DEGRADATION KINETICS OF MONOSACCHARIDES IN HYDROCHLORIC, SULFURIC, AND SULFUROUS ACID

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The degradation kinetics of monosaccharides during sulfurous acid treatment was compared to hydrochloric acid and to sulfuric acid treatments. Reaction conditions corresponded to the range found in previous research to allow for the production of hemicelluloses-derived monosaccharides through hydrolysis of wood. Degradation behavior of monosaccharides during treatment with each acid was expressed by a second-order reaction rate constant with respect to substrate and acid concentrations, and the activation energy and frequency factor were calculated using the Arrhenius equation. Results demonstrated that the second-order reaction rate of a monosaccharide was dependent on the type of acid, indicating that monosaccharides degrade at different rates under different acids, even when the molar concentration of the acid is the same. The degradation of monosaccharides in sulfurous acid was much slower than that in hydrochloric acid and in sulfuric acid. A comparison of two sequential treatments with sulfuric acid, with and without the bisulfite ion, showed that sulfurous acid has a protective effect on the degradation of monosaccharides.

Keywords: Monosaccharide; Sulfurous acid; Degradation kinetics; Acid hydrolysis; Hemicellulose

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INTRODUCTION

Dilute acid treatment has many potential applications for the chemical and biochemical conversion of lignocellulosic biomass, including wood, into useful products. When acid treatment is applied under high temperatures (160 to 230°C) and pressures (~10 atm), it leads to relatively low conversion rates (about 70% glucose) of monosaccharide from polysaccharides, such as recalcitrant cellulose (Iranmahboob *et al*. 2002; Korolkov *et al*. 1961). Usually two-stage acid hydrolysis with the range of 2 to 5% acid concentration in the dilute-acid hydrolysis process and the range of 10 to 30% in the concentrated-acid hydrolysis process, is adopted (Broder *et al*.1995; Patrick Lee *et al*. 1997). When acid treatment is applied as a pretreatment to enzymatic saccharification, it is expected to make the remaining cellulose more digestible to cellulolytic enzymes through the partial degradation and removal of lignin and hemicelluloses (Kumar *et al*. 2009; Pingali *et al*. 2010; Saha *et al*. 2005; Taherzadeh and Karimi 2007; Wyman 1994). Most dissolving pulp is produced from softwood fiber, using either the acid-sulfite or prehydrolysis kraft process (Durbak 1993), and acid prehydrolysis prior to kraft pulping

is an attractive approach for production of high purity cellulose pulp (Bouiri and Amrani 2010). Dilute acid treatment, for example sulfurous acid treatment, can also be expected to be used as the prehydrolysis stage prior to the kraft pulping process to produce dissolving pulp (DP), and recently with this purpose, pertinent work was done in our laboratory.

In the acid hydrolysis of polysaccharides, the acid catalyzes not only the hydrolysis of polysaccharides into monosaccharides, but also there are further degradation reactions of monosaccharides into furans and carboxylic acids (Chandel *et al* 2011; Sjostrom 1993). The latter is a substantial problem because it lowers the overall yield of monosaccharides and leads to the production of undesired compounds during the subsequent fermentation process employed to convert monosaccharides to useful compounds, such as ethanol (Carvalheiro *et al.* 2008; Mamman *et al.* 2008; Marzialetti *et al.* 2008). Therefore, the conversion of monosaccharides to other compounds is one of the primary concerns in processes using acids to hydrolyze lignocellulosic biomass.

Recently, dilute acid treatment with sulfurous acid (H_2SO_3) has renewedly attracted more attention as a promising pretreatment process for biomass conversion (Yang *et al.* 2010; Zhu *et al.* 2009; Yu *et al.* 2010; Takahashi *et al.* 2010; Tanifuji *et al.* 2011). Until about 40 years ago, sulfurous acid-mediated pulping was one of the most frequently used chemical pulping process in the world, similar to sulfite pulping. The behavior of wood components, especially lignin, during the sulfite pulping process had been well studied (Rydholm 1965). However, when sulfurous acid is applied in the pretreatment process, reaction conditions are usually different from those used during acid sulfite pulping, and the main concern is the prehydrolysis of hemicelluloses, not the removal of lignin. In our opinion, several clear advantages can be postulated in the use of sulfurous acid as a pretreatment method: (1) as an acid catalyst, it hydrolyzes polysaccharides and lignin; (2) the formation of carbonyl adducts may prevent monosaccharides from further degradation; (3) by the introduction of sulfonic acid groups into lignin, it causes partial delignification and softening of the wood, which can contribute to delignification during the second stage; (4) by the formation of organic sulfonic acid groups, it can increase the acidity of the system, although sulfurous acid itself is a weak acid. Therefore, it is important to quantitatively understand the behavior of monosaccharides during sulfurous acid treatment as the prehydrolysis stage.

Sulfurous acid is a weaker acid than either hydrochloric or sulfuric acid. However, previous studies, including our preliminary work, indicated that in contrast to strong mineral acids (HCl and H_2SO_4), the use of sulfurous acid retains the yield of cellulose (though there is some depolymerization), while the hemicelluloses of wood are equally well hydrolyzed to monosaccharides in comparable yields with hydrochloric acid and sulfuric acid (Shi *et al.* 2010; Shi *et al.* 2011; Wang *et al.* 2011). Generally, yields of monosaccharides from hemicelluloses during acid treatment can be affected by both the efficiency of polysaccharide hydrolysis and the preservation of monosaccharides that are produced. Production of monosaccharides during dilute acid treatment has been previously investigated in many studies (Aguilar *et al.* 2002; Herrera *et al.* 2004; Khajavi *et al.* 2005; Kumar and Wyman 2008; Qi *et al.* 2008; Téllez-Luis *et al.* 2002; Xiang *et al.* 2004). In these studies, a discussion of the degradation of monosaccharides was also presented, just based on the decrease in monosaccharide yield from the hydrolysis of

polysaccharides under prolonged reaction times or increased acid concentrations. Few comprehensive studies or reviews discussing and comparing the degradation kinetics of monosaccharides in different dilute acids have been published.

In this work, we analyzed the degradation behavior of several monosaccharides (arabinose, xylose, galactose, mannose, and glucose) in three dilute acids (hydrochloric acid, sulfuric acid, and sulfurous acid) and compared the stability of these monosaccharides during treatment with these three acids.

EXPERIMENTAL

Materials

All monosaccharides, including D-glucose, D-xylose, L-arabinose, D-mannose, D-galactose, sodium borohydride ($NaBH_4$), $NaHSO_3$, and other reagents were all from Wako Pure Chemical Industry (Japan). Monosaccharides were used without further purification.

Acid Treatment

From a stock solution of five mixed monosaccharides in water, similar portions were added to three volumetric flasks, with equal volumes and varying acid concentrations. The concentration of monosaccharides in the prepared reaction mixture was 0.002 mol/L for each monosaccharide. The monosaccharide solution in each acid (4 mL volume) was applied to a TAF-SR reactor (maximum working pressure: 10 MPa; maximum working temperature: 180°C; seal o-ring: Fluorinated gum; total volume: 50 mL; Taiatsu Techno Corp., Japan) equipped with an internal teflon tube and subjected to heat treatment in an oil bath shaker (RSO-200TE, Riko, Japan) at selected temperatures and indicated times (Table 1). As a reference sample, the same portion of stock solution was mixed with the internal standard (inositol) and directly subjected to GC determination as alditol acetates. The value obtained for the reference sample was used as the initial yield for each monosaccharide at reaction time 0 h.

Table 1. Treatment Conditions Selected for Acid Treatment

Acid	Acid concentration (mol/L)	Temperature (°C)	Time (h)
HCl	0.14 (0.5%)*	120, 130, 140	0.75–5.75
	0.27 (1.0%)*		
	0.41 (1.5%)*		
H_2SO_4	0.20 (2.0%)*	120, 130, 140	0.75–5.75
	0.41 (4.0%)*		
	0.61 (6.0%)*		
H_2SO_3	0.16 (1.3%)*	120, 130, 140	1.75–13.75
	0.39 (3.2%)*		
	0.63 (5.1%)*		

*approximate weight concentration, % (w/w)

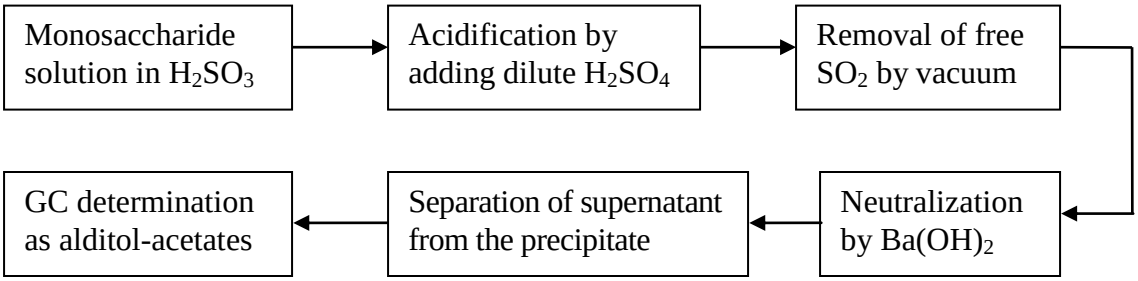
Analytical Procedures

GC determination of monosaccharide yield by alditol-acetate method (Borchardt and Piper 1970)

After cooling and addition of an internal standard (inositol), the reaction mixture from acid treatment was neutralized to pH 5.5 with NaOH for HCl treatment and $Ba(OH)_2$ for sulfuric acid treatment (for the neutralization of H_2SO_3, see next section). Supernatants of neutralized samples were reduced by $NaBH_4$ for 24 h. The excess $NaBH_4$ was destroyed by the addition of acetic acid, and borate was removed by repeating methanol addition and evaporation. Produced alditols were converted into acetates by the addition of acetic anhydride and subjected to Gas Chromatograph determination (GC-14B, Shimadzu, Japan) under the following conditions: column, TC-17, 30 m × 0.25 mm; column temperature, 220°C; injection temperature, 220°C; detector temperature, 230°C.

Determination of monosaccharides from sulfurous acid treatment

For the determination of monosaccharides from sulfurous acid treatment, the reaction mixture was subjected to the conditions outlined in Scheme 1. Namely, after the addition of the internal standard (inositol), the reaction mixture was further acidified to pH 1 by the addition of dilute sulfuric acid and then kept under reduced pressure for about 1 h to eliminate SO_2 from the solution. After neutralization with $Ba(OH)_2$ to pH 5.5, the supernatant was converted into alditol acetates in the same manner as described in the above section and subjected to GC determination.



Scheme 1. Sample preparation for determination of monosaccharides during sulfurous acid treatment

RESULTS AND DISCUSSION

Determination of Monosaccharides from Sulfurous Acid Treatment

The degradation of pentoses into furfural and hexoses into hydroxymethylfurfural (HMF), levulinic, and formic acids are typical acid-catalyzed reaction products that contribute to the loss of monosaccharide yield (Chandel *et al.* 2011; Sjostrom 1993). However, these reactions only account for a portion of the yield loss observed during mild acid treatment (Mansilla *et al.* 1998). During acid treatment, some bimolecular reactions will also take place, contributing to the loss of monosaccharide yield. Therefore, degradation of monosaccharides cannot be accurately expressed based on the formation

of some selected degradation products. In this work, we described the degradation behavior of each monosaccharide during acid treatment based on the precise determination of recovery yields when monosaccharides were subjected to acid treatment under strictly controlled conditions. Reaction mixtures of each monosaccharide were analyzed and expressed by second-order reaction rate constants with respect to substrate and acid concentrations.

However, when reaction mixture from sulfurous acid treatment was analyzed for monosaccharide content using the same methods as those for hydrochloric acid or sulfuric acid treatment, the recovery yield was sometimes quite low. This was thought to be caused by the formation of monosaccharide-sulfite adducts (bisulfite adducts) through the carbonyl group of the monosaccharide products. In order to destroy these adducts and measure the actual yield, a post-treatment method was developed (seeing Scheme 1). By the comparison of three samples prepared by different methods, we examined whether the conditions shown in Scheme 1 could result in higher and more accurate yields. As shown in Table 2, samples prepared from sulfurous acid solutions gave quite different yields depending on the post-treatment method. When post-treatment was applied, the recovery yield of each monosaccharide was the same as the reference sample, while recovery yields were quite low if post-treatment were not applied. Based on this result, all the samples prepared from sulfurous acid treatment were subjected to the conditions presented in Scheme 1 for the determination of residual monosaccharides.

Table 2. The Effect of Post-Treatment on Monosaccharide Recovery Yield during Sulfurous Acid Treatment (at room temperature)

Samples	Recovery yield (%)				
	L-arabinose	D-xylose	D-mannose	D-glucose	D-galactose
Water (reference)	100	100	100	100	100
With Scheme 1	100.1	100.4	99.9	100.1	99.8
Without Scheme 1	16.6	17.4	17.3	16.8	17.4

Comparison of Monosaccharide Degradation during Treatment with the Three Acids

The degradation experiment with three acids was repeated two times, showing good repetitiveness except in the case of degradation of arabinose at 120 ^{o}C with 0.5% (w/w) HCl. Figure 1 shows the dependence of monosaccharide recovery yield with treatment times at comparable acid concentrations at 140°C. Degradation of each monosaccharide was faster in HCl than in H_2SO_4 at the same acid concentration (0.41 mol/L, Fig. 1(a) and 1(b)). Monosaccharide degradation also differed for HCl and H_2SO_4 treatments under other treatment conditions (different temperatures and acid concentrations), but with the opposite tendency at times; this will be discussed in the next part by comparison of kinetic parameters. Because the proton activity of dilute HCl and H_2SO_4 solutions are almost the same when they are present at the same molar concentration in water (Phan *et al.* 2011), the differences in monosaccharide degradation for these two acids suggest that not only protons, but also counter anions of the acids (conjugate bases), participate in the degradation of monosaccharides (Marcotullio and De Jong 2010). This may be important during the design of an effective prehydrolysis stage

using dilute acids for a chemical pulping process. Since H_2SO_3 is a weaker acid than the other two acids tested in this study, the degradation of each monosaccharide was much slower in 0.39 and 0.63 mol/L H_2SO_3 (Fig. 1(c) and 1(d)) than in the other two acids at 0.41 mol/L. Although the stable nature of monosaccharides in H_2SO_3 may not be surprising, it has great practical value because it indicates that the prehydrolysis stage can be performed under a variety of conditions without significant loss of monosaccharides.

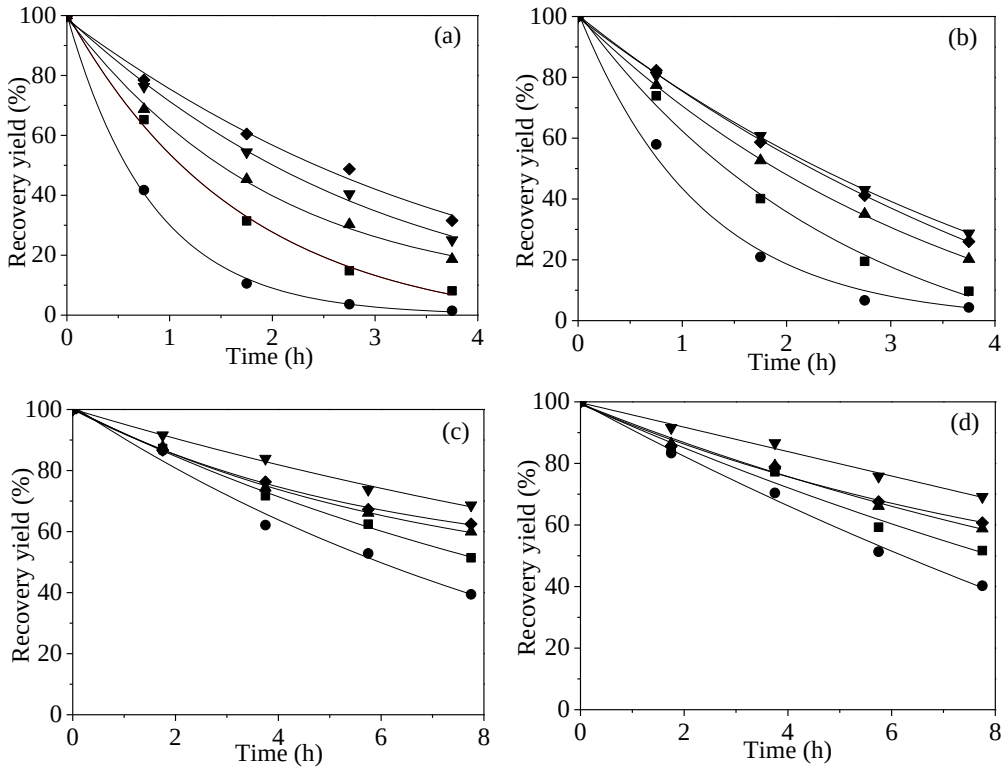


Fig. 1. Differences in monosaccharide degradation during treatment with different acids at 140°C under comparable acid concentrations ((a) in 0.41 mol/L HCl; (b) in 0.41 mol/L H_2SO_4; (c) in 0.39 mol/L H_2SO_3; and (d) in 0.63 mol/L H_2SO_3)

Kinetic Parameters of Monosaccharide Degradation during Treatment with the Three Acids

Table 3 shows the reaction rate constant (*k*) of each monosaccharide during treatment with HCl, H_2SO_4, or H_2SO_3. Rate constants are expressed as second-order reaction rate constants with respect to substrate and acid concentrations (as shown in Equation (1)). The results clearly showed that degradation of pentoses was more rapid than the degradation of hexoses under all conditions examined, with the exception of galactose in H_2SO_3 at 130°C. Among these monosaccharides, xylose seemed to be the most unstable.

$$-\frac{dc}{dt} = k\,[C_{sugar}][\,C_{acid}\,] \quad (1)$$

Table 3. Second Order Rate Constant (*k*) of Each Monosaccharide during Treatment with the Three Acids

	Temp. (°C)	*k* (L· mol^{-1}· h^{-1})				
		L-arabinose	D-xylose	D-mannose	D-glucose	D-galactose
in HCl	120	0.311	0.504	0.162	0.132	0.095
	130	1.010	2.095	0.768	0.695	0.633
	140	1.512	2.124	1.120	0.962	0.764
in H_2SO_4	120	0.292	0.483	0.160	0.112	0.121
	130	1.406	1.542	0.916	0.633	0.768
	140	1.553	2.157	1.282	0.975	1.066
in H_2SO_3	120	0.019	0.016	0.006	0.004	0.006
	130	0.020	0.035	0.013	0.016	0.045
	140	0.130	0.168	0.056	0.066	0.057

The data also demonstrated that the second-order rate constants of most monosaccharides, except galactose at 120°C, and xylose and glucose at 130°C in H_2SO_4 were smaller than those in HCl. However, at 140°C, the second-order rate constants for each monosaccharide in H_2SO_4 were greater than those in HCl. In this research, the second-order rate constants (*k*) were simply obtained as an average of three pseudo-first order reaction rate constants at three different acid concentration levels. Because of this, if degradation behavior of each monosaccharide is compared only at one acid concentration level, the second-order rate constants could be different from what is expected, as shown in Table 3. This means that three pseudo-first order reaction rate constants do not stay in a simple line, indicating complexity of acid-catalyzed degradation of monosaccharides. This may also indicate that at higher temperatures, different types of reactions other than simple acid-catalyzed degradation occur and are enhanced during degradation of monosaccharides in H_2SO_4. Because of this, reaction with conjugate bases (HSO_4^-) or bimolecular reactions with the monosaccharides themselves or their degradation products are suggested.

In addition, it was found that each monosaccharide was much more stable in the H_2SO_3 system than in HCl or H_2SO_4 under all the conditions examined in this study (Table 3). Such discrepancies in degradation behaviors among different acid treatments also seemed to imply the involvement of the acids' conjugate bases in the degradation of monosaccharides in dilute acid systems.

Table 4. Activation Energy (*Ea*) and Pre-exponential Factor (*A*) of Each Monosaccharide during Treatment with the Three Acids

	in HCl		in H_2SO_4		in H_2SO_3	
	Ea (kJ/mol)	*A* (L· mol^{-1}· h^{-1})	*Ea* (kJ/mol)	*A* (L· mol^{-1}· h^{-1})	*Ea* (kJ/mol)	*A* (L· mol^{-1}· h^{-1})
L-arabinose	107.1	3.02×10^{13}	113.5	4.46×10^{14}	126.6	9.56×10^{14}
D-xylose	97.9	6.48×10^{12}	101.4	1.66×10^{13}	159.4	2.07×10^{19}
D-mannose	131.0	5.00×10^{16}	141.3	1.20×10^{18}	146.0	1.42×10^{17}
D-glucose	134.8	1.33×10^{17}	146.5	4.10×10^{18}	190.8	8.68×10^{22}
D-galactose	141.6	8.21×10^{17}	147.5	6.16×10^{18}	148.3	4.21×10^{17}

Activation energies for the degradation of monosaccharides in HCl and H_2SO_4 were highest for galactose, and they decreased sequentially for glucose, mannose, arabinose, and xylose (Table 4). However, activation energies of each monosaccharide, especially xylose and glucose in the H_2SO_3 system, were much higher than those in HCl or H_2SO_4. These data indicated that degradation of xylose and glucose was inhibited by H_2SO_3, and the temperature dependency of the degradation reaction of monosaccharides was lower in the case of H_2SO_3. These observations seemed to suggest that differences in conjugate bases result in different activation energies for the reaction of each monosaccharide in different acids.

Protective Effects of Sulfurous Acid on Monosaccharides during Acid Treatment

The reduced degradation of monosaccharides in H_2SO_3 must be primarily due to the weaker nature of this acid compared to the other two acids. However, as mentioned in the Introduction, H_2SO_3 can hydrolyze hemicellulose in wood very well, resulting in a monosaccharide yield that is comparable to yields obtained from the other two acids. In addition, previous studies demonstrated that the formation of furfural and HMF was low when wood chips were treated with sulfurous acid (Zhu *et al.* 2009; Yu *et al.* 2010). These results prompted us to examine the effects of H_2SO_3 on the protection of monosaccharides to further degradation during acid treatment. Generally, the degradation of monosaccharides in acids proceeds from the protonation of carbonyl groups. Monosaccharides could be lost not only by this type of degradation, but also by bimolecular reactions, such as aldol condensation-type reactions, in which carbonyl groups participate. As was suggested in the Experimental section (Determination of monosaccharides from sulfurous acid treatment), carbonyl groups of monosaccharides potentially undergo adduct formation during treatment with sulfurous acid. The actual species that participates in adduct formation is the bisulfite ion derived from sulfurous acid. Because of adduct formation, reactions due to the carbonyl group could be suppressed. This expectation is schematically illustrated in Fig. 2.

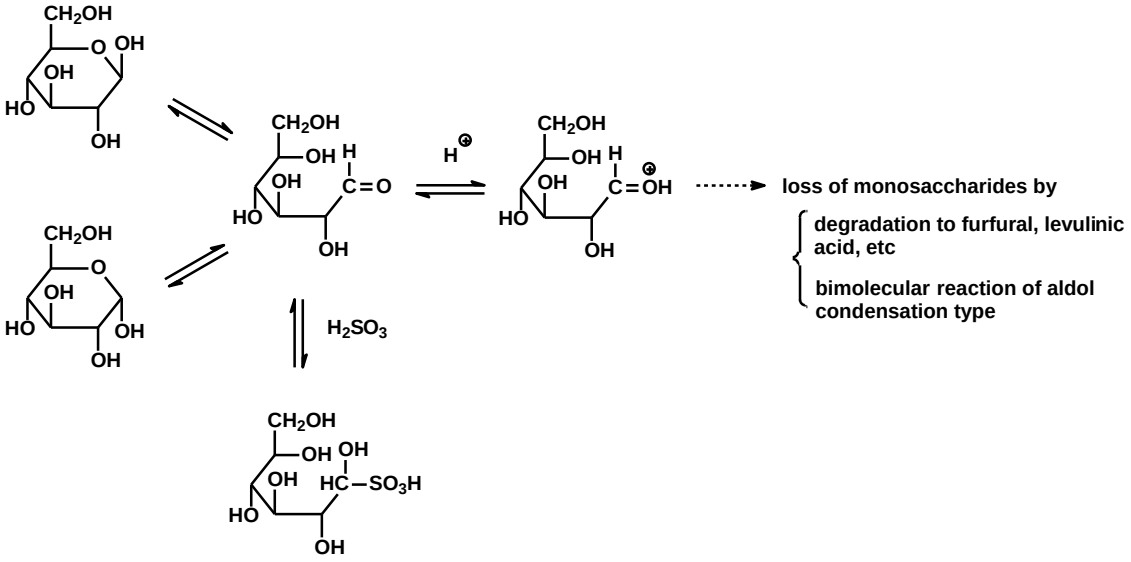


Fig. 2. Possible effects of sulfurous acid on the protection of monosaccharides

In order to examine this possibility, monosaccharides were subjected to H_2SO_4 treatment with and without the addition of $NaHSO_3$. The pH of the two solutions was adjusted to the same value, 0.70 (Table 5). This experiment was repeated twice, showing better repetitiveness (shown in Table 6) within the accuracy of the experiment. The minimum difference between two cases was selected in order to clearly show contrasting results. As shown in Fig. 3, each monosaccharide showed better stability in H_2SO_4 with $NaHSO_3$ treatment than in H_2SO_4 without $NaHSO_3$ treatment. These results demonstrated that the bisulfite ion has a certain role in protecting monosaccharides.

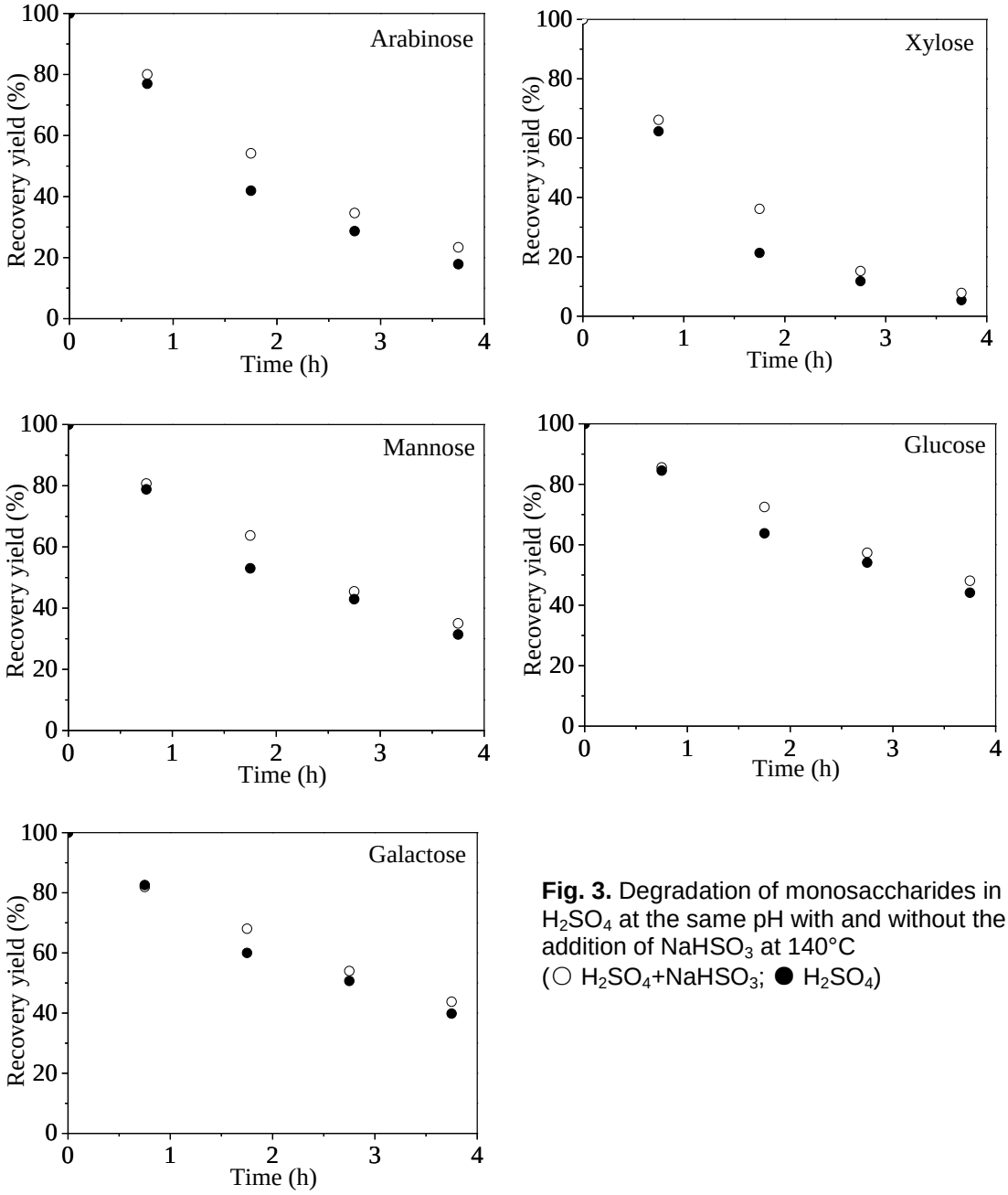


Fig. 3. Degradation of monosaccharides in H_2SO_4 at the same pH with and without the addition of $NaHSO_3$ at 140°C (○ H_2SO_4+$NaHSO_3$; ● H_2SO_4)

Table 5. Treatment of Monosaccharides in H_2SO_4 with and without the Addition of $NaHSO_3$

Composition of System		Initial pH
No. 1	0.60 mol/L H_2SO_4 and 0.32 mol/L $NaHSO_3$	0.70 (26.9°C)
No. 2	0.34 mol/L H_2SO_4 without $NaHSO_3$	0.70 (27.8°C)

Table 6. Recovery Yield of Monosaccharides in H_2SO_4 at the same pH with and without the Addition of $NaHSO_3$ at 140°C

*concentration of each monosaccharide was 0.002 mol/L.

Time (h)	$NaHSO_3$	Recovery Yield (%)				
		L-arabinose	D-xylose	D-mannose	D-glucose	D-galactose
0		100	100	100	100	100
0.75	without	77.83±1.22	62.91±0.86	79.11±0.40	84.48±0.07	81.52±0.06
0.75	with	78.56±1.07	65.29±1.20	80.08±0.88	85.58±0.01	81.75±0.24
1.75	without	41.21±1.01	21.13±0.26	53.03±0.05	64.02±0.34	59.97±0.05
1.75	with	55.56±1.97	36.63±0.64	64.01±0.36	72.79±0.42	68.66±0.88
2.75	without	29.85±1.69	12.10±0.42	43.31±0.56	54.44±0.48	51.24±0.77
2.75	with	33.84±1.06	15.01±0.28	45.04±0.61	56.93±0.60	53.51±0.68
3.75	without	18.04±0.27	5.39±0.01	31.18±0.30	43.76±0.51	39.60±0.33
3.75	with	23.07±0.41	7.86±0.02	35.09±0.11	48.22±0.21	43.90±0.18

CONCLUSIONS

1. The second-order reaction rate of a monosaccharide was dependent on the type of acid used.
2. Monosaccharides degrade at different rates in different acids even when the molar concentrations of the various acids are constant.
3. Pentoses and hexoses degrade much slower in sulfurous acid than in HCl or H_2SO_4.
4. Sulfurous acid was suggested to have a protective effect on the degradation of monosaccharides due to the formation of carbonyl-sulfite adducts.

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