Degradation of Polysaccharides in Alkaline Solution to Organic Acids: Product Characterization and Identification

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Synopsis

Agricultural products have considerable potential for conversion to valuable oxychemicals. Analyses by ether extraction, titration, and anion-exchange classification of the alkaline degradation products of totally converted starch and cellulosics showed that the product compounds are mainly organic acids. Almost all the organic acids are monocarboxylic in nature, with an average equivalent weight in the range 76–84. The organic acids identified thus far by HPLC and GC are formic, acetic, glycolic, lactic, 2-hydroxybutyric, 2-hydroxyisobutyric, and 2-hydroxyvaleric acids. Together, these compounds represent 41–46% of the starting material weight.

INTRODUCTION

Recent crop surpluses in the United States have helped fuel interest in the conversion of agricultural products into oxychemicals. One possible approach involves alkaline degradation of polysaccharide material to organic acids. As well as having numerous direct uses, many organic acids have the potential of being important intermediates in the production of other valuable products.[1,2]

Starch and cellulose are, by far, the most abundant polysaccharides. Much of the work on alkaline degradation of starch and cellulose has been conducted at 100°C or lower.[3-6] These studies have addressed the mechanisms of degradation and reaction termination, the effects of molecular structure, and identification of the acids produced at these conditions.[7-11] However, little conversion of polysaccharide to acids occurs at these low temperatures. Almost all the investigations at greater temperatures have involved study of the alkaline pulping process, where polysaccharide degradation is limited and not desired.[12,13]

One study of alkaline degradation of cellulose[14] focused on production of formic, acetic, glycolic, and lactic acids; results showed a maximum total yield of these acids of approximately 30% based on cellulose. However, the rest of the material was unaccounted for, and optimum reaction conditions were not clear. Our previous work with cellulose[15,16] reported the total equivalents of organic acids produced and confirmed that formic, acetic, glycolic, and lactic acids were important alkaline degradation products. In addition, we also determined kinetics of cellulose degradation at reaction conditions leading to entirely water-soluble products. However, most of the products remained uncharacterized and unidentified.

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The objectives of the research reported here are to: (a) compare the effect of temperature, time, and alkali concentrations on the alkaline degradation of starch and cellulose to organic acids; and (b) characterize, identify, and compare the reaction products from alkaline degradation of starch and cellulose using HPLC, GC, ether extraction, titration, and anion-exchange classification. In addition, the cellulosic material rice straw was included in the study. Aside from interest as a possible feedstock, rice straw has considerable mineral content with potential catalytic effect. For comparison, product characterization and identification were also performed on the alkaline degradation products of glucose, the monomer of starch and cellulose.

EXPERIMENTAL

Materials

Starch used 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%. Rice straw was hammer-milled to give particles less than 2 mm in length, with 98% of mass consisting of particles less than 1 mm in size. Moisture and ash contents were found to be 9 and 15%, respectively. Glucose used was a commercial, laboratory-grade, anhydrous product (J. T. Baker Chemical Co., Phillipsburg, NJ).

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 run using 10% (w/w) slurries of starch, cellulose, or rice straw (calculated on a moisture and ash-free (maf) basis) in aqueous solutions of 4 or 6% (w/w) NaOH. Reactions were performed under nitrogen atmosphere in magnetically stirred autoclaves equipped with cooling coils in direct contact with reactants, and using Hastelloy C liners (Autoclave Engineers, Erie, PA).

Experiments to determine the effect of temperature, time, and NaOH concentration were conducted in a 300-mL autoclave (Model ABP-300) with 100 g of reactants. The time needed to raise the temperature of the reactants to selected temperature was typically 30–60 min. The experiments were conducted at temperatures between 240 and 320°C, with pressures between 3340 and 11,300 kPa (485–1640 psi). The reactants were held at the selected temperature for 0–40 min to assess the effect of reaction time. For reactants held 0 min at the selected temperature, the reactants were cooled immediately

upon achievement of the selected temperature. The time required to cool the reactants to below 100°C was 5–10 min, and the time required to cool to room temperature was approximately 30 min.

After cooling reactants to room temperature, the autoclave was opened, and the liner with reaction products was removed. Any solid starch, cellulose, or rice straw residue remaining was filtered from the liquid and then extracted with water. The filtrate was combined with extract, and a sample of the combined solution was titrated for total organic acids as described below. The extracted solid residue was dried at 40°C in a forced-air oven and then at 98°C in a vacuum oven. The yield of maf solid residue for the rice straw was obtained by subtracting the weight of the original ash content. The ash content was assumed insoluble in the liquid phase because it consisted mostly of silica,[17] which is insoluble in water, and other oxides of very low solubility.

An aliquot of the combined solution was titrated with 0.5*N* HCl to determine total organic acids produced. Titration to pH 8.0 allowed the determination of residual hydroxide ion concentration and thus production of organic acids by difference between original and final hydroxide ion content. Continued titration to pH 1.7 allowed another determination of the equivalents of organic acids produced.[18] The value for equivalents of organic acid produced was taken as the average of the two determinations.

After desirable reaction conditions were determined using the 300-mL autoclave [10% (w/w) slurries of starch, cellulose, or rice straw in 6% (w/w) NaOH solutions at 280°C for 10 min], runs were carried out in a 1-L autoclave (Model AFP 1005) with 400 g of reactants to obtain product solution for analyses (HPLC, GC, ether extraction, titration, and anion-exchange classification.) A 10% (w/w) solution of glucose in 6% (w/w) NaOH was run for comparison. In these cases, while cool-down times were similar to those for the 300-mL autoclave, heat-up times were approximately double. However, this did not appear to give different results when compared to the 300-mL autoclave.

High-Performance Liquid Chromatography

Filtered product solutions from reactions with starch, cellulose, rice straw, and glucose were analyzed using a Waters Associates Model ALC 201 HPLC 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 × 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 0.002*N* H_2SO_4 at a flow rate of 0.5 mL/min. Data acquisition from the chromatographic system was by a 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 BF_3–propanol according to the method of Salwin and Bond.[19] 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., Deerfield, IL) fused-silica capillary column (25 m × 0.25 mm i.d., 0.2–μm film thickness). The temperature program was 100–240°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 1 μL with a split ratio of 80:1.

Ether Extractions

To characterize the compounds being produced beyond what specific identification could be made by HPLC and GC at this time, the product solutions from alkaline degradation of starch, cellulose, rice straw, and glucose were each treated according to the scheme in Figure 1. The initial amount of filtered product solution was 100 g in each case.

In this scheme, fraction A represents ether-soluble, nonionic compounds. Because of the initial high pH of the product solution, organic acids would exist as fully ionized salts and thus not be soluble in ether. Reduction to pH 2 produces nonionized acids having a range of solubilities in ether. Thus, fraction B represents organic acids with solubility in ether. Fraction C includes organic acids having poor solubility in ether and/or compounds (e.g., sugars) having no solubility in ether.

After removal of ether by vacuum distillation, aliquots of fractions A and B were redissolved in water and analyzed by HPLC using the same column and conditions used for analyzing the original, filtered product solutions. Fraction C was also analyzed by HPLC after concentration by removal of some of the

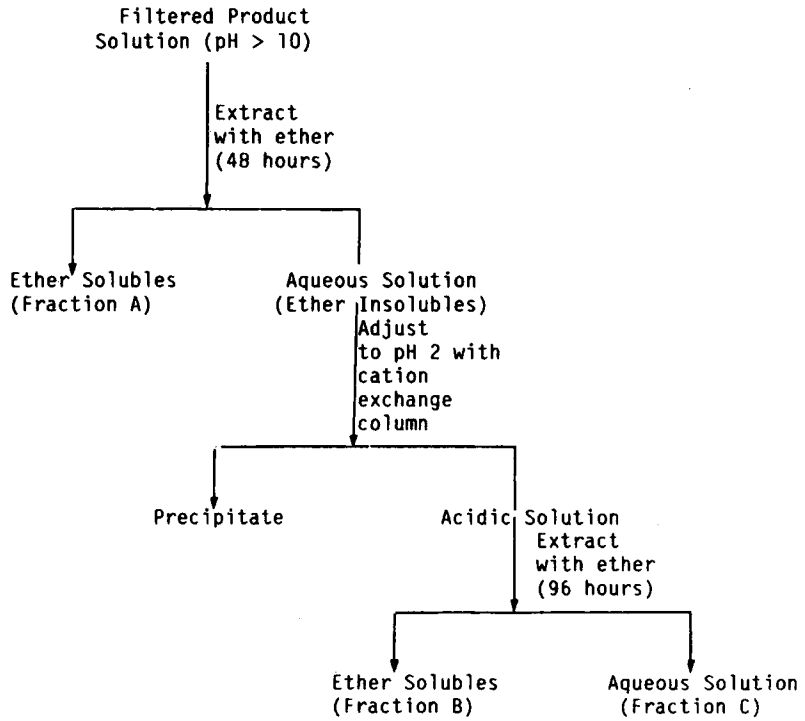

Fig. 1. Ether extraction scheme for product solutions.

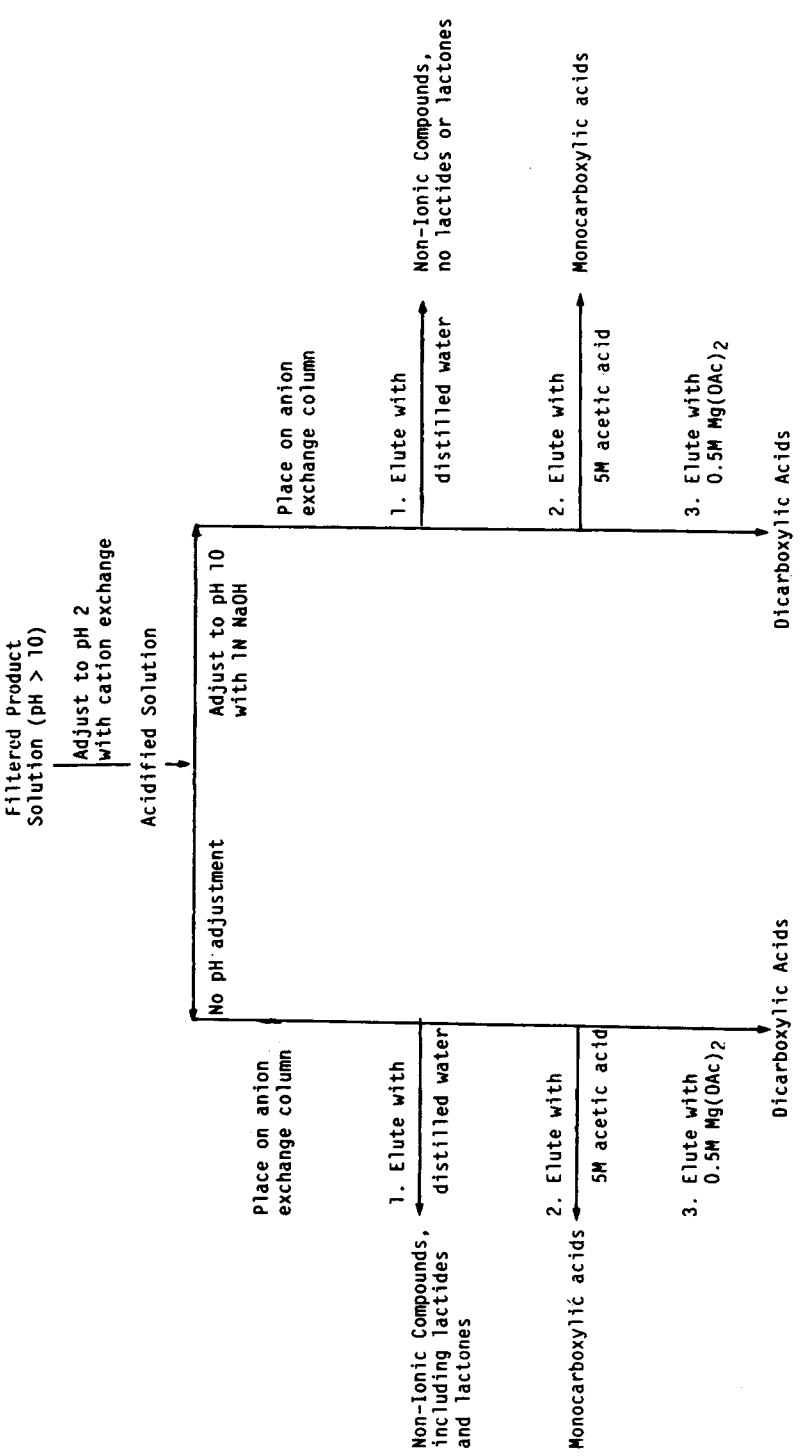

Fig. 2. Anion-exchange classification of product solutions.

water. These HPLC analyses allowed designation of unknown chromatogram peaks as nonionic compounds, definite organic acids, and possible organic acids.

The precipitate which formed when the aqueous solution from the first extraction was acidified by cation exchange (AG 50W-X8, 20–50 mesh, hydrogen form, Bio-Rad Laboratories) was difficult to recover quantitatively. Therefore, a separate determination was made by adjusting the pH of a separate aliquot of product solution to pH 2 with 2*N* HCl followed by filtration and determination of precipitate weight.

Anion-Exchange Classification

Product compounds were further classified into nonionic, monocarboxylic, and dicarboxylic compound fractions by using the anion-exchange classification procedure[20] shown in Figure 2. In this procedure, filtered product solution was first placed through a cation exchange column filled with AG 50W-X8, 20–50 mesh, hydrogen form (Bio-Rad Laboratories) to convert organic acid salts to nonionized acids, remove any acid-insoluble material by precipitation, and liberate any dissolved carbon dioxide generated in the alkaline degradation reactions. The product solution was then divided into two fractions, with one fraction readjusted to pH 10 with 1*N* NaOH and held for at least 3 h, and the other fraction allowed to remain acidic. Any hydroxy acids susceptible to formation of lactides or lactones would produce a larger amount of nonionic compounds in the fraction allowed to remain acidic as compared to that readjusted to pH 10.

Each fraction was then separated on an anion-exchange column filled with AG1-X8, 100–200 mesh, in the acetate form (Bio-Rad Laboratories). Elution sequentially with distilled water, 5*M* acetic acid and 0.5*M* magnesium acetate produced fractions that were, respectively, nonionic, monocarboxylic, and dicarboxylic in nature. Collected eluate fractions were analyzed using oxidation by dichromate followed by colorimetry.[21,22] Eluate fractions were also analyzed by HPLC using the same column and conditions discussed earlier. This allowed designation of unknown HPLC chromatogram peaks as nonionic, monocarboxylic, or dicarboxylic acid.

RESULTS AND DISCUSSION

Tables I–III give results for the alkaline thermochemical degradation of 10% (w/w) slurries of starch, cellulose, and rice straw in various NaOH solutions over a range of temperature and time. Total conversion of starch to water-soluble products occurred in 4% NaOH by just heating to 240°C before cooling, as measured by the absence of residual material. However, total degradation of cellulose and rice straw required reaction times as long as 40 min at 280°C in 4% NaOH; shorter reaction times were adequate at 320°C for total degradation. With 6% NaOH, reaction times of 0–10 min at 280°C gave total degradation and yielded the greatest number of milliequivalents of organic acid for all the polysaccharide materials.

The effect of the initial NaOH concentration on the amount of organic acids produced was quite similar for all the polysaccharides. For 4% NaOH at 280°C, the milliequivalents of organic acids produced equaled approximately

TABLE I
Effect of Alkaline Thermochemical Degradation of 10% (w/w) Slurries of Starch[a]

NaOH (%)	Temp (° C)	Time[b] (min)	Residue[a] (%)	Final soln (pH)	Acids produced (meq)
4	240	0	0	12.8	55
4	280	0	0	8.4	90
4	280	10	0	8.6	88
4	320	0	0	8.7	88
6	280	0	0	12.8	116
6	280	10	0	11.1	122

[a] Based on moisture and ash-free content of starch.
[b] Time at reaction temp after 30–60 min heat-up from room temp.

TABLE II
Effect of Alkaline Thermochemical Degradation of 10% (w/w) Slurries of Cellulose[a]

NaOH (%)	Temp (° C)	Time[b] (min)	Residue[a] (%)	Final soln (pH)	Acids produced (meq)
4	240	0	42.2	12.1	62
4	240	40	17.5	8.4	85
4	280	0	15.0	8.0	85
4	280	10	3.8	7.6	88
4	280	40	0	7.9	88
4	320	0	0	8.2	91
4	320	40	0	8.4	88
6	280	10	0	11.8	116
6	280	40	0	10.7	118

[a] Based on moisture and ash-free content of cellulose.
[b] Time at reaction temp after 30–60 min heat-up from room temp.

TABLE III
Effect of Alkaline Thermochemical Degradation of 10% (w/w) Slurries of Rice Straw[a]

NaOH (%)	Temp (° C)	Time[b] (min)	Residue[a] (%)	Final soln (pH)	Acids produced (meq)
4	240	0	20.3	10.9	73
4	240	40	14.1	9.5	83
4	280	0	5.8	9.1	80
4	280	40	0	9.2	87
4	320	0	2.0	8.5	86
4	320	40	0	9.4	82
6	280	0	0	10.6	114
6	280	10	0	10.4	110
6	280	40	0	9.9	108

[a] Based on moisture and ash-free content of rice straw.
[b] Time at reaction temp after 30–60 min heat-up from room temp.

the milliequivalents of NaOH in the starting reaction solution. At 6% NaOH, production of organic acids was somewhat less than starting NaOH availability. Previous results with cellulose[15] showed that increasing NaOH concentration beyond 6% did not increase organic acid production proportionately, but quickly reached a plateau. Therefore, a reaction solution of 6% NaOH at 280° C for 10 min was selected for subsequent degradation conversions of 10% starch, cellulose, rice straw, and glucose to obtain product solutions for analyses.

High Performance Liquid Chromatography and Gas Chromatography

The HPLC chromatograms of the alkaline degradation products of all the polysaccharide materials and glucose were quite similar; and those from starch and cellulose were nearly identical. Table IV lists the 18 peaks observed in these chromatograms. Based on retention times of standards, six of the product compounds were identified: glycolic (peak 11), lactic (peak 12), formic (peak 13), 2-hydroxybutyric (peak 14), acetic (peak 15), and 2-hydroxyvaleric (peak 17) acids. Fourteen of the peaks were common to all chromatograms. Peak 5 appeared only for rice straw, and peaks 16–18 did not appear for glucose. In addition, peaks 1–3, 16, and 18 were quite small in all the

TABLE IV
Chromatogram Peaks from High-Performance Liquid Chromatography of Starch, Cellulose, Rice Straw, and Glucose Alkaline Degradation Products[a] on HPX-87H Organic Acid Column[b]

Peak	Retention time (min)	Capacity factor (κ')	Compound
1	7.21	1.03	Unknown #1
2	7.42	1.06	Unknown #2
3	8.35	1.19	Unknown #3
4	10.05	1.44	Unknown #4
5[c]	10.35	1.48	Unknown #5
6	11.39	1.63	Unknown #6
7	11.88	1.70	Unknown #7
8	12.53	1.79	Unknown #8
9	12.99	1.86	Unknown #9
10	13.40	1.91	Unknown #10
11	14.02	2.00	Glycolic acid
12	14.68	2.10	Lactic acid
13	15.83	2.26	Formic acid
14	16.57	2.37	2-Hydroxybutyric acid
15	17.59	2.51	Acetic acid
16[d]	19.10	2.73	Unknown #11
17[d]	20.49	2.93	2-Hydroxyvaleric acid
18[d]	22.00	3.14	Unknown #12

[a] Each reaction run with 10% (w/w) starting material in 6% (w/w) NaOH at 280° C for 10 min.
[b] 60° C, 0.5 mL/min, 0.002 *N* H_2SO_4.
[c] Appeared only for rice straw degradation product.
[d] Did not appear for glucose degradation product.

TABLE V
Yields of Organic Acids in Alkaline Degradation Product from 10% (w/w) Starch, Cellulose, Rice Straw, and Glucose in 6% (w/w) NaOH at 280° C for 10 min

Organic acid	Yields[a] (%)			
	Starch	Cellulose	Rice straw	Glucose
Formic[b]	13.0	13.3	9.7	5.4
Acetic[b]	1.8	1.6	3.6	3.4
Glycolic[c]	5.7	4.7	4.9	4.8
Lactic[c]	19.8	18.1	15.3	36.1
2-Hydroxybutyric[c]	2.5	2.9	5.2	1.1
2-Hydroxyisobutyric[c]	2.0	1.7	1.6	0.9
2-Hydroxyvaleric[c]	1.6	1.5	0.6	0
Total 7 acids	46.4	43.8	40.9	51.7

[a]Yield based on moisture and ash-free weight of starting material.
[b]HPX-87H organic acid column, 60° C, 0.5 mL/min, 0.002 N H_2SO_4.
[c]Superox FA fused silica capillary column, He, 100–250° C at 5° C/min, FID.

chromatograms except for rice straw, for which peaks 1 and 2 were fairly large.

The gas chromatograms of the propyl esters of the polysaccharide material and glucose degradation products were also quite similar. Again, those from starch and cellulose were nearly identical. Seventeen peaks were common to the four chromatograms. 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 acids were hidden under the GC solvent peak; thus, their yields were calculated from the HPLC chromatograms. In addition, 2-hydroxyisobutyric was identified with GC. With HPLC 2-hydroxyisobutyric was found to elute as a shoulder on the trailing edge of the lactic acid peak. At very low levels (1–2% of product solution), it became hidden under the lactic acid HPLC peak.

Product yields are shown in Table V. The major reaction product was lactic acid, followed by formic acid. The yields of each organic acid from starch and cellulose were quite similar and differed markedly from glucose. Previous work on cellulose[8] and starch[9] showed that degradation in alkaline solution involved modification of the glucose units before elimination from the polymer molecule. The markedly different yields of organic acids from glucose compared to cellulose and starch in our study appears to confirm a difference in reaction pathways.

The product yields from rice straw show some similarities to those from starch, cellulose, and glucose. In particular, both rice straw and glucose yielded approximately twice as much acetic acid and little or no 2-hydroxyvaleric acid when compared to the yields from starch and cellulose. Rice straw produced the largest yield of 2-hydroxybutyric acid, approximately twice that for starch and cellulose and five times that for glucose. Alkaline degradation of rice straw involves conversion of hemicellulose, sugars, and lignin, as well as cellulose. Since amounts of total organic acids and total identified organic

acids from rice straw are quite similar to those produced from pure cellulose, noncellulose components of rice straw were apparently also converted to organic acids. Given the complicated composition of rice straw, it is difficult to separate out any catalytic effects of its mineral content. However, the similarities of the rice straw results with the other materials studied indicate no dramatic effect.

Although the conversion pathways for the alkaline degradation of the polysaccharide materials differ somewhat from glucose, many of the same organic acids are produced. Only the relative amounts of these acids appear to differ.

Ether Extractions

Table VI compares ether extractions of the alkaline degradation products treated according to the scheme in Figure 1. The total amount of nonionic, ether-soluble material extracted into fraction A was quite small. HPLC of fraction A revealed that it contained only unknown #11, as shown in Table VII.

The greatest amount of material was extracted into fraction B from the acidified product solution. However, there was not a clean-cut distinction between fraction B and fraction C compounds. Table VII shows that several compounds had moderate to large solubility in ether, but were not totally extracted from the aqueous phase. Only unknowns #1, 3, and 6 appeared to have little or no solubility in ether. Unknown #5, present only in rice straw degradation product, was not detected in any fraction, and can only be assumed lost in the precipitate upon acidification of the alkaline product solution after the initial ether extraction or irreversibly absorbed on the HPLC column.

Based on ether solubilities, it appears that, with the possible exception of unknown #1, 3, 5, and 6 and definite exception of unknown #11, all the other compounds produced by alkaline degradation were organic acids. Even unknowns #1, 3, 5, and 6 could be organic acids with very small ether solubility.

TABLE VI
Comparison of Ether Extractions of Alkaline Degradation Product (Fig. 1) from 10% (w/w) Starch, Cellulose, Rice Straw, and Glucose in 6% (w/w) NaOH at 280° C for 10 min

	% of Degradation product[d]			
	Starch	Cellulose	Rice straw	Glucose
Fraction A[a]	4.2	2.6	5.8	1.8
Acid ppt.[p]	5.2	2.5	11.2	15.5
Fraction B[b]	69.3	70.4	61.0	67.6
Fraction C[c]	21.3	24.5	22.0	15.1

[a] 48-h ether extraction of filtered, alkaline product.

[p] Precipitate formed when aqueous, alkaline solution from step a is acidified to pH 2.

[b] 96-h ether extraction of filtered, acidified, aqueous solution from step a.

[c] Material remaining in acidified, aqueous solution after ether extraction in step b.

[d] % (w/w) based on total material recovered in ether extraction classification procedure (> 95% of starting dry organic material).

TABLE VII
Appearance of Starch, Cellulose, Rice Straw, and Glucose Alkaline Degradation Product Compounds[a] in Various Fractions from Ether Extraction of Product Solution (Fig. 1) as Determined by HPLC[b]

Compound[c]	Location of compounds		
	Fraction A	Fraction B	Fraction C
Unknown #1			+ +[d]
Unknown #2		+[d]	+ +
Unknown #3			+ +
Unknown #4		+	+ +
Unknown #5			
Unknown #6			+ +
Unknown #7		+	+ +
Unknown #8		+	+ +
Unknown #9		+	+ +
Unknown #10		+ +	
Glycolic acid		+ +	+
Lactic acid		+ +	+
Formic acid		+ +	
2-Hydroxybutyric acid		+ +	
Acetic acid		+ +	
Unknown #11	+ +		
2-Hydroxyvaleric acid		+ +	
Unknown #12		+ +	

[a] Each reaction run with 10% (w/w) starting material in 6% (w/w) NaOH at 280° C for 10 min.
[b] HPX-87H organic acid column, 60° C, 0.5 mL/min, 0.002 *N* H_2SO_4.
[c] See Table IV.
[d] + = moderate solubility; + + = largest solubility.

Anion-Exchange Classification

Classification by anion exchange showed that only unknown #11 was not an organic acid. Figure 3 shows classification by anion exchange of the product solutions into nonionic compounds, monocarboxylic acids, and dicarboxylic acids. The figure takes into account the amount of material found earlier to precipitate when product solution is adjusted to pH 2. The amount of material classified as nonionic at pH 10 was 3.7, 2.5, 6.6, and 2.8% for starch, cellulose, rice straw, and glucose, respectively. These results are quite close to the results found by ether extraction of nonionics (fraction A). HPLC analyses of the nonionic fraction from anion-exchange classification at pH 10 found only unknown #11. Again, this was in agreement with the results for ether-extracted fraction A.

The difference in nonionics between classifying product at pH 2 and pH 10 represents that portion of monocarboxylic acids susceptible to lactide or lactone formation. The percentage of product solution material susceptible to lactide or lactone formation is fairly small: 4.5, 11.2, 12.9, and 4.6% for starch, cellulose, rice straw, and glucose, respectively.

Clearly, most of the product compounds were monocarboxylic acids, representing between 79.3% for rice straw and 90.5% for cellulose of the classified product at pH 10. A relatively small percentage of product was classified as

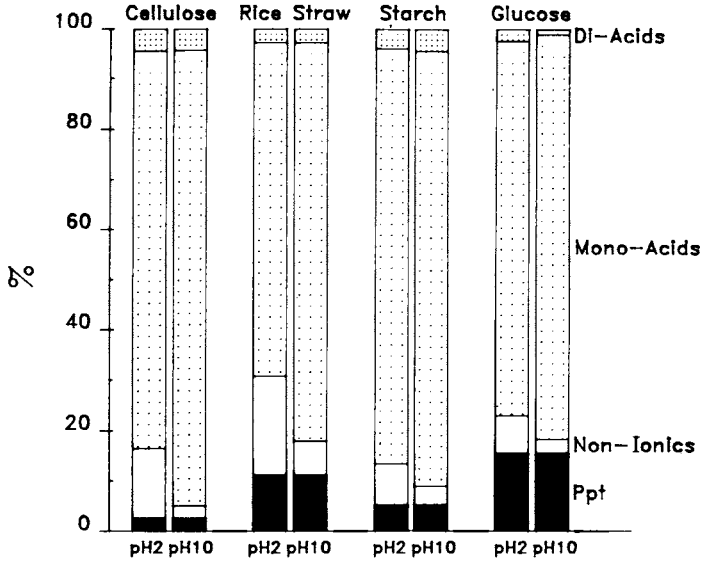

Fig. 3. Classification by anion exchange of product from alkaline degradation of 10% (w/w) starch, cellulose, and rice straw in 6% (w/w) NaOH at 280° C for 10 min. For pH 2 data, alkaline product is first acidified by cation exchange. For pH 10 data, acidified product is then adjusted back to pH 10.

dicarboxylic in nature. Analyses of this fraction by HPLC revealed that only unknown #4 appeared as a dicarboxylic acid in all the product solutions.

It appears that all of the compounds in fractions B and C from the ether extraction procedure are organic acids. With data from the titration of the product solutions plus the weight of fractions B and C taken into account, the calculated average equivalent weights of carboxylic acids produced by alkaline degradation were starch, 77; cellulose, 84; rice straw, 76; and glucose, 82. These average equivalent weights are all fairly small, indicating thorough degradation of the polysaccharide molecules as well as breakdown of glucose to approximately two organic acids.

CONCLUSIONS

Starch, cellulose, and rice straw can each be totally converted to water-soluble products by degradation of 10% (w/w) slurries in 4–6% (w/w) NaOH at 280° C. The amount of organic acids produced in each case corresponds closely to the equivalents of NaOH in the reaction solution at 4% (w/w) NaOH and falls slightly below at 6% (w/w) NaOH.

Monocarboxylic acids are the main products of alkaline degradation of starch, cellulose, and rice straw. They represent, respectively, 86.6, 90.5, and 79.3% of the starting material weight. Much smaller amounts of dicarboxylic acids, nonionics, and acid-insoluble precipitate are formed. The ether solubilities of the monocarboxylic acids cover a large range, from very soluble to insoluble. Seven of the organic acids have been identified as formic, acetic, glycolic, lactic, 2-hydroxybutyric, 2-hydroxyisobutyric, and 2-hydroxyvaleric acids. When the amounts of these acids produced from each starting material

are totaled, they represent 46.4, 43.8, and 40.9% of the initial dry organic weights of starch, cellulose, and rice straw, respectively. Furthermore, they represent 53.6, 48.4 and 51.6% of the monocarboxylic acids produced from these respective polysaccharide materials.

The results for starch and cellulose were quite similar. This is of interest for both theoretical and practical reasons. Any commercial process would benefit from the ability to switch between feedstocks, depending on price and availability.

The results for glucose were quite different from those for the other materials studied. Biggest differences were a larger amount of lactic acid and no 2-hydroxyvaleric acid produced from glucose. The total yield of identified organic acids produced from glucose was 51.7% based on glucose starting weight.

The organic acids identified thus far all have either numerous existing or potential uses. Additional work remains to be done to determine remaining unidentified organic acids and to optimize the production of the most valuable compounds.

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