Pretreatment–Catalyst Effects and the Combined Severity Parameter

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ABSTRACT

Fractionation of lignocellulosic materials into high-yield cellulosic solid components can be accomplished with acid-catalyzed aqueous and mixed aqueous and nonaqueous media, with the latter leading to high lignin and xyland removal. Concepts combining only time and temperature pulping profile with catalyst concentration are presented to correlate these two types of fractionation methods with pulping variables. Severity concepts combining time and temperature only are often used in the pulp and paper industry. The present extension of this concept produces *phenomenological* descriptions that permit comparisons of different proceses and yield some pseudokinetic parameters for aspen (*Populus tremuloides*) acid-catalyzed fractionation.

Index Entries: Catalyst effects; severity parameters; lignin; xylan; lignocellulosics.

INTRODUCTION

Organosolv delignification of wood was originally studied by Kleinert and Tayenthal (1) and Kleinert (2,3) as a high-yield process to replace kraft pulping. More recently, both acid and base as well as non-catalyzed ethanol and methanol organosolv processes have been studied at the laboratory and pilot plant levels (4–10). One of these, the ALCELL™ process, is now being demonstrated at the 36 t/d level at REPAP's New Brunswick mill (7).

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Advantages of organosolv processes include high yields of cellulosic materials, high selectivity for lignin removal, and probable environmental improvements compared to conventional pulping, because of the extensive recycle of solvents and the wide range of potential catalysts. These processes could also be applied to the preparation of substrates for fuel and chemical production from the enzymatic hydrolysis of the cellulosic fraction (11). Compared to acid hydrolysis pretreatments, the increased removal of lignin could be advantageous in increasing digester capacity and decreasing enzyme losses (12,13). The enzymatic digestibility of organosolv pulps prepared from *Populus spp.* is markedly enhanced if at least 50% of the original xylan is removed (14). Similar findings hold for other types of pretreatments (15–19). We report here on the systematic evaluation of the effect of sulfur dioxide and mineral acid catalysts on the methanol–water organosolv pretreatment of aspen. These data are compared, by means of a severity concept, with those of dilute aqueous acid pretreatments of aspen, as reported by Grohmann et al. (15).

The severity concept is developed from previous similar concepts, such as Vroom's H-factor (20), and the P-factor of Brasch and Free (21) which are used to control the extent of pulping and of prehydrolysis processes in the pulp and paper industry. The concept of combining temperature and time in a single parameter has been shown to describe the noncatalyzed aqueous and steam pretreatment of hardwoods (22). By also incorporating an acidity function, we demonstrate here that catalyzed aqueous and organosolv pretreatments can also be correlated by this tool. Although severity concepts are *phenomenological* descriptions, they do permit comparison of different processes, and it is possible to derive some pseudokinetic parameters from such correlations.

EXPERIMENTAL

The central composite design employed in the sulfur dioxide catalyzed experiments aimed at the removal of at least 50% of the starting xylan content ($\leq$ 15% of residual xylan in the pulp) for high enzymatic digestibility of the resulting celulosic substrates. In addition, the design attempted to minimize lignin content and maximize hexosan retention. Experimental conditions were 125°–145 °C, 40–200 min residence time, regular size aspen (*Populus tremuloides*) chips, and methanol concentrations of 40–70% by volume. The SO_2 concentration ranged from 0.2–1.7% (wt) of the incoming liquor with an average 10:1 liquor-to-wood ratio. In addition, mineral acids, such as sulfuric and phosphoric, were employed. Experiments were also performed without catalysts to compare the degree of recovery and isolation of the various fractions with those from the catalyzed experiments. A flow-through delignification system (23) was employed in these experiments. A few comparative points were made with nonflow conditions (static experiments). Results and conditions are shown in Table 1.

Table 1
Effect of Liquor Composition, Pulping Temperature,
Time, and Catalyst on the Composition and Yield
of the Cellulosic Residue from Organosolv Pulping of Aspen Wood

Catalyst concn, %	MeOH concn, %	T, °C	Time, min	Pulp Sugar Content (%ODW)[a]			Residual lignin %ODW	Lignin free yld, %[b]
				Xyl	Mann	Gluc		
				Sulfur dioxide				
0.2	55.0	136	70	13.2	1.9	73.4	12.9	57.6
0.5	47.5	131	53	10.4	3.6	66.0	13.2	55.0
0.5	47.5	130	105	9.6	1.7	67.3	11.9	51.7
0.5	47.5	141	53	9.0	2.2	82.0	9.2	49.4
0.5	47.5	140	105	11.7	2.2	76.3	7.6	50.6
0.5	55.0	135	70	10.4	2.1	76.4	10.4	53.5
0.5	62.5	131	53	13.7	3.0	61.2	14.3	59.0
0.5	62.5	131	105	11.0	2.0	72.2	9.9	55.5
0.6	62.5	141	53	10.7	3.0	67.6	14.0	53.3
0.5	62.5	141	105	10.0	1.9	87.0	5.3	51.6
0.9	40.0	136	70	11.0	1.5	74.6	14.1	51.6
0.9	55.0	126	70	17.1	2.1	67.4	15.4	61.7
0.9	55.0	136	42	16.6	1.1	67.4	14.9	56.3
0.9	55.0	135	70	8.8	3.7	69.3	12.3	52.3
0.9	55.0	136	70	10.5	2.1	81.1	6.8	51.3
0.9	55.0	135	70	10.9	2.1	77.9	9.3	52.3
0.9	55.0	135	204	8.8	2.5	83.4	5.3	48.6
0.9	55.2	145	70	9.0	1.9	86.0	7.1	49.5
0.9	70.0	135	70	12.7	3.3	75.1	10.6	53.6
1.3	47.5	131	53	10.6	1.8	74.8	11.5	53.1
1.3	47.5	131	105	10.4	2.0	85.2	6.9	51.2
1.3	47.5	140	53	9.1	1.9	83.0	6.5	50.5
1.3	47.5	140	105	7.1	1.6	88.0	5.5	46.8
1.3	55.0	136	70	10.1	2.0	79.4	5.7	51.2
1.3	62.5	131	53	13.3	2.3	80.4	9.9	54.6
1.3	62.5	131	105	12.2	2.2	78.8	8.5	54.2
1.3	62.5	141	53	10.7	4.5	77.2	8.0	53.6
1.3	62.5	140	105	8.8	4.2	82.3	6.1	50.9
1.7	55.0	136	70	10.5	1.3	85.3	7.0	51.7
				Sulfuric acid				
.01	50.0	161	60	9.8	2.1	78.6	7.2	50.3
.01[c]	50.0	162	60	7.1	1.6	88.4	5.7	46.1
				Phosphoric acid				
.02	50.0	165	60	6.8	2.2	78.1	4.6	48.9
.02	50.0	166	60	8.0	2.5	85.3	4.7	49.0
.007	50.0	166	60	9.2	1.8	78.1	6.2	51.2
none								
-	50.0	175	95	14.2	1.8	64.9	13.6	56.7

[a]Sugar contents of the pulps on an anhydro basis; arabinose and galactose were not present (Xyl=xylan, Mann=mannan, Gluc=glucan).
[b]Based on the oven-dried weight (ODW) of the original wood.
[c]Static experiment.

The pH data were obtained with a combination glass electrode (Orion #8103) using an Orion (Cambridge, MA) (#601A) Digital Ionalyzer and an acetate buffer in 50% methanolic solutions as the calibration standard; data were obtained at 20 and 40 °C. Because of the difference in calibration solutions and temperature, the pH values presented here differ somewhat from the values in the literature (14). The values used here are corrected for liquid-junction potentials and media effects on the hydrogen ion concentrations at low temperatures (40 °C) (24).

Analyses included Klason and soluble lignin, according to the Tappi standard method and useful method, respectively. Individual sugars were measured after hydrolysis of pulps or liquor residues as alditol acetates by gas chromatography (25).

RESULTS AND DISCUSSION

Severity Factors to Describe Complex Kinetic Processes

Lignin and xylan solubilization from the matrix of cellulose, hemi-celluloses, and lignin (the main polymeric components of wood) are important both to commercial pulping processes and to the understanding of the fundamental physical and chemical phenomena at the cell wall and overall composite levels. The bulk observations employed in this work include measurements of the mass of lignin and xylan solubilized as a function of time, temperature, cooking chemicals, and solvent system, based on the detailed composition of the residual pulp. The process description employed generates a correlation tool that allows better planning of experiments (and of the technical process) and is part of a data base necessary for the more complete understanding of such processes.

Mass loss of these polymers from the solid wood is a key observation, not suitable, however, for rigorous kinetic treatment based on activity changes and polymer theory. We propose here a data treatment of mass loss that reflects the non-first-order nature of the lignin loss. Experimentally, the observed initial high rate of lignin mass loss is followed by a diminishing rate, and when the data are plotted on the basis of remaining log mass vs time, a curve is obtained that suggests that the first-order rate constant is changing with the extent of reaction. Such behavior is often interpreted as being multiphasic, with a rapid pseudo-first-order initial dissolution, which is then followed by the bulk-phase delignification, also interpreted as pseudo-first-order, followed by a very slow (residual) final dissolution (26–28). A biphasic description has also been ascribed to the xylan dissolution in dilute acid hydrolysis of aspen (15).

Severity parameters have been used in the pulp and paper industry since the 1957 introduction of the H-factor (20), in which the delignifica-

tion is treated as a first-order reaction (based on mass loss) having Arrhenius temperature-dependent rates. Relative reaction rates (in which reaction rates at a pulping temperature were referenced to that at the base temperature [(T_b)] of 100°C), can be translated into H-factors, which can guide cooking time, and more importantly, allow the operator to adjust cooking cycles when operational difficulties dictate changes from standard temperature–time nonisothermal cooking profiles, a practical application.

The proposed severity factor is based on an approximation to Arrhenius temperature behavior, but is not limited to first-order kinetics and allows the well-known reduction in reaction rate with extent of reaction to be accommodated. The formalism presented here linearizes the temperature behavior for convenience, and is equivalent to the Arrhenius formal treatment. Like the Vroom factor, the only experimental variables required are the cooking temperature and time history once the appropriate values of the three fitted parameters have been determined for the particular species of wood employed.

The basis of the severity factor is a reaction ordinate given by

$$R_\omega = \exp\left[(T_r - 373) / \omega\right] \cdot \Delta t \tag{1}$$

in which T_r is the absolute reaction temperature, and the term Δt is the duration (min) of the reaction. The term ω is determined experimentally, as described below. If the reaction ordinate is applied to a first-order reaction with an Arrhenius temperature behavior, the ω term can be shown to be related to the reduced activation energy,

$$\Theta = E_a / R \tag{2}$$

in which R is the appropriate gas constant, via the equation

$$\omega = T_f{}^2 / \Theta \tag{3}$$

where T_f is a temperature chosen to be in the middle of the range of experimental conditions (floor temperature). This choice is necessary, because the error in the approximation of the reaction ordinate to the correct Arrhenius-temperature-based first-order expression increases with the increased temperature range of the experiments. It is given by the difference between the two expressions below, where α is the degree of conversion:

$$\ln[-\ln(1 - \alpha)] = \ln(A) - \Theta / T_r + \ln(t) \tag{4}$$

and

$$\ln[-\ln(1 - \alpha)] = \ln(A) - \Theta / T_r + \ln(R_\omega) - \left[(T_r - T_f) / \omega\right] \tag{5}$$

Equation (4) is the usual form for a first-law equation, and Eq. (5) is the value calculated with the severity parameter ω. The difference between these two equations is $\Theta[(1/T_r) - (1/T_f)] + [(T_r - T_f)/\omega]$. Operation far from the floor temperature incurs a large error in the predicted extent of conversion.

The data of conversion vs time for various temperatures is treated by the following linearizing transforms: for conversion: $Y = \ln[-\ln(1-\alpha)]$; for temperature-time: $X = [\ln(t) + (T_r - T_b)/\omega] = \ln(R_\omega)$. The value of ω is established by performing sequences of linear least squares on the data as $Y = mX + C$ and graphing r^2 against ω, for maximization of r^2, or by applying a simplex optimization routine to give the best value of ω. Note that the value of the intercept will depend on the units of time. Also, the transformation is best if conversion values are in the range of 0.2–0.8. For values outside of this range, statistical weighting functions can be used to correct the transformed values (e.g., with functions in which the initial σ value, prior to the transformation, is multiplied by $-[(1-\alpha)\ln(1-\alpha)]^{-1}$). Also, if the temperature range employed is very large, corrections to the $\ln(R_\omega)$ should be applied. For instance, assuming an Arrhenius-dependent behavior with temperature and first-order kinetics, the correction is given by

$$\ln(R_\omega)_{corr} = \ln(R_\omega) - [(T_r - 2T_f + T_f^2 / T_r) / \omega] \qquad (6)$$

The final fitted equation, $Y = mx + C$, can be interpreted in terms of a first-order reaction mechanism, as described below. The three constants that describe the conversion are ω, m, and C. From these, some pseudo-kinetic parameters can be derived, such as the reduced activation energy ($\Theta = T_f^2/\omega$) and the intercept, which can lead to the Arrhenius preexponential factor. Heat-up and cool-down times have been included in the calculation of the severity parameters.

If we assume that the polymer dissolution involves the hydrogen ion activity as a first-order reaction,

$$\text{Pol} + \text{H}^+ \xrightarrow{\text{k}'} \text{Products}$$

$$d[\text{Pol}] / dt = -\text{k}'[\text{Pol}][\text{H}^+] \qquad (7)$$
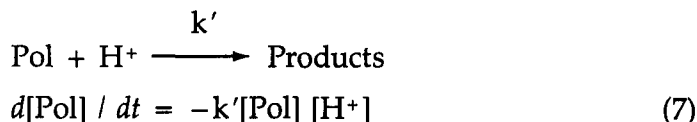
or, when integrated,

$$\ln\{[\text{Pol}] / [\text{Pol}]_0\} \propto [\text{H}^+]\exp[-E_a / R(T_r + 273)]\Delta t \qquad (8)$$

We can derive a combined severity parameter that includes time and temperature parameters, and the hydrogen ion activity parameters, as:

$$\ln\{[\text{Pol}] / [\text{Pol}]_0\} \propto [\text{H}^+]\exp[T_r - T_b) / \omega]\Delta t \qquad (9)$$

Equation (9) can be represented as the sum of the log of the severity parameter minus the pH of the pulping liquor at pulping temperature, or another appropriate acidity function for the solutions under the pretreatment conditions. As a first approximation, the pH of the liquor at a lower temperature can be employed as a measure of the hydrogen ion concentration for aqueous and methanol–water solutions of dilute acids or well-buffered solutions. Measurement of the relative hydrogen ion activity in aqueous alcoholic solutions is possible with the usual glass electrode,
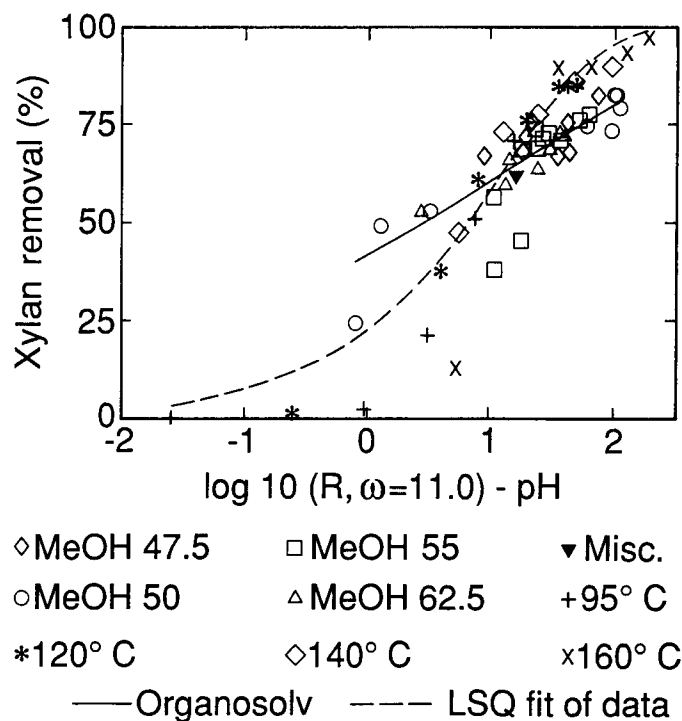
Fig. 1. Comparison of % xylan removal for dilute acid hydrolysis and organosolv pretreatments as a function of the combined severity parameter. Experimental points and model-generated data are given. Errors of the estimates are ±4% of xylan removal and ±0.2 in the calculated combined severity factors.

provided that the alcohol concentration is below 90% (wt) (93.2% (vol) (27). The liquid-junction potential and the medium effects on the hydrogen ion are under 0.15 pH U, and corrections have been made to generate the numbers employed in the calculations of log R_ω – pH.

Alternatively, the possibly more correct Hammett acidity functions could be employed from data obtained from spectroscopic properties of acid–base indicators or reaction kinetics in these media at the appropriate temperatures (29,30). However, such data are not available for the range of solvents, temperature, and catalysts employed in these experiments.

The Acid Pretreatment of Aspen

The data from the dilute acid hydrolysis of Grohmann et al. (15) were analyzed for the efficiency of removal of xylan. The data give a good fit to the model described above, and the transformed linear data gave an r^2 of 0.86, with $\omega = 11 \pm 1$ and the equation:

$$\ln[-\ln(1-\alpha)] = 1.3 \cdot \{\log 10([R_{\omega(corr)} - pH])\} - 1.0 \qquad (10)$$

The data are plotted in Fig. 1, along with the curve derived from Eq. 10. The standard deviation of the data, which is estimated at 5% of the statis-
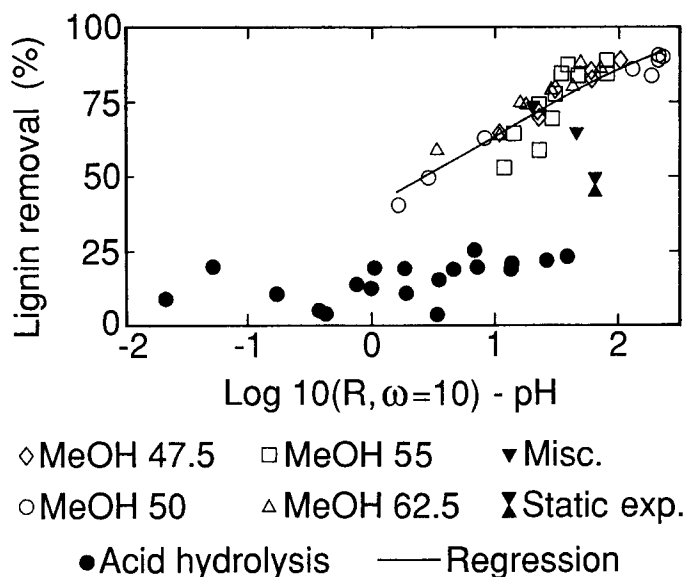
Fig. 2. Comparison of % lignin removal for dilute acid hydrolysis and organosolv pretreatments as a function of the combined severity parameter. Experimental points and model-generated data are given. Errors of the estimates are ±5% of lignin removal and ±0.2 in the calculated combined severity factors.

tical weight of the points, is fair for most points, except those having less than 20% xylan removal. The slope corresponds to a reaction whose order varies as the severity increases. This is expected, since xylan dissolution is recognized in the literature, to be a multiphasic process, with activation energy ranging between 28 and 37 kcal/mol, using the biphasic kinetics in the 95–140°C range (15). The activation energy of the time-varying rate constant is calculated, from the value of ω at floor temperature, to be 29±4 kcal/mol, a value in reasonable agreement with the biphasic kinetic interpretation. These experiments are at a constant pH of 1.5, and therefore, log 10(R_ω) correlation have the same form and are shifted by 1.5.

On examining these dilute-acid-hydrolysis data for the efficiency of lignin removal, no correlation with severity can be found ($r^2 = 0.01$); such a lack of correlation is expected, since lignin is barely removed under these conditions; in addition, the experimental numbers represented by Klason ligin determinations contain ash and extractives as well. These data are shown in Fig. 2.

The correlation for glucan removal from the solid residue was only fair, with an r^2 of 0.38 for an ω value of 11±1. The fit of the data is given by:

$$\ln[-\ln(1-\alpha)] = 0.24 \cdot \{\log10[R_{\omega(corr)}] - pH\} - 1.7 \qquad (11)$$

This data is plotted in untransformed form, along with the regression line in Fig. 3, for the combined log10(R_ω)-pH severity parameter. Again it

○MeOH 47.5   □ MeOH 55

○MeOH 50   △ MeOH 62.5   ▼Misc.
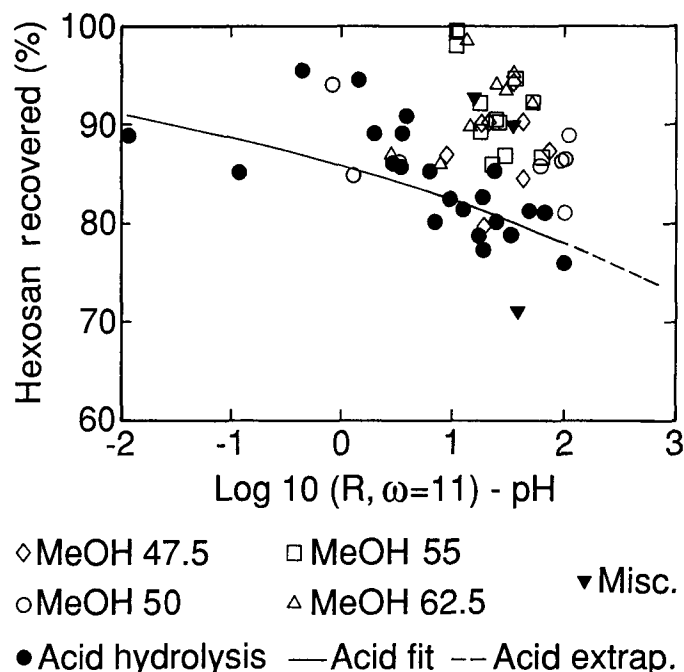
●Acid hydrolysis   —Acid fit   -- Acid extrap.

Fig. 3.   Comparison of % hexosan recovered for dilute acid hydrolysis and organosolv pretreatments as a function of the combined severity parameter. Experimental points and model-generated data are given. Errors of the estimates are ±5% in hexosan recovery and ±0.2 in the calculated combined severity factors.

should be noted that the points near to 100% are of low statistical weight and have little impact on the correlation and the fitted coefficients.

Organosolv Treatment of Aspen

The data set used was composed of 38 data points at different concentrations of methanol. The data points at 50% methanol used sulfuric and phosphoric acid catalysts; SO_2 was the acid catalyst in the remainder of the experiments.

There was no correlation of xylan removal with the simple severity parameter, R_ω, based only on temperature and time. The use of the combined thermal–acidity severity parameter, however, gave an r^2 of 0.7 at $\omega = 11 \pm 1$, and the linear regression in the transformed coordinates was

$$\ln[-\ln(1-\alpha)] = 0.55 \cdot \{\log 10[R_{\omega(corr)}] - pH\} - 0.6 \qquad (12)$$

The data and the regression line are plotted in Fig. 1, along with the line and data for the acid hydrolysis results. Within the experimental errors, between combined severities of 0 and 2, there is no discernible trend with methanol concentration nor with the type of catalyst. This lack of sensitivity to alcohol concentration was also observed in the regression treatment

of the SO_2-catalyzed data. At low combined severities (<1), the removal of xylan in the flow-through organosolv experiments is higher than that observed in the batch dilute acid hydrolysis. At higher combined severities (>1), xylan is protected and recovered in higher amounts in the organosolv pretreatment than in the diluted acid hydrolysis experiments.

Lignin removal is, of course, favored by the solvolytic action of the methanol, as is shown in Fig. 2, in which the comparison between the acid hydrolysis and the organosolv experiments is made. The regression curve for lignin removal at an ω value of 10 ± 1 is shown to be fair, with an r^2 of 0.8 and a fitted transformed equation of the form

$$\ln[-\ln(1-\alpha)] = 0.66 \cdot \{\log 10[R_{\omega(corr)}] - pH\} - 0.7 \tag{13}$$

The point for the static experiment at a severity factor of 1.8 was excluded from the regression, since the lignin removal was lower than those from the continuous experiments because of different mass transfer conditions. With the combined severity factor accounting for 80% of the variance in the data set, and with the standard deviation of 5% estimated from duplicate experiments, no strong correlation with either catalyst type or with solvent concentration is found. The activation energy of the time-varying rate constant, calculated from the ω value at the floor temperature, is 36 ± 5 kcal/mol. Activation energies for the bulk delignification in the 20–25 kcal/mol range are given for deashed black cottonwood and interpreted as either lignin or lignin-carbohydrate bond cleavage reactions, which have about 19 kcal/mol activation energy (26,28).

As with the pentosans at higher combined severities, the organosolv system clearly preserves the hexosan potential of the solid residues. No correlation with severity was found for the hexosan recovery, and the data are presented for comparison with the trend for the acid hydrolysis in Fig. 3. Higher recoveries of hexosan are obtained from organosolv experiments than from dilute acid hydrolysis at combined severities >1.

THEORY

The development of the relation between the use of a temperature-compensated concept and the traditional kinetic parameter is given by the following development. For a generalized kinetic expression,

$$d\alpha / dt = -k(t)f(\alpha) \tag{14}$$

By assuming that the rate constant, k, is a function of time itself, i.e.,

$$d\alpha / dt = -\beta t^{r-1} f(\alpha) \tag{15}$$

and that the reaction is first order in α, we obtain the form

$$d\alpha / \alpha = -\beta t^{r-1} dt \tag{16}$$

Table 2
Example of the Linear Least-Squares Optimization for ω,
and Derivation of m and C from $Y = mX + C$ Based on Percentage
Xylan Recovered from Dilute Acid Hydrolysis of Aspen

ω	r^2	m	C
Uncorrected $\ln(R_\omega)$			
10	0.792	1.15	-1.42
10.5	0.803	1.21	-1.44
10.75	0.804	1.23	-1.45
11	0.802	1.25	-1.44
12	0.770	1.28	-1.38
Corrected $\ln(R_\omega)$			
10	0.783	1.10	-0.93
10.5	0.810	1.18	-0.97
11	0.826	1.25	-1.00
11.5	0.831	1.30	-1.02
12	0.825	1.33	-1.02

On integration with the limits, i.e., at $t = 0$, $\alpha = 0$ and at t, $0.0 \le \alpha \le 1$, we find

$$- \ln(1 - \alpha) = \beta / \gamma \Delta t^\gamma \qquad (17)$$

On rearranging this equation, the time required for any given level of conversion is given by

$$\Delta t_\alpha = [-\ln(1 - \alpha)]^{1/\gamma} (\gamma/\beta)^{1/\gamma} \qquad (18)$$

We have already defined the severity concept as

$$R_\omega = \exp[(T_r - T_b) / \omega]\Delta t \qquad (19)$$

Substituting the kinetic value of Δt_α, we find that

$$R_\omega = \exp[(T_r - T_b) / \omega][-\ln(1 - \alpha)]^{1/\gamma}(\gamma/\beta)^{1/\gamma} \qquad (20)$$

On taking logarithms, we obtain

$$\ln(R_\omega) = (T_r - T_b) / \omega + (1/\gamma)[\ln(\gamma/\beta)] + (1/\gamma)\{\ln[-\ln(1 - \alpha)]\} \qquad (21)$$

On multiplying through by γ and rearranging,

$$\ln[-\ln(1 - \alpha)] = \gamma \ln(R_\omega) - \ln(\gamma/\beta) - \gamma(T_r - T_b) / \omega \qquad (22)$$

Thus, a plot of the equation in the form $Y = mX + C$ should be linear for the appropriate value of ω, with $Y = \ln[-\ln(1 - \alpha)]$ and $X = \ln(R_\omega)$. The derived slope is γ, and the intercept value, C, is the term $\{-\ln(\gamma/\beta) + \gamma[(T_f - T_b)/\omega]\}$. In C, T_f replaces T_r if the corrected form of $\ln(R_\omega)$ is used. If the uncorrected form is used, the value of C will be a function of temperature.

Examples of the linear least-square optimization procedure for the percentage of xylan recovered are shown in Table 2 for two sets of calcul-

Table 3
Slopes (*m*) and γ Values for Acid-Catalyzed Polymer Dissolution

Case	Slope *m*	γ	γ-1
Xylan acid hydrolysis	1.2	0.5	−0.5
Lignin organosolv	0.5	0.2	−0.8
Glucan acid hydrolysis	0.2	0.1	−0.9

ations, using uncorrected and temperature-corrected $\ln(R_\omega)$ values. The optimum ω values are 10.75 and 11.5, respectively, for uncorrected and corrected values; within the ±1 error of the estimate, these values are identical. Very little variation is observed in the slope (*m*) values, within the model errors. The intercepts, however, can vary more with the method of calculation, and exhibit temperature dependence.

CONCLUSIONS

The slopes for acid-catalyzed polymer dissolution according to the methods related here are summarized in Table 3. The *m* and γ values in Table 3 suggest that, indeed, these processes exhibit strongly multiphasic kinetics with a rapid reaction at low severity and a rate that severely slows down with increased severity.

The values of ω along with the floor temperature of the data set can be used to derive the activation energy of the time-varying rate constant proposed in this treatment. The value for acid-catalyzed removal of xylan in the aqueous system was found to be 29±4 kcal/mol; for the organosolv system, the removal of lignin was found to have an activation energy of 36±5 kcal/mol. These values are slightly higher than those derived from the traditional treatment of the process as a multiphasic series of kinetics. Those values, however, are usually derived from the bulk-phase segment of the curve, a point at which the rate constant, according to the above interpretation, would already be modified by time. Thus we find the two interpretations to be reasonably in accord with each other.

Severity parameters and combined parameters that reflect acidity functions can be very useful tools in the planning of experiments. In addition, they may allow compensating adjustments to be made in a simple way to time, temperature, and acidity conditions useful to operating mills. These concepts need to be validated for other species and wider ranges of conditions.

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