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Thermochemical Conversion of Polysaccharides in Concentrated Alkali to Glycolic Acid

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ABSTRACT

Degradation of starch and cellulose in alkaline solutions above 8N NaOH favored the production of glycolic acid. In 16N NaOH, starch and cellulose degraded at 240°C to produce, respectively, 46 and 43% yields of glycolic acid. At these same conditions, 24 and 12% yields of oxalic acid were also produced from starch and cellulose. Raising the amount of starch or cellulose above 10 g in 250 mL 16 N NaOH lowered the percent yields of glycolic and oxalic acids, but increased absolute yields sufficiently to consider larger polysaccharide:16 N NaOH ratios for commercial use. Substituting KOH for NaOH lowered glycolic and oxalic acid yields, and demonstrated the effect of the alkali cation on the conversion reactions.

Index Entries: Thermochemical; alkali; cellulose; starch; glycolic acid; oxalic acid.

INTRODUCTION

Previous research directed toward optimizing conversion of polysaccharide materials in alkaline solution has focused on reaction of 4–10% (w/w) mixtures in pressure vessels at 240–300°C in 1–4 N alkali (*1–6*), and reaction in the atmosphere at 170–240°C by fusing approximately 1 part polysaccharide material with 3 parts 50% alkali (19 N) (*7–9*). In the first case, productions of lactic and formic acids have been optimized at 20 and 10%, respectively, and production of acetic, glycolic, 2-hydroxybuty-

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ric, 2-hydroxyisobutyric, and 2-hydroxyvaleric totaled 15%, based on starting polysaccharide (*6*). In the second case, productions of oxalic and acetic acids have been optimized at 46 and 12%, respectively (*8*).

The work reported here involves reaction of polysaccharides, specifically starch and cellulose, at conditions intermediate to those discussed above. In an analogy to acid hydrolysis of cellulose, it was hypothesized that degradation of polysaccharide materials in quite concentrated alkaline solution would produce different results compared to degradation in relatively dilute alkaline solution. The reaction conditions of interest were such that stirable mixtures of polysaccharide (4–12% [w/v]) in concentrated alkali required containment in a pressure vessel. However, because of the concentrated nature of the alkaline solution, reaction pressure was considerably lower than that in dilute alkali. Reaction vessel material requirements for handling concentrated alkali would be somewhat mitigated because of the lower pressure requirement.

Thus, the goals of this work were

1. Determination of the effect of alkali concentration on polysaccharide degradation to organic acids,
2. Identification and quantitation of as many organic acids as possible,
3. Determination of the effect of reaction temperature, time, and polysaccharide concentration with a selected concentrated alkaline solution,
4. Determination of the effect of KOH compared to NaOH.

METHODS

Materials

Starch used in experiments was commercial, food-grade (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, acetic, oxalic, glycolic, L(+)-lactic, DL-2-hydroxybutyric, 2-hydroxyisobutyric, DL-2-hydroxyvaleric, and succinic acids were used as standards in HPLC and GC analyses. Glutaric acid was used as an internal standard in the GC analyses. Boron trifluoride (14% in propanol) 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 using a Hastelloy C liner (Autoclave Engineers, Erie, PA). The time needed to heat reactants to selected temperatures was approximately one h. The time required to cool the reactants to below 100°C was 20–30 min, and the total time required to cool to room temperature was approximately one h.

In initial experiments to determine the effect of NaOH concentration, any solid material in the reaction product was filtered from the liquid and then extracted extensively with water. The filtrate was combined with extract, and a sample of the combined solution was used for HPLC and GC analysis. Later the solid material was found to be mainly sodium oxalate. In subsequent experiments at 16 N alkali, the filtration and extraction steps were eliminated. Thus, for experiments performed to determine the effects of temperature, time, and effect of KOH compared to NaOH, the well-mixed product slurry was used for the GC analysis procedure.

High-Performance Liquid Chromatography

Filtered product solutions were analyzed with a high-performance liquid chromatograph equipped with a refractive index detector. A 300 mm × 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 .002N H_2SO_4 at a flow rate of .5 mL/min.

Gas Chromatography

To verify the compounds identified by HPLC, both standards and product solutions were converted to their propyl esters with BF_3-propanol, according to the method of Salwin and Bond (*10*). The pH of standard and product solutions was adjusted to neutral before beginning the procedure, and the product solution was diluted 1:5. Analysis of the esterified compounds was performed on a gas chromatograph equipped with a flame ionization detector and a bonded FFAP (Quadrex Corp., New Haven, CT) fused-silica capillary column (25 m × .25 mm id, .25 μm film thickness). The temperature program was 100–240°C at 5°C/min and 19 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 1 μL with a split ratio of 80:1.

RESULTS

Product Identification

Table 1 lists the organic acids identified. Since GC gave much better separation of peaks than HPLC, the GC chromatograms were used to calculate the yields of most of the compounds. Formic and acetic acids were hidden under the GC solvent peak; thus, their yields were calculated from the HPLC chromatogram. For 2-hydroxyisobutyric acid, the HPLC peak was hidden under the lactic peak.

Table 1
Organic Acids Identified in Alkaline Degradation Products of Starch and Cellulose

Formic acid ($HCOOH$)[a]
Acetic acid (CH_3COOH)[a]
Glycolic acid ($CH_2OHCOOH$)[a,b]
Lactic acid ($CH_3CHOHCOOH$)[a,b]
2-Hydroxybutyric acid ($CH_3CH_2CHOHCOOH$)[a,b]
2-Hydroxyisobutyric acid ($CH_3CCH_3OHCOOH$)[b]
2-Hydroxyvaleric acid ($CH_3CH_2CH_2CHOHCOOH$)[a,b]
Oxalic acid ($HOOCCOOH$)[a,b]
Succinic acid ($HOOCCH_2CH_2COOH$)[a,b]

[a] Identified by HPLC.
[b] Identified by GC.

Alkali Concentration

Figures 1a and 1b show the effect of alkali concentration on the conversion of cellulose to organic acids. Reaction temperature and time were selected because they were close to optimum for formic and lactic acid yields in 1 N NaOH (6). Yield is based on starting dry cellulose. Oxalic acid yield is not shown for the largest alkali concentrations, since it produces an insoluble salt at high sodium hydroxide concentration and was not totally accounted for in this series of experiments. The results show a large effect of alkali concentration on glycolic acid yield, starting at 8 N and peaking at 16 N NaOH. Acetic and succinic acid yields were also greater in concentrated alkali, and later results showed the same held for oxalic acid. In contrast, formic, lactic, 2-hydroxybutyric, 2-hydroxyisobutyric and 2-hydroxyvaleric acid yields were lower at 16 N than at 1 N NaOH. Because of the large yield of glycolic acid in 16 N NaOH, this concentration was selected for subsequent reactions with starch and cellulose.

Temperature and Time

Figure 2 shows the effect of reaction temperature on starch conversion to organic acids in 16 N NaOH. Glycolic acid increased through 260°C and then dropped sharply at 280°C, indicating glycolic acid degradation or favoring of competing reactions. The results also show that large amounts of oxalic acid can be produced in concentrated alkali. Increasing temperature improved succinic acid yields and had very little effect on lactic acid production. Only trace amounts of 2-hydroxybutyric, 2-hydroxyisobutyric, and 2-hydroxyvaleric acid were found. HPLC chromatograms of product solutions from reactions run in 16 N NaOH became less sharp, indicating column deterioration. Thus, formic and acetic acid yields were not obtained for these and later experiments.

Subsequent experiments to determine the effect of reaction time on starch and cellulose conversion in 16 N NaOH were performed at 240°C

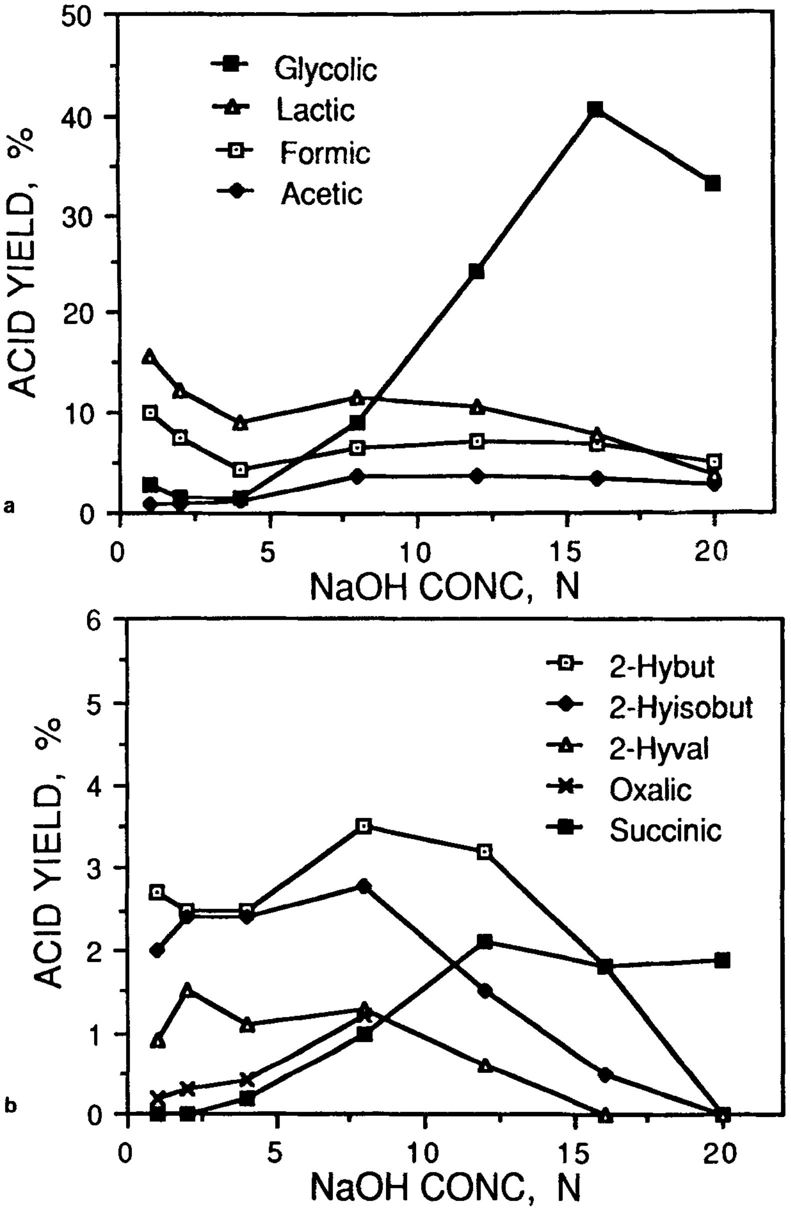

Fig. 1. *a.* Effect of alkali concentration on the conversion of cellulose to organic acids. Reaction conditions: 10 g cellulose in 250 mL alkali solution at 240°C for 17 min. *b.* Effect of alkali concentration on the conversion of cellulose to organic acids. Reaction conditions: *see* Fig. 1a.

and 260°C. Figures 3 and 4 show that maximum yields of glycolic acid at 240°C were similar for cellulose and starch. However, the maximum glycolic acid yield from cellulose was obtained in approximately 8 min, compared to 45 min for starch. Largest oxalic and lactic yields at 240°C from cellulose also occurred at shorter times compared to starch.

At 260°C compared to 240°C, glycolic acid yield from cellulose dropped slightly, whereas oxalic acid yield increased by about one-third.

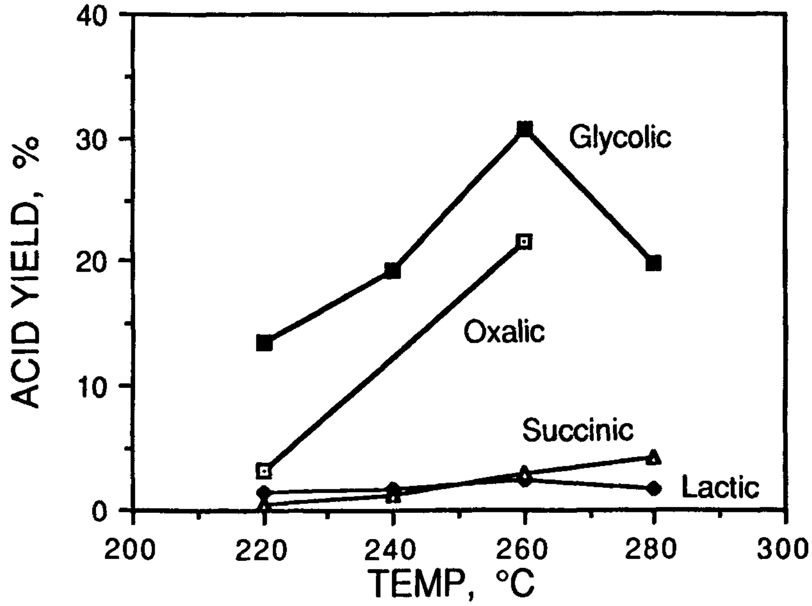

Fig. 2. Effect of reaction temperature on the conversion of starch to organic acids. Reaction conditions: 10 g starch in 250 mL 16 N NaOH for 17 min.

Lactic acid yield remained approximately the same. At 260°C compared to 240°C, maximum glycolic acid yield from starch dropped by one-third and occurred much earlier. Maximum oxalic acid yield also occurred earlier, but remained approximately the same for both temperatures. Lactic acid yield did not change markedly over the times investigated.

Only trace amounts of 2-hydroxyisobutyric and 2-hydroxyvaleric were found from cellulose and starch conversion in 16 N NaOH at 240°C

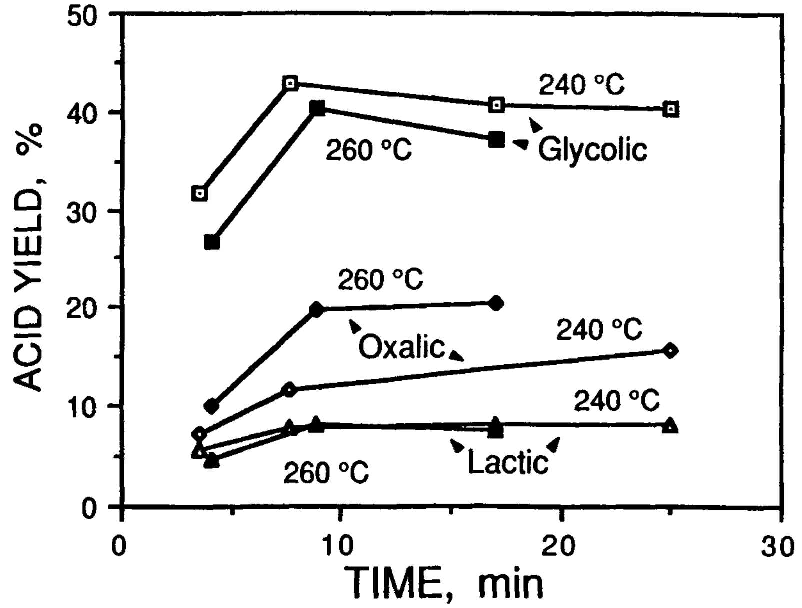

Fig. 3. Effect of reaction temperature and time on the conversion of cellulose to organic acids. Reaction conditions: 10 g cellulose in 250 mL 16 N NaOH.

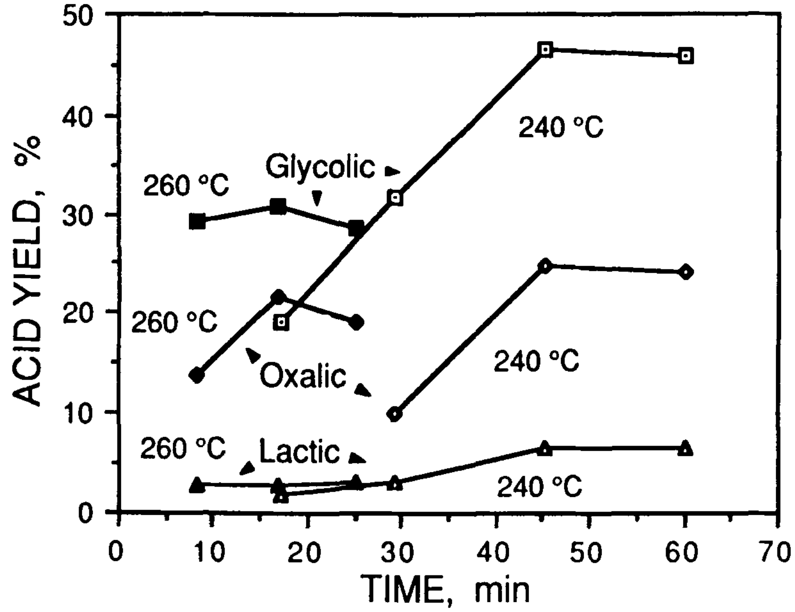

Fig. 4. Effect of reaction temperature and time on the conversion of starch to organic acids. Reaction conditions: 10 g starch in 250 mL 16 N NaOH.

and 260°C. Maximum yields of both 2-hydroxybutyric and succinic acids from cellulose or starch were approximately 2% each at both 240°C and 260°C.

Polysaccharide Concentration

Figures 5 and 6 show the effect of changing the amounts of starch and cellulose relative to 16 N NaOH solution on the conversion reaction products. The reaction conditions in each case were selected because they provided: near-optimum yields of glycolic acid in reaction slurries of 10 g polysaccharide:250 mL 16 N NaOH, and reaction times well beyond the minimum required for optimum yields in the 10 g:250 mL case (*see* Figs. 3 and 4). The percent yields of glycolic and oxalic acids decreased as the amount of starch or cellulose was doubled and tripled relative to 16 N NaOH. In each case, the yield of lactic acid increased slightly. When the amount of starch or cellulose was reduced to 5 g, glycolic acid percent yield decreased and oxalic acid increased. The effect was especially evident with starch. Thus, it is clear that increasing the amount of polysaccharide beyond 10 g:250 mL 16 N NaOH decreases the percent yields of glycolic and oxalic acids. However, it increases the absolute amount of these acids produced per unit volume (i.e., production capacity of the reactor.) Table 2 shows the effect of polysaccharide concentration increases on the production of glycolic, lactic, and oxalic acids. Deciding which polysaccharide:alkali solution ratio to select in a commercial process will depend on the economic tradeoff between raw material cost and equipment plus operating costs.

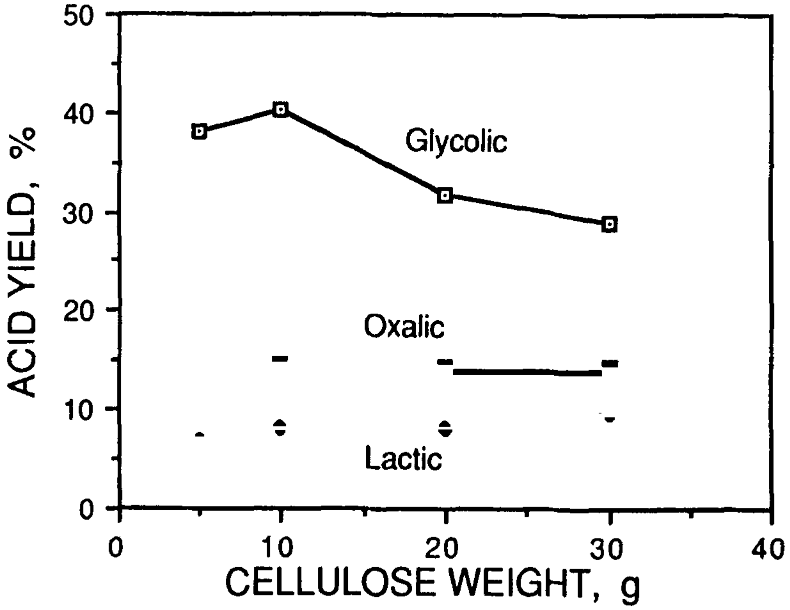

Fig. 5. Effect of starting cellulose weight on the conversion to organic acids. Reaction conditions: 250 mL 16 N NaOH at 240°C for 25 min.

KOH Compared to NaOH

Few alkalis have the solubility in water necessary to achieve high concentrations such as 16 N. Since KOH does, it was selected to determine if the K^+ cation would have a different effect on organic acid yields compared to the Na^+ cation. Table 3 shows that for both starch and cellulose, 16 N KOH appears less effective than 16 N NaOH in promoting

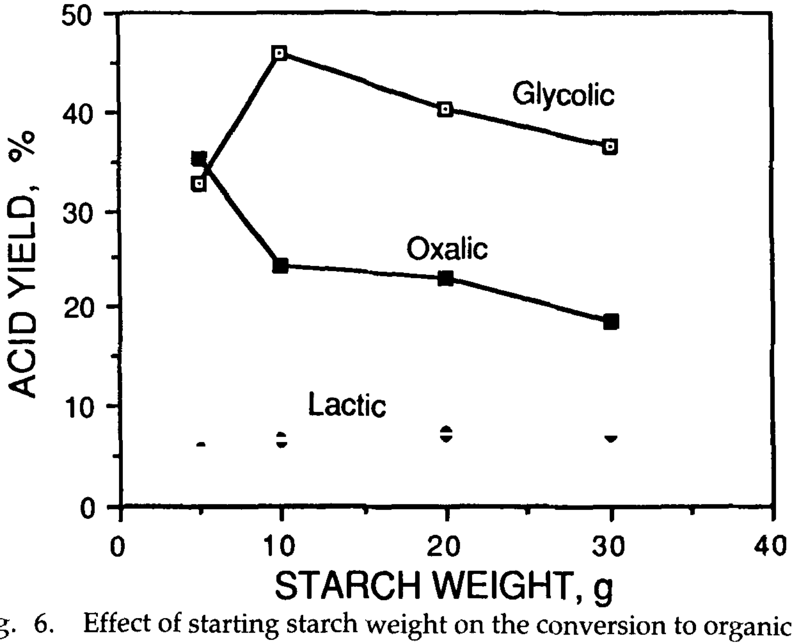

Fig. 6. Effect of starting starch weight on the conversion to organic acids. Reaction conditions: 250 mL 16 N NaOH at 240°C for 60 min.

Table 2
Effect of Polysaccharide Concentration Increases on Production of Organic Acids

	Product Increase,%[a]			
	Starch Increase		Cellulose Increase	
	100%	200%	100%	200%
Glycolic	76	139	58	116
Lactic	111	221	102	251
Oxalic	90	131	86	177

[a] Relative to production from reaction of 10g polysaccharide in 250 mL 16 N NaOH

high yields of glycolic and oxalic acids. The fact that the alkali cation influences product yield indicates that cations do effect the reaction mechanisms in degradation of polysaccharides.

DISCUSSION

Degradation of polysaccharides, such as starch and cellulose, in concentrated NaOH solutions, uniquely promotes the production of glycolic and oxalic acids. Conversion of starch in 16 N NaOH at 240°C produces yields of 46% glycolic and 24% oxalic, and conversion of cellulose in 16 N NaOH at 240°C gives yields of 43% glycolic and 12% oxalic. Increasing the amount of starch or cellulose beyond 10g:250 mL 16 N NaOH decreases the percent yields, based on starting polysaccharide, but increases the absolute amounts produced sufficiently to consider using the largest polysaccharide:alkali solution ratio consistent with economic optimization.

Substitution of KOH for NaOH gives lower yields of glycolic and oxalic acids. Apparently, the alkali cation does effect the degradation reactions leading to organic acids from polysaccharides. Unfortunately, the solubilities of other alkalis are so low that the concentration of cations in solution would be limited.

Table 3
Comparison of NaOH and KOH in Degradation of Starch[a] and Cellulose[a]

	Yields,%[b]			
	Starch (240°C, 60 min)		Cellulose (240°C, 25 min)	
	NaOH	KOH	NaOH	KOH
Glycolic	45.8	37.5	40.2	27.1
Lactic	6.7	7.7	8.2	8.0
Oxalic	24.2	18.3	15.6	14.7

[a] 10 g in 250 mL 16 N NaOH or 16 N KOH.

[b] Based on starting dry weight of starch or cellulose.

At present, glycolic acid is produced commercially as an intermediate in one of the synthesis routes used for manufacture of ethylene glycol. This synthesis route starts with a hydrocarbon, and involves production of methanol and formaldehyde as intermediates before glycolic acid. The conversion of formaldehyde to glycolic acid requires reaction with carbon monoxide, water, and an acid catalyst at very high pressures. Glycolic acid is converted to an ester, which is then reacted with hydrogen to produce ethylene glycol. The more commonly used and simpler route to ethylene glycol involves oxidation of ethylene to ethylene oxide, which is then hydrated to ethylene glycol. If the former route to ethylene glycol is ever abandoned, the present source of glycolic acid could be lost. Nonetheless, the simple alternative of degrading polysaccharide material in concentrated alkali may compare favorably with the multistep procedure now used to convert hydrocarbon material to glycolic acid.

Glycolic acid has many existing uses, including textile and leather processing, metal cleaning and plating, and production of detergents, adhesives, coatings, and biodegradable polymers. Production of biodegradable polymers from glycolic acid is an especially attractive use that has great growth potential (*11*). Glycolic acid from polysaccharide materials also has potential for use as an intermediate in the production of formaldehyde, methanol, a variety of esters, and ethylene glycol (*see* above).

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