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Cellulose and Hemicellulose Hydrolysis Models for Application to Current and Novel Pretreatment Processes

Sigrid E. Jacobsen and Charles E. Wyman*

Chemical and Biochemical Engineering, Thayer School of Engineering, Dartmouth College, Hanover NH 03755-8000, E-mail: charles.wyman@dartmouth.edu

Abstract

Acids catalyze the hydrolysis of cellulose and hemicellulose to produce sugars that organisms can ferment to ethanol and other products. However, advanced low- and no-acid technologies are critical if we are to reduce bioethanol costs to be competitive as a pure fuel. We believe carbohydrate oligomers play a key role in explaining the performance of such hydrolysis processes and that kinetic models would help us understand their role. Various investigations have developed reaction rate expressions based on an Arrhenius temperature dependence that is first order in substrate concentration and close to first order in acid concentration. In this article, we evaluate these existing hydrolysis models with the goal of providing a foundation for a unified model that can predict performance of both current and novel pretreatment process configurations.

Index Entries: Biomass; hydrolysis; kinetics; bioethanol; pretreatment.

Introduction

When used as a transportation fuel, ethanol produced from lignocellulosic biomass, often termed *bioethanol*, has the potential to provide significant, and, in many cases, unique, environmental, economic, and strategic benefits. Included are significant reductions in greenhouse gas emissions, disposal of problematic solid wastes, less air pollution (particularly when used as a pure fuel in advanced propulsion systems), reduced trade deficits, and improved energy security. Most important, biomass is the only known resource for sustainable production of organic fuels and chemicals that integrate into our existing infrastructure so readily *(1,2)*. However, although dramatic progress has been made in reducing the cost

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

of bioethanol production over the last two decades to the point that it is now competitive with ethanol from other sources, continued advances are needed to make it cost competitive with conventional fuels and realize its tremendous benefits on a large scale in a market-driven economy. Fortunately, there are no foreseeable insurmountable obstacles to achieving such cost reductions, and in fact, a number of important opportunities have been identified to lower bioethanol production costs substantially. The primary challenge is to focus on those that have the greatest potential to realize dramatic cost reductions through leap-forward technology advances *(3)*.

Hydrolysis of the hemicellulose fraction of biomass to sugars also prepares the cellulose fraction for subsequent conversion by acids or enzymes and presents particularly promising opportunities for research that could radically reduce biomass processing costs. Recent techno-economic studies of bioethanol production by enzymatic processes clearly show that hemicellulose hydrolysis (i.e., pretreatment) is the single most expensive element for the process, representing about one-third of the overall processing cost *(3,4)*. However, the total costs for converting the cellulose fraction into fermentable sugars are close behind at about 25–30% of the overall processing costs, depending on how process costs are grouped. Thus, because radical improvements in hemicellulose and cellulose hydrolysis technologies could clearly have a significant impact on the cost of manufacturing bioethanol, these opportunities merit particular attention if the goal is to make bioethanol competitive in the open market.

A promising alternative to current processes for hemicellulose hydrolysis is the use of very dilute acid (~0.07%) or even no-acid flow through technologies because such approaches could radically reduce the costs of pretreatment *(3)*. These technologies have several powerful attributes, including high yields, high cellulose digestibility, far less costly materials of construction, good lignin removal, and reduced chemical costs *(5,6)*. Similar results have been found for very dilute acid–catalyzed breakdown of cellulose, and these systems could prove promising for glucose release from cellulose in flow through configurations, at least until cellulase costs are reduced for enzymatic conversion technology or novel organisms are developed that eliminate the currently costly enzyme production step. However, flowthrough approaches suffer from very high energy use during both hydrolysis and subsequent processing owing to the large volumes of water currently used in hydrolysis. As presently configured, the concentrations of sugars from these promising hemicellulose and cellulose systems are very low, the process configurations are complex, and most of the hemicellulose sugars are released in oligomeric form, raising questions about subsequent processing impacts. Thus, we believe it is vital to understand the fundamental mechanisms that explain their performance if we are to develop ways to capitalize on the advantages and overcome the limitations of such systems. Mechanisms such as transport limitations, the effect of structure, the heterogeneous nature of the reaction, and interactions owing to molecular forces have been proposed *(7)*, but a more

systematic consideration of these factors is still needed to clarify their importance.

Because we feel that kinetic models are an invaluable component of this strategy, this article focuses on reviewing existing models to determine their ability to predict hydrolysis performance with the goal of developing unifying mechanisms that explain both more-established and promising alternative hemicellulose and cellulose hydrolysis technologies. Our discussion focuses on kinetic models of hydrolysis work devised for batch or plug-flow reactors using sulfuric acid concentrations above 0.4%. We judge that new perspectives can be gained by examining the similarities and differences between such models for hemicellulose and cellulose hydrolysis. Against this background, we briefly describe mechanisms we are considering to explain the behavior of advanced hydrolysis approaches, and we assess how well the existing models can be used to describe these postulated mechanisms for hemicellulose and cellulose hydrolysis.

Overview of Biomass Composition and Hydrolysis

Lignocellulosic biomass primarily comprises three major fractions—cellulose, hemicellulose, and lignin—plus lesser amounts of minerals (ash) and other compounds often termed *extractives*. Cellulose comprises between 35 and 50% of the total dry mass and consists of long chains of β-anhydroglucose units linked by β1,4-glucoside bonds. About 50–90% of the cellulose in lignocellulosic materials is bound laterally by hydrogen bonds and forms crystalline structure. The remaining portion is less ordered, and is often called amorphous cellulose *(8)*. It is the crystallinity of cellulose that poses the first of the major challenges in effective hydrolysis. Related to crystallinity is the concept of accessible surface area; Burns et al. *(9)* reported that the rate of enzymatic hydrolysis is a function of the surface area available to the cellulase enzyme. Another significant challenge in cellulose hydrolysis is the physical protection of cellulose provided by hemicellulose and lignin *(8)*.

Hemicellulose represents up to about 35% of total lignocellulosic mass, and, like cellulose, its monomer units can also be fermented to ethanol. Sometimes mistakenly termed *xylan*, hemicellulose consists of branched chains of sugars whose units include mostly aldopentoses, such as xylose and arabinose, and some aldohexoses, such as glucose, mannose, and galactose. In addition to high degrees of polymerization, a hemicellulose polymer typically has substituents on the main chain or its branches. The variety of linkages, branching, and different monomer units contribute to the complex structure of hemicellulose and thereby its variety of conformations and function. Within biomass, hemicellulose is connected to lignin and cellulose by covalent bonds, but because few hydrogen bonds are involved, it is much more easily broken down than crystalline cellulose. Unlike homogeneous cellulose, the heterogeneity of hemicellulose and the resulting variety of hydrolysis reaction mechanisms involved challenge understanding of the hydrolysis process *(8)*.

The third significant fraction in biomass is lignin. However, because this portion of biomass remains as a solid after most hydrolysis methods and cannot be fermented to ethanol, it is often burned as boiler fuel. Although lignin can impact fermentation, its removal is typically considered complex and expensive *(10)*.

Basic Models for Dilute Acid Hemicellulose Hydrolysis

In general, hemicellulose hydrolysis models are based on acid-catalyzed breakdown of long chains of hemicellulose to form shorter oligomers that continue to break down to monomeric sugars. These models only apply to work done at pH values below 2.0 because at pH values above 2.0 hydronium ion catalysis competes with hydroxyl catalysis *(11)*. However, a key assumption of many kinetic models is that the rate of oligomer-to-monomer reaction is so much faster than the rate of oligomer production that this reaction step can be omitted; but, few physical data support this hypothesis *(12–14)*. On the other hand, xylose yields include monomers and oligomers in other models without defining the role of oligomers *(15)*. Although a considerable fraction of sugars in hydrolysate are typically oligomers, more detailed study and classification of the types have not been reported. Secondary hydrolysis using 3.25% acid has been considered to further hydrolyze any oligomer products into monomers *(16)*, but when xylose is subjected to acid for extended times, it is converted into furfural, reducing yields and creating compounds that are inhibitory to fermentation.

Almost all models in the literature use one of the three following basic approaches we call models A, B, and C to describe hemicellulose hydrolysis:

Model A

The simplest model describing hemicellulose hydrolysis kinetics is based on a two-step first-order reaction approach Saeman *(17)* proposed in 1945 for cellulose hydrolysis. According to this approach, hemicellulose is hydrolyzed to xylose, which in turn breaks down to degradation products in a second reaction:

$$\text{Hemicellulose} \xrightarrow{k_1} \text{Xylose} \xrightarrow{k_2} \text{Degradation products}$$

The reactions are assumed to follow a first-order dependence on reactant concentration with an Arrhenius temperature relationship for k_i. The latter can be calculated by determining the three parameters, k_{io}, m_i, and E_i, in the following equation:

$$k_i = k_{io} \times A^{mi} \times e \exp\left(-E_i/RT\right)$$

in which k_{io} is the preexponential factor; A is the concentration of acid (wt%); m_i is a power; and E_i is the activation energy. We found three articles that were based on this model with the predicted maximum theoretical xylose

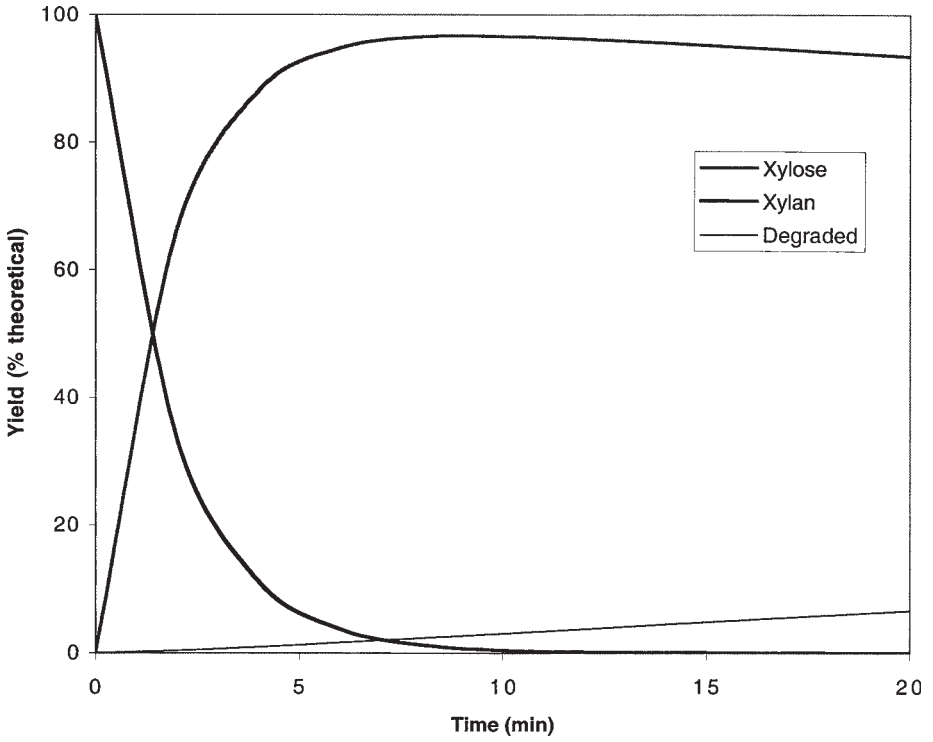
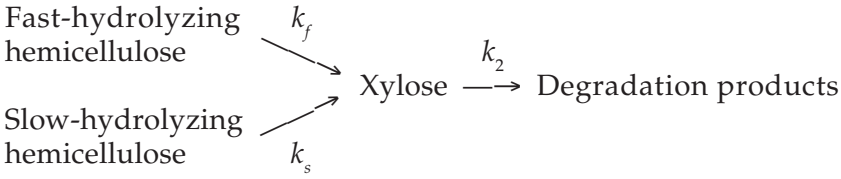


Fig. 1. An example of hydrolysis curves as predicted by model A, using kinetic constants for wheat straw hydrolysis at 160°C and 0.5% acid *(11)*.

yield varying from 83 to 95% *(12,13,18)*. Figure 1 shows a representative example of model A prediction.

Model B

In 1955, Kobayashi and Sakai *(19)* introduced a model that included two types of hemicellulose, one fast hydrolyzing and one slow, each with its own kinetic constant. This modification was based on the observation that the hydrolysis reaction rate decreased significantly after about 70% conversion. Since then, the majority of hemicellulose modeling has been based on this reaction scheme:



The fast and slow fractions differ only slightly per substrate and typically are calculated to be about 65 and 35%, respectively, of most materials.

For this present article, nine sets of constants from seven studies using this model were used to predict yields for a range of acid concentrations

and temperatures *(14,15,19–23)*. Some models predicted an increase in the maximum yield with increasing reaction temperature whereas others showed no change in the maximum value. Figure 2 presents examples of both types of models.

Model C

Whereas model B assumed that oligomers break down to monomers much more quickly than they are formed, so that little accuracy was believed to be lost by omitting this step, a third variation of the basic model is the inclusion of an oligomeric intermediate. The reaction mechanism is represented as follows:

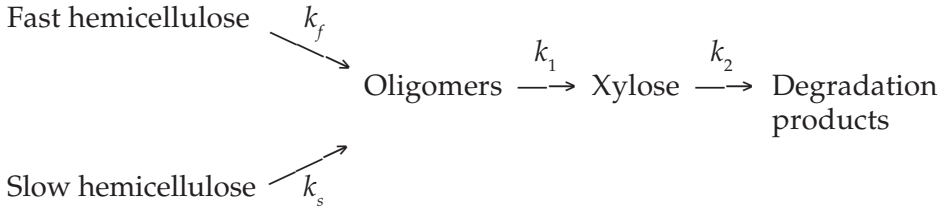


Figure 3 shows the two fractions of fast- and slow-hydrolyzing xylan and how model C predicts oligomer formation and breakdown to monomers. This is the only hemicellulose model that includes any role for oligomers.

Basic Models for Dilute Acid Cellulose Hydrolysis

The initial kinetic study of cellulose hydrolysis was by Saeman *(17)*. From experiments using Douglas fir in a batch reactor and 0.4% acid, dilute acid hydrolysis was described using two pseudohomogeneous consecutive first-order reactions:

$$\text{Cellulose} \xrightarrow{k_1} \text{Glucose} \xrightarrow{k_2} \text{Degradation products}$$

The reaction rate equations describing cellulose and glucose concentrations are as follows:

$$dC/dt = -k_1 \times C \quad dG/dt = k_2 \times G - k_1 \times C$$

for which the reaction rate constants follow an Arrhenius temperature dependence of the following form:

$$k_i = k_{io} \times A^{mi} \times e \exp(-E_i/RT)$$

Glucose yield, the focus of most hydrolysis studies, is evaluated by the following integrated equation:

$$G = C_o [k_1/(k_1 - k_2)] \times (e^{-}k2t - e^{-}k1t) + G_o \times e^{-}k2t$$

in which G is the fraction of the total potential glucose since glucose and C_o and G_o are the initial fractions of potential cellulose and glucose, respectively.

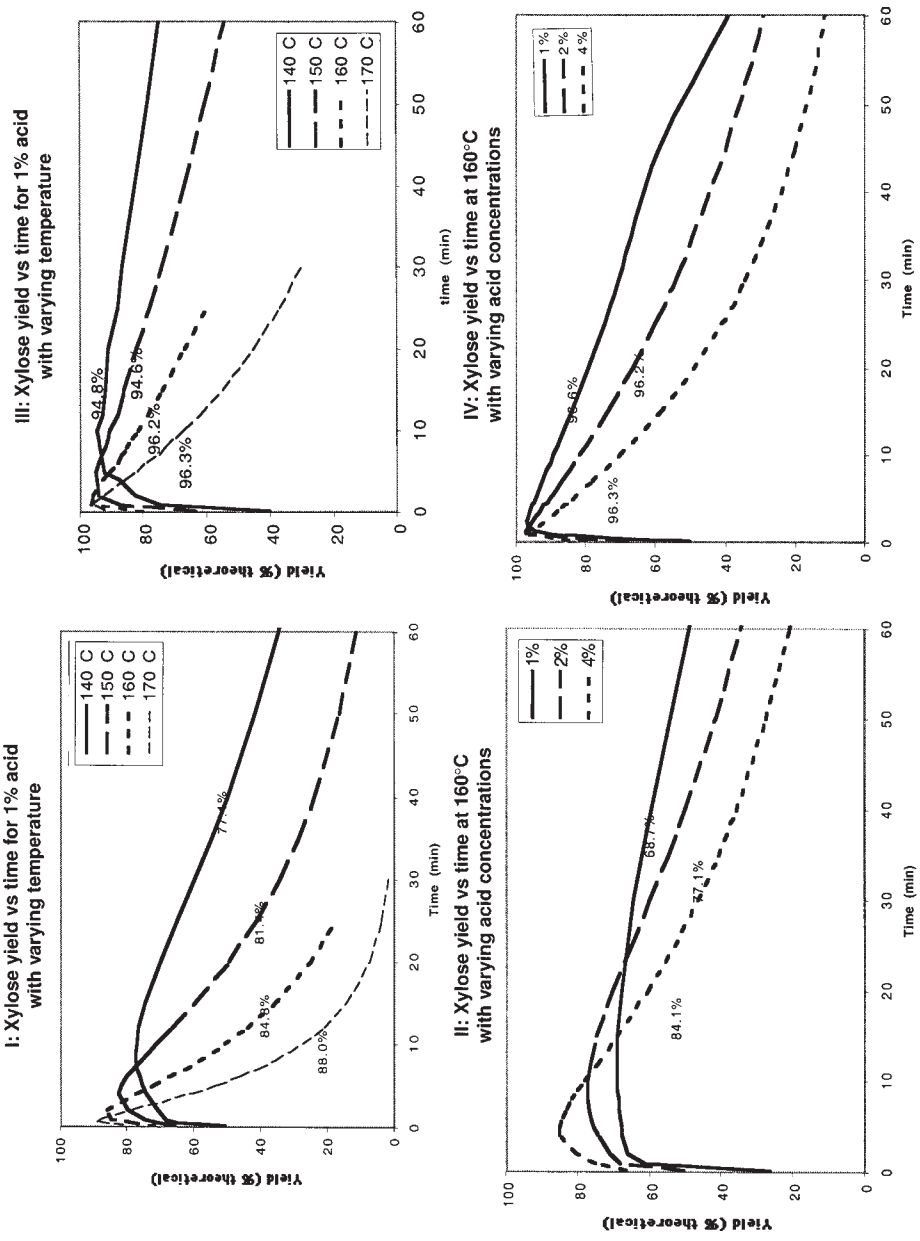


Fig. 2. I and II are representative of model B studies, which predict xylose yield changing with different acid concentration or temperature. III and IV are examples of those studies that predict no change in maximum xylose yield. The maximum yield of each curve is noted along the curve.

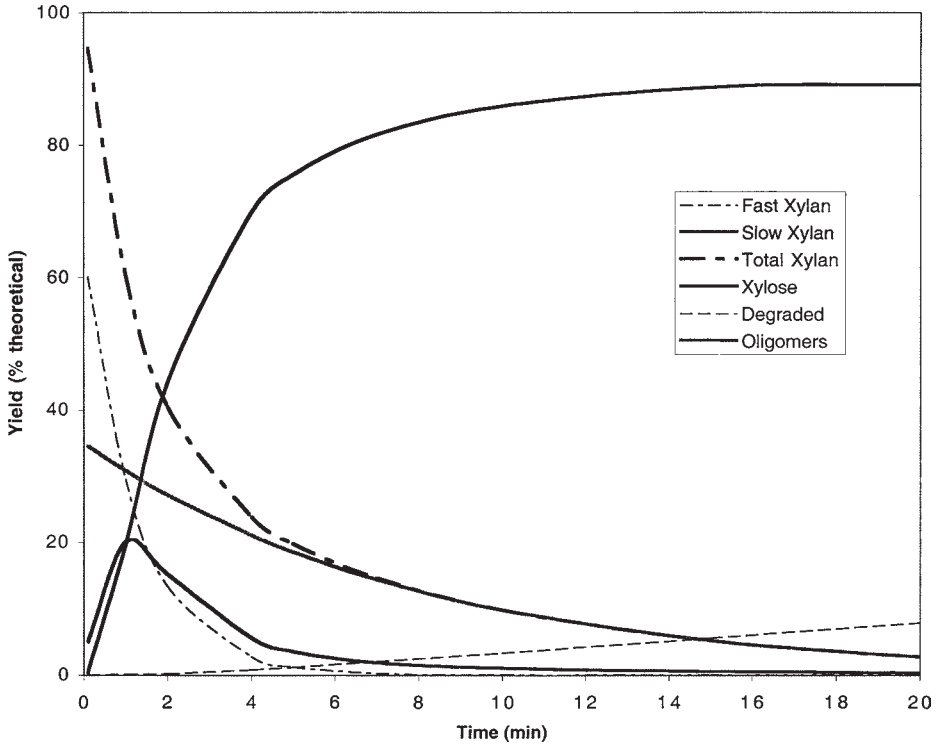


Fig. 3. An example of hydrolysis curves as predicted by model C, using kinetic constants for corn stover hydrolysis at 160°C and 0.5% acid.

The models for dilute acid hydrolysis of cellulose are based on formation of a conjugated acid, leading to cleavage of the glycosidic bond as a water molecule is added and an H^+ ion is released. The amorphous portion of cellulose breaks down almost instantly to its monomer glucose units, which are then immediately subject to degradation reactions leading to products such as hydroxymethyl furfural, levulinic acid, and formic acid. McKibbins et al. *(23)* have provided a thorough examination of the subsequent glucose degradation reactions.

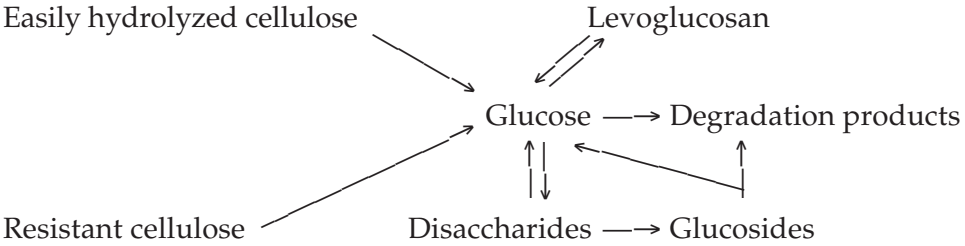
Least-squares fits have generally been used to determine the parameter values for these expressions that match the experimental yield profiles for each substrate, and more than 10 models developed between 1945 and 1990 were collected to compare the results for these traditional studies *(18,24–33)*. Each used Saeman *(17)* kinetics to describe and predict the hydrolysis of various lignocellulosic materials in either a plug-flow or batch reactor. For the present study, each set of reported kinetic parameters was used to predict glucose concentration profiles for the same temperature and acid conditions as the original work. All models predict that the glucose yield will increase with increasing acid concentration and temperature, but no model predicts yields higher than 70% of theoretical for the range of conditions examined.

Refinements in Hydrolysis Kinetic Models

Since the first kinetic model for hydrolysis was introduced, several significant modifications have been made as research revealed where additional factors should be included. It is worthwhile to review these to create a complete picture of the current status.

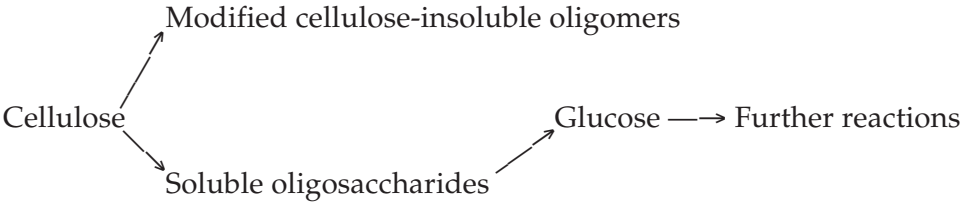
Missing in the original Saeman *(17)* model for cellulose hydrolysis is a factor for the more easily hydrolyzed cellulose. Because the amorphous cellulose hydrolyzes almost instantaneously to glucose, an initial glucose concentration must be assumed. This factor is easily incorporated into the original model, and all subsequent models have done so.

Conner et al. *(34)* further developed this model by studying the reversion reactions of glucose. The extended model describes the glucose decomposition reactions in more detail:



By including these reversion reactions, the fit of experimental data to the predicted model curves was greatly improved.

Another important development was the discovery of parasitic pathways. Using thermogravimetric analysis, differential scanning calorimetry, and diffuse reflectance infrared, Bouchard et al. *(35)* detected highly significant changes in the chemical structure of unhydrolyzed cellulose during plug-flow hydrolysis. A study using a semibath flowthrough system by Mok and Antal *(36)* reported that, indeed, a portion of cellulose, or nonhydrolyzable oligomers, cannot be hydrolyzed to glucose. However, this study concluded that this is owing to an acid-catalyzed parasitic pathway that competes with the acid-catalyzed hydrolysis pathway and that there is no significant chemical change in the cellulose itself. These studies *(35,36)* shed light on the limit of glucose yields at 60–65% by incorporating a reaction scheme that includes a parallel pathway for cellulose degradation:



This model implies that low glucose yields are not necessarily owing only to glucose degradation or reversion reactions and that a parallel path should be incorporated into any kinetic model that aims to predict glucose

yields accurately. A secondary result of this study is the finding that high severity processes induce structural rearrangement that affects the thermal properties of the cellulose. Thus, modifications of cellulose during high-severity reactions are more structurally than chemically related.

Several modifications have been applied to both hemicellulose and cellulose models. Several studies found that it is important to include the neutralizing capacity of the substrate in the kinetics *(15,20,35)*. As one example, Cahela et al. *(15)* reported that minerals in the substrate would neutralize up to 70% of the acid, making this an important factor to include in kinetic models. Harris et al. *(37)* provided detailed calculations of acidity and neutralizing capacity to find $[H^+]$, the molal hydrogen ion concentration, which is used in the rate equation in place of the wt% acid concentration. All other terms are defined as previously.

$$k_i = k_{io} \times [H^+]^{mi} \times \exp(-E_i/RT)$$

In the same manner, Conner et al. *(35)* recorrelated constants using $[H^+]$ in which the effective acid concentration was determined from the neutralizing capacity of the substrate and the amount and concentration of the applied acid. It was assumed that all the cations in the substrate were immediately available and effective to give

$$[H^+] = \text{molality of added acid} - \text{molality of the cations}$$

A different approach was employed by Malester et al. *(24)* with municipal solid waste as a substrate. Their conclusion was that using wt% acid concentrations as a measure of acidity does not account for the nonlinearity of the $[H_3O^+]$ nor neutralizing capacity. This study proposed the use of pH as a measure of acidity with the rate constants calculated as follows:

$$k_i = k_{io} \times \exp(-E_i/RT - 2.303_{mi}(\text{pH}))$$

The observation that the use of pH or $[H^+]$ in the place of wt% acid concentration results in more accurate kinetic constants could explain the range of yield curves observed when comparing models using only the applied acid concentration.

Cellulose and hemicellulose experiments have both reported evidence of oligomer intermediates. This was evidenced by Kim and Lee *(16)*, who reported improvements in yields following secondary hydrolysis. Oligomers were also particularly significant in a hydrothermal pretreatment study by Kubikova et al. *(38)*, who observed that the maximum concentration of solubilized material can be more than tripled by recirculation of the eluate. Also, Torget et al. *(5)* showed that in a reverse-flow, two-temperature configuration, the fraction of monomeric xylose relative to oligomeric xylose can be as low as 31%.

Abatzoglou et al. *(31)* observed an oligomer presence during cellulose hydrolysis when using alpha cellulose in a cascade reactor with 0.2–1.0 wt% H_2SO_4. Significant amounts of oligoderivatives in the hydrolysate were

detected in the early stages of hydrolysis. To include this result, this study extended the Saeman *(17)* model as follows:

$$\text{Cellulose} \xrightarrow{\alpha k_1} \text{Oligoderivatives} \underset{\gamma k_1}{\overset{\beta k_1}{\rightleftharpoons}} \text{Glucose} \xrightarrow{k_2} \text{Degradation products}$$

Then three new models were derived for the following conditions:

1. For oligoderivatives-to-glucose reaction in equilibrium, $\beta k_1 = \gamma k_1$.
2. For oligoderivatives-to-glucose reaction not in equilibrium, $\beta k_1 \neq \gamma k_1$.
3. For repolymerization reactions, $\gamma = 0$.

The third model was the most accurate in predicting experimental results, and it was reported that for cellulose conversion up to 30%, oligoderivatives are the major product. Because the conversion of oligomers to glucose is two to three times faster than hydrolysis of cellulose to soluble oligomers *(15)*, oligomer formation had not been recognized previously. Abatzoglou et al. *(31)* suggest using a two-step process for optimal glucose yield in which the cellulose-to-oligomer reaction would be catalyzed in a first stage followed by the oligomer-to-glucose reaction under milder conditions. This would decrease the production of degradation products.

A valuable contribution to hemicellulose modeling is the concept of using a reaction ordinate of a severity parameter. This parameter, introduced by Overend and Chornet *(39)*, combines treatment temperature and time to describe the depolymerization of lignocellulose for steam-aqueous pretreatment and is based on the observation that one can trade the treatment temperature for time and vice versa. As expected, because cellulose needs higher temperatures for hydrolysis, it was found that the majority of the cellulose remains in pulp residue until very high severities. Abatzoglou et al. *(40)* extended the severity parameter to include the effect of acid catalysts and formally linked solid hydrolysis to basic kinetics. Though it is unclear in what pH range this tool is valid, it was found that for dilute acid hydrolysis, the reaction ordinate or severity parameter, relates time (t) and temperature (T) as follows:

$$R_o = [H^+] \times \exp[(T - 100)/14.75] \times t$$

Because this relation shows that the yield and composition for the cellulose or hemicellulose fraction is a function of a single variable combining time, temperature, and acid level, it is a valuable tool for both process control and prediction of yield.

Discussion

We believe that oligomers play an important role in distinguishing the performance of various process configurations for breakdown of hemicellulose and perhaps cellulose into sugars. In particular, based on results

from several studies (e.g., *see* refs. *41–44*), we have postulated that limitations in the solubility of hemicellulose or cellulose and their oligomers in hydrolysate liquid coupled with hydrolysis kinetics could explain why batch and cocurrent systems differ in performance from percolation and other flowthrough operations that show promise for reducing hydrolysis costs. Longer chains are assumed to be less soluble than shorter oligomers formed as intermediates during hydrolysis, but the solubility of both should increase with temperature. Thus, according to the proposed mechanism, if the liquid is drawn off during the reaction as in flowthrough systems, oligomers are removed, allowing more to be dissolved in the freshwater that enters and recovering sugar monomers and oligomers before they can degrade at the reaction conditions. Otherwise, on cooling to quench the reaction, most of the oligomers still in the presence of biomass would reprecipitate back onto its surface as a result of lower solubility at lower temperatures. Reactive lignin and sugar degradation products are also suspected of promoting reattachment of hemicellulose or cellulose, their oligomers, and lignin in solution to the solid biomass and possibly complexing with monomeric sugars. All such reattached components will appear to have not reacted in subsequent analytical measurements that characterize sugar yields. Thus, the time of reaction for batch and cocurrent systems must be sufficient to maximize soluble sugar concentrations in solution on quenching the reaction, but this reduces yields to balance sugar degradation against hydrolysis of the more recalcitrant fraction.

Our research has focused on understanding the pathways to oligomer and monomer formation to determine the suitability of this mechanism and other possibilities in explaining biomass hydrolysis for different reactor configurations. The development of a unified model that can explain performance in all configurations should facilitate the development of novel approaches that can best capitalize on the chemistry involved to realize the advantages observed for flowthrough systems while overcoming their current limitations. The existing models we have discussed are assessed here with the goal of providing a strong basis for understanding such systems.

In hemicellulose hydrolysis, one is struck by the very different dependence of xylose yield on reaction conditions as seen in Fig. 2 with about half of the studies examined based on model B following each pattern. Such variation could reflect real changes with substrate, differences with experimental configurations, experimental problems in gathering data, or limitations with the kinetic models. To gain a better understanding of these differences, we examined the predicted change in xylose concentration alone based on xylose degradation kinetics reported in the literature and found a significant variation in the yields, as shown in Fig. 4. This result suggests either that there are some problems in the experimental measurements or that each substrate introduces different components that influence xylose losses. It is important to remember that all the kinetic models assume that acid hydrolysis is random and all bonds are equally reactive

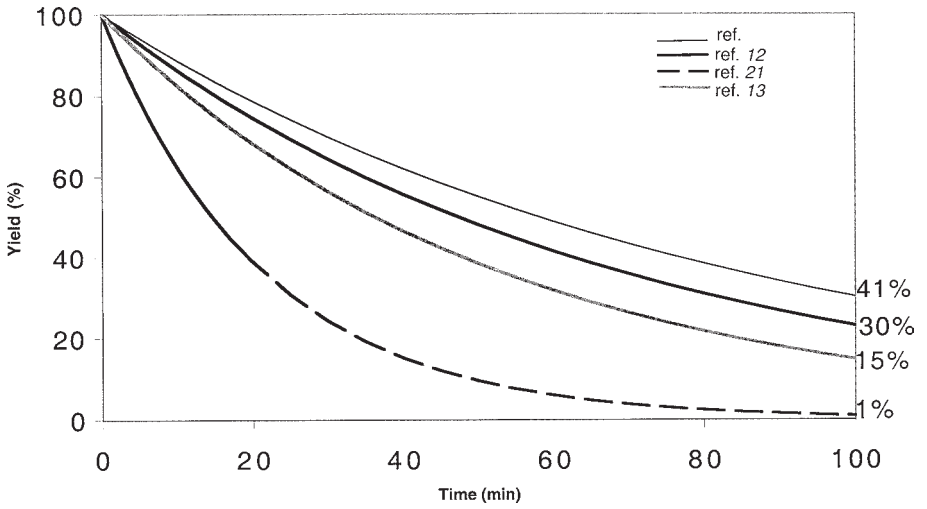


Fig. 4. Pure xylose degradation curves as predicted by several studies at 160°C and 1% acid.

(i.e., a homogeneous system). Even the various monomers are treated as xylose, whereas in reality, hemicellulose consists of a variety of monomers. This raises the question, Can models based on assumptions of homogeneity accurately describe a system as heterogeneous as hemicellulose?

An issue that deserves attention is reversion reactions. Reversion reactions in cellulose hydrolysis have been studied, but the concept has not been applied to hemicellulose hydrolysis. In their hydrothermal pretreatment study, Kubikova et al. *(38)* observed that water-insoluble products in the hydrolysis of straw were adsorbed. This issue should be examined in the context of acid-catalyzed hydrolysis as well as different reactor configurations.

Several reasons have been proposed to explain the change in reaction rate during hemicellulose hydrolysis. Instead of being owing to two types of hemicellulose (fast and slow hydrolyzing) the change could be caused by the following:

1. Transport limitations, i.e., diffusion *(7)*
2. Nonhomogeneous reactions at the xylan-water interface *(7)*
3. Accessibility, i.e., some xylan being more tightly bound to lignin

None of these three options has been incorporated into existing kinetic modeling. The study of these possible mechanisms could lead to valuable insight.

Reaction mechanisms and kinetics have been more extensively studied for cellulose than hemicellulose hydrolysis. This is partly because of the more homogeneous nature of cellulose but also because all aspects of cellulose structure and behavior are better understood. However, cellulose

and hemicellulose models do share some common areas where further research is needed.

Interestingly, hydrolysis models do not include the effects of lignin and cellulose or hemicellulose interactions, but actual experience shows that these effects can be significant. The assumption that cellulose or hemicellulose reacts independently of other biomass components should be validated.

The influence of reactor configuration on results may be significant and deserves attention. For example, different configurations could affect the solubilization environment and the significant amount of the variation in kinetics models could be linked to experimental setup.

Conclusion

Dilute-acid cellulose and hemicellulose hydrolysis kinetics models are both based on a first-order term for reactants with an Arrhenius temperature dependence and an acid concentration raised to a power. Although such an approach is simple to apply, it raises questions about the use of a homogeneous reactant concentration to describe a nonhomogeneous system. The use of acid concentrations in wt% and not in terms of more typical concentration units such as weight fraction is puzzling. This suggests that more work is needed to understand the basic nature of biomass hydrolysis.

It is commonly accepted that hemicellulose is best described by consideration of two fractions breaking down to sugars. However, some investigators show that a continuum approach is more appropriate. Only limited modeling has included the formation of oligomers that we believe is vital to describe the performance of a wide range of reactor configurations on a consistent basis. Also, the heterogeneity of hemicellulose and the reaction of sugars with lignin and other biomass components has not been fully considered.

Cellulose hydrolysis has been more extensively modeled than that of hemicellulose. These models incorporate a number of side reactions that lead to degradation of cellulose to nonreactive material and loss of glucose to various degradation products. However, limited modeling has been done to predict the formation of cellulose oligomers that could be important for flowthrough systems. Once again, little has been done to incorporate reactions of glucose with other biomass components.

Existing models provide a useful tool for describing the performance of batch and cocurrent process configurations. However, they do not appear to describe adequately the role of oligomers, and these components are felt to be central to explaining the performance of all systems on a unified basis. Existing models also may not adequately factor in side reactions that impact yields. With improvement of the overall understanding of the pathways of oligomer and monomer formation and hydrolysis kinetics, a unified model to describe biomass hydrolysis in all configurations can be developed.

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