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Background, Design, and Preliminary Experiments

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SUPERCRITICAL WATER OXIDATION OF HAZARDOUS CHEMICAL WASTE

KINETICS EXPERIMENTS AND BENCH-SCALE SYSTEM

Background, Design, and Preliminary Experiments

by

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ABSTRACT

The project, "Supercritical Water Oxidation of Hazardous Chemical Waste," is a Hazardous Waste Remedial Actions Program (HAZWRAP) Research and Development task being carried out by the Los Alamos National Laboratory. It has been in progress since February 1986. Its objective is to obtain information for use in understanding the basic technology and for scaling up and applying oxidation in supercritical water as a viable process for treating a variety of DOE-DP waste streams. This report gives the background and rationale for kinetics experiments on oxidation in supercritical water being carried out as a part of this HAZWRAP Research and Development task. It discusses supercritical fluid properties and their relevance to applying this process to the destruction of hazardous wastes. An overview is given of the small emerging industry based on applications of supercritical water oxidation. Factors that could lead to additional applications are listed. Modeling studies are described as a basis for the experimental design. The report describes plug flow reactor and batch reactor systems, and presents preliminary results.

I. BACKGROUND

A. Overview of the Process

Above a high enough temperature and pressure (647 K and 22.13 MPa), water becomes a fluid that is neither a liquid nor a gas but has some of the characteristics of both. In this state, water's solvent properties reverse so that nonpolar, oily compounds become soluble and salts become insoluble. Under these conditions, oxidation of hazardous organic chemicals such as PCBs and solvents takes place rapidly and completely. Carbon becomes carbon dioxide, hydrogen becomes water, and other components of the hazardous organic become their oxidized compounds.

Although this oxidation is similar to combustion, it takes place at a much lower temperature than incineration (about 800 K in contrast to 2300 K) and in a completely contained system. No NO_x is created at these low temperatures, and the effluent can be completely controlled. Because the supercritical state can be produced by pressure or temperature increases without a phase change, less energy is needed than in processes in which a phase change takes place, such as incineration of aqueous wastes. This process has the promise of destroying low concentrations of hazardous chemicals in water, such as groundwater contaminated with chlorinated hydrocarbons, at reasonable cost. Depending on the nature and concentration of the hazardous chemicals, the process may produce net heat which can be used to cogenerate electricity. Because supercritical water can easily and quickly diffuse into small spaces in solid particles, the process should be applicable to decontamination of solid materials such as soil.

The chemistry of oxidation in supercritical water is poorly understood. Little investigation has been carried out on the mechanisms operative in this environment. Because the temperatures are much lower than those of normal combustion, the very efficient destruction observed is somewhat surprising. The purpose of this project is further understanding of the chemical mechanisms of oxidation in supercritical water, directed toward development of a practical process that can be applied to a variety of hazardous wastes.

In order to plan experiments that will yield useful kinetic data that can be used both to interpret chemical mechanisms and to form a basis for development of a process, the physical properties of the system to be studied and previous work in the area of reaction kinetics and mechanisms must be considered. These are discussed in following parts of this section, along with the forms a viable process might take in different applications. Industrial activity in this area is summarized.

B. Physical Properties of Supercritical Water Solutions

The physical properties of the system under study are extremely important in designing kinetics experiments. For reliable kinetic measurements, the mixtures must remain homogeneous. This is an important consideration and potentially a major source of experimental error. However, many properties, such as solubility and heat capacity, change rapidly in the vicinity of the critical point. For this project, multicomponent mixtures will be studied, containing initially an organic compound, water, and O_2, with N_2 as well if air is used as the oxidant. In addition, reaction intermediates, including a number of oxygenated organic compounds, will be produced, and the final products will include carbon dioxide, water, and, in some cases, inorganic acids or salts. Very little is known about phase diagrams for multicomponent mixtures in the supercritical region. However, phase diagrams are available for some binary mixtures in which one of the components is water. Some general observations can also be made about the behavior of supercritical fluid systems.

Under supercritical conditions, two immiscible gas phases can exist in equilibrium with each other or with one or more liquid phases. Gas-gas equilibria of the first type have a critical curve starting at the critical point of the less volatile component and continuing to increase with temperature and pressure. Gas-gas equilibria of the second type show a minimum temperature in the critical curve and decreasing critical temperature with increasing pressure for some pressure range near the critical point; at higher pressures, critical temperatures and pressures for the mixture both increase. Gas-gas equilibria of the second type provide a wider range of complete miscibility, the more desirable situation for kinetics experiments.

Many of the components likely to be present in reaction mixtures are known to give gas-gas equilibria of the second type in binary systems with water. Gases such as O_2 (Ref. 1), N_2 (Ref. 2), and carbon dioxide (Ref. 3); nonpolar organics such as ethane (Ref. 4), propane (Ref. 5), butane (Ref. 4), n-pentane (Ref. 6), n-hexane (Ref. 7), 2-methylpentane (Ref. 6a), cyclohexane (Ref. 8), n-heptane (Ref. 6), benzene (Refs. 6a,9) toluene (Ref. 6a), fluorobenzene, and 1,4-difluorobenzene (Ref. 10) give temperature minima in their critical curves with water ranging from 540 K for carbon dioxide (Ref. 3) to 640 K for oxygen (Ref. 1) and nitrogen (Ref. 2).

Oxidation of some hazardous organic compounds produces inorganic acids. For example, HCl is produced in the oxidation of chlorinated hydrocarbons. The phase diagram for HCl and water[11] shows a gas-gas equilibrium of the first type, with no temperature minimum. Thus, HCl is somewhat more likely than the nonpolar compounds to form two fluid phases in aqueous supercritical systems.

Neutralization of acids such as HCl as they form may be desirable, and thus hydroxides may be added to the process water. In this case, the products will be salts rather than acids. The phase behavior of ionic solids such as salts and hydroxides in supercritical water can be expected to be very different from that of both polar (HCl) and nonpolar (hydrocarbons) liquids and gases. Water is significantly more ionized at supercritical temperatures and pressures than at STP.[12] However, at supercritical conditions the thermal energy of water molecules is greater than the association energy of hydrogen bonding between them, as is illustrated by the increase in the static dielectric constant.[13] Further, the density of water changes rapidly with small changes in temperature and pressure in the vicinity of the critical point. The net result of all these changes in water's properties in the supercritical state is that the solvating environment of supercritical water is very different from that of water at STP.

As might be expected, the phase behavior of aqueous salt solutions under supercritical conditions is much more complex than that of the lower-boiling substances. A theoretical treatment of mixtures of high- and low-boiling substances, such as ionic solids and water,[14] shows that, under supercritical conditions, the difference in boiling points appears to be a primary factor in phase behavior. Solubility of NaCl is much less in supercritical water than in liquid water.[15] The precipitation of solid products may be part of the driving force to complete oxidation and thus beneficial to the overall process. Low salt solubility must be considered a factor in planning the kinetics experiments.

The similarity in behavior of supercritical aqueous systems of nonpolar compounds such as the reactant organics and gases and most of the intermediates and products suggests that multicomponent mixtures of water with nonpolar compounds should also show large regions of complete miscibility at temperatures and pressures above the critical point of water. However, HCl and the salts behave quite differently, and the addition of even small amounts of a third component to a binary mixture is known to have large effects in supercritical systems, leading to the separation of a liquid phase. For example, at temperatures (580-610 K) near, but lower than, the critical point of water, a mixture of water with two nonpolar compounds, benzene and n-heptane, gives two phases. Ternary mixtures of carbon dioxide, water, and NaCl have been found to have higher critical temperatures than CO_2-water binary systems and contain less carbon dioxide at the same temperatures.[16] The phase interaction of reactants, intermediates, and products in the reacting mixture is unpredictable, and multiple liquid and gaseous phases are possible.

C. Reactions in Supercritical Water

The small published literature on reactions in supercritical water falls largely into two categories: patent literature on oxidation of hazardous wastes and report literature on coal processing with supercritical water. Some work on the wet oxidation of organic compounds may also be relevant.

Reactions in a variety of supercritical fluids have recently been reviewed.[17] The potential advantages of supercritical fluids are discussed, such as reducing coking in pyrolysis reactions, reactivating catalysts, allowing the effect of solvent viscosity to be studied, improved product separation, and reaction enhancement. Water is somewhat more difficult to use as a supercritical solvent than other solvents generally reported in the literature, because its critical temperature (647 K) and pressure (22.13 MPa) are relatively high. Only two of the applications reviewed use water as solvent: the hydrolysis of aniline to phenol and the oxidation of hazardous chemicals. Neither of these examples contains significant kinetic or mechanistic information.

The most recent information available on oxidation of organic compounds in supercritical water is by M. Modell and his associates[18] and a thesis by R. K. Helling, prepared at MIT under the direction of J. W. Tester, on the oxidation of ammonia and carbon monoxide in supercritical water.[19] Modell's work has been directed toward proving the effectiveness of a process and contains little mechanistic or kinetic information. Helling has provided preliminary data on the kinetics of the oxidation of ammonia and carbon monoxide.

Another system that is partially relevant to this project is the conversion of coal in supercritical water.[20] Coal is treated with a catalyst and hydrogen or synthesis gas to give hydrocarbon gases and liquids, and a carbonaceous char. This reduction reaction is the opposite of oxidation, but some aspects of this work may be relevant because pyrolysis reactions may also be taking place in both systems.

Some further partially relevant information is available on the mechanism of the wet air oxidation of organic compounds.[21] The temperature and pressure range is lower than that for the supercritical process: about 420-570 K and 6.9-12.4 MPa. Some general conclusions can be drawn about wet air oxidation from the literature. The reaction appears to be homogeneous and to take place mainly in the liquid phase. Some compounds, such as short-chain organic acids, do not oxidize readily. The mechanism appears to be a free radical mechanism similar to that of conventional combustion. It is not clear to what degree these conclusions will carry over to the supercritical regime, and there are indications that supercritical reaction kinetics and mechanisms will be quite different. For example, the overall rate of reaction for wet air oxidation is much slower than that reported for oxidation under supercritical conditions.

D. Potential Applications of Supercritical Water Oxidation

Many hazardous compounds can be destroyed by oxidation in supercritical water. In principle, any organic compound (that is, any compound composed of carbon and other elements such as hydrogen, nitrogen, phosphorus, sulfur, and the halogens) can be oxidized to relatively innocuous compounds. Under typical supercritical water oxidation conditions, the carbon in organic compounds gives carbon dioxide, hydrogen gives water, nitrogen gives ammonia and dinitrogen, phosphorus gives phosphoric acid, sulfur gives sulfuric acid, and the halogens give the corresponding halogen acids. The mineral acids are likely to be produced in relatively small concentrations and can be neutralized to salts by use of caustics.

The requirement for water as a reacting solvent allows the process to be used for a variety of organic wastes containing water or water contaminated with organics. There appears to be no upper or lower limit to the concentration of organic in water that can be destroyed by the process. An economic constraint, however, on the organic concentration is the amount of heat generated by oxidation of the organic. For autogenous (heat supplied by the process without added fuel) operation of a supercritical water oxidation plant, the optimum concentration of organic in water is about 10%. The optimum concentration will vary with the heat of oxidation of the particular organic compounds present. Above this optimum organic concentration, if more heat is generated than can readily be removed from the processing vessel, water can be added to maintain the concentration of organic and therefore the heat produced. Below the optimum organic concentration, heat must be added to maintain the temperatures needed for reaction. For high concentrations of organics, process water can be recycled. The economic lower concentration that can be treated will depend on the cost of supplying heat to the process or recycling heat within it.

The gas-like properties of supercritical water allow its penetration into extremely small pores, which suggests that this process could be used for decontamination of soils and other wastes containing solids. Supercritical carbon dioxide is being used to extract hazardous compounds from soils.[22] These methods, however, do not destroy the hazardous compounds, and another step, usually oxidation, is required. Supercritical water oxidation could extract and destroy hazardous compounds from soil in a single step. For this application, methods of handling the solids must be developed.

Mixed waste (containing both hazardous organic chemicals and radioactive isotopes) and wastes containing organic chemicals and metals could also be treated to remove the organics. Metal ions could later be removed by ion exchange or other treatment, or might be removed by precipitation during the supercritical step. Metals that are complexed with an organic or that are contained in organometallic compounds can be converted to their inorganic form, which normally is more readily removed, by oxidation of the organic portion of the molecule. The completely closed system used for oxidation in supercritical water will contain radioactive species or other hazardous metal ions. Although the metal ions may be converted to a more favorable form for removal, they will not be eliminated from the solution in the same way the organics are. However, judicious engineering of a system might make use of the relative insolubility of metal salts in supercritical water as a removal mechanism.

Some of the many streams that might be treated by supercritical water oxidation thus include: liquid aqueous and organic streams as they are originated, including machining wastes, paint wastes, automobile grease and lubricant wastes, PCB-contaminated oil, and waste solvents; groundwater contaminated with organics; stored wastes, including those that contain sludges or other solids; soil contaminated by spills or burial of organics; vermiculite and other mineral absorbers used to clean up spills of organics; mixed wastes containing both organics and radioisotopes, including uranium-machining wastes; and organometallic compounds, including stream and lake sediments containing organomercury compounds.

A great range of sizes appears to be possible for supercritical water oxidation plants. Standard pressure-vessel technology can be used to provide small- to medium-sized installations, with capacities ranging up to tens of gallons per minute. In addition, plants with very large capacities (up to 300 gal/min) have been proposed, in which the heat exchange and reaction take place in the same vessel. This vessel and its containment are emplaced in the ground by use of oil-field drilling technology. The containment vessel is a very long cylinder. The depth of the cylinder provides pressure by hydrostatic head, and the emplacement in the earth provides structural strength for containment of the pressure. Concentric tubes within the containment vessel provide downcomer and upcomer sections, and a variety of methods of oxygen introduction and heating have been proposed.

Neither aboveground nor subsurface plants require a large land area. Standard plants processing tens of gallons per minute can be skid-mounted and carried on one or two semitrailers. An in-ground unit processing sewage from a medium-sized city requires about an acre of land.

E. Industrial Activity

Four companies were visited that are active in developing particular applications of supercritical water oxidation and wet air oxidation, which is closely related to supercritical water oxidation in chemistry and equipment, but takes place below the critical point of water. Additional materials requirements are imposed by the supercritical pressure and temperature regime. The wet oxidation processes require an additional biological polishing step, which, the companies report, can be carried out in an ordinary sewer plant if the effluent meets legal requirements. The four companies are MODAR (Natick, Massachusetts, and Houston, Texas), Oxidyne (Cincinnati, Ohio, and Dallas, Texas), Zimpro (Rothschild, Wisconsin), and VerTech (Denver, Colorado). MODAR and Oxidyne offer supercritical oxidation technology; Zimpro and VerTech offer wet oxidation technology. MODAR and Zimpro hold patents relating to aboveground processing units. Oxidyne and VerTech hold patents relating to units emplaced in the ground with oil-field drilling technology.

Zimpro reports 200 operating wet air oxidation installations, 18 of which are used for cleanup of hazardous chemical waste streams. VerTech has operated a subsurface wet air oxidation system for processing sewage sludge from the city of Longmont, Colorado. MODAR has a skid-mounted unit that has been used for several demonstrations. Oxidyne is preparing to build a test unit. Information is available on demonstrations carried out by Zimpro[23] under contract to the State of California, by VerTech[24] under contract to the EPA, and by MODAR in collaboration with CECOS International, Inc.[25] Destruction efficiencies are also available for wet oxidation for some compounds,[26] but these do not give any but the broadest information about mechanisms. None of the companies has the resources to carry out experiments on the basic kinetics of the process.

II. DESIGN OF KINETICS MEASUREMENTS

In order to obtain meaningful data for the understanding and development of supercritical water oxidation as a useful process, three interactive paths are being pursued: (1) basic chemical kinetics experiments are being carried out; (2) these experiments are being used to develop a predictive chemical kinetics model; and (3) a demonstration experiment at pilot scale is being planned.

Although some industrial development is proceeding on this process, very little general understanding is available on the rates and mechanisms of the chemistry involved. It is not clear at present what constitutes the set of reactions currently referred to as supercritical oxidation, nor the basis for the notable rapidity and completeness of reaction. It is likely that mass transfer effects, in particular the increased solubility and diffusivity of O_2 and the organic in the supercritical water solvent, play a part in the rapidity and completeness of reaction. The precipitation of salt products may also be important as a driving force to completion. Mass transfer effects, however, must be separated from chemical kinetics for the understanding necessary for application of the method at industrial scale to cleanup of defense-related hazardous wastes.

The chemistry itself may be complex. At supercritical water temperatures, many organic compounds pyrolyze in air or inert gas environments. Pyrolysis is a set of chemical reactions induced by heat that lead to a carbonaceous char and gases or liquids as major products. However, reactions at pyrolysis temperatures in supercritical water produce much less char than conventional pyrolysis.[17] It is not clear whether the pyrolysis reactions are suppressed in supercritical water or the reactive intermediates react with water to produce non-char products. The latter case in particular could contribute to complete and rapid destruction of the organics. The questions of mass transfer and pyrolysis must be separated from that of oxidation before it can be determined whether the oxidation mechanism is similar to that of air oxidation.

Critical phenomena themselves may contribute to reaction rate enhancement. However, this contribution is likely to be small and to occur only in the vicinity of the critical point. A recent controversy in this field[27] illustrates that both experimental and interpretive difficulties are associated with kinetic measurements near the critical point. Large, rapid changes in properties such as solubility and heat capacity near the critical point make measurements particularly difficult. Therefore, it is desirable either to avoid this region for kinetic measurements or to make the range of measurement necessary to fully characterize the system. At this time, there appears to be no reason why the vicinity of the critical point needs to be explored in the early kinetic measurements. Thus, most experiments will be done at pressures and/or temperatures significantly above the critical point.

In order to simplify some of the issues above and to answer basic questions about reaction mechanisms, it is useful to choose a model compound whose chemistry is inherently relatively simple and reasonably well understood in other conditions. Methane, CH_4, is the simplest hydrocarbon. It has been studied extensively under conventional combustion conditions and computer kinetic models are available to describe its chemistry. Thus, it is a reasonable compound for initial studies of oxidation in supercritical water. In addition, because it is the simplest hydrocarbon, its chemistry can serve as a baseline for other aliphatic compounds, including chlorinated hydrocarbons.

A. Plug Flow Reactor

A tubular reactor system allows isothermal operation with radially well-mixed, one-dimensional plug flow. A schematic diagram of the system used in this study is shown in Fig. 1. The reactor is 4.24 m of 0.635-cm o.d. x 0.211-cm i.d. (0.25 x 0.083 in.) Inconel 625 tubing immersed in a fluidized-bed sand bath for temperature control. Dilute concentrations of reactants in water are prepared by dissolution in room temperature water in one-liter agitated tanks. The feed solutions are preheated separately to reaction conditions in less than 10 s in 0.108-cm i.d. Hastelloy C276 tubing and mixed at the reactor inlet. The reactor effluent is cooled quickly in a heat exchanger, depressurized, and separated into measured gas and liquid flows. The composition of the gas phase is determined by gas chromatography.

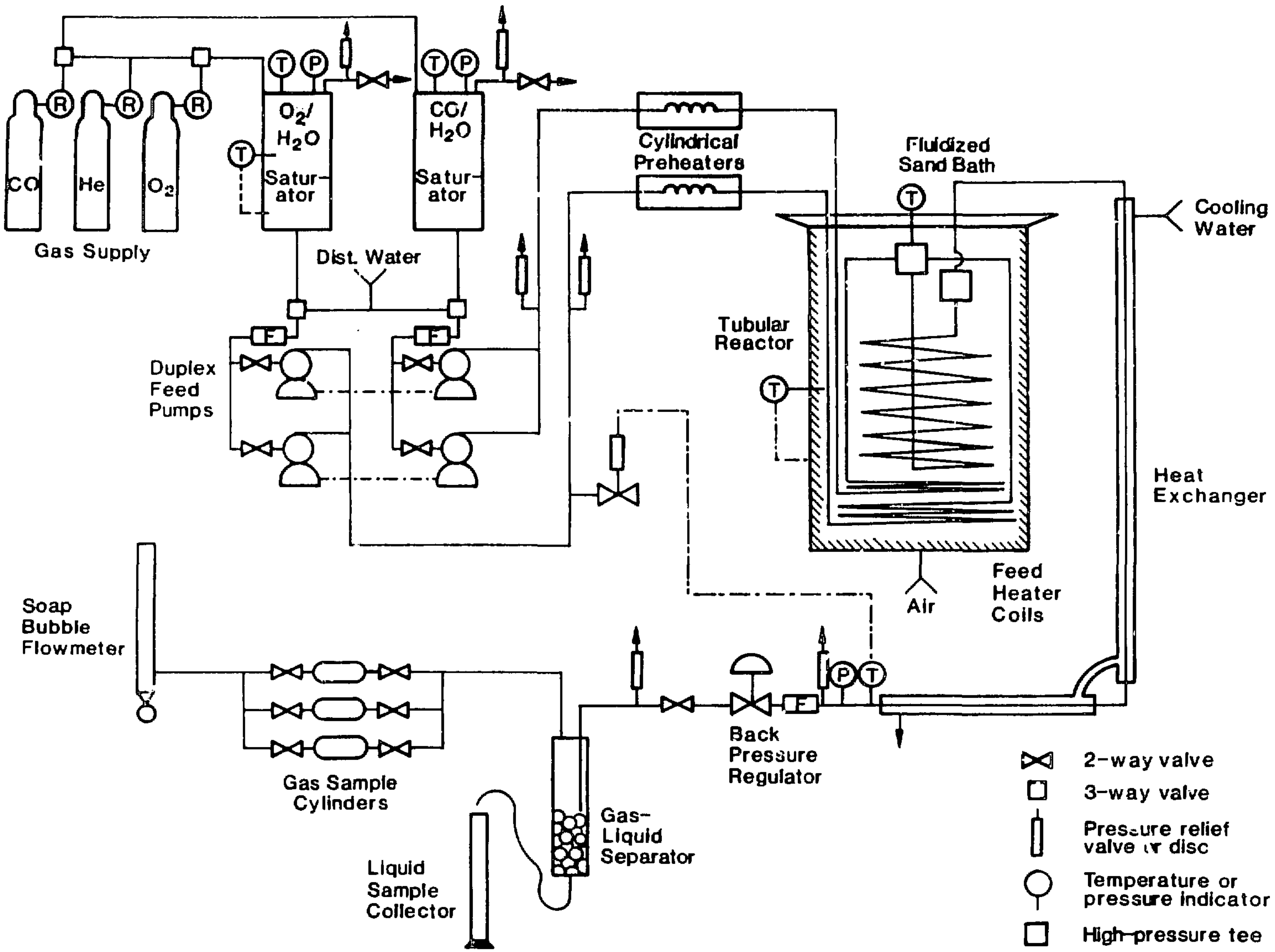

Figure 1. Schematic of plug flow reactor.

B. Batch Reactor

To complement and extend the kinetics measurements made in the plug flow reactor, a batch kinetics reactor that can be sampled at several regular intervals is under construction. The schematic of this apparatus is given in Fig. 2. Water or other input liquid is stored in liquid reactant tanks 1 and 2. It is then introduced into one-liter injectors by evacuating the injectors and feed lines. Gaseous reactants or oxidants can be added from reactant gas supplies 1 and 2. Pressure is increased at the injectors by means of a large-diameter piston driving a smaller-diameter piston. Fluids in the injectors can be pressurized to 5000 psi by applying low-pressure air to the large piston. This pressurization will cause gases at the dilute concentrations required for these experiments to dissolve in the water, forming a single phase. Solenoid-operated valves allow the pressurized fluid from one or both injectors to be introduced rapidly into the preheated pressure vessel. The amounts of fluids injected are precisely measured by the use of a magnetic sensing system that provides readout of the position of the piston in the injector. Multiple small samples can be removed and cooled rapidly from several locations in the autoclave by means of solenoid-operated high-temperature valves and subsequently routed to sample bottles.

The reaction vessel (autoclave) has a capacity of one liter and is made from A-286 steel. It is externally heated and rated to withstand 5000 psi at the maximum operating temperature of 700°C. All other components, including valves and tubing, are 300 grade stainless steel. Valves, tubing, and fittings that are in a region subjected to high temperature are rated to 60 000 psi to accommodate the material's weakening due to the temperature.

Instrumentation consists of thermocouples with continuously recording readouts to measure temperature at several locations within the reaction vessel. Pressures for both the injectors and the reaction vessel are measured with strain-gage-type pressure transducers with continuous recording capability. Analysis of samples will be by gas chromatography.

C. Chemical Kinetic Modeling

Chemical kinetic modeling is an important and extremely valuable tool in the analysis of the complex chemical systems that underlie such phenomena as combustion and air pollution. The increasing availability of fundamental rate constant data, the development of computational methods for solving large systems of "stiff" equations, and the extraordinary growth in both the power

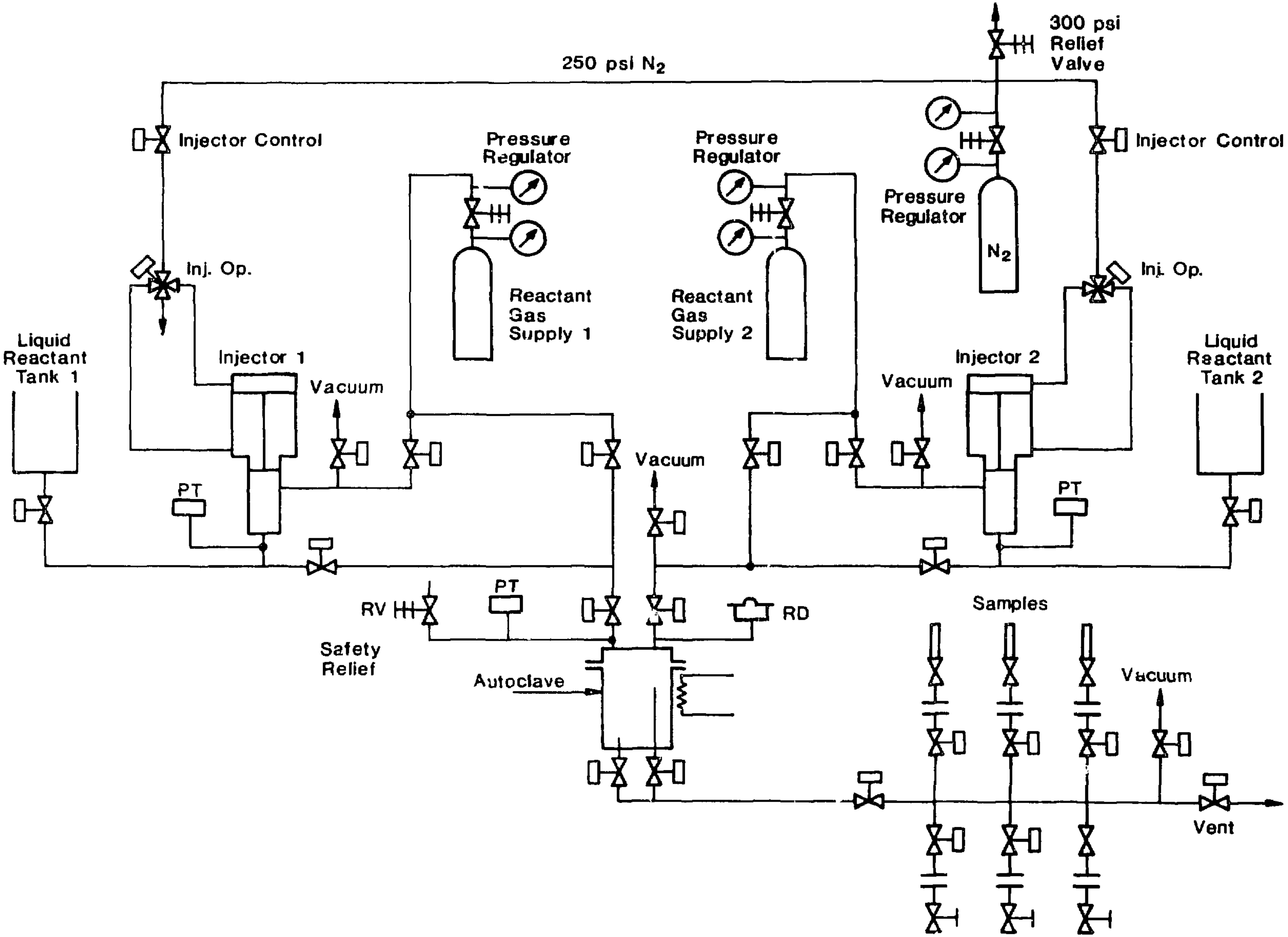

Figure 2. Schematic of batch reactor.

and availability of computing have simultaneously spurred and allowed the increased application of detailed kinetic modeling. By far the most common applications have been in the fields of combustion and atmospheric chemistry. Detailed combustion mechanisms have been developed for numerous fuels and applied to practical problems such as internal combustion engines, power plant burners, jet and rocket propulsion, and stack gas cleanup. Atmospheric applications have ranged from urban air pollution to stratospheric ozone chemistry to regional acid deposition models. All of these applications have common goals: to develop a better understanding of the complex chemistry and the critical pathways, to determine important gaps in our knowledge of fundamental rate constants, to identify the possibility of "missing" or previously unrecognized chemical reactions, and to develop validated predictive tools that can be used to explore means to control these complex processes.

Detailed kinetic modeling is accomplished by assembling a multistep mechanism of elementary reactions with the thermochemical data and fundamental rate constants that describe the elementary reactions. This information is then translated into a set of differential equations that describes the time variance of species concentrations and of temperature. With starting conditions and concentrations specified, this becomes an initial value problem and is readily solved by any one of a number of available "stiff" equation packages. "Stiff" equation arrays occur when both fast and slow reactions are included, the usual case in detailed kinetic modeling.

An elementary reaction step is one that describes a single molecular event. In combustion or atmospheric chemistry, transient free radical species are usually involved. An example is the well-known and very important reaction of hydroxyl radicals with methane:

$$CH_4 + OH \rightarrow CH_3 + H_2O.$$

This is but 1 step of more than 100 in the complex mechanism that describes the oxidation of methane. Elementary reactions can be contrasted to global reactions of the type

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O.$$

This reaction is a proper chemical description of an overall process, but it provides no insight into such questions as the role of formaldehyde (CH_2O)

or the effect of pressure in the combustion of methane. The many elementary steps of a mechanism represent the global process described by this reaction in a very detailed way, giving insight into the roles of intermediates and a basis for prediction of the behavior of the process under a variety of conditions.

If all the steps and all the rate constants in the methane oxidation mechanism were perfectly known, then the oxidation of methane could be modeled perfectly for any reactor, any initial conditions, any diluent, etc. Unfortunately, this is not the case. However, several mechanisms have been compiled that model methane oxidation very closely for limited ranges of conditions.

The use of an elementary reaction model to model a process that is known to be beyond the original scope of the model allows an iterative process to take place in which new chemical steps appropriate to the process conditions are postulated and new fundamental rate constant data are estimated or calculated in order to reproduce the experimental results observed. Eventually, the model is developed to a point of predictive capability. This type of interaction leads to new understanding and chemical insight that cannot be obtained from the use of a global model.

In order to develop both an analytical capability for deriving mechanistic data from the kinetics experiments and eventually a predictive capability for application to supercritical water oxidation plants, we are proceeding with detailed kinetic modeling of the oxidation of simple fuels in water under supercritical conditions. This is, without doubt, a regime that is beyond the scope of any previously developed combustion mechanisms. Densities are equivalent to pressures of 200 or more atmospheres and the fuel is dilute in, what is under those conditions, a reactive medium. Very few combustion mechanisms have been intentionally developed for pressures much higher than one atmosphere, although a methane combustion mechanism has been developed at Los Alamos in which the pressure dependent behavior of about a dozen reactions is described up to 250 atm. Additionally, the role of water as a reactant in bimolecular reactions and as a third body in termolecular reactions has not been determined at the temperatures and pressures common to the supercritical regime.

III. RESULTS

Preliminary results have been obtained from the plug flow reactor. Analysis of these results and earlier comparable results on the oxidation of carbon monoxide in supercritical water by means of chemical kinetics modeling is providing insight into the chemical mechanisms operative in these systems.

Results of the preliminary experiments are given in Table I. For all experiments, the pressure was held constant at 24.5 MPa, and the liquid and gas flow rates were 9.8 ml/min and 7 ml/min, respectively, at ambient pressure and temperature. The mass balances indicate the probable degree of error. The purpose of these experiments was to scope the temperature conditions necessary for oxidation of methane and ethane in supercritical water and to obtain preliminary data for modeling.

The product of methane oxidation at 650°C was carbon dioxide. No carbon monoxide was detected at a detection limit of 0.001%. The products of ethane oxidation at 500°C were methane and carbon dioxide. Again, no carbon monoxide was detected.

On the basis of these results, four model simulations were run. Simulation conditions (intended to match experimental conditions) and results are shown in Table II. For the first three simulations the Los Alamos high-pressure methane oxidation mechanism mentioned above was used with a small number of reactions described to 250 atm, but with the remainder of the mechanism unchanged. The mechanism was developed to describe the low-temperature oxidation of methane at pressures usually below 100 atm. For these three simulations, the initial mole fractions for methane and O_2 were calculated from room temperature solubility data. For the fourth simulation, four reactions describing the high-pressure limited unimolecular dissociation of H_2, methane, formaldehyde, and water were added and the initial mole fractions of methane and O_2 were increased to experimental values. With these changes a slight amount of methane oxidation was predicted by the model, but the still significant underprediction as well as the fact that carbon monoxide rather than carbon dioxide was predicted as the dominant product made it clear that the model was not adequately describing the role of supercritical water. That is not surprising since the mechanism, as with most available combustion mechanisms, was developed to describe gas-phase combustion with fuel mole fractions of 0.1 or greater, far removed from supercritical water conditions.

TABLE I

EXPERIMENTAL RESULTS FROM PLUG FLOW REACTOR
(Pressure = 24.5 MPa)

Substrate	T(C)	Residence Time (s)	O_2 Feed (10^{-6} mole/s)	Substrate Feed (10^{-6} mole/s)	Reactor Fluid Density (kg/m^3)	% Conversion	O_2 Mass Balance Closure	Substrate Mass Balance Closure
Methane	520	7.2	3.4	2.9	82.62	0	96	95
	550	6.7	2.6	2.9	76.67	0	89	93
	600	6.1	2.4	2.9	69.09	<0.05	88	90
	650	5.8	2.3	2.5	63.3	11.7	89	86
Ethane	460	6.6	3.0	2.5	101.03	0	90	84
	500	8.4	2.6	4.5	87.50	32.2	90	88

TABLE II

SIMULATION OF METHANE OXIDATION IN SUPERCRITICAL WATER

	SIMULATION IDENTIFIER			
	1	2	3	4
Temperature (°C)	550	600	650	650
(K)	823	873	923	923
Pressure (MPa)	24.5	24.5	24.4	24.4
(Atm)	241.8	241.8	240.9	240.9
Density (molecules cm^{-3})	$2.57x10^{21}$	$2.31x10^{21}$	$2.11x10^{21}$	$2.11x10^{21}$
Perfect Gas Pressure (Atm)	288.0	275.3	265.7	265.7
Initial Mole Fractions				
CH_4	$2.4x10^{-5}$	$2.4x10^{-5}$	$2.4x10^{-5}$	$1.0x10^{-3}$
O_2	$5.0x10^{-5}$	$5.0x10^{-5}$	$5.0x10^{-5}$	$1.0x10^{-3}$
H_2O	0.9999	0.9999	0.9999	0.998
Residence Time (s)	6.7	6.7	5.53	5.53CH4
CH_4 Conversion (%)	0	0	0.5	0.5

Since the oxidation of carbon monoxide is simpler and is contained as a submechanism in the oxidation of methane, the oxidation of carbon monoxide in supercritical water is a useful simplified system in which to understand the role of water in the oxidation process. Additionally, some preliminary modeling results and experimental data on carbon monoxide oxidation in supercritical water are available.[19]

In Table III are listed the experimental conditions and experimental results for carbon monoxide oxidation. These experiments were modeled by Helling and serve as the basis for our model development. The mechanism used by Helling was a simple 42-step mechanism taken from Westbrook, Dryer, and Schug[28] with very slight modification. Since this mechanism is intended for combustion in the gas phase with high fuel concentrations and relatively low pressures, the lack of agreement observed by Helling between his experimental results and the model calculations is not surprising.

In Table IV are shown model results starting with those of Helling and our reproduction of his results through various modifications to the mechanism. The mechanism is still in an active state of development and further improvements are fully expected. Helling observed that the poor agreement with

TABLE III

EXPERIMENTAL DATA: CO-OXIDATION IN SUPERCRITICAL WATER

	EXPERIMENT NUMBER 1	 2	 3
Temperature (°C)	400.5	484.0	543.0
(K)	673.6	757.1	816.1
[BPressure (MPa)	24.51	24.56	24.
(Atm)	241.9	242.4	242.9
Density (molecules cm^{-3})	5.22×10^{21}	3.10×10^{21}	2.62×10^{21}
Perfect Gas Pressure (Atm)	479.3	319.3	291.6
Initial Mole Fractions			
CO	2.97×10^{-4}	4.91×10^{-4}	2.77×10^{-4}
O_2	4.58×10^{-4}	4.17×10^{-4}	6.11×1^{-4}
H_2O	0.9992	0.9991	0.9991
Residence Time (s)	13.18	7.66	6.57
CO Conversion (%)	11.6	36.5	81.3
Product Ratio $[H_2]/[CO_2]$	0.73	0.32	0.22

experimental H_2 ratios was a deficiency of the model. This is also seen in our reproduction of his calculation, which is designated A-1. Model A-2 uses the same mechanism but updates the rate constants to more recently reviewed values and describes pressure falloff for those reactions for which pressure falloff had been calculated for the above-mentioned methane mechanism. The poor agreement between model and experiment at this point was expected.

In model B-1 the mechanism was expanded from 42 to 66 reactions. The additional chemistry primarily describes the formation and reactions of HCO and formaldehyde. It is evident that this additional chemistry has little effect, apparently because no reactions have been added or modified to account for the role of water as a reactant.

In model B-2 the rate constant for the reaction

$$H + O_2 + M \rightarrow HO_2 + M$$

is set to a high pressure limit and the six least important reactions are dropped from the mechanism. The effect of reducing this rate constant is to increase the steady state H atom concentration and consequently the H_2 product by a small amount. Of note at this point is that H_2 is still far lower than observed experimentally and that the temperature dependence of the model is

TABLE IV

CO-OXIDATION AND PRODUCTS: EXPERIMENT AND MODEL

	EXPERIMENT NUMBER					
	1		2		3	1
Identifier	%CO Oxidized	$[H_2]/[CO_2$	% CO Oxidized	$[H_2]/[CO_2]$	% CO Oxidized	$[H_2]/[CO_2]$
Experiment	11.6	0.73	36.5	0.32	81.3	0.22
Model (Helling)	3.98		87.7		99.8	
Model A-1	3.88	0.0016	70.5	0.0028	99.7	2.4x10-5
Model A-2	0		50.2	7.0x10-4	99.97	5.3x10-7
Model B-1	0		50.2	7.0x10-4	99.97	5.3x10-7
Model B-2	0		50.2	0.002	99.96	1.2x10-8
Model B-3	0		2.59	0.0027	54.1	0.0025
Model C-1	0		2.70	0.055	54.1	0.033

much steeper than measured in the experiment. In model B-3, the rate of the reaction

$$HO_2 + M \rightarrow H + O_2 + M$$

was increased by a factor of 2 to reflect the efficiency of water as a collision partner (in comparison to methane for which the rate constant had been set), and the rate constant for the reaction

$$H_2O + HO_2 \rightarrow H_2O_2 + OH$$

was reduced by a factor of 16. This was in keeping with the rate of the reverse reaction, which was reduced in going from model A-1 to model A-2. The effect of the first change should be to increase H atom and H_2 concentration. The effect of the second change should be to slow the oxidation; this reaction, followed by the very rapid collisional dissociation of H_2O_2 to yield 2OH, converts one HO_2 radical into three OH radicals. The hydroxyl radical drives the oxidation of carbon monoxide as well as the oxidation of H_2. The B-3 results show slowed oxidation and increased H_2 yield, a closer approach to the experimental results than the earlier simulations.

In order to begin to account for the role of supercritical water in the oxidation, it is reasonable to postulate the reaction

$$H + H_2O + H_2O \rightarrow H_2 + OH + H_2O.$$

For the rate constant we assume a reasonable three-body collision coefficient and an activation energy just equal to the enthalpy of the reaction. This assumption lowers the activation energy by 3.4 Kcal compared to the bimolecular reaction, suggesting a somewhat more facile reaction due to energy transfer from a third body. However, the extremely high density of water, which is squared in the rate equation for this reaction, is actually the more dominant effect in increasing the effectiveness of this reaction. Model C-1 shows the results with this reaction added to the mechanism. There was little effect on the oxidation rate, but the H_2 production increased more than an order of magnitude.

This work remains in progress. Results so far are very encouraging. Changes to the basic gas-phase mechanism have been relatively minor so far, but the carbon monoxide oxidation model has rapidly progressed toward matching the experimental results. Further modifications, carefully considered, will be made to better model the chemistry of water itself in these systems. Once the carbon monoxide oxidation mechanism is satisfactorily developed, it will be used as a submechanism in the further development of the methane mechanism.

The carbon monoxide oxidation mechanism, as it currently stands, is given in Table V. Rate constants are given in the form $AT^n\exp(-E_a/T)$ and A is given in molecular units. The reactant M represents a collision partner and the density of M is equivalent to the density of the system.

IV. SUMMARY AND RECOMMENDATIONS

Although the unusual properties of supercritical fluids were first reported more than a hundred years ago, industrial applications of supercritical fluids have been investigated only recently. Over the past decade, there has been considerable interest in both the fundamentals and applications of supercritical fluids as solvents, but chemical reactions in supercritical fluids have been investigated very little.

Interest in development of supercritical water oxidation for destruction of hazardous wastes results from several factors:

High destruction efficiencies can be achieved. A supercritical fluid provides a single-phase reaction medium, without significant limitation by phase transport processes.

Overall reaction rates can be very rapid, despite the relatively mild temperatures of the oxidation. Rapid reaction implies that the residence time in the reaction vessel can be small and yet provide a significant throughput. This is a key factor related to both economics and process efficiency. It also suggests that the process is inherently scalable.

The mild temperatures prevent NO_x from being formed. All effluents can be completely controlled, and most are relatively harmless. The bulk and molecular transport properties of supercritical fluids suggest that oxidation in supercritical water may be a superior technique for decontamination of hazardous organics associated with solids, such as machine parts or soils.

The obvious niche for application of this technology is in the treatment of contaminated water streams, from very dilute to very concentrated.

TABLE V

CO-OXIDATION MECHANISM USED FOR SIMULATION C-1

THE REACTIONS				A	n	Ea(K)
1	M + 2H	=	H2	4.500E-29	-1.30	0.000E+00
2	H2 + M	=	2H	5.000E-05	-1.10	5.253E+04
3	0 + H + M	=	0H	1.300E-29	-1.00	0.000E+00
4	0 + H2	=	H + 0H	1.800E-20	2.80	2.980E+03
5	20 + M	=	02	6.200E-34	0.00	-9.000E+02
6	0H + H	=	0 + H2	8.100E-21	2.80	1.950E+03
7	0H + H + M	=	H20	1.200E-25	-2.00	0.000E+00
8	0H + H2	=	H20 + H	1.060E-17	2.00	1.490E+03
9	0H + 0	=	02 + H	7.500E-10	-0.50	3.000E+01
10	20H	=	H20 + 0	3.500E-16	1.40	-2.000E+02
11	20H	=	H02 + H	2.000E-11	0.00	2.018E+04
12	20H	=	H202	1.270E-03	-2.77	0.000E+00
13	02 + M	=	20	2.000E-10	0.00	5.425E+04
14	02 + H	=	0H + 0	2.800E-07	-0.90	8.750E+03
15	02 + H	=	H02	7.500E-11	0.00	0.000E+00
16	02 + H2	=	H + H02	2.400E-10	0.00	2.850E+04
17	02 + 0H	=	0 + H02	3.700E-11	0.00	2.650E+04
18	H20 + M	=	H + 0H	3.600E-08	0.00	5.290E+04
19	H20 + H	=	H2 + 0H	1.000E-16	1.90	9.265E+03
20	H20 + 0	=	20H	7.600E-15	1.30	8.605E+03
21	H20 + 02	=	H02 + 0H	1.050E-09	0.00	3.717E+04
22	H20 + H02	=	H202 + 0H	3.000E-12	0.00	1.650E+04
23	H02 + M	=	H + 02	1.200E-04	-1.18	2.436E+04
24	H02 + H	=	H2 + 02	1.100E-10	0.00	1.070E+03
25	H02 + H	=	20H	2.800E-10	0.00	4.400E+02
26	H02 + H2	=	H202 + H	5.000E-11	0.00	1.310E+02
27	H02 + 0	=	02 + 0H	2.900E-11	0.00	-2.000E+02
28	H02 + 0H	=	H20 + 02	2.400E-08	-1.00	0.000E+00
29	2H02	=	H202 + 02	4.500E-14	0.00	-1.200E+03
30	H202	=	20H	7.830E+13	0.00	2.348E+04
31	H202 + H	=	H02 + H2	8.000E-11	0.00	4.000E+03
32	H202 + H	=	H20 + 0H	4.000E-11	0.00	2.000E+03

TABLE V (continued)

THE REACTIONS				A	n	Ea(K)
33	$H_2O_2 + O$	=	$OH + HO_2$	1.600E-17	2.00	2.000E+03
34	$H_2O_2 + OH$	=	$H_2O + HO_2$	2.900E-12	0.00	1.600E+02
35	$H_2O_2 + O_2$	=	$2HO_2$	9.000E-11	0.00	2.000E+0
36	$CO + H + M$	=	HCO	1.400E-36	1.00	7.800E+02
37	$CO + H_2$	=	$HCO + H$	2.200E-09	0.00	4.529E+04
38	$CO + O = M$	=	CO_2	7.300E-33	0.00	2.180E+03
39	$CO + OH$	=	$CO_2 + H$	3.400E-16	1.00	0.000E+00
40	$CO + H_2O$	=	$HCO + OH$	4.700E-09	0.00	5.292E+04
41	$CO + O_2$	=	$CO_2 + O$	4.200E-12	0.00	2.400E+04
42	$CO + HO_2$	=	$CO_2 + OH$	2.500E-10	0.00	1.190E+04
43	$CO + HO_2$	=	$HCO + O_2$	1.500E-11	0.00	1.977E+04
44	$CO_2 + H$	=	$CO + OH$	2.500E-10	0.00	1.330E+04
45	$HCO + M$	=	$H + CO$	8.900E-04	-1.74	1.024E+04
46	$HCO + H$	=	$CO + H_2$	2.000E-10	0.00	0.000E+00
47	$HCO + H_2$	=	$CH_2O + H$	3.000E-18	2.00	8.970E+03
48	$HCO + O$	=	$CO + OH$	5.000E-11	0.00	0.000E+00
49	$HCO + O$	=	$CO_2 + H$	5.000E-11	0.00	0.000E+00
50	$HCO + OH$	=	$CO + H_2O$	5.000E-11	0.00	0.000E+00
51	$HCO + H_2O$	=	$CH_2O + OH$	3.900E-16	1.35	1.315E+04
52	$HCO + O_2$	=	$CO + HO_2$	8.500E-11	0.00	8.500E+02
53	$HCO + HO_2$	=	$OH + H + CO_2$	5.000E-11	0.00	0.000E+00
54	$HCO + H_2O_2$	=	$CH_2O + HO_2$	1.700E-13	0.00	3.486E+03
55	$2HCO$	=	$CH_2O + CO$	3.000E-11	0.00	0.000E+00
56	$CH_2O + H$	=	$HCO + H_2$	3.640E-16	1.77	1.510E+03
57	$CH_2O + O$	=	$HCO + OH$	3.100E-11	0.00	1.550E+03
58	$CH_2O + OH$	=	$HCO + H_2O$	5.700E-15	1.18	-2.250E+02
59	$CH_2O + O_2$	=	$HCO + HO_2$	3.400E-11	0.00	1.960E+04
60	$CH_2O + HO_2$	=	$HCO + H_2O_2$	3.300E-12	0.00	5.870E+03
61	$H_2O + H + H_2O$	=	$H_2 + OH + H_2O$	2.000E-32	0.00	7.550E+03

Supercritical water oxidation may be superior to conventional incineration for many applications with liquid wastes, including mixed wastes.

The most important near-term issues relate to the kinetics and mechanism of oxidation of organics in supercritical water. The kinetics determines the residence time and conditions necessary for oxidation, and the mechanism gives information necessary for application to a wide range of wastes.

Meaningful kinetics experiments to supply a basis for development of supercritical water oxidation as a technology for destruction of hazardous chemical wastes must provide information on mechanisms and rates necessary to design and size equipment. They must also address issues related to operability and reliability. In particular, a single phase must be maintained during measurements and the rapid changes in thermodynamic properties near the critical point must be avoided. The issues relevant to the understanding of the technology and the development of a viable process include appropriate choice of model compounds, separation of mass transfer effects, pyrolysis, and other non-oxidation reactions taking place, and how these factors affect residence time, the critical parameter in plant design.

In this task, two types of kinetics apparatus, a plug-flow reactor and a batch reactor, are being applied to the determination of kinetic parameters. In addition, a computational chemical kinetic model is being developed to simulate the process and to analyze and direct the kinetics experiments. Because the phenomenology is complex, the initial model compound for study is methane. Early experiments and modeling results show promise for representing the mechanism of methane oxidation in supercritical water on the basis of a gas-phase kinetic model modified for the high pressures of supercritical water systems and for the additional participation of water in the reactions.

In addition to this portion of the task, a demonstration at pilot scale is planned early in the program. This demonstration would provide additional data with which the bench-scale measurements and the kinetic modeling could be compared.

Our recommendations for continuing work are:

(1) Utilize the model compound to develop an understanding of basic kinetics and mechanisms.
    a. Continue kinetics measurements on methane oxidation above 650°C.
    b. Improve the carbon monoxide oxidation module of the kinetics model and incorporate it into the methane oxidation model.

    c. Improve other parts of the methane model after the carbon monoxide module has been incorporated into it.

(2) Extend the reaction kinetics experimental and computational studies to include other organic compounds found in hazardous waste.
    a. Aliphatic hydrocarbons (gasoline, kerosene, oils).
    b. Halogenated hydrocarbons (PCBs, solvents).
    c. Other hazardous chemicals (pesticides, organometallic compounds).
    d. Mixtures of several compounds (synergistic and interference effects).
    e. Organics associated with solids (soils, machine parts, spill absorbers).
    f. Mixed radioactive and organic wastes.

(3) Couple the kinetics and mechanism studies with a series of demonstration experiments on actual waste streams, designed to address increasingly difficult problems.

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