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WET OXIDATION OF MODEL CARBOHYDRATE COMPOUNDS

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ABSTRACT

The major product formed by wet oxidation of a series of model compounds: D-xylose, D-glucose, D-glucitol, cellulose, and dextran, was formic acid. Its yield varied according to the structure of the carbohydrate, oxygen pressure, temperature, and the presence or absence of ferric sulfate. Acetic acid was also formed; its yield was much less dependent on the structure of the carbohydrate. Other products formed include methanol, acetaldehyde, acetone, and a series of hydroxylated acids.

INTRODUCTION

Wet oxidation, a process of treating materials with air or oxygen and water at temperatures >100°, has been used commercially for producing vanillin from pulped lignin[1], decreasing the bulk of municipal solid-waste[2], and in pulping-recovery systems[3]. There has been considerable recent interest in using this process for converting plant materials into organic chemicals[4–8]. Plant materials undergo two general types of wet-oxidation reactions depending on the temperature, oxygen pressure, and the presence or absence of metal catalysts[7]. At low oxygen pressures (827–1655 kPa) and temperatures (120–170°), the major reactions involve acid-catalyzed hydrolysis of the lignin and hemicellulose into low-molecular-weight, water-soluble products. At higher temperaures (170–220°) and pressures (1655–3310 kPa) and with addition of metal catalyst, the major products are carboxylic acids (mainly acetic and formic acid), formed by oxidation and fragmentation of the polysaccharides (cellulose and hemicelluloses)[7].

The maximum yield of formic acid from wood was 14.6%, based on the starting weight of wood. This yield was obtained at 200° and decreased at both higher and lower temperaures. The yield of formic acid was increased to 22% by increasing the oxygen pressure to 3310 kPa, or to 28% by the addition of such metal catalysts as ferric sulfate or copper sulfate. In contrast, the maximum yield of acetic acid obtained was 12%. The yield of acetic acid increased with temperature and with oxygen pressure up to 2482 kPa of oxygen and then decreased. Addition of metal catalysts also decreased the yield of acetic acid.

The purpose of this study was to learn more about the high-temperature wet-

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oxidation process that leads to the formation of carboxylic acid. Five model compounds were used; D-xylose, D-glucose, D-glucitol, cellulose, and dextran, in order to determine what effect the structure and the types of linkage had upon the high-temperature, wet-oxidation reaction.

EXPERIMENTAL

Procedures — The carbohydrates and other chemicals used in this study were the best grade commercially available and were used without further purification. The dextran used was produced by *Leuconostoc mesenteroides* (strain no. B-512) and had an average molecular weight of 151,000. The wet-oxidation reaction was performed in a 600-mL high-pressure (316 stainless steel) reactor (Model 4563, Parr Instrument Company, Moline, IL). Table I outlines the conditions of the wet-oxidation reaction.

In a typical wet-oxidation experiment, the carbohydrate and water are mixed in the reactor and the reactor is sealed, pressurized with oxygen, and heated to the desired temperature (15 min). Once the reaction temperature is reached, it is held constant with stirring for 30 min and then cooled.

Analyses. — The amount of D-xylose and D-glucitol remaining after the reaction was determined by using high-performance liquid chromatography[9] with an amino-bonded polar column (LiChrosorb NH_2). The amount of D-glucose remaining was determined by using a glucose analyzer (YSI Model 23A Glucose Analyzer, Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio 45387). Cellulose was determined by filtering the solution and determining the amount of insoluble cellulose remaining; the amount of degradation of the solid cellulose was determined by hydrolyzing the cellulose to D-glucose and analyzing for total D-glucose. The liquid solution from the wet oxidation of cellulose was also analyzed for D-glucose directly and after hydrolysis with 4.5% percent sulfuric acid for 4 h in order to determine how much material was solubilized during the wet-oxidation reaction. Dextrans, which are water soluble, were determined by hydrolysis (4.5% sulfuric acid for 4 h at 100°) and analysis of the liberated D-glucose by using a glucose analyzer.

TABLE I

WET-OXIDATION CONDITIONS

Temperature range	171–227°
Time	30 min
Oxygen pressure[a]	1655–3310 kPa
Carbohydrate[b]	15 g
Water	150 mL
Reactor volume	600 mL

[a] These values are the initial oxygen pressures at room temperature. [b] The weight of all carbohydrates was 15 g, except for cellulose, which was 7.5 g.

The low-molecular-weight acids were isolated from the liquid fraction by using small reverse-phase columns (Waters C-18 Sep-Pak No. 51910). Samples of the wet-oxidation product were passed through the reverse-phase columns with water as the eluent. The carboxylic acids are not retained on the column, whereas other, less-polar organic compounds are bound. After this purification step, the liquid sample containing the acids was analyzed by high-performance liquid chromatography (l.c.) with a cation-exchange column (Bio-Rad HPX-87). The volatile products, including methanol, acetaldehyde, and acetone, were determined quantitatively by gas chromatography at 150°, with a Porapak-Q column (100–120 mesh, 3.05 m × 3.175 mm) and a flame-ionization detector.

The higher-molecular-weight acids were separated and analyzed by using gas chromatography–mass spectrometry after conversion into their trimethylsilyl derivatives. A Varian Model 2700 gas chromatograph interfaced with a DuPont Model 490-F mass spectrometer was used; the column was 1.83 m × 3.175 mm 3% SE-30 packed on Chromosorb W; and the column temperature was programmed from 100 to 210° at 6°/min.

RESULTS AND DISCUSSION

The stability of the individual model compounds to wet oxidation is shown in Figs. 1 and 2. This group of reactions was performed at an oxygen pressure at 1655 kPa for 30 min. D-Xylose was the least stable monosaccharide, with 80% being lost after 30 min at 171°. D-Glucose showed more stability, with ~98% remaining at 171°. However, at 182°, >90% of the D-glucose was broken down. The most stable compound was D-glucitol. Even at temperatures as high as 198°, >88% of the start-

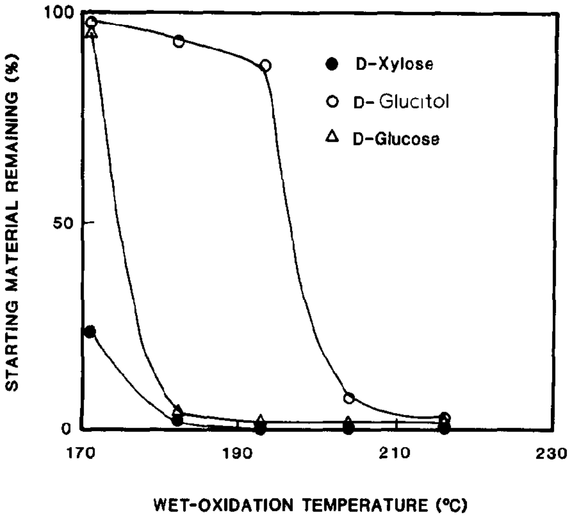

Fig. 1. Rate of decomposition of monosaccharides during wet oxidation.

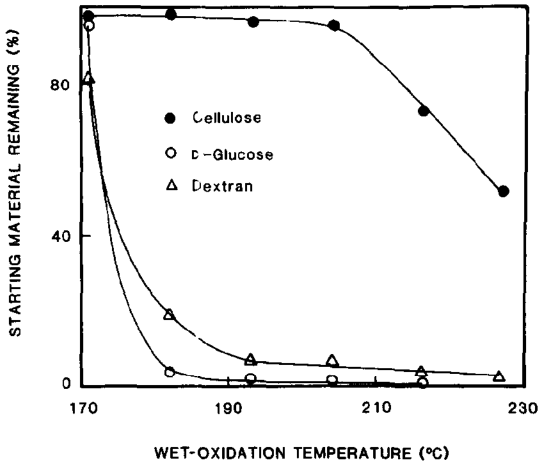

Fig. 2. Rate of decomposition of cellulose and dextran during wet oxidation.

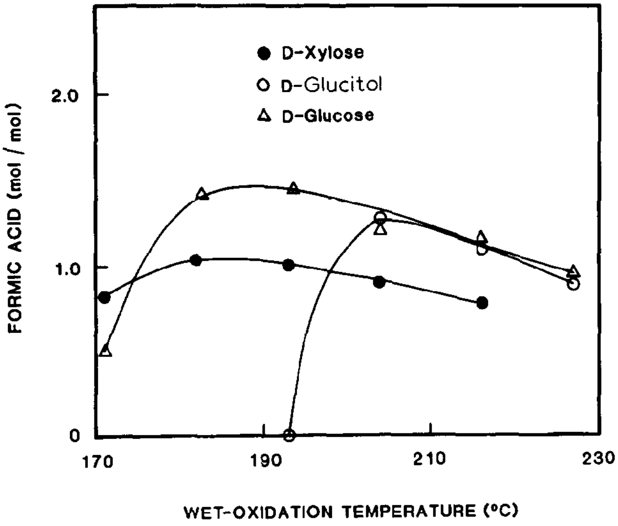

Fig. 3. Yield of formic acid from monosaccharides.

ing material remained. Apparently, the aldehyde group at C-1 plays an important role in initiating the wet-oxidation reaction.

There was a large difference in the stabilities of the two polysaccharides. Cellulose was relatively stable to wet oxidation and did not start breaking down until the wet-oxidation temperature reached 203°. Analysis of the solid cellulose material remaining after wet oxidation indicated that 95–99% of the D-glucose residues in the solid cellulose remained intact at all temperatures studied. Only traces (0–

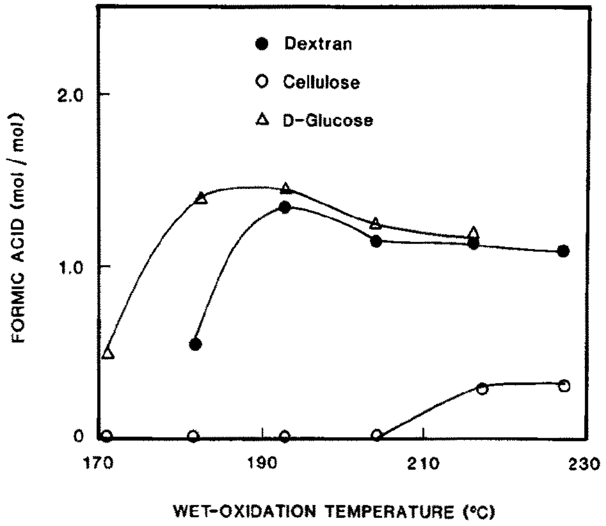

Fig. 4. Yield of formic acid from dextran and cellulose.

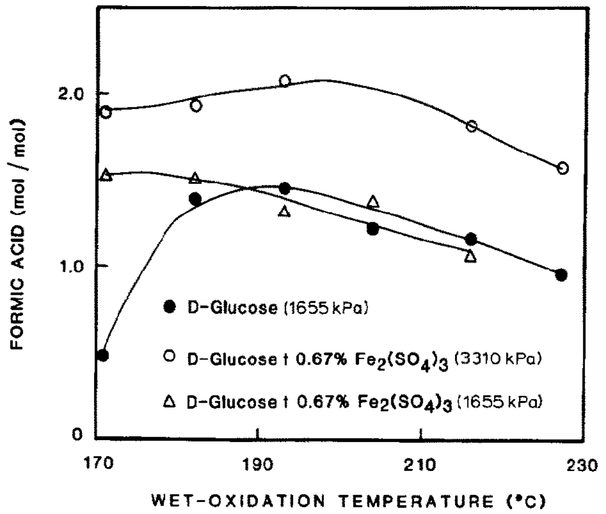

Fig. 5. Yield of formic acid from D-glucose.

0.5%) of D-glucose, from hydrolysis of the cellulose, were found in the liquid until the wet-oxidation temperature reached 216–227°, at which point the concentration of D-glucose reached 4.25–4.50% based on the weight of starting material. Traces of water-soluble cello-oligosaccharides were also formed during wet-oxidation; the concentration of these varied from 0.25–1.0% over the temperature range.

Dextran, in contrast, was degraded very rapidly by wet oxidation. Even at 171°, the lowest temperature studied, almost 20% of the dextran had decomposed.

The major product from all carbohydrates was formic acid. Figs. 3 and 4

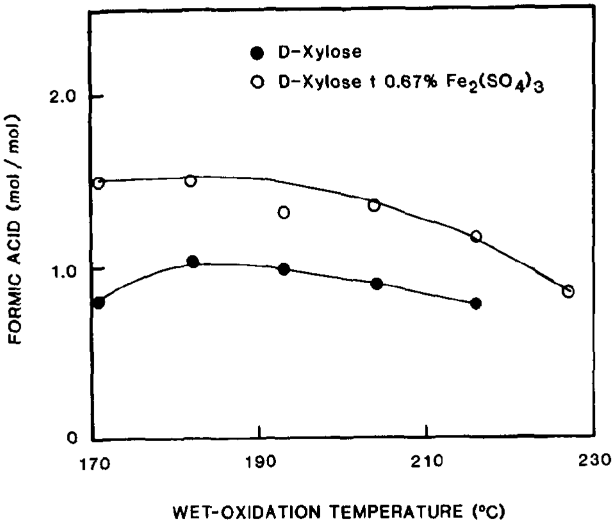

Fig. 6. Yield of formic acid from D-xylose.

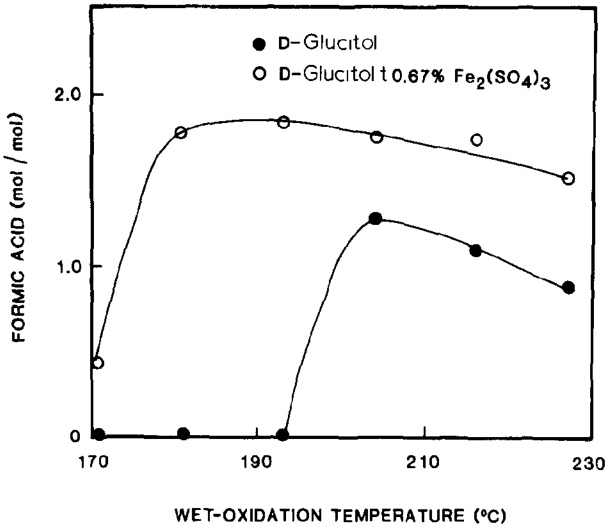

Fig. 7. Yield of formic acid from D-glucitol.

show the yields from each model compound in mol of formic acid/mol of sugar. For D-glucose, the maximum yield of formic acid at 1655 kPa was 1.45 mol/mol of sugar at 190°. With D-xylose, the yield was 1.05 mol/mol of sugar at 190°. D-Glucitol produced 1.25 mol/mol of sugar at 205°. Yields of formic acid from dextran and cellulose correspond to their relative stability: dextran gave 1.35 mol/mol of sugar; cellulose gave the lowest yield of formic acid of all the compounds studied—0.3 mol/mol of sugar residues at 227°.

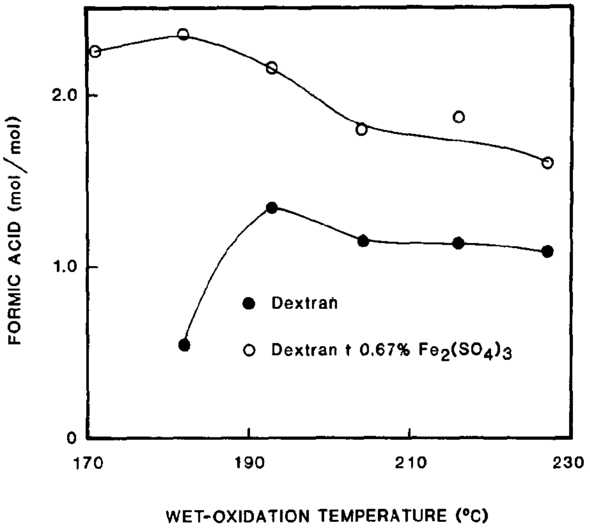

Fig. 8. Yield of formic acid from dextran.

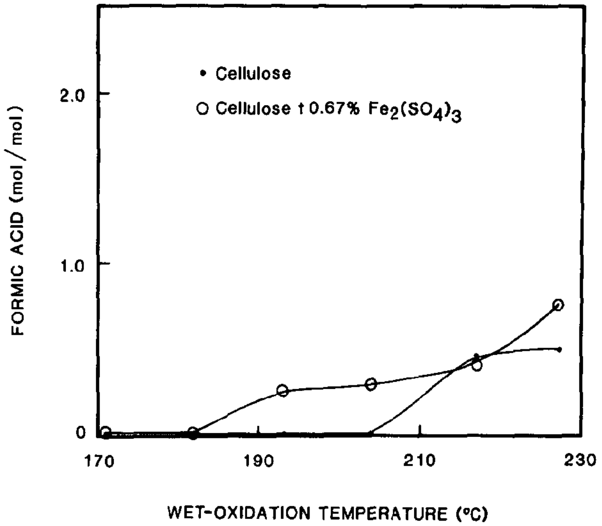

Fig. 9. Yield of formic acid from cellulose.

The yield of formic acid could be increased by using higher oxygen pressures or by the addition of ferric sulfate. This effect is illustrated in Fig. 5–7. The addition of ferric sulfate led to higher yields of formic acid at a lower temperature in the case of D-glucose. With 0.67% of ferric sulfate present, D-glucose gave 1.55 mol/mol of sugar versus 1.45 mol/mol of sugar for the uncatalyzed reaction. Higher oxygen pressure (3310 kPa) increased the yield to 2.09 mol/mol of sugar at 190–200°.

For D-xylose, the presence of ferric sulfate caused an increase from 1.05 mol

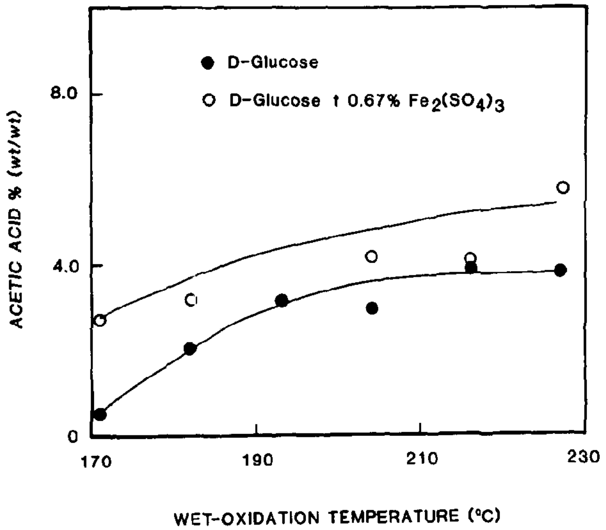

Fig. 10. Formation of acetic acid from D-glucose.

TABLE II

MAXIMUM YIELD OF FORMIC AND ACETIC ACID[a]

Compound	*Formic acid*		*Acetic acid*	
	mol/mol	*%*	*mol/mol*	*%*
D-Glucose	1.55	39.7	0.18	6.0
D-Xylose	1.50	47.0	0.18	7.2
D-Glucitol	1.87	47.2	0.18	6.1
Dextran	2.35	67.5	0.23	8.4
Cellulose	0.75	21.3	0.19	6.9

[a] Reactor conditions: 1655 kPa of oxygen, 0.67% $Fe_2(SO_4)_3$, 10% carbohydrate or 5% cellulose, 30-min reaction time.

of formic acid to 1.50 mol of formic acid (Fig. 6). The largest effect of ferric sulfate was seen with D-glucitol (Fig. 7). The yield of formic acid increased from 1.30 mol at 203° to 1.85 mol at 190°. The ferric sulfate not only increased the yield of formic acid but also lowered the temperature of the wet-oxidation reactions.

The yield of formic acid from the polysaccharides was increased both by oxygen pressure and by addition of ferric sulfate (Figs. 8 and 9). The yield of this acid from dextrans increased from 1.35 mol at 193° to 2.35 mol at 182° after addition of ferric sulfate. With cellulose, the yield increased from 0.50 to 0.75 mol.

The yield of acetic acid increased as the wet-oxidation temperature increased, or by addition of ferric sulfate; however, it was much less dependent on the structure of the carbohydrate (Fig. 10). The maximum yield of acetic acid and formic acid for the various model compounds studied is summarized in Table II.

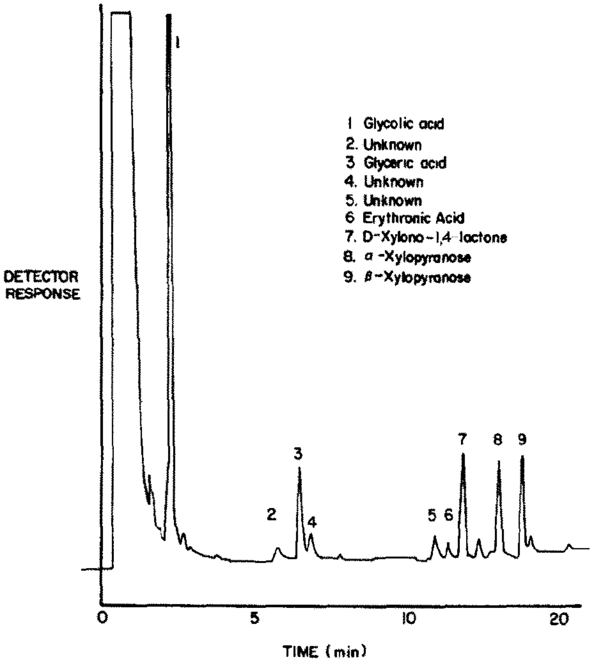

Fig. 11. Gas-chromatographic separation of products from the wet oxidation of D-xylose (silylated).

There are several other products formed during wet oxidation: traces of methanol (0.5%), acetaldehyde, and acetone (<0.5%). Also formed is a series of hydroxylated acids. A chromatograph of the products formed by the wet oxidation of D-xylose is shown in Fig. 11. These acids are apparently formed by oxidation of the terminal group on the carbohydrate. A similar pattern of products was seen with all of the model compounds.

The results of this study indicate that relatively high yields of formic acid and acetic acid are obtained from all the carbohydrates studied. The most likely mechanism for this reaction involves the formation of hydroperoxy radicals which interact with the carbohydrates. Studies have shown that certain metals react directly with oxygen to produce hydroperoxy radicals[10,11]. Studies by Isbell[12,13] have shown that aldoses, ketoses, uronic acids, and alditols are rapidly broken into formic acid, oxalic acid, and carbon dioxide by alkaline hydrogen peroxide.

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