

## HETEROLYSIS AND HOMOLYSIS IN SUPERCRITICAL WATER

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### INTRODUCTION

Efficient thermochemical processes underlie the conversion of crude oil and natural gas liquids to higher value chemicals and fuels. Unfortunately, attempts to develop similar conversion processes for biomass feedstocks (such as wood chips and bagasse) have been frustrated by the non-specificity of high temperature pyrolysis reactions involving biopolymer substrates (1,2). For example, the pyrolysis of bagasse yields a liquid mixture of carbohydrate sirups and phenolic tars, a gas composed primarily of carbon oxides and hydrogen, and a solid charcoal. Variations of the conventional engineering parameters (temperature, heating rate, residence time and pressure) do not provide a good control over the complex set of concurrent and consecutive pyrolysis reactions. Thus it has not been possible to engineer the pyrolysis reactions to produce a few high value products from biomass materials.

Recent advances in materials technology, high pressure pumps and other high performance liquid chromatography (HPLC) equipment, have created new opportunities (3) for fundamental studies of chemical reactions in solvents at very high pressures ( $>30$  MPa) and temperatures ( $>400^{\circ}$  C). For sufficiently dilute solute-solvent mixtures at pressures  $P > P_c$ , no liquid-vapor phase transition occurs as the mixture is heated. Furthermore, when the temperature  $T$  is near the solvent's critical temperature  $T_c$  and  $P > P_c$  many solvents manifest extraordinary properties (4,5). These unusual properties provide new parameters for the control of chemical reactions involving biopolymers and other substrates.

As discussed in the following sections, when the density of supercritical (SC) water exceeds  $0.4$  g/cm $_3$  the fluid retains its ionic properties (high dielectric constant and ion product) - even at high temperatures. These properties provide new opportunities to catalyze a variety of heterolytic bond cleavages with a high degree of specificity. Examples discussed in this paper include the dehydration of ethanol to ethylene, the dehydration of glycerol to acrolein, and the conversion of 1,3 dioxolane to glycol and formaldehyde. In each of these examples the specificity of the heterolytic bond cleavage is high (approaching one mole of desired product per mole of reactant); whereas the conventional, higher temperature, free radical reactions offer lower yields of the same desired products. In the case of ethanol dehydration, findings reported here have exciting implications for the production of ethylene from ethanol, which may find early application in Brazil.

## PRIOR WORK

Interest in the use of SCF solvents as a reaction media is founded upon recent advances in our understanding of their unique thermophysical and chemical properties. Worthy of special note are those thermophysical properties (6) which can be manipulated as parameters to selectively direct the progress of desirable chemical reactions. These properties include the solvent's dielectric constant (7), ion product (8,9), electrolyte solvent power (10,11), transport properties (viscosity (12), diffusion coefficients (13) and ion mobilities (14)), hydrogen bonding characteristics (15), and solute-solvent "enhancement factors" (6). All these properties are strongly influenced by the solvent's density  $\rho$  in the supercritical state.

For example, SC water with  $\rho = 0.47 \text{ g/cm}^3$  at  $400^\circ \text{C}$  ( $P = 35 \text{ MPa}$ ) enjoys a dielectric constant of about 10 (comparable to a polar organic liquid under normal conditions), an ion product of  $7 \times 10^{-14}$  (vs  $10^{-14}$  at room conditions) and a dynamic viscosity = 0.57 millipoise (vs 10 at room conditions). Under these conditions SC water behaves as a water-like fluid with strong electrolytic solvent power, high diffusion coefficients and ion mobilities, and considerable hydrogen bonding. These properties favor chemical reactions involving heterolytic (ionic) bond cleavages which can be catalyzed by the presence of acids or bases.

Dramatic changes occur when the temperature of the SC water is raised to  $500^\circ \text{C}$  at constant pressure ( $\rho = 0.144 \text{ g/cm}^3$ ). Decreases in the dielectric constant to a value of 2 and ion product to  $2.1 \times 10^{-20}$  cause the fluid to lose its water-like characteristics and behave as a high temperature gas. Under these conditions homolytic (free radical) bond cleavages are expected to dominate the reaction chemistry. Thus by using the engineering parameters of temperature and pressure one can dramatically change the chemical properties of the solvent (dielectric constant and ion product) to favor heterolytic or homolytic bond cleavages. This paper emphasizes the manipulation of these parameters as a means for engineering the reaction chemistry of biopolymer materials.

## APPARATUS AND EXPERIMENTAL PROCEDURES

Figure 1 is a schematic of the SC flow reactor. Prior to the initiation of flow, the system is brought up to pressure by an air compressor. Afterwards, an HPLC pump forces a pure solvent into the reactant accumulator at a measured rate of flow. This flow displaces the solvent/solute reactant mixture out of the accumulator, through the reactor and a 10 port valve dual loop sampling system, and into the product accumulator. The flow of products into the second accumulator displaces air through a back-pressure regulator and into a water displacement apparatus, which measures the rate of air flow at ambient conditions. The

reactant flow is rapidly heated to reaction temperature by the entry heat guard, and maintained at isothermal conditions by a Transtemp Infra-red furnace and an exit heat guard. Samples captured in 5.4 ml sample loops are released into sealed, evacuated test tubes for quantitative analysis by GC, GC-MS, and HPLC instruments within the laboratory. The outer annulus of the reactor is a 4.572 mm ID Hastelloy C-276 tube, and the inner annulus is a 3.175 mm OD sintered alumina tube, giving the reactor an effective hydraulic diameter of 3.2 mm. The alumina tube accommodates a movable type K thermocouple along the reactor's axis, which provides for the measurement of axial temperature gradients along the reactor's functional length. Radial temperature gradients are measured as differences between the centerline temperature and temperatures measured at 10 fixed positions along the outer wall of the reactor using type K thermocouples. The location of the movable thermocouple within the reactor is measured electronically to within 0.01 mm by a TRAK digital position read out system. The entire reactor and sampling system is housed in a "bullet proof" enclosure which can be purged of air (oxygen) during studies involving flammable solvents (such as methanol).

The reactor can be characterized by the following representative nondimensional numbers:  $Re = 33$ ,  $Pr = 1.3$ ,  $Sc = 0.43$ ,  $Pe_{\text{thermal diffusion}} = 43$ ,  $Pe_{\text{species diffusion}} = 56$  and  $Da = 0.15$ . Figure 2 displays a typical temperature profile of the reactor during operation. Because the thermal diffusivity of SC water is comparable to that of many high quality insulation materials, gross radial temperature gradients can easily exist in a flow reactor. As shown in Figure 2, radial temperature gradients within the annular flow reactor are negligible. A computer program, which accurately accounts for the effects of the various fluid (solvent, solvent and solute, air) compressibilities on flow measurements, calculates mass and elemental balances for each experiment. A typical experiment evidences mass and elemental balances of  $1.00 \pm 0.05$ .

## RESULTS AND DISCUSSION

Results of experiments probing the dehydration chemistry of ethanol in SC water ( $P = 34 \text{ MPa}$ ) are summarized in Table 1. The low temperature ( $400^\circ \text{C}$ ), uncatalyzed dehydration is very slow, and little ethylene is formed. However, in the presence of  $0.1 \text{ M H}_2\text{SO}_4$  the reaction is both rapid and highly specific. The effectiveness of the acid catalyst is a result of the high degree of dissociation of  $\text{H}_2\text{SO}_4$  in SC water at  $400^\circ \text{C}$  and  $34 \text{ MPa}$ , as well as the high mobility of  $\text{H}^+$  ions in SC water. These results contrast with the conventional (16) acid catalyzed dehydration, which requires heating the alcohol in  $95\% \text{ H}_2\text{SO}_4$  at  $170^\circ \text{C}$ . Figure 3 displays the acid catalyzed heterolytic reaction mechanism for ethanol dehydration.

Table 1 also reveals a dramatic loss in specificity at higher temperatures ( $500^\circ \text{C}$ ) due to the increasing role of homolysis in the reaction chemistry. Unwanted products of

homolysis include  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{C}_2\text{H}_6$ , which serve to decrease the yields of the desired product ethylene. Homolysis is favored under these conditions because the water has lost its ionic properties (ion product =  $10^{-20}$ ) and will not facilitate the dissociation of acid catalysts or the formation of carbonium ion intermediates.

Table 2 summarizes similar results for the dehydration of glycerol (40). As shown in Figure 4, the observed products (acetaldehyde, acrolein, and the gases  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ ) can be explained by any one of several different pathways and mechanisms. However, an experiment with the posited intermediate acetol as the reactant produced only gases; hence pathway 1 cannot be the source of acrolein. The dramatic increase in the relative yield of acrolein in the presence of  $\text{NaHSO}_4$  at  $360^\circ\text{C}$  supports the role of the heterolytic pathway 2 in forming acrolein. The significant influence of the free radical scavenger hydroquinone in reducing acrolein yields supports the role of homolytic bond cleavage (pathway 3) in the formation of acrolein at higher temperatures ( $500^\circ\text{C}$ ). These findings are in accord with earlier studies of the vapor phase pyrolysis of glycerol (17), and the results of experiments involving ethanol given in Table 1. Here again we observe the high specificity of dehydration reactions involving acid catalyzed, heterolytic bond cleavages.

In addition to the dehydration of ethanol and glycerol, we have also completed less detailed studies of the reaction chemistry of 1,3 dioxolane, glycol, acetaldehyde and acetic acid in SC water, and (in some cases) SC methanol. At  $350^\circ\text{C}$  and 34 MPa the facile reaction of 1,3 dioxolane with water produces glycol and formaldehyde (99.8% yield) via a carbonium ion intermediate. Here again is an example of the extraordinary specificity heterolytic reaction chemistry. The model compounds glycol, acetaldehyde and acetic acid undergo negligible decomposition in SC water at temperatures up to  $500^\circ\text{C}$ , pressures to 34 MPa, and residence times approaching 3 minutes.

Because of the potential commercial significance of ethanol dehydration in SC water, we are presently developing kinetic expressions for the rate of ethylene formation in the SC water environment. We are also measuring the rate of ethanol dehydration in the vicinity of the critical point of water to determine if the properties of the fluid near the critical point have any influence on the reaction rates. In the near future we plan to begin studies of the reaction chemistry of glucose and related model compounds (levulinic acid) in SC water.

## CONCLUSIONS

The significance of this work is its identification of SC water as a media which supports and enhances aqueous phase chemistry ordinarily observed at much lower temperatures. Fundamental studies of the reaction chemistry of biopolymer related model compounds described in this paper offer insights

into the details of reaction mechanisms, and facilitate the choice of reaction conditions which enhance the yields of valuable products. Chemical reaction engineering in supercritical solvents, based on the ability to choose between heterolytic and homolytic reaction mechanisms with a foreknowledge of results, holds much promise as a new means to improve our utilization of the vast biopolymer resource.

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TABLE 1  
Ethanol Dehydration in Supercritical Water  
at 34.5 MPa

PRODUCT	YIELD (%)*			
C <sub>2</sub> H <sub>4</sub>	71	93	65	56
C <sub>2</sub> H <sub>6</sub>	6	--	16	21
CH <sub>4</sub>	--	--	22	22
CO	47	1	--	6
CO <sub>2</sub>	--	14	15	19
H <sub>2</sub>	57	--	10	560
REACTANT CONCENTRATION(M)	1.02	1.02	0.53	0.53
CATALYST	--	H <sub>2</sub> SO <sub>4</sub>	--	NaHSO <sub>4</sub>
TEMPERATURE (° C)	400	400	500	500
RESIDENCE TIME(S)	151	151	79	76
Degree of Conversion (%)	7.2	26.0	4.2	0.7

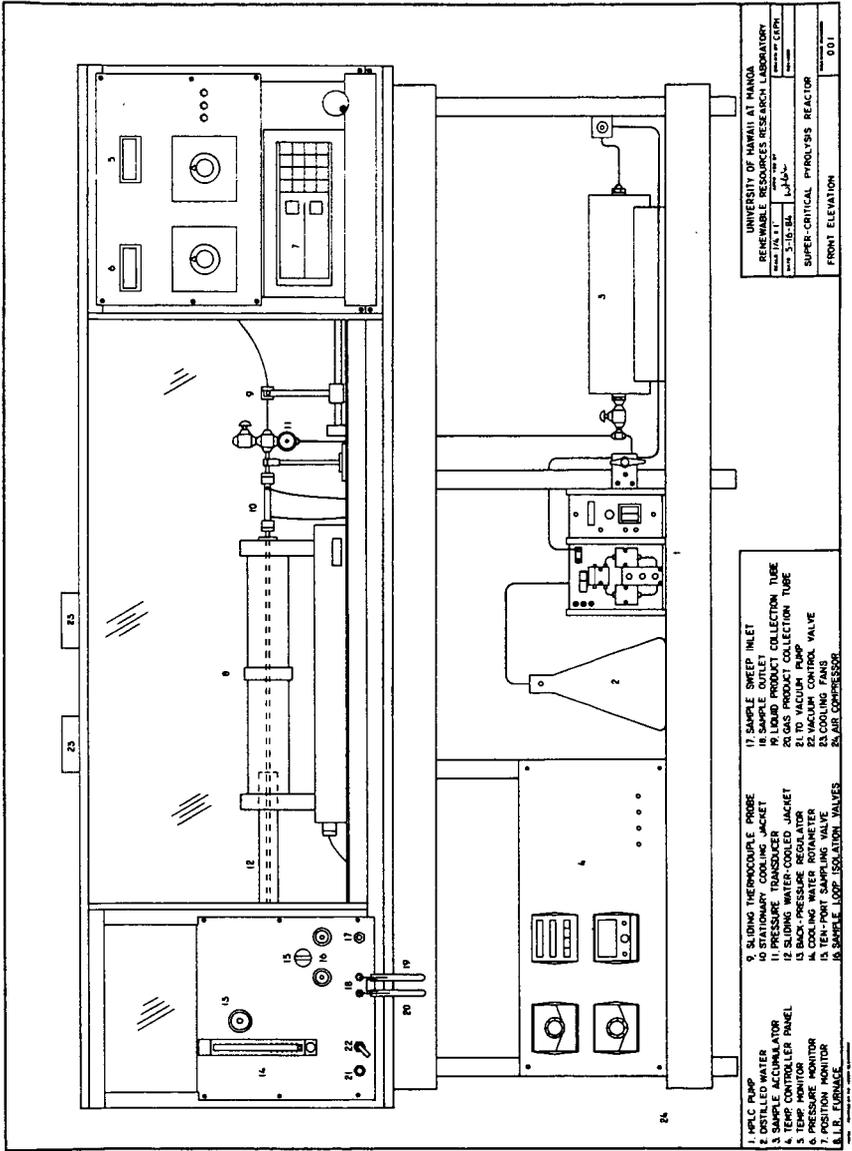
\*100 (mole product/mole reactant converted)

TABLE 2  
Glycerol Dehydration in Supercritical Water  
at 34.5 MPa

PRODUCT	YIELD (%)*			
	360° C		500° C	
	w/o NaHSO <sub>4</sub>	w NaHSO <sub>4</sub>	w/o scav.	w scav.
Acrolein (x)	24	70	34	11
Acetaldehyde (v)	38	35	74	88
Ratio (x/v)	0.6	2.0	0.5	0.1

\*100 (mole product/mole reactant converted)

FIGURE 1. SUPERCRITICAL FLOW REACTOR



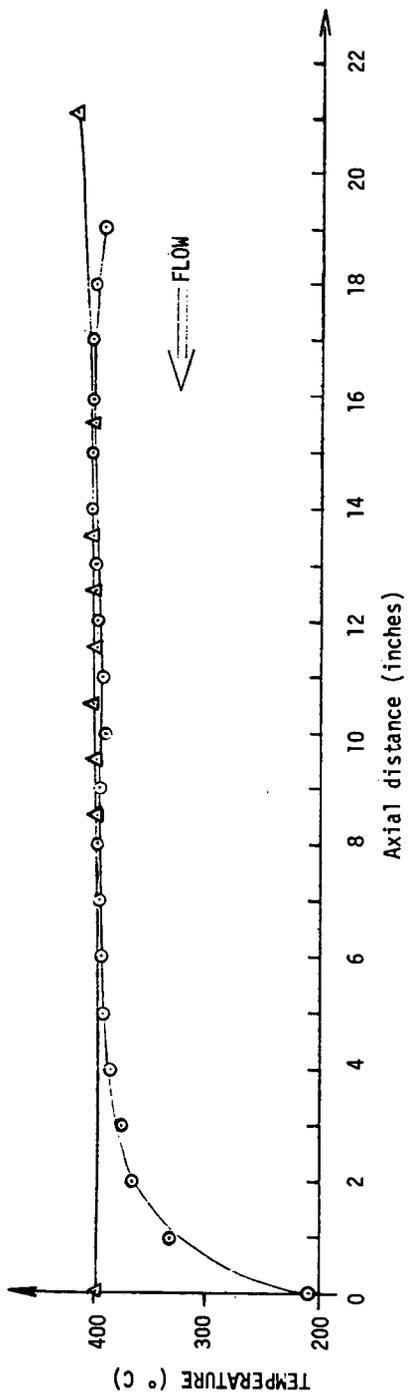


FIGURE 2. TYPICAL WALL ( $\Delta$ — $\Delta$ ) AND CENTERLINE ( $\circ$ — $\circ$ ) TEMPERATURE PROFILES OF THE SUPERCRITICAL FLOW REACTOR

