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FINAL REPORT

SUPERCRITICAL WATER OXIDATION  
OF PRODUCTS OF HUMAN METABOLISM

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## 1.0 INTRODUCTION

Future long-term manned spaceflights or space stations will require regenerative methods of life support. Previous investigations at M.I.T. and MODAR, Inc. indicated that urine and feces can be oxidized in supercritical water with high efficiencies (Price, 1982; Timberlake et al., 1982). Supercritical conditions exist for water at temperatures above 374°C (705°F) and pressures above 22.1 MPa (3200 psia). Supercritical water properties are much different from those of room temperature water and depend strongly on the density of the water. The solvation properties of supercritical water at temperatures between 400 and 700°C and near critical pressures (22-30 MPa or 3190-4350 psia) are also much different than those of normal water. Under these conditions, the water behaves like a dense gas with a high solubility of organics (Connolly, 1966), complete miscibility in all proportions with oxygen (Pray et al., 1952), high diffusivities (Franck, 1976; Flarsheim et al., 1985), low viscosity (Todheide, 1972), and low solubility and dissociation of inorganics, particularly ionic salts (Marshall, 1976; Martynova, 1976). The changes in solubility are due in part to the reduction in hydrogen bonding, since hydrogen bonding is a short range force, and has a diminished influence as the density of water decreases in the critical region. The solvation properties make supercritical water an excellent medium for oxidation of wastes, since organics and oxygen can be intimately mixed in a

single, homogeneous phase, and inorganics can be readily removed from solutions by precipitation.

The oxidation of other organics in supercritical water was demonstrated by Modell et al. (1982), Cunningham (1986), and Wightman (1981). Modell et al. (1982) oxidized several toxic chlorinated hydrocarbons in supercritical water, destroying at least 99.99% of the organic chlorides and 99.97% of the TOC (total organic carbon). The maximum destruction efficiencies were limited by the resolution of the analytical techniques. Cunningham et al. (1986) demonstrated the applicability of this process to the complete destruction of biopharmaceutical wastes. Oxidative reaction kinetics in supercritical water were investigated by Wightman (1981) for phenol, a common component in industrial waste, and acetic acid, a characteristic by-product of conventional wet oxidation. A detailed review of the relevant literature is available in a thesis supported by this contract by Helling (1986) and in a previous progress report for this contract (Huff et al., 1984).

Pyrolysis reactions in supercritical water have also been studied. The unique solvent properties of the fluid and the possibility of promoting hydrolysis reactions have led to the use of supercritical water in the pyrolysis of wood, coal, and model compounds related to these. The initial work by Amin, Reid and Modell (1975), Woerner (1976) and Whitlock (1978) demonstrated the profound influence of supercritical water on pyrolysis products: no char formed from pyrolysis of glucose in supercritical water and gasification increased over

that possible in subcritical water. Recent work has confirmed the lack of char formation, and provided evidence of carbonium ion, free radical, and hydrolysis reactions from the products pyrolysis of glycerol (Antal et al., 1985), guaiacol (Lawson and Klein, 1985), and benzylphenylamine (Abraham and Klein, 1985). The fundamental pyrolysis investigations have highlighted specific mechanisms for the influence of supercritical water on chemical reactions, which could aid the interpretation of oxidation data.

## 2.0 SCOPE

Although the efficient destruction of organic material has been demonstrated in the supercritical water oxidation process, the reaction kinetics and mechanisms are unknown. The work described here was divided into three primary parts:

- 1) Study experimentally the kinetics and mechanisms of carbon monoxide and ammonia oxidation in and reaction with supercritical water;
- 2) Perform experimental oxidations of urine and feces in a microprocessor controlled system; and
- 3) Design a minaturized supercritical water oxidation process for space applications, including preliminary mass and energy balances, and power, space and weight requirements.

Carbon monoxide and ammonia were selected as they are the simplest reactive carbon and nitrogen compounds and have been well-studied

in the uncatalyzed and catalyzed gas-phase reactions. They also oxidize more slowly than other materials, and limit the overall conversion of organic nitrogen and organic carbon from complex molecules to molecular nitrogen and carbon dioxide. Part 1 was conducted at M.I.T.; Parts 2 and 3 were conducted at MODAR, Inc.

### 3.0 ACCOMPLISHMENTS

#### 3.1 Oxidation of Urea

The work on the oxidation of urea in supercritical water, by itself and with other organics, for the development of the supercritical water oxidation process for CELSS was conducted at MODAR, and is described in more detail in the progress report for October, 1983, to March 1984, for this contract, hereafter referred to as Huff et al. (1984). Mixtures of 4.4-4.8% by weight urea in water were oxidized with 36-67% excess oxygen, at a normal liquid flow of about 21 cm<sup>3</sup>/min, and at an average external wall temperature between 640 and 710°C. The conversion of urea to molecular nitrogen increased with temperature from 16% at 640°C to 60% at 710°C. The true fluid temperature in the reactor was not known, but was between the reactor inlet temperature near 400°C and a maximum about 50°C above the average external wall temperature.

Dilute solutions of urea (about 1% by weight) were oxidized to approximate isothermal reaction conditions at two residence times. The conversions for both times were about 2% at 600°C and 30% at

650°C. The insensitivity of conversion to residence time could reflect an approach to an equilibrium conversion to molecular nitrogen, or it could be a result of the different (and unquantified) mixing, flow regime and temperature profiles at the two residence times.

The activation energy for oxidation of ammonia from urea, calculated from conversion data at different temperatures, was between 68 and 980 kJ/mole (16 and 234 kcal/mole). Different activation energies were calculated for different sub-groups of the experimental data. The variation by an order of magnitude in the calculated activation energy is probably due to the non-isothermal temperature profile in the reactor and unknown variation in flow regime.

Ethanol in a three-to-one weight ratio to urea was added to the feed in oxidation experiments for comparison with experiments with the same amount of urea but no ethanol (Huff et al., 1984). The destruction of ammonia was in all cases greater with ethanol than without, being between 76 and 99.9% for estimated adiabatic reaction temperatures between 582 and 657°C; the conversion to molecular nitrogen ranged from 18 to 67%. The reaction was again insensitive to residence time, as was the pure urea oxidation data. The increased conversion at lower temperatures possible with the ethanol addition may be due to local hot regions or increased concentrations of free radicals from the oxidation of ethanol. Local hot regions could arise due to poor mixing of the various feed streams or uneven heating from the reactor-wall heaters. The destruction of ethanol was in all cases greater than 99.9%, indicating it is more reactive than ammonia.

## 3.2 Process Design

The preliminary process design for this applicataion was conducted by T.B. Thomasson of MODAR, Inc., and is described fully in Huff et al. (1984).

## 3.3 Oxidation Kinetics of Carbon Monoxide and Ammonia

This portion of the work was conducted at M.I.T. It is described in detail in the thesis by Helling (1986). The remainder of this report summarizes the conduct of and results from this work. The results will also be published in the open literature (Helling and Tester, 1987a; 1987b).

### 3.3.1 Apparatus and Procedures

A tubular reactor system was designed to produce well-characterized data for the quantitative determination of reaction kinetics in supercritical water. A schematic of the system for oxidation of carbon monoxide is shown in Figure 1. Analysis of kinetics was simplified by the reactor being both isothermal and in radially well-mixed, one-dimensional plug flow. The reactor was 4.24 m of 0.635-cm O.D. x 0.211-cm I.D. (1/4 x 0.083 in.) Inconel 625 tubing. The alloy was selected for its high strength and corrosion resistance, and the reactor was immersed in a fluidized-bed sand bath for temperature control.

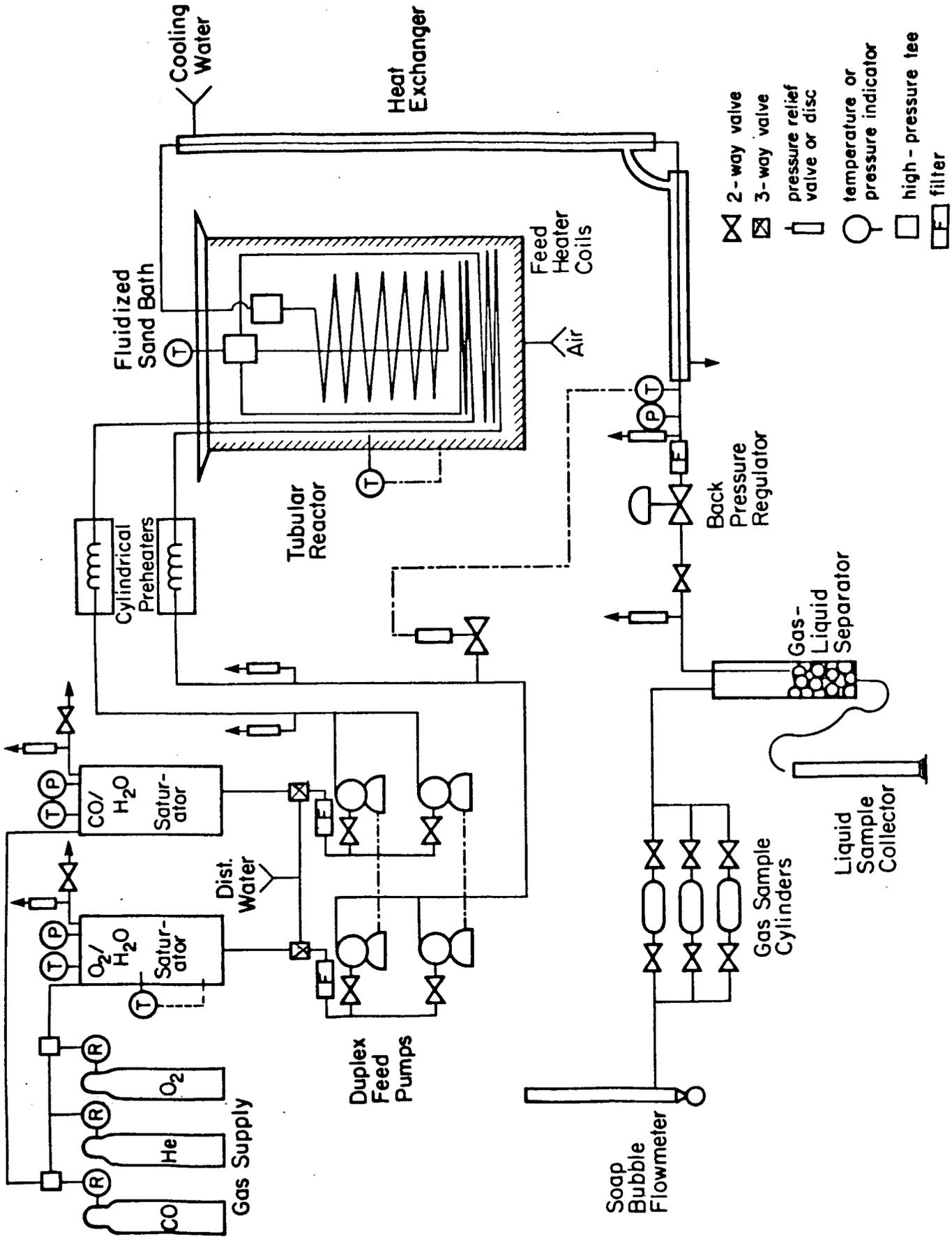


Figure 1. Schematic of Experimental Apparatus

Dilute inlet concentrations of combustibles (ammonia, carbon monoxide and ethanol) and oxidant (oxygen) were used in this system. Dilute concentrations were prepared by dissolving reagents in room temperature water in one-liter, agitated tanks. The two feed solutions were heated separately to reaction conditions in less than 10 s in a narrow (0.108 cm-I.D.) Hastalloy C276 tubing, and mixed at the reactor inlet. This avoided the operating difficulty of controlling the composition of the feed by mixing a large flow of water with a low flow of compressed oxygen or combustible. The reactor effluent was cooled quickly (at least 200°C in the first 0.5s) in a heat exchanger, depressurized, and separated into measured gas and liquid flows. The composition of the gas phase was determined by gas chromatography. The system for oxidation of ammonia or water-soluble hydrocarbons used the carbon monoxide saturator as a simple tank with a low pressure, inert atmosphere.

### 3.3.2 Experimental Results

Over ninety experiments were performed with the apparatus described above. Fifty-nine of the experiments were either at conditions to oxidize carbon monoxide in supercritical water containing dissolved oxygen (38) or to react the carbon monoxide with the supercritical water to produce carbon dioxide and hydrogen by the water-gas shift reaction (21). These experiments produced consistent and reproducible results and represent the main thrust of the experimental work in this thesis.

Reactor conditions for these experiments ranged in temperature from 400 to 540°C at nominally constant pressure of 24.6 MPa (3550 psig) and mass flowrate ( $1.67 \times 10^{-4}$  kg/s or 10 g/min). The typical Reynolds numbers in the reactor were  $3100 \pm 400$ , and residence times between 6 and 14 s. Inlet concentrations ranged between  $0.75$ - $3.9 \times 10^{-3}$  mole/L for carbon monoxide,  $0.59$ - $4.2 \times 10^{-3}$  mole/L for oxygen in the oxidation experiments, and the mole fraction of water was greater than 0.999. The oxygen was usually in excess in the oxidation experiments although four experiments were conducted at or below stoichiometric oxygen levels. The variation in inlet concentrations arises both from changing the mole fraction of the components in the feed and also by the change in fluid density with temperature, from  $160. \text{ kg/m}^3$  at 400°C to  $78. \text{ kg/m}^3$  at 540°C. The remaining experiments were conducted to investigate the oxidation of ammonia, ethanol, hydrogen and the effect of hydrogen and reactor surface area on the carbon monoxide reactions.

The measured quantities in all experiments included the system temperatures and pressures, gas and liquid flowrates, and gas-phase composition. With these data and an appropriate set of assumptions, the reactor residence time, concentrations in the inlet and outlet, conversion, apparent first-order rate constant, average reaction rate, and the solubilities in the saturators were all calculated. The key assumptions were that equilibrium existed between carbon dioxide in the gas phase and dissolved carbon dioxide in the water effluent, the reactor inlet concentrations were found from outlet concentrations

by a mass balance, and the fluid properties were those of water.

The form of the global expression for the reaction of carbon monoxide was assumed as:

$$-\frac{d[\text{CO}]}{dt} = A \exp(-E_a/RT) [\text{CO}]^a [\text{O}_2]^b [\text{H}_2\text{O}]^c \quad (1)$$

where:

- A = pre-exponential factor (L/mole)<sup>a+b+c-1</sup> s<sup>-1</sup>
- E<sub>a</sub> = activation energy, kJ/mole
- R = universal gas constant, 8.31 J/mole-K
- T = absolute temperature, K
- a, b, c = reaction orders

The orders of the reaction were sometimes fixed to specific values (such as zero or one) before regression of the other parameters.

The temperature dependence of a reaction can be simply demonstrated by graphing the natural log of the apparent first-order rate constant k\* in s<sup>-1</sup>, which is obtained from the data by setting a=1 and b=c=0 in Eqn.(1), as a function of the reciprocal absolute temperature in an Arrhenius plot. The slope yields the activation energy and the intercept yields the pre-exponential constant.

The Arrhenius plot for the thirty-eight oxidation experiments is shown in Figure 2, and is certainly linear over this temperature range (400-541°C), with an apparent activation energy of 112±5 kJ/mole (26.7 kcal/mole) and pre-exponential factor of 10<sup>6.5±3.5</sup> s<sup>-1</sup>. The data are not very scattered despite the 5-8 fold range in the carbon monoxide and oxygen concentrations, so the assumed reaction orders may be close to being correct.

Various techniques were tried to regress all the constants in

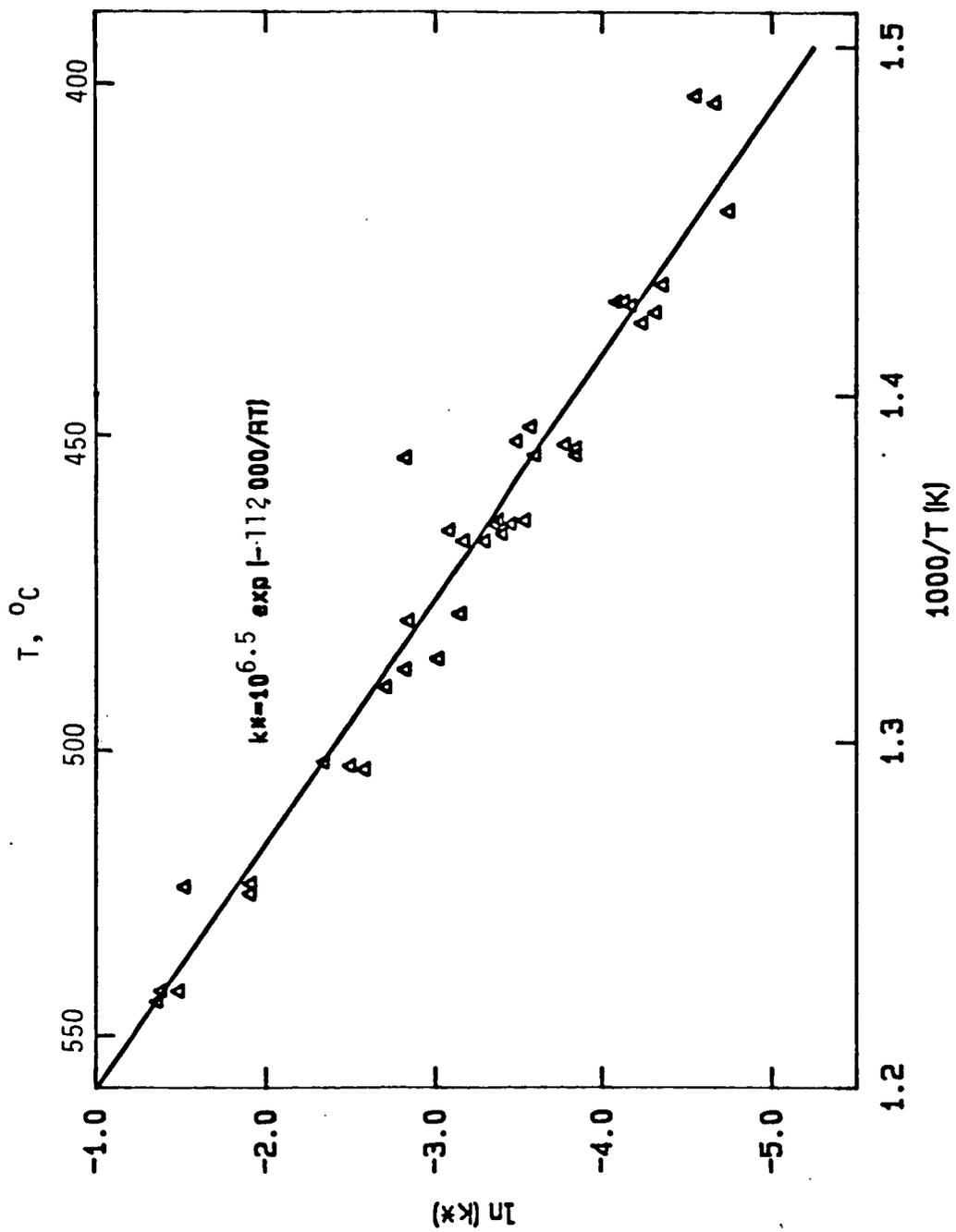


Figure 2. Arrhenius Plot for First-Order Oxidation of Carbon Monoxide in Supercritical Water at 24.5 MPa

Eqn.(1) from the experimental data. An attempt to linearize the equation by estimating initial rates for low conversion experiments was limited by the lack of data at conversions less than 10%, so the parameters were determined by a Gauss-Newton non-linear optimization technique. The "best-fit" equation is:

$$-\frac{d[\text{CO}]}{dt} = 10^{7.25 \pm 0.53} \exp(-120. \pm 7.7/RT) [\text{CO}]^{1.018 \pm 0.09} [\text{O}_2]^{0.03 \pm 0.04} \quad (2)$$

where the stated uncertainties are the 95% confidence limits, the activation energy is in kJ, and the concentrations are in mole/L.

The model fits the data to within a conversion of  $\pm 6\%$ . This equation is truly a global expression, and does not attempt to separate contributions to the production of carbon monoxide of the water-gas shift pathway, or:



from a direct oxidation pathway, represented as:



The lack of a statistically significant dependence of the conversion on the oxygen concentration in Eqn.(2) is surprising. The oxygen concentration was varied by a factor of eight in these experiments ( $0.59-4.8 \times 10^{-3}$  mole/L), and from near stoichiometric (98%) to excess (515% of stoichiometric), with no consistent trends by visual observation or statistical analysis of the data. The oxidation of carbon monoxide in supercritical water is independent of the specific oxygen level in the range of conditions studied here, but the presence of oxygen can still have an effect on the pathway of the reaction. Setting the oxygen term to zero did not change the other parameters

significantly. Including a term for the concentration of water did not improve the fit to the data enough to warrant the additional term, and since the water concentration was not changed except by changing the temperature, its effect could not be confidently separated from that of temperature. Regressed parameters for different assumed forms of the rate law are listed in Table 1.

The two major pathways to produce carbon dioxide can be distinguished because hydrogen is only produced by the water-gas shift. Thus the ratio of hydrogen produced to carbon dioxide produced is approximately the fraction of the carbon dioxide that was produced by the water-gas shift reaction. The ratio would be the exact fraction if none of the hydrogen produced reacted with oxygen to form water. The ratio of hydrogen produced to carbon dioxide produced is plotted in Figure 3 for the 38 oxidation experiments, and decreases from 75% to 20% with increasing temperature. The water-gas shift reaction, by this measure, is clearly an important part of the total carbon dioxide production rate. The decrease in this ratio shows that the water-gas shift reaction apparently proceeds by a less activated, parallel reaction to the direct oxidation pathway.

Twenty-one experiments were conducted with no oxygen intentionally added to the reactor to determine kinetic parameters for the global water-gas shift reaction. Air leakage during gas sampling and analysis made it impossible to rule out the presence of some oxygen in the reactor (from dissolved air in the water, or gas pockets in the apparatus), although at worst, the level of oxygen was still two orders

Table 1. Summary of Empirical Rate Expressions

<u>Model Type</u>	<u>Parameters</u> (a,b)					<u>Objective</u> (c)
	k ((L/mole) <sup>(a+b+c-1)</sup> s <sup>-1</sup> )	E <sub>a</sub> (J/mole)	orders a	orders b	orders c	
	log <sub>10</sub> A					
Water-Gas Shift	1.60	62,900	0.5677	-	-	0.0419
	± 1.70	± 4100	± 0.051			
	5.24	80,930	0.5863	-	1	0.0414
	± 1.57	± 4749	± 0.026			
	5.09	79,750	0.5621	-	1.001	0.0413
	± 1.65	± 4925	± 0.066		± 0.041	
Global Oxidation of Carbon Monoxide	7.251	120,300	1.014	0.03	-	0.0374
	± 0.260	± 3816	± 0.043	± 0.02		
	7.121	122,300	1.011	-	0.25	0.0364
	± 0.247	± 3590	± 0.016			
	7.213	127,600	1.001	-	0.596	0.0362
	± 0.249	± 3632	± 0.042		± 0.0261	
Direct Oxidation of Carbon Monoxide	17.38	237,600	1.874	0.03	0.0338	
	± 0.803	± 11,910	± 0.011	± 0.03		
	18.08	251,800	2.066	-	0.25	0.0327
	± 0.816	± 12,070	± 0.043			
Dryer and Glassman(1973)	12.35	167,500	1	0.5	0.25	
	± 0.40	± 5000				
Hydrogen Oxidation	10.9	192,000	1	-	-	
	± 6.9	± 122,000				
Ethanol Oxidation	21.81	340,000	1	-	-	
	± 6.0	± 50,000				

a) Parameters in: rate = A exp (-E<sub>a</sub>/RT) [CO, EtOH or H<sub>2</sub>]<sup>a</sup> [O<sub>2</sub>]<sup>b</sup> [H<sub>2</sub>O]<sup>c</sup>

b) Uncertainties are standard deviations; if no uncertainty is listed, the stated value was assumed

c) Objective is the mean deviation  $\left(\frac{1}{N} \sum (X_{obs} - X_{calc})^2\right)^{1/2}$  with this model

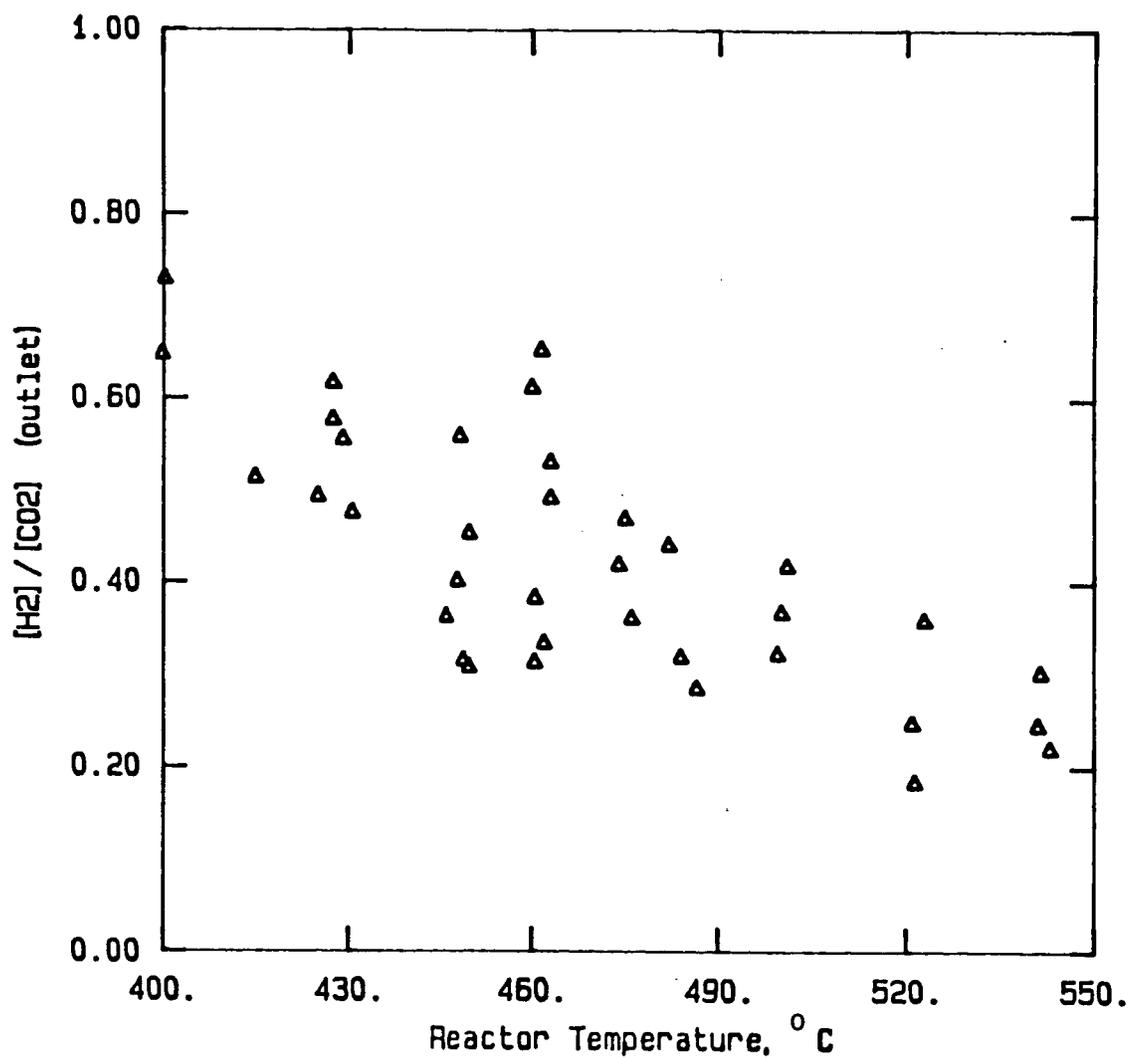


Figure 3. Fraction of Carbon Dioxide Produced by the Water-Gas Shift During Oxidation of Carbon Monoxide in Supercritical Water.

of magnitude less than in the oxidation experiments.

The first step in the analysis of the data was to generate an Arrhenius plot of the natural log of the apparent first-order rate constant versus the reciprocal temperature, as was done with the oxidation experiments. This plot is shown in Figure 4, where the broken line shows the best-fit line for the oxidation experiments. In contrast to the Arrhenius plot for the global oxidation experiments (Figure 2), the water-gas shift data show more scatter and the best-fit line has a lower slope, indicating a lower activation energy.

A non-linear dependence of the rate on the concentration of carbon monoxide was discovered by performing a non-linear regression of the data, as was done with the oxidation experiments. The resulting best expression is:

$$-\frac{d[\text{CO}]}{dt} = 10^{1.60 \pm 3.57} \exp(-62.9 \pm 8.6 / RT) [\text{CO}]^{0.568 \pm 0.107} \quad (5)$$

The key differences between the two global rate expressions (Eqns.(2) and (5)) is that the water-gas shift rate has about half the activation energy of the oxidation, a much lower pre-exponential term, and also an order with respect to carbon monoxide 44% lower than the oxidation experiments. The two rate expressions and data sets overlap at low temperatures (400-450°C), but they diverge significantly at increasing temperatures, so that above 500°C the difference in the two pathways is clear. Neither expression has a dependence on oxygen concentration, although the presence of oxygen seems to allow the more highly activated reaction path to be followed.

The experimental results for the oxidation of carbon monoxide and

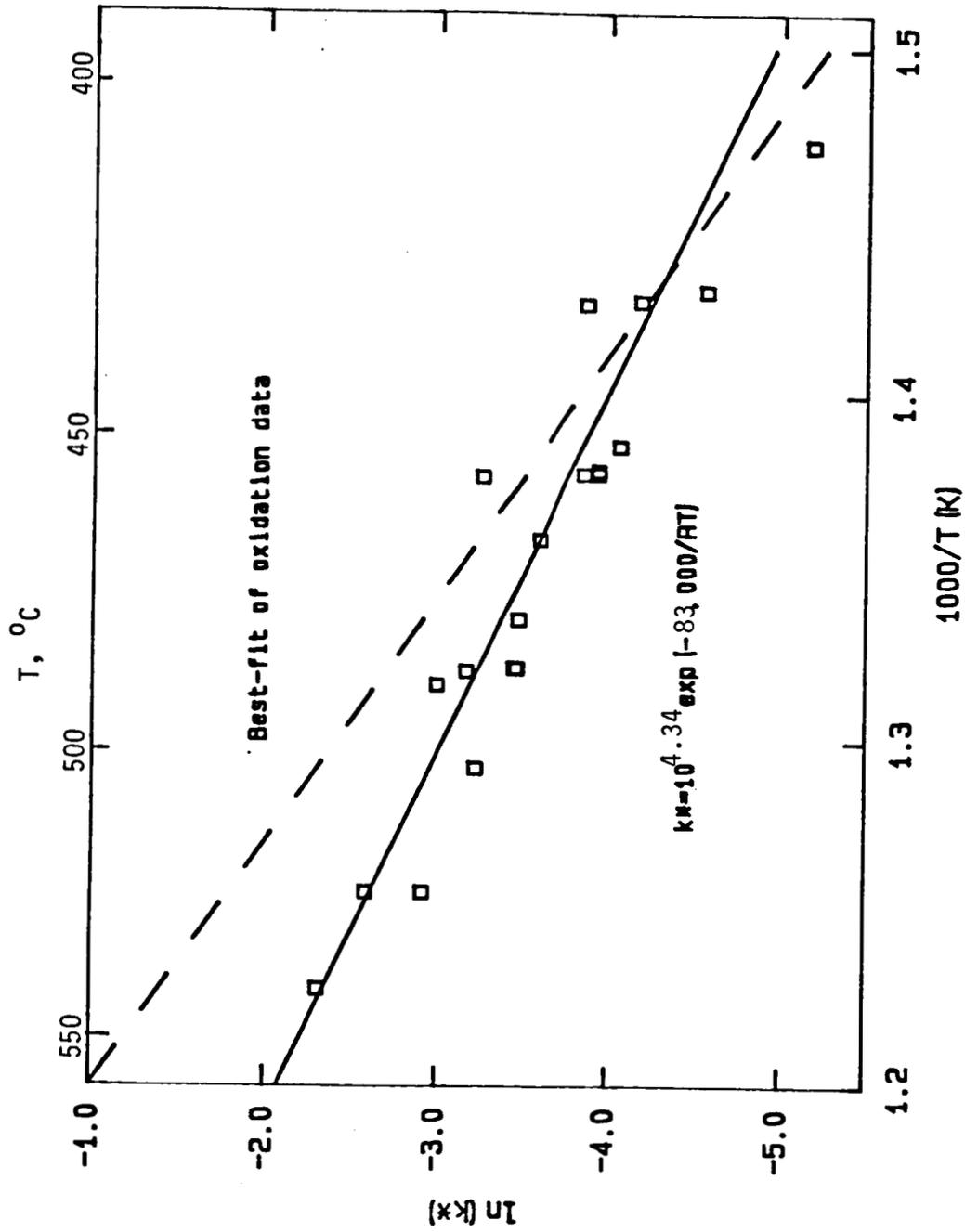


Figure 4. Arrhenius Plot for First-Order Water-Gas Shift Reaction in Supercritical Water at 24.5 MPa

the water-gas shift reaction could be modeled by at least three sets of global reactions. The first is parallel oxidation and water-gas reactions, as described by Eqns.(3) and (4) above. The second is assuming the water-gas shift reaction is completely reversible (so that increasing hydrogen concentrations will decrease the rate of carbon dioxide production) and the hydrogen is consumed at higher temperatures in the oxidation experiments by reaction with oxygen. The third model includes reactions at the reactor wall (catalysis), especially for the water-gas reaction. The data presented so far are sufficient to fully characterize the first parallel reaction model; qualitative conclusions can be made on the others.

The best, non-linear, empirical model for the water-gas shift reaction (Eqn.(5)) was included in a regression of the data from the oxidation experiments so that the overall conversion of carbon monoxide was calculated from two parallel and simultaneous paths: one due to an oxygen facilitated pathway, or direct oxidation, and the other to the water-gas shift. The resulting regressed expression for the separated direct oxidation rate was:

$$-\frac{d[\text{CO}]}{dt} = 10^{17.4 \pm 1.63} \exp(-238. \pm 24. / RT) [\text{CO}]^{1.87 \pm 0.02} [\text{O}_2]^{0.03 \pm 0.06} \quad (6)$$

The order with respect to oxygen again is not statistically significantly different from zero (at a 95% confidence level). Other regressed parameters are reported in Table 1.

Five experiments were performed with dilute solutions of carbon monoxide and hydrogen fed to the reactor at three nominal temperatures (425, 483 and 541°C). The amount of hydrogen in the inlet was two

to four times as great as the hydrogen in the outlet of a similar water-gas shift experiment, with the ratio being lower for the high temperature experiments, where more hydrogen was produced in the comparable water-gas shift experiment. If the hydrogen concentration in the water-gas shift experiments is assumed to increase linearly with time from an initial concentration of zero, then the ratio of the average hydrogen concentration for these experiments to the corresponding water-gas shift experiments is about four to eight. This large excess in hydrogen should have been enough to demonstrate if hydrogen had an effect on carbon dioxide production.

The results of these experiments showed little effect of the excess hydrogen. A slight decrease in conversion occurred in the excess hydrogen experiments at 541 and 483°C (22 and 32 relative percent), but this is within possible experimental error and is a much smaller effect than would be observed for this great excess of hydrogen and any reasonable order with respect to hydrogen (greater than 0.2 for the reverse reaction). The set of experiments at low temperature (425°C) suggest a possible reaction acceleration due to the presence of hydrogen, but again much of the apparent acceleration could be due to experimental uncertainties. One experiment was made to measure directly the rate of the reverse water-gas shift reaction at 483°C by reacting dilute solutions of hydrogen and carbon dioxide. The conversion of carbon dioxide to carbon monoxide was at most 0.4%, and even this amount of carbon monoxide could have been an analytical artifact or a residual trace left in the reactor from previous experi-

ment. These experiments indicate that the reverse reaction is negligible at dilute conditions in supercritical water.

Inconel 625, an alloy composed primarily of nickel, chromium and molybdenum, was the primary material used in the tubular reactor. It is not known to be a catalyst for either oxidation of carbon monoxide or the water-gas shift reaction, but many metals do catalyze these reactions to some extent. A series of experiments was conducted to evaluate the magnitude of any potential catalytic effects in which the surface area was increased by 52% and the reactor volume decreased by 14% by packing the tubular reactor with irregularly shaped shavings of Inconel 625. The nominal mesh size of the pieces was -16 +20 mesh (0.084 - 0.10 cm), and the estimated specific surface area was 3.0 m<sup>2</sup>/kg. This is very low compared to typical porous catalysts, which are in the range of square meters per gram (Satterfield, 1980). Attempts to pack the reactor with a fine powder of Inconel 625 (-80 +100 mesh) were unsuccessful, as the pressure drop was excessive, greater than 2.38 MPa (350 psi) over the approximately 1.8 m packed length of the reactor and 5 micron frit (used as a screen), at typical flowrates ( $1.67 \times 10^{-4}$  kg/s or 10 g/min).

Nine experiments were conducted with carbon monoxide fed to the packed reactor. All were conducted at temperatures for which previous experimental data existed: nominally 425, 475 and 523°C. Seven of the experiments were oxidation tests, since if any effects existed, they should occur in this system where more reactions are possible. Two water-gas shift conditions were studied. In addition to the

temperatures, most of the other operating variables for all nine experiments were very close to specific previous runs, except that two experiments used a lower inlet concentration of carbon monoxide than the earlier run. These results suggest that the reactor surface has a small or negligible effect on carbon monoxide reaction rates, although experiments with a greater increase in the surface area should be conducted to confirm this. No tests with excess hydrogen, hydrogen and oxygen, or carbon dioxide and hydrogen were attempted in the packed reactor.

Two other compounds studied, in addition to carbon monoxide, whose oxidation kinetics are important to the understanding of reactions in supercritical water, were ammonia and ethanol. Ammonia was selected as it is known to oxidize slower than other species and is the rate-limiting reaction in the conversion of organic nitrogen to molecular nitrogen. Difficulty in reaching and controlling high sand-bath temperatures limited operations with the present apparatus to below 550°C. These lower temperatures resulted in such low conversions of ammonia that kinetics parameters for oxidation in supercritical water could not be quantitatively determined. Measurable ammonia conversions of about 5% were only observed at 540°C. At this temperature, addition of ethanol at a mass concentration equal to 73% of the ammonia did not alter the measured conversion. Much higher reaction temperatures (probably above 600°C) will be required to study the kinetics of ammonia oxidation as well as the co-oxidation of ammonia and ethanol in supercritical water.

The direct oxidation of ethanol in supercritical water was investigated in a series of exploratory experiments. The inlet species for four of these experiments included only ethanol, water and oxygen in order to estimate the effect of temperature on the oxidation of this simple organic compound between 484 and 541°C, at oxygen levels between 2.2 and 3.6x10<sup>-3</sup> mole/L, and ethanol levels between 6.7 and 7.9x10<sup>-4</sup> mole/L. The variation in ethanol and oxygen concentrations were due solely to the changes in the reactor fluid density with temperature. The feed solution for all the experiments with ethanol was a 0.1 vol% aqueous solution prepared at normal temperature and pressure.

No experiments were conducted where the concentrations of ethanol or oxygen were varied significantly, so the reaction was assumed to be first order in ethanol and zero in oxygen, which is consistent with the observed global rate law for carbon monoxide oxidation in supercritical water. A plot of the log of the first-order rate constant versus the reciprocal absolute temperature is shown in Figure 5 for four ethanol oxidation experiments and three other experiments with ethanol. The reaction is clearly highly activated, going from a conversion of 16% at 484°C to 99.5% at 541°C, and the data are reasonably linear. A least-squares linear regression of the four oxidation data yielded a rate expression as:

$$-\frac{d[\text{EtOH}]}{dt} = 10^{21.8 \pm 6} \exp(-340. \pm 215. \text{ kJ/RT}) [\text{EtOH}]^1 \quad (7)$$

The conversion of ethanol reported here is conversion of ethanol to any product (disappearance of ethanol). The closure of the mass

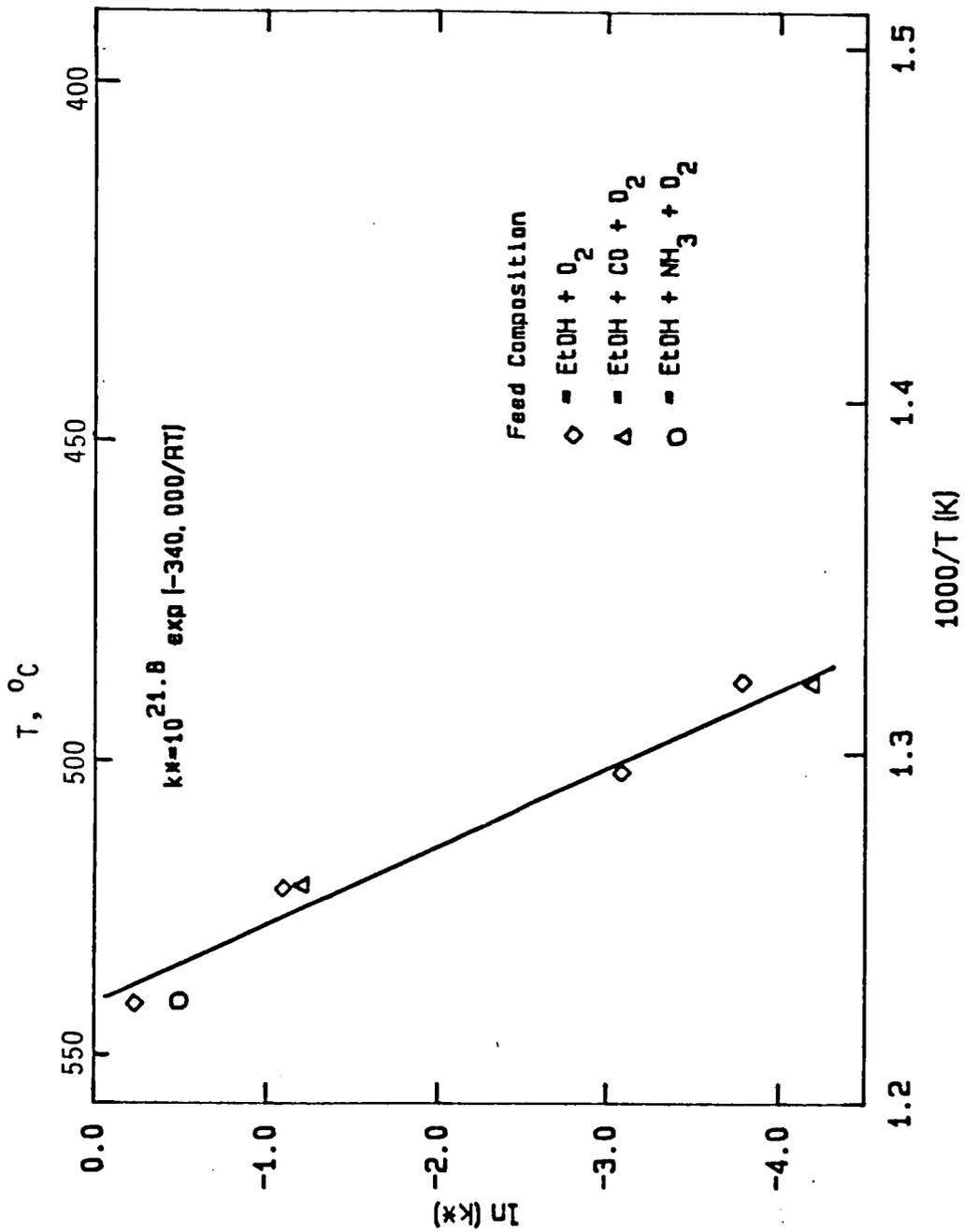


Figure 5. Arrhenius Plot for First-Order Oxidation of Ethanol in Supercritical Water

balance for carbon is adequate, being between 93.5 and 105.8%. Most (greater than 85%) of the ethanol was converted to either carbon monoxide or carbon dioxide at temperatures above 520°C, and more carbon dioxide was formed at higher temperatures, as would be expected. Only one other liquid product of reaction was identified, which was acetaldehyde, which usually accounted for 1% or so of the carbon.

### 3.3.3 Modeling of Experimental Data

Expressions have been developed for gas-phase oxidation of wet carbon monoxide that could apply to reactions in supercritical water, and several were tested by comparing their predictions of conversion for a given set of conditions to the experimentally determined values. Such calculations were done for global rate expressions proposed by Hottel, et al. (1965), Lavrov (1962), Dryer, et al. (1973), Howard, et al. (1973), and Graven and Long (1954); the results are listed in Table 2. The experiments are listed by the reaction temperature, as this is the key operating condition that affects reaction rates. The three experiments were not at similar concentrations or residence times.

None of the global expressions for gas-phase reactions accurately predict the conversion of carbon monoxide to carbon dioxide in supercritical water. The best results were obtained with the correlation by Dryer and Glassman (1973), which predicted rates at least 2.5 times greater than those observed in supercritical water. The other oxidation expressions over-predicted the conversions by one to four orders

Table 2. Comparison of Predictions to Experimental Data:

Conversion at Specific Residence Times and Temperatures

<u>Model</u>	Conversion, %, in (Residence Time), s, at:		
	Temperature of Experiment, °C		
	400	484	543
<u>Global Expression</u>			
Hottel, Williams, Nerheim and Schneider (1965)	99.99 (0.013)	99.99 (0.008)	99.99 (0.006)
Lavrov (1968)	99.96 (13.18)	99.99 (2.89)	99.99 (0.51)
Dryer and Glassman (1973)	26.95 (13.18)	92.40 (7.66)	99.99 (3.22)
Howard, Williams and Fine (1973)	99.99 (2.49)	99.99 (0.43)	99.99 (0.05)
Graven and Long (1954)	0.0015 (13.18)	0.014 (7.66)	0.36 (6.57)
<u>Elementary Network</u>			
Westbrook, Dryer and Schug (1983)	3.98 (13.18)	67.7 (7.66)	99.6 (6.57)
<u>Experimental Data</u>	11.6 (13.18)	36.5 (7.66)	81.3 (6.57)

of magnitude. The variation by several orders of magnitude is a larger difference than typical for predictions of gas-phase combustion, where the models usually agree to within a factor of ten, but the accuracy of the predictions with a given model falls off rapidly outside the range of conditions for which the correlation was developed. The one correlation for the water-gas shift reaction (Graven and Long, 1954) under-predicted the conversion by at least two orders of magnitude.

One likely reason for the error in the predictions of oxidation rates in supercritical water is the explicit dependence on the concentration of water. The composition and pressure of the supercritical water environment produces concentrations of water that are two to five orders of magnitude greater than those for which these expressions were developed. The correlations included water as a minor but essential component of the reaction gas, but in the experiments conducted here, water is the major component of the supercritical mixture, so it is not surprising that the correlations could overpredict the effect of the water on the reaction rate. The role of water in the reaction mechanism could be much different when it is the one major species than when it is a minor species.

Although the prediction of carbon monoxide conversion using gas-phase rate expressions for reaction in supercritical water are off by an order of magnitude or more for most of the expressions, the more important error is the failure of these global expressions to include the importance of the water-gas shift. Hydrogen was a key experimental

reaction product in all reactions of carbon monoxide in supercritical water, indicating the presence of the water-gas shift reaction, but it would be impossible to predict this with the correlations from the gas-phase oxidation of carbon monoxide, since these expressions do not allow for the formation of hydrogen. Since 20-75% of the carbon dioxide that was produced experimentally came from the water-gas shift, the overprediction of the conversion from an oxidation pathway is even greater than it was for the global reaction. Because of the failure to account for hydrogen production, the fit of the global expressions to other experiments was not tested.

Elementary reaction models were used in this study as one means to fundamentally model the reactions that could occur on a molecular level during the oxidation of carbon monoxide and ammonia in supercritical water. The experimental reaction environment was modeled as one that was isothermal, isobaric, constant density, and in plug flow. The assumption of constant temperature and pressure, and plug flow are all reasonable from the design and operation of the reactor; the assumption of constant density cannot be rigorously true in an isobaric system, but is still reasonable for the dilute reaction environment. The experimental variation in temperature and pressure produced a maximum variation in the calculated density of 5%, but usually below 1.5%. The use of dilute reagents also legitimizes the assumption of ideal mixtures in the fluid phase. The fugacity coefficients of the dilute reagents (which were also well above their critical temperatures and pressures) were estimated to be between 0.95 and 1.2, so were

assumed to be unity, as were those for all radicals. The real concentration of the major component, steam, was found for each experimental condition from the literature (Keenan et al., 1978), and its fugacity coefficient ranged from 0.68 to 0.85. The thermodynamic properties of all the species were found as a function of temperature only from the JANAF tables (Miller, Branch and Kee, 1980). Low-pressure (or density) rate constants were used for all third-body reactions due to the lack of available rate constants for the more appropriate high-pressure (or density) conditions. The specific set of reactions used in the simulations of carbon monoxide reaction were those presented in Westbrook, Dryer and Schug (1982).

The first test of the elementary model was to compare predictions made with the known set of rate constants to experimental data. This is shown in Table 2 for the same three experiments that were modeled with the global rate expressions. The elementary model predicted conversions of carbon monoxide to carbon dioxide slightly better than the best global model, typically being within a factor of two of the experimentally determined conversion. Unfortunately the elementary model was consistent with the global models and did not predict any significant formation of hydrogen. Predictions were lower by a factor of 50 of the observed values. Unlike the global models, the elementary model did include the possibility of hydrogen production, as hydrogen was one of the ten species that was included in the mechanism and presumably modeled as accurately as carbon monoxide and dioxide.

Several methods were tried to improve the prediction of hydrogen

production with the elementary model. These included modifying the reaction set, the thermodynamics, and specific rate constants. The attempted improvements were conducted on a simulation of an experiment at 484°C, with rate constants arbitrarily adjusted only one reaction at a time. The program ODESSA (Leis, 1986), which can both numerically integrate and calculate sensitivity parameters for a system of ordinary differential equations, was used to identify important reactions to try adjustments of rate constants. None of these attempts produced satisfactory results (that is increasing hydrogen production by several orders of magnitude, and also decreasing the carbon dioxide production). Simulations of the water-gas shift at supercritical and gas-phase conditions were as unsuccessful as simulations of oxidations at supercritical conditions. The model and program were verified by correct simulation of gas-phase combustion data.

The failure of existing models to predict the reaction rates in supercritical water leads to speculation on the effect of the solvent on the reaction rates and mechanisms. A solvent can affect reaction rates in both radical processes and ionic processes. The influence of solvent on ionic reactions is well-understood, as presented in many texts on organic chemistry (Streitweiser and Heathcock, 1974), but the supercritical water environment studied in this work was not likely to support ionic reactions due to the low density. The possible effects of a solvent on radical processes include altered formation and stabilization of radicals or intermediates. For either kind of reaction, a solvent can influence the transport on a molecular

scale of reactive solutes to each other.

Water can enter radical, third-body reactions directly as the energy carrier for a reaction. Water is very effective in this role, but the simulations with the elementary model discussed in the previous section suggest that this is not the most important effect of the supercritical water on the reaction rates. Supercritical fluids as solvents may also form loosely ordered structures on a molecular level about solute molecules, as speculated by Abraham and Klein (1985). Association on a microscopic scale in supercritical water may be due to the limited hydrogen bonding still possible at those conditions. Raman spectral evidence reported by Franck (1976) suggests that 5-8% of water molecules at 500°C are still in a weakly associated state with neighboring molecules. A "cage" of water molecules associated around solute molecules could stabilize the existence of radicals or transition states, prevent solute radicals from reacting with other solutes, or both. A cage structure could certainly promote reactions between dilute, solute molecules and the predominant solvent. This kind of structure is consistent with lower than predicted rates for oxidation and higher than expected rates for the water-gas shift reaction (the solute-solvent reaction).

#### 3.3.4 Conclusions and Recommendations from Kinetics Studies

1. Empirical kinetics expressions were determined for oxidation of carbon monoxide and the water-gas shift reaction in supercritical water. The best global model incorporates parallel reaction

pathways of the water-gas shift and direct oxidation, where rates of each reaction depend explicitly only on the carbon monoxide concentration and temperature.

2. Carbon monoxide reacts in supercritical water by a radical pathway for the densities studied here. A qualitative model consistent with the data is a water (solvent) cage surrounding reactive solutes, promoting the water-gas shift reaction between solvent and solute, and retarding the direct oxidation reactions.
3. No existing global or elementary model predicted the importance of the water-gas shift reaction to produce hydrogen. Small adjustments to the elementary model did not improve the prediction of hydrogen production. Conversions of carbon monoxide to carbon dioxide were predicted to within a factor of two, but this agreement is insignificant since the production of hydrogen was not predicted.
4. Expressions were also determined including dependences on water, but these did not improve the fit to data enough to warrant the additional parameter. No significant dependence was observed on the concentration of hydrogen or oxygen.
5. Limited kinetics parameters were determined for oxidation of ethanol between 484 and 540°C; ammonia was unreactive up to 540°C.

### 3.3.5 Recommendations from Kinetics Studies

1. Study oxidation of ammonia with and without added organics in an improved heater, capable of producing stable temperatures

up to 650°C, or in a batch reactor capable of long (1-60 minute) residence times at lower (400-500°C) temperatures.

2. Investigate the transition of the water-gas shift from a radical mechanism to an ionic one, which may exist near the critical point, by conducting experiments at higher densities and with added hydrogen peroxides as a free-radical generator or hydroxides to promote ionic reactions.
3. Explore the oxidation in supercritical water of other simple organics, representative of classes of molecules, such as methane, methanol, methyl-ethyl ketone, acetic acid, chloromethane, or urea.

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