_2O, carbon monoxide, CO, and hydrogen peroxide, H_2O_2. Both hydrocarbon radicals produced by R3 and R4 lead to formaldehyde:

$$CH_2OH + O_2 = CH_2O + HO_2 \qquad (R5)$$

$$CH_3O + O_2 = CH_2O + HO_2 \qquad (R6)$$

and the consumption of formaldehyde gives carbon monoxide. Most of the hydrogen peroxy radicals, HO_2, produced by reactions R5 and R6 self-react to form hydrogen peroxide, H_2O_2,

$$HO_2 + HO_2 = H_2O_2 + O_2 \quad . \tag{R7}$$

This reaction along with the decomposition of hydrogen peroxide,

$$H_2O_2 + M = OH + OH + M \quad , \tag{R8}$$

leads to chain propagation where each hydrogen peroxy radical is converted to an hydroxyl radical, OH, which is available to react with the fuel.

The production of radicals under the present conditions is characteristic of intermediate-temperature chemistry dominated by hydrogen peroxy radicals and hydrogen peroxide reaction intermediates. The chain branching sequence is as follows:

$$CH_2O + HO_2 = HCO + H_2O_2 \tag{R9}$$

$$CH_3OH + HO_2 = CH_2OH + H_2O_2 \tag{R10}$$

$$H_2O_2 + M = OH + OH + M \tag{R8}$$
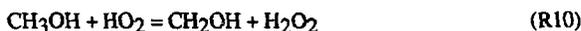
The sequence of reaction (R9) and (R10) followed by reaction (R8) give a net production of radicals. The very reactive hydroxyl radicals consume methanol via reactions (R3) and (R4). This reaction sequence accelerates the oxidation of methanol under the present conditions.

RESULTS

To quantify real-gas effects in this plug-flow reactor model, we have calculated the specific volume of supercritical water at 25 MPa as the water is heated from 300 K to 900 K. The slight dilution of 2% methanol will not change these results appreciably. Figure 3 shows the specific volume of pure water at 25 MPa over this temperature range using the Peng-Robinson and ideal-gas equations of state, compared to water. The upper, chain-dashed line is the Peng-Robinson equation of state. The compressibility factor is plotted on the second Y-axis and shows a wide variation from 0.2 to 0.9, with a dramatic increase near the critical temperature of water (647 K). We see that the Peng-Robinson equation of state predicts the specific volume of water quite well in this regime. The accuracy is quantified in Figure 4, where we have plotted the percent error in the calculated specific volume with respect to data from the steam tables (plotted for reference on the second Y-axis). The ideal gas equation of state is in error by more than 100% at low temperatures (less than 650 K), and approaches 15% error in the operating temperature regime. The

Peng-Robinson equation of state predicts specific volume within 1% above 650 K, and within 20% below this temperature, with a small spike in the error close to the critical point. Even with an error at low temperature, the Peng-Robinson equation of state is still a substantial improvement over the ideal-gas expression.
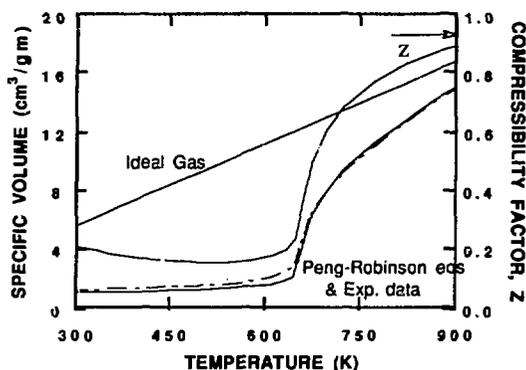

Figure 3. Temperature-volume relationship of supercritical water at 25 MPa calculated using the Peng-Robinson equation of state and compared to experimental data. The bottom solid line is the experimental data. Compressibility factor, Z, is calculated from experimental data, and is shown as the top solid S-shaped curve, corresponding to the second Y-axis..
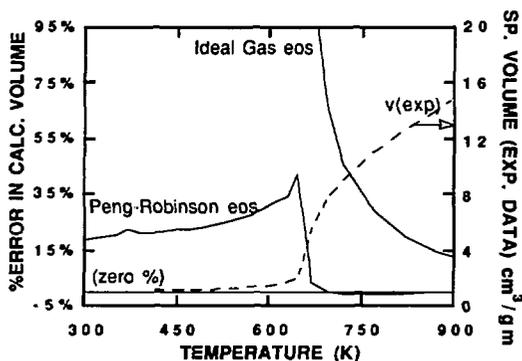

Figure 4. Percent errors in calculated specific volume of supercritical water at 25 MPa from 300 K to 900 K, expressed as percent of experimental data (from steam tables).

Figures 5 - 7 show mole fraction, X_k, profiles for CH_3OH, CO, and CO_2, respectively. Figure 8 presents an overlay of the mole fraction profiles for these three species. In each plot, the distance coordinate is presented as the dimensionless parameter $X = x/L$. Overlayed on each of the mole-fraction profiles is the experimentally determined temperature profile, $T(X)$. The general shape of the temperature profile indicates the preheat zone for this particular case extends from $X = 0$ to approximately $X = 0.3$, the reactor covers $0.3 < X < 0.8$, and the cooldown section extends from $0.8 < X < 1.0$.

Figure 5 shows that methanol destruction begins at a dimensionless distance of $X = 0.13$ and is 99% complete at $X = 0.21$. Likewise, the production and/or destruction of other primary species occurs at the same approximate location in the reactor. A study of the overlayed reactor temperature and species profiles shows a significant increase in rate of reaction when the reactor profile exceeds approximately 600 K. The profiles also indicate the CH_3OH is 99% destroyed when the reactor reaches a temperature of 750 K, or 150 K below the maximum temperature of the preheater. As mentioned previously, composition of the fluid in the supercritical reactor was not sampled, however, mass flow rates and thermal profiles on the outside of the reactor suggest that most of the chemical reaction is over in the first 1/4 to 1/3 of the total reactor length. Our model concurs with this observation.

Results from ideal-gas calculations show nearly identical chemical profiles as the real-gas calculations shown in Figures 5 through 8 plotted versus distance. However, real-gas effects are highly pronounced in reactor residence times. As shown in Figures 3 and 4, ideal-gas overpredicts specific volume of the mixture by more than 100% at temperatures below the critical point. Since mass flow is conserved, this error in specific volume is directly related to the error in velocity, resulting in residence times nearly 150% too long using an ideal-gas assumption. Although the Peng-Robinson equation of state is not exact in the low-temperature, compressed liquid state, it shows a marked improvement over the ideal-gas assumption, and provides a sufficient means to study the role of chemistry in supercritical water reactors. Future models can incorporate equations of state specifically designed for supercritical water, such as found in Ref. 23.
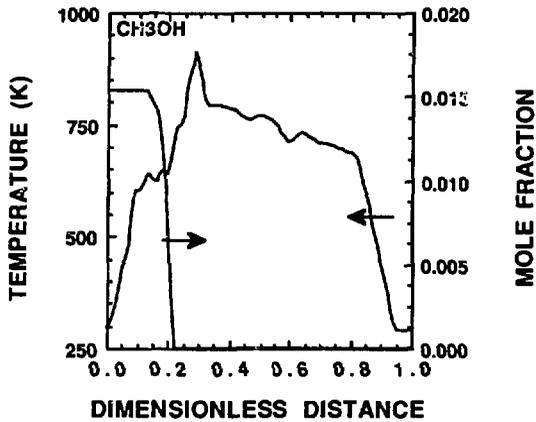
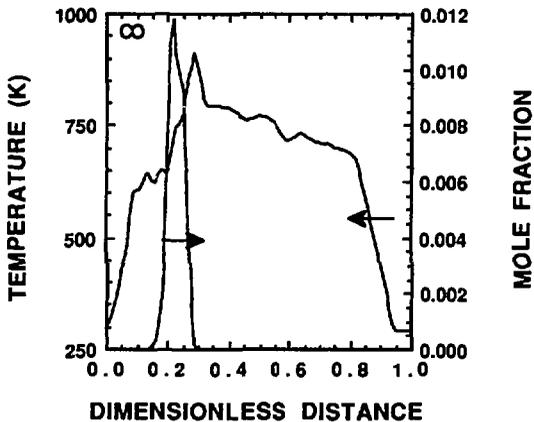Figure 5. Methanol mole fraction and temperature profiles for SCWO reactor.

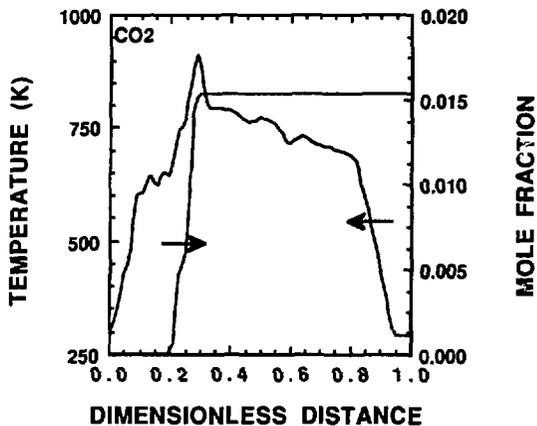Figure 6. CO mole fraction and temperature profiles for SCWO reactor.

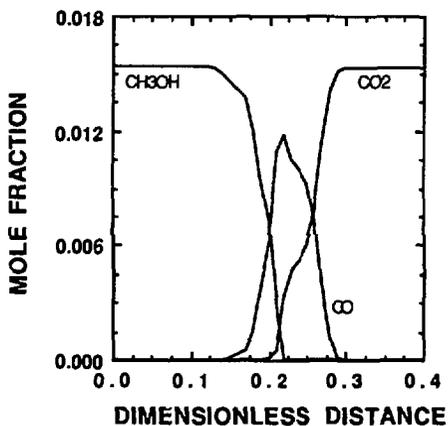Figure 7. CO_2 mole fraction and temperature profiles for SCWO reactor.

Figure 8. Overlay of species concentration profiles shown in Figures 5, 6, & 7.

CONCLUSIONS

Results from our calculations show that the methanol is 99.9% destroyed at 1/3 the total reactor length. Although the composition of the fluid inside the supercritical reactor was not sampled, mass flow rate and temperature data from the outside of the reactor also suggested[1] (prior to this calculation) that most of the chemical reaction is over in the first 1/4 to 1/3 of the total reactor length. This implies that the chemical reaction is triggered by thermal effects, rather than kinetic rates, an important implication that warrents further study.

Results from ideal-gas calculations show nearly identical chemical profiles inside the reactor in dimensionless distance. However, real-gas effects are highly pronounced in reactor residence times. Ideal-gas overpredicts specific volume of the mixture by more than 100% at temperatures below the critical point, resulting in residence times nearly 150% too long using an ideal-gas assumption.

Our results indicate that this oxidation process can be successfully modeled using gas-phase chemical mechanisms. The oxidation process is characteristic of intermediate temperature chemistry dominated by hydroxyl and hydrogen peroxy radicals and formaldehyde, carbon monoxide, and hydrogen peroxide reaction intermediates. Future work will study the effects of different thermal profiles and perturbations on reaction rates on the location of the reaction zone. Our next step is to add chlorinated species to the model to study supercritical oxidation of organics in the presence of halogenated species.

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[1]Bramlette, T.T., Mills, B.E., Hencken, K.R., Brynildson, M.E., Johnston, S.C., Hruby, J.M., Feemster, H.C., Odegard, B.C., Modell, M., "Destruction of DOE/DP Surrogate Wastes with Supercritical Water Oxidation Technology," Sandia National Laboratories, Livermore, CA, SAND90-8229, November 1990.

[2]Thomason, T.B. and Modell, M., "Supercritical Water Destruction of Aqueous Wastes," Hazardous Waste, 1, 4, pp. 453-467, 1984.

[3]Timberlake, S.H., Hong, G.T., Simson, M., and Modell, M., "Supercritical Water Oxidation for Wastewater Treatment: Preliminary Study of Urea Destruction," SAE Technical Paper Series, No. 820872, 1982.

[4]Modell, M., Gaudet, G.G., Simson, M., Hong, G.T., and Biemann, K., "Supercritical Water," Solid Wastes Management, August 1982.

[5]Staszak, C.N., Malinowski, K.C., and Killilea, W.R., "The Pilot-Scale Demonstration of the MODAR Oxidation Process for the Destruction of Hazardous Organic Waste Materials," Environ. Progress, 6, 1, pp. 39-43, February 1987.

[6]Lawson, M., "New Technology Tackles Dilute Wastes," Chemical Week, pp. 40-43, October 1986.

[7]Swallow, K.C., Killilea, W.R., Malinowski, K.C., and Staszak, C.N., "The MODAR Process for the Destruction of Hazardous Organic Wastes--Field Test of a Pilot-Scale Unit," Waste Management, 2, pp. 19-26, 1989.

[8]Johnston, J.B., Hannan, R.E., Cunningham, V.L., Daggy, B.P., Sturm, F.J., and Kelly, R.M., "Destruction of Pharmaceutical and Biopharmaceutical Wastes by the MODAR Supercritical Water Oxidation Process," Bio/Technology, 6, p. 1423, 1988.

[9]Modell, M., "Supercritical Water Oxidation," in Standard Handbook of Hazardous Waste Treatment and Disposal, H.M. Freeman, ed., McGraw-Hill Book Co., New York, 1989.

[10]Anon., "Assessment and Development of an Industrial Wet Oxidation System for Burning Waste and Low-Grade Fuels--Final Report," DOE/ID-12711-1, Stone and Webster Engineering Corporation, September 1989.

[11]Bergan, N.E., Butler, P.B., Dwyer, H.A., "Chemkin Real-Gas: A Fortran Package for Analysis of Thermodynamics and Chemical Kinetics in High-Pressure Systems," Sandia National Laboratories, SAND report draft, to be published, 1991.

[12]Wilk, R.D., Cernansky, N.P., Pitz, W.J., and Westbrook, C.K., "Propene Oxidation at Low and Intermediate Temperatures: A Detailed Chemical Kinetic Study", Combustion and Flame, 77, 145 (1989).

[13]Norton, T.S., and Dryer, F.L., "Some New Observations on Methanol Oxidation Chemistry", Comb. Sci. Tech., 63, 107 (1989).

[14]Hindmarsh, A. C., "LSODE and LSODI, Two Initial Value Ordinary Differential Equation Solvers," ACM SIGNUM Newsletter 15 10-11 1980.

[15]Peng, D.Y., Robinson, D.B., "A New Two-Constant Equation of State," Ind. Eng. Chem., Fundam, Vol. 15, No. 1, 1976.

[16]Reid, R. C., Prausnitz, J. M., Poling, B. E., The Properties of Gases & Liquids, 4th ed., Appendix A, Donnelley & Sons Co, 1987.

[17]Knapp, H., Doring, R., et al., "Vapor-Liquid Equilibria for Mixtures of Low Boiling Sub.", Chem. Data Ser., Vol. VI, 771-793, 1982.

[18]Griffiths, J.F., Coppersthwaite, D., Phillips, C.H., Westbrook, C.K., Pitz, W.J., "Auto-Ignition Temperatures of Binary Mixtures of Alkanes in a Closed Vessel: Comparisons between Experimental Measurements and Numerical Predictions", 23rd (International) Combustion Symposium, Orleans, France (1990).

[19]Miller, J.A., and Bowman, C.T., "Mechanisms and Modeling of Nitrogen Chemistry in Combustion", Prog. Energy Combust. Sci., 15, 287 (1989).

[20]Westbrook, C.K. and Dryer, F.L., Combust. Sci. and Tech., 20, 125 (1979).

[21]Tsang, W., "Chemical Kinetic Data Base for Combustion Chemistry. Part 2. Methanol", J. Phys. Chem. Ref. Data, 16, 471 (1987).

[22]Kaiser, E.W., Westbrook, C.K., and Pitz, W.J., "Acetaldehyde Oxidation in the Negative Temperature Coefficient Regime: Experimental and Modeling Results", Int. J. Chem. Kin. 18, 655 (1986).

[23]Christoforakos, M., and Franck, E. U., "An Equation of State for Binary Fluid Mixtures to High Temperatures and High Pressures", Ber. Bunsenges. Phys. Chem. 90, 780-789 (1986).