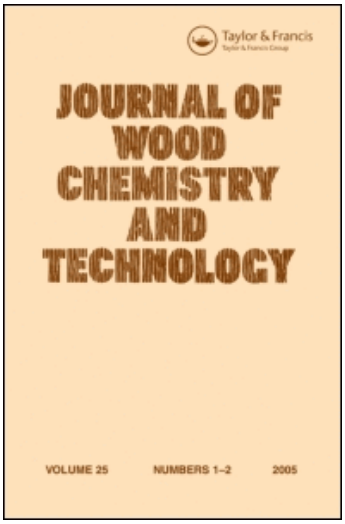

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KINETIC MODEL FOR THE DILUTE SULFURIC ACID SACCHARIFICATION OF LIGNOCELLULOSE

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ABSTRACT

Despite continuing interest in various processes for producing ethanol or other chemicals from agricultural and wood residues, little attention has been given to improving the kinetic modeling of dilute acid saccharification of cellulosics, a key step in many of these processes. A new model for cellulose saccharification is proposed. It incorporates the effect of the neutralizing capacity of the substrate, the presence of readily hydrolyzable cellulose, and the reversion reactions of glucose. Although general in nature, the model was developed specifically for application to the dilute sulfuric acid saccharification of prehydrolyzed wood lignocellulose. A computer program to simulate the new model under various reaction conditions was prepared. This program reasonably predicts yields of fermentable (monomeric) sugar, reducing sugar, reversion material, remaining cellulose, as well as glucose lost by dehydration, all as a function of acid concentration, temperature, and reaction time.

INTRODUCTION

Despite continuing interest in various processes for producing ethanol from agricultural residues and wood, little attention has been given to improving the kinetic modeling of cellulose saccharification. Kinetic modeling plays an important role in the design, development, and operation of many chemical processes.

Kinetic data are also important in the design and evaluation of processes to hydrolyze cellulosic materials to glucose for fermentation into ethanol or a variety of other chemical intermediates.

Luers[1] first recognized that the rate of glucose production from cellulose depends on the reaction rates for its formation and destruction and that these reactions proceed independently. However, he concluded that the two reactions were similarly affected by changes in acidity and temperature, and thus maximum glucose yields were unaffected by such changes. Saeman[2] showed that the rate of the hydrolysis reaction is increased more rapidly than that of the sugar dehydration reaction by both increased temperature and increased acid concentration. He modeled the system as two consecutive pseudo-first order reactions in which the rate constants were functions of the applied acid concentration and temperature.

The model based on two consecutive reactions is presently the only model used to simulate cellulose saccharification. However, this model is an oversimplification of the reactions that actually occur in dilute acid solution. Saeman recognized that glucose yields would be affected by the presence of neutralizing material (i.e., ash-forming constituents) in the cellulose substrate and by the formation of reversion materials from glucose in dilute acid solution. Because these effects were less pronounced at the reaction conditions of the percolation process he was investigating, he did not incorporate them into his model. However, both factors are especially important in predicting glucose yields at the lower acidities and liquid-to-solid ratios encountered in some of the current processes under study. In addition, Saeman's model does not include the fact that all celluloses contain material that is rapidly hydrolyzed. However, this factor can be readily introduced into his model.[3]

We propose a new model that includes elements to correct the shortcomings of the model limited to two consecutive psuedo-first order reactions (Fig. 1). The new model can be used to predict yields of fermentable (monomeric) sugar, yields of reducing sugars, yields of total anhydroglucose units in the hydrolysate, and the

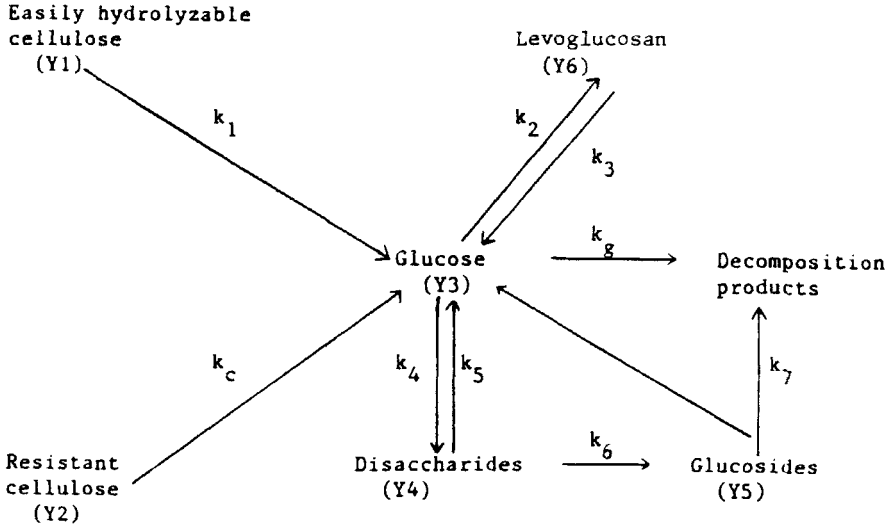


FIGURE 1. Model for dilute acid hydrolysis of cellulosics.

amount of cellulose remaining, all as a function of acid concentration, temperature, and reaction time. The construction of this new model entailed the development of a submodel for the reversion phenomenon and a recorrelation of rate data for both cellulose hydrolysis and glucose decomposition. The values for parameters used in this model are based on data gathered at the USDA Forest Products Laboratory (FPL) and reported in the following references classified as to subject matter:

rate of glucose degradation,[2,4,5,6,7]

rate of cellulose hydrolysis,[2,4,7]

glucose yields from lignocellulose saccharification,[2,4,8]

and reversion equilibria.[9]

Although the model is general in nature, the values of parameters used in the various equations were developed specifically for application to the dilute sulfuric acid hydrolysis of prehydrolyzed wood lignocellulose.

EVALUATION OF PARAMETERS AND RATE CONSTANTS

Cellulose Hydrolysis

Kirby,[4] Saeman,[2] and Saeman et al.[7] report cellulose hydrolysis rate constants for the dilute sulfuric acid hydrolysis of the resistant or difficultly hydrolyzable portion of Douglas-fir [Pseudotsuga menziesii (Mirb.) Franco] wood and prehydrolyzed Douglas-fir wood. The effect of liquid-to-solid ratio on the rate of hydrolysis was significant, especially at low acid concentrations. This was properly ascribed to the ash content. Kirby used three separate equations, one for each liquid-to-solid ratio, to correlate his data, but the correlation was not satisfactory. We have used the data from these investigators to establish the effect of acidity and temperature on the hydrolysis rate of the resistant portion of cellulose in the following manner.[10]

The acidity of the reacting system, $[H^+]$, is a function of the amount and concentration of the applied acid solutions, the neutralizing capacity of the substrate, and, for sulfuric acid, the extent of the secondary ionization. This latter factor may be ignored because measurements of the bisulfate dissociation constant[11] indicate that under the usual conditions of cellulose hydrolysis less than 1% of the bisulfate ion dissociates and sulfuric acid may thus be considered monovalent. The neutralizing capacity for various substrates differs greatly, ranging from 10 to 120 meq/kg,[12] and should be determined experimentally for each substrate. Assay methods for the neutralizing capacity of prehydrolyzed lignocellulose are the same as those described for wood.[13]

To evaluate the hydrogen-ion concentration the sulfuric acid is assumed to release only one hydrogen ion. It is also assumed that all the cations in the substrate are readily accessible and are effective immediately. For prehydrolyzed lignocelluloses this assumption is valid because most of the ash constituents of these materials result from ion-exchange during the wash that follows prehydrolysis. Thus, with the further assumption that the

hydroxide-ion concentration is negligible, the hydrogen-ion concentration is the difference between the molality of the added acid solution and the molality of the cations (i.e., eq/kg of water). At low liquid-to-solid ratios and low acid concentrations the neutralizing capacity of the lignocellulose significantly lowers the effective acid concentration $[H^+]$. For example, the applied acid concentrations in Kirby's group of data ranged from 0.04 to 0.327 molal H_2SO_4, which in the absence of any neutralizing effect corresponds to the hydrogen-ion concentration. With correction for the neutralizing capacity of the residue the resulting range of $[H^+]$ was 0.0055 to 0.327. Notice the extreme drop at the lower end of the range.

The rate constant for hydrolysis of the resistant portion of cellulose, k_c, was assumed to be related to acidity and temperature as follows:

$$k_c = A[H^+]^a \, EXP(-E/RT) \qquad (1)$$

where

$[H^+]$ = molal hydrogen-ion concentration,
A = constant,
a = constant,
E = activation energy,
R = gas constant, and
T = temperature (°K).

Data for the hydrolysis of two prehydrolyzed Douglas-fir lignocelluloses were available.[2,7] We assumed various neutralizing capacities for these materials because they had not been determined. For an assumed neutralizing capacity and with a knowledge of the amount of added acid and the liquid-to-solid ratio one could calculate $[H^+]$ as outlined above. The experimental rate constant for cellulose hydrolysis and the calculated $[H^+]$ were fit to eq. (1) by a least-squares method to determine A and a; an activation energy of 42,900 calories per mole[2] was used. This process was repeated iteratively for different assumed neutralizing capaci-

ties for the two substrates. The values of the neutralizing capacities that resulted in the lowest value for the sum of squares of the differences between the experimental and calculated k_c values were chosen as the neutralizing capacities of the substrates.

These methods resulted in the following correlation:

$$k_c = 2.472 \times 10^{20} [H^+]^{1.218} \text{ EXP}(-42900/RT) \text{ min}^{-1}. \quad (2)$$

Equation (2) applies specifically to the sulfuric acid hydrolysis of cellulose contained in Douglas-fir lignocellulose. Although the functional form would probably remain the same, the values of the parameters change with catalyst and substrate. Sufficient data are not available on catalyst systems other than sulfuric acid to make comparative correlations, but large differences would be expected. Saeman[2] measured the rates of hydrolysis of the resistant cellulose in five different wood species using dilute sulfuric acid. Analysis of these data indicates that rates differing by as much as 20% can be expected to accompany changes in wood substrates.

In addition to the resistant portion of cellulose whose hydrolysis rate is obtained from eq. (2), all celluloses contain material that reacts at a much greater rate. Native celluloses contain readily hydrolyzable hemicellulosic material. Isolated celluloses contain a portion of easily hydrolyzable material, the quantity of which depends on both the origin and prior treatment of the cellulosic subtrate.[14] The data of Millett et al.[15] show that approximately 10% of the cellulose contained in wood pulps and native celluloses hydrolyzes at a rate 20 to 100 times as fast as the remaining 90%. The cellulose in prehydrolyzed Douglas-fir lignocellulose after drying contained about 10% of readily hydrolyzable material.[4] We assumed that 10% of the cellulose content of our wood lignocelluloses were hydrolyzed at 50 times the rate of the resistant portion, i.e., $k_1 = 50 \times k_c$ (Fig. 1).

Reversion

In aqueous acid solutions, glucose not only reacts to form small quantities of its isomers, mannose and fructose, but also undergoes reversible reactions that result in disaccharides, oligosaccharides, and anhydrosugars. This latter group of reactions is referred to as reversion and the reaction products as reversion products. In this study we defined the quantity of reversion products in a given solution as the difference between the total amount of all glucose-containing components and the amount of monomeric glucose in that solution. In our model we assumed that cellulose hydrolysis produces only monomeric glucose and that all oligosaccharides in solution result from the reversion reactions.

Total glucose is measured either by Scott's method[16] or by diluting the solution and hydrolyzing the reversion products (correction being made for losses) under reaction conditions that favor the existence of free glucose in solution.[17] The resulting solution can then be analyzed for monomeric glucose by either a specific enzymatic method (glucose oxidase), paper chromatography,[17] or high performance liquid chromatography (HPLC).[18 21] Monomeric glucose in the original solution can be determined directly by any of these same methods.

Another frequently used analytical procedure measures the copper-reducing power of the sugar solution.[22] This procedure, which was used extensively in much of the previous work at FPL, estimates the reducing end groups of carbohydrates while discriminating against other aldehydic groups. Reducing sugars are reported as equivalents of glucose. Although there are small differences, we have assumed that the reducing capacity of glucose and the various disaccharide reversion products are the same on a molar basis, i.e., 1 mole of disaccharide has the same reducing power as 1 mole of glucose.

The reversion reactions result in components bonded only by glucosidic bonds; no evidence of ether bond formation exists. Although most of the isomeric disaccharides of glucose have been

isolated under reversion-type reaction conditions,[23 25] it has been found that the preferrential mode of condensation is between the anomeric hydroxyl and the C6-primary hydroxyl, i.e., the most prominent constituents of the reversion mixture are [1,6]-linked glucosides. Minor[9] showed that at glucose concentrations below 20% the reversion products formed from glucose in dilute sulfuric acid solution consist almost exclusively of the disaccharides gentiobiose and isomaltose, and the internally [1,6]-linked glucosans levoglucosan and 1,6-anhydro-β-D-glucofuranose. At 180 °C the disaccharides accounted for most of the reversion products, the glucosans constituting less than 30%. However, at 230 °C the glucosans were the major reversion products. Smith[26] also observed large amounts of levoglucosan in reversion products obtained at 220 °C.

These facts led us to develop a submodel for the formation of reversion products from glucose. The reaction scheme for this submodel was incorporated into the cellulose saccharification model (Fig. 1). In this scheme, the reversion products are assumed to consist only of monomeric, nonreducing glucosans (exemplified by levoglucosan) and of reducing disaccharides such as gentiobiose and isomaltose. Also incorporated into this part of the model was the fact that in acid solution the reducing end of the disaccharide can be dehydrated to give a glucoside (Fig. 1). Indeed, 2-furfuryl-5-methylglucoside, the expected product from a degradation reaction of this type, has been observed among reversion products.[27]

Equilibrium constants for the two reversion reactions shown in Figure 1 can be defined as:

$$KL = [\text{Levoglucosan}]/[\text{Glucose}] = k_2/k_3 \qquad (3)$$

and

$$KD = [\text{Disaccharides}]/[\text{Glucose}]^2 = k_4/k_5 \qquad (4)$$

where KL and KD are the equilibrium constants for the formation of

levoglucosan and disaccharides, respectively. The molal concentrations of each component are indicated by brackets. The rate constants k_2, k_3, k_4, and k_5 refer to Figure 1. Values for KL and KD at 180 and 230°C were determined by Minor.[9] These can be expressed analytically as:

$$KL = 9.91 \times 10^2 \, EXP(-4521/T) \qquad (5)$$

and

$$KD = 7.902 \times 10^{-7} \, EXP(5444/T). \qquad (6)$$

Minor's data were taken at a single acid concentration; however, the principle of thermodynamic consistency requires that the forward and reverse reactions be accelerated to the same degree by increased acidity. Hence, KL and KD are independent of acidity.

If one assumes that the rate constants for the hydrolysis of 1,6-glucosidic bonds are similar (i.e., $k_3 \cong k_5 \cong k_7$) and if one knows this hydrolysis rate relative to the glucose decomposition rate (k_g), then one can use eqs. (5) and (6) to obtain estimates of the rate constants k_2 and k_4, expressed in terms of k_g. The rates for the hydrolysis of all glucosides[28] are much greater than the decomposition rate for glucose. The hydrolysis rate of isomaltose is approximately 35 times the glucose decomposition rate; the ratio is higher for gentiobiose. In this study we have assumed that $k_3 = k_5 = k_7$ and we estimate that these rate constants are all equal to 35 k_g. Hence, as a conservative estimate, $k_2 = KL \times 35 \times k_g$ and $k_4 = KD \times 35 \times k_g$.

Glucose and Disaccharide Dehydration

Of the available information on glucose degradation[2,4,7] only McKibbins[5,6] data include the complete range of temperature and acidity of interest in cellulose hydrolysis. He measured the rate constant for the disappearance of reducing sugars, k_r, for glucose in dilute sulfuric acid solution. The formation of reversion

products in acid solution contributes to the reducing power of the sugar solutions as noted above. Hence, k_g (Fig. 1), the true rate constant for glucose dehydration, is related to k_r but cannot be equated with it. Values of k_g were calculated from McKibbin's experimental values of k_r using the submodel developed for the reversion reactions.

The calculated k_g values were then correlated by a least squares method using the following fundamental equation:[29]

$$k_g = \text{constant} \times [H^+](\gamma_a/\gamma^{\neq})\gamma_g \, EXP(-E/RT) \qquad (7)$$

where

γ_a = activity coefficient of the hydrogen ion,

$\gamma^{\neq}$ = activity coefficient of the transition complex, and

γ_g = activity coefficient of glucose.

A statistical analysis based on this least squares fit indicated that the ratio, $\gamma_a/\gamma^{\neq}$, was not significantly different from unity for the sulfuric acid system. The final correlation[30] between glucose dehydration rate and acid concentration was found to be:

$$k_g = 5.580 \times 10^{15} \, [H^+] \, \gamma_g \, EXP(-33800/RT) \; min^{-1} \qquad (8)$$

where

$\ln \gamma_g = 0.183 \times [G]$, and

$[G]$ = molal glucose concentration.

The rate constant k_g relates only to the acid catalyzed degradation reactions of glucose, but glucose and other sugars are also destroyed by various base catalyzed and uncatalyzed reactions.[29] Above 0.05 m $[H^+]$ the rate constant for the disappearance of glucose is correctly predicted by eq. (8). However, at lower acid concentrations the nonacid catalyzed reactions become significant. Equation (8) should not be used below acid concentrations of 0.05 m. Because only limited information is available[5,6] on the rates of glucose destruction at hydrogen-ion

concentrations below 0.05 m, applications of the saccharification model are limited by this same restriction.

In addition to hydrolytic cleavage of the glucosidic bond, reducing disaccharides undergo destructive dehydration reactions. These affect only the reducing-end group and are identical to the reactions by which the monomer is destroyed. The disaccharides may be regarded as C6 substituted glucose derivatives. Because such derivatives would be expected to react at approximately the same rate as glucose, we have assumed $k_6 = k_g$. This is not a critical assumption--large variations in the assumed value of k_6 may be tolerated because the quantity of anhydroglucose combined in the disaccharides seldom exceeds 5% of the total.

COMPUTER SIMULATION OF THE CELLULOSE SACCHARIFICATION MODEL

The cellulose saccharification model depicted in Figure 1 can be described in terms of the following differential equations:

$$\frac{d[Y1]}{dt} = -k_1[Y1] \tag{9}$$

$$\frac{d[Y2]}{dt} = -k_c[Y2] \tag{10}$$

$$\frac{d[Y3]}{dt} = k_1[Y1] + k_c[Y2] - k_2[Y3] + k_3[Y6] - 2k_4[Y3]^2 + 2k_5[Y4] + k_7[Y5] - k_g[Y3] \tag{11}$$

$$\frac{d[Y4]}{dt} = k_4[Y3]^2 - k_5[Y4] - k_6[Y4] \tag{12}$$

$$\frac{d[Y5]}{dt} = k_6[Y4] - k_7[Y5] \tag{13}$$

$$\frac{d[Y6]}{dt} = k_2[Y3] - k_3[Y6] \tag{14}$$

From the previous discussion it is readily apparent that these equations can be rewritten in terms of the known constants k_c (the hydrolysis rate constant for resistant cellulose), k_g (the glucose dehydration rate constant), KL (the equilibrium constant for the formation of levoglucosan from glucose), and KD (the equilibrium constant for the formation of disaccharides from glucose).

A computer program[31] that numerically integrates the transformed differential equations by the Runge-Kutta fourth order method[32] was prepared. This program allows yields of monomeric glucose, total anhydroglucose, reducing sugar, and remaining cellulose to be calculated as a function of acid concentration, temperature, and reaction time.

In the program the temperature is assumed to vary in a manner that approximates the variation that occurs in the particular experimental apparatus. In the laboratory procedure[4,7] small reactors (glass or copper) containing the reactants were heated for various intervals in a molten salt bath. The temperature of the contents is assumed to have no spatial variation but to change with time according to Newton's law:

$$\frac{dT}{dX} = \alpha(TB - T) \tag{15}$$

where

T = temperature of reactants,

TB = temperature of bath,

X = time (minutes),

α = characteristic heat transfer coefficient for reaction,

= 13.8 min^{-1} for 5-mm glass ampoules,

= 3.1 min^{-1} for 16-mm glass ampoules, and

= 28.0 min^{-1} for 10-mm copper reactors.

Calculation is simplified by assuming the water content of the reactants to be constant throughout the reaction. Although water is involved in the reactions--it is produced by glucose

dehydration and consumed by cellulose hydrolysis--the net variation in water content was less than 1% over the range of experimental data examined. Assuming the water content to be constant, it is equivalent to a constant acid molality throughout the reaction. This assumption was also used to correlate the rate constants, k_c and k_g.

COMPARISON OF MODEL WITH EXPERIMENTAL DATA

For saccharification in dilute sulfuric acid, two groups of experimental data were available with which to compare calculations based on the previously described model. The first group was an extensive set of measurements of the maximum reducing power yields from Douglas-fir lignocellulose.[4,7,8] The substrate was the same as that used to obtain the kinetic data[4] on which eq. (2) is based. The intent of the study was to determine the variation of maximum yield with changing reaction conditions, and data were collected over a wide range of temperatures, acidities, and liquid-to-solid ratios (Table 1). However, for each set of reaction conditions, data were only collected at a few time intervals in the region near the occurrence of the maximum yield. Based on these observations the maximum reducing power yield, time to maximum, and remaining cellulose were reported for each set of reaction conditions.

The second group of data, in which southern red oak lignocellulose was used, covers only a narrow range of temperatures at a single concentration of applied acid and a single liquid-to-solid ratio (Table 2). However, at each set of reaction conditions measurements of reducing power yield, monomeric glucose yield, and remaining cellulose were made at time intervals covering a wide extent of reactions. As with the previous group of data, two substrates were used, differing only in their neutralizing capacity. This results in a difference in the effective hydrogen-ion concentration between groups.

TABLE 1
Comparison of Experimental Data (EXP) for Saccharification of Prehydrolyzed Douglas-fir Lignocellulose[1] with Values Calculated (CALC) with the Model.

Temperature	Added acid concentration	L/S ratio	$[H^+]$	Time to maximum reducing sugar yield		Cellulose remaining at maximum reducing sugar yield		Maximum reducing sugar yield		
				EXP	CALC	EXP	CALC	EXP	CALC	Difference
°C	%		Mols/1,000 g H_2O	Min				%		
				LOW ASH LIGNOCELLULOSE (52 meq/kg)						
150	1.6	2.0	0.14	360	409	40.7	47.9	26.8	25.4	1.4
	1.6	6.0	0.16	360	365	38.0	47.0	28.0	26.8	1.2
	3.2	6.0	0.33	180	166	28.2	43.7	29.8	29.2	0.6
160	1.6	2.0	0.14	100	148	38.7	43.0	29.9	28.9	1.0
	1.6	2.5	0.14	160	143		42.7	30.0	29.4	0.6
	1.6	6.0	0.16	130	133	31.3	41.9	31.3	30.6	0.7
170	1.6	2.0	0.14	40	56	39.0	38.5	32.3	32.5	-0.2
	1.6	2.5	0.14	65	54		38.2	33.0	33.0	0.0
	0.8	6.0	0.07	105	114	38.2	40.5	32.3	31.8	0.5
	1.6	6.0	0.16	40	50	39.2	37.4	34.4	34.5	-0.1
	3.2	6.0	0.33	25	22.9	27.8	34.5	35.0	37.2	-2.2
180	1.6	2.0	0.14	22	22.3		34.4	35.5	36.0	-0.5
	1.6	2.0	0.14	20	22.3	22.4	34.4	35.6	36.0	-0.4

180	1.6	2.5	0.14	20	21.5		34.1	38.5	36.6	1.9
	0.8	3.0	0.06	56	50.9		37.0	34.3	34.2	0.1
	1.6	3.0	0.15	22	21.1		33.9	36.7	37.1	-0.4
	1.6	6.0	0.16	15	20.1	32.6	33.3	38.3	38.3	0.0
	0.8	6.0	0.07	47	44.9		36.1	35.6	35.5	0.1
	1.6	6.0	0.16	22	20.1		33.3	37.9	38.3	-0.4
	3.2	6.0	0.33	10	9.5		30.5	39.5	41.0	-1.5
	1.6	12.0	0.16	22	19.7		32.9	38.7	39.0	-0.3
190	1.6	2.0	0.14	6.0	9.6	27.5	30.8	38.8	39.5	-0.7
	1.6	2.5	0.14	8.0	9.3		30.3	42.0	40.1	1.9
	0.8	6.0	0.07	14.0	18.7	28.8	32.2	40.0	39.1	0.9
	1.6	6.0	0.16	6.0	8.7	26.7	29.3	41.6	41.9	-0.3
	3.2	6.0	0.33	2.0	4.5	24.0	26.8	43.0	44.6	-1.6

(continued)

TABLE 1 (continued)
Comparison of Experimental Data (EXP) for Saccharification of Prehydrolyzed Douglas-fir Lignocellulose[1] with Values Calculated (CALC) with the Model.

Temperature	Added acid concentration	L/S ratio	$[H^+]$	Time to maximum reducing sugar yield		Cellulose remaining at maximum reducing sugar yield		Maximum reducing sugar yield		
				EXP	CALC	EXP	CALC	EXP	CALC	Difference
°C	%		Mols/1,000 g H_2O	Min				%		
210	1.6	2.5	0.14	1.7	2.6	23.7		45.0	46.3	-1.3
230	1.6	2.5	0.14	0.5	1.3	19.1		50.5	50.0	0.5
240	1.6	2.5	0.14	0.3	1.1	17.6		51.5	51.2	0.3
250	1.6	2.5	0.14	0.2	0.9	16.6		48.5	52.3	-3.8
HIGH ASH LIGNOCELLULOSE (108 meq/kg)										
160	1.6	3.0	0.13	215	162	43.1		29.4	29.3	0.1
	1.6	6.0	0.15	185	142	42.3		31.4	30.4	1.0
	1.6	12.0	0.16	165	133	41.9		31.7	31.0	0.7
170	1.6	3.0	0.13	76	61	38.6		33.0	32.9	0.1
	1.6	6.0	0.15	66	54	37.6		34.2	34.3	-0.1
	1.6	12.0	0.16	59	51	37.3		34.7	35.0	-0.3

180	0.8	3.0	0.05	80	74	38.4	30.0	33.0	-3.0
	1.6	3.0	0.13	26	24	34.3	36.3	36.6	-0.3
	3.2	3.0	0.30	11.2	10.3	31.1	38.0	39.6	-1.6
	0.8	6.0	0.06	60.0	52.0	36.7	34.8	35.0	-0.2
	1.6	6.0	0.15	22.0	21.4	33.5	37.2	38.1	-0.9
	3.2	6.0	0.32	11.1	9.8	30.6	39.3	40.9	-1.6
	0.8	12.0	0.07	60.0	45.4	36.0	36.6	36.0	0.6
	1.6	12.0	0.16	22.0	20.2	33.1	38.2	38.9	-0.7
	3.2	12.0	0.33	10.7	9.6	30.3	40.0	41.7	-1.7
190	1.6	3.0	0.13	9.2	10.5	30.5	40.5	40.1	0.4
	1.6	6.0	0.15	7.0	9.3	29.6	42.0	41.7	0.3
	1.6	12.0	0.16	6.8	8.8	29.2	42.4	42.5	-0.1

[1]Hydrolysis in dilute H_2SO_4; experimental data from references ([4,7,8]).

TABLE 2
Comparison of Experimental Data (EXP) for Saccharification of Prehydrolyzed Southern Red Oak Lignocellulose[1] with Values Calculated (CALC) Using the Model.

Time	Weight loss[2]	Glucan remaining		Monomeric glucose yield			Reducing sugars yield		
		EXP[3]	CALC	EXP[4]	CALC	Difference	EXP[5]	CALC	Difference
Min	- % -								
	230 °C-LOW ASH LIGNOCELLULOSE (27.2 meq/kg, $[H^+]$ = 0.073 m)								
0.46	30.1±2.2			30.7±2.9	38.7	-8.0	33.5±2.3	39.3	-5.8
0.67	48.1±0.9			48.1±2.8	49.1	-1.0	49.8±0.6	50.2	0.4
0.93	58.4±0.8			51.6±1.6	50.6	1.0	53.4±0.4	51.7	1.7
1.25	62.1±0.5			45.1±1.9	45.1	0.0	46.6±0.9	46.0	0.6
1.58	61.0±1.1			34.7±0.9	37.2	-2.5	36.3±0.7	37.9	-1.6
2.01	55.8±1.2			23.3±0.1	27.8	-4.5	25.4±0.9	28.2	-2.8
	230 °C-HIGH ASH LIGNOCELLULOSE (107.2 meq/kg, $[H^+]$ = 0.046 m)								
0.58	32.5±0.9	64.4	53.8	29.2±1.2	36.3	-7.1	34.5±1.3	36.8	-2.3
0.75	41.9±0.4	45.2	41.3	39.0±0.8	43.3	-4.3	43.6±0.5	44.1	0.5
0.92	48.9±1.5	32.0	31.6	45.2±1.2	47.3	-2.1	49.4±0.4	48.2	1.2
1.08	51.7±1.2			44.2±1.1	49.1	-4.9	49.2±1.0	50.2	-1.0
1.25	58.1±1.8	17.6	18.9	44.9±2.4	49.6	-4.7	50.0±1.5	50.7	-0.7
1.42	56.9±1.6			42.8±1.4	48.9	-6.1	47.9±1.7	50.1	-2.2
1.58	58.1±0.7	15.6	11.3	43.6±0.4	47.7	-4.1	46.7±0.9	48.7	-2.0
2.00	59.0±1.3	9.1	5.9	36.5±3.2	42.6	-6.1	40.6±1.4	43.5	-2.9

210 °C-LOW ASH LIGNOCELLULOSE (27.2 meq/kg, $[H^+]$ = 0.073 m)

1.0	23.1±0.3	74.8	63.4	21.0±0.8	29.8	-8.8	24.5±0.6	30.3	-5.8
2.0	38.9±1.1	38.8	40.1	37.8±0.3	42.1	-4.3	39.7±0.5	43.4	-3.7
3.0	48.3±1.7	29.8	25.2	44.1±2.2	45.6	-1.5	45.7±0.7	47.0	-1.3
3.5	50.7±0.3	24.8	20.0	43.2±1.7	45.4	-2.2	46.9±0.5	46.8	0.1
4.0	53.1±0.5	18.9	15.9	44.0±0.5	44.4	-0.4	46.5±0.6	45.8	0.7
6.0	56.4±0.1	5.3	6.3	35.5±0.6	36.4	-0.9	38.4±0.4	37.4	1.0
8.0	56.1±0.5	1.6	2.5	27.1±2.2	27.3	-0.2	29.8±1.4	27.9	1.9

210 °C-HIGH ASH LIGNOCELLULOSE (107.2 meq/kg, $[H^+]$ = 0.046 m)

2.0	28.7±0.6	57.0	56.6	27.0±1.1	33.6	-6.6	31.4±0.8	34.4	-3.0
3.0	36.8±1.0	48.6	43.5	37.6±2.0	40.0	-2.4	38.7±0.8	41.0	-2.3
4.5	45.3±1.4	30.4	29.2	40.9±0.5	43.8	-2.9	43.9±0.5	45.2	-1.3
6.0	49.5±1.0	23.7	19.6	41.7±1.0	43.5	-1.8	44.5±0.4	44.9	-0.4

(continued)

TABLE 2 (continued)
Comparison of Experimental Data (EXP) for Saccharification of Prehydrolyzed Southern Red Oak Lignocellulose[1] with Values Calculated (CALC) Using the Model.

Time	Weight loss[2]	Glucan remaining		Monomeric glucose yield			Reducing sugars yield		
		EXP[3]	CALC	EXP[4]	CALC	Difference	EXP[5]	CALC	Difference
Min	- - - - - - - - - - - - - - - - - -			%		- - - - - - - - - - - - - - - - - -			
	210 °C-HIGH ASH LIGNOCELLULOSE (107.2 meq/kg, $[H^+]$ = 0.046 m)								
7.5	52.9±0.6	13.6	13.2	40.0±2.3	41.0	-1.0	42.0±0.9	42.2	0.2
9.5	53.1±0.9	9.9	7.8	34.7±1.1	36.0	-1.3	36.6±0.7	36.9	-0.3
12.5	53.3±0.2	3.8	3.5	27.1±1.6	27.9	-0.8	29.4±0.9	28.4	1.0

[1]Cellulose content = 57%; applied acid solution = 0.8% H_2SO_4; liquid to solid ratio = 3.
[2]Percent of original ovendry prehydrolyzed residue ± standard deviation.
[3]Percent of original glucan.
[4]Percent of potential glucose available from residue ± standard deviation.
[5]Percent of potential reducing sugars available from residue ± standard deviation.

Douglas-fir Lignocellulose

Calculated and experimental values for maximum reducing sugar yield, cellulose remaining at maximum yield, and time to reach the maximum, at various reaction conditions using this substrate are listed in Table 1. The two materials, high- and low-ash lignocellulose, were identical except for their ash content and, consequently, their neutralizing capacity. The low-ash material was prepared by washing the high-ash material with a dilute HCl solution.[5] The range of reaction conditions is broad, the temperature range is 100 °C, and variation in the concentration of applied acid and liquid to solid ratio is fourfold and sixfold, respectively. Forty-eight data sets are included. The original data include an additional 11 sets in which the applied acid concentration was 0.4%. However, these were excluded from consideration because, as previously explained, the information on the degradation of glucose at low acidities is too limited.

The calculated values of both time necessary to reach maximum sugar yield and the quantity of cellulose remaining at that time differ, often significantly, from the experimental values. In the case of time to maximum sugar yield, this difference is more pronounced at the higher reaction temperatures. At the higher temperatures, it was difficult to accurately determine the experimental reaction times due to the shorter reaction time frame. In addition, the experimental time to maxiumu was taken as the time to obtain a more precise estimate of the time to maximum sugar yield. Both experimental error, especially at the higher temperatures, and the method used to define the experimental maximum explain the differences between the calculated and the experimental times to maximum.

In almost all cases the calculated amount of cellulose remaining is greater than determined experimentally. We are unable to explain this difference. However, the available experimental data for cellulose remaining were limited as compared to the other types of experimental data. Thus, comparison of the experimental amounts of cellulose remaining with the calculated

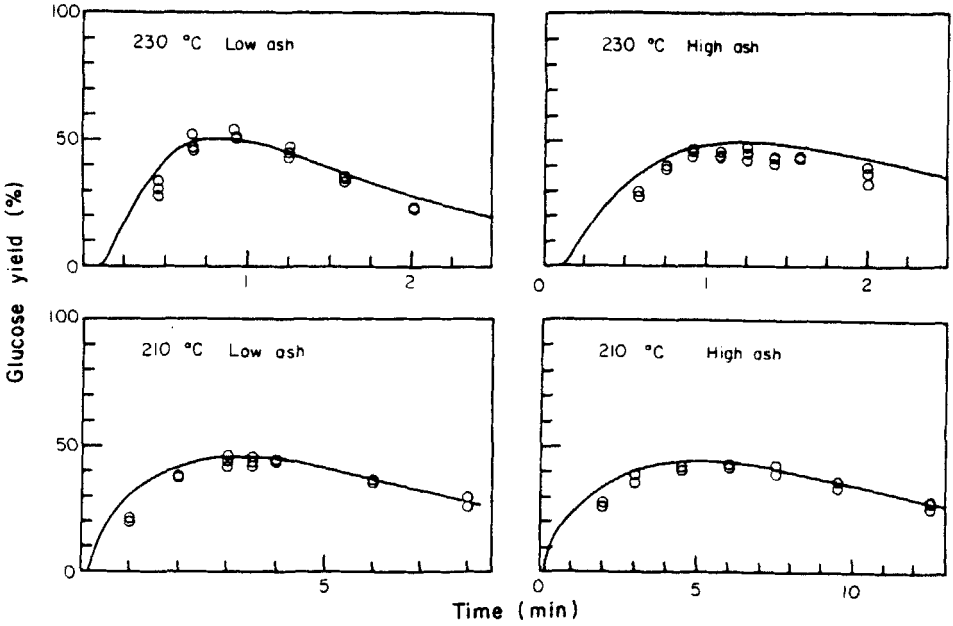
amounts may not be a good test of the validity of the model. Near the maximum for sugar yield, the change of sugar yield with reaction time is at a minimum. Although the experimental time to maximum sugar yield may not be known precisely (as previously discussed), the experimental maximum sugar yield was thus fairly well established. Therefore, the best indication of the validity of the model is provided by a comparison of the reducing sugar yields determined experimentally and by calculation. The average of the differences between experimental and calculated maximum reducing sugar yields (right-hand column) is less than -0.2 ± 1.1%. The maximum difference (-3.8%) occurs at 250 °C. At this temperature with the experimental procedure used, much of the reaction occurs at nonisothermal conditions. This large difference probably occurs because the assumptions used to model the temperature rise are inadequate. The agreement between actual values and those predicted using this model is very good. Similar calculations using the model and parameters[2] currently in general use give an average difference of -3.52 ± 3.79%.

Southern Red Oak Lignocellulose

Two prehydrolyzed southern red oak residues, differing only in their neutralizing capacity, were hydrolyzed in 0.8% H_2SO_4 at two temperatures. The four groups constitute a 2^2 factorial experiment with two temperatures and two acidities, the difference in acidity resulting from the difference in neutralizing capacity (Table 2, Figs. 2 and 3). The values of the various parameters used in the calculation were the same as those used previously for the Douglas-fir lignocellulose, except the frequency factor that was 2.472×10^{20} in eq. (2) was changed to 2.870×10^{20} in eq. (16):

$$k_c = 2.870 \times 10^{20} [H^+]^{1.218} \text{ EXP } (-42900/RT) \text{ min}^{-1}. \quad (16)$$

Equation (16) was obtained by assuming the hydrolysis rates of Douglas-fir and southern red oak lignocelluloses to be similarly



ML84 5649

FIGURE 2. Comparison of glucose yields calculated from the model (solid line) with experimentally determined glucose yields (open symbols) for hydrolysis of prehydrolyzed southern red oak wood. The temperature for the hydrolysis reaction and the neutralizing capacities of the substrates are indicated in the figure. The liquid-to-solid ratio was 3:1. The added acid was 0.8% sulfuric. (ML84 5649)

affected by temperature and acidity changes and evaluating the frequency factor from the experimental values of glucan remaining (Table 2). Comparison of eq. (16) with eq. (2) shows that at similar conditions the rate of hydrolysis for prehydrolyzed southern red oak is greater than that for prehydrolyzed Douglas-fir. Saeman[2] found a similar difference between these species when comparing the hydrolysis rates of cellulose in various woods.

The differences between the calculated and experimental values of the reducing sugar yields have a mean of -1.1 ± 2.0% (Table 2). Similar differences for the monomeric glucose yields have an average of -3.2 ± 2.6%. The greatest differences occur at the

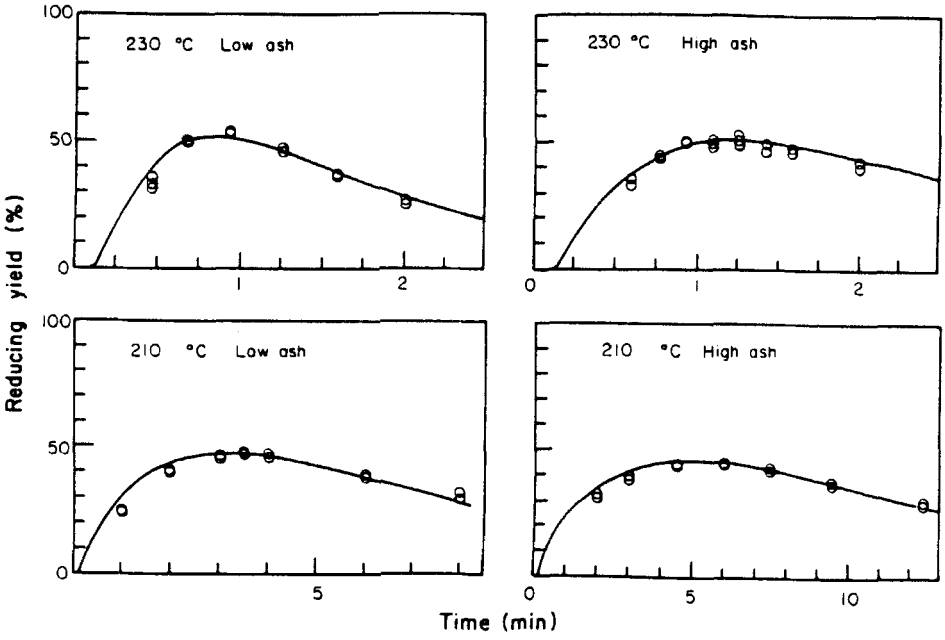


FIGURE 3. Comparison of reducing sugar yields calculated from the model (solid line) with experimentally determined reducing sugar yields (open symbols) for hydrolysis of prehydrolyzed southern red oak wood. The temperature for the hydrolysis reaction and the neutralizing capacities of the substrates are indicated in the figure. The liquid-to-solid ratio was 3:1. The added acid was 0.8% sulfuric. (ML84 5648)

extremities of the time range. The large differences occurring early in reaction are perhaps due to an inadequate estimate of the effective reaction temperature during heat up while those at the other extreme may result from interference in the assay incurred by degradation products.

Predictions of maximum yields are much better. The differences between calculated and experimental maximum reducing sugar yields have an average of 0.1 ± 1.1%, and the maximum monomer yield -1.8 ± 2.2%.

CONCLUSIONS

The model presented successfully simulates the dilute sulfuric acid saccharification of prehydrolyzed Douglas-fir and southern red oak lignocelluloses as determined by comparison of the experimental data with the values predicted for a given set of reaction conditions. The model is a considerable improvement over the simple model based on two consecutive reactions. It takes into consideration the facts that the neutralizing capacity of the cellulosic substrate lowers the effective concentration of the added acid, that glucose gives reversion products in dilute acid solution, and that all cellulosics contain material that is readily hydrolyzable.

Although the model was developed specifically for application to the dilute sulfuric acid saccharification of prehydrolyzed wood lignocellulose, it can in principle be used if other substrates or catalysts are used. However, the values of parameters in the various equations of the model will be different and must be evaluated. Thus as previously discussed, large differences in the rate of cellulose hydrolysis have been observed depending on the cellulosic substrate used.[15] Also changes in the catalyst can affect the rates of the saccharification reactions. For example, hydrochloric acid is a much more effective catalyst for glucose degradation than sulfuric acid when compared at equal hydrogen-ion concentrations.[33]

The model has several advantages for use in process calculations. The various forms of glucose-containing species in solution can be estimated separately and thus may be treated as entities in process schemes. The estimated values can be used to interrelate values obtained from the various analytical methods used to assay carbohydrate content, e.g. reducing sugars, HPLC, and enzymatic methods. The model also estimates the amount of material lost through glucose dehydration. From this, one can then estimate the quantities of various sugar degradation products (i.e. hydroxymethylfurfural and levulinic acid) that would contaminate the final glucose solution.

Further experimental data are required to fully test the model and make it applicable to a variety of other substrates and catalysts. This includes data to more accurately describe glucose dehydration, glucose reversion, and cellulose hydrolysis in sulfuric acid as well as other acid solutions. Further research in these areas is being undertaken.

EXPERIMENTAL

Douglas-Fir Lignocellulose

Details of the procedures used to obtain the data reported in Table 1 are given in the original publications.[4,7,8]

Southern Red Oak Lignocellulose

Chips (9 mm) of southern red oak wood (Quercus falcata Michx.) impregnated with dilute sulfuric acid were prehydrolyzed by direct steam heating for 6 minutes at 170 °C as described elsewhere.[10] One-half of the lignocellulosic residue was slurried, fiberized, and washed using distilled water, the other half was treated similarly using tap water. After washing, the wet residues were pressed to remove as much water as possible and air dried. The ash contents were determined using ASTM Method No. D 1102. Ash samples were titrated with dilute acid to determine their neutralizing capacity,[13] and these values were reported on the basis of the original material as meq/kg of ovendry lignocellulose. The distilled water-washed residue contained 0.18% ash and had a neutralizing capacity of 27.2 meq/kg. Corresponding values for the tap-water-treated material were 0.47% and 107.2 meq/kg.

Samples of the two residues were reacted in glass ampoules at a liquid-to-solid ratio of three using 0.8% H_2SO_4 at 230 and 210 °C. Approximately 200 mg of residue were placed in a tared 20-cm x 5-mm od glass tube sealed at one end. The sample was then dried (60 °C in vacuo) and weighed. The tube was fitted with a rubber septum and evacuated. To obtain the desired liquid-to-solid ratio acid solution was injected with a syringe. The con-

tents were mixed by shaking, brought to atmospheric pressure with N_2, and sealed.

The reaction was carried out by placing the ampoule in a molten salt bath controlled to ±0.1 °C. The reaction time was taken as the interval from immersion in the salt bath to quenching in an adjacent water bath. After reaction the ampoules were opened and the contents washed onto a tared sintered glass funnel with hot water. The solids were washed with approximately 100 ml of boiling water, dried over night in vacuo at 60 °C, and weighed. The collected filtrate was diluted to a known volume.

The filtrates were analyzed for both total reducing sugars and monomeric glucose. The procedure for the former was Nelson's colorimetric modification of the Somogyi method[22] while HPLC[21] was used for the latter. The HPLC method used a Bio-Rad HPX-85 carbohydrate column maintained at 85 °C. The column was eluted with distilled water. The column effluent was monitored with a refractive index detector.

Carbohydrate analyses on the solids were performed using ASTM Method No. D 1915[17] except that the sugars were analyzed using the aforementioned HPLC procedure rather than paper chromatography. The original lignocellulose contained 57% glucan, 3% xylan, and 33% Klason lignin (ASTM Method No. D 1106), reported on an ash-free, ovendried basis. The unaccounted 7% is probably soluble lignin.

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