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A Comprehensive Kinetic Model for Dilute-Acid Hydrolysis of Cellulose

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Abstract

Acid-catalyzed hydrolysis is controlled not only by temperature and acid concentration but also by the physical state of the cellulose. Under low temperature and acid condition the cellulose structure stays in stable crystalline form. Therefore, the prevailing reaction mode is endwise hydrolysis. Glucose then becomes the main sugar product. However, when temperature and/or acid concentration is raised to a certain level, the cellulose structure becomes unstable by breakage of hydrogen bonding, the primary force that holds the cellulose chains. Once the crystalline structure of the cellulose is disrupted, acid molecules can penetrate into the inner layers of the cellulose chains. In support of this hypothesis, we have experimentally verified that a substantial amount of oligomers is formed as reaction intermediates under extremely low-acid and high-temperature conditions. We also found that the breakage of hydrogen bonds occurs rather abruptly in response to temperature. One such condition is 210°C, 0.07% H_2SO_4. Glucose, once it is formed in the hydrolysate, interacts with acid-soluble lignin, forming a lignin-carbohydrate complex. This occurs concurrently with other reactions involving glucose such as decomposition and reversion. On the basis of these findings, a comprehensive kinetic model is proposed. This model is in full compliance with our recent experimental data obtained under a broad range of reaction conditions.

Index Entries: Acid hydrolysis; cellulose; kinetics; model; hydrogen bond; oligomer; lignin.

Introduction

The origin of the organized kinetic study of cellulose hydrolysis dates back to that of the work of Saeman *(1)*. This kinetic model describes dilute-

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acid hydrolysis as two pseudo-homogeneous consecutive first-order reactions:

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

Hydrolysis of glycosidic bonds of soluble reactants in homogeneous phase has indeed been verified to follow first-order reaction *(2,3)*. The reaction rate constants are expressed in the form of an Arrhenius equation with an additional term indicating the effect of acid:

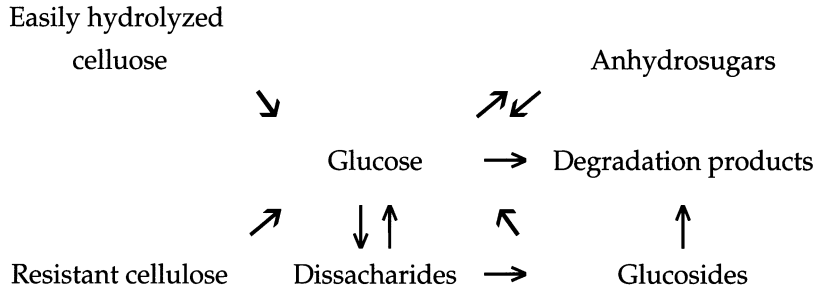
$$k_1 = k_{i0} \times A^{m_i} \times e^{(E_i/RT)}$$

in which k_{i0} is the preexponential factor, A is the acid concentration, m_i is the acid exponential, and E_i is the activation energy.

This simple kinetic model was established on the basis of data obtained under a limited range of reaction conditions: the conventional dilute-acid hydrolysis conditions of 180–200°C, 0.2–2% acid. The question is, can this model be extrapolated beyond the aforementioned region, and if so, how far? This question arises because the reaction is heterogeneous and factors other than chemical reaction may influence the overall process. Limitation of this model is also seen in the case of partial hydrolysis with highly dilute acids, yielding so-called hydrocellulose, a product with reduced degree of polymerization (DP) but higher crystallinity *(4)*.

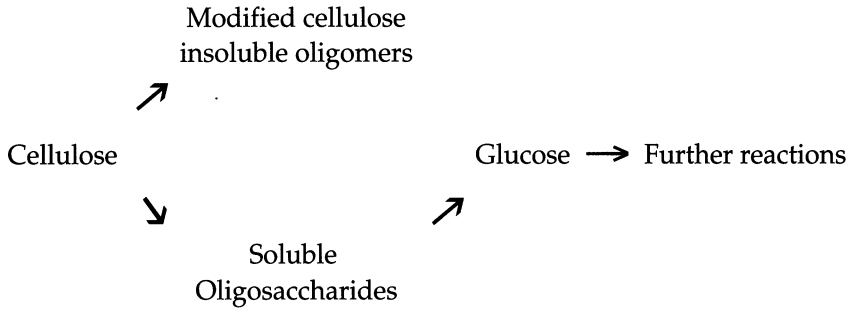
The rate of heterogeneous hydrolysis of celluloses is one to two orders of magnitude lower than those of homogeneous hydrolysis of model compounds. Heterogeneous hydrolysis has been found to be influenced by such physical factors as the degree of crystallinity, the state of swelling, and mechanical disintegration *(5,6)*.

Significant advances have been made to the original model of Saeman *(1)*. The presence of amorphous cellulose and reversion reactions of glucose were implemented in a model suggested by Conner et al. *(7)*:



Another important development in the kinetics was the finding of parasitic pathways. Using thermogravimetric analysis, differential scanning calorimetry, and diffuse reflectance infrared, Bouchard et al. *(8)* detected some significant changes in the chemical structure of unhydrolyzed cellulose. Mok et al. *(9)* confirms this finding. For these studies, the hydrolysis conditions were within the 200–240°C temperature ranges

and at low sulfuric acid concentrations (0.2–1.0% [w/w]). Both studies reported that a portion of the cellulose turns into nonhydrolyzable oligomers and, thus, cannot be hydrolyzed to glucose on further treatment. This was cited as the major reason that glucose yields above 60–65% are not attainable. The reaction pattern of the parasitic pathway is as follows:



Cellulose and hemicellulose experiments have both reported evidence of oligomer intermediates. Kim and Lee *(10)* reported improvements in yields following secondary hydrolysis. Abatzoglou et al. *(11)* observed the presence of oligomers during hydrolysis of α-cellulose in a cascade reactor under conditions within 200–240°C and at low sulfuric acid concentrations (0.2–1.0% [w/w]). Significant amounts of oligoderivatives were observed in the hydrolysate of the early stages of hydrolysis, and conversion of oligomers to glucose was two to three times faster than hydrolysis of cellulose to soluble oligomers.

Our laboratory, in cooperative research with the National Renewable Energy Laboratory (NREL), explored the use of a bed-shrinking flow-through (BSFT) reactor *(12)* under extremely low-acid and high-temperature conditions. We have obtained experimental data in which glucose yields surpassed 80%. This certainly contradicts the current kinetic models. We conducted an experimental investigation seeking a plausible explanation for this contradiction. From the results, we propose a comprehensive kinetic model for cellulose acid hydrolysis. This model recognizes the heterogeneous nature of the reaction and offers a potential application for a broader range of reaction conditions.

Materials and Methods

Sawdust, Feedstock, and Chemicals

Yellow poplar sawdust was provided by NREL. It was milled and stored frozen at NREL before being sent to our laboratory. It was further milled to pass through a 2-mm screen. The chemical composition of the yellow poplar was 42.8 wt% glucan, 14.8 wt% xylan, 2.5 wt% mannan, 0.9 wt% galactan, 0.5% arabinan, 24.3 wt% klason lignin, 2.8 wt% acid-soluble lignin (ASL), and 0.7 wt% ash, on an oven-dried basis. Sugarcane bagasse feedstock was provided by BCI (Jennings, LA). The chemical

composition of bagasse, which was milled to pass through a 0.8-mm screen, was determined to be 37.4% glucan, 17.9% xylan, and 21.7% klason lignin.

Chemicals were of chemical grade, purchased from Sigma-Aldrich. The chemical composition of α-cellulose (P. no. C-8002) (20 micro) was analyzed to be 92.2% glucan, 3.4% xylan, and 3.2% mannan on a dry basis.

Experimental Apparatus and Procedures

Hydrolysis of pretreated yellow poplar was performed in both batch and BSFT reactors. For dilute-acid-catalyzed hydrolysis at high-temperature conditions, experiments were performed using sealed, tubular batch reactors. The reactors (19.0 cm^3 of internal volume) were constructed of Hastelloy C-276 tubing (1/2-in. id × 6-in. lenght) capped with Swagelok end fittings. Approximately 0.6 g of a-cellulose and 12 g of 0.07% H_2SO_4 solution were loaded into the reactor. The solid/liquid ratio was maintained at the same level of 1/20 in all batch operations. The reactors were first submerged into the preheating bath set at 30°C above the desired reaction temperature for rapid preheating. The reactors were then quickly transferred into another sand bath set at the desired reaction temperature after 1.5 min. The reactor temperature was monitored by a thermocouple inserted into the reactor. After the desired reaction time, each reactor was taken out of the sand bath and quenched in a cold-water bath. The experimental parameters were the time variation of the solid composition and the monomeric sugar concentrations in liquid. For batch hydrolysis under high concentration of acid (4% H_2SO_4) at 120°C, experiments were conducted in an autoclave using Pyrex glass bottles with 150-mL volume capacity. Hydrolysis experiments were also conducted in a semi-batch flow-through reactor and BSFT reactor. Details of the flow-through kinetic experiments are described elsewhere *(12)*.

α-Cellulose was treated by concentrated H_2SO_4 for the study of the effect of cellulose structure on hydrolysis. Three grams of cellulose was added to 50-mL solutions with varying H_2SO_4 concentrations. The treatment was conducted at 25°C for 4 h. After the pretreatment, distillated water was added to dilute the acid. The reprecipitated cellulose was filtered and washed to neutral. It was then stored in a wet condition with 50–70% moisture content for further experiments.

Analytical Methods

Solid samples from experiments were analyzed for glucan content according to the NREL analysis procedures *(13)*. Oligomeric sugars in the hydrolysate liquor were converted into monomers using 4% (w/w) H_2SO_4 hydrolysis at 120°C for 60 min. Sugars and other compounds were determined by an high-performance liquid chromatography (HPLC) using a Bio-Rad Aminex HPX-87P column. Oligomer samples were also analyzed by HPLC using a Bio-Rad Aminex HPX-42A column.

Table 1
Observed Glucose Yields from Various Reactor Operations

Feedstock	Condition	Reactor	Maximum yield (%) 250°C	220°C	235°C
Yellow poplar	0.07% H_2SO_4	BSFT	87.5	90.3	90.8
		Nonshrinking flow-through	—	64.4	—
α-cellulose	0.07% H_2SO_4	Batch	—	40.2	—
		BSFT	—	80.6	—
Sugarcane bagasse	0.07% H_2SO_4 and BSFT reactor	Untreated	—	52.6	—
		50% Delignified	—	61.3	—
		85% Delignified	—	76.5	—

Results and Discussion

Observed Glucose Yields from BSFT Reactors

The unique characteristic of the BSFT reactor is that a spring is placed inside the reactor to press the biomass during the hydrolysis reaction. The BSFT reactor, which was originally developed at NREL, keeps a dense bed condition and minimizes the residence time of the liquid. During the acid hydrolysis process, degradation of glucose occurs concurrently. Short residence time in the BSFT reactor reduces such degradation, resulting in high glucose yields. For the present work, we modified the BSFT reactor by adding a quick quenching heat exchanger at its outlet. With this modification, we were able to eliminate posthydrolysis degradation, raising the accuracy in the kinetic experiments. The superior performance of the BSFT reactor is reaffirmed when it is operated at extremely low-acid and high-temperature conditions. Table 1 summarizes the glucose yields obtained in our work. With yellow poplar feedstocks, the highest yield obtained using the BSFT reactor was 90%, occurring at 205–235°C and 0.07% H_2SO_4. This result agrees closely with the work at NREL *(14)*. However, with use of a normal nonshrinking flow-through reactor, the glucose yield was only 64.4%, which is in line with the prediction from the conventional hydrolysis kinetic theory. For α-cellulose, the maximum yield in a batch reactor was about 40.2% under 0.07% H_2SO_4 and 205°C. The yield was greatly improved to 80.6% when the BSFT reactor was used. A number of BSFT experiments were also conducted with sugarcane baggase. Among the notable points of these experiments is that hydrolysis of sugarcane bagasse was strongly affected by the amount of lignin present in the feedstock. For hydrolysis of untreated bagasse, an average yield of 52.6% was obtained under 0.07% H_2SO_4 and 220°C using the BSFT reactor. For bagasse pretreated with 1% H2O2 solution at 170°C, about 50% of the

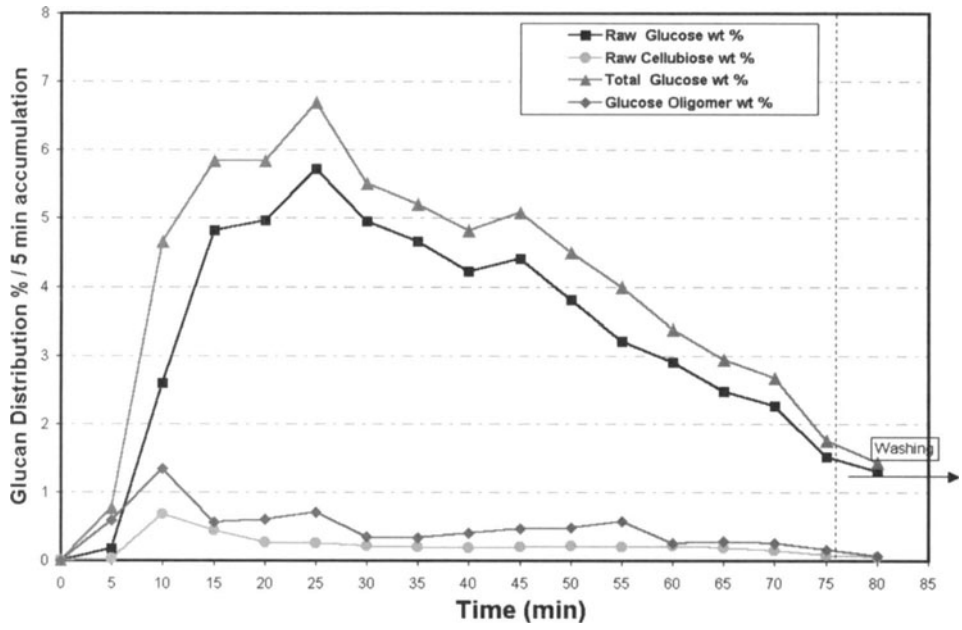


Fig. 1. α-Cellulose hydrolysis in BSFT reactor at 205°C and 0.07% H_2SO_4.

lignin was removed. Using this substrate, the glucose yield was improved to 61.3%. The substrate was also pretreated with 10% aqueous ammonia to remove 85% lignin. When this substrate was applied, the yield was further improved to 76.5%. The level of glucose yield observed in our work and its dependency on pretreatment and reactor type cannot be explained by existing hydrolysis kinetic theory.

Presence of Oligomers in Hydrolysate

Figure 1 shows the hydrolysis profile for a-cellulose in a BSFT reactor at 205°C and 0.07% H_2SO_4. The observed yield of total soluble sugars (glucose, cellobiose, and oligomers) is 80.6%. The yield is substantially higher than those observed in our previous experiments using batch reactors and percolation reactors. One notable feature of this run is the presence of oligomers that were not observed in our previous experiments. We believe this is owing to the unique characteristics of the BSFT reactor and the quick quenching of the hydrolysates, which prevented further reactions of intermediates. A sample HPLC chromatogram is shown in Fig. 2. Glucose and cellobiose contents were obtained from HPLC chromatograms of raw hydrolysate samples. The same liquid samples were put through a secondary hydrolysis that was carried out with 4% H_2SO_4 at 121°C for 1 h. The glucose yield was calculated from the total glucose value after secondary hydrolysis. The yields of this magni-

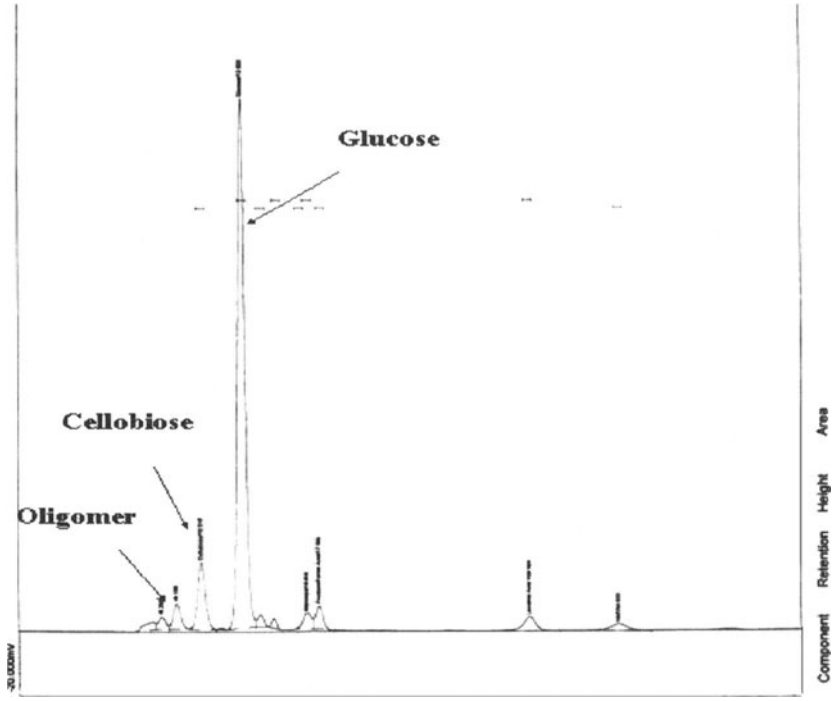


Fig. 2. Evidence of oligomer presence in HPLC chromatogram.

tude and the presence of oligomers in the hydrolysate cannot be explained by published cellulose hydrolysis kinetic models. To validate these experimental results, selected samples from these experiments were sent to NREL for further analysis on sugar contents and oligomers. A sample chromatogram with high resolution of oligomers is shown in Fig. 3. The chromatogram shows that glucose and short-chain oligomers are the major products under the hydrolysis conditions applied for a-cellulose. The amount of oligomers existing in the hydrolysates decreased with the increase in degree of polymerization.

Acid hydrolysis of crystalline cellulose in biomass is a heterogeneous reaction. According to the kinetic model of Saeman *(1)*, glucose monomer is the only sugar product in the hydrolysate. The results obtained from BSFT reactor experiments (Figs. 1–3) obviously disprove it since we found a significant amount of oligomers as well as glucose monomer. The oligomers are produced either through a parallel pathway or as intermediate products before glucose. The facts that glucose is the predominant component among the three different species of sugar products (glucose, cellobiose, and higher oligomers) and that the amount of oligomer decrease with increasing DP indicate that the serial (intermediate) pathway is unlikely. With this understanding, we modified the hydrolysis kinetic model by inserting a parallel pathway for release of oligomers.

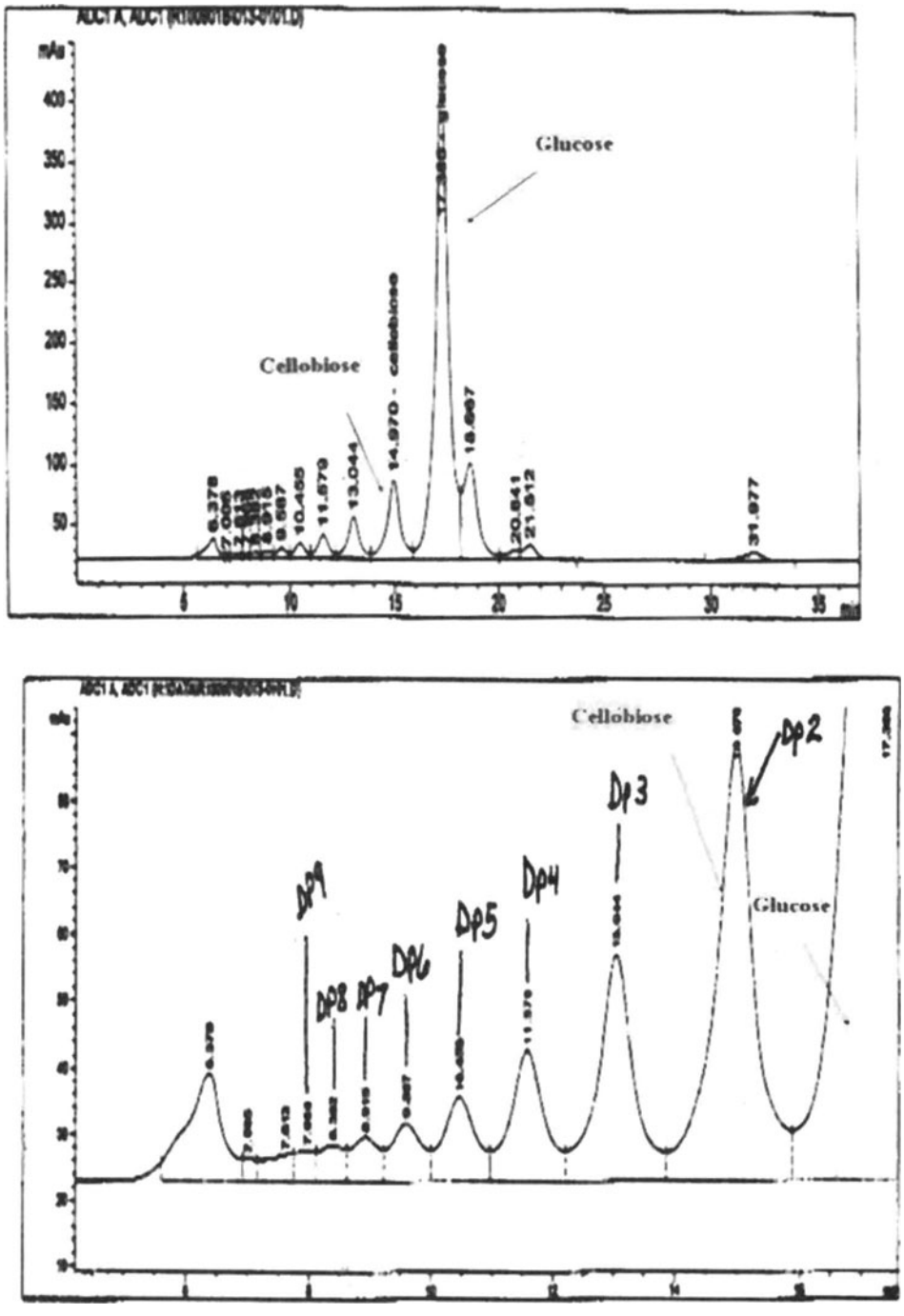


Fig. 3. HPLC chromatogram with high resolution of oligomers (courtesy of Dr. Raymond Ruiz, NREL).

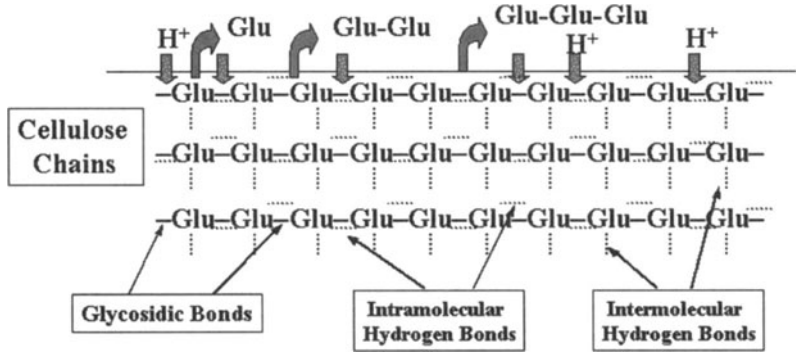


Fig. 4. Illustration of crystalline cellulose structure and acid hydrolysis mechanism.

Association of Glucose/Oligomer with Cellulose into Kinetic Model

We are also investigating on the heterogeneous nature of cellulose hydrolysis and the role of hydrogen bonding on the kinetics of cellulose hydrolysis in a parallel research in our laboratory *(15)*. From this study we find that the supramolecular structures of cellulose must be taken into consideration in the mechanism of cellulose hydrolysis. Since cellulose supramolecular structures are built on various types of hydrogen bonding between OH groups, we now propose a hypothesis that the acid hydrolysis of cellulose is influenced by hydrogen bonding within the macrostructure of crystalline cellulose. Figure 4 illustrates the hydrogen bonds within crystalline cellulose and the association between glucose/oligomers and the cellulose. Hydrogen bonding is believed to be the major factor that controls the structure and the physical property of cellulose *(16–18)*. There are several levels of hydrogen bonding in the cellulose structure: intramolecular hydrogen bonding, intermolecular hydrogen bonding, and hydrogen bonding between the surface of cellulose and water/medium molecules *(16)*. Formation of intramolecular hydrogen bonds has been proven to contribute directly to certain physical properties of cellulose such as crystallinity and solubility in various solvents having different polarities. It also affects the relative reactivity of the cellulose *(18)*. In the overall molecular structure, glucose ($C_6H_{12}O_6$) is quite similar to xylose ($C_5H_{10}O_5$). However, hydrolysis of cellulose is about one to two orders of magnitude lower than xylan. By comparing the ring structures of both glucose and xylose pyranose form, the additional CH_2OH group connected to the cyclic structure of glucopyranose (the stable structure form for glucose) provides much higher probability for the formation of intra–hydrogen bonding and inter–hydrogen bonding than the cyclic structure of xylopyranose (the stable structure form for xylose). The strength of the hydrogen bonds in cellulose makes it stable to the attack by acidic catalytic elements in aqueous solution. The hydrogen bonds impede the access of the catalyst to the active site

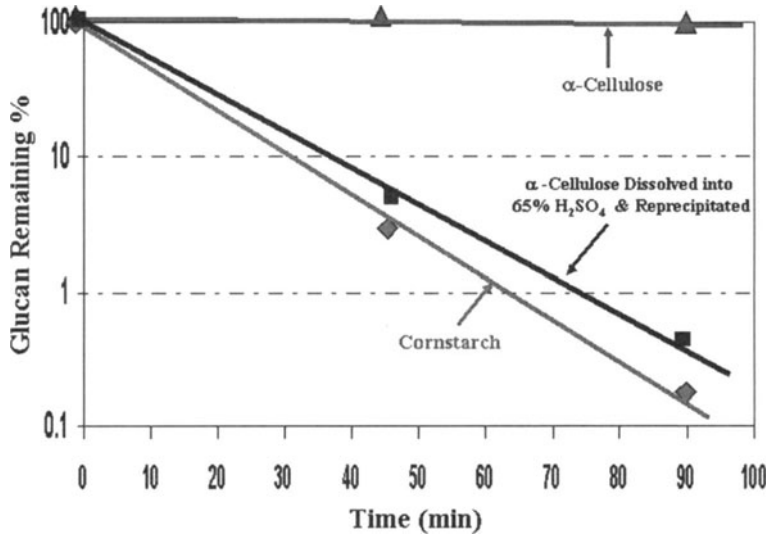


Fig. 5. Comparison of hydrolysis rates of starch, and treated and untreated cellulose (120°C, 4% H_2SO_4).

and the release of glucose. During the catalytic acid-hydrolysis process shown in Fig. 4, the hydronium ions in the liquid randomly attack the glucosidic bonds and consequently lower the stability of hydrogen bonds. When both glucosidic bonds and hydrogen bonds are cleaved, glucose and oligomers are readily released to bulk liquid.

The observed kinetics of acid hydrolysis follows a first-order reaction and the temperature effect conforms to an Arrhenius equation. However, we find that the Arrhenius equation is applicable only within a limited range of temperature and acid concentration. The kinetics of cellulose hydrolysis strongly depends on the physical state of cellulose. Particularly notable is the drastic difference in hydrolysis rate between crystalline cellulose and the dissolved and reprecipitated cellulose (Fig. 5). Cellulose is totally dissolved in 65% H_2SO_4 at room temperature. The cellulose is reprecipitated when it is diluted with water. The reprecipitated cellulose is hydrolyzed at a rate two orders of magnitude higher than that of crystalline cellulose and at about the same rate as cornstarch (Fig. 5). Sasaki et. al. *(19,20)* reported a similar case. They discovered that cellulose is rapidly dissolved and depolymerized in supercritical water at 300–320°C without any acid. The cellulose hydrolysis rate under these conditions is again far above the prediction by extrapolation of the Arrhenius equation based on the data over 260–280°C. The investigators reported a one- order-of-magnitude jump of hydrolysis rate when the temperature was raised from a subcritical temperature to near or above critical temperature (~300°C). We observed similar phenomenon in the hydrolysis of pretreated yellow poplar carried out at high-temperature and extremely low-acid conditions. In Fig. 6, an abrupt

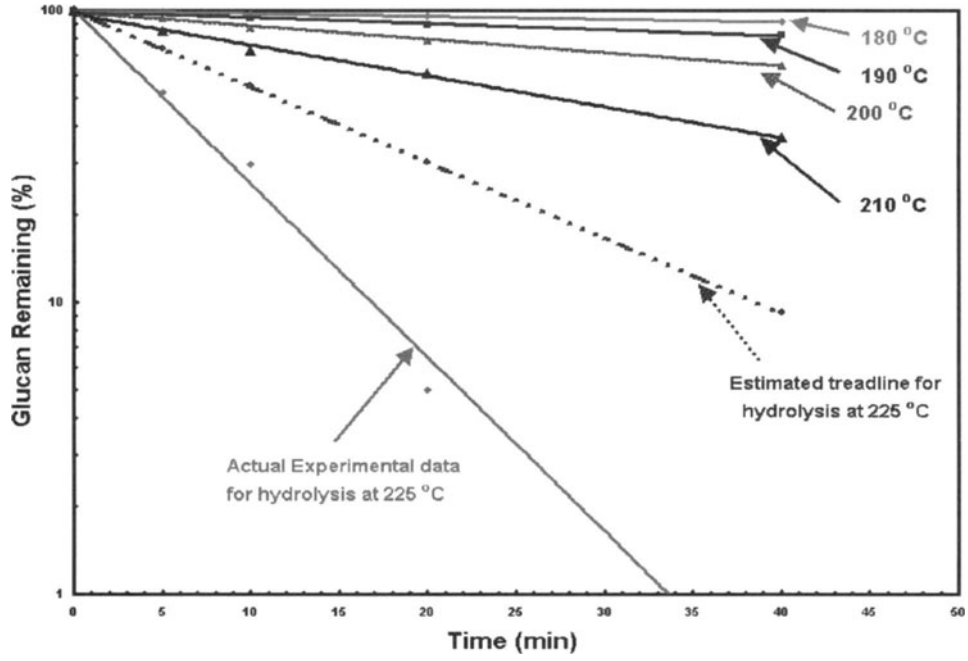


Fig. 6. Influence of temperature on hydrolysis rate. Kinetic profiles from hydrolysis of pretreated yellow poplar in batch reactor with 0.07% H_2SO_4 are shown.

jump of reaction rate is observed between 210 and 225°C. The actual measured rate constant at 225°C is 0.137, which is 2.3 times larger than the value extrapolated by Arrhenius equation based on the data at 180–200°C.

We have also observed similar behavior with hydrolysis of α-cellulose in that a discontinuity of reaction behavior occurred at a certain temperature *(15)*. This was owing to a temperature-induced disruption of cellulose physical structure. On devastation of cellulose supramolecular structure, catalytic hydrolysis becomes much more rapid since the catalytic group can gain much easier access to cellulose without having to penetrate into the crystalline barrier. Furthermore, the hydrolysis products, including glucose and oligomers, are readily released into liquid owing to weakened hydrogen bonding. This finding partly explains why the cellulose hydrolysis rate is drastically improved and high glucose yields are obtained under high-temperature and extremely low-acid conditions.

For the sake of discussion, we introduce a reaction index applicable for the hydrogen bonds, called the instability index (I_0). It is an index similar to the severity factor in that it involves two parameters: temperature and acid concentration. The ionic strength of the solution may also be included into the definition of the instability index. The exact mathematical expression of I_0 is yet to be determined. It is an entity that increases when acid concentration and/or temperature increases.

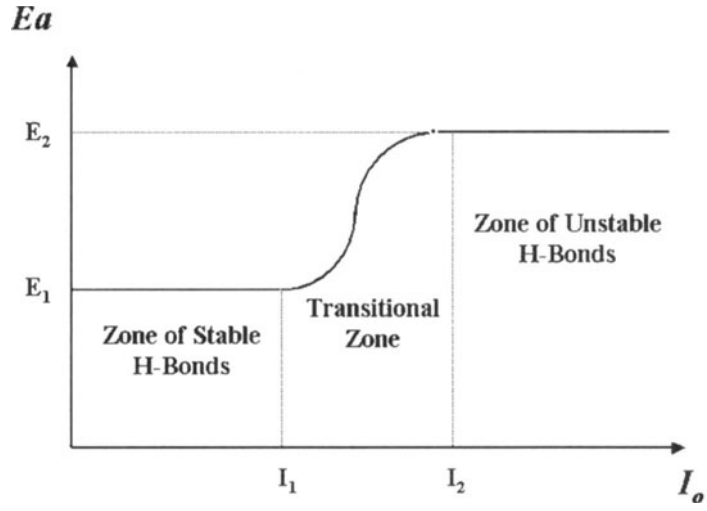


Fig. 7. Activation energy vs instability index of hydrogen bonds.

Because of the direct involvement of hydrogen bond in the hydrolysis reaction, its instability affects the kinetics, especially the activation energy or the temperature dependency (Fig. 7). For convenience, the hydrolysis conditions are divided into three different zones according to different instability index. Each zone has different activation energy for the acid hydrolysis reaction. At low instability index region, which means low temperature or low acid concentration, the hydrogen bonds are relatively stable and the hydrolysis rate constant has low activation energy. According to our experimental data, temperatures under 210°C and <0.07% H_2SO_4 fall under the stable zone. Above this zone, hydrogen bond becomes progressively unstable. Thus, the experimental data taken in the stable zone cannot be extrapolated to the unstable zone, and vice versa.

We have observed oligomers in the hydrolysates. The distribution of oligomers with varying DP is determined by reaction conditions and reactor configurations. According to its definition, the I_0 determines the state of hydrogen bonds, and thus determines how easily the crystalline structure is broken up and products are released into liquid medium. The higher-DP oligomers have a higher number of hydrogen bonds to the residual cellulose; thus, it is more difficult to be released into the liquid medium than the low-DP oligomers. Obviously, glucose is released most easily. At lower I_0, hydrogen bonds are so stable that only glucose monomer is released. The long-chain oligomers stay on the surface of the cellulose because of the strong binding force of hydrogen bonds until they are further hydrolyzed to monomer. We believe that is the reason why glucose is the predominant product under low I_0 conditions. This would explain why the amount of oligomer decreases with DP in the hydrolysate (Fig. 3). On the other hand,

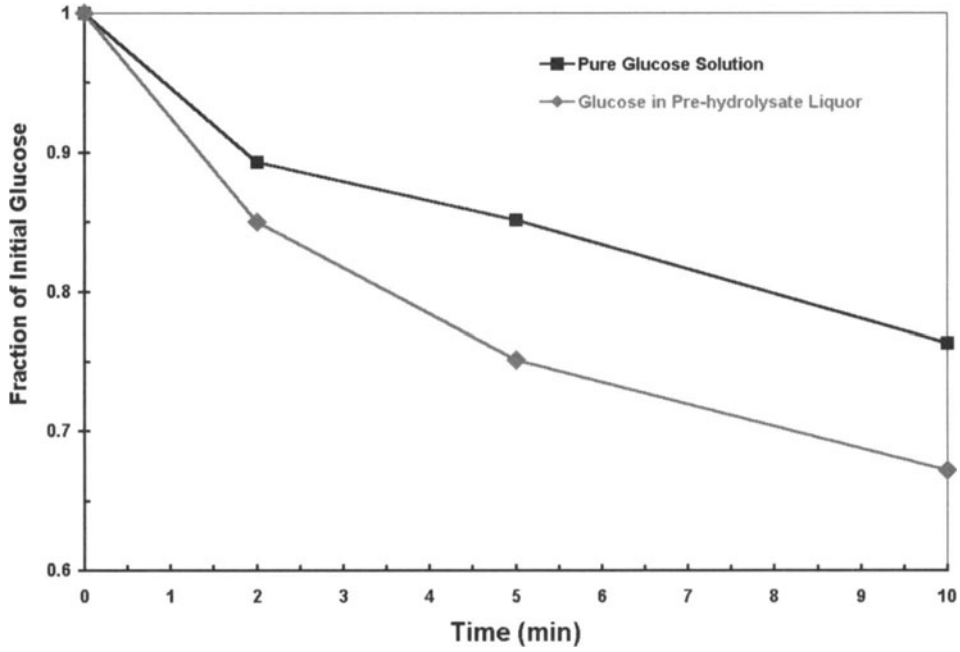


Fig. 8. Effect of lignin on glucose decomposition at 200°C and 0.1% H_2SO_4.

at high I_0 conditions such as concentrated H_2SO_4 or above 210°C, hydrogen bonds become unstable and eventually disrupted. Only then, are the oligomers directly released. When this happens, the high-DP oligomers are less likely to be released than the low-DP ones because high DP induces a high number of hydrogen bonds, and thus high binding force.

Glucose-Lignin Interaction

In several of our experiments, we have observed that the disappearance of glucose during acid hydrolysis of lignocellulosic biomass was faster than that of model prediction. We speculate that glucose may recombine with ASL in hydrolysates; the data in Table 1 support this hypothesis. Glucose yield from hydrolysis of sugarcane bagasse increases substantially when the lignin content in the feedstock is reduced by pretreatment. We also observed that glucose decomposed faster when the medium was supplemented with ASL (Fig. 8). From these observations, we conclude that there exists an additional pathway for glucose decomposition caused by the glucose-lignin interaction, most likely recondensation between glucose and ASLs. With part of lignin being solubilized into medium at high temperature, the presence of protons causes the formation of intermediate carbonium ions that have a high affinity for nucleophilic reaction moiety. This in turn causes lignin fragmentation or lignin condensation reactions, depending on the type of the active nucleophile *(21)*. Thus, the active sites

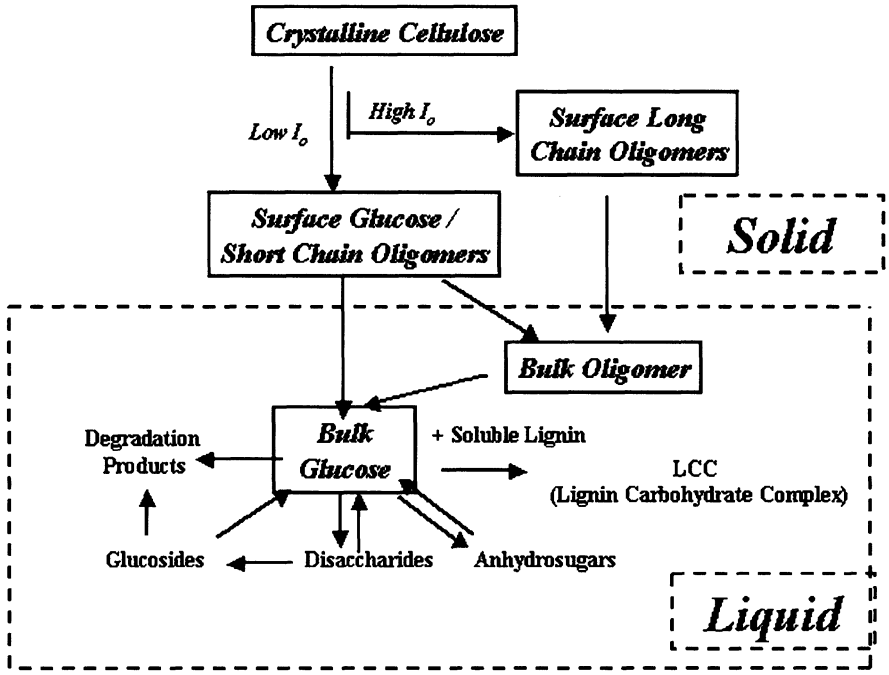


Fig. 9. Proposed comprehensive kinetic model for acid hydrolysis of lignocellulose.

on ASL will lead to the condensation reaction between ASL and glucose as follows:

$$\text{ASL} + \text{Glucose} \rightarrow \text{ASL} - \text{Glucose}$$

However, we have yet to positively identify the lignin-carbohydrate complex in the hydrolysates. Further investigation on this topic is currently under way in our laboratory.

Proposed Hydrolysis Kinetic Model

On the basis of our experimental findings, we propose a comprehensive kinetic model as described in Fig. 9. This model accounts for factors pertaining to the heterogeneous nature of the reaction, the hydrogen-bonding theory, and posthydrolysis reaction, specifically glucose-ASL interaction. In the solid phase during the hydrolysis process, the strength of hydrogen bonds controls the release of either glucose or oligomers to the liquid. Oligomers are released at high I_0 conditions, whereas glucose is released at low instability conditions. Within the high I_0 reaction zone, oligomers are released into the liquid and further hydrolyzed to glucose in the acidic liquid medium. In the liquid phase, glucose takes an additional pathway owing to interaction with ASL at high-temperature conditions. This occurs concurrently with other reactions involving glucose such as decomposition and reversion.

Conclusion

The conventional kinetic model of two sequential reactions is inadequate as a general model since it does not account for the heterogeneous nature of the reaction. The heterogeneity of the reaction creates physical resistances that are far greater than the reaction resistance. The primary factor controlling the physical resistance is the state of the hydrogen bonding in cellulose molecular structure.

The state of hydrogen bonding affects the kinetic behavior. If the hydrolysis reaction is carried out under a condition that severely disrupts hydrogen bonding (high I_0 condition), glucose and its oligomers are formed. Since oligomers are more stable than monomer against decomposition, adoption of such a reaction condition may increase sugar yield. Quick quenching of the reactor effluent is an efficient way to raise the glucose yield, especially in the high I_0 zone. Glucose-lignin recondensation occurs during acid hydrolysis of cellulose and is an important factor causing loss of sugar.

A comprehensive kinetic model is proposed implementing additional factors into the conventional model: a parallel oligomer pathway, association of glucose/oligomers with cellulose through hydrogen bonding, and interaction of glucose with ASL. The proposed kinetic model provides valid explanations for our recent laboratory data that contradict the conventional acid hydrolysis model.

Acknowledgments

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