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Kinetics of Thermochemical Pretreatment of Lignocellulosic Materials

A. O. CONVERSE,[1] I. K. KWARTENG,[1]
H. E. GRETHLEIN,*,[2] AND H. OOSHIMA[1]

[1]Thayer School of Engineering, Dartmouth College, Hanover, NH 03755; and [2]Present address, Michigan Biotechnology Institute, Lansing, MI 48909

ABSTRACT

The results of an experimental study of the acid hydrolysis of hardwood are presented in the form of values for the three parameters, activation energy, power on the acid concentration, and pre-exponential factor, of the first order kinetic constants for each of the following reaction participants: xylan remaining, glucan remaining, xylose formed, and xylose decomposed. These are used as a base for a quantitative theory to predict the temperature, time, and acid concentrations needed for effective pretreatment of the substrate for subsequent enzymatic hydrolysis of the glucan. This theory is based on the assumption that successful pretreatment requires >90% removal of the xylan, <10% removal of the glucan, and >80% xylose yield. This theory is compared with selected published data.

Index Entries: Pretreatment; lignocellulosic substrates; kinetics; hydrolysis; enzyme.

INTRODUCTION

As pointed out by Conner (*1*), prehydrolysis, catalyzed either by added mineral acid or acid formed from acetate groups in the hemicellulose, has been utilized for some time and for a number of purposes, e.g., in the Masonite process (2), and in the preparation of Kraft pulp (3). More recently, it has been employed in the Iotech (*4*) and Stake (*5*) processes for increased animal digestion and enzyme hydrolysis of wood substrates. Having made the case for the importance of quantifying the prehydroyl-

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*Author to whom all correspondence and reprint requests should be addressed.

sis kinetics, Conner then proceeds to treat the xylan hydrolysis kinetics but does not relate it to the effectiveness of pretreatment.

Lamptey et al. (*6*) assert, in discussing their results, that optimal conditions for autohydrolysis are both mild enough to preserve the pentose sugars, and yet strong enough to provide rapid enzymatic hydrolysis. Wright has also pointed out the economic importance of preserving the pentose sugars that are formed during the pretreatment (*7*). Grohmann et al. (*8*) conclude from their study of mild acid hydrolysis that removal of the hemicelluloses is a necessary requirement for effective pretreatment.

It appears to us that there are three requirements that must be satisfied by a technically successful pretreatment.

1. Removal of the xylan;
2. Preservation of the glucan; and
3. Preservation of the xylose produced.

Actually, there is good reason to believe that there is a fourth: melting and partial removal of the lignin. Tanahashi et al. (*9*) have shown that steam explosion gives rise to small flecks of lignin that are solid but separated from the cellulosic portion of the substrate. Grethlein et al. (*10*) have shown that prehydrolysis is less effective on white pine than on hardwoods. Perhaps this effect is simply caused by the fact that there is less hemicellulose to remove in soft woods, and therefore less pore volume is generated when it is removed. However, this remains unexplained. For hardwoods, in any event, it appears that the above three requirements are sufficient, probably because the conditions that remove the xylan also modify the lignin.

It should be noted that the rapid decompression of the heated biomass has been neglected in the above discussion. This is in accord with the conclusion by Brownell and Saddler that it is not required (*11*). In our own studies of acid hydrolysis as well as steam explosion, however, there is a very rapid decompression.

In this paper we have used Kwarteng's (*12*) study of xylan hydrolysis, xylose decomposition, and glucan hydrolysis to generate contours on the temperature–time plane to identify the region in which xylan hydrolysis exceeds 90%, xylose yield exceeds 80%, and glucan hydrolysis is less than 10%. This provides a quantitative theory of pretreatment, assuming that the rate and extent of the enzymatic hydrolysis is correlated with the extent of xylan removal. Evidence supporting such correlation has been presented by Grohmann et al. (*8*) and further evidence is presented later in this paper. The results of Kwarteng's kinetics studies and the resulting contours, are presented here. Finally, a few of the studied pretreatment conditions are compared with the theory. The contours extrapolate the kinetic model far outside the region in which the supporting data were obtained, and may, therefore, be in error in certain regions. We hope that this approach will eventually lead to a successful quantitative theory of pretreatment.

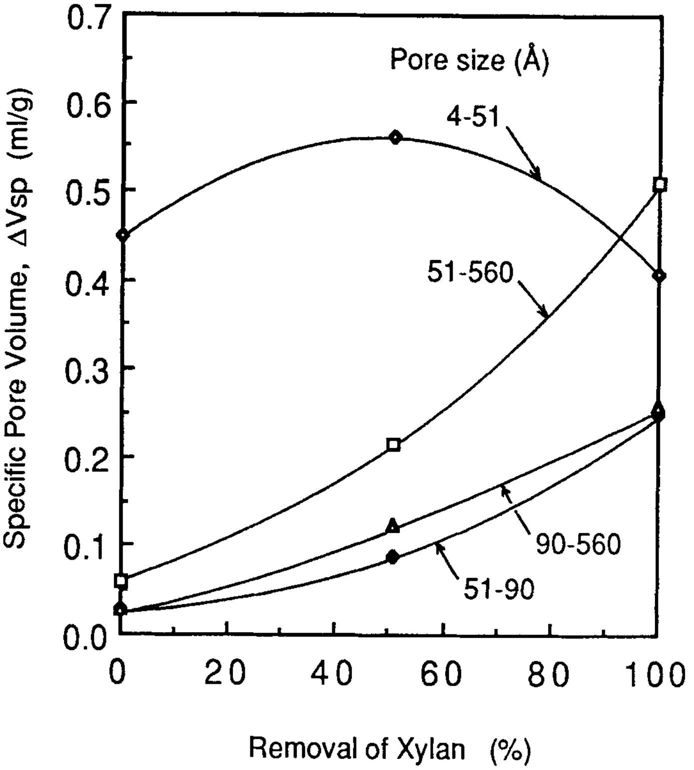

Fig. 1. The effect of xylan removal on pore size distribution. The curves indicate the volume whose width is in the range indicated. For example, the curve labeled 51-560 is the volume available to molecules less than 560 A in diameter less the volume available only to molecules smaller than 51 A in diameter.

CORRELATION BETWEEN XYLAN REMOVED, PORE SIZE, AND THE ENZYMATIC HYDROLYSIS OF GLUCAN

Figure 1 represents the relationship between the specific pore volume, V_{sp}, and the percent removal of xylan from the wood pretreated by acid under various conditions. The figure shows that the pore volume accessible to enzyme, which is assumed to be 50–100 Å, increases as xylan is removed. On the other hand, the behavior of the small pores with sizes of 4–51 Å is different from that of the large pores. That is, in the initial stage of the removal of xylan the volume of small pores increases and as the removal proceeds, it decreases. This behavior may be caused by the competition of the formation of new pores caused by the removal of xylan with the disappearance of pores within the xylan removed. Figure 2 shows that the potential glucose of the pretreated wood is increased as the removal of xylan proceeds. The increase in the volume of pores accessible to enzyme by the removal of xylan without the significant loss of glucan enhances the rate of the enzymatic hydrolysis of the glucan, as shown in Fig. 3.

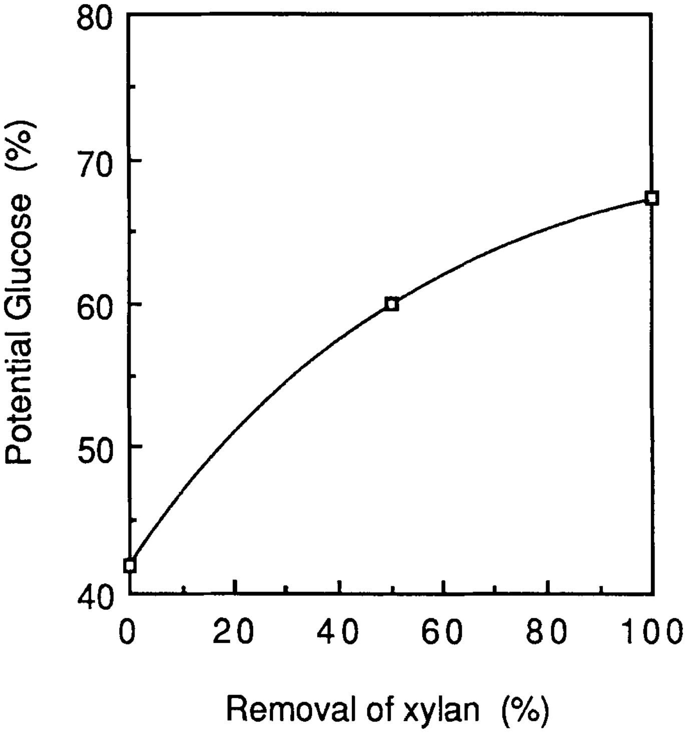

Fig. 2. Glucan content, as percent potential glucose, of pretreated solids as a function percent xylan removed.

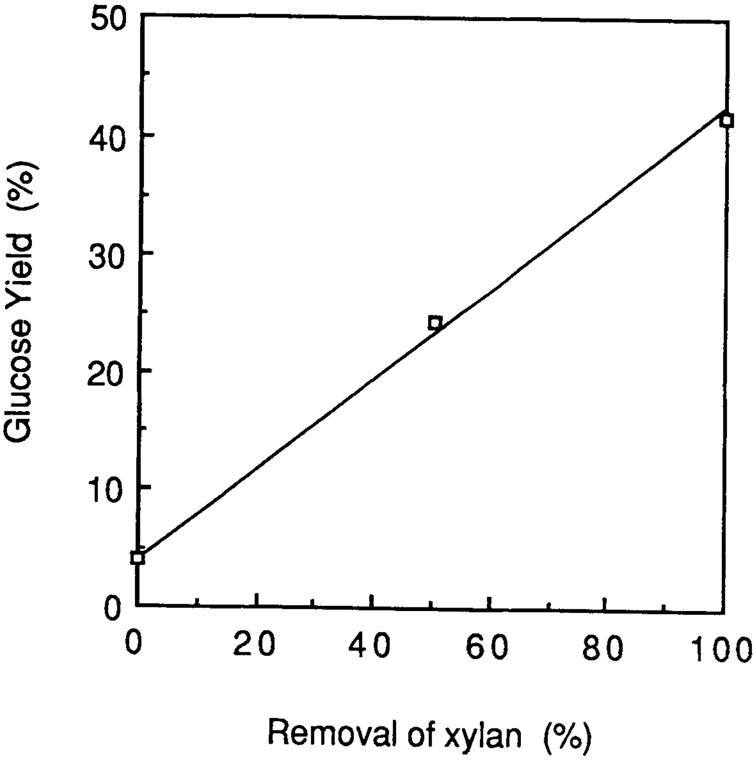

Fig. 3. Glucose yield in the first 2 h of enzymatic hydrolysis as a function of the xylan removed in pretreatment.

Table 1
Composition of Wilner-60 Mixed Hardwood

Component	Mass fraction, percentage
Moisture	6.71
Extractives	3.84
Ash	0.33
Carbohydrates	
Glucan	36.58
Xylan	18.42
Galactan	2.84
Arabinan	2.46
Mannan	0.83
Lignin, uronic anhydride, and acetyl groups	28.03

ACID HYDROLYSIS KINETICS OF XYLAN, XYLOSE, AND GLUCAN

Experimental

Acid hydrolysis was carried out in a plug-flow reactor with direct steam injection to rapidly increase the temperature and initiate the reaction, as described previously (*13*). Sulfuric acid (technical grade, J. T. Baker Chemical Co.) was added to the substrate slurry before pumping. The substrate was Wilner 60 hardwood flour, 90% birch and 10% maple, from Wilner Wood Co. The composition is presented in Table 1.

The reaction products, the hydrolyzates, were analyzed for the following quantities at each reaction temperature as follows

1. Acid content (wt%) in the liquid phase was obtained by titrating 10 mL against standardized 0.1 *N* NaOH;
2. The concentrations (mg/mL) of the hydrolysis products—cellobiose, glucose, xylose, galactose, arbinose, mannose, HMF, and furfural—were determined by a high pressure liquid chromatograph (HPLC), using the Biorad Carbohydrate Column, HPX-87, with water as the eluent;
3. The potential sugars (mg/mg) in the feed slurry and unreacted hydrolyzate solids were obtained by quantitative saccharification (Saeman (*14*)) and by HPLC analysis;
4. The solids concentrations in both feed slurries to the reactor and the hydrolyzate slurries from the reactor were also determined by drying and weighing the residue.

Results

Xylose decomposition was studied independently by feeding the reactor with a xylose solution. The xylose decomposition in the flow reactor was found to be first order with the reaction rate constant given by

$$\begin{aligned} k &= \mathrm{P} * \mathrm{A}^{n} * \exp(-\mathrm{E}/\mathrm{RT}) \\ \text{where } E &= 27{,}100 \text{ cal} \\ n &= 0.69 \\ 1n(P) &= 28.48 \end{aligned} \tag{1}$$

with a standard deviation as percent of the mean of 3.8%. Experimental conditions ranged as follows: acid concentration, 0.2–2.0 wt%; temperature, 160–265°C; residence time, 0.125–0.35 min; and initial xylose concentration, 5–10 wt%. The above parameters are statistically different from those that were determined by Kwarteng from Root's batch reactor data (*15*). This difference between batch and flow reactor kinetics was also found in Smith's study of glucose (*16*).

The above xylose decomposition kinetics were imposed in the determination of the xylose formation kinetics. Assuming a single type of xylan, the xylose yield data was fit as a first order reaction with the reaction rate constant given by

$$\begin{aligned} k &= \mathrm{P} * \mathrm{A}^{n} * \exp(-\mathrm{E}/\mathrm{RT}) \\ \text{where } E &= 27{,}800 \text{ cal} \\ n &= 1.17 \\ 1n(P) &= 31.76 \end{aligned} \tag{2}$$

with a standard deviation as percent of the mean of 9.3%. Experimental conditions ranged as follows: acid concentration, 0.2–2.4 wt%; temperature, 160–265°C; residence time, 0.125–0.60 min; and initial solids concentration, 33–106 mg/mL. The above data was also fit with a two-fraction xylan model (*12*). However, in this study the above parameters Eq. (2) were used because the fit of the two-fraction model, 9.5%, was no better. This differs from the results obtained in batch experiments by Conner (*1*) and Grohmann et al. (*8*). In the work reported in the next section, the above parameters are used to compute the xylose yield.

Assuming a single type of xylan, the residual xylan data was fit as a first order reaction with the reaction rate constant given by

$$\begin{aligned} k &= \mathrm{P} * \mathrm{A}^{n} * \exp(-\mathrm{E}/\mathrm{RT}) \\ \text{where } E &= 25{,}500 \text{ cal} \\ n &= 0.73 \\ 1n(P) &= 29.84 \end{aligned} \tag{3}$$

with a standard deviation as percent of the mean of 6.5%. Experimental conditions were the same as for the xylose yield data.

The residual glucan data was fit as a first order reaction with the reaction rate constant given by

Table 2
Comparison of Experimental Values
of Xylan Autohydrolysis with Predicted Values

		Fraction xylan remaining	
Temperature, C	Residence time, min	Experimental (Kwarteng (*11*))	Predicted with A = 0.0033%
160	.622	.969	.989
177	.596	1.02	.967
189	.584	1.017	.933
199	.566	.969	.885
209	.548	.876	.813
219	.536	.637	.706
230	.528	.498	.545
243	.529	.28	.314
252	.501	.17	.187
262	.461	.099	.087

$$\begin{aligned} k &= \mathrm{P} * \mathrm{A}^{\mathrm{n}} * \exp(-\mathrm{E/RT}) \\ \text{where } E &= 36{,}500 \text{ cal} \\ n &= 1.15 \\ \ln(P) &= 37.76 \end{aligned} \tag{4}$$

with a standard deviation as percent of the mean of 7.8%. Experimental conditions were the same as for the xylose yield data.

The above expressions for the rate constant indicate that k would equal zero when there is no acid added, i.e., A = 0. However,the data in Table 2 indicate that xylan hydrolysis does occur, as is well known. Presumably this is caused by the protons formed from the acetate groups in the biomass. To represent this behavior, the value of the acid content, that causes Eq. (3) for the xylan hydrolysis rate constant to best fit the data in Table 2, was determined. The value obtained was 0.0033 wt%. The fraction of xylan remaining, as predicted by Eq. (3) with this value for A, is compared with the experimental values in Table 2.

CONTOURS OF SUCCESSFUL PRETREATMENT

The objective of this section is to identify conditions of residence time, temperature, and acid concentration that will cause >90% of the xylan to be removed and yet remove <10% of the glucan and preserve the xylose formed. In principle, it would be possible to allow more of the glucan to be removed so long as the glucose is preserved. However, it is known from acid hydrolysis studies that the maximum yield of glucose from a plug-flow acid hydrolysis reactor is about 50% (*13*), whereas for

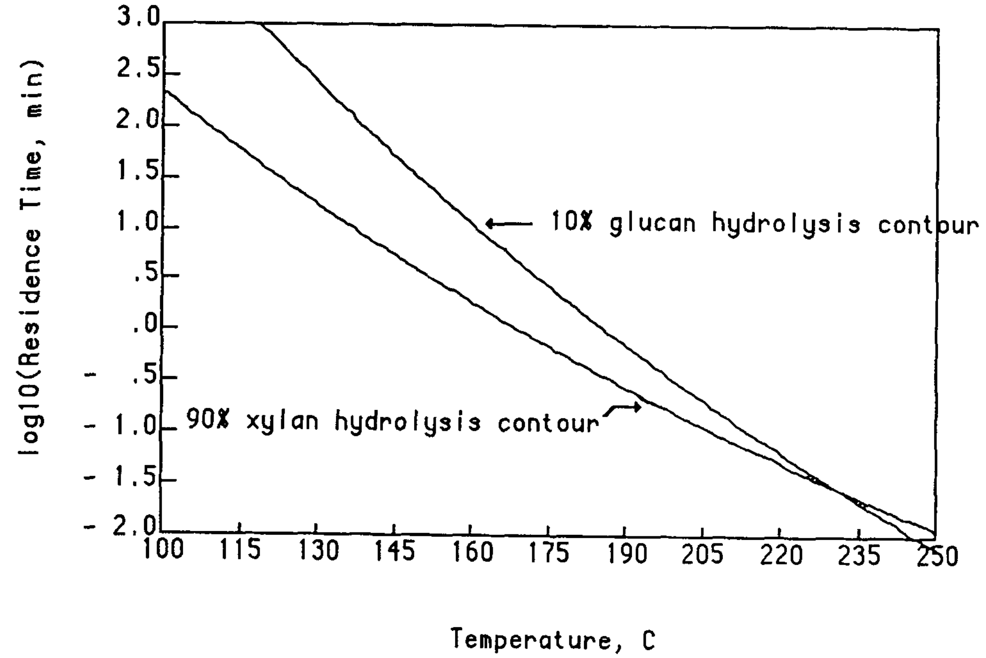

Fig. 4. Xylan and glucan conversion contours on the residence time vs temperature plane. The area between the contours contains the acceptable pretreatment conditions. Acid concentration = 1 wt%.

xylose the maximum yield is >85% (*11*). Hence, it is not possible to remove a significant fraction of the glucan without decomposing some of the glucose. This not only decreases the yield but also generates products that interfere with the fermentation.

Figure 4 presents, for the case in which 1 wt% sulfuric acid is added, the contours for 10% glucan hydrolysis and 90% xylan hydrolysis, and the region in which the above constaints are satisfied. The contours cross at about 230°C, indicating that pretreatment should be carried out below this temperature in the region between the two contours. The residence time varies from 1000 to 0.05 min, as the temperature is varied from 100 to 230°C. The xylan contour is calculated from the kinetic parameters based on residual xylan data. The glucan contour is calculated from the kinetic parameters based on residual glucan data.

Figure 5 presents the corresponding xylose yields as a function of temperature. For each temperature, the time is set so that 90% of the xylan is removed. Two values of the xylose yield are presented. The upper value is calculated from the kinetic parameters based on residual xylan data. The lower value is calculated from the kinetic parameters based on xylose concentration data. The xylose decomposition kinetics parameters is used in both sets of computations. The difference between the two values is owing to: the formation of xylose oligimers, and inconsistency

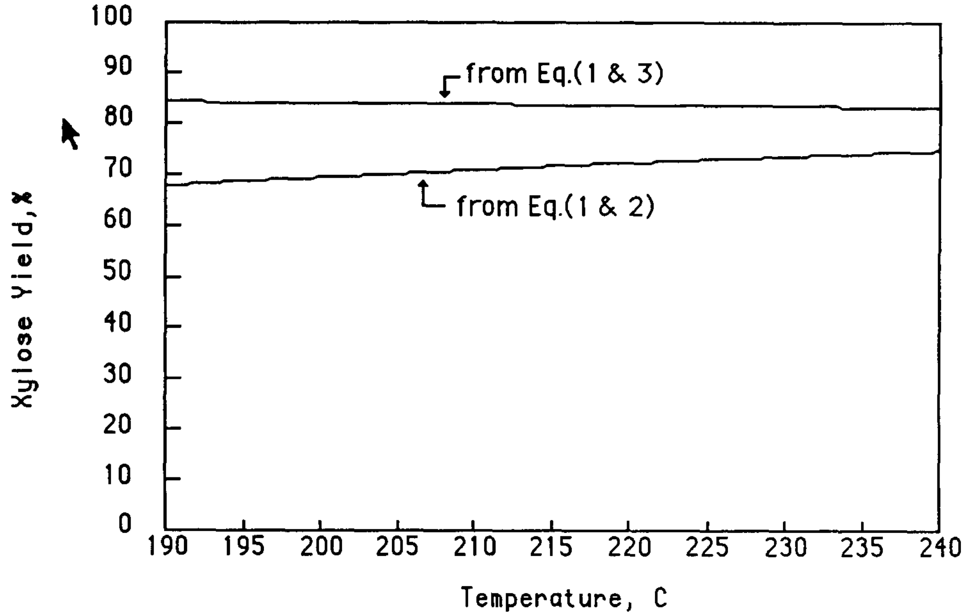

Fig. 5. Xylose yield vs temperature based on xylan-remaining and xylose-formed kinetics. Acid concentration = 1 wt%. Xylan conversion = 90%.

between the kinetic parameters. The kinetic parameters derived from the xylose formation data, underpredict the observed xylose yields at conditions that give rise to the highest xylose yields (*12*). Xylose yields in excess of 85% were obtained at temperatures in the 200–210°C range (*12*). Hence, it is known that high xylose yields can be obtained at conditions that provide effective pretreatment. Further study is needed to clarify the situation at lower temperatures.

Figures 6 and 7 present the corresponding results for autohydrolysis, i.e., with no added acid. As discussed in the previous section, the effective acid concentration when no acid is added is 0.0033 wt%. This was used to determine the results presented in Figs. 6 and 7. Figure 6 demonstrates that the residence times required for pretreatment are an order of magnitude greater than in Fig. 4 when acid is added. Figure 8 presents more detailed reslts over the more restricted range encountered in steam-explosion pretreatment. The glucan contour is absent, off the plot to the right. Figure 7 shows a large difference between the xylose yield based on remaining xylan and that based on xylose formed. Possibly, this is owing to oligomer formation. It should be noted, however, that this plot extrapolates the kinetics model far beyond the experimental conditions used in the parameter evaluations.

The computer programs used to prepare Figs. 4–8 are available from the author.

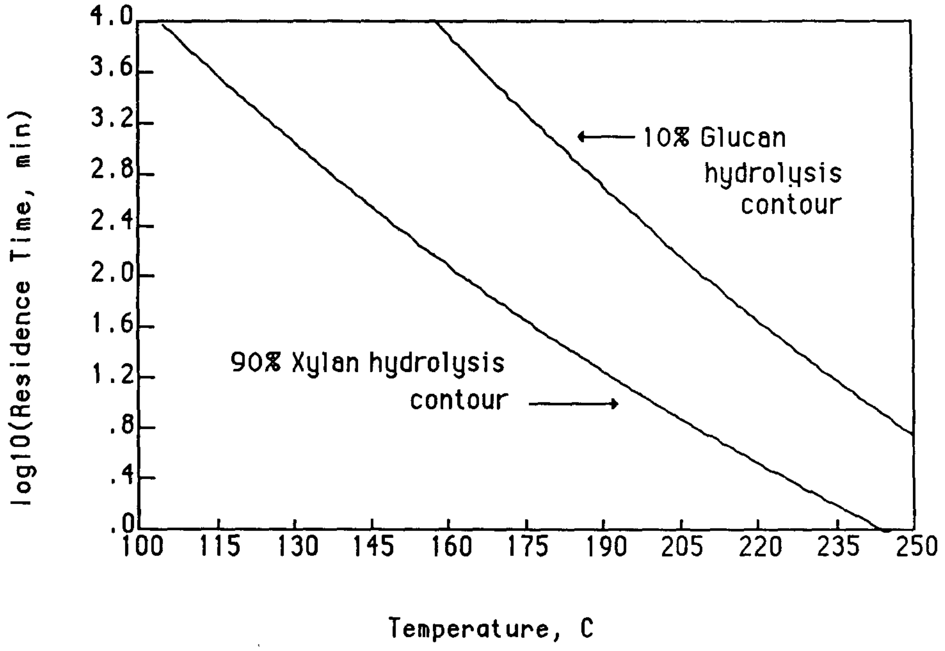

Fig. 6. Xylan and glucan conversion contours on the residence time vs temperature plane. The area between the contours contains the acceptable pretreatment conditions. Acid concentration = 0.0033 wt%, i.e., the condition for autohydrolysis.

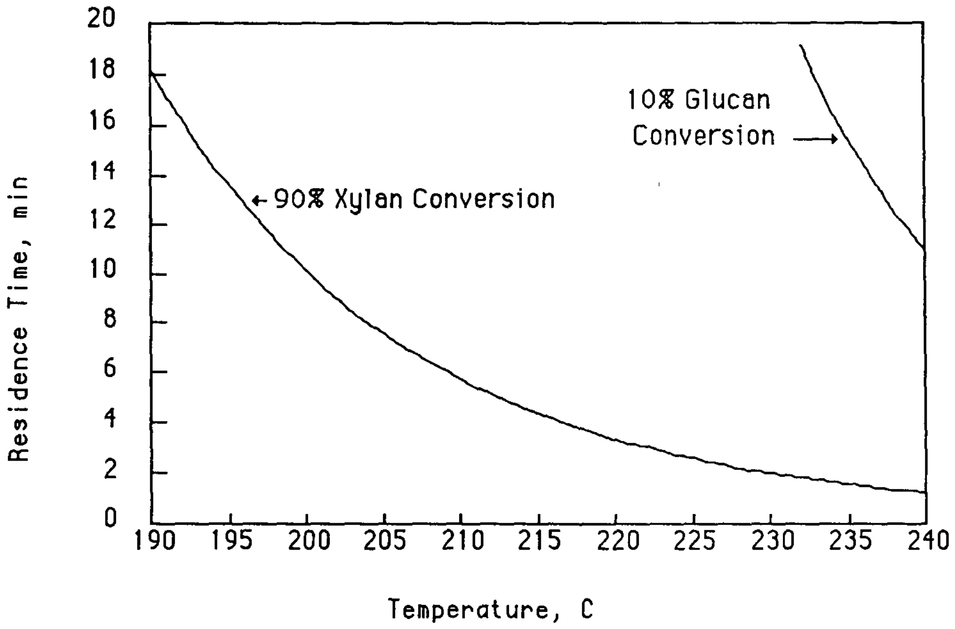

Fig. 7. Zoom projection of region of special interest from Fig. 6.

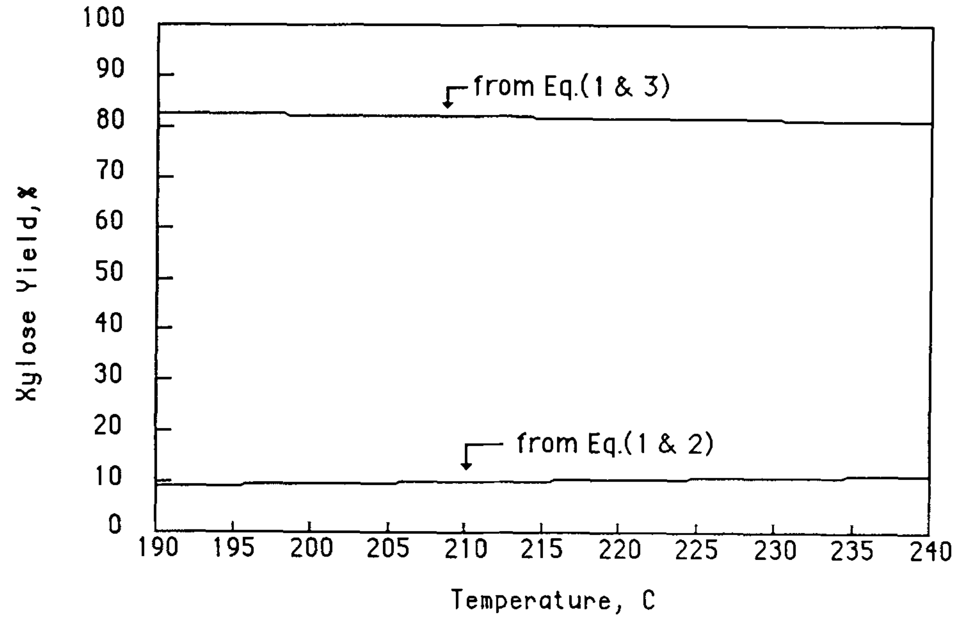

Fig. 8. Xylose yield vs temperature based on xylan-remaining and xylose-formed kinetics. Acid concentration = 0.0033 wt% (autohydrolysis). Xylan conversion = 90%.

COMPARISON OF THEORY WITH EXPERIMENT

In Fig. 9, the steam explosion pretreatment conditions studied by Grous (*17*) are displayed by the nine dark square points on the plot previously presented as Fig. 7. The numerical values next to these points are the glucose yields after 48 h of enzymatic hydrolysis of the pretreated poplar wood. The corresponding value for poplar that has not been pretreated was found to be 17%. Given that the 90% xylan contour comes from Kwarteng's independent study of acid hydrolysis, and that to use his kinetic parameters the effective acid concentration of 0.0033 wt% had to be estimated from a limited amount of data, the agreement shown in Fig. 9 is rather fortuitous.

In Fig. 10, the total yield of xylan and xylose recovered by Grous (*17*) in both the liquid and the solid products from steam explosion are presented on the plot previously presented as Fig. 8. The yields are indicated by the crossbars on the vertical lines at the three temperatures used; the numerical values are the corresponding residence times, in minutes. The yield values are on the low side of the wide range between the values of the xylose yield based on the remaining xylan kinetics and the xylose yield based on the xylose-formation kinetics. These data indicate that over 50% of the xylan is lost as volatile products, presumably furfural. Thus, although the steam explosion pretreatment conditions used by Grous satisfy the requirements for good glucose yield from enzymatic

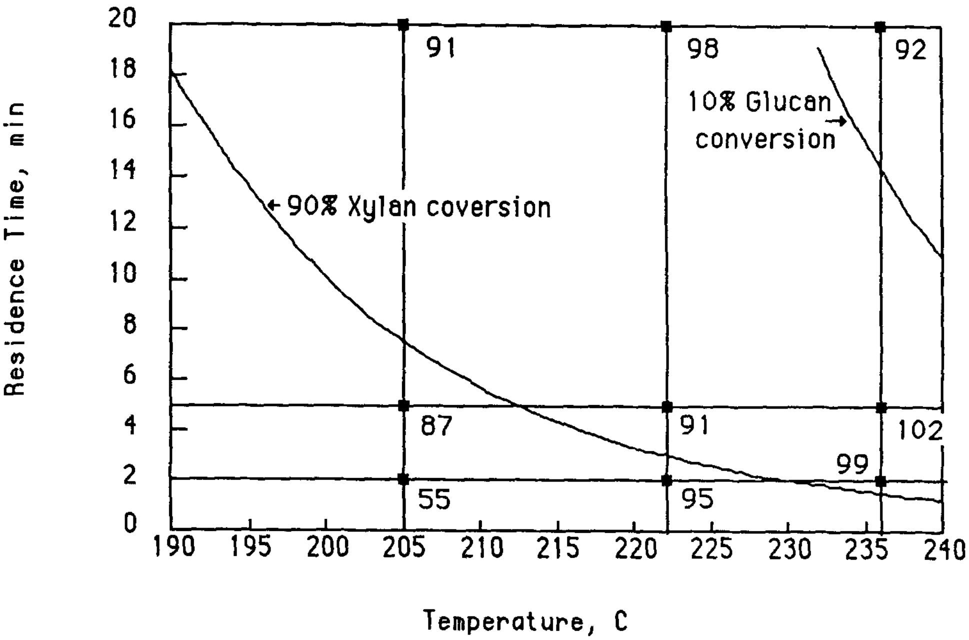

Fig. 9. Projection of steam explosion pretreatment conditions employed by Grous et al. (*17*) on the corresponding xylan and glucan conversion contour plot.

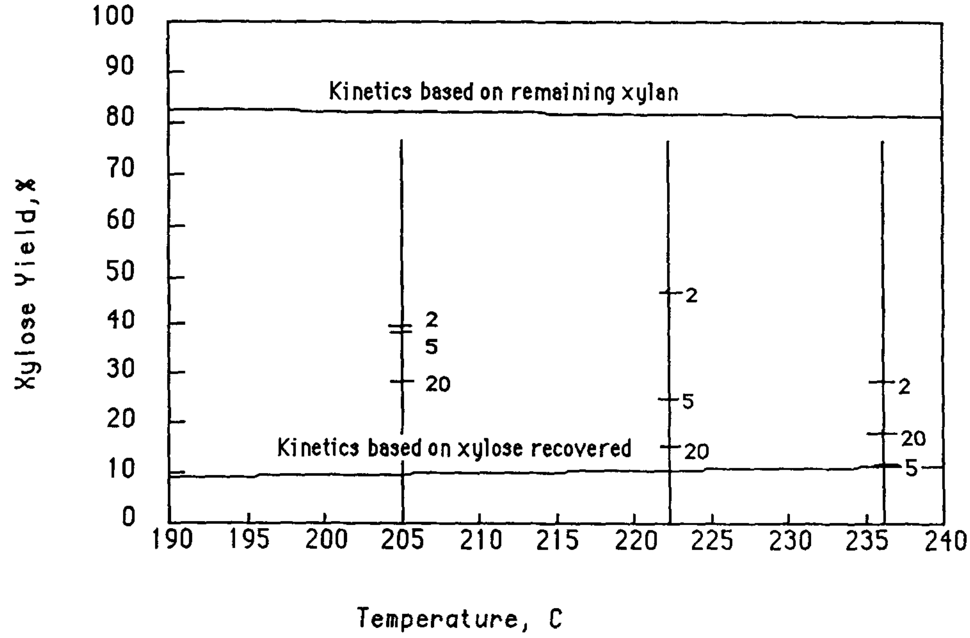

Fig. 10. Xylose plus xylan recovery found by Grous et al. (*17*) compared to the predicted xylose yield.

hydrolysis, they do not satisfy the requirement for good xylose recovery. It should be noted, however, that total product recovery was difficult in the apparatus used by Grous; the low yield may have been caused in part by experimental limitations.

In Table 3 the pretreatment conditions reported by Grethlein et al. (*10*) are summarized. The substrate was Wilner mixed hardwood (maple and birch). The values of the percent glucan hydrolyzed during pretreatment as predicted by Eq. (4) are presented in column 4; column 6 presents the corresponding experimental value. The percent xylan hydrolysis as predicted from Eq. (3) is presented in column 5; and the glucose yields, after 48 h of enzymatic hydrolysis with 0.34 IU/mL of *Trochoderma reesei* Rutgers C-30 strain, are presented in column 7. Yields (col. 7) in excess of 80% are obtained only for pretreatment conditions at which the xylan hydrolysis is >90%, the value postulated to be a satisfactory criterion for successful pretreatment. Unfortunately, the data do not provide a very good check on this assumption, since the percent xylan hydrolysis jumps from 67.6% in run 2 to 95.4% in run 3.

Data on the batch acid-hydrolysis pretreatment of poplar wood from Grohmann et al. (*8*) as shown on Fig. 11 show the 80% xylan conversion contour to be well above, rather than below, the 90% contour predicted from the theory. This may be a result of the fact that different substrates were employed as well as the difference in the temperature range. Nevertheless, the two contours are parallel. In Fig. 12, furthermore, the xylose yield data from Grohmann et al. are in good agreement with the upper value predicted by the theory.

CONCLUSIONS

The paper presents a quantitative theory of auto- and mild-acid-hydrolysis pretreatment of lignocellulosic substrates for subsequent enzymatic hydrolysis of the glucan. The theory compares well with limited published data from Dartmouth. Comparison with batch data from Grohmann et al. is not as favorable but the trends are correct. Comparison with the results of other investigators is invited.

ACKNOWLEDGMENT

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Table 3
Enzyme Hydrolysis Compared to Xylan Removal[a]

Temperature, °C	Acid, percentage	Time, min.	Glucan hydrolysis, percentage	Xylan hydrolysis, percentage	Experimental value glucan hydrolysis	48-h Enzyme hydrolysis glucan yield Ref. 9)
180	.51	.14	.4	31.8	1.2	45.3
200	.48	.13	1.9	67.6	2.9	72.9
220	.47	.12	7.8	95.4	8.2	83.1
220	.57	.13	10.4	97.9	6.0	86.0
220	1.22	.12	21.6	99.8	9.5	79.0
230	.59	.12	19.9	99.8	9.8	91.3
230	1.17	.12	38.5	100.0	18.8	93.0

[a] Substrate: Wilner mixed hardwood.

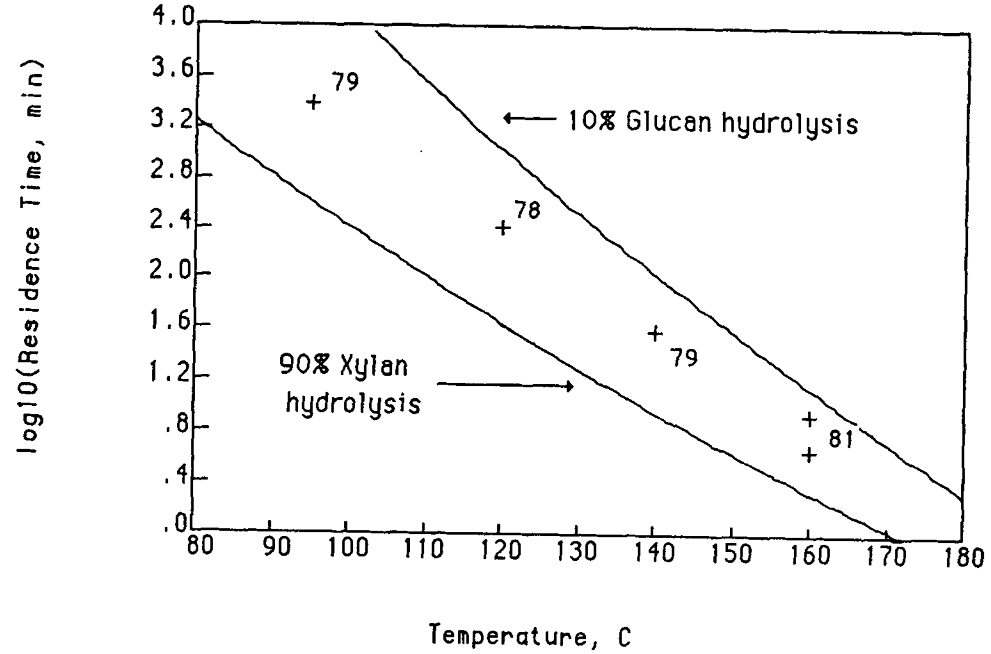

Fig. 11. Xylan hydrolysis results obtain by Grohmann et al. (*8*) compared to the xylan hydrolysis contour based on kinetic parameters presented in this paper. The numerical values are the percent xylan hydrolysis obtained by Grohmann et al. (*8*).

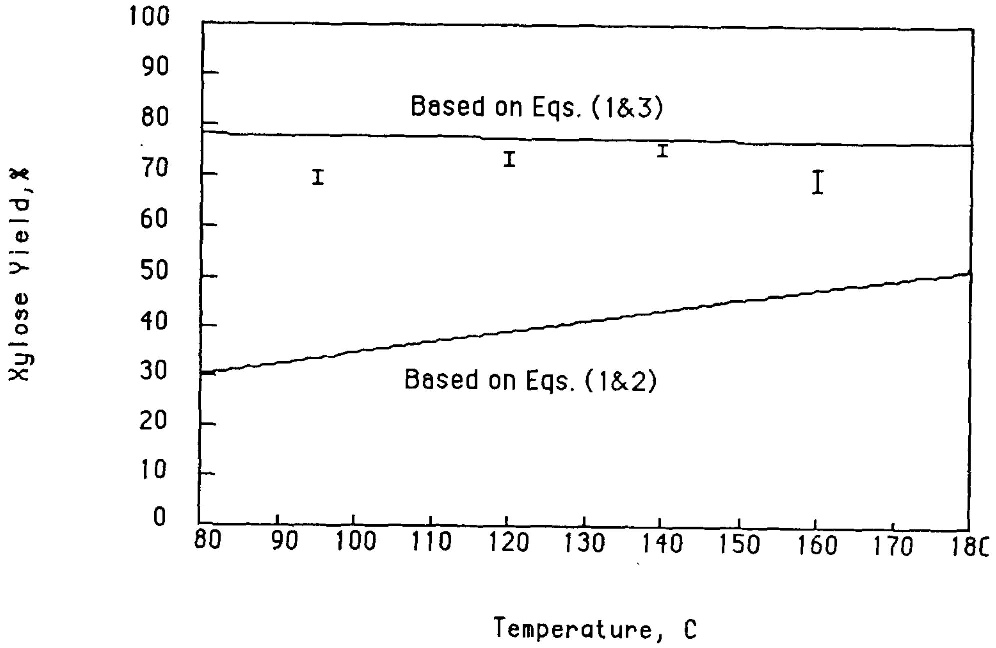

Fig. 12. Xylose yields obtain by Grohmann et al. (*8*) compared to the xylose yields based on kinetic parameters presented in this paper. Acid concentration = 0.825 wt%.

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