Glucose Hydrolysis and Oxidation in Supercritical Water

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Glucose hydrolysis and oxidation occurred rapidly in supercritical water at 246 bar and at 425 to 600°C. A diverse set of products, present in the liquid-phase reactor effluent and also subject to hydrolysis, was formed. At 600°C and a 6-s reactor residence time, glucose is completely gasified, even in the absence of oxygen. In the presence of oxygen, destruction of liquid-phase products is enhanced, with none found above 550°C at a 6-s reactor residence time. Major products formed were acetic acid, acetonylacetone, propenoic acid, and acetaldehyde in the liquid phase, and carbon monoxide, carbon dioxide, methane, ethane, ethylene, and hydrogen in the gas phase. Methane and hydrogen were present among the products at temperatures up to 600°C for reactor residence times of 6 s.

Introduction

Supercritical water oxidation (SCWO) is an attractive alternative technology for the treatment of aqueous organic wastes (Tester et al., 1993), including those with high solids contents, such as activated sludges (Shanableh and Gloyna, 1991), pulp mill sludges (Hossain and Blaney, 1991; Modell et al., 1992), and human waste (Takahashi et al., 1989). For wastes with solids contents from 0 to 20 wt. %, complete oxidation to CO_2, N_2, and H_2O by SCWO can be carried out without addition of auxiliary fuel, and a significant fraction of the heating value of the waste can be recovered. Furthermore, SCWO treatment of this class of waste is more economical than incineration, since burning a high-water-content waste requires dewatering of the sludge combined with addition of auxiliary fuel to supplement the waste's heating value. In some cases, SCWO of sludges may even be cheaper than the common disposal method of landfilling (Modell et al., 1992). Supercritical water oxidation has also demonstrated the ability to quickly and efficiently destroy dioxins and furans, which are frequently present as trace contaminants in pulp mill sludges (Hossain and Blaney, 1991; Modell et al., 1992). In addition, SCWO conditions can be controlled to give only partial oxidation of nitrogenous waste constituents to ammonia, while carbon-containing species are oxidized completely to CO_2 and H_2O; human waste can thus be converted to a clean fertilizer for plants, a critical capability for controlled ecological life support systems (Takahashi et al., 1989).

A common feature of sludges and human waste is their high fiber content, most of which is cellulose. In the case of pulp mill sludges, the waste will also contain significant amounts of lignin. Sludges and human waste are typically at least somewhat acidic, and heating of aqueous cellulose under acidic conditions hydrolyzes and depolymerizes cellulose to its monomer, glucose (Skaates et al., 1981). Yields of glucose from cellulose hydrolysis, however, are less than 100% because secondary destructive pathways reduce the glucose yield either by hydrolyzing the glucose (Saeman, 1945) or by converting the cellulose to a nonglucose product (Bobleter and Bonn, 1983; Mok et al., 1992). Nevertheless, a significant fraction of the cellulosic waste in an SCWO reactor is likely to decompose to glucose. Furthermore, a glucose molecule contains the same functional groups as the cellulose polymer. Glucose is thus an appropriate model compound for sludges and human waste.

Figure 1 shows the structure of D-glucose, or dextrose, the common form of glucose. The Fischer projection illustrates the straight-chain (acyclic) form of glucose, which is a six-carbon sugar terminated by an aldehyde group (an aldohexose). An intramolecular rearrangement of the acyclic form

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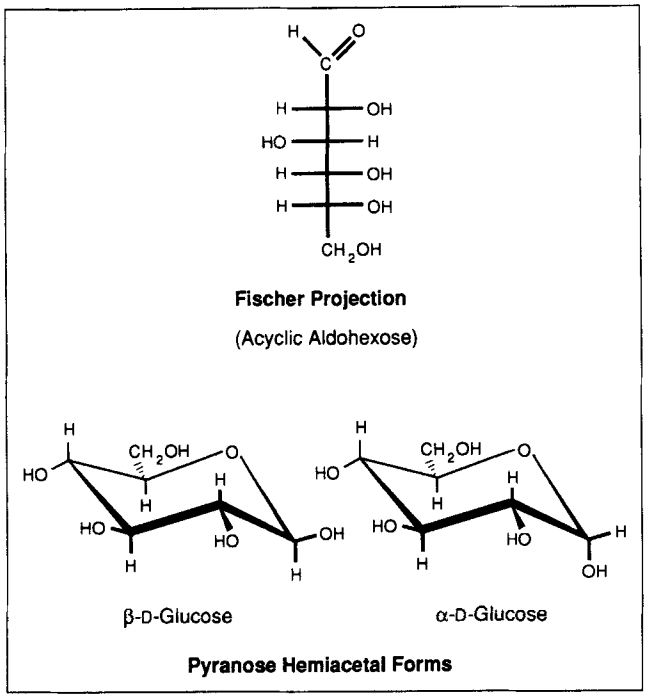

Figure 1. Structures of D-glucose.

results in the heterocyclic, hemiacetal forms of glucose shown in Figure 1. The fundamental ring structure is a pyran, and the ring form of glucose is referred to as a pyranose. The ring closure occurs at a chiral carbon, and there are thus two distinct optical forms of the pyranose (α and β). Cellulose is formed from glucose by an intermolecular dehydration (condensation polymerization) of the pyranose.

Despite the potentially widespread application of SCWO to sludges and human waste, very few studies have been conducted to investigate the destruction characteristics or oxidation kinetics of glucose. Rather, most studies have been concerned with proving the ability of SCWO to treat these wastes with high efficiency (Takahashi et al., 1989; Hossain and Blaney, 1991; Modell et al., 1992). Several kinetic studies of glucose oxidation have been carried out under wet-air oxidation conditions, however, at temperatures of 180–260°C and oxygen pressures of 23–34 bar (Ploos van Amstel and Rietema, 1970; Brett and Gurnham, 1973; Skaates et al., 1981). In those studies, oxidation rates were determined by the reduction in glucose concentration or in chemical oxygen demand (COD), and exhibited an activation energy of about 130 kJ/mol (Skaates et al., 1981). Since wet-air oxidation occurs at temperatures and pressures much lower than those used in the SCWO process, global kinetic measurements and correlations obtained under wet-air oxidation conditions cannot be applied with confidence to SCWO. In addition, none of the wet-air oxidation studies made an extensive effort to ascertain identities or yields of oxidation products, except for Ploos van Amstel and Rietema (1970), who reported that the hydrolysis products of glucose were more refractory than glucose itself, and Skaates et al. (1981), who listed several identified oxidation products, with acetic acid the major product.

The oxidation of glucose in supercritical water, as a model for the oxidation of more complex cellulosic wastes, remains poorly understood. A study of the oxidation characteristics of glucose in supercritical water was therefore undertaken. Initial experiments revealed that hydrolysis of glucose occurred rapidly, and subsequent glucose experiments examined both the hydrolysis and oxidation reactive pathways. Previous experimental results for glucose pyrolysis and hydrolysis were examined to obtain anticipated identities for the products of the hydrolysis and oxidation of glucose in supercritical water.

Previous Experimental Studies of Glucose Hydrolysis/Pyrolysis

While relatively few studies have examined glucose oxidation, there exists an extensive literature concerning the pyrolysis and hydrolysis of cellulose and glucose. Much of this work has been directed toward the utilization of biomass through its conversion to liquid fuels or chemical feedstocks. Efforts to maximize product yields have led to the examination of a wide range of reaction conditions.

Biomass pyrolysis, in which biomass is heated and decomposed in an inert atmosphere or under a vacuum, has been reviewed by Antal (1982). Pyrolysis of cellulosic carbohydrates leads to a variety of smaller compounds, including liquid organics, light gases, and char (Antal, 1982; Evans and Milne, 1987). Destruction of cellulose by pyrolytic reactions proceeds through an intermediate species, levoglucosan (1,6-anhydro-β-D-glucopyranose), which is distinct from the glucose intermediate formed during cellulose hydrolysis. Levoglucosan is apparently formed through intramolecular condensation, although the mechanism is not well understood, with evidence for both heterolytic (ionic) and homolytic (free-radical) pathways found experimentally (Theander and Nelson, 1978; Antal, 1982; Evans and Milne, 1987). Evans and Milne (1987) identified by mass spectrometry over 80 products of the pyrolysis of wood, including many phenolics that were attributed to the pyrolysis of lignin.

Hydrolysis of glucose has been the subject of experimental studies for over a century. Many early studies were concerned with the role of glucose hydrolysis in the discoloration of sugar solutions. For example, aqueous, liquid solutions of glucose at 100 to 250°C were found to form 5-hydroxymethylfurfural, which subsequently either hydrolyzed to levulinic acid and formic acid or polymerized to form colored products (Wolfrom et al., 1948; Singh et al., 1948; Newth, 1951; Mednick, 1962). More recently, Antal and co-workers (Antal and Mok, 1988; Antal et al., 1990a,b, 1991) studied the hydrolysis of fructose, sucrose, and xylose, both with and without an acid catalyst, at 250°C and 345 bar, to investigate the potential for enhancing yields of valuable products. The hexoses (fructose and sucrose) produced significant yields of 5-hydroxymethylfurfural and smaller quantities of furfural, while the pentose (xylose) produced furfural. Small yields of other products were also found, including formic acid, lactic acid, levulinic acid, pyruvaldehyde, and glyceraldehyde (Antal et al., 1990, 1991). Product formation was explained on the basis of ionic, acid-catalyzed mechanisms.

Modell and co-workers were the first to study the hydrolysis and reforming of glucose in near and supercritical water (Amin et al., 1975; Woerner, 1976; Modell, 1985). Amin et al. (1975) reported that, for temperatures below the critical temperature (374°C), glucose hydrolysis produced liquid organics

and char, with little formation of gas. On the other hand, for temperatures above the critical temperature and at 221 bar, gasification of the glucose (after 30 to 60 min) increased significantly (up to 20%), while char formation was suppressed, and most of the hydrolyzed glucose appeared as furans or furan derivatives (furfurals). The gaseous product consisted mostly of carbon monoxide, carbon dioxide, and hydrogen, with smaller amounts of methane and C_2 (two-carbon) gases. Woerner (1976) found similar results in his continuation of the same work.

Most recently, Antal and coworkers (Antal et al., 1992; Yu et al., 1993) studied the reforming reactions of glucose in supercritical water at higher pressures (345 bar) and temperatures (450 to 650°C). At 600°C, the glucose was completely gasified for a residence time of 20 to 30 s, with the major products being carbon dioxide and hydrogen. Carbon monoxide, methane, and ethane were formed in smaller yields. At a given temperature, the yield of gases showed little sensitivity to residence time, whereas gasification increased markedly with increasing temperature. Both the extent of gasification and the composition of the gas produced were found to be sensitive to the reactor material, with Inconel 625 and "corroded" Hastelloy C276 favoring gasification to a greater extent than new Hastelloy. Inconel and corroded Hastelloy also appeared to catalyze the water-gas shift pathway, such that carbon monoxide yields decreased sharply while hydrogen and carbon dioxide yields increased in the reactors constructed of those materials (Antal et al., 1992; Yu et al., 1993).

With the exception of the work of Modell and Antal and their coworkers (Modell, 1985; Antal et al., 1992; Yu et al., 1993), little of the prior work on glucose pyrolysis and hydrolysis is directly relevant to the conditions in the supercritical water oxidation process. Glucose pyrolysis studies lack the presence of water as a reactive medium at relevant densities and temperatures. Glucose hydrolysis studies are carried out in liquid water, typically with acid catalysis, such that ionic chemistry is dominant; in the SCWO process, at temperatures above 425°C and pressures of 230–250 bar, ionic chemistry is likely to be of much more minor (if any) importance. Nevertheless, the foregoing studies provide a framework within which to develop an expectation of the types and identities of products that may be formed during the reactions (hydrolysis and oxidation) of glucose in supercritical water.

Experimental Techniques

Experiments for glucose hydrolysis and oxidation were conducted over a temperature range of 425 to 600°C at a constant pressure of 246 bar. The experimental apparatus and procedures have been described in greater detail elsewhere (Holgate and Tester, 1993; Holgate, 1993). Briefly, a dilute aqueous feed solution of oxygen was prepared by dissolving the gas in purified water in a high-pressure 3-L saturator; the corresponding dilute glucose feed solution was prepared and loaded into an identical feed reservoir. The feed solutions were delivered separately to the reactor by a duplex high-pressure feed pump. The reactor was 4.71 m of 0.635-cm OD $\times$0.171-cm ID Inconel 625 tubing contained in a fluidized sand bath. The feeds were preheated separately to reaction temperature in two 2.8-m lengths of 0.159-cm OD$\times$0.108-cm ID Hastelloy C276 tubing contained in the reactor sand bath. The preheated feeds met and mixed at the reactor inlet, where the oxidation reaction was initiated. Reactor temperature was taken as the average of the mixing and exit fluid temperatures. Upon exiting the reactor, the reaction mixture was quenched to ambient temperature in a countercurrent shell-and-tube heat exchanger, and the pressure was reduced to ambient upon passing through a back-pressure regulator. The resulting gas and liquid phases were disengaged in a gas-liquid separator and the flow rate of each phase was measured. Reactor flow rates in the experiments ranged from 5.9 to 13.8 g/min, yielding residence times of 5.1 to 9.9 s.

Compositional analyses of the reactor effluents were accomplished by gas chromatography (GC) for the gaseous effluent and high-performance liquid chromatography (HPLC) for the liquid effluent. Primary gas sample analysis was accomplished with a Hewlett-Packard 5890 Series II GC using helium as the carrier gas, which provided accurate determination of O_2, N_2, CO, CO_2, and light hydrocarbons using a thermal conductivity detector, but detection of H_2 was poor except at high concentrations. The gas analysis scheme employed two columns, an 80/100-mesh Porapak T and a 60/80-mesh molecular sieve 5A, connected through an air-actuated switching valve that allowed the column order to be reversed. The method provided relatively rapid sample analysis without sacrificing peak resolution. Secondary gas sample analysis was provided by a Perkin Elmer Sigma 1B GC using nitrogen as the carrier gas; this GC was used exclusively for hydrogen and helium detection by thermal conductivity, for which it was very sensitive. Reported gas-phase product yields are the average of multiple (5–10 or more) sample analyses. Detection limits for gas-phase species were about 0.2% by volume in the gaseous effluent. Depending on the gas flow rate, this limit can correspond to a minimum detectable yield of less than 10^{-3}.

Aqueous glucose concentrations were determined by a standard enzymatic technique (Sigma Chemical Co.) in which the glucose concentration is determined indirectly by absorption at 340 nm using a UV/visible spectrophotometer (Shimadzu UV160U). This method is specific to glucose and is not readily subject to interference by other compounds. The method was sufficiently sensitive to allow determination of glucose concentrations in the liquid effluent as low as 5×10^{-5} mol/L.

Compositional analysis of the liquid effluent was accomplished by isocratic HPLC, using a Rainin HPXL solvent delivery system with an Interaction ORH-801 analysis column (chosen for its ability to resolve organic acids) and an Interaction Ionguard guard column. Detection was by UV absorption at 210 or 290 nm using a Rainin Dynamax UV-1 UV/visible detector. Column temperature was maintained by a Timberline column heater. The mobile phase was 0.002-M H_2SO_4 delivered at 0.5 mL/min, with a column temperature of 65°C; sample injection volumes were 100 μL. Peak identification was accomplished by comparison of sample peak retention times with those of standard solutions of pure compounds. Once peaks were identified, calibrations were performed with standard solutions of varying concentrations. Calibration by peak height or peak area gave equally good results; sample peaks were subsequently quantified by peak height since peak overlap frequently occurred and peak areas could not be determined accurately in all cases. Reported

liquid-phase product analyses are the average of three separate sample analyses.

Product Identification

Gas-phase analyses and product identifications were relatively straightforward owing to the limited number of possible products. Species identified in the gas-phase effluent included hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene. No acetylene was detected. Higher-molecular-weight gases, for example, three-carbon and higher, were not specifically searched for, but had they been present they should have caused spurious peaks during the consecutive sample analyses. No such peaks were observed, and furthermore, under conditions where the glucose was completely converted to gaseous species, carbon-balance closures were excellent (95 to 97% or better). These observations led us to conclude that C_3 (or higher) gases were formed to a negligible extent under all of our experimental conditions.

Product identifications for the liquid-phase effluent presented more of a challenge. A list of suspected products was obtained from earlier studies of glucose pyrolysis and hydrolysis (Woerner, 1976; Shallenberger and Birch, 1975; Antal, 1982; Evans and Milne, 1987; Antal et al., 1990a, 1991). This list was then condensed on the basis of commercial availability (for calibration purposes) and the importance (abundance) of the products in the earlier studies. The resulting list of almost 40 suspected products is shown in Table 1. Suspected compounds were tested by injection of authentic standard solutions (prepared using distilled, deionized water) in the HPLC, and observed retention times for the standards were compared with retention times of peaks in a sample of the liquid-phase effluent.

Peak detection was accomplished by UV absorption at two

Table 1. Compounds Tested as Possible Liquid-Phase Products

Compound	RT*, min	λ**, nm	Present in Effluent from Hydrolysis	Present in Effluent from Oxidation
Acetaldehyde	15.9	290	✓	✓
Acetic acid	13.1	210	✓	✓
Acetol (hydroxyacetone)	10.4,14.8	210	?	
Acetone	18.3	290		
Acetonylacetone (2,5-hexanedione)	19.75	210	✓	✓
2-Acetylfuran	42.9	290	✓	
Crotonaldehyde	28.9	210	?	?
Crotonic acid	21.7	210	?	
2-Cyclopenten-1-one	29.7	210	?	?
3,4-Dihydro-2H-pyran	ND†	—		
Dihydroxyacetone	11.9	210		
2,5-Dimethylfuran	M‡	—		
Formaldehyde	ND	—		
Formic acid	11.8	210	✓	
Furfuryl alcohol	36.1	290		
2-Furaldehyde (furfural)	35.8	290	✓	✓
Furan	31.9	210	?	?
2,5-Furandimethanol	M	—		
2-(5H)-Furanone	23.1	210		
2-Furoic acid	22.9	210		
Glucaric (saccharic) acid	6.8	210		
Gluconic acid	8.0	210		
Gluconic acid lactone	8.0	210		
Glucose	ND	—	✓	✓
Glyceraldehyde	10.1	210	?	
Hydroxyacetic (glycolic) acid	10.7	210	?	
5-Hydroxymethylfurfural	25.1	290	✓	✓
Lactic acid	11.1	210	✓	
Levulinic acid	13.7	210		
5-Methyl-2(3H)-furanone	M	210		
2-Methyl-2-cyclopenten-1-one	41.7	210		
2-Methylfuran	ND	—		
5-Methylfurfural	51.9	290	✓	
Oxalic acid	5.2	210		
Propenal (acrolein)	21.0	210		
Propenoic (acrylic) acid	15.6	210	✓	✓
Propionaldehyde	19.6	290		
Propionic acid	15.3	210		
Succinic acid	10.1	210	?	

*Retention time.
**Wavelength for detection/maximum absorbance.
†Not detectable at either 210 or 290 nm.
‡Gives multiple unidentified peaks.

different wavelengths, 210 and 290 nm. Analysis at dual wavelengths enabled discrimination between peaks by functional group, and allowed identification of additional species not detectable at a single wavelength. For example, UV absorption by a compound requires the presence of a double bond, either C = C or C = O. Carboxylic acids have their maximum UV absorbance at approximately 210 nm, as do unsaturated or conjugated ketones and aldehydes. On the other hand, saturated aldehydes and ketones have their maximum absorbance at about 290 nm (Silverstein et al., 1991). Consequently, detection at a single wavelength limits the ability to identify all species: at 210 nm, simple aldehydes have virtually no absorbance, while carboxylic acids have no absorbance at 290 nm. Furthermore, for compounds that absorb at both 210 and 290 nm, the wavelength that maximizes sensitivity (with maximum absorption) can be chosen. For example, the detection limit (at ambient conditions) for furaldehydes by absorbance at 290 nm was about 10^{-7} mol/L, or yields of about 10^{-5}. Carboxylic acids, with their much weaker absorbance, had much higher detection limits; the limit for acetic acid at 210 nm was about 5×10^{-4} mol/L, or yields on the order of 10^{-2}. Other compounds had detection limits between these two extremes.

The ability to discriminate on the basis of functional group is illustrated by acetaldehyde and propenoic (acrylic) acid in Table 1. Both compounds have almost the same retention time, but propenoic acid absorbs exclusively at 210 nm while acetaldehyde absorbs only at 290 nm. Thus the two compounds may be "separated" by the dual-wavelength analysis, even though their peaks overlap. Table 1 lists the better of the two wavelengths for the detection of each test compound. Detection by UV absorption has the disadvantage of not allowing determination of compounds (at concentrations of interest) that lack a double bond, such as methanol, which may be present in the liquid effluent; should detection of such species be desired, alternative analytical methods would be required.

Not all of the test compounds in Table 1 have an associated retention time. In those cases, clear assignment of a retention time for a standard solution was not possible. In some cases, detection of the compound was not possible. For example, glucose was not detectable at the concentrations of interest, because in aqueous solution glucose exists almost exclusively in its cyclic, hemiacetal (glucopyranose) form, shown in Figure 1, which lacks the aldehyde group and which therefore cannot be easily detected by UV absorption. Fortunately, an alternate enzymatic method is available for glucose determinations. Formaldehyde was similarly not detectable, because it exists in solution in a form (formalin or methanediol) that lacks the C = O group.

Other test compounds in Table 1 were detectable, but gave multiple peaks even for ostensibly pure standard solutions. In these cases, the test compound apparently undergoes reaction while standing in aqueous solution. A compound that is sufficiently labile to undergo hydrolysis in room-temperature water is likely not stable under reactor conditions, although the compound may represent an important step in a degradative pathway, and the room-temperature hydrolysis products may also be present in the reactor effluent. Identification of these products was not attempted, however.

Figure 2 shows two HPLC chromatograms, with detection

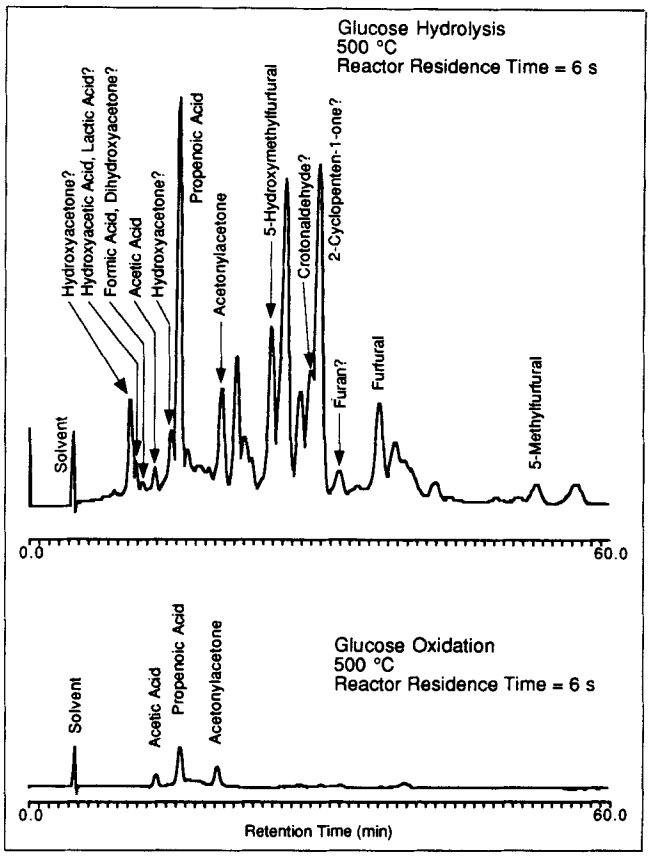

Figure 2. HPLC chromatograms of liquid effluent from glucose hydrolysis vs. oxidation in supercritical water.

Nominal initial conditions: 500°C, 1×10^{-3} mol/L glucose, 6×10^{-3} mol/L oxygen (for oxidation), 6-s reactor residence time. UV detection at 210 nm.

at 210 nm, for hydrolysis and oxidation of glucose in supercritical water at 500°C and 246 bar, with nominal initial conditions of 1×10^{-3} mol/L glucose, 6×10^{-3} mol/L oxygen (for the oxidation experiment), and a 6-s reactor residence time. Peak identities, when known or suspected, have been indicated. Clearly the number of liquid-phase products is greatly reduced under oxidizing conditions.

Many peaks formed during glucose hydrolysis remain unidentified, as Figure 2 shows. Of the 26 or more peaks detected in the hydrolysis effluent, only half have been identified, with many of those identifications tentative. Positive identifications were made for acetaldehyde (not shown in Figure 2 because it can only be detected at 290 nm), acetic acid, acetonylacetone (2,5-hexanedione), 2-acetylfuran (present in very low concentrations and not quantified), formic acid, furfural (2-furaldehyde), 5-hydroxymethylfurfural, lactic acid, 5-methylfurfural, and propenoic (acrylic) acid. Structures of the positively identified compounds are shown in Figure 3. The rationale for these identifications, whether tentative or positive, deserves further elaboration.

Formic acid and dihydroxyacetone have virtually identical retention times (11.8 vs. 11.9 min; see Table 1). However, the sample peak at this retention time is probably formic acid (Antal et al., 1990a, 1991). This peak appears to be fairly

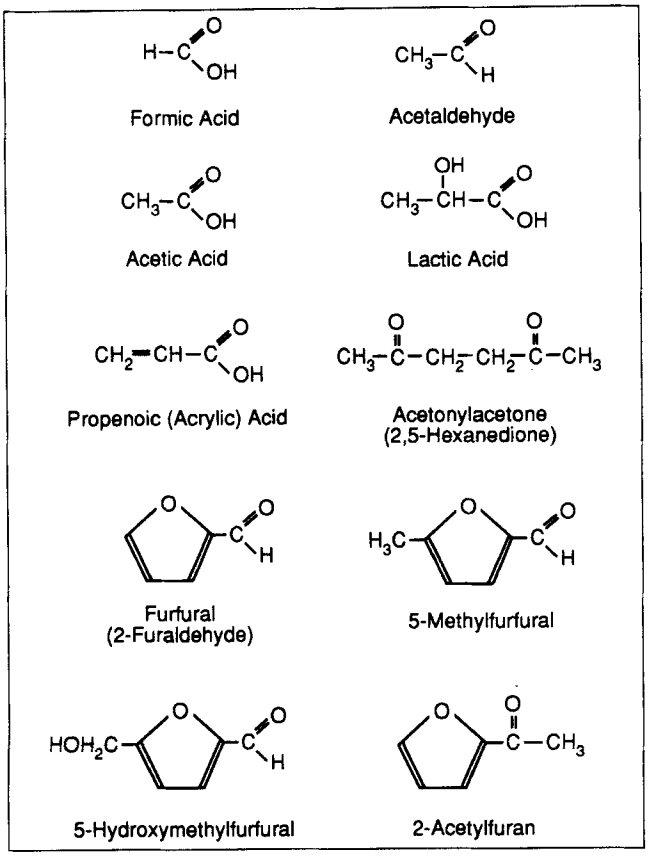

Figure 3. Compounds identified in liquid effluent of glucose hydrolysis and/or oxidation.

unstable and disappears from the hydrolysis effluent for temperatures above 500°C.

Acetol (hydroxyacetone) gives two peaks (at 10.4 and 14.8 min), indicating that it undergoes rearrangement in solution, most likely forming 2-hydroxypropanal. Comparison of relative times from the work of Antal et al. (1991), whose HPLC method was the basis for the one used here, indicates that the peak at 14.8 min probably corresponds to acetol; the peak at 10.4 min is probably 2-hydroxypropanal.

A cluster of peaks with similar retention times exists near the 10-min mark. These peaks are not adequately resolved and no positive identifications are possible. At higher temperatures (450°C and above for oxidation, 525°C and above for hydrolysis), these peaks are unimportant. The identification of lactic acid at a retention time of 11.1 min is tentative, because Antal et al. (1991) indicate that glycolaldehyde (not tested here) elutes at the same time; however, Antal et al. (1990a) did not detect glycolaldehyde during fructose hydrolysis at 250°C and 345 bar. Like the peaks at ~10 min, the lactic acid peak disappears at higher temperatures.

Propenoic (acrylic) acid and propanoic (propionic) acid have very similar retention times; the very tall sample peak at ~15.5 min could belong to either compound. However, the height of the peak suggests that it is probably propenoic acid, because of its much higher absorption due to conjugation. To create such large peaks, propionic acid would have to be present at unrealistically large concentrations.

Crotonaldehyde, crotonic acid, and 2-cyclopenten-1-one all exhibit retention times near those of peaks observed in effluent samples. Unfortunately, retention times are not sufficiently close to warrant a positive assignment of identity to the peaks. Furthermore, a peak at ~30 min exists in the samples at both 210 nm and 290 nm. If the peak at 210 nm is 2-cyclopenten-1-one, then the peak at 290 nm must correspond to another unknown species, because 2-cyclopenten-1-one does not absorb at 290 nm.

The peak in the effluent samples at ~36 min was quantified as furfural rather than furfuryl alcohol, since furfuryl alcohol did not absorb at 210 nm and gave a small peak at 290 nm; the peak in the effluent sample, on the other hand, occurred at both 210 and 290 nm and was large at 290 nm, consistent with the behavior of furfural.

Acetonylacetone was identified since it appears to be a hydrolysis product of 2,5-dimethylfuran, which has been detected among the products of cellulose pyrolysis (Antal, 1982) and glucose caramelization (Shallenberger and Birch, 1975). A path to acetonylacetone from glucose through 2,5-dimethylfuran therefore apparently exists. Acetonylacetone was also listed as a suspected product by Woerner (1976) for hydrolysis of glucose in near-critical water. However, oxidation experiments in the present study at 450 and 475°C gave excessive carbon recovery (118 and 111%, respectively), and suggested that acetonylacetone may not be the proper peak assignment. Were the peak a C_3 instead of a C_6, carbon-balance closures would have been much improved. The assignment of the acetonylacetone peak is therefore the most tenuous of the peak identifications.

Phenolics or other six-membered aromatics were not tested as possible products. Without synthesis or condensation pathways, compounds larger than phenolics cannot form. The results of Antal and coworkers for hydrolysis of sugars (Antal et al., 1990a,b, 1991) indicate that furans, furaldehydes, and their derivatives are the dominant products, while Evans and Milne (1987) attribute the presence of phenolics among the products of biomass pyrolysis to the decomposition of lignin, not cellulose. However, Antal et al. (1990b) have noted that 1,4-butanediol may form tetrahydrofuran with acid catalysis, and West and Gray (1987) observed the formation of dioxanes from 1,4-butanediol in supercritical water. Similarly, Theander and Nelson (1978) indicate that dihydroxyacetone may form aromatics (hydroxybenzenes) in acid solution. These results suggest that phenols or other condensation products cannot be completely eliminated from consideration as possible products, and future studies of glucose reactions in supercritical water may wish to consider these species.

Finally, larger condensation products, such as oligomers of 5-hydroxymethylfurfural or dibenzofurans, cannot be ruled out *a priori* as possible products. HPLC chromatograms were run for retention times as long as 90 min, however, without detecting any peaks beyond retention times of 60 min. Moreover, detection by UV absorption should be highly sensitive to these conjugated species, even in minute quantities. Furthermore, any long-retention-time peaks should eventually appear during the consecutive sample analyses, and should create spurious peaks in the sample chromatograms. No spurious peaks were seen, however, and consecutive chromatograms showed excellent reproducibility. From these observations we concluded that there were no products of high molecular weight in the liquid reactor effluent.

High-molecular-weight products may also form as suspended or deposited solids. This possibility was not examined. Higher temperatures and oxidizing conditions gave good mass-balance closures, so that any solids could only be present in very small amounts. Low-temperature hydrolysis gave poor mass-balance closures and yellowish, odorous liquid effluents, and could have produced solids. The color and odor can be accounted for by the liquid-phase products listed in Table 1, however, and any solids, if present, were not visually apparent and caused no operational difficulties.

Identification of analytes by retention time alone inherently entails a degree of uncertainty. For example, sample matrix effects (such as pH or analyte-analyte interactions) may cause some sample retention times to shift relative to those of standard solutions. More definitive assignment of sample peak identities will require the use of liquid chromatography/mass spectrometry (LC/MS) and/or GC/MS techniques, which are currently being pursued in our laboratory.

Product Distributions for Glucose Hydrolysis and Oxidation

The global hydrolysis or "reforming" of glucose

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2 \qquad (1)$$

can produce significant quantities of hydrogen, if complete reaction to CO_2 and H_2 is achievable, and motivates the glucose gasification research of Antal and co-workers (Antal et al., 1992; Yu et al., 1993). The global oxidation of glucose

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad (2)$$

is of more relevance to SCWO treatment of cellulosic wastes, where complete destruction of organics is desired. Since glucose hydrolysis occurs at significant rates at supercritical-water temperatures and pressures, oxidation of glucose via reaction 2 cannot occur without a simultaneous contribution from reaction 1. In the present study, glucose hydrolysis and oxidation were examined at conditions relevant to the SCWO process (246 bar, 425 to 600°C) to evaluate the relative contributions of the two reactive pathways.

In a series of experiments, an initial concentration (at reactor conditions) of 1×10^{-3} mol/L of glucose was used at a fixed residence time of 6 s and over the temperature range 425 to 600°C. Experiments with and without stoichiometric (6×10^{-3} mol/L) oxygen were conducted, in order to distinguish the products and rates of the hydrolysis and oxidation pathways. The concentration of oxygen required to achieve a stoichiometric glucose/oxygen ratio was high and was limited by solubility constraints in the oxygen saturator. The upper limit of oxygen concentration restricted the maximum glucose concentration, since the glucose concentration was to be the same during both oxidation and hydrolysis experiments. The concentrations used reflect the highest attainable oxygen concentration over the range of reactor temperatures studied.

Hydrolysis and oxidation experiments were performed in pairs. Following heatup of the system, the aqueous glucose feed was switched on to begin a hydrolysis experiment; the oxygen-side feed was pure water. After data had been collected for hydrolysis, the aqueous oxygen feed was introduced and an oxidation experiment was begun. In this manner, hydrolysis and oxidation pathways could be examined under otherwise identical conditions. Switching to the oxygen feed perturbed reaction conditions slightly, since the high-pressure oxygen solution causes an increased flow at the oxygen-side pump head, diluting the glucose feed somewhat and slightly decreasing the overall reactor residence time. These perturbations were very minor, however, and conditions of the hydrolysis and oxidation experiments were essentially identical except for the presence or absence of oxygen.

Even at the lowest temperature studied (425°C), glucose concentrations in the liquid effluent (as determined enzymatically) indicated a conversion of glucose *by hydrolysis* of 97% for a reactor residence time of 6 s, demonstrating the high reactivity of glucose even in the absence of oxygen. Measurements of the kinetics of glucose consumption by either global pathway were therefore not feasible at these temperatures and pressures. Glucose destruction rates under SCWO conditions were significantly faster than under wet-air oxidation conditions, where reaction times of 10 min or greater were required to achieve similar conversions (Ploos van Amstel and Rietema, 1970; Skaates et al., 1981).

Both hydrolysis and oxidation of glucose produced large quantities of gas, as shown in Figure 4. The extent of gasification in Figure 4 is defined as the moles of carbon present in the gaseous effluent divided by the moles of carbon fed to the reactor. Gasification was obviously more prevalent under oxidizing conditions, with 60% of the glucose carbon appearing in the gaseous effluent at 425°C, increasing to virtually 100% for temperatures of 500°C and higher. Under hydroly-

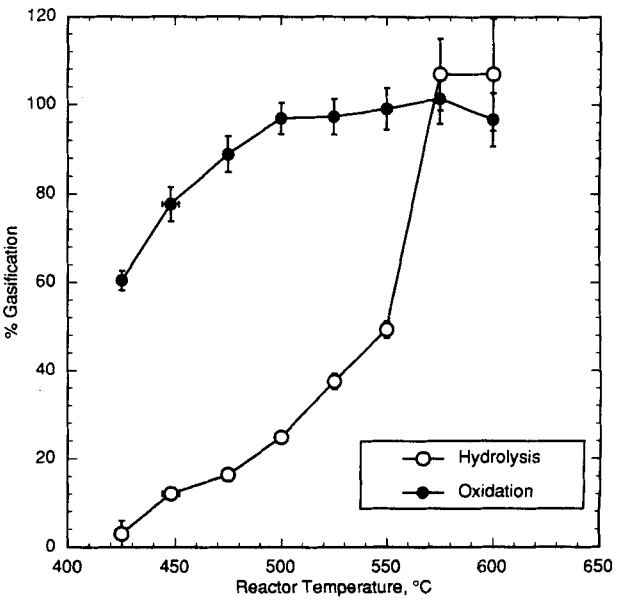

Figure 4. Variation of extent of glucose gasification with temperature during hydrolysis and oxidation.

Nominal initial conditions: 1×10^{-3} mol/L glucose, 6×10^{-3} mol/L oxygen; 6-s reactor residence time.

sis conditions, gasification was less extensive at low temperatures (~ 12% at 450°C), but rose quickly to 100% at 575 to 600°C. The large error in the extent of hydrolytic gasification at high temperatures stems from the very high gas flow rates (~ 40 mL/min) caused by the large amounts of gas produced (18 mol of gas per mol of glucose; see Eq. 1); in the present experimental system, high gas flow rates are difficult to measure precisely.

Products of glucose hydrolysis

Figure 5 shows the yields of major identified products from the glucose hydrolysis experiments. In this and subsequent figures, the product yield is defined as the moles of product divided by the moles of glucose reacted. Thus the maximum yield of carbon dioxide is 6, while the maximum yield of hydrogen is 12. Since the conversion of glucose was 97% or higher in all experiments, the product yield on a per-mole-reacted basis, as used here, is essentially the same as the yield on a per-mole-fed basis. Figure 5 indicates that the major constituents of the gaseous product of glucose hydrolysis are carbon dioxide, carbon monoxide, hydrogen, and methane, with smaller quantities of ethylene and ethane. Small quantities of ethylene in the presence of large quantities of carbon dioxide (such as at the higher hydrolysis temperatures) may have been lost due to inadequate GC peak separation; thus

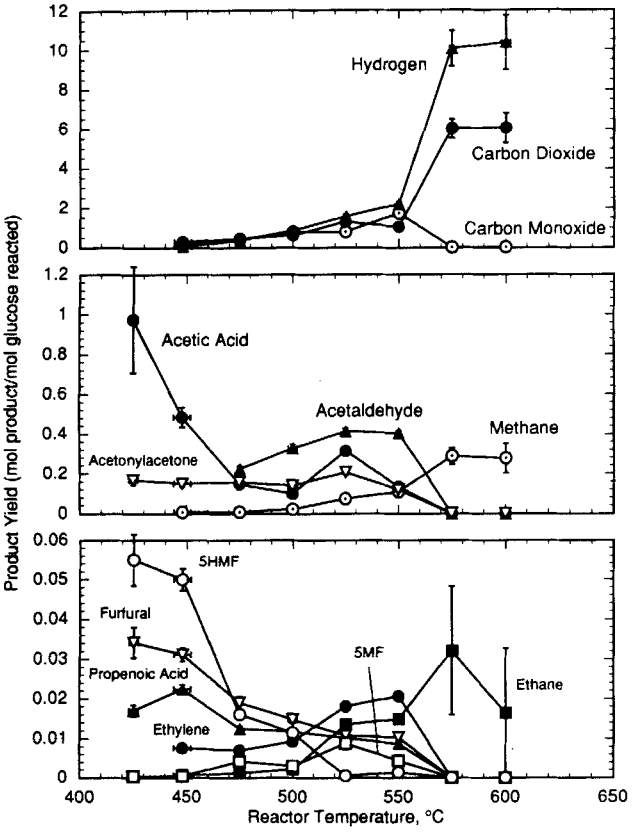

Figure 5. Variation of product yields with temperature for glucose hydrolysis at 246 bar.

Experimental conditions: $(1.02 \pm 0.02) \times 10^{-3}$ mol/L glucose, 6.1 ± 0.3-s reactor residence time.

the disappearance of ethylene at 575 and 600°C may be an artifact of analytical error. Hydrolysis at the highest temperatures yielded a gaseous effluent consisting almost exclusively of hydrogen and carbon dioxide in a 1.7:1 ratio, indicating the presence of a fast, water-gas-shift-type pathway ($CO + H_2O \rightarrow CO_2 + H_2$). These observations are generally consistent with the recently reported results of Antal and coworkers (Antal et al., 1992; Yu et al., 1993).

In particular, the hydrolysis results at 600°C show quite good agreement with the equilibrium calculations of Yu et al. (1993), which predict that carbon dioxide and hydrogen will be virtually the exclusive products. The small yield of methane in Figure 5 may be due to the conversion of methane to hydrogen and CO_2 by a slower steam-reforming pathway ($CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$). At higher glucose concentrations (> 0.1 mol/L), the equilibrium calculations indicate that CH_4 becomes increasingly stable, at the expense of CO_2 and H_2. Yu et al. also observed experimentally that the extent of glucose gasification (at 600°C, 345 bar, and 30 s) decreased with increasing glucose concentrations, for concentrations of 0.1 to 0.8 mol/L. These concentrations are more than two orders of magnitude greater than those used in the present work; at these lower concentrations the glucose was completely gasified at 600°C.

Hydrolytic reactions of glucose also produced large numbers of products in the liquid effluent (for example, see Figure 2). At the lowest temperatures, the majority of these products was unidentified, resulting in poor carbon balance closures. Typically only about 50% of the carbon was accounted for in identified products. As the temperature was increased, the extent of gasification increased and the carbon balance improved, with complete closure at 575 to 600° C, where the glucose was completely gasified and no liquid-phase products remained. The identified liquid-phase products of glucose hydrolysis were acetic acid, acetaldehyde, acetonylacetone, 5-hydroxymethylfurfural (5HMF), furfural, propenoic acid, and 5-methylfurfural (5MF). Acetaldehyde was not detectable below 475°C because its HPLC peak was obscured by a large, broad peak of unknown origin. The yields of all the liquid-phase products decrease steadily with increasing temperature, indicating that the stability of those species decreases sharply with increasing temperature. The exceptions are 5MF and acetaldehyde, whose formation is apparently favored at 475 to 550°C; these species may be intermediates in the destruction (hydrolysis) of more complex species. Similarly, the yields of methane, ethane, and ethylene increase steadily with temperature up to the highest temperatures, implying that these small gases are products of the hydrolysis of liquid-phase intermediates.

Products of glucose oxidation

Yields of identified products from the corresponding glucose oxidation experiments are shown in Figure 6. Yields of liquid-phase products are greatly reduced compared to hydrolysis conditions, and decrease with increasing oxidation temperature, with no liquid-phase products detected at temperatures above 550° C. Temperatures above 550° C are thus sufficient to ensure complete destruction of all intermediates produced from glucose, including acetic acid and furan derivatives. At the highest temperatures, glucose is converted

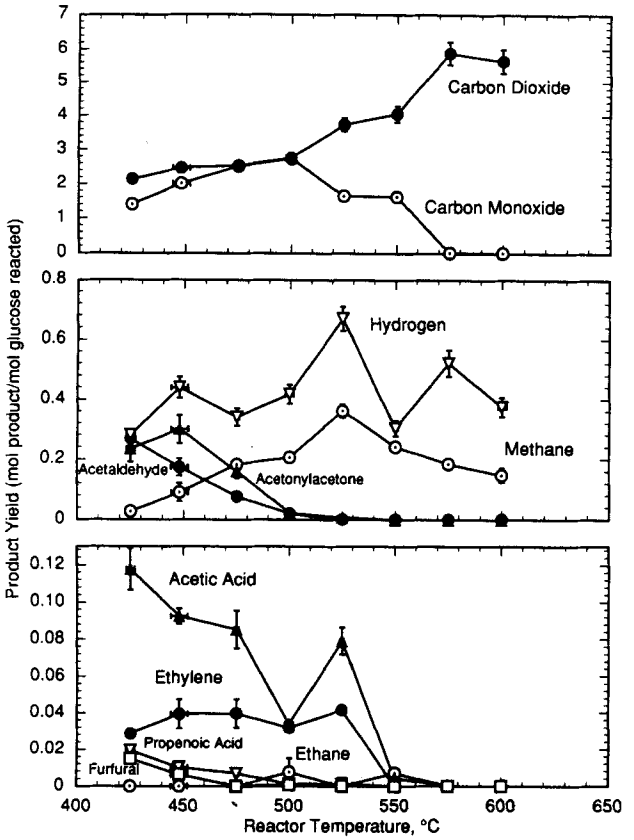

Figure 6. Variation of product yields with temperature for glucose oxidation at 246 bar.

Experimental conditions: $(0.99 \pm 0.02) \times 10^{-3}$ mol/L glucose, $(6.2 \pm 0.2) \times 10^{-3}$ mol/L oxygen, 5.9 ± 0.3-s reactor residence time.

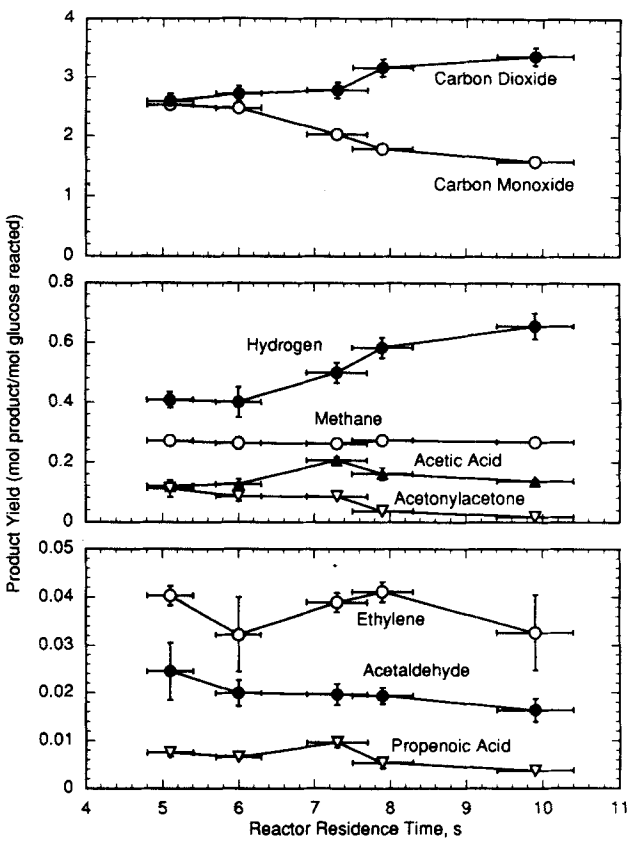

Figure 7. Variation of product yields with residence time for glucose oxidation at 500 ± 2°C and 246 bar.

Experimental conditions: $(1.01 \pm 0.02) \times 10^{-3}$ mol/L glucose, $(6.1 \pm 0.2) \times 10^{-3}$ mol/L oxygen.

almost entirely to carbon dioxide, with small quantities of hydrogen and methane also present. Ethylene may also be present at the highest temperatures, but it was not resolved by the GC from the high concentration of carbon dioxide. The average carbon-balance closure for the oxidation experiments was $103.4 \pm 7.1\%$. The stability of methane even at the highest temperatures is consistent with the earlier methane oxidation study in our group reported by Webley and Tester (1991), who found methane to be one of the more refractory species under SCWO conditions.

The pH (at ambient conditions) of the liquid effluent from the hydrolysis experiments ranged from 3.5 at the lowest temperatures to 4.75 at 600°C, while the pH of the oxidation effluent ranged from 4.25 at 425°C to 4.75 at 600° C. The seemingly low pH values at the high reaction temperatures are consistent with the presence of dissolved CO_2 in the liquid effluent. At the lower temperatures, the lower pH values for the hydrolysis experiments indicate that the yield of organic acids is higher than in the oxidation experiments, which is consistent with the yields in Figures 5 and 6.

Effect of feed preheating

The potential exists for reaction (hydrolysis) of the glucose during feed preheating in these experiments. Using heat-transfer coefficients derived earlier for our experimental system (Holgate et al., 1992), the residence time of the glucose feed in the feed preheating tubing was estimated to range from 14.7 s at 600° C to 11.7 s at 425° C. A significant fraction of this residence time (~ 4 s) is spent near the reaction temperature, such that the actual reaction time may be over 50% longer than the reactor residence time. In the oxidation experiments, the glucose may undergo hydrolysis prior to mixing with oxygen; the high efficiency of the oxidation indicates that any prehydrolysis of the glucose does not produce compounds that are refractory relative to oxidation.

Effect of residence time

Figure 7 shows the results of a series of stoichiometric oxidation experiments conducted at 500°C in order to evaluate the effect of reactor residence time on the observed product yields. In these experiments, the average extent of gasification was 89.1%, with an average of 101.7% carbon-balance closure. All products were thus well accounted for in these experiments. Comparison of the yields at 6 s in Figure 7 with the yields at 500°C in Figure 6 demonstrates the good agreement between the two sets of data (with the exception of the acetic acid yield), despite the fact that the two sets of results were obtained in different experiments. Figure 7 shows that over a 5-s span of residence times, the yields of the major products do not change markedly, indicating that reactions (oxidation) of these species occur relatively slowly at this

temperature. In fact, the range of residence times is effectively expanded by the change in flow rate required to vary the reactor residence time, combined with the effects of the changing flow rate on feed preheating. For example, at the longest reactor residence time (9.9 s), heat-transfer calculations indicate that the glucose feed spends an additional 16 s in the preheating tubing, with an additional 3 s at ~ 500°C. At the shortest reactor residence time (5.1 s), the glucose feed spends an additional 9 s in the preheating tubing, with only an additional 1 s at ~ 500° C. Thus the residence times at or near reaction temperature effectively range from 6.1 to 12.9 s. The lack of a pronounced change in species yields over this range of times is remarkable, but is in accordance with the observations of Antal et al. (1992) for hydrolysis at longer residence times. Rapid oxidation of these species requires higher temperatures. On the other hand, primary decomposition/oxidation of glucose, as well as secondary destruction of the more complex intermediates, must occur quite rapidly, in the first 5 to 6 s and/or during preheating of the glucose feed. The compounds shown in Figure 7 therefore represent the destruction-limiting species for treatment of glucose.

Effect of reactor surface

Reactor surface effects were not explicitly examined in this study. However, as noted earlier, Antal and co-workers (Yu et al., 1993) found evidence that Inconel and corroded Hastelloy catalyzed glucose gasification and the water-gas shift, resulting in high CO_2 yields and low CO yields. The reactor in our laboratory has been exposed to SCWO conditions for a total of several hundred hours and produces hydrolysis yields similar to Antal's "catalyzed" results. Other studies in our laboratory, using a packed-bed reactor, demonstrated that the role of the reactor surface is one of inhibition of reaction rate (Holgate and Tester, 1994). The "catalyzed" results seen here and in Antal's work may be more accurately characterized as less rate-inhibited, with newer reactor surfaces tending toward greater inhibition.

Mechanistic Implications of Product Spectra

The data in Figures 5 through 7 allow certain conclusions to be drawn regarding the mechanisms of glucose hydrolysis and oxidation in supercritical water. First, the absence of levulinic acid from the liquid effluent in all experiments is significant. Levulinic acid is typically formed from the ionic, acid-catalyzed hydrolysis of 5HMF (Kuster and Temmink, 1977). While 5HMF is present in the effluent of hydrolysis experiments, the absence of levulinic acid suggests that it either is not formed or is rapidly hydrolyzed. Experiments by Amin et al. (1975) and Woerner (1976) indicate that levulinic acid is relatively stable, and we thus conclude that the acid-catalyzed hydrolysis of 5HMF is not an operative pathway in supercritical water under these conditions. Disappearance of 5HMF must occur through another, possibly free-radical, mechanism.

The presence of propenoic acid among the products both of hydrolysis and of oxidation is consistent with the work of Mok et al. (1989), provided that lactic acid is first formed to a significant extent. Lactic acid is at least formed at lower temperatures and is identifiable in the effluent; at higher temperatures, lactic acid formation may continue, but degradative pathways may render the lactic acid concentration too low to be quantified. According to Mok et al. (1989), lactic acid undergoes parallel free-radical pathways: decarboxylation to CO_2, H_2, and acetaldehyde, and dehydration to propenoic acid. The acetaldehyde may then undergo further free-radical reactions to form acetic acid, acetone, and methane. Methane (along with carbon monoxide) is also a primary product of the gas-phase pyrolysis and oxidation of acetaldehyde (Colket et al., 1975a,b). Furthermore, propenoic acid may decarboxylate to ethylene and CO_2. Note that in Figures 5 and 6 the yields of methane and ethylene at the high temperatures are approximately equivalent to the yields of acetaldehyde and propenoic acid, respectively, at lower temperatures. This behavior supports the notion that methane is formed from acetaldehyde while ethylene is formed from propenoic acid.

Under the conditions of the present study, the pathway for formation of acetic acid from acetaldehyde does not appear to be operative, or acetic acid is significantly less stable than acetaldehyde. For example, once the decline in acetaldehyde yield begins, acetic acid concentrations are very low; if acetic acid is a major product of acetaldehyde decomposition, it must subsequently degrade quickly. Gas-phase studies of acetic acid decomposition (oxidation studies are virtually nonexistent) suggest that acetic acid decarboxylates to methane and carbon dioxide (Bamford and Dewar, 1949; Blake and Jackson, 1969). A consecutive pathway, in which acetaldehyde first formed acetic acid that then rapidly formed methane, would be indistinguishable from the direct formation of methane from acetaldehyde. The precise mechanistic relationship between acetic acid, acetaldehyde, and methane unfortunately cannot be determined from the present data. However, subsequent studies in our group of acetic acid hydrolysis in supercritical water have confirmed the existence of the decarboxylation pathway (Meyer, 1993).

Figure 5 indicates that between 550 and 575°C a fast water-gas-shift-type pathway becomes important, with carbon monoxide quickly converted to carbon dioxide for temperatures of 575°C and above. This behavior contrasts with other observations of the water-gas shift in the same reactor (Holgate et al., 1992; Holgate and Tester, 1994), in which the water-gas-shift reaction pathway was actually quite slow, even at temperatures approaching 600°C. The mechanism for this accelerated water-gas shift remains unexplained.

The limited response of the product yields in Figure 7 to increases in residence time, combined with the yield behavior in Figures 5 and 6, suggests that there are three kinetic regimes for the reactions of glucose in supercritical water. First, glucose undergoes rapid hydrolysis or oxidation to form a wide array of products, the more stable of which include acetic acid, acetaldehyde, acetonylacetone, and propenoic acid. The secondary reactions of these species are slower, and result in the formation of small quantities of stable light gases, including methane and ethylene. The tertiary destruction of these trace light gases ultimately limits the complete conversion of glucose to carbon dioxide and water.

Conclusions

Glucose hydrolysis and oxidation proceed rapidly and completely in supercritical water at 246 bar and 425 to 600°C, for

a glucose concentration of 1×10^{-3} mol/L and reactor residence times of 5 to 10 s. Diverse products are formed that are also susceptible to hydrolysis; at 600°C and a 6-s reactor residence time, glucose is completely gasified, even in the complete absence of oxygen. The presence of stoichiometric oxygen accelerates the destruction of the intermediate products, with no liquid phase products found above 550°C at a 6-s reactor residence time. The major, persistent intermediate products of glucose hydrolysis and oxidation were acetic acid, acetonylacetone, propenoic acid, and acetaldehyde in the liquid phase, and carbon monoxide, carbon dioxide, hydrogen, methane, ethane, and ethylene in the gas phase. Methane and hydrogen were present at trace levels in the effluent at temperatures up to 600°C at a reactor residence time of 6 s. The relative stability of certain intermediate products at 500°C suggests that rapid, high-efficiency oxidation of glucose requires temperatures of 500–600°C.

While this limited study of glucose hydrolysis and oxidation in supercritical water was not able to provide global kinetic data, important products of both pathways have been characterized. The identified products were frequently the most refractory products formed, indicating that their destruction may, under certain circumstances, limit complete destruction of glucose; for this reason alone, the identification of these species was important. Future experiments at lower, subcritical temperatures (150 to 280°C) should provide more quantitative kinetic information. More sophisticated analytical techniques, including additional liquid chromatography and/or gas chromatography with mass spectrometry using improved columns and EPA standard methods, will be required to identify positively the liquid-phase products formed at the lower temperatures.

Acknowledgments

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