Cellulose Hydrolysis Under Extremely Low Sulfuric Acid and High-Temperature Conditions

JUN SEOK KIM,[1] Y. Y. LEE,*,[1] AND ROBERT W. TORGET[2]

[1]*Department of Chemical Engineering,
230 Ross Hall, Auburn University, Auburn, AL 36849,
E-mail: yylee@eng.auburn.edu;
and [2]National Renewable Energy Laboratory, Golden, CO, 80401*

Abstract

The kinetics of cellulose hydrolysis under extremely low acid (ELA) conditions (0.07 wt%) and at temperatures >200°C was investigated using batch reactors and bed-shrinking flow-through (BSFT) reactors. The maximum yield of glucose obtained from batch reactor experiments was about 60% for α-cellulose, which occurred at 205 and 220°C. The maximum glucose yields from yellow poplar feedstocks were substantially lower, falling in the range of 26–50%. With yellow poplar feedstocks, a large amount of glucose was unaccounted for at the latter phase of the batch reactions. It appears that a substantial amount of released glucose condenses with nonglucosidic substances in liquid. The rate of glucan hydrolysis under ELA was relatively insensitive to temperature in batch experiments for all three substrates. This contradicts the traditional concept of cellulose hydrolysis and implies that additional factors influence the hydrolysis of glucan under ELA. In experiments using BSFT reactors, the glucose yields of 87.5, 90.3, and 90.8% were obtained for yellow poplar feedstocks at 205, 220, and 235°C, respectively. The hydrolysis rate for glucan was about three times higher with the BSFT than with the batch reactors. The difference of observed kinetics and performance data between the BSFT and the batch reactors was far above that predicted by the reactor theory.

Index Entries: Yellow poplar; cellulose hydrolysis; bed-shrinking flow-through reactor; kinetics.

Introduction

The acid-based treatment of biomass is gaining its position as a viable saccharification process. Among the notable indicators of such is the

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

emergence of the BCI biomass-to-ethanol plant (Jennings, LA) and the Total Hydrolysis Process of National Renewable Energy Laboratory (NREL), Golden, CO *(1)*. The latter is built on three unique technical elements: employing extremely low acid (<0.1%) and high reaction temperature, applying a countercurrent moving bed scheme in the reactor design, and utilizing the bed-shrinking phenomena as a means to improve the reactor performance.

There are distinct advantages of using extremely low acid (ELA) conditions for hydrolysis of lignocellulosic biomass. The low acidity minimizes the gypsum production, if any. The corrosion characteristics of ELA are close to those of neutral aqueous reaction so that standard-grade stainless steel equipment can be used instead of high nickel alloy. ELA gives a significant cost advantage in the equipment. A process using ELA also qualifies as a "green technology" because it has a minimal environmental effect. The recent advancement made in this technology has brought the acid hydrolysis process to a position where it can compete with the enzymatic hydrolysis process in the overall process economics. This breakthrough technology has been proven on an ideally behaving bench-scale kinetic reactor system. An upscale experimental investigation using a continuous countercurrent reactor is being conducted at NREL.

The ELA reaction conditions are beyond the region normally explored in the conventional acid hydrolysis processes. Recent findings at NREL have proven that yields in the vicinity of 90% are attainable under ELA conditions. The NREL data also suggest that the reaction mechanism may be quite different in this region from those found in conventional processes. The present study was undertaken to provide further insights and kinetic data on the reactions taking place under ELA conditions.

Materials and Methods

Material

Yellow poplar sawdust feedstock was provided by NREL. The chemical composition of a representative sample was 45.2% glucan, 15.8% xylan, and 18.4% Klason lignin. It was milled to pass through a 2-mm screen before use. The composition of prehydrolyzed yellow poplar was 68.9% glucan and 26.9% Klason lignin. The prehydrolysis conditions were 174 and 204°C/10 min using 0.07 wt% sulfuric acid by percolation reactor *(2)*.

Batch Kinetic Experiments

All batch reactor experiments were performed using sealed tubular reactors. The reactors (13.5 cm^3 of internal volume) were constructed out of Hastelloy C-276 tubing (0.5 in. [1.27 cm]). Both ends of the reactor were capped with Swagelok end caps measuring 0.5 in. (1.27 cm) wide and 6 in. (15.24 cm) long. The reactors were packed with 0.8 g of solid substrate and 8 mL of acid solution to achieve a solid-to-liquid ratio of 1:10. The sulfuric acid concentration was 0.07 wt% (pH 2.2). The reaction temperatures were
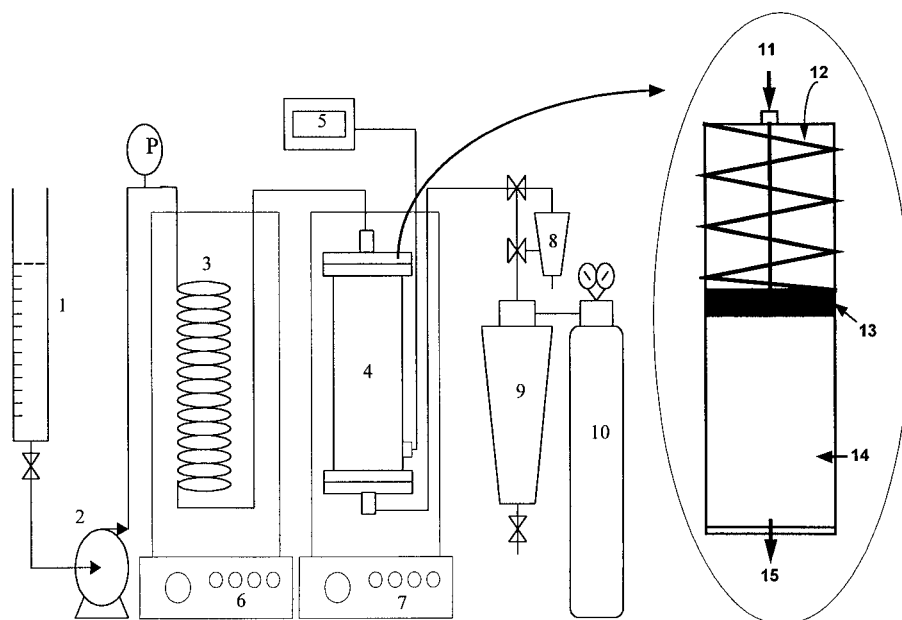
Fig. 1. Laboratory setup for BSFT reactor system: 1, liquid tank; 2, metering pump; 3, preheating coil; 4, bed-shrinking reactor; 5, thermometer; 6 and 7, temperature programmable sand bath; 8, sampling port; 9, pressure holding tank; 10, N_2 gas; 11, acid fluid inlet; 12, spring; 13, movable end; 14, compressed solid biomass; 15, liquid outlet.

controlled in sand baths. The reactors were first submerged into a sand bath set at 50°C above the desired reaction temperature for rapid preheating. The reactors were then quickly transferred into another sand bath set at the precise desired reaction temperature. The reactor temperature was monitored by a thermocouple inserted into the reactor. Reaction temperatures of 205, 220, and 235°C were applied. After the desired reaction time, the reaction was quenched in an ice bath. The contents of the reactor were separated into liquid and solid by filtration and subjected to analyses.

Bed-Shrinking Flow-Through Kinetic Experiments

The bed-shrinking flow-through (BSFT) reactor system invented by NREL is described in Fig. 1. The main body of the reactor is Hastelloy C276 tubing (2 in. [5.08 cm]). The internal volume was 294.4 cm^3. The Hastelloy C276 tubing (1/8 in. [1.6 mm] od ×0.03 in. [0.8 mm] id) was used to connect the reactor with other components of the system as well as for the preheating coil. The reactor, ancillary tubing, pump assembly, and collection system were connected and pressurized to 400 psig with N_2 gas. The flow rate of the BSFT runs was kept at 30 mL/min. The amount of initial biomass was 60 g. The reactor is equipped with an internal spring to compress the bed in the reactor as hydrolysis occurs. When the reaction reached the desired time, the flow was stopped and the reactor was quenched in cold water. The

liquid sample was collected from the liquid holding tank, and the remaining solid was taken from the reactor for further analysis of composition.

Analytical Methods

The sugars were determined by high-performance liquid chromatography using Bio-Rad Aminex, HPX-87P columns *(3,4)*. A refractive index detector was used. The compositional analysis of all biomass solid samples was carried out by the NREL standard methods *(5)*. The sugars in the liquid sample were determined after being subjected to a secondary acid hydrolysis. The conditions of secondary hydrolysis were 4 wt% sulfuric acid, 121°C, and 1 h.

Results and Discussion

The ELA conditions have been applied mostly for hemicellulose hydrolysis, primarily as a method of pretreatment for the enzymatic hydrolysis. For the past several years, however, it has been investigated from a different angle and with a different purpose at NREL—as a means of cellulose hydrolysis. This work has produced remarkable results in that unusually high glucose yields have been achieved. Yields were particularly high when the experiments were conducted with a BSFT reactor. The observed yields are far above the level projected by the known kinetics, often exceeding 90%. The high yields could not be explained solely from the reactor analysis. In our opinion, there are factors in the kinetics of hydrolysis unique to ELA yet to be identified. Consequently, we became interested in reconfirming the NREL experiments and in seeking explanations for these findings.

Batch Reactions

The reaction kinetics under ELA is far from being established. The literature data on acid hydrolysis of glucan under the ELA conditions are currently limited to those of NREL. In the initial experiments, we conducted a series of batch runs for α-cellulose using 0.07 wt% of sulfuric acid, at varying temperatures of 205, 220, and 235°C. The reaction progress is summarized in Fig. 2. The results are shown in terms of the percentage of glucan remaining in solid and the percentage of glucose released in liquid. The maximum yield of glucose obtained from the α-cellulose was about 60% for 205 and 220°C. However, the maximum yield at 235°C was actually <40%. This is contrary to the conventional concept of cellulose hydrolysis, in which higher yields are obtained at higher temperature, because the activation energy for hydrolysis is higher than that of the decomposition reaction.

The same batch experiments were also conducted using yellow poplar as the feedstock. The overall reaction profiles on the percentage of glucan remaining and the percentage of glucose released were similar to those of α-cellulose runs (Fig. 3). The yield of glucose released increased slightly as
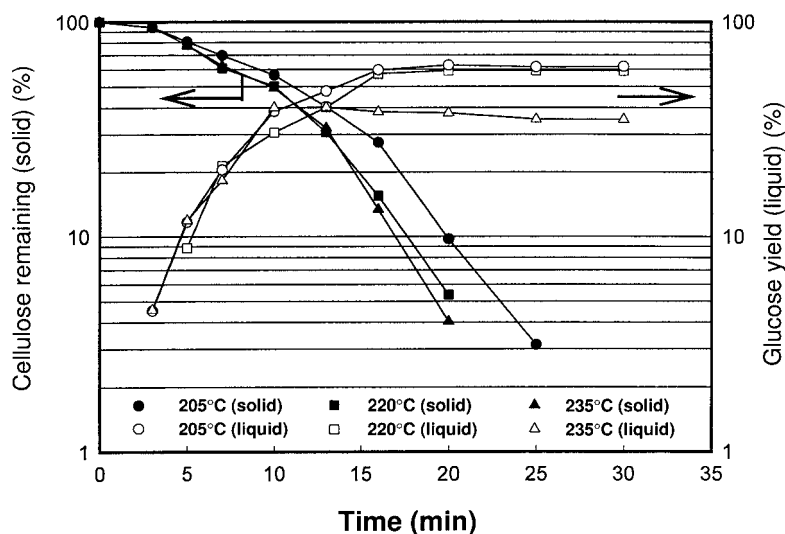
Fig. 2. Semilog plot of cellulose remaining and glucose yield in batch reaction of α-cellulose (0.07 wt% H_2SO_4).
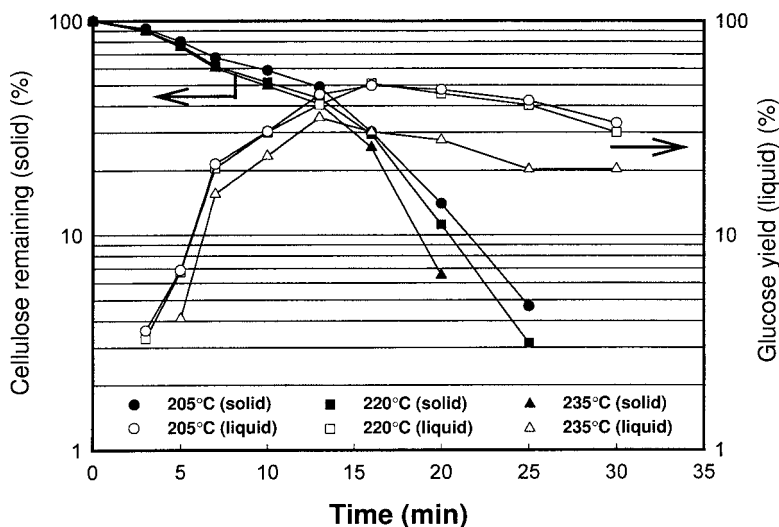

Fig. 3. Semilog plot of glucan remaining and glucose yield in batch reaction of untreated yellow poplar (0.07 wt% H_2SO_4).

the temperature was raised. However, the maximum yield of glucose from yellow poplar was much lower than that from α-cellulose for all three temperatures. The difference was most significant at 235°C, at which the maximum observed batch yield was only 35.2% for yellow poplar feedstock, a drastic departure from the 59.2% observed for α-cellulose. Although there was a similar tendency in the reaction profiles, the batch glucose yields obtained with prehydrolyzed (xylan-free) yellow poplar feedstocks were
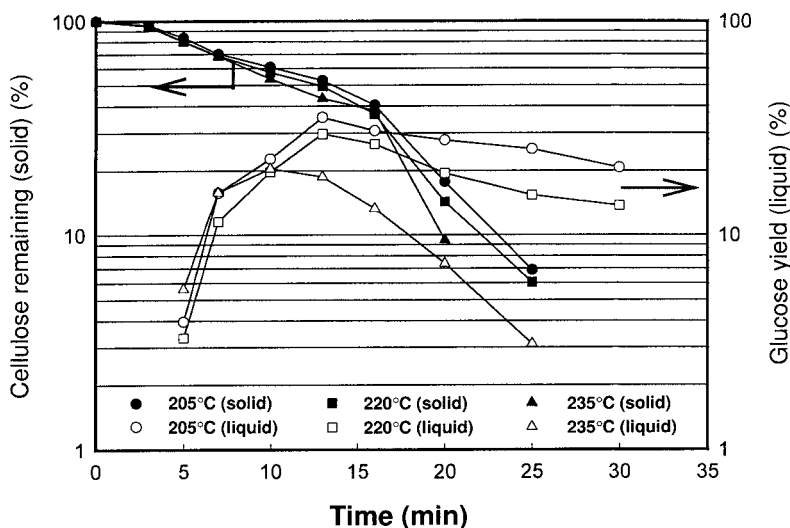
Fig. 4. Semilog plot of glucan remaining and glucose yield in batch reaction of pretreated yellow poplar (0.07 wt% H_2SO_4).

substantially lower than those of the untreated feedstocks for all temperatures (Fig. 4). This is not unique to the ELA conditions; it has been observed in hydrolysis with a higher acid level. The pretreated biomass had a higher fraction of crystalline cellulose, since the easily hydrolyzable glucan was removed during the prehydrolysis process. Prehydrolysis therefore makes the feedstock more difficult to hydrolyze when it comes to acid hydrolysis.

The batch data clearly indicate that the glucose yields from lignocellulosic feedstock (yellow poplar) are substantially lower than those from α-cellulose. One of the potential reasons is that the extraneous materials in the lignocellulosic biomass have a certain degree of buffering capacity for acids *(6)*. The acidity of the liquid, and thus the reactivity, might have been affected. The data in Figs. 2–4, however, preclude this because the decay curves of glucan are essentially the same for α-cellulose and yellow poplar. The hydrolysis reactivity is obviously not affected significantly by the presence of the extraneous materials. Furthermore, the solid-to-liquid ratio applied in the batch experiments was high enough (1:10) to mimic the buffering effects of the biomass.

Another interesting point seen from the batch hydrolysis experiments is that the glucan hydrolysis in solid was relatively insensitive to temperature for all three substrates. The difference in overall slope, although not straight lines, was <10% over the temperature span of 40°C. If one calculates the activation energy for the glucan hydrolysis with the data obtained in this study (ELA), it is approx 1 kcal/mol, an order of magnitude lower than those reported for conventional cellulose hydrolysis. This again contradicts the traditional cellulose hydrolysis and further indicates that there are additional factors and reactions in the hydrolysis under ELA. The estimated rate of glucose decomposition in the traditional sense (glucose to
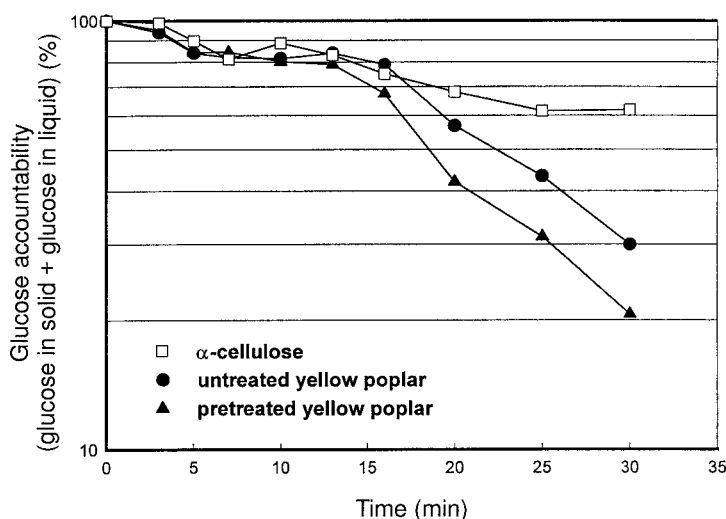
Fig. 5. Semilog plot of glucose accountability for various substrates at 220°C.

hydroxymethyl furfural [HMF]) under the ELA conditions does not fully account for the low yields observed with the yellow poplar feedstocks. What happens to the released glucose under the ELA conditions is uncertain. Some of it would decompose to HMF *(7–9)*, some may recondense with remaining cellulose or lignin (soluble and insoluble), and some may repolymerize as suggested by Conner et al. *(10)*. To verify this point, we prepared a separate plot from the batch data. In this plot, the accountability of glucose, defined as glucan in solid plus the glucose in liquid, is plotted against time for both α-cellulose and yellow poplar (Fig. 5). The difference in the accountability is relatively small between the prehydrolyzed and untreated yellow poplar (lower two curves). However, there is a substantial difference between α-cellulose and yellow poplar. The difference of the accountability occurs only at the latter phase of the reaction, at which the soluble lignin and extraneous compounds tend to accumulate and the released glucose is at a high level. We also note that the true decomposition of glucose under acidic conditions is independent of the feedstock. These findings collectively indicate that the low yields for the lignocellulosic feedstock are primarily owing to the interaction of the released glucose with the nonglucosidic compounds in the liquid. The unaccounted glucose would most likely exist in a condensed form with nonglucosidic substances, which includes the solubilized lignins. However, the existence of the condensed products is yet to be proven. In any event, there is much to be learned regarding the fundamental aspects of the reactions occurring under the ELA conditions.

BSFT Reactor

A series of experiments were conducted using the BSFT reactor invented by NREL. This reactor was used in its original design without any
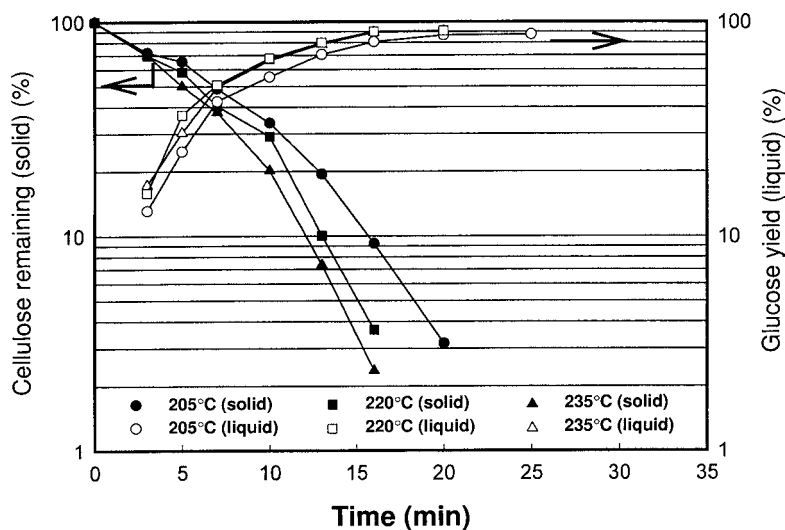
Fig. 6. Semilog plot of cellulose remaining and glucose yield for BSFT reactor, untreated yellow poplar (0.07 wt% H_2SO_4).

Table 1
Maximum Glucose Yields of Batch and BSFT Reactor

Reactor/feedstock	Maximum yield (%)/ reaction time (min)		
	205°C	220°C	235°C
Batch (alpha-cellulose)	61.77/30	59.23/25	40.17/16
Batch (pretreated yellow poplar)	26.62/16	35.45/13	20.43/10
Batch (untreated yellow poplar)	49.82/16	50.98/16	35.22/13
Bed-shrinking (untreated yellow poplar)	87.54/25	90.32/20	90.78/20

modification. The experiments were conducted at 205, 220, and 235°C using 0.07 wt% H_2SO_4. The feedstock was untreated yellow poplar. The shrinking-bed reactor operation was stopped at a desired point in the reaction time; therefore, each run provided only one data point. For each reaction condition, the experiments were repeated to obtain nine data points over the reaction time. The results are summarized in Fig. 6 and Table 1.

The results we obtained are indeed astonishing in that the glucose yields of 87.5, 90.3, and 90.8% were obtained at respective temperatures of 205, 220, and 235°C. The concentrations of glucose in these runs were 2.25, 2.37, and 2.47 wt%, respectively—certainly in a usable range. We have essentially reproduced the results obtained at NREL involving BSFT reactors that can achieve yields in the vicinity of 90%. In addition, we expanded the temperature range down to 205°C. Although the yield is somewhat lower at 87.5%, the low-temperature (205°C) run offers economic benefits
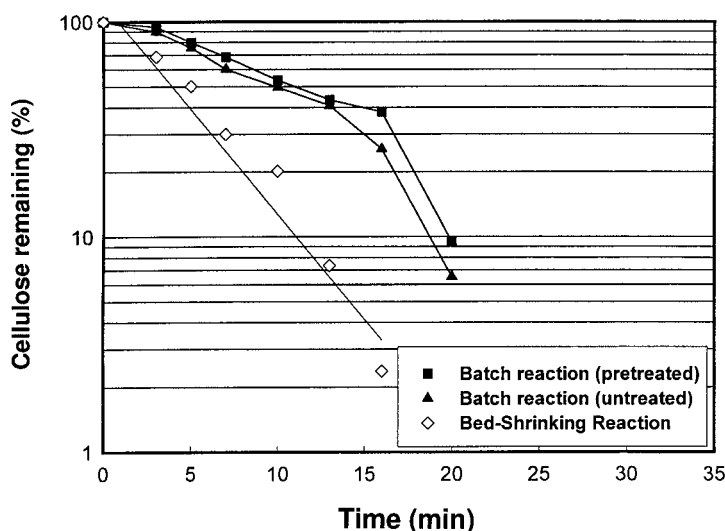
Fig. 7. Hydrolysis profiles of remaining glucan for batch and BSFT reactors at 235°C.

in other areas (lower equipment cost and energy input). It may prove to be a desirable operating condition.

We have previously conducted a modeling investigation that ascertains the positive effect of a bed-shrinking reactor *(11)*. However, the difference in observed kinetics and performance data between the BSFT and batch reactors is far above that predictable by the reactor theory in lieu of the solid-liquid contact pattern. One should also realize that the simplistic approach of representing the acid hydrolysis of cellulose as one set of serial-parallel reaction patterns is grossly inadequate under the ELA conditions.

The drastic difference in reactor performance between the batch and BSFT reactors is reaffirmed in Fig. 7. Here, the semilog plots for the remaining glucan are shown for the batch and BSFT reactors. It is clearly seen that the hydrolysis rate for glucan (estimated from the initial slopes) is about three times higher with the BSFT reactor than with the batch reactors. What causes this difference remains a mystery. For it to be fully understood, the detailed reaction mechanism of this heterogeneous catalytic reaction must be verified, and, therefore, further research is necessary.

Acknowledgments

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