

# Fundamental Aspects of Dilute Acid Hydrolysis/Fractionation Kinetics of Hardwood Carbohydrates. 1. Cellulose Hydrolysis

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Previous kinetic modeling and bench-scale demonstration efforts using batch, percolation, or plug-flow reactors for the dilute sulfuric acid hydrolysis of cellulose have concluded that glucose yields above 70% of theoretical were not possible. This has been explained to be a result of reactions involving glucose or the cellulose itself in a destructive manner, as well as hydrolyzed soluble oligomers which have been modified chemically so as not to release glucose. However, recently, we have demonstrated that near-quantitative yields of glucose from cellulose can indeed be obtained using a bench-scale shrinking-bed percolation reactor in which an internal spring compresses the biomass as the reaction progresses. The present study was initiated to gain a fundamental understanding of the kinetic sequences involved in these high yields. Three reactor configurations (batch, percolation, and shrinking-bed percolation) were studied using similar hydrolysis severities to begin addressing chemical, physical, and hypothesized boundary layer phenomenon governing rate-limiting steps of glucose release from two prehydrolyzed yellow poplar cellulosic substrates. The characteristics of the logarithmic release of glucose as well as the logarithmic disappearance of cellulose as a linear function of time were found to be reactor dependent. Use of a percolation reactor was described where the initial hydrolysis rate constant for cellulose using 0.07% w/w sulfuric acid at 225 °C is enhanced 5-fold compared to a batch reactor. Additionally, when lower hydrolysis severities are used for hydrolyzing yellow poplar cellulose in batch mode, biphasic kinetics were observed. Several hypothesized boundary layer resistances, such as structured water, viscosity, and re-hydrogen bonding of released glucose, will be suggested as diffusion resistances for released glucose to the bulk medium, which would be a function of the reactor configuration and define potential glucose yields.

## Introduction

From the late 1970s through the late 1980s, a concerted research and development effort was phased in to improve the saccharification of cellulose in ligno-cellulosic feedstocks using enzymatic processes to ultimately convert the released glucose to fuels and chemicals.<sup>1</sup> This increased research activity was due to the potential of enzymatic processes to convert the cellulose to glucose nearly quantitatively.<sup>2</sup> Alternative thermochemical processes, such as a two-stage fractionation<sup>3</sup> which used dilute sulfuric acid for the saccharification, lost favor because of the relatively low yields of glucose which could be obtained using batch reactors (55–60%<sup>3–6</sup>) or slightly better yields using percolation reactors.<sup>7–9</sup> Although work continues on aqueous fractionation processes using dilute acids, these processes are thought to be only near-term options because raising the glucose yields much higher than 70% in an economically viable industrial process holds little promise. Dilute acid processes were industrialized in the early part of the 20th century,<sup>10</sup> and even with continued research and development, no significant breakthroughs have been made to raise the glucose yields much higher

than 65–70%. If dilute acid saccharification processes are to compete in the mid-to-long term, significantly higher yields, in an economically viable process scenario, must be developed.

There have been several improvements to the kinetic model originally suggested by Saeman,<sup>11</sup> in which he proposed a hydrolysis sequence of cellulose → glucose → degradation products. However, these more recent models substantiate the results whereby it was predicted that glucose yields higher than 65–70% are not attainable using dilute sulfuric acid. Conner et al.<sup>12</sup> suggested that once glucose is formed under reaction conditions, it can derivatize and/or degrade at a significant rate. Bouchard et al.<sup>13</sup> suggested that only about 60–70% of the theoretical glucose yield from cellulose can be obtained using a plug-flow reactor because the cellulose is chemically altered after about 70% conversion. Therefore, the resulting solid substrate is not quantitated as cellulose and can no longer be hydrolyzed to release glucose. Mok and Antal<sup>14</sup> suggested that when using a percolation reactor, about 30% of the hydrolyzed cellulose gives rise to oligomers, which cannot be converted to glucose either at reaction temperature or after traditional posthydrolysis conditions using 4% sulfuric acid. However, Torget et al.,<sup>15</sup> using a simulated countercurrent shrinking-bed reactor system for the aqueous fractionation of yellow poplar, have produced glucose yields higher than 85%<sup>15</sup> using 0.07% w/w

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sulfuric acid and 225 °C. This cannot be explained by previously published cellulose hydrolysis kinetic models, so the proposed kinetic fractionation of glucose from hardwood cellulose using dilute sulfuric acid was revisited.

Although the acid-catalyzed hydrolysis of crystalline cellulose is a heterogeneous reaction, the models described in the literature<sup>3,10–14</sup> have successfully been able to model the data using homogeneous first-order reaction kinetics to describe the hydrolysis behavior, even though it is known that the hydrolysis liquor cannot penetrate the crystallite domain in cellulose. This assumes that (1) the observed global rate of glucose release from the crystalline cellulosic microfibrils is controlled kinetically independent of the transport processes, (2) the glucose migrates unhindered to the bulk medium and no further electrostatic interactions occur in the form of hydrogen-bonding or van der Waals interactions, i.e., readsorption, and (3) no physical boundary layer effects, e.g., viscosity or structured water, interfere with the glucose being released to the bulk medium.

This study uses three reactor configurations (batch, percolation, and shrinking-bed percolation) employing similar dilute sulfuric acid hydrolysis severities to address “hypothesized” rate-limiting boundary layer phenomenon restricting the free diffusion of hydrolyzed glucose to the bulk medium. Ramifications of liberated glucose from cellulose that remains in close proximity to the crystallite structure are discussed in conjunction with reactor configurations as well as potential yields of glucose found in the bulk medium.

## Materials and Methods

*Liriodendron tulipifera* L. (yellow poplar) sawdust substrate was provided by Eric Miller of Saw Miller Inc., Haydenville, OH. It was shipped in 1-ton parcels from Lannes Williamson Pallets, Inc., Southside, WV. It arrived at NREL as fresh green sawdust with a moisture content of 43 wt %. The sawdust was double-bagged in plastic and stored frozen at –20 °C. The chemical composition of a representative sample after being milled to pass through a 2-mm rejection screen was 41.9 wt % glucan, 19.4 wt % xylan, 2.7 wt % mannan, 0.8 wt % galactan, 0.6 wt % arabinan, 23.4 wt % Klason lignin (determined on unextracted sawdust), 3.2 wt % soluble lignin, 0.6 wt % ash, 3.4 wt % acetyl, and 4 wt % others. For dilute acid hydrolysis runs, the sawdust was thawed and separated into two size fractions using a portable sieve shaker (Tyler Industrial Products, Mentor, OH) equipped with a 4-mm-mesh screen (USA Standard Testing Sieves). The material that passed through the 4-mm screen was used “as is”.

## Analytical Methods

Compositional analyses of all biomass solid samples were carried out by standard methods.<sup>16</sup> Monomeric sugars were determined by HPLC using Bio-Rad Aminex HPX-87P columns.<sup>17–19</sup> The decomposition products of sugars were determined by HPLC with a Bio-Rad Aminex HPX-87H column. A refractive index detector was used in both cases. The sugars in liquid samples were determined after being subjected to a secondary acid hydrolysis. The conditions in the secondary hydrolysis were 4 wt % sulfuric acid, 121 °C, and 1 h.

## Batch Kinetic Experiments

All batch reactor experiments (Figures 1, 3, and 4) were performed at Auburn University, using the biomass and acid loading conditions listed below.<sup>20</sup> Sealed tubular reactors (13.5 cm<sup>3</sup> of internal volume) were used for batch reaction experiments. The reactors were constructed of Hastelloy C-276 tubing (0.5 in. [1.27 cm]). Both ends were capped with Swagelok end caps into a nominal size of 0.5 in. (1.27 cm) diameter × 6 in. (15.24 cm) length. The reactors were packed with 0.9 g of a solid substrate and 9 mL of an acid solution to achieve a solid-to-liquid ratio of 1:10. The sulfuric acid concentration was 0.07–0.8 wt % (pH 1.2–2.2). The reaction temperatures were controlled in oil baths. The reactors were first submerged into an oil bath set at 50 °C above the desired reaction temperature for rapid preheating. The reactors were then quickly transferred into another oil bath set at the desired reaction temperature (180–225 °C), which was monitored by a thermocouple inserted into the reactor. The heat up time to reach a reaction temperature was 3–5 min with only about 30–60 s spent at a temperature at which cellulose could hydrolyze. The reported reaction times were started from the time the reaction vessel reached the desired hydrolysis temperature to the time the vessel was quenched in an ice bath. The reactor contents were separated into liquid and solid by filtration and subjected to analyses.

## Flow-Through Kinetic Experiments

Acid-catalyzed flow-through hydrolysis experiments used semibatch flow and continual shrinking-bed reactors.<sup>21–24</sup> All wetted parts were constructed from a Hastelloy C-276 because of its strength at elevated temperatures, corrosion resistance, and commercial availability.

Two dilute acid (0.07 wt % sulfuric acid) treated substrates were used: one for the comparative kinetic curves following the disappearance of cellulose as a function of hydrolysis time using either a percolation reactor or a batch ampule reactor (Figure 1) and the other for studying the mechanisms for cellulose hydrolysis and glucose yields in both the batch and percolation modes as a function of both hydrolysis time and acid concentrations (Figures 2–4). For the former, the substrate was prepared exactly as previously described<sup>22</sup> using the two-temperature regime of 174 °C/10 min and 204 °C/10 min using 0.07 wt % sulfuric acid. The solid substrate was washed extensively and chemically analyzed to contain 71% glucan and 28% lignin (both Klason and soluble lignin). The physical appearance of the treated particles did not change significantly; i.e., the pretreated wood particles were still discernible as particles even though nearly half of the mass had been solubilized. For the latter, the substrate's pretreatment was designed to mimic the composition where the “curvature” was observed (Figure 1) for the batch reactor, i.e., when about 50% of the crystalline cellulose was hydrolyzed. Therefore, the advanced two-stage hydrolysis, as described by Nagle,<sup>23</sup> was used with native sawdust being loaded into a single shrinking-bed reactor. Moist yellow poplar was packed into the spring-loaded reactor and set into a sand bath set at 185 °C. Once the reactor contents were at 170 °C (about 10 min), hot compressed water at 183 °C was pumped through the bed to completely saturate the biomass for

1.2 min. The flow was stopped, and the reactor was isolated at temperature in a nonflowing static mode for an additional 8.8 min. The reactor was then transferred to a 225 °C sand bath, and dilute sulfuric acid (0.07 wt %) was then pumped (90 mL/min) for a 4-min residence time. The reactor was immediately quenched in cold water and the solid substrate removed. The resulting substrate now changed to the consistency of very fine particulate "mud" with no discernible wood structure.

For the kinetic curve, depicted in Figure 1 for the percolation mode, the 1-in. (2.54 cm) reactors were used.<sup>21</sup> The reactors were packed with 6 g of wet (water saturated, about 30 wt % solids), pretreated biomass and sealed. The ancillary tubing, pump assembly, and collection system were connected and pressurized to 400 psig, and the reactor was submerged in a 225 °C sand bath. Once the reactors were at about 210 °C (which took about 10 min), two reactor voids<sup>21</sup> were pumped using 0.07 wt % sulfuric acid over 2 min to quickly heat the biomass to 225 °C. For each kinetic point, one reactor volume of the acid was pumped each minute during the reported total residence time, after which flow was stopped and the reactors were quenched in cold water. The contents were removed and analyzed for its cellulose content.

To demonstrate the effect of the two different reactor designs on glucose yields from prehydrolyzed sawdust in which 50% of the crystalline cellulose had been removed, the small percolation reactor system was used with slight modifications. Two sets of reactors were made using two single reactors that were bolted together end-to-end. Biomass that was prehydrolyzed using percolation (as described above, using a 183 °C first stage (10 min residence time) for prehydrolysis followed by a 4 min residence time at 225 °C) to remove all of the hemicellulose, 60% of the lignin, and 50% of the cellulose (with the consistency of "mud") was loaded into the bottom half of each reactor set. For the traditional percolation reactor scenario, a Teflon plug was inserted into one reactor cavity and a small hole was drilled down the center to allow the hydrolysis liquor to flow. In the continual shrinking-bed reactor scenario, a handmade titanium spring made from 0.125 in. (0.32 cm) tubing was inserted into the second reactor cavity and lodged against a thin movable Teflon plug to which a 20- $\mu$ m-pore-size titanium frit was attached to allow the fluid to move from the cavity to the biomass. The reactors were connected to the pump and collection system<sup>21</sup> and pressurized to 400 psig. The reactors were submerged one at a time in 225 °C sand baths. Once the shrinking-bed reactor was at about 210 °C (about 10 min), 0.07 wt % sulfuric acid (at 225 °C) was pumped at one-third void/min<sup>23</sup> for 10 min and the reactor quenched in cold water. The fixed-volume percolation reactor was treated exactly the same except that the flow rate was continually increased as a function of the hydrolysis time to account for estimated solubilization of the biomass to address the nonideality of the liquor residence time as compared to the shrinking-bed reactor. The solids were collected, washed with water, and analyzed. The collected liquors were likewise analyzed.

## Experimental Results

In the study of dilute sulfuric acid fractionation catalysis of lignocellulosics, acid concentrations of about 0.4 wt % to about 1–2 wt %<sup>3,11–14</sup> are commonly used. These conditions require that exotic alloys for corrosion

**Table 1**

reactor mode for hydrolysis of yellow poplar cellulose using 0.07 wt % sulfuric acid and 225 °C	glucose yields from crystalline cellulose (%)
3-stage continual shrinking-bed progressing batch-simulated countercurrent operation <sup>15</sup>	85–87
1-stage continual shrinking-bed continuous percolation operation	92

resistance be used to construct the hydrolysis reactors. Also, the higher the acid concentration used, the more gypsum is produced because lime is used for neutralization. This creates fouling concerns and increased disposal costs in downstream processing. Although these concentrations were used, acid concentrations as low as 0.07 wt % were also used to compare reaction rates and residence times. This could allow for lower-cost alloys for constructing reactors. It will also reduce the amount of gypsum produced in the process. Additionally, Zucher–Hammet plots of cellobiose hydrolysis<sup>25</sup> and glucose degradation<sup>26</sup> suggest that a pH (measured at ambient conditions) of 2.2–2.5, which translates into an acid concentration of about 0.05–0.07 wt % sulfuric acid (as measured at 25 °C), would favor higher glucose yields due to lower degradation rates of the released glucose found in the bulk medium. Therefore, acid concentrations from 0.07 to 0.8 wt % were used for the following experiments.

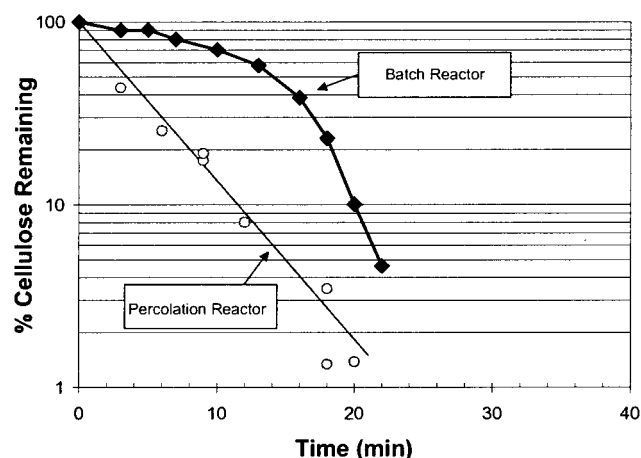
## Cellulose Hydrolysis Kinetics Relative to Reactor Configuration

To study the kinetic sequences in hardwood (yellow poplar) cellulose hydrolysis, a traditional semilog plot of cellulose disappearance as a function of hydrolysis time (due to the fact that batch kinetic data have been reported to model homogeneous first-order kinetic behavior) was developed using 0.07% w/w sulfuric acid and a hydrolysis temperature of 225 °C (using prehydrolyzed yellow poplar sawdust<sup>22</sup>). After some initial screening of hydrolysis rates versus hydrolysis times at various temperatures (data not shown), 225 °C was chosen because reasonable residence times gave good saccharification rates and pilot-scale reactor designs would be able to accommodate them. Although all published kinetic curves studying cellulose hydrolysis use batch ampule reactors and acid concentrations of about 0.4–1.6 wt % sulfuric acid,<sup>3,11–14</sup> this study uses traditional ampule batch reactors and a flowing percolation reactor. We justified using a flowing reactor because we recently demonstrated that a continual shrinking-bed reactor can produce glucose yields of 85–92%<sup>15</sup> (see Table 1). The reactor uses an internal spring to compress the bed in a percolation reactor as hydrolysis occurs, thus maintaining a well-behaved packed-bed column with a relatively constant bulk packing density throughout the entire hydrolysis process.

Thus, because our bench-scale hydrolysis work was done in a flowing shrinking-bed reactor, we felt that any anomalies might be manifested in the kinetic curves. The kinetics of yellow poplar cellulose hydrolysis using prehydrolyzed sawdust in either a batch or a non-shrinking-bed (no internal spring) percolation reactor is seen in Figure 1.

Because of the unexpected initial hydrolysis rates that resulted from using the two types of reactors and 0.07% w/w sulfuric acid, we repeated each curve several times





**Figure 1.** Hydrolysis of prehydrolyzed yellow poplar at 225 °C using 0.07 wt % sulfuric acid using batch ampules and a percolation reactor.

to ensure the data were real and reproducible. The most telling observation is the 5-fold initial rate difference between using a flowing percolation reactor and the batch, nonstirred ampule reactor. This implies that cellulose hydrolysis is reactor dependent (at least using 0.07 wt % sulfuric acid); further, the proposed simplified homogeneous kinetic schemes<sup>10–12,14</sup> are inadequate. Saeman's<sup>11</sup> extrapolated hydrolysis kinetic equations and constants from Douglas Fir cellulose at 225 °C and 0.07% w/w sulfuric acid (Saeman's lowest acid concentration was 0.4%) result in an extrapolated rate constant of 0.07 min<sup>-1</sup>. Our batch data produce a rate constant (taken from the initial slope of Figure 1 (0–5 min) and multiplied by 2.303) of 0.06 min<sup>-1</sup>, which is in good agreement. This suggests that the hydrolysis reaction mechanism in batch mode employing very dilute sulfuric acid (0.07 wt %) is similar to those using higher sulfuric acid concentrations (0.4–1.6% w/w) using Douglas Fir as the substrate.

Another striking observation is the curvature of the hydrolysis kinetic curve using a batch reactor. It may suggest that, as the hydrolysis progresses, the rate constant (as determined from the slope of the curve) continually increases with time or that the reaction rate slowly increased because of heat-up anomalies. If indeed the reaction rate intrinsically increased as a function of conversion, one would expect faster release and, thus, greater survivability of glucose. However, we did not observe this (data not shown). Also, as stated in the Materials and Methods section, the total heat-up time for the batch ampules was 3–5 min, with only about 30–60 s spent at temperatures at which cellulose could possibly hydrolyze. Therefore, the curvature in the rate curve using 0.07 wt % acid is most likely due to a real global or intrinsic catalytic event which has not been observed using higher acid concentrations for the hydrolysis of cellulose.

### Batch Cellulose Hydrolysis as a Function of Temperature and Acid Concentrations

To investigate further on the “curvature” shown in Figure 1, hydrolysis temperatures of 180 and 195 °C and acid concentrations from 0.07 to 0.8 wt % were studied. The cellulose substrate chosen for this stage of the study was one which already had 50% of the cellulose, all of the hemicellulose, and about 50–60% of the lignin removed from yellow poplar (see the

Materials and Methods section). The reasoning was 2-fold. First, if the cellulose had been chemically altered in any way up to 50% conversion,<sup>13</sup> mass balance closures of both cellulose and glucose as a function of hydrolysis time might reveal some insight as to the kinetic mechanisms involved. Second, the “curvature” characteristics of the cellulose at 50% conversion could be studied as a function of conversion, temperature, and acid concentration.

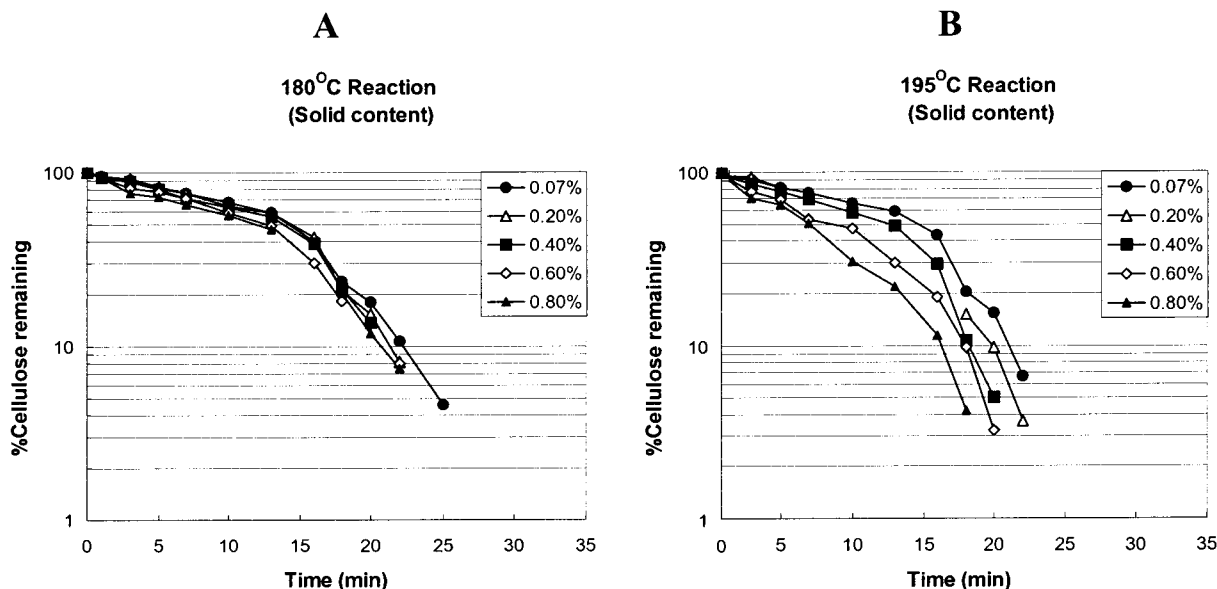
Figure 2 follows the hydrolysis of this “special” cellulosic substrate from previously hydrolyzed yellow poplar sawdust and plots the results in a semilog plot versus hydrolysis time at various acid concentrations and temperatures. “Curious” kinetics are again observed as previously described (see Figure 1). At all acid concentrations using 180 °C and with the more dilute sulfuric acid curves at 195 °C, there is a definite curvature to the lines which becomes apparent at about 50–60% conversion. As the acid concentration increases to more than 0.4 wt % at 195 °C, the more traditional first-order rate curves are observed.<sup>3,11,12</sup>

The initial rates of cellulose hydrolysis using 0.07 wt % sulfuric acid in a batch reactor configuration seem to deviate from the typical exponential Arrhenius relationship. During comparison of the initial hydrolysis rate of yellow poplar cellulose at 180 and 195 °C (Figure 2) and 225 °C (Figure 1), the rate constant increases only marginally with temperature—more of a linear relationship with absolute temperature (as determined from the initial slopes of the curves). This suggests that there appears to be a noncatalytic step in the observed global hydrolysis of hardwood cellulose at least when using 0.07 wt % sulfuric acid. However, if one uses higher acid concentrations, e.g., >0.4 wt %, the observed global hydrolysis shows stronger temperature dependency (Figure 2) in line with the Arrhenius relationship.<sup>11</sup>

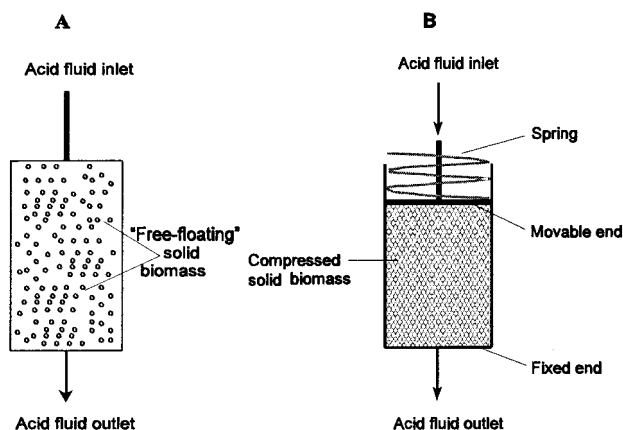
### Glucose Yields As Affected by Percolation Reactor Design

Mok and Antal<sup>14</sup> have reported that the highest yield of glucose from purified cellulose using a fixed-volume percolation reactor and very dilute sulfuric acid is about 70% of theoretical. However, Torget et al.<sup>15</sup> have reported that glucose yields from pretreated yellow poplar can be in excess of 85% using very dilute sulfuric acid and (which has recently been independently verified<sup>27</sup>) a shrinking-bed percolation reactor (a reactor in which an internal spring compresses the biomass bed as a function of hydrolysis). The question is, is this yield difference due to the substrate nature or the percolation reactor design?

To initially address this question, two percolation reactors were used to study dilute-acid-catalyzed cellulose hydrolysis, a traditional fixed-volume percolation reactor, similar in design to the one described by Mok and Antal,<sup>14</sup> and the “shrinking-bed” percolation reactor used by Torget et al.<sup>15</sup> The “special” cellulosic substrate described above was used in which 50% of the cellulose, all of the hemicellulose, and about 50–60% of the lignin had been hydrolyzed previously (see the Materials and Methods section). The major reason for using the “special” substrate for this experiment was the desire to use a more physically uniform substrate in terms of both size and shape to minimize nonidealities due to flow considerations around submerged particles, which may have an impact on hydrolysis behavior.



**Figure 2.** Semilog plot of cellulose hydrolysis as a function of acid concentration and temperature (A, 180 °C; B, 195 °C) versus hydrolysis time.



**Figure 3.** (A) Traditional fixed-volume percolation reactor that does not adjust for solubilization of biomass. (B) Continual shrinking-bed reactor that maintains a relatively constant bulk packing density.

A schematic representation of the two experimental reactors is seen in Figure 3.<sup>15,23,24</sup> However, in reactor A, as more and more biomass is solubilized, the percolation reactor becomes more of a continuous stirred tank reactor (CSTR) with more nonideality associated with the liquor phase; thus, more glucose/unit liquor flow might degrade compared to reactor B, depending on the degradation rate constant. This needs to be accounted for when comparing the two reactors performances.

The hydrolysis experiments were performed at 225 °C for a 10-min residence time (see the Materials and Methods section). To account for the continual shrinking volume of the spring-loaded reactor, liquor flows in the fixed-volume percolation reactor were constantly increased as a function of time to help mitigate the increased linear velocity of the flowing medium caused by the decreased volume. This is due to the solubilization of biomass with the concomitant decrease in the reactor volume caused by the spring tension. This increased flow rate in the fixed-volume reactor maintained similar linear velocities in both reactor systems. The results were startling in that the traditional percolation reactor, after accounting for nonideality, resulted in very low glucose yields of 35% of theoretical.

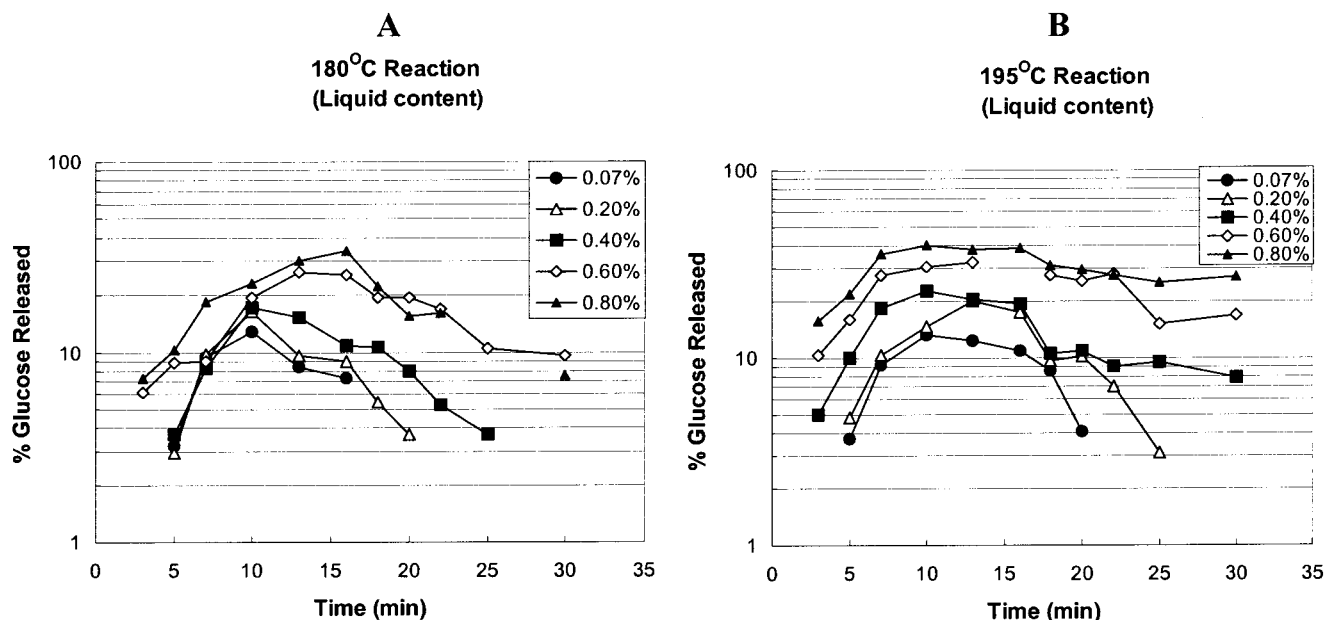
No cellulose was detected in the solid residue. The continual shrinking-bed percolation reactor yielded 84% glucose yields with no cellulose detected in the solid residue. The extreme yield difference was unexpected and will be discussed later.

#### Glucose Yields as a Function of Temperature and Acid Concentrations

The glucose yields obtained from the batch experimental setup shown in Figure 2 as a function of temperature and hydrolysis time of the pretreated yellow poplar substrates are depicted in Figure 4. Many striking observations fall out of the data. First, the initial rate constants of sugar release (3–10 min) in all curves are faster than the initial rate constant of cellulose hydrolysis, as seen by the initial slopes of the curves in Figure 2 compared to those in Figure 4. This suggests that the initial rate of release of glucose is faster than the rate of cellulose hydrolysis, which of course is not possible. These data suggest an extra kinetic step between the hydrolysis of cellulose and the release of glucose equivalents to the bulk medium, which will be discussed later. Second, the shapes of the curves in Figure 4 differ and seem to follow a trend of “flattening” out as the acid concentration is increased, indicating that the “released” glucose has a longer survival rate in the presence of increasing acid concentrations at a given hydrolysis temperature. Third, increased yields are seen with increased acid concentrations.

#### Discussion

When the kinetic modeling work of the “shrinking-bed” percolation reactor was first initiated by the authors in 1995 and subsequently published,<sup>24,28</sup> the work of Mok and Antal<sup>14</sup> and Bouchard et al.<sup>13</sup> was not included in the modeling exercises. This was due to an incomplete understanding of why the shrinking-bed reactor was giving near-quantitative yields of glucose from yellow poplar cellulose from a bench-scale demonstration using 225 °C and 0.07 wt % sulfuric acid, while the literature<sup>13,14</sup> suggested that yields above 70%



**Figure 4.** Semilog plot of glucose yields in the hydrolyzate as a function of acid concentration and temperature (A, 180 °C; B, 195 °C) versus hydrolysis time.

were not likely. Bouchard et al.<sup>13</sup> suggested that up to 30% of pure cellulose was derivatized in the presence of dilute acid in a plug-flow reactor and could not be hydrolyzed to glucose. Mok and Antal<sup>14</sup> suggested that although pure cellulose could be hydrolyzed completely in a percolation reactor, oligomers, up to 30% of the original cellulose and which could not be hydrolyzed to form glucose, formed. We have now continued our investigation into the fundamentals of hardwood cellulose hydrolysis kinetics using yellow poplar and three reactor designs, batch, fixed-volume percolation, and shrinking-bed percolation reactors, and address the previous work.

One of the more striking observations made during this study was the 5-fold initial hydrolysis rate constant difference for yellow poplar cellulose using a batch ampule versus a percolation reactor with 0.07 wt % sulfuric acid as the catalyst. Two obvious phenomenon can help explain this: either the hydronium ion diffusion to the cellulose surface is "slowed" in a batch reactor as compared to a percolation reactor or the released glucose at the cellulose surface has a more difficult time "escaping" to the bulk medium in a batch reactor and can reattach to the cellulose polymer. In regards to the former resistance, it has been postulated<sup>29</sup> that water molecules at the boundary layer of crystalline cellulose can form an "ice-like" structure two to four molecular layers deep. This is hypothesized to be a result of the hydrogen bonding of water hydrogens to the negative charge distribution on the hydroxyl oxygens of the crystallite-glucose moieties. This structural organization of water molecules could conceivably form a physical barrier to both hydronium ion and glucose diffusion as well as a charge barrier due to dipole-dipole interactions. It is unlikely, however, that the hydronium ion activity for hydrolysis would be effected because of the fact that this ion can transfer its charge to the cellulose surface via the Grotthuss mechanism.<sup>30</sup> Therefore, the most probable resistances may be separating the hydrolyzed glucose from the hydrogen-bonding and van der Waals attractions as well as probable viscous forces caused by the high concentration of glucose and the low concentration of solvating water molecules at the cel-

lulose surface. Additionally, the glucose would have to diffuse through a hypothesized charge and physical barrier due to the structured water boundary layer. Any perturbation of these resistances to diffusion of the released glucose to the bulk medium would lead to a faster observed hydrolysis rate constant. Such perturbation seems to be inherent in a percolation reactor in which the solids are contained and the hydrolysis medium flows.

Another striking observation in the batch hydrolysis of yellow poplar cellulose is the apparent "curvature" of the semilog plots of cellulose remaining as a function of hydrolysis time and temperature as well as acid concentrations. This "curvature" is seen using prehydrolyzed poplar which has its full compliment of crystalline cellulose (Figure 1) or partially hydrolyzed crystalline cellulose in which 50% of the cellulose has been previously hydrolyzed (Figure 2). At 195 °C and using 0.8 wt % sulfuric acid, however, the traditional linear hydrolysis response on a semilog plot is observed with no apparent "curvature". Although Bouchard et al.<sup>13</sup> suggest that only about 70% of pure cellulose is available for glucose release, the literature<sup>11,12,14</sup> suggests that all of the cellulose is hydrolyzed completely and at a constant rate using batch or percolation flow reactors. Our data suggest that, at lower severities, a change in the "apparent" hydrolysis rate takes place after about 50–60% conversion with the "apparent" rate constant increasing steadily as a function of conversion after 60%. However, at the highest severities tested in this study, there appears to be no distinction between the rate constant for the first 60% conversion and the last 40% conversion. These data do not dispute the conclusions drawn by Bouchard et al.<sup>13</sup> in that one could conclude that there are two distinct reactions occurring involving the quantitation of cellulose remaining as a function of hydrolysis: (1) the hydrolysis of the 1,4- $\beta$ -glycosidic linkages and the concomitant diffusion of the released glucose away from the solid surface and (2) a "destructive" hydronium ion catalyzed reaction between released glucose moieties and the cellulose surface which would lead to lost glucose potential as well as lost cellulose potential. We hypothesize that, at higher severities, the



constructive hydrolysis pathway and the destructive (parasitic<sup>14</sup>) derivatization pathway have similar rate constants.

As has been eluded to above, many additional parameters need to be considered in the heterogeneous catalysis of cellulose in addition to the breaking of the covalent linkages. These may include re-hydrogen bonding of hydrolyzed glucose, van der Waals forces, viscosity at the boundary layer due to released glucose, structured water at the boundary layer, and diffusion rates as a function of distance from the cellulose surface. It is also interesting to note that viscosity has an inverse exponential relationship to absolute temperature whereas diffusion has a linear relationship to absolute temperature. With that said, it appears that a linear function of temperature, such as the diffusion of glucose away from the cellulose boundary layer, is a rate-limiting factor governing the "effective" cellulose hydrolysis rate using 0.07 wt % sulfuric acid in a batch mode. This is because the rate constant, as determined from the slope of the semilog plots, only increases linearly with absolute temperature instead of the more traditional exponential Arrhenius relationship.

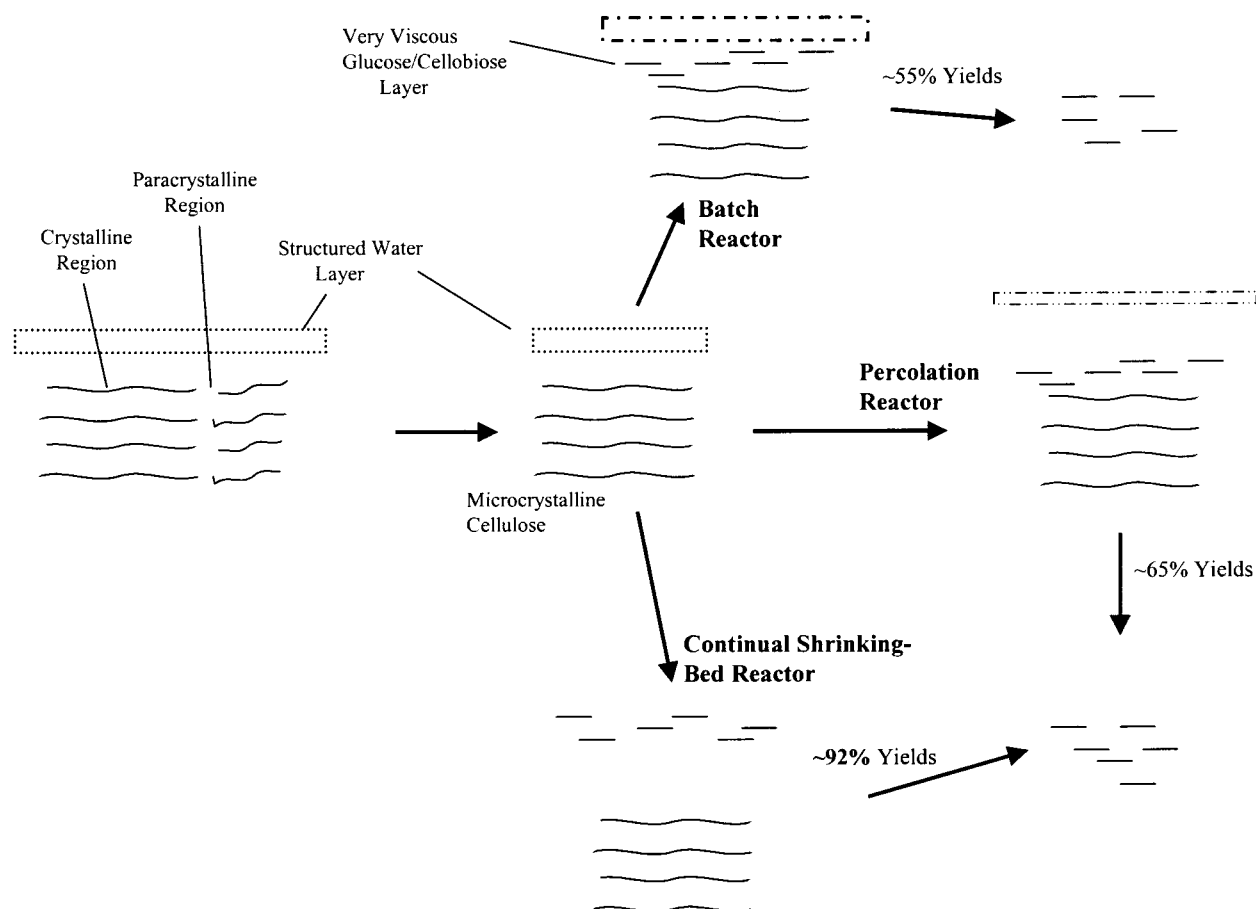
An intriguing observation of this study was the extremely different yields of glucose obtained from two differently designed percolation reactors using the "special" yellow poplar derived cellulose. As described previously, the chosen substrate had already had 50% of the crystalline cellulose removed. Using a standard fixed-volume percolation reactor, glucose yields of only about 35% of theoretical were obtained, whereas using a continual shrinking-bed percolation reactor, glucose yields of 84% of theoretical were obtained. In both cases, no cellulose was detected in the remaining solid (which was analyzed as Klason lignin) and similar linear velocities of hydrolysis liquor were used. As hydrolysis occurred in the continual shrinking-bed reactor, the spring maintained a tightly and uniformly packed bed that forced the hydrolysis medium very close to the solid surface. However, in the fixed-volume percolation reactor, as biomass was hydrolyzed over time, the reactor behaved more like a CSTR and thus would not have the same velocity profiles at the solid surface boundary as compared to the shrinking-bed reactor. From this experiment, it appears that a "scouring" of the solid phase by the liquor phase is necessary to achieve high yields of glucose from crystalline cellulose. This very close shearing action caused by the flowing liquor probably influences the hypothesized structured water layer (thus influencing diffusion), possible re-hydrogen bonding of released glucose, as well as the cellulose surface viscosity profiles (thus influencing chemical reactions as well as diffusion) caused by the released glucose. The unexpectedly very low yields (~35%) of glucose from the traditional percolation reactor could be due to anomalies of the hydrolysis due to the smaller dp fragments of cellulose expected in the "special" chosen substrate.<sup>13</sup> However, 65% of the glucose potential in the nonshrinking-bed reactor probably was not degraded but rather suffered the fate observed by Mok and Antal<sup>14</sup> or Bouchard et al.<sup>13</sup> The degradation rate of free glucose in the bulk medium under these conditions was  $0.04 \text{ min}^{-1}$ <sup>31</sup> and thus would not account for the lack of mass balance closure on glucose, supporting the contention of alternative destructive pathways of the glucose potential using these hydrolysis conditions. These very low yields (~35%) could be a fortuitous

observation in that continued studies using this substrate could provide greater insight into the observed destructive (parasitic) pathway.

As has been extensively reported in the literature<sup>3,11,12</sup> and reported here, yields of glucose from crystalline cellulose increase in a batch reactor with increasing acid concentrations at a given temperature. Although the literature ascribes this observation to a larger exponent on the acid term in the hydrolysis rate expression as compared to the glucose disappearance rate expression, other factors need to be considered because of the heterogeneous nature of the reaction. They include viscosity, reversibility of hydrogen bonding of released glucose, and possible structured water near the cellulose surface. The higher glucose yields obtained with increasing acid concentration could possibly be a result of the increased charge perturbation at the boundary layer of the released cellulose fragments. The hypothesized aligned water molecules at the solid-liquid interface, which because of the dipole moments at the boundary layer form an electrostatic barrier, become more misaligned because of increased ionic disturbance with increasing hydronium ion concentration. This could provide channels or pores for glucose to escape to the bulk medium. Alternatively, the hydrolyzed glucose at the boundary layer could be in hydrogen-bonding equilibrium and provide a resistance to diffusion to the bulk medium. Increased hydronium ion concentration would favor glucose in the "released" state and increase the flux of glucose to the bulk medium. Again, because of the heterogeneous nature of the catalytic events, more careful experimental designs are needed to elucidate all of the possible catalytic reactions, equilibrium states, and physical interactions involved in the release of glucose from cellulose.

### Proposed Heterogeneous Cellulose Hydrolysis Model

From these data sets and selected literature,<sup>13,14</sup> we propose a model for dilute acid hydrolysis of hardwood cellulose (Figure 5) which accounts for the heterogeneous nature of the hydrolysis process. The cellulosic substrate is made up of microcrystalline bundles attached to each other by paracrystalline regions<sup>32</sup> and surrounded by a charged water boundary layer that results from dipole-dipole interactions caused by the aligning of water molecules around the polar surface of the cellulose exterior.<sup>29</sup> The hydronium ion either penetrates the charged water boundary layer or transfers its charge to successive layered water molecules<sup>30</sup> and first attacks the "easily" accessible paracrystalline region, yielding microcrystalline cellulose bundles again surrounded by the charged water boundary layer. The hydronium ion then catalyzes the release of glucose or cellobiose from the most outer layer of the crystallite. The released moieties are held in close proximity to the cellulose surface possibly by hydrogen-bonding potential with the structured cellulose surface, van der Waals attraction forces, as well as the resistance of diffusion imparted by the charged structured water layers. As hydrolysis continues, an additional resistance to glucose diffusion is imparted because of increased viscosity at the boundary layer with the build up of glucose and/or cellobiose. Several external factors will effect the rate of release of glucose as well as the glucose yield potential in the bulk medium. These external factors appear to be related to the microenvironment conditions at the



**Figure 5.** Schematic representation of hypothesized boundary layer effects which affect the dilute-acid-catalyzed release of glucose from hardwood crystalline cellulose using batch, percolation, or continual shrinking-bed percolation reactors.

solid-liquid interface. The primary factors affecting the surface conditions are the fluid dynamics (agitation and flow rate) and the ionic charge disturbances of the structured water layer at the interface. The latter can be induced by addition of external ionic components such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{NH}_4^+$  salts.<sup>33</sup> It may further influence the level of hydronium ion, its penetration through the water layer, and the hydrogen bonding between the glucose and the unreacted cellulose. Additionally, the temperature affects not only the hydrolysis of the glycosidic linkages but also the ordering energies in the structured water layer, the viscosity, and the diffusion resistances. The fact that the global hydrolysis rate (using 0.07 wt % acid) deviates considerably from the Arrhenius-type temperature dependency indirectly supports these hypotheses.

## Conclusions

We learned early in this study that the dilute-acid-catalyzed rates of cellulose hydrolysis using a flowing reactor were greatly enhanced over those using batch reactors. We therefore surmised that the empirical modeling approaches using batch reactors in the literature described only the global kinetic behavior, not the intrinsic kinetic hydrolysis. We therefore took a more chemical-mechanistic approach and developed hypotheses which may better describe, in a global sense, various physical and chemical phenomena. The elements in this discussion include glucose diffusion and both glucose and cellulose modification chemistry, thus affecting potential yields of glucose in the bulk phase. The key observations made in this regard are as follows:

(1) Using very dilute sulfuric acid (0.07 wt %), the initial yellow poplar cellulose hydrolysis rate constant is five times faster using a flowing percolation reactor as compared to using static batch ampule reactors.

(2) Using very dilute sulfuric acid and a batch reactor, the yellow poplar cellulose hydrolysis constant does not follow the traditional Arrhenius temperature dependence, but rather more of a linear dependence is observed.

(3) Using relatively mild hydrolysis severities, biphasic catalysis is observed. However, at higher severities, the traditional single phasic curves are observed in semilog plots.

(4) To date, only a continual shrinking-bed reactor is able to attain near-quantitative yields of glucose from yellow poplar cellulose using dilute sulfuric acid with no additional co-ions or cosolvents. These yields appear to be dependent on a continual "scouring" of the boundary layer at the cellulose-aqueous interface.

(5) To add insight into the possible global heterogeneous catalysis and chemistry, several physical external factors were discussed in terms of unexplored hypotheses. The primary factor is considered to be the molecular level surface conditions at the solid-liquid interface. The surface conditions are influenced by fluid dynamic conditions (agitation and flow velocity) and charge disturbance of the structured water. It can further influence potential re-hydrogen bonding. Under certain reaction conditions, the global reaction rate did not follow the Arrhenius pattern and can be explained by the fact that the temperature influences not only the hydrolysis of the glycosidic linkages but also the non-reactive external factors.



(6) A working kinetic model was proposed which attempts to depict why yields of glucose from yellow poplar cellulose vary with reactor configuration.

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