INTRODUCTION

The State of Hawaii is a leading producer of sugarcane and pineapples. The phytomass waste that results from this production is mainly burned to generate electric power. To use lignocellulose materials more effectively some programs are under development. One of the most promising seems to be the conversion of phytomass under pressure and temperature higher or near the critical point of the solvent into chemicals. Near this point the chemical and physical properties of solvent are both liquid- and gas-like and the fluid could be very useful for production of chemicals with higher yields and selectivity obtained using more conventional conditions. The factors affecting supercritical (SC) processing are solvent, catalyst, parameters of the reactor and accessibility of substrate.

The dehydration of cellulose and chitin in supercritical acetone resulted in the formation of anhydrosugars with acceptable yields (1). We used water as a solvent because of its excellent characteristics as a solvent for carbohydrates, its ionic strength, and lower solubility of dehydration products. The reactions which we could suppose to take place under SC conditions in the presence or without inorganic acids or bases are mutarotation, epimerization, dehydration, degradation reaction to levulinic acid, saccharinic acids, as well as, aldol- and retro-al dol reaction. From all the products the most important seems to be 1,6-anhydro-β-D-glucopyranose, 5-hydroxymethylfuraldehyde, 2-furaldehyde, and levulinic acid.

Most of the authors who studied production of chemicals from phytomass or its model compounds under SC conditions used batch or semi-continuous reactors (1-6). The negative effect of these reactors on reactions taking place are diminished heat transfer, lower reproducibility, and industrial applicability in comparison to flow reactors. In this paper we discuss the processing of D-glucose using the SC flow reactor under sub- and supercritical conditions.

EXPERIMENTAL

Prior to the initiation of flow, the system is brought up to pressure by an air compressor. Premixed reactant solutions were pumped into the reactor at a controlled flow rate by an HPLC pump. The solution flow through the reactor, pass a 10 port valve dual loop sampling system, and is collected in product accumulator. The flow of products into the accumulator displaces air through a back-pressure regulator which maintains the reactor system at the desired pressure.
The reactant flow is rapidly heated to reaction temperature by the entry heat guard, and maintained at isothermal conditions by a Trans-temp Infrared 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 1.4 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 temperatures and temperatures measured at 10 fixed positions along the outer wall of the reactor using type K thermocouples. The entire reactor and sampling system is housed in a protective enclosure which can be purged of air (oxygen) during studies involving flammable solvents (such as methanol).

The reactor apparatus can be characterized by the following representative nondimensional numbers: \( Re = 420, \) \( Pr = 1.86, \) \( Sc = 0.86, \) \( Pe_n = 776 \) (thermal diffusion), \( Pe_m = 358 \) (species diffusion), and \( Da = 0.40. \) We have determined from the temperature profile of the reactor during operation that 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.

**RESULTS AND DISCUSSION**

Results of experiments probing the dehydration chemistry of D-glucose in SC water \( (P = 34.5 \text{ MPa}) \) are summarized in Table 1. We began the first experiment at 200°C. As can be seen under this condition no dehydration products were observed and only a small amount of D-glucose was epimerized to D-mannose. At 250°C we observed 5-hydroxymethylfuraldehyde as the only dehydration product. The presence of sulphuric acid or sodium hydroxide increased the conversion of substrate. The acid increased the yield of dehydration product and also 2-furaldehyde occured as product of pentose dehydration. On the other hand, base decreased the yields of furan derivatives and produced lactic acid as a beta elimination, benзilic acid rearrangement, and retro-aldol reaction product. The decrease of flow rate and omission of catalysts increased the yield of 5-hydroxymethylfuraldehyde, as well as the conversion. A further increase of temperature to 275°C increased the conversion of substrate and yield of dehydration product. The presence of acid decreased yield of furan derivatives. In the presence of sodium hydroxide lactic acid was the predominant product. At 300°C and in absence of catalyst the yield of furan derivatives increased further. These results confirm that water is more selective for dehydration when used without catalyst in the SC flow reactor. In some experiments we were not able to identify some degradation products. This resulted in lower carbon balances than have been reported in our earlier work.
When the reaction was run under supercritical conditions (385°C, residence time of 24 seconds) the yield of furan derivatives decreased dramatically and products of retro-aldol reaction (acetol and formaldehyde) were observed. The levulinic acid was probably destroyed in this way. Under SC conditions gaseous products were also observed. Their presence indicate that decarbonylation, decarboxylation, and other fragmentation reactions were taking place. These were probably due to homolytic reaction processes.

CONCLUSIONS

The reactions of D-glucose at 34.5 MPa and temperature interval from 200 to 385°C in SC flow reactor are epimerization, dehydration, degradation to acids, and retro-aldolization. The experiments confirmed that water when used without catalyst is more selective for dehydration. Further research will follow to increase the yield of selected products.

REFERENCES


131
TABLE 1
Processing of D-Glucose in SC Flow Reactor at 34.5 MPa

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>YIELD (%)^a</th>
</tr>
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<tbody>
<tr>
<td>C₆H₁₂O₆^b</td>
<td>52 24 11 3 20 8 1 1 -- --</td>
</tr>
<tr>
<td>C₆H₁₂O₆^c</td>
<td>-- 4 2 2 1 1 -- -- -- --</td>
</tr>
<tr>
<td>C₆H₁₀O₃^d</td>
<td>-- 23 27 25 5 31 18 5 21 3</td>
</tr>
<tr>
<td>C₅H₄O₂^e</td>
<td>-- -- -- 9 -- 10 12 -- 13 1</td>
</tr>
<tr>
<td>C₃H₆O₃^f</td>
<td>-- -- -- -- 10 -- -- 81 -- --</td>
</tr>
<tr>
<td>C₃H₆O₂^g</td>
<td>-- -- -- -- -- -- -- -- -- 23</td>
</tr>
<tr>
<td>C₂H₄O₂^h</td>
<td>-- -- -- -- 7 -- -- -- -- 10</td>
</tr>
<tr>
<td>CH₂O^i</td>
<td>-- -- -- -- -- -- -- -- -- 36</td>
</tr>
<tr>
<td>CATALYST^j</td>
<td>-- -- -- H₂SO₄ NaOH -- H₂SO₄ NaOH -- --</td>
</tr>
<tr>
<td>TEMPERATURE^k</td>
<td>200 250 250 250 250 275 275 275 300 385</td>
</tr>
<tr>
<td>RESIDENCE TIME^l</td>
<td>41 38 76 38 38 35 36 36 49 24</td>
</tr>
<tr>
<td>CONVERSION (%)</td>
<td>5 38 57 53 89 62 82 97 98 97^m</td>
</tr>
</tbody>
</table>

^a100 (moles of product/moles of reactant converted). ^bD-Mannose.
^cD-Fructose. ^d5-Hydroxymethylfurfuraldehyde. ^e2-Furaldehyde. ^fLactic acid.
^gAcetol. ^hGlyceraldehyde. ^iFormaldehyde. ^j5 mM of catalyst. ^kDegrees of
Centigrade. ^lSeconds. ^mAlso gaseous products: Carbon monoxide (9.3 %), carbon
dioxide (55.7 %), hydrogen (34.5 %), methane (0.2 %), ethylene (0.3 %), and ethane (0.1 %).
PYROLYSIS AND SOLVOLYSIS OF BIOMASS IN SUPERCRITICAL FLUID SOLVENTS
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ABSTRACT
The reactions of diaryl ethers and alkanes were examined in water at varying densities. The ethers, namely benzyl phenyl ether (BPE), phenethyl phenyl ether (PPE) and dibenzyl ether (DBE) underwent parallel pyrolysis and hydrolysis. The former paths led to the usual products described in the literature, whereas the latter led to benzyl alcohol plus phenol, phenethyl alcohol plus phenol and two mols of benzyl alcohol for BPE, PPE and DBE, respectively. 1,2-Diphenylethane (DPE) and 1,3-diphenylpropane (DPP) fragmented according to the neat pyrolysis pathway only, even at the highest water density studied.

The solvolysis was evidently substitution at a saturated carbon atom to which was attached a heteroatom-containing leaving group. Kinetics analysis of the DBE experiments allowed decoupling of the pyrolysis and solvolysis rates, which further permitted correlation of the solvolysis rate constant with the solvent dielectric constant. Good correlation on this Kirkwood plot suggests the solvolysis proceeds through a transition state that is more polar than the reactants.

INTRODUCTION
The extreme pressure-volume-temperature behavior of fluids at or near their critical point has focussed considerable attention on the extraction of volatiles from, and synfuels-related processing of, high molecular weight, low-volatility materials including biomass [10]. More recently, it has been established that reaction in and with the solvent might assist [1, 7, 15]. However, information about the kinetics and mechanisms controlling these reactions is usually obscured during experiments with actual biomass by the complexity of the substrate and its structure. This motivates the use of model compounds whose structures and product spectra are well enough characterized to allow the deduction of reaction pathways, kinetics and mechanisms.

The present report is of a probe into the effect of supercritical water on the reaction paths of the
diaryl ethers BPE, PPE and DBE and the diaryl alkanes DPE and DPP. The thermal reactions of these compounds having been well studied previously, they afforded an excellent opportunity to explore the effect of supercritical water on their reactions.

**EXPERIMENTAL**

The model compounds were reacted neat and in water at conditions summarized in Table 1. The reduced density of water \( (\rho_{r,w} = \rho / \rho_{c,w}) \) ranged from 0.0 to 2.1. Except for PPE, the reactants, solvents, and GC standards were commercially available and used as received. PPE was synthesized according to the method of Mamedov and Khydyrov [8].

A typical experimental procedure was as follows: measured amounts of the reactant, solvent and the demonstrably inert [15] internal standard biphenyl were loaded into "tubing-bomb" reactors comprising one 1/4 in. stainless steel Swagelok port connector and two end caps. These constant volume batch reactors had a volume of 0.59 cm³. Sealed reactors were immersed into a fluidized sand bath and reached the desired reaction temperature, ±2 °C, in about 2 minutes. After the desired time had passed, the reactions were quenched by immersion in a cold water bath.

Reaction products were collected as a single phase in acetone. Subsequent product identification was by GC-MS; and routine quantitation was by gas chromatography on an HP 5880 instrument equipped with a 50 M SE-54 or DB-5 fused silica capillary column and flame ionization detector. Response factors were estimated by analysis of standard mixtures.

**RESULTS**

Experimental results are presented in sections allotted to each model compound. Within each section, results are presented in terms of reaction products and kinetics, first for pyrolysis and then for reaction in water.

**Benzyl Phenyl Ether.** Neat pyrolysis of benzyl phenyl ether (BPE) at 332°C led to phenol and toluene as stable primary products, as indicated by their positive initial and zero final slopes in Figure 1, a plot of molar yield \( (n_r/n_{1,0}) \) vs. reaction time. Minor products included, in order of decreasing yield, o-hydroxydiphenylmethane (OHD), p-hydroxydiphenylmethane (PHD), diphenylmethane, benzaldehyde, benzene, 1,2-diphenylethane and t-stilbene. Linear regression showed the apparent first-order disappearance rate constant for BPE at 332°C to be 9.45 x 10⁻¹⁴ s⁻¹.

BPE reaction in water, at 332°C and an overall water loading \( \rho_{r,w} = 1.6 \), was almost four times as fast as neat pyrolysis at the same reaction temperature. Figure 1 also illustrates the differences
between the product spectra for neat pyrolysis of BPE and its reaction in water at $\rho_{t,w}=1.6$. Benzyl alcohol, produced in only trace quantities during neat pyrolysis, was a major hydrolysis product. After reaching its maximum yield of 0.45 at 8 minutes, benzyl alcohol underwent secondary reaction to extinction by 45 minutes.

The ultimate yields of the stable products OHD and PHD were also dependent upon $\rho_{t,w}$. The maximum OHD yield of 0.098 observed during neat pyrolysis at 332°C was about one third of the value of 0.26 observed from reaction in water at $\rho_{t,w}=1.6$. Similarly the yield of PHD increased from a value of 0.05 after 45 minutes during neat pyrolysis to a value of 0.18, after only 30 minutes, during reaction of BPE in water.

The effect of $\rho_{t,w}$ on reaction of BPE in water is illustrated in Figure 2 as a plot of product selectivity ($s = \frac{y_i}{x}$) vs. $\rho_{t,w}$ for a constant reaction time of 5.6 minutes. BPE conversion (x) increased monotonically with reduced water density from a value of 0.85 at $\rho_{t,w}=0.0$ to essentially unity for $\rho_{t,w} \geq 1.5$. Selectivity to the pyrolysis product toluene decreased with increasing water density from 0.25 at $\rho_{t,w}=0.0$ to 0.05 at $\rho_{t,w}=2.1$. Selectivity to phenol, which resulted from both pyrolysis and solvolysis, increased from a low value of 0.58 at $\rho_{t,w}=0.0$ to 0.80 at $\rho_{t,w}=1.1$. Selectivity to benzyl alcohol increased from 0.0 at $\rho_{t,w}=0.0$ to a maximum of about 0.50 at $\rho_{t,w}=1.2$, at which point secondary reactions of benzyl alcohol were significant by 5.6 minutes. Furthermore, but not illustrated in Figure 2, the selectivity to both OHD and PHD increased, as $\rho_{t,w}$ increased from 0.0 to 2.1, from lows of 0.08 and 0.03 to highs of 0.21 and 0.13 for OHD and PHD, respectively.

These results suggest that reaction of BPE in water is a combination of a thermal pathway leading to phenol and toluene and a hydrolysis pathway that yields phenol and benzyl alcohol. The thermal pathway is like that reported for BPE thermolysis by Brüker and Kölling [2], Schlosberg et al. [13], Sato and Yamakawa [11] and Kamiya et al. [5]. The hydrolysis reaction is the addition of one mol of water to one mol of BPE producing one mol each of phenol and benzyl alcohol. Selectivity to the hydrolysis pathway increased with increases in reduced water density.

**Phenethyl Phenyl Ether.** The major primary products from the neat pyrolysis of phenethyl phenyl ether (PPE) were phenol and styrene. Styrene underwent secondary decomposition to ethyl benzene, toluene, benzene and other minor products. PPE reaction in water also led to phenol and styrene, but in addition afforded phenethyl alcohol. Reactions in $\text{H}_2^{18}\text{O}$ showed incorporation of the label into the phenethyl alcohol.
The influence of $\rho_{r,w}$ on the selectivity to products at 413°C is summarized in Figure 3 as a plot of $s_1$ vs. $\rho_{r,w}$ for a constant reaction time of 16 minutes. PPE conversion was about 0.40 at $\rho_{r,w}=0.0$ and leveled off at 0.25 for $\rho_{r,w} \geq 0.2$. Selectivity to styrene increased from 0.29 at $\rho_{r,w}=0.0$ to an average value of 0.52 for $\rho_{r,w} \geq 0.2$. Selectivity to phenol averaged at about 1.0. The selectivity to phenethyl alcohol increased from essentially zero at $\rho_{r,w}=0.0$ to 0.06 at $\rho_{r,w}=1.4$.

These results suggest that the overall reaction of PPE in water is by two paths, the first of which being pyrolysis to phenol and styrene and the second of which being hydrolysis to phenol and phenethyl alcohol. The neat pyrolysis pathway is identical to that observed by Klein and Virk [6]. The hydrolysis of PPE was equivalent to the addition of one mol of water to one mol of PPE to produce one mol each of phenol and phenethyl alcohol.

Dibenzyl Ether. Neat pyrolysis of dibenzyl ether (DBE) at 374°C led to toluene and benzaldehyde as major primary products. Its reaction in water at 374°C led to benzyl alcohol, toluene, benzaldehyde, and oligomers. DBE decomposition in water at $\rho_{r,w}=1.6$ was about 3.5 times as fast as neat pyrolysis; benzyl alcohol was the major and essentially the only primary product at this water density. The yield of benzyl alcohol reached a maximum and then decreased at longer times as it reacted to oligomers. The foregoing suggests that DBE reaction in water comprises two parallel pathways, with the first being identical to the neat pyrolysis reported by Schlosberg et al. [12] and also thermolyses in hydrogen donor noted by Bröcker and Kölling [2], Cronauer et al. [3] and Simmons and Klein [14]. The second pathway is hydrolysis of one DBE mol to two benzyl alcohol mols.

1,2-Diphenylethane. Neat pyrolysis of 1,2-diphenylethane (DPE) at 500°C produced toluene as the major and primary product; t-stilbene, benzene, ethyl benzene, phenanthrene, and diphenylmethane were all minor primary products. Trace amounts of styrene and triphenylethylene were also present.

Reaction of DPE in water at 500°C and $\rho_{r,w}=1.4$ also led to toluene as the major primary product. Observed minor products were those formed during neat pyrolysis. Products' yields from neat pyrolysis and reaction in water were virtually identical. Thus, no additional pathways were identified for the reaction of DPE in water.

1,3-Diphenylpropane. Neat pyrolysis of 1,3-diphenylpropane (DPP) at 420°C led to toluene and styrene; styrene underwent secondary conversion to other products including ethyl benzene.
Minor products included 1,2-diphenylethane, benzene, and n-propyl benzene, all present in molar yields of less than 0.05. Reaction of DPP in water at 420°C and $\rho_{r,w}=1.6$ led to the same products in approximately the same molar yields as did pyrolysis. Thus pyrolysis was the lone operative pathway during reaction of DPP in water.

**DISCUSSION**

Reaction of the diaryl ethers BPE, PPE and DBE in water was via parallel pyrolysis and solvolysis pathways. The diaryl alkanes DPE and DPP, on the other hand, fragmented by only a neat pyrolysis pathway, even at the largest $\rho_{r,w}$ studied. Since all of the model compounds pyrolyse by a set of free-radical elementary steps, it is reasonable to suspect that solvolysis does not proceed through a transition state involving water and a thermally generated radical. In fact, the empirical observation that solvolysis occurred between water and an organic molecule with a saturated carbon to which was attached a heteroatom-containing leaving group suggests the chemistry may be like the classic liquid-phase nucleophilic substitution at saturated carbon. Solvolysis involving supercritical methanol and also a N-containing organic has been observed also [1]. Note that heterocyclics, devoid of saturated carbons, did not undergo solvolysis. Another mechanism must therefore govern the solvolysis reaction.

Thus the transition state is likely more polar than the reactants, which are neutral molecules. The class of reaction illustrated in Equation (1)

\[ \text{molecule} + \text{molecule} \Leftrightarrow \text{polar transition state} \Rightarrow \text{products} \quad (1) \]

is amenable to division of the free energy of activation $\Delta G^\\text{f}$ into an electrostatic and a non-electrostatic part, the former being influenced by the solvent dielectric constant as developed in the classic Kirkwood analysis. For the present reactions, where the activated complex is more polar than the reactants, the solvolysis rate constant should increase with increasing solvent dielectric constant [9] and afford a linear correlation of $\ln k_s$ with the function $(\epsilon-1/\epsilon)$.

The kinetics data for reaction of DBE in water at 374°C were reduced for pyrolysis and solvolysis rate constants for each $\rho_{r,w}$ studied. The solvolysis rate constant and Franck's [4] measurements of $\epsilon$ vs. $\rho$ for water allowed construction of the Kirkwood plot of Figure 4. The linear relationship between $\ln k_s$ and $\rho_{r,w}$ supports the proposed polar transition state.
SUMMARY AND CONCLUSIONS

1. Reaction in water of the diaryl ethers was by parallel pyrolysis and solvolysis. The diaryl alkanes afforded only pyrolysis products, even at reduced water densities of greater than 1.4.

2. Whereas the pyrolysis occurred via a set of free-radical elementary steps, the solvolysis was likely via nucleophilic substitution that proceeded through a polar transition state.

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<table>
<thead>
<tr>
<th>Reactant</th>
<th>T(°C)</th>
<th>$r_{w}$</th>
<th>t (min)</th>
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<tr>
<td><img src="image" alt="BPE" /></td>
<td>332</td>
<td>0, 1.6</td>
<td>0-60</td>
</tr>
<tr>
<td><img src="image" alt="PPE" /></td>
<td>377</td>
<td>0.0-2.1</td>
<td>5.6</td>
</tr>
<tr>
<td><img src="image" alt="DBE" /></td>
<td>413</td>
<td>0.0-1.4</td>
<td>16</td>
</tr>
<tr>
<td><img src="image" alt="DPE" /></td>
<td>374</td>
<td>0.0-1.6</td>
<td>0-60</td>
</tr>
<tr>
<td><img src="image" alt="DPP" /></td>
<td>500</td>
<td>0.0, 1.4</td>
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<tr>
<td><img src="image" alt="DPP" /></td>
<td>420</td>
<td>0.0, 1.6</td>
<td>0-60</td>
</tr>
</tbody>
</table>

Table 1: Summary of Experimental Conditions
Figure 1: Reaction of Benzyl Phenyl Ether, Neat and in Water
$T = 332^\circ C$

Figure 2: Reaction of Benzyl Phenyl Ether in Water
$T = 377^\circ C$, $t = 5.6$ minutes
Figure 3: Reaction of Phenethyl Phenyl Ether in Water
\[ T = 413^\circ C, \, t = 16 \text{ minutes} \]
Figure 4: Variation of $k_s$ with Solvent Dielectric Constant
Reaction of DBE in Water, $T = 374^\circ C$
Formation of Aromatic Compounds from Carbohydrates. X
Reaction of Xylose, Glucose, and Glucuronic Acid in Acidic Solution at 300°C

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David A. Nelson* and Richard T. Hallen
Chemical Sciences Department, Pacific Northwest Laboratory, Richland, WA 99352 USA

INTRODUCTION

For several years our respective groups have investigated the formation of aromatic compounds from carbohydrates in aqueous solution at various pH-values under reflux or hydrothermolytic conditions. For instance, previous papers (1-6) in this series concerned the degradation of hexoses, pentoses, erythrose, dihydroxyacetone, and hexuronic acids to phenolic and enolic components. Of particular interest were the isolation and identification of catechols, an acetophenone, and chromones from pentoses and hexuronic acids at pH 4.5 (1,2). The formation of these compounds, as well as reductic acid (7), was found to be more pronounced than that of 2-furaldehyde (2) under acidic conditions. The aromatic precursors of 3 and 4 were also isolated from these reaction mixtures. This is in contrast to the high yield of 2 obtained from pentoses (8) and hexuronic acids (9) at very low pH. Similar products were obtained in lower yield from glucose and fructose under acidic conditions (10). However, the predominant product of these hexoses was 5-hydroxymethyl-2-furaldehyde (1) as would be expected from prior work (11). Surprisingly, similar products are noted at neutral and even alkaline pH with glucose and xylose (12). Previous hydrothermolytic studies of cellulose indicated that certain aromatic products could be obtained when the pH was maintained in the range of 4-11 (13). This suggested that aldol condensation, a prime route for the production of aromatics from saccharides, could function under moderately acidic conditions.

The current research was initiated to study the competition between the formation of phenolic compounds (aldol involvement) and that of furans (dehydration and cyclization). Hydrothermolytic (liquefaction) conditions, 5-7.5 minutes at 300°C, were chosen to examine the effect on potential biomass
materials while exposed to mild acid. Xylose and glucuronic acids were previously found to provide higher yields of phenols than glucose. It is also of increasing interest for those involved with the hydrolysis of biomass, including steaming and autohydrolysis under slightly acidic conditions at 170-250°C, to obtain substrates for various fermentation processes or as a pretreatment for other uses. It is very likely that the aromatic products, particularly those formed from pentosans and polyuronides, may have an inhibiting effect on fermentation processes. More information, therefore, is needed concerning the formation of aromatic components and their precursors from the high temperature, aqueous processing of biomass.

EXPERIMENTAL

A series of 3.0 mL capacity tubing autoclaves (316 stainless steel) were used. Each tube was 0.6 x 9 cm and sealed with Swagelok™ fittings. The tubes were charged with 0.27 g sodium glucuronate, 0.19 g D-xylose, or 0.22 g D-glucose, respectively. Buffered acid solutions (2.0 mL) were added to the tubes. For instance, sodium acetate-acetic acid buffer was used for the pH 3 to 4 reactions, while a potassium chloride-hydrochloric acid buffer was used for the pH 1.7-1.9 reactions. The void space of each tube was swept with nitrogen prior to insertion into a 300°C sand bath. Interior tube temperature was reached 300°C within 2.5 minutes, while quenching to below 100°C required only 0.1 minute. The solutions after cooling, which in all nine experiments were dark brown, contained minimal or no precipitate. The tube contents were extracted with ethyl acetate, dried, and the solvent was removed. Gas chromatographic analyses were obtained with a Hewlett-Packard 5880A instrument using a DB capillary column.

RESULTS AND DISCUSSION

The yields of the solvent free extracts are presented in Table 1. Column A shows the standard wt.% yields. Column B was formulated to show a loss of

Table 1. Yields of Ethyl Acetate Extracts After Acidic Treatment of Glucose, Xylose, and Glucuronic Acid at 300°C

<table>
<thead>
<tr>
<th>pH</th>
<th>Time(min.)</th>
<th>Glucose</th>
<th>Xylose</th>
<th>Glucuronic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>5</td>
<td>37</td>
<td>27</td>
<td>20</td>
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<tr>
<td>3.6</td>
<td>5</td>
<td>40</td>
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<td>31</td>
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<tr>
<td>3.0</td>
<td>5</td>
<td></td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>7.5</td>
<td></td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>5</td>
<td></td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>

*A equals wt.% based on the amount of carbohydrate.

**B equals wt.% based on glucose or xylose minus 3 H2O, and glucuronic acid minus 3H2 and CO2.
three moles of water for glucose and xylose and a loss of one mole of carbon
dioxide for glucuronic acid. This represents the conversion of carbohydrates
to furan or phenolic components. The standard yields (column A) give mixed
results when pH is compared; i.e., xylose shows higher yields at higher pH,
while glucuronic acid does not. This may reflect two different mechanisms,
however. These solvent extracted yields are rather close to those obtained
under basic conditions (13).

There was some change in pH after the acidic hydrothermolysis of glucose,
xylose, and glucuronic acid. The aqueous phase of glucose and xylose increased
from pH 1.7 to about 2.6 after 5 min at 300°C. Those reactions of xylose
buffered at pH 3.6 held that acidity level rather well. The pH of the
glucuronic acid reactions tended to increase more than those of xylose
regardless of buffer; i.e., pH 1.9 to 3.2, 3.0 to 3.4, 3.6 to 3.8, and 4.0 to
5.2. This probably could be partially attributed to the decarboxylation of
the glucuronic acid.

Table 2 presents the quantitative results of those components volatile
enough for gc analysis. At low pH the furan compounds predominate when both
Table 2. Major Identified Components of Glucose, Xylose, and Glucuronic Acid
After Hydrothermolysis at 300°C with Various Times and pH

<table>
<thead>
<tr>
<th>Component</th>
<th>Glucose* pH 1.7 5 min</th>
<th>Xylose pH 1.7 5 min</th>
<th>Xylose pH 3.6 5 min</th>
<th>Xylose pH 3.6 7.5 min</th>
<th>Glucuronic Acid pH 1.9 5 min</th>
<th>Glucuronic Acid pH 3.0 5 min</th>
<th>Glucuronic Acid pH 3.6 5 min</th>
<th>Glucuronic Acid pH 2.8 5 min</th>
<th>Glucuronic Acid pH 4.0 5 min</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>19.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>8.4</td>
<td>46.5</td>
<td>6.9</td>
<td>2.9</td>
<td>2.7</td>
<td>0.7</td>
<td>—</td>
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</tr>
<tr>
<td>3</td>
<td>—</td>
<td>—</td>
<td>3.5</td>
<td>6.5</td>
<td>3.8</td>
<td>4.2</td>
<td>16.7</td>
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<td>8.6</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>0.5</td>
<td>4.1</td>
<td>0.9</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>—</td>
<td>0.4</td>
<td>8.3</td>
<td>8.5</td>
<td>2.3</td>
<td>3.3</td>
<td>—</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

* Values are reported as mole%; oil yields are reported in Table 1; those values
not reported are <0.1%.

Glucose and xylose are exposed to 300°C. This is not unexpected since all
pentoses form 2-furaldehyde (2) in high yield when exposed to aqueous acid
solution (14). However, the presence of 2 in the glucose reaction mixture is
of interest. The major product obtained from hexoses at elevated temperatures
and aqueous acid is 5-hydroxymethyl-2-furaldehyde (1) with minor amounts of 2-
(hydroxyacetyl)furan (15). The 2-furaldehyde has been detected after acidic
treatment of fructose(16), glucose(15,17), and is a major component after the thermolysis of cellulose in distilled water(13). One plausible explanation for the formation of 2 may involve loss of formaldehyde(18) from glucose with consequent pentose formation. It should be noted that the pyrolysis of 1 does produce a small amount of 2(19). However, the reaction conditions are sufficiently different to suggest a different mechanism for hydrothermolysis.

The xylose results are also notable with the increase of 3 and 5 at pH 3.6 and longer time. In contrast, 2 decreased with increased pH and time. During previous work(1) with xylose in refluxing acid at pH 4.5, 1,2-dihydroxybenzene (3) was not detected. However, 3 has been detected after xylose was exposed to refluxing caustic solution(12). The presence of 3 in basic solutions of xylose was attributed to retro-aldol and re-aldol reactions since both xylose and glucose yielded the same type of products. Unfortunately, this does not explain the presence of 3 in the acidic hydrothermolysis product, but it has been shown that the aldol reaction can occur at pH 4.0(13). Detection of 3,8-dihydroxy-2-methylchromone(5) has been noted previously in xylose solutions at pH 4.5(1,20). Since 5 is a ten-carbon product, it is presumed that at least two moles of xylose were necessary for its composition. Thus, the mole % values of 5 (Table 2) should be doubled to reflect this. Further support for this was recently demonstrated by E. Olsson, N. Olsson, and O. Theander in unpublished work during the preparation of 5 at pH 5 and 100° from 1-13C-pentose (prepared by a Kilinj synthesis involving erythrose and K13CN). The major distribution of the 13C-label was at the 2-methyl and C-8a positions.

The results from glucuronic acid do not appear quite as informative as those from xylose. The 2-furaldehyde content decreased with increasing pH; none was observed beyond pH 3.0. Correspondingly, the amount of phenolic components (3 and 4) increased with pH, but reached a maximum at pH 3.6. The decrease of 3 and 4 after 7.5 min at pH 3.6 may be due to instability of those components toward the thermal conditions, however degradation of 3 at pH 4.5 was negligible at 100°(1). The results at pH 4.0 do suggest a contribution from the decreasing acidity. The decrease of 5 with increasing pH is also of interest since it had previously been isolated from glucuronic acid exposed to pH 4.5 and 100°(1,20). The Table 2 values obtained for 3, 4, and 5 from glucuronic acid may also represent only 50% of the mole percentage since each component may require more than one mole of glucuronic acid for its preparation.

Several unidentified components were also observed in the reaction mixtures of hydrothermolized glucuronic acid and xylose. Unfortunately, isolation attempts were not successful for these products. These components (m/e 164 and 162 from glucuronic acid and xylose, respectively) were found in moderate amounts.

It is evident from the results of this research that phenolic products, especially 3, may be obtained by the acidic hydrothermolysis of xylose and glucuronic acid containing materials. The phenolics and 2-furaldehyde could contribute toward the inhibition of fermentation organisms if acidic pretreatment procedures are not carefully controlled.
ACKNOWLEDGMENTS

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REFERENCES

INTRODUCTION

Very little research has been done to explore commercial application of the thermochemical degradation of polysaccharide materials to organic acids in alkaline solution. Much of the work on alkaline degradation of polysaccharides has been conducted at 100°C or lower to investigate mechanisms of degradation, reaction termination and the effects of molecular structure (1-4). However, little conversion of polysaccharides to acids occurs at these low temperatures. Most investigations at higher temperatures have involved study of the alkaline pulping process at approximately 170°C (5,6), where polysaccharide degradation is limited and not desired. Chesley et al. (7) proposed a commercial method for producing formic, acetic, glycolic and lactic acids from cellulosic materials. However, optimum process parameters were not clear, kinetic data was not obtained, additional acids were not identified, and most of the starting polysaccharide material was not accounted for. More recent work has provided additional information on the thermochemical degradation of cellulose to organic acids at reaction conditions of practical interest (8,9). However, no additional organic acids were identified, and the acid production data was difficult to interpret because of long heat-up times. No data has been reported for the important polysaccharide, starch, at reaction conditions of practical interest.

The object of this study was to obtain and compare kinetic data for the thermochemical degradation of starch and cellulose to organic acids in alkaline solution. Reaction conditions leading to substantial or complete degradation in short times were selected so that the results could have practical application to the production of organic acids. Data for the formation of seven identified acids were also collected to allow determination of reaction conditions leading to optimum yields. The reaction system used in a previous study (8) was modified to allow rapid attainment of reaction temperatures, thus making kinetic data more easily analyzed.
EXPERIMENTAL

Materials

Starch used in experiments was commercial, food-grade starch (CPC International Inc. Englewood Cliffs, NJ) having a moisture content of 13%. Cellulose was purchased commercially as a highly purified, finely powdered product (Cellulay-Cellulose, United States Biochemical Corp., Cleveland, OH) and had a moisture content of 6%.

Formic acid (88%) (Fisher Scientific Co., Fair Lawn, NJ), glacial acetic acid (J. T. Baker Chemical Co., Phillipsburg, NJ), glycolic acid, L(+)-lactic acid (grade L-1), DL-α-hydroxybutyric acid (sodium salt), α-hydroxyisobutyric acid and DL-α-hydroxyvaleric acid (sodium salt) (Sigma Chemical Co., St. Louis, MO) were used as standards in HPLC and GC analyses. Glutaric acid (Mallinckrodt, Inc., St. Louis, MO) was used as an internal standard in the GC analyses. Boron trifluoride (14% in propanol) (Eastman Kodak Co., Rochester, NY) was used as a derivatizing agent to produce propyl esters of the organic acids for GC analyses.

Reactions

All reactions were performed under nitrogen in a 1-L magnetically stirred autoclave equipped with a cooling coil (Model AFP 1005, Autoclave Engineers, Erie, PA). Each experiment was run by first adding 1679 of aqueous solution containing 10g of NaOH to the autoclave and heating the sealed autoclave to the desired temperature plus 5-10°. A well-mixed slurry of 10g of starch or cellulose (moisture free) in 859 of water was then added to an adjacent Kuentzel vessel (Vessel KD-19.3-SS11, Autoclave Engineers, Erie PA) which had tubing with a ball valve leading from its bottom to the stirred autoclave. The tubing extended through the head of the stirred autoclave to below the surface of the alkaline solution. After addition of the starch or cellulose slurry, the Kuentzel vessel was quickly sealed and connected to a nitrogen cylinder. The Kuentzel vessel was pressured to 100 psi above the pressure in the stirred autoclave, and the starch or cellulose slurry was injected into the hot alkaline solution in the stirred autoclave by opening the ball valve. The resulting solution volume was 250ml and it contained 10g of starch or cellulose (0.25M based on glucose monomer) and 10g of NaOH (1.00M). This solution dropped below the target reaction temperature for a short time, but returned to the desired temperature in 1-3 min. The reaction was timed from the moment of injection.

Experiments were conducted at temperatures between 180 and 300°C, and the reactants were held at the selected temperature for varying times to determine the effect of reaction time. The temperature dropped quickly upon flow of water through the cooling coil and removal of the autoclave heater. The time required to cool the reactants to below 100°C was 5-15 min.

After cooling to room temperature, the autoclave was opened and the reaction products were suctioned out. In the case of cellulose, any unreacted material appeared as a solid residue in the reaction solution. Any residue was filtered from the reaction solution and then extracted with water. The filtrate was combined with extract, and an aliquot of the combined solution was titrated for total organic acids. The solid residue was dried at 40°C for 24 hr. in a forced-air oven and then at 90°C for 24 hr. in a vacuum oven. In the case of starch, any unreacted starch was soluble in the alkaline product solution. An aliquot of the solution was titrated for total acids. Unreacted
starch was precipitated quantitatively with acetone (10). A 5.0g aliquot of the product solution was neutralized with 2.0N HCl to pH 7 and 25ml of acetone was added. After sitting overnight, the starch precipitate was separated by centrifugation, washed with 20ml of a 1:3 acetone-water solution, separated again by centrifugation, and finally dried in the same manner as for cellulose solid residue.

**High-Performance Liquid Chromatography**

Filtered product solutions from reactions with starch and cellulose were analyzed using a Waters Associates high-performance liquid chromatograph model ALC 201 equipped with a refractive index detector model R-401 (Waters Associates, Milford, MA) to identify water-soluble products. This was accomplished by matching retention times of product compound peaks with retention times of standards. A 300 mm x 7.8 mm Aminex HPX-87H organic acid analysis column (Bio-Rad Laboratories, Richmond, CA) was used. Elution was carried out at 60°C using 0.002N H2SO4 at a flow rate of 0.5 ml/min. Data acquisition from the chromatographic system was by the Hewlett-Packard integrating recorder model 3388A (Hewlett Packard Co., Palo Alto, CA).

**Gas Chromatography**

To verify the compounds identified by HPLC, both standards and product solutions were converted to their propyl esters with BF3-propanol according to the method of Salwin and Bond (11). Analysis of the esterified compounds was performed on a Hewlett Packard 5880A gas chromatograph equipped with a flame ionization detector and a bonded Superox FA (Alltech Assoc., Inc. Deerfield, IL) fused-silica capillary column (25m x 0.25mm I.D., 0.2 μm film thickness). The temperature program was 100°C to 240°C at 5°C/min and 10 min at 240°C. The injector temp was 225°C and the detector temp was 300°C. Carrier flow (He) was 1.0 ml/min. Injection volume was 1μl with a split ratio of 80:1.

**RESULTS AND DISCUSSION**

**Degradation of Starch and Cellulose**

An analysis of the data was performed to determine whether starch and cellulose degradation in alkaline solution could be described by second-order kinetics according to the equations:

\[
\text{polysaccharide} + \text{N·alkali} \rightarrow \text{products}\]

\[
\frac{dC_p}{dt} = -k_{d}C_p C_a
\]

\[
\ln \frac{C_a}{C_p} = \ln M + C_p (M-N) k_d t
\]

\[
M = \frac{C_{a_0}}{C_p}
\]

\[
N = \frac{(C_{a_0} - C_a)}{(C_p - C_p)}
\]
where $k_a$ is the reaction rate constant for starch or cellulose in alkaline solution, $C_P$ is the concentration of starch or cellulose, $C_{P0}$ is the concentration of starch or cellulose at $t=0$, $C_a$ is the concentration of alkali, $C_{A0}$ is the concentration of alkali at $t=0$, $t$ is the reaction time, and $N$ is the stoichiometric reactant ratio between hydroxide ion and polysaccharide.

The catalytic effect of the hydroxide ion would normally be represented as part of the reaction rate constant ($k_a$) for each temperature, because catalyst concentration normally remains constant. However, in the case of alkaline degradation of starch or cellulose, organic acids are produced which are converted to their salts by the alkali present, thus reducing the hydroxide ion concentration. Therefore, it seemed that this degradation reaction could be represented by second-order kinetics, with the hydroxide ion concentration determined by the stoichiometry of conversion of starch or cellulose to organic acids.

Figures 1 and 2 show experimental data plotted according to Equation 3 on semilogarithmic graphs to determine applicability of second-order kinetics. The linear plots indicate that the results conform to second-order kinetics quite well. Table 1 shows the reaction parameters determined for each temperature plotted in Figures 1 and 2.

Table 1. Reaction Parameters for Alkaline Degradation

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Starch</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N$</td>
<td>$k_a$</td>
</tr>
<tr>
<td></td>
<td>liter/mole min.</td>
<td>liter/mole min.</td>
</tr>
<tr>
<td>180</td>
<td>1.44</td>
<td>0.0026</td>
</tr>
<tr>
<td>200</td>
<td>1.17</td>
<td>0.0243</td>
</tr>
<tr>
<td>220</td>
<td>1.16</td>
<td>0.1334</td>
</tr>
<tr>
<td>240</td>
<td>1.16</td>
<td>0.3733</td>
</tr>
</tbody>
</table>

Interestingly, although $M = C_{A0}/C_{P0} = 4.0$ for both starch and cellulose, extrapolating the data plotted in Figures 1 and 2 back to $t = 0$ gives $M = 5.0$ for starch and $M = 4.6$ for cellulose. Thus, $M$ increased from 4.0 to 5.0 for starch and 4.6 for cellulose in very little or no time instead of the expected finite time. Considering that $M$ eventually reaches infinity for the systems studied, this represents a small fraction of more easily degraded polysaccharide. The results of this paper apply to the more resistant fractions of starch and cellulose, which constitute the bulk of those polysaccharides.

Figure 3 shows the reaction rate constants determined from the slopes of the lines in Figures 1 and 2 plotted against the reciprocal of absolute temperature on a semilogarithmic graph. The slope of the line through the points allows determination of the reaction activation energy according to the Arrhenius equation: $k = k_0 e^{(-E/RT)}$. The value of $E$ determined in this manner is 39,500 calories/mole, which appears to apply equally well to the degradation of starch or cellulose.

151
Production of Organic Acids

The values of N calculated for starch and cellulose shown in Table 1 reveal that as these polysaccharides were degraded by alkali, a smaller number of organic acid molecules were formed from each glucose monomer in starch compared to cellulose. This means that the organic acids produced initially from starch had a greater molecular weight than those produced from cellulose. This is illustrated clearly in Figure 4, which shows equivalents of organic acids produced from the degradation of starch or cellulose as a function of time. Although starch and cellulose degrade at the same rate, the rate of total organic acid formation was less for starch, and fewer equivalents of organic acids were produced in a given time from starch than from cellulose. The relative difference decreased as the temperature increased, and at higher temperatures the difference in total equivalents of organic acids produced disappeared at short times. A maximum concentration of approximately 0.45 equivalents/L of total organic acids was produced for both starch and cellulose for the reaction systems studied. Apparently, in starch degradation, the initially larger molecules of organic acids eventually break down into a larger number of smaller organic acids. Therefore, the total organic acid formation for starch ultimately equals that for cellulose. Since the starting concentration of starch and cellulose was 0.25 mol/L based on the glucose monomer, the average equivalent weight for the organic acids produced is (0.25)(180)/(0.45) = 100g/eq. This assumes that all the polysaccharide material degrades to acids.

The HPLC chromatograms of the alkaline degradation products of starch and cellulose were quite similar. Based on retention times of standards, formic, acetic, glycolic, lactic, 2-hydroxybutyric and 2-hydroxyvaleric acids were identified. The GC chromatograms of the propyl esters of the starch and cellulose chromatograms were also quite similar. Since GC gave much better separation of degradation products than HPLC, the GC chromatograms were used to calculate the yields of glycolic, lactic, 2-hydroxybutyric and 2-hydroxyvaleric acids. Formic and acetic were hidden under the GC solvent peak; thus, their yields were determined from the HPLC chromatograms. In addition, 2-hydroxyisobutyric, which was hidden under the HPLC lactic peak, was identified and quantified with GC. Tables II and III give the maximum yields of these acids at several temperatures. The corresponding times at temperatures to achieve maximums are included in the headings.

Table II. Maximum Organic Acid Yields from Degradation of Starch in Alkaline Solution

<table>
<thead>
<tr>
<th></th>
<th>240°C</th>
<th>260°C</th>
<th>280°C</th>
<th>300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 min</td>
<td>30 min</td>
<td>20 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Formic</td>
<td>10.5</td>
<td>10.9</td>
<td>10.5</td>
<td>10.2</td>
</tr>
<tr>
<td>Acetic</td>
<td>1.6</td>
<td>1.9</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Glycolic</td>
<td>3.4</td>
<td>4.5</td>
<td>5.3</td>
<td>5.6</td>
</tr>
<tr>
<td>Lactic</td>
<td>16.9</td>
<td>17.5</td>
<td>19.1</td>
<td>19.0</td>
</tr>
<tr>
<td>2-Hydroxybutyric</td>
<td>2.3</td>
<td>2.9</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>2-Hydroxyisobutyric</td>
<td>2.4</td>
<td>2.6</td>
<td>2.7</td>
<td>2.5</td>
</tr>
<tr>
<td>2-Hydroxyvaleric</td>
<td>1.4</td>
<td>1.4</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>Total</td>
<td>38.2</td>
<td>41.7</td>
<td>45.1</td>
<td>44.3</td>
</tr>
</tbody>
</table>

1Based on starting dry weight of starch
2Maximum not yet attained
Table III. Maximum Organic Acid Yields from Degradation of Cellulose in Alkaline Solution

<table>
<thead>
<tr>
<th>Yields(1) %</th>
<th>240°C</th>
<th>260°C</th>
<th>280°C</th>
<th>300°C</th>
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</thead>
<tbody>
<tr>
<td>Formic</td>
<td>10.8</td>
<td>10.9</td>
<td>10.7</td>
<td>10.2</td>
</tr>
<tr>
<td>Acetic</td>
<td>1.6</td>
<td>1.9</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Glycolic</td>
<td>4.6</td>
<td>4.8</td>
<td>5.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Lactic</td>
<td>19.8</td>
<td>19.9</td>
<td>20.4</td>
<td>18.5</td>
</tr>
<tr>
<td>2-Hydroxybutyric</td>
<td>3.4</td>
<td>3.3</td>
<td>3.5</td>
<td>3.4</td>
</tr>
<tr>
<td>2-Hydroxyisobutyric</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>1.9</td>
</tr>
<tr>
<td>2-Hydroxyvaleric</td>
<td>1.3</td>
<td>1.6</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>Total</td>
<td>43.6</td>
<td>44.5</td>
<td>45.3</td>
<td>42.2</td>
</tr>
</tbody>
</table>

1Based on starting dry weight of cellulose

Consistent with the results for rates of total acids produced shown in Figure 4, it took a longer time to reach the maximum yields starting with starch compared to cellulose. The maximum yields of the identified product acids at each temperature were quite similar for starch and cellulose starting materials. The time required to reach the maximum yields decreased as temperature increased. The trade-off is the higher operating pressure at higher temperature. The total yields of the identified acids appear to reach an optimum at approximately 280°C for both starch and cellulose.

The similarity in maximum yields for the identified product acids from starch and cellulose suggests similar or identical reaction pathways. The slower rate for acid formation from starch could be explained by dissolved starch polymer or partially degraded starch polymer interfering with additional degradation of initial conversion products. The greater ease with which starch polymer dissolves in alkaline solution compared to cellulose is consistent with this possibility.

Although significant amounts of other organic acids are produced, lactic acid is the major product for the reaction conditions studied. As well as having numerous direct uses, lactic acid has the potential of being an important intermediate in the production of other valuable products (12, 13). Preliminary economic analysis indicates that production of lactic acid from alkaline degradation of cellulose has economic merit (9). It is also conceivable that all the hydroxy acids produced could be used together without separation to produce polyester materials.

CONCLUSIONS

Starch and cellulose can both be thermochemically degraded in alkaline solution to water soluble compounds of relatively low molecular weight. (A parallel study examines more completely the nature of these compounds (14).) Both starch and cellulose degradation processes can be described by second-order kinetics, with the hydroxide ion concentration determined by the stoichiometry of polysaccharide conversion to organic acids. The thermochemical degradation activation energy in alkaline solution for both starch and cellulose is 39,500 calories/mole.
The production of organic acids from starch proceeds more slowly than from cellulose. Ultimately, however, the yields of acids are quite similar from both. Formic, acetic, glycolic, lactic, 2-hydroxybutyric, 2-hydroxyisobutyric and 2-hydroxyvaleric acids are produced in significant amounts. The maximum yield of lactic acid is approximately 20%, and the maximum sum total yield of all identified acids is approximately 45% for the conditions investigated.

Increasing the yields of the desirable acids produced from the thermochemical, alkaline degradation of polysaccharides will require additional understanding of the reaction mechanisms and kinetics involved. Additional research should also proceed to determine the effect of other bases and supplementation of alkali catalysis by other catalytic materials.

REFERENCES

6. E. Sjostrom, Tappi, 60(9), 151 (1977).
Figure 1. Effect of time on thermochemical degradation of starch in alkaline solution according to Eq. 3.

Figure 2. Effect of time on thermochemical degradation of cellulose in alkaline solution according to Eq. 3.
Figure 3. Relation of second-order reaction rate constants for starch and cellulose to temperature according to Arrhenius equation.

Figure 4. Effect of time on organic acid production from thermochemical degradation of starch and cellulose in alkaline solution.