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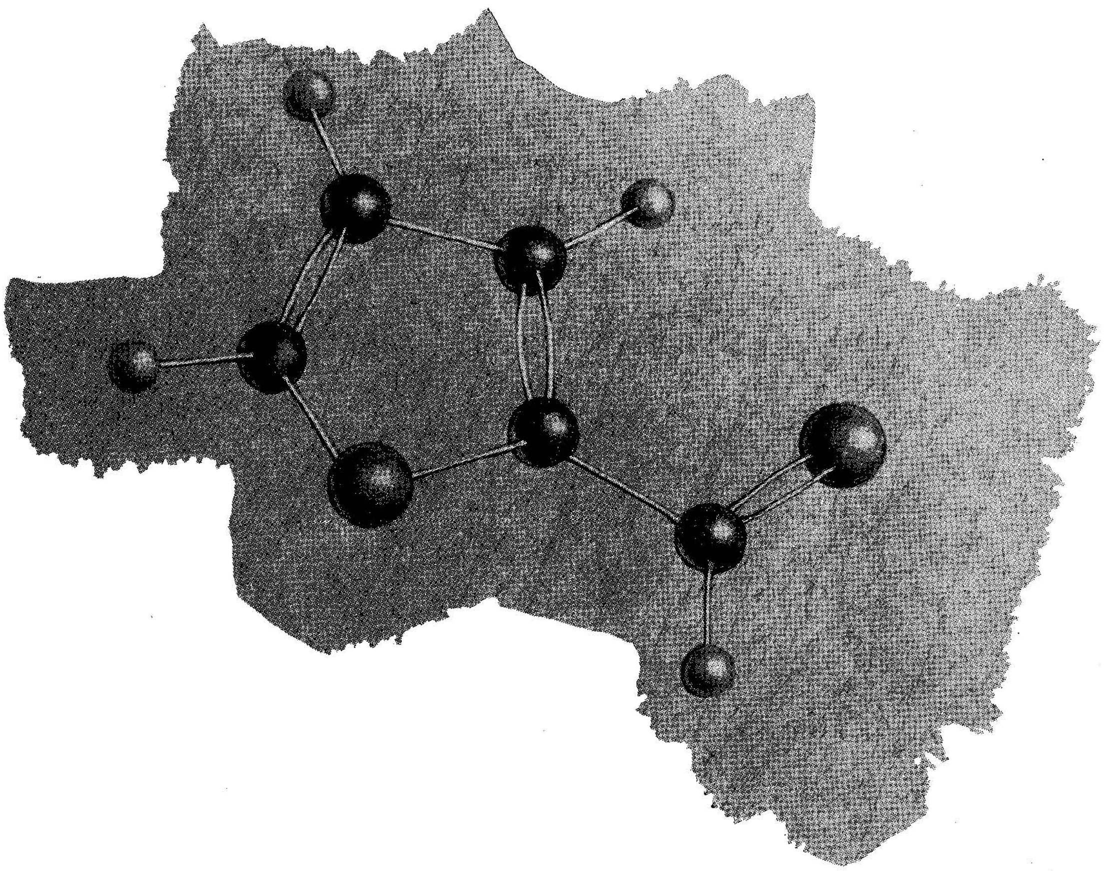
Furfural Yield and Decomposition in Sodium 2, 4–Dimethylbenzenesulfonate–Sulfuric Acid – Water Solutions



SUMMARY

Batch–type microreactors (about 1/40 milliliter of reactants) were used to measure furfural yields from acidified xylose solutions containing sodium xylene–sulfonate. Initial xylose concentration was 0.666 molar. Two levels of sulfuric acid catalyst were used, 0.05 and 0.2 molar, while the sodium xylenesulfonate concentration ranged from 0 to 1.68 molar (close to saturation at room temperature). The reaction temperatures were 150°, 200°, and 240° C. It was found that presence of the salt did not affect the quantity of furfural produced, but greatly increased the rate of formation. The regular increase in rate of furfural formation was directly related to the increase in the rate of xylose decomposition, and furfural yields for all salt and acid concentrations at a given temperature were uniquely described by the xylose half–life.

Furfural Yield and Decomposition in Sodium 2, 4–Dimethylbenzenesulfonate–Sulfuric Acid– Water Solutions

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INTRODUCTION

The purpose of this Research Paper is to present experimental data on the yield of furfural from aqueous, acidified xylose solutions containing sodium 2,4-dimethylbenzenesulfonate (xylenesulfonate). This particular system became of interest through other studies which demonstrated the possibility of generating a hemicellulose solution containing sodium xylenesulfonate. In view of the important role of furfural in the chemical utilization of hardwoods and waste pentose streams, it was desirable to examine the effect of the hydrotropic agent on the furfural yield from xylose. Data of this type are fundamental to design calculations for sizing reaction equipment and for ascertaining the actual feasibility of furfural production in an integrated scheme where sodium xylenesulfonate is used for delignification and hemicellulose removal.

EXPERIMENTAL

Measurements of furfural yield and the decomposition rates of furfural and xylose were made according to techniques reported earlier.[2,3] Briefly, the method involves reacting solutions isothermally in small glass ampoules and quantitatively measuring the concentration of the component in question. A procedure for calculating the first–order rate constant from concentration–time data was also reported[3] and this was used in processing the furfural and xylose decomposition data.

Reactant solutions involving xylose were prepared from chemically pure xylose, reagent grade sulfuric acid, and sodium 2,4–dimethylbenzene–sulfonate. The salt was the purest form obtainable from Distillation Products Industries, Rochester, N.Y.; it was used as received with correction for moisture content. Furfural for the determination of decomposition rate was

[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

[2] Root, D. F., Saeman, J. F., Harris, J. F., and Neill, W. K. Chemical conversion of wood residues, Part II: Kinetics of the acid-catalyzed conversion of xylose to furfural. Forest Products Jour., Vol. 9 (5): 158–165, 1959.

[3] Smuk, J. M., Harris, J. F,, and Zoch, L. E. Rate of D–xylose decomposition in sulfuric acid––sodium 2,4–dimethylbenzenesulfonate––water solutions. U.S. Forest Serv. Res. Paper FPL 20, Forest Products Lab., Madison, Wis., 1965.

derived from technical grade furfural by distilling twice under reduced pressure (less than 1 millimeter of mercury). The middle third of the distillate was taken from each distillation. Solutions were made by weighing either 10grams of xylose or 2.4 grams of furfural into a 100–milliliter–volumetricflask. The desired quantity of salt (0, 5, 10, 20, 30, or 35 grams) was added and sufficient standard sulfuric acid was pipetted into the flask to give the required concentration on diluting to the mark.

The ampoules containing the reacted solution were analyzed for either xylose or furfural. Xylose was determined according to the Somogyl method, and furfural was done by quantitative distillation followed by optical density measurement at 276 millimicrons. Both analyses have been described in detail.[2] In the analysis for furfural, no interference was found to be caused by the presence of the salt. Known solutions containing only furfural, acid, and salt agreed within 0.5 percent with the spectrophotometric measurements at all salt concentrations used.

DISCUSSION

Figure 1 shows furfural yield as a function of time for solutions containing sodium xylene–sulfonate and 0.05–molar sulfuric acid reacted at 150° C. Furfural yields for all experimental reaction conditions are given in tables 1, 2, and 3. The effect of the salt is to increase the net rate of furfural formation without significantly altering the maximum yield. By converting the measure of time to a dimensionless basis (kt) all of the furfural yields are brought together as a single function, dependent only implicitly upon salt concentration, The new time basis (kt) involves the rate of xylose degradation at the reaction conditions where furfural yield was measured and, consequently, relates furfural yield directly to the amount of xylose decomposed. Figures 2, 3, 4, and 5 present all of the furfural yield data in graph form using dimensionless time as the independent variable. Experimental values for the first–order disappearance of xylose in the various sodium xylenesulfonate solutions are reported in table 4.

These results have an important bearing on wood utilization processes employing sodium xylenesulfonate as a delignification agent; that is, the resulting hemicellulose solution may be converted directly to furfural without concern for ill effects due to the presence of the salt. The major process correction occurs in the reaction zone where the residence time must be

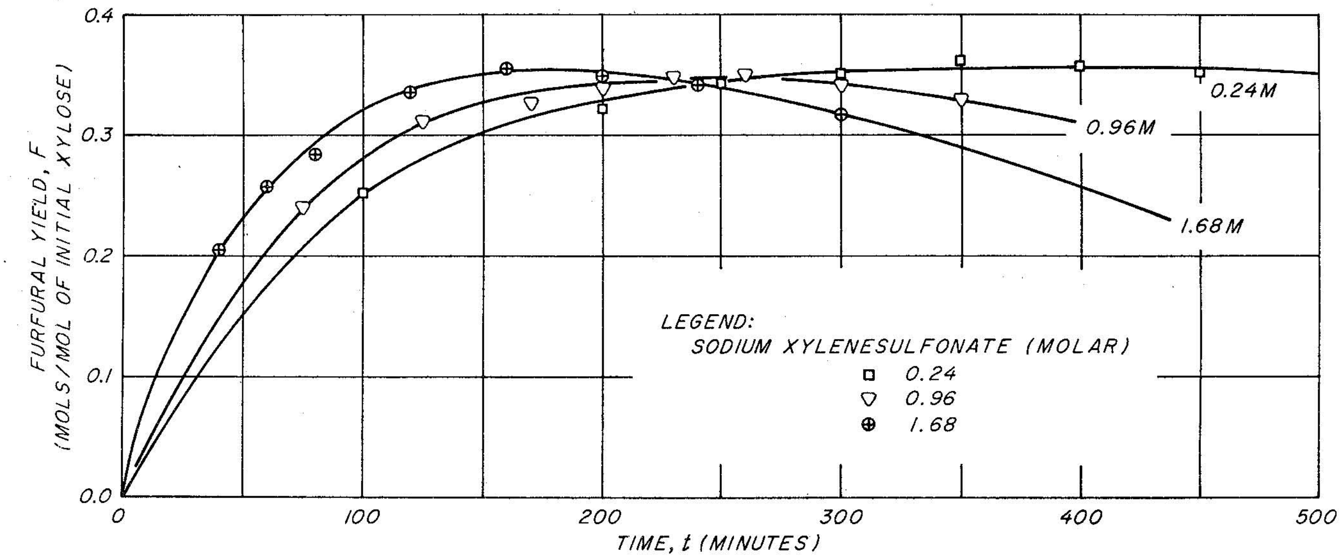

Figure 1.--Effect of sodium xylenesulfonate on furfural yields at 150° C. Acid concentration = 0.05 molar, and initial xylose concentration = 0.666 molar.

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Table 1.--Furfural yields from solutions containin xylose-sulfuric acid-sodium xylenesulfonate at 150° C.[1]

Salt concentratio: C_s	Acid concentration = 0.05 molar[2]			Acid concentration = 0.2 molar[2]		
	Furfural yield F[3]	Time t	Dimensionless time kt[4]	Furfural yield F[3]	Time t	Dimensionless time kt[4]
Molarity		Minutes			Minutes	
0	0.112	40	0.161	0.287	40	0.596
	.195	80	.322	.322	60	.894
	.261	140	.564	.337	80	1.192
	.317	200	.806	.343	100	1.49
	.340	260	1.048	.336	120	1.788
	.301	300	1.209	.....	.....	......
	.365	360	1.449	.....	.....	......
	.368	400	1.612	.....	.....	......
0.24	.253	100	.456	.087	6.0	.0971
	.321	200	.912	.170	15.0	.243
	.342	250	1.14	.251	30.0	.485
	.351	300	1.368	.295	45.0	.728
	.363	350	1.596	.330	60.0	.971
	.358	400	1.824	.339	75.0	1.214
	.352	450	2.052	.331	90.0	1.456
.48	.093	25	.147	.096	6.0	.105
	.162	50	.254	.170	15.0	.264
	.212	75	.381	.273	30.0	.527
	.255	100	.508	.306	45.0	.791
	.295	140	.711	.323	60.0	1.05
	.322	180	.914	.336	75.0	1.32
	.344	220	1.118	.328	90.0	1.58
	.350	260	1.321	.....	.....	......
	.348	300	1.524	.....	.....	......
	.346	340	1.727	.....	.....	......
.96	.240	75	.461	.101	6.0	.113
	.313	125	.768	.197	15.0	.281
	.326	170	1.044	.230	30.0	.563
	.339	200	1.228	.318	45.0	.844
	.348	230	1.412	.334	60.0	1.13
	.350	260	1.596	.336	75.0	1.41
	.341	300	1.842	.323	90.0	1.69
	.330	350	2.149	.....	.....	......
1.44	.157	30	.229	.123	6.0	.124
	.248	60	.458	.217	15.0	.311
	.288	100	.764	.298	30.0	.622
	.307	130	.99	.332	45.0	.932
	.329	160	1.22	.340	60.0	1.24
	.321	190	1.45	.339	75.0	1.55
	.317	220	1.68	.323	90.0	1.86
	.304	280	2.14	.....	.....	......
1.68	.206	40	.338	.127	6.0	.136
	.257	60	.508	.227	15.0	.339
	.288	80	.677	.312	30.0	.678
	.334	120	1.015	.334	45.0	1.02
	.355	160	1.354	.345	60.0	1.36
	.347	200	1.692	.335	75.0	1.70
	.341	240	2.03	.314	90.0	2.03
	.317	300	2.538	.....	.....	......

[1] Xylose concentration, 0.666 molar.

[2] Stoichiometric molarity at 24° C.

[3] Expressed as fraction of theoretical on a molar basis; molar concentration of furfural ÷ 0.666.

[4] Values of *k* listed in table 4.

Table 2.--Furfural yields from solutions containin xylose-sulfuric acid-sodium xylenesulfonate at 200° C.[1]

Salt concentration C_s	Acid concentration = 0.05 molar[2]			Acid concentration = 0.2 molar[2]	
	Furfural yield F[3]	Time t	Dimensionless time kt[4]	Furfural yield F[3]	Time t
Molarity		Minutes			Minutes
0	0.281	2	0.5	.....	.....
	.419	4	1.0	.....	.....
	.472	6	1.5	.....	.....
	.504	8.33	2.08	.....	.....
	.509	10	2.5	.....	.....
	.512	11.66	2.92	.....	.....
	.475	15	3.75	.....	.....
	.451	20	5.0	.....	.....
0.24	.387	2.5	.734	0.254	0.417
	.491	5	1.47	.413	.83
	.516	5.83	1.62	.462	1.25
	.520	8.33	2.45	.508	1.66
	.517	10	2.94	.504	2.09
	.495	11.66	3.43	.501	2.5
	.473	14.16	4.16	.497	2.92
	.451	16.66	4.89	.....	.....
.48	.296	1.66	.538	.270	.417
	.433	3.33	1.08	.409	.83
	.486	5	1.61	.477	1.25
	.507	6.66	2.15	.510	1.66
	.512	8.33	2.69	.512	2.09
	.500	10	3.23	.502	2.5
	.485	11.66	3.76	.491	2.92
	.473	13.33	4.30	.....	.....
	.453	15	4.84	.....	.....
	.386	20	6.45	.....	.....
.96	.244	.83	.333	.211	.25
	.389	1.66	.667	.350	.5
	.465	2.5	1.0	.441	.75
	.505	3.33	1.33	.477	1
	.534	4.17	1.67	.510	1.25
	.533	5	2.0	.521	1.5
	.534	5.83	2.33	.521	1.66
	.521	6.67	2.67	.....	.....
1.44	.314	.83	.439	.241	.25
	.461	1.66	.878	.389	.5
	.512	2.5	1.32	.475	.75
	.550	3.33	1.76	.510	1
	.552	4.17	2.20	.527	1.25
	.545	5	2.63	.529	1.5
	.538	5.83	3.07	.532	1.66
	.522	6.67	3.51	.....	.....
1.68	.229	.67	.354	.256	.25
	.371	1.33	.708	.413	.5
	.455	2	1.06	.493	.75
	.502	2.66	1.42	.525	1
	.522	3.33	1.77	.536	1.25
	.523	4	2.12	.533	1.5
	.530	4.67	2.48	.539	1.66
	.528	5.33	2.83	.....	.....
	.523	6	3.19	.....	.....
	.516	6.67	3.54	.....	.....

[1]Xylose concentration, 0.666 molar.

[2]Stoichiometric molarity at 24° C.

[3]Expressed as fraction of theoretical on a molar basis; molar concentration of furfural ÷ 0.666.

[4]Values of <u>k</u> listed in table 4.

Table 3.--Furfural yields from solutions containing xylose-surfuric acid-sodium xylenesulfonate at 240° C.[1]

Furfural yield F[2]	Time t	Dimensionless time kt[3]	Furfural yield F[2]	Time t	Dimensionless time kt[3]
	Seconds			Seconds	
SALT CONCENTRATION = 0 MOLAR			SALT CONCENTRATION = 0.24 MOLAR		
0.374	9.9	0.593	5.431	10.1	0.715
.553	20.2	1.2	.570	20	1.42
.609	30	1.78	.617	29.9	2.13
.619	40	2.37	.614	40.1	2.86
.626	50	2.97	.609	50	3.56
.614	60	3.56	.603	60	4.28
.606	69.9	4.15	.595	70	4.99
579	100	5.93	.583	80	5.71
SALT CONCENTRATION = 0.48 MOLAR			SALT CONCENTRATION = 0.96 MOLAR		
.422	9.9	.81	.453	7.9	.738
.595	20.2	1.65	.607	16	1.5
.621	30	2.45	.625	24.1	2.25
.622	40	3.27	.643	32	2.99
.622	50	4.1	.627	40	3.74
.610	60	4.91	.629	48.1	4.5
.597	69.9	5.72	.613	55.9	5.22
.565	80	6.55	.593	64	5.98
SALT CONCENTRATION = 1.44 MOLAR			SALT CONCENTRATION = 1.68 MOLAR		
.538	7.9	.895	.511	7	.857
.640	16	1.81	.639	14.1	1.73
.658	24.1	2.73	.668	21	2.51
.652	32	3.63	.656	28	3.43
.623	40	4.53	.644	35	4.29
.618	48.1	5.45	.630	42.1	5.16
.599	55.9	6.34	.615	48.9	5.99
.589	64	7.25	.....	.....	.....

[1] Xylose concentration, 0.666 molar; stoichiometric acid molarity at 24° C., 0.05.

[2] Expressed as fraction of theoretical on a molar basis; molar concentration of furfural ÷ 0.666.

[3] Values of k listed in table 4.

calculated on the basis of the appropriate xylose degradation rate. Minor alterations in the recovery system may be necessary because of changes in the vapor–liquid equilibria, but the reaction system remains essentially the same as when processing pure, aqueous pentose solutions.

The unique dependence of furfural yield on xylose degradation is very striking for the data at 150° C. While the data at 200° and 240° C. exhibit more scatter, the points are well grouped on a single curve and no trend can be noticed with salt concentration. The effect of the sodium xylenesulfonate appears to be analogous to that of sulfuric acid, where it has been observed that furfural yield is not dependent upon acid concentration for solutions at least 0.05 molar in sulfuric acid.[2] Confirmation of this fact is obtained by comparing figures 2 and 3. In pure, aqueous acid solutions this result may be interpreted by taking all reactions to be acid catalyzed, so that an increase in acid concentration produces a proportional increase in all reaction rates. Furfural yields for the pure, aqueous acid solutions have been well correlated by the following equation.[2]

$$\frac{dF}{dt} = -k_2F - k_3 x F + kx \qquad (1)$$

where x and F refer to xylose and furfural concentrations at time t, as fractions of the initial xylose concentration; k_2 and k are first–

order rate constants for furfural and xylose decomposition at the particular reaction conditions; and $\underline{k}_3$ is a constant closely related to a second-order rate constant involving furfural and an intermediate.

On the basis of the above equation, the observed salt effect is not to be expected. In contrast to the pure acid solutions, the salt will not only affect the acid activity, but it will also cause more profound changes in the activity coefficients of the xylose, furfural, and transition states of the furfural and xylose decomposition. In general, these salt effects will be reflected in changes in the relative rates of xylose and furfural decomposition, making furfural yields dependent upon salt concentration at any given fraction of xylose reacted.

Some attempt was made to examine more closely

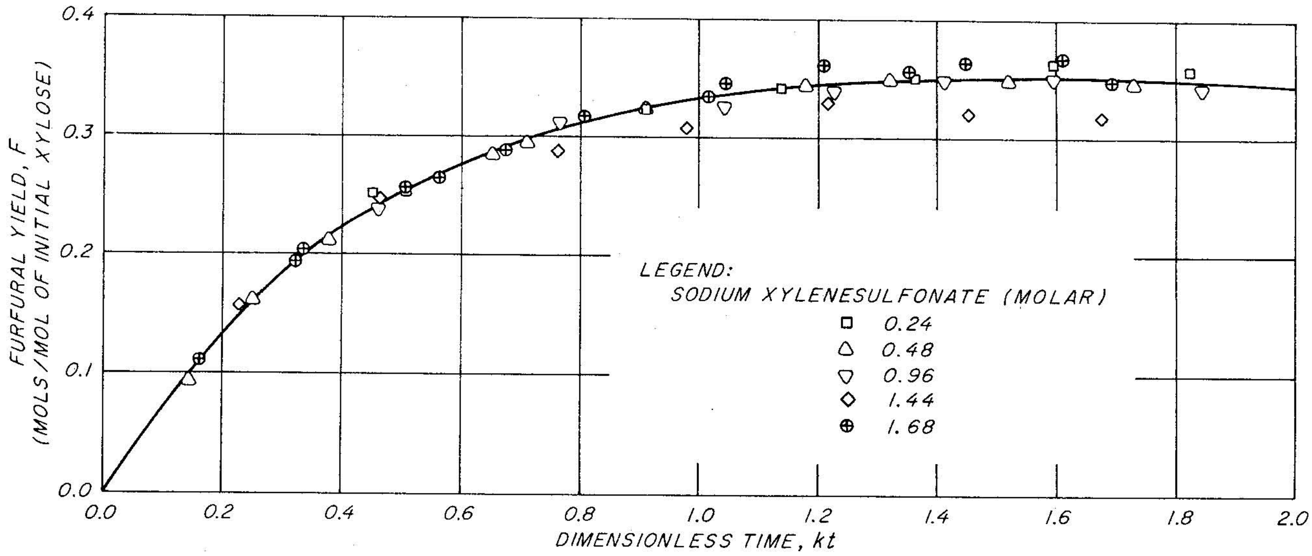

Figure 2.--Furfural yield as a function of dimensionless time at various concentrations of sodium xylene-sulfonate. Acid concentration = 0.05 molar; temperature = 150° C.; and initial xylose concentration = 0.666 molar.

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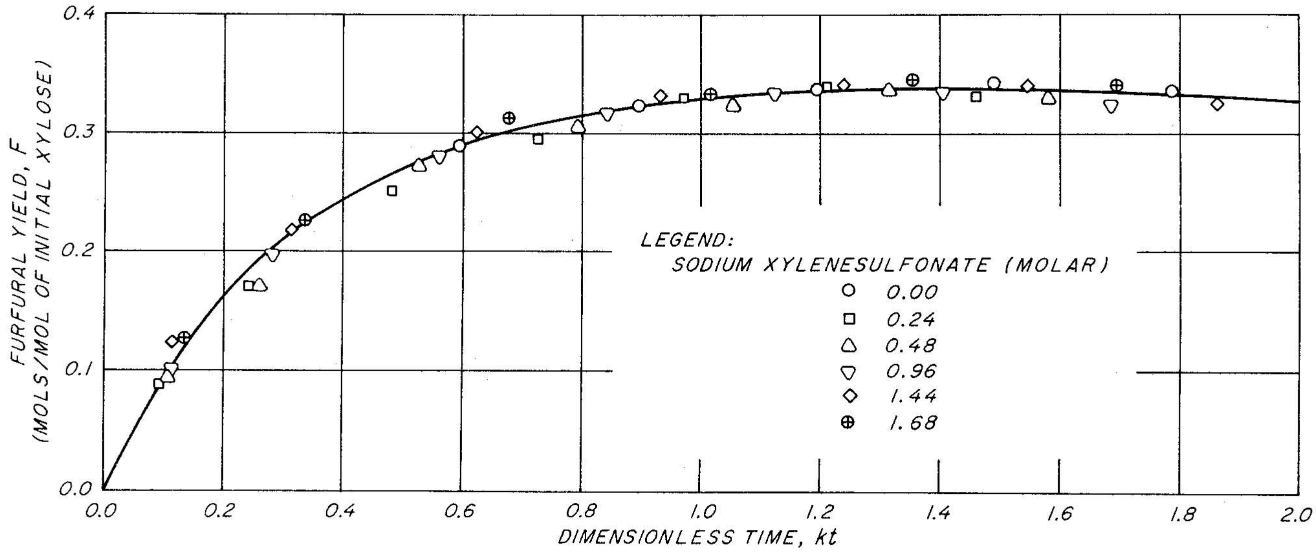

Figure 3.--Furfural yield as a function of dimensionless time at various concentrations of sodium xylene-sulfonate. Acid concentration = 0.2 molar; temperature = 150° C.; and initial xylose concentration = 0.666 molar.

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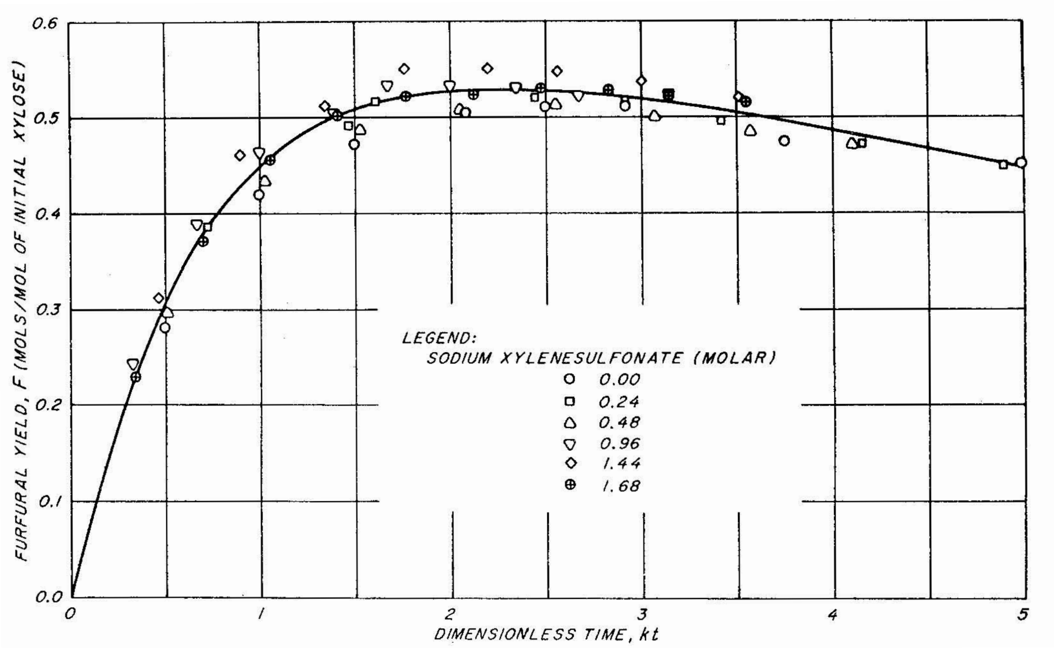

Figure 4.--Furfural yield as a function of dimensionless time at various concentrations of sodium xylene-sulfonate. Acid concentration = 0.05 molar; temperature = 200° C.; and initial xylose concentration = 0.666 molar.

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the apparent conflict between expected and observed results. Additional experiments were performed on the decomposition of furfural in the various sodium xylenesulfonate solutions. The calculated first-order rate constant, as well as the values for the ratio $\frac{k_2}{k}$ are listed in table 5.

As indicated in table 5, there is approximately a 25-percent decrease in $\frac{k_2}{k}$ between the 0.24 and 1.68-molar-salt solutions. With a change of this magnitude, $\frac{k_2}{k}$ can confidently be taken as sensitive to salt concentration. The change in furfural yield associated with this change in $\frac{k_2}{k}$ can be calculated from the integrated form of equation (1), assuming $\frac{k_3}{k}$ is independent of salt. Such a calculation shows the variation in furfural yield will not be more than a 10-percent increase. This small difference cannot be experimentally detected with a high degree of confidence, which introduces some question as to the precise validity of the observed dependency of furfural yield upon xylose degradation only. A much broader change in furfural decomposition rate might clarify this point, but solubility limitations of the salt make further increases in concentration impractical, Such experiments can be of importance in the interpretation of the overall mechanism for furfural formation. For example, starting from equation (1), it is easily

Table 4.--Experimental rates of xylose decomposition in sodium xylenesulfonate-sulfuric acid-water solutions

Temperature T	Acid concentration C_A	Salt concentration C_S	First-order rate constant k
°C.	Molarity	Molarity	$Minutes^{-1}$
[1]150	0.05	0	0.00402
		.24	.00457
		.48	.00507
		.96	.00614
		1.44	.00764
		1.68	.00845
	.2	0	.0149
		.24	.0162
		.48	.0176
		.96	.0188
		1.44	.0207
		1.68	.0226
200	.05	0	.248
		.24	.294
		.48	.323
		.96	.373
		1.44	.473
		1.68	.531
240	.05	0	3.56
		.24	4.28
		.48	4.91
		.96	5.61
		1.44	6.80
		1.68	7.35

[1]Rates at 150° C. from: Rate of D-xylose decomposition in sulfuric acid--sodium 2.4-dimethylbenzenesulfonate--water solutions, by Smuk, J. M., Harris, J. F., and Zoch, L. L. U.S. Forest Serv. Res. Paper FPL 20, Forest Products Lab.. Madison, Wis., 1965.

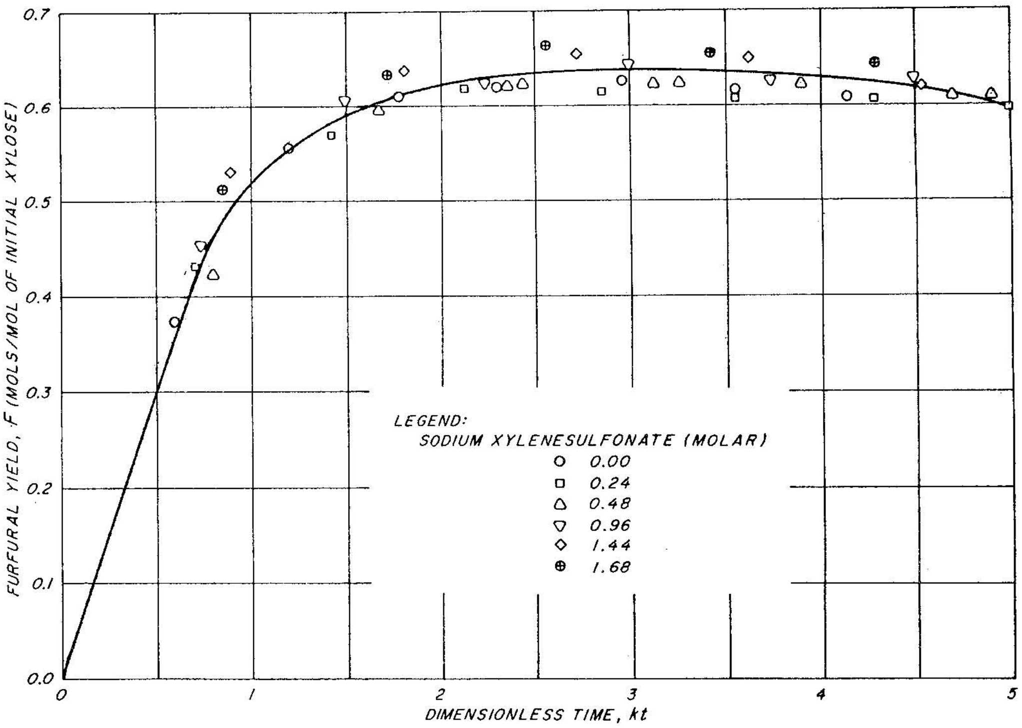

Figure 5.--Furfural yield as a function of dimensionless time at various concentrations of sodium xylene-sulfonate. Acid concentration = 0.05 molar; temperature = 240°C.; and initial xylose concentration = 0.666 molar. ZM 128 681

Table 5.--Experimental rates of furfural decomposition in sodium xylenesulfonate-sulfuric acid-water solutions [1]

Temperature T	Acid concentration C_A	Salt C_s	First-order rate constant $k_2 x 10^3$	Ratio of rate constants k_2/k
°C.	Molarity	Molarity	$Minutes^{-1}$	
150	0.05	0.24	0.794	0.174
		.48	.863	.170
		.96	.989	.162
		1.44	1.07	.142
		1.68	1.08	.128
	.2	.24	2.96	.182
		.48	3.11	.177
		.96	3.16	.168
		1.44	3.43	.166
		1.68	3.37	.149
200	.05		12.5	.0426
			13.4	.0415
			15.8	.0395
			18.5	.0351
			19.4	.0358
	.2		46.5	......
			47.5	......
		.96	50.6	......
		1.44	56.6	......
		1.68	56.7	......

[1] Initial furfural concentration, 24 grams per liter.

shown that if

$$\left(\frac{\delta F}{\delta s}\right)_x = 0$$

in which s is the concentration of salt, then

$$\frac{da}{ds} = \frac{db}{ds} = 0$$

Therefore, if $\frac{k_2}{k}$ is found dependent upon salt concentration, the assumed mechanism must be incorrect. The data presented here are inconclusive in this respect because of the possibility of subtle changes in furfural yield at equal xylose half-lifes.

furfural yield is dependent only upon the amount of xylose decomposed in acidified solutions containing sodium xylenesulfonate. This observation is apparently valid for temperatures as high as 240° C. and all salt concentrations up to saturation. The presence of sodium xylenesulfonate accelerates the rate of furfural production and has no adverse effects on yield.