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	<i>Kinetics of Supercritical Water Oxidation</i> <i>QR Jan 1 - Mar 31, 1996</i> DOCUMENT IDENTIFICATION 1996																															
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1996	3. REPORT TYPE AND DATES COVERED Quarterly Report, Jan 1 - March 31, 1996	
4. TITLE AND SUBTITLE Kinetics of Supercritical Water Oxidation			5. FUNDING NUMBERS N/A	
6. AUTHOR(S) S.F. Rice, R.R. Steeper, R.G. Hanush, J.D. Aiken, E. Croiset, J.W. Tester, K. Brezinsky				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Sandia National Laboratories Combustion Research Facility			8. PERFORMING ORGANIZATION REPORT NUMBER Case 8610.000	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203			10. SPONSORING / MONITORING AGENCY REPORT NUMBER N/A	
11. SUPPLEMENTARY NOTES This work was supported in part by SERDP. The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein. All other rights are reserved by the copyright owner.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution is unlimited				12b. DISTRIBUTION CODE A
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14. SUBJECT TERMS Kinetics, Supercritical water oxidation, Supercritical flow reactor, SERDP				15. NUMBER OF PAGES 16
				16. PRICE CODE N/A
17. SECURITY CLASSIFICATION OF REPORT unclass.	18. SECURITY CLASSIFICATION OF THIS PAGE unclass.	19. SECURITY CLASSIFICATION OF ABSTRACT unclass.		20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

DTIC QUALITY INSPECTED 1

Kinetics of Supercritical Water Oxidation

SERDP Compliance Technical Thrust Area

Quarterly Report

Sandia National Laboratories
Combustion Research Facility
Case 8610.000

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Reporting Period: January 1 - March 31, 1996

Project description

This project consists of experiments and theoretical modeling designed to improve our understanding of the detailed chemical kinetics of supercritical water oxidation (SCWO) processes. The objective of the four-year project is to develop working models that accurately predict the oxidation rates and mechanisms for a variety of key organic species over the range of temperatures and pressures important for industrial applications. Our examination of reaction kinetics in supercritical water undertakes *in situ* measurements of reactants, intermediates, and products using optical spectroscopic techniques, primarily Raman spectroscopy. Our focus is to measure the primary oxidation steps that occur in the oxidation of methanol, higher alcohols, methylene chloride, aromatics, and some simple organic compounds containing nitro groups. We are placing special emphasis on identifying reaction steps that involve hydroxyl radicals, hydroperoxyl radicals, and hydrogen peroxide. The measurements are conducted in two optically accessible reactors located at Sandia's Combustion Research Facility (CRF), the supercritical flow reactor (SFR) and the supercritical constant volume reactor (SCVR), designed to operate at temperatures and pressures up to 600°C and 500 MPa. The combination of these two reactors permits reaction rate measurements ranging from 0.1 s to many hours.

The work conducted here continues the experimental approach from our previous SERDP-funded project by extending measurements on key oxidant species and expanding the variety of experimental methods, primarily spectroscopic in nature, that can be used to examine reactions at SCWO conditions. Direct support is provided to the project collaborators at MIT and Princeton who are contributing to model development for phenol, other aromatics, and halogenated species. These researchers are examining these processes using more conventional sample-and-quench methods. The experiments at Sandia and at the universities all focus on determining the primary oxidation steps that involve the OH and HO₂ radicals, generating data that will be used to evaluate and refine SCWO reaction kinetic schemes. The primary technical difficulty in this stage of the project will be recasting existing high temperature (1100 °C) chemical kinetic models for these simple molecules to 400-600 °C.

Executive Summary of Progress this Period

Programmatic

FY95 funds were fully expended at the end of February and FY96 funds arrived at Sandia in early March, preserving continuity of the project. Some of the time during this period was devoted to applied experiments in support of Sandia's work for DARPA and the Office of Naval Research for the application of SCWO to Naval shipboard excess hazardous material (EHM). This work will be presented in a Sandia Technical Report to be prepared next quarter.

This quarter marked the arrival of Dr. Eric Croiset from the Université Orleans and CNRS Orleans, France. He will be working with the project team as a visiting scientist through December 1996. Additionally, the project is in the process of finding a suitably qualified postdoctoral associate join the team in late 1996. Commencing June 3, Melissa Pecullan, the primary graduate student working on the research on this project at Princeton University, will begin a three-month visit to Sandia. She will conduct experiments at low, intermediate, and high pressure designed to correlate the results on the oxidation and pyrolysis of anisole and phenol at atmospheric pressure that she recently obtained at Princeton to hydrothermal conditions.

The contract with the Massachusetts Institute of Technology was renewed with an updated statement of work for the second year (April 1, 1996 - March 31, 1997).

H₂O₂ thermal decomposition

Improvements in the reactant feed and sampling methods used in the SFR for the DARPA/ONR tests, permitting quenched samples to be taken with reaction times much less than one second, have enabled measurements on the thermal

decomposition of H_2O_2 up to 450 °C over a range of pressures from 5 to 25 MPa. Preliminary results show that the decomposition rate has a dramatic dependence on the density of the fluid.

CO/CO₂ water-gas shift chemistry

Considerable progress on this task was made this quarter. Although the identity of several of the low-concentration intermediates have not been determined, a key goal of the experimental component of this work has been realized. Previous experiments at pressures up to 30 MPa failed to show the effect of excess water predicted by Melius et. al.¹ for $\text{CO} + \text{H}_2\text{O} \Rightarrow \text{CO}_2 + \text{H}_2$ and experimental difficulties had prevented operation at higher pressure. These difficulties were overcome this quarter and operation of the supercritical constant volume reactor (SCVR) up to 50 MPa is now routine. Kinetics experiments at this higher pressure and at 450 °C have revealed a dramatic change in the rate of the water-gas shift reaction. This result suggests that the water-stabilized transition state structures predicted by Melius' calculations may indeed exist at densities near the critical density of water. To capitalize on this preliminary result, however, some additional modifications of the SCVR are necessary to reduce the mixing timescale from about 2 minutes to less than 10 s.

Massachusetts Institute of Technology, Department of Chemical Engineering

We have completed our initial investigation into the use of hydrogen peroxide as an alternative means of introducing oxygen (O_2) into our bench-scale, tubular flow reactor. The results from a series of experiments show that there is no discernible difference between a direct oxygen feed system and one based on decomposing H_2O_2 to produce oxygen. As described in our previous report, we have redesigned the mixing tee at the entrance to our bench-scale tubular reactor in an effort to improve the degree of micromixing in the reactor entrance region. Methanol oxidation experiments with the new tee design exhibit much shorter induction times (approx. 1 second or less) than those observed with the old tee design (approx. 2-2.5 seconds). Efforts are currently underway with the new tee to reexamine key compounds and to determine the extent to which past data and their associated global rate expressions are affected by the mixing time phenomena. It appears that there is now much better agreement between the results from Sandia and MIT on the oxidation rate of methanol over a wide range of temperatures.

Princeton University, Mechanical and Aerospace Engineering Department

Time profiles of reaction intermediate mole fractions for the atmospheric pressure, gas phase, water-perturbed pyrolysis and oxidation of anisole have been obtained. Experiments were performed at initial water concentrations of 2 and 4%. At these

water loadings, the anisole pyrolysis and oxidation chemistry appears to be unaffected. Species profiles from the water-perturbed experiments are, within experimental error, indistinguishable from those obtained from the unperturbed system. The next phase of the experimental work will be carried out at Sandia in the Supercritical Fluids Reactor (SFR) during the visit of Princeton student M. Pecullan. The gas phase anisole oxidation model (in progress) may then be extrapolated stepwise to the supercritical water oxidation of anisole and other related compounds. The modeling effort has led to the development of a multichannel reaction scheme to form a number of the major species directly from recombination of the phenoxy and methyl radicals.

Future work

The primary goal of the next quarter is to complete the H_2O_2 measurements, analyze the data, and prepare the results for publication. We will also initiate an elementary reaction modeling approach to account for the discrepancies between the present experimental observations and the simplest four-step pseudo-first-order description for this process. In addition, the water-gas shift experiments will continue. A fairly large experimental matrix is required to determine whether the quantitative aspects of the Melius model for the reaction as a function of water density are accurate. Melissa Pecullan's visit begins in June, which marks the beginning of the experimental effort to determine the high pressure detailed reactivity of phenol and anisole in the SFR.

Publications & presentations

S.F. Rice, T.B. Hunter, and R.G. Hanush "Oxidative Reactivity Of Simple Alcohols In Supercritical Water Using *In Situ* Raman Spectroscopy, presented at Second International Symposium on Environmental Applications of Advanced Oxidation Technologies February 28 -March 1, 1996, San Francisco CA, paper to appear in EPRI proceedings.

Detailed Summary of Technical Progress this Period

Sandia Combustion Research Facility

H_2O_2 thermal decomposition

The thermal decomposition of H_2O_2 has been identified as a key rate-determining step in the oxidation of alcohols in supercritical water.² We had planned to use an optically accessible reactor in another laboratory in the Combustion Research Facility to use pulsed laser photolysis combined with transient absorption spectroscopy to monitor the kinetics of the disproportionation reaction



It has been suggested³ that this reaction proceeds by the pathway



producing

$$-d[\text{H}_2\text{O}_2]/dt = k_2^{\text{hp}}[\text{H}_2\text{O}_2] + k_3[\text{H}_2\text{O}_2][\text{OH}] - k_5[\text{HO}_2]^2 \quad (6)$$

The parentheses surrounding the collision partner in Reaction 2 indicate that at lower pressures the rate for hydrogen peroxide unimolecular dissociation requires a collision. At our densities, RRKM calculations indicate⁴ that the reaction rate is in the high pressure limit and that an increased frequency of collisions will not increase the rate.

Assuming steady state for HO_2 and OH yields

$$-d[\text{H}_2\text{O}_2]/dt = 2k_2^{\text{hp}}[\text{H}_2\text{O}_2] \quad (7)$$

Experimentally, if the concentration of H_2O_2 is measured as a function of time as it is permitted to thermally decompose, the kinetics are expected to be first order with respect to H_2O_2 . In addition, the observed first order rate will be twice the elementary first order rate constant for Reaction 2 in the high pressure limit.

Delays associated with equipment availability for the pulsed laser experiments have prevented us to date from making the measurements needed to verify the rate and mechanism used for this key reaction in our elementary model. As a result, we have modified the supercritical fluids reactor (SFR) to permit significantly more rapid quenching of short-residence-time reactions. This allows us to take samples of rapidly quenched reactions with a minimum time resolution of 1 second at pressures above the critical point. Using this new operating scheme, we can measure the decomposition rate of H_2O_2 by taking short-residence-time samples followed by iodometric analysis. Figure 1 shows preliminary results for the thermal decomposition of H_2O_2 in high pressure liquid water and supercritical water up to 425 °C. The reaction appears to follow first order kinetics. However, more data are required for the higher temperature points. The slope of the data for the H_2O_2

reaction at each temperature represents the first order rate of Reaction 7 at that temperature.

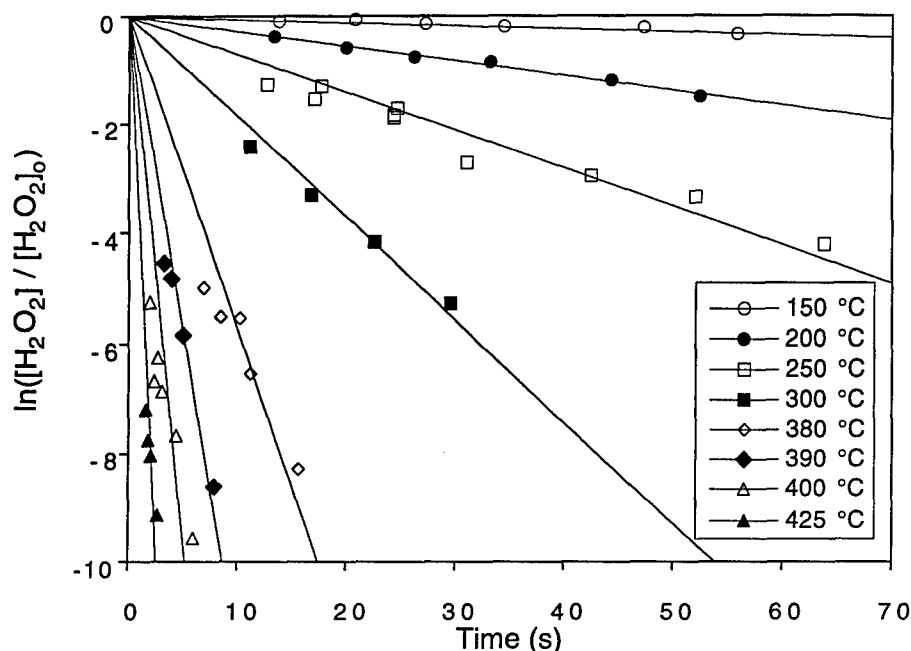


Figure 1. Plot of normalized measured hydrogen peroxide concentration vs. time where $[H_2O_2]$ is the measured hydrogen peroxide concentration after reaction and quenching and $[H_2O_2]_0$ is the initial concentration. The good straight-line fits indicate that first order kinetics are followed.

In Figure 2, these data are shown in Arrhenius format. The data reveal very well defined Arrhenius behavior for the reaction when water is at liquid-like densities (below 380 °C). Above this temperature there is a significant change in the variation in the rate constant with temperature. This suggests that there is one mechanism for liquid thermal decomposition of H_2O_2 and a different mechanism for the gas phase reaction. That is, when the density drops below the critical density, the identity of the rate controlling reaction (or reactions) changes.

There are many possible explanations for this observation that require further investigation. In addition, because of this complexity, it is even more important to implement the spectroscopic approach to examine this reaction. Using the laser diagnostics, we will be able to access higher temperatures and hopefully probe some of the assumptions accompanying the steady state approximation described above.

We are also concerned about the possibility that catalytic effects involving the reactor walls may significantly influence the quantitative accuracy of the data. The wall effects will be investigated next quarter.

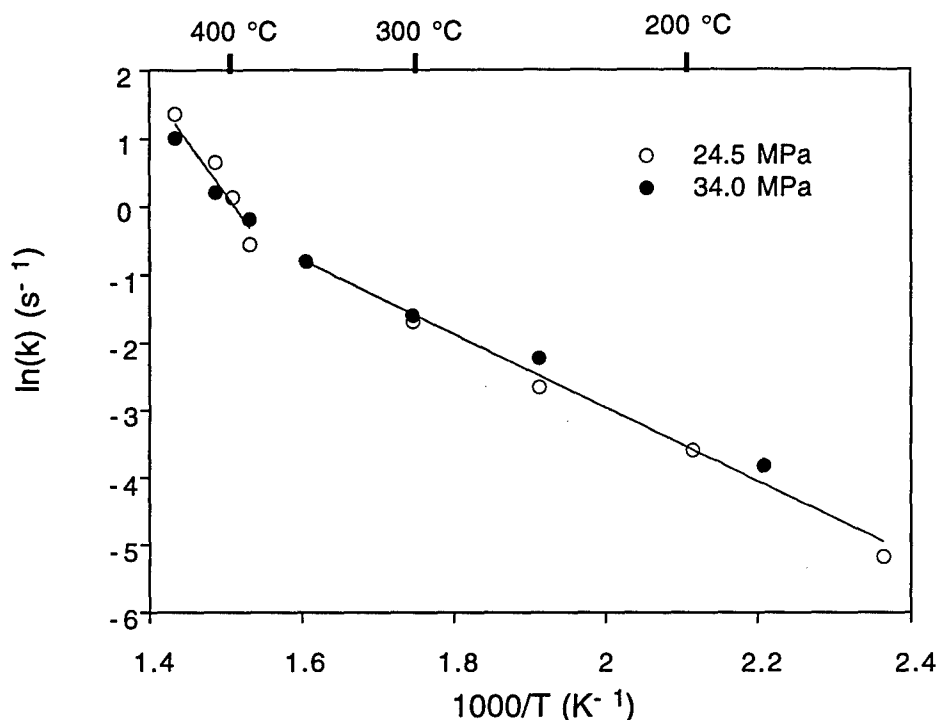


Figure 2. Arrhenius plot of first order rate constants for the thermal decomposition of hydrogen peroxide at 24.5 and 34.0 MPa. Note the distinct change in slope of the plot when the density changes from liquid-like ($>0.8\text{g/cc}$) to supercritical conditions ($<0.3\text{ g/cc}$) at approximately 380°C .

CO/CO₂ water-gas shift chemistry

In the previous quarter, reasonable experimental reproducibility was established for measuring CO, CO₂, and H₂ concentrations as a function of time and system pressure for the water-gas shift reaction. These experiments were carried out over a pressure range of 2 -27 MPa (300 - 4000 psi) at 450°C . The reaction rate was found to vary linearly with water concentration. The presence of side products was observed and still remains an unresolved issue in the overall interpretation of the results, but the biggest concern existing to this point was whether we could observe the predicted¹ dramatic change in reaction rate with increased water concentration.

The supercritical constant volume reactor (SCVR) is rated to operate as high as 8000 psi (540 MPa). After some difficulty, we were successful this quarter in sealing the system at this pressure and were able to observe the effect that had been predicted. Figure 3 shows the results of a typical experiment at 450 °C and 29.0 MPa. The effective initial rate for the disappearance of CO is 1.04×10^{-5} mole/l-s. The water concentration is 7.72 mole/l. Figure 4 shows nearly identical experimental conditions with pressure at 51.0 MPa (water concentration 22.8 mole/l). At this water concentration, if the rate continued to vary linearly, we would expect the initial effective rate to be about 3.0×10^{-5} mole/l-s. The observed rate is 7.2×10^{-4} . Obviously, a more detailed analysis is required in the future, since the rate slows significantly as CO₂ is accumulated. However, this observation is critical. It clearly shows that there is a change in the mechanism in the reaction of CO with water as the microscopic structure of water begins to appear more liquid-like.

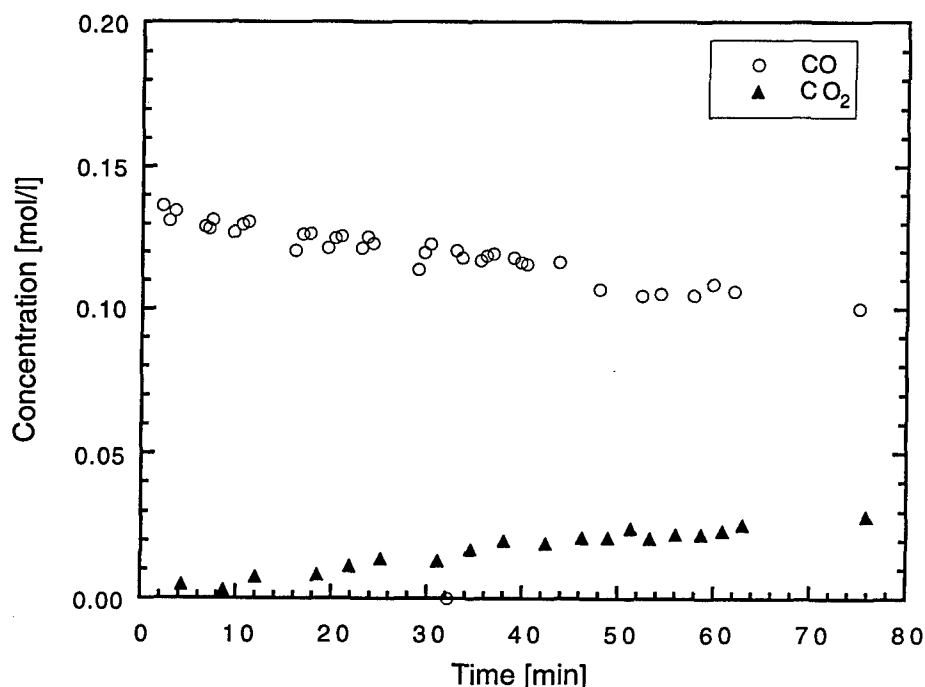


Figure 3. Concentrations of CO and CO₂ as a function of time after injection of CO into supercritical water at 450 °C and 29.2 MPa. The concentrations are measured by *in situ* Raman spectroscopy in the SCVR.

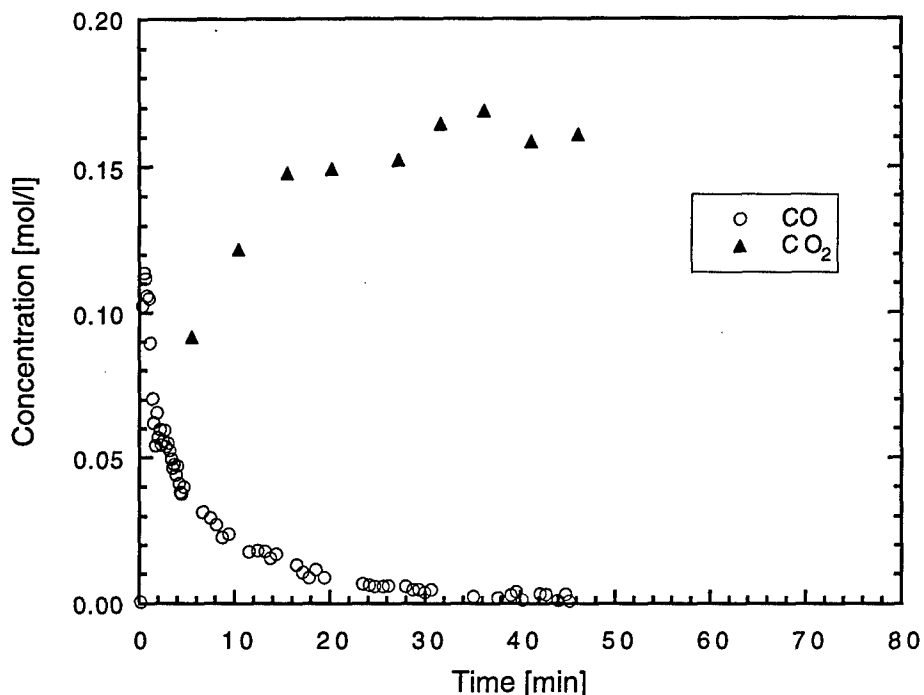


Figure 4. Concentrations of CO and CO₂ as a function of time after injection of CO into supercritical water at 450 °C and 51.0 MPa. The concentrations are measured by *in situ* Raman spectroscopy.

Massachusetts Institute of Technology, Department of Chemical Engineering

This work is supported partly by the SERDP program and partly by an Army Research Office University Research Initiative program.

Hydrogen Peroxide/Dissolved Oxygen Studies:

We have completed our initial investigation into the use of hydrogen peroxide as an alternative means of introducing oxygen (O₂) into our bench-scale, tubular flow reactor. The work was motivated, in part, by the desire to overcome the 0.4 wt% inlet oxygen concentration limit imposed by our saturator-based oxygen feed system. It was also motivated by the desire to directly compare the oxidation rate data obtained in our reactor with those obtained from Sandia's larger tubular flow reactor (which employs hydrogen peroxide as the oxidant source).

In the new oxidant delivery system, a volumetrically-prepared hydrogen peroxide solution is pressurized to system pressure (23.0-26.0 MPa), heated to supercritical

temperatures (approx. 400-425 °C), and fed to a packed-bed tubular reactor. Within the reactor, the preheated hydrogen peroxide solution passes across a bed of 200-250 μm Inconel 625 beads which promote the surface-catalyzed decomposition of hydrogen peroxide to oxygen and water. The oxygen produced is completely soluble in the supercritical water solution and flows into the primary reactor where it is mixed with a preheated aqueous organic waste stream.

In an effort to determine if hydrogen peroxide is decomposing completely to oxygen and water before reaching the primary reactor, two sets of studies were conducted. The first examined the amount of oxygen evolved from the peroxide stream after exiting the packed-bed reactor. The measured oxygen flowrates indicated complete decomposition of the peroxide (within measurement error) and are consistent with the global stoichiometry of the hydrogen peroxide decomposition reaction: $\text{H}_2\text{O}_2 \Rightarrow 1/2 \text{O}_2 + \text{H}_2\text{O}$. The second set of experiments compared the rate of oxidation of methanol using the saturator-based feed system with the oxidation rate using a hydrogen peroxide solution prepared to deliver an equivalent amount of oxygen upon complete decomposition of peroxide. The results from this series of experiments appear in Figure 5. At 500 °C, 24.2 MPa, and a 1:1 methanol-to-oxygen molar feed ratio there is no discernible difference between the two systems over a residence time range of 2 to 5 seconds. The distribution of the measured concentrations of the oxidation product species (H_2 , CO , CO_2 , CH_2O), for both feed arrangements as a function of time, are likewise identical within measurement error.

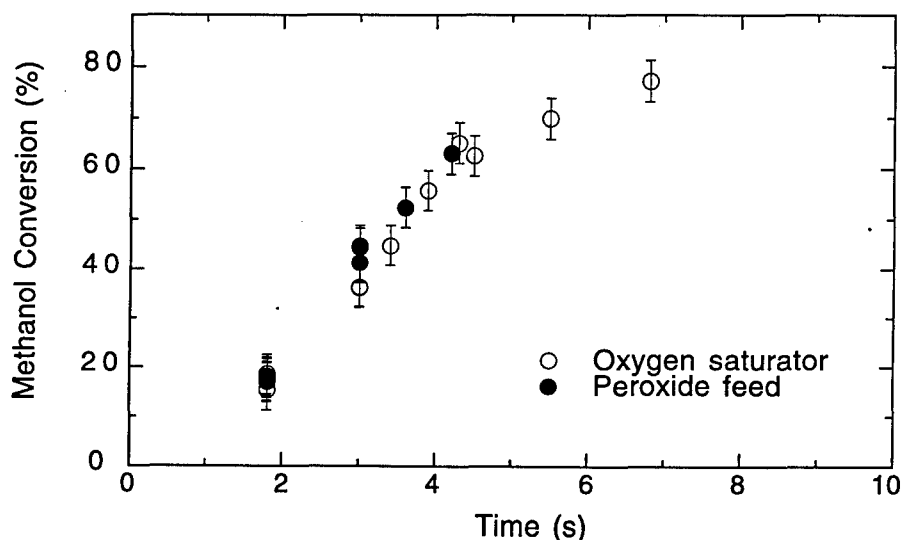


Figure 5. Comparison of methanol conversion obtained at 500 °C, 24.1 MPa, and a 1:1 O_2 :MeOH molar feed ratio using an oxygen saturator and equivalent H_2O_2 feed.

Feed Mixing Effects

As described in our previous report, we have redesigned the mixing tee at the entrance to our bench-scale tubular reactor in an effort to improve the degree of micromixing in the reactor entrance region. The redesign was initiated by an observed mixing problem, illustrated in Figure 6. Figure 6 shows methanol conversion as a function of time at 500 °C, 24.2 MPa, and a 1:1 methanol-to-oxygen molar feed ratio using three different mixing tee configurations. Initially, 8.1 and 2.5 meter reactors were constructed, each with their own mixing tee, in order to study the oxidation of methanol at short and long residence times. It was observed that methanol conversions obtained in these two reactors differed substantially (see 8.1m "slow" tee and 2.5m "fast" tee).

Close inspection of the tees (Figure 7) revealed that the critical parameters controlling the mixing process (jet and main stream Reynolds numbers (Re_j), jet-to-main stream velocity ratio (v_j/V_{rx}) and jet-to-main stream diameter ratio) were different for the two tees. As a result, the "fast" tee was providing more efficient mixing of the incoming oxidant and organic streams. To further test this hypothesis, the "fast" tee was removed from the 2.5m reactor and placed on the 8.1 m reactor. As shown in Figure 6 (8.1m "fast" tee) the resulting oxidation rates were in good agreement with those obtained using the 2.5 m reactor.

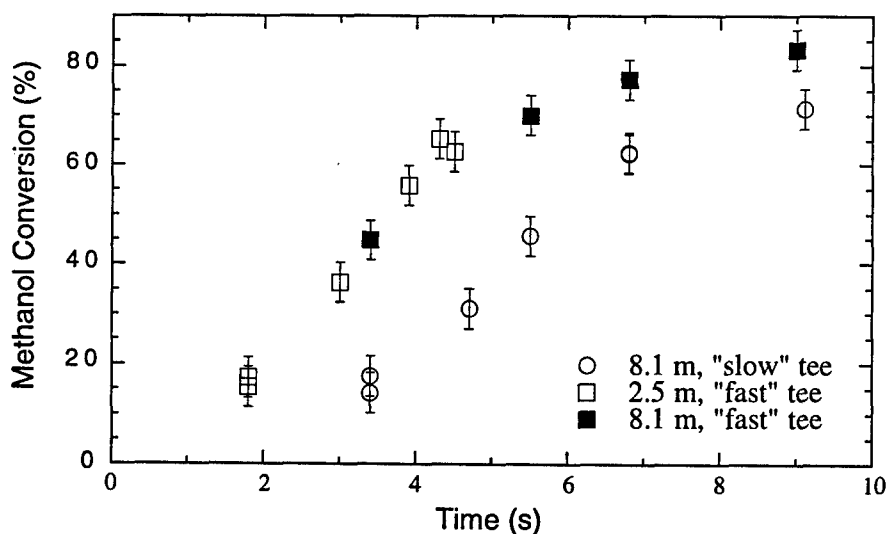
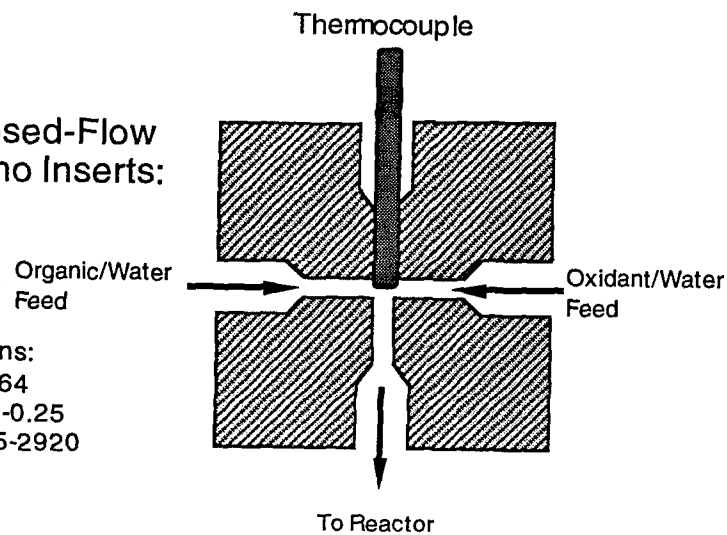


Figure 6. Comparison of methanol conversion obtained at 500 °C, 24.1 MPa, and a 1:1 O₂:MeOH molar feed ratio using original and optimized mixing tees.

Old Opposed-Flow Tee with no Inserts:

Flow Conditions:
 v_j (cm/s) = 20-64
 v_j/V_{rx} = 0.2-0.25
 Re_j = 905-2920



New Side-Entry Tee with 0.01" ID inserts:

Flow Conditions:
 v_j (cm/s) = 775-2,500
 v_j/V_{rx} = 7.5-9.3
 Re_j = 5,700-18,000

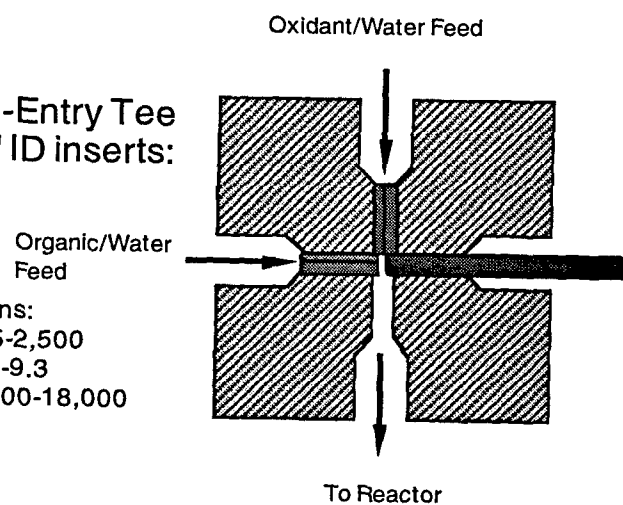


Figure 7. Schematics of two different mixing tee configurations. The inserts are designed to increase turbulence in the mixing region.

In response to these observations, efforts were made to design a mixing tee that was easy to fabricate and that ensures good mixing. Following a review of recent literature aimed at identifying optimal micromixing conditions in pipeline tees, we adopted a side-entry inlet tee configuration (feed streams enter the tee at a 90 degree angle to each other). The inner diameter of the two inlet branches was reduced to 0.01" and Reynolds numbers for both the main and side-branch streams range from 11,000 to 15,000 under normal operating conditions. Results of methanol oxidation experiments using the new tee design are consistent with the "fast" tee results described above and exhibit much shorter induction times (approx. 1 second or less) than those observed with the old tee design (approx. 2-2.5 seconds). Efforts are currently underway with the new tee to reexamine key compounds and to determine the extent to which past data and their associated global rate expressions are affected by the mixing time phenomena.

Princeton University, Mechanical and Aerospace Engineering Department

Experimental Results

Reaction intermediate mole fraction versus time profiles for the atmospheric pressure, gas phase, water-perturbed pyrolysis and oxidation of anisole have been obtained. This data set was collected for comparison with data acquired from the unperturbed anisole/oxygen system at the same nominal temperature (727 °C) and stoichiometries (pyrolysis and $\phi=0.6$). Observed shifts in species profiles due to the addition of water were expected to aid in the identification of chemical pathways involving water and thereby provide a starting point for the development of a detailed kinetic model for the supercritical water oxidation of anisole. Experiments were performed at initial water concentrations of 2 and 4%. At these water loadings, the anisole pyrolysis and oxidation chemistry appears to be unaffected. Figure 8 shows that species profiles from the water-perturbed experiments are, within experimental error, indistinguishable from those obtained from the unperturbed system.

Unfortunately, the current reactor configuration would not allow water concentrations in significant excess of 4%. This limitation is detailed as follows. Anisole and water cannot be premixed as liquids since they are not soluble in one another. The flow reactor's one evaporator had to be reserved for fuel vaporization. Therefore the water was injected into the inlet section of the reactor, just downstream of the arc heater, and vaporized in the hot flow of nitrogen and oxygen. Water has a substantial heat of vaporization (40.7 kJ/mol) and, at a molar concentration of 4%, cools the bulk inlet flow significantly; the arc gas temperature had to be maintained at 855 °C in order to achieve a temperature of 727 °C at the entry of the test section. So, ultimately the upper bound on water loading was defined by the maximum arc gas temperature at which the plasma torch can be safely operated, approximately 900 °C.

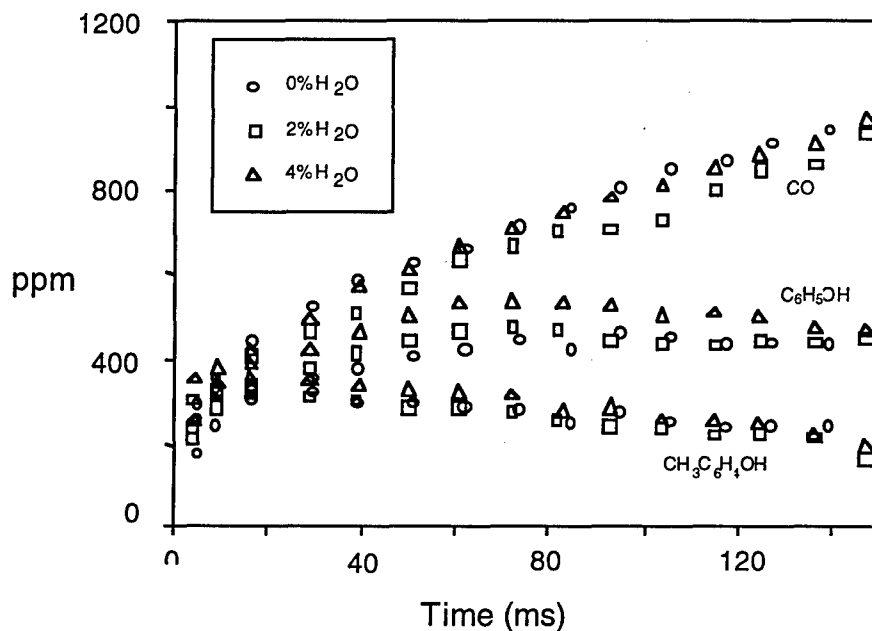


Figure 8. Carbon Monoxide, Phenol, and Cresol profiles for lean oxidation of anisole with and without water at 727 °C and $\Phi=0.6$.

The next phase of the experimental work will be carried out at Sandia's Combustion Research Facility using the Supercritical Fluids Reactor (SFR). Above the critical pressure of water (22.1 MPa), the maximum operating temperature of the SFR is 650 °C. At pressures of only tens of atmospheres (1-5 MPa), however, the reactor may be operated safely at 750 °C. In order to provide an intermediate situation (i.e., between the high temperature, atmospheric pressure oxidation of anisole in a nitrogen bath and the low temperature oxidation of anisole in supercritical water) the initial SFR experiments will be performed at the same nominal temperature as the Princeton work and at high (1.0-6.0 MPa), but *subcritical*, pressures. The gas phase anisole oxidation model that is being developed at Princeton may then be extrapolated stepwise to the supercritical water oxidation of anisole and other related compounds.

Following a flow reactor modification (reported last quarter) to allow for the melting and subsequent vaporization of a room-temperature solid reactant, an oxidation study of phenol was executed. The data set spans a range of stoichiometries ($\phi=0.64$ -1.73) at 896 °C. The phenol oxidation data is expected to assist in the development of the anisole model, and will also serve as a benchmark for investigation of the supercritical-water-oxidation of phenol.

Modeling

As was previously reported, the modeling effort has led to the development of a multichannel reaction scheme to form a number of the major species directly from recombination of the phenoxy and methyl radicals. QRRK analysis was employed in order to estimate reaction rate constants and validate the proposed chemistry. Recent work has revealed the necessity for greater detail in the description of certain substituted benzenes and cyclopentadienes that exist in several isomeric forms. Such species (i.e. cresols and methylcyclopentadienes) constitute a significant fraction of the major reaction intermediates. Initially a simplified approach to modeling these species was attempted wherein isomers are represented by a single molecule. An "average molecule," one possessing an equilibrium ratio weighted average of the thermodynamic properties of each isomer, was constructed for both cresol and methylcyclopentadiene. However, although the thermodynamics are very similar for all three isomeric forms of each of these two species, the activation energies for some isomerization and decomposition pathways are very different among isomers. The MOPAC code (a general semi-empirical Molecular Orbital PACKage) was used to estimate heats of formation and entropies of transition states for several isomerization reactions and thereby obtain estimates for rate parameters. These calculations have allowed a more accurate description of the chemistry resulting in an enhanced agreement between model predictions and the experimental data.

Future Work

The primary goal for work next quarter is completion of the H_2O_2 measurements, analysis of the data, and preparation of the results for publication. Specific tasks to be done include a considerable amount of routine data collection to ensure that the kinetics data set covers a sufficiently wide range of temperatures and pressures and allows an evaluation of wall effects in the SFR. Because the thermal decomposition of H_2O_2 is catalyzed by metals (and the SFR is a metal-walled reactor), a significant concern is whether the rates that are measured are due to a homogeneous reaction or whether the data are representative of a surface-catalyzed wall reaction. We will also initiate an elementary reaction modeling approach to account for the discrepancies between the present experimental observations and the simplest four - step pseudo-first-order description for this process.

In addition, the water gas shift experiments will continue in Sandia's SCVR. A fairly large experimental matrix is required to determine whether the quantitative aspects of the Melius model for the reaction as a function of water density are accurate. We will also focus on adding a mixing device to the SCVR to reduce the experimental time resolution to several seconds from the present value of a little over a minute.

Melissa Pecullan's visit from Princeton begins in June which marks the beginning of the experimental effort to determine the detailed reactivity of phenol and anisole at high pressure. Hopefully, most of the experimental work will be completed during Pecullan's 3 month visit, but the entire task probably will not be completed until the mid-fall. The most important activity during Pecullan's visit will be acquiring extensive data on phenol and anisole oxidation at pressures in the range of 20 -100 bar at temperatures as near to 730 °C as possible, thus matching the temperature of the ambient pressure data taken at Princeton. Some modification of the gas chromatographic equipment at Sandia will be required, however, the primary experimental challenge will be extending the operational temperature range of the SFR above 650 °C. The combination of the high temperature and reduced fluid density will require an extension of the preheater to accommodate the high-velocity flow in the tubing.

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