Bed-Shrinking Flow-Through Reactor in Dilute Acid Hydrolysis of Cane Bagasse Cellulose

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Abstract: The kinetics of cellulose hydrolysis under dilute acid conditions (1.0, 2.0, and 3.0 wt.%), including extremely low acid (ELA) conditions (0.07 wt.%) and a temperature range of 180-220°C were investigated using batch reactors and bed-shrinking flow-through (BSFT) reactors. The maximum yield of glucose obtained from the batch reactor experiments is about 30% from sugarcane bagasse which occurred at 200 and 210°C. The maximum glucose yields from pre-treated bagasse feedstocks based on a BSFT reaction increased to 55%. With sugarcane bagasse feedstocks, a large amount of glucose is unaccounted for in the latter phase of batch reactions. Therefore, to improve the BSFT reactor performance, a two-stage BSFT reaction was applied using hydrogen peroxide. It appears that a half amount of K. lignin was released during the first-stage reaction, while the maximum glucose yield increased through the second-stage BSFT reaction. The maximum yield of glucan hydrolysis using the two-stage BSFT reaction under ELA conditions at a high reaction temperature was much higher than that from the batch and BSFT reactions. In the experiments using a two-stage BSFT reaction, a glucose yield of 63% was obtained for sugarcane bagasse feedstocks at respective temperatures of 210 and 220°C under ELA conditions.

Keywords: sugarcane bagasse, cellulose hydrolysis, bed-shrinking flow-through reactor

Introduction

Biomass treatment using an acid based treatment has a much longer history than the enzymatic process. Acid-catalyzed wood saccharification has been used in Germany as early as the 1940s [1]. In recent years, however, the treatment of a lignocellulosic biomass with dilute sulfuric acid has become the primarily means of pretreatment in the enzymatic hydrolysis of cellulose. Conventional dilute-acid based cellulose hydrolysis is an unpopular concept as it is known to pose inherent technical problems yet. Despite the diminished interest in acid technology, a number of different reactor configurations have still been proposed and investigated, and such a plug-flow reactor, percolation reactor [2,3], progressive batch/percolation reactor [4], and counter-current and co-current reactors [5]. The current authors, in coordination with a research team at the New Renewable Energy Lab (NREL), have been working on the development of a novel biomass saccharification process using an extremely low acid (ELA) catalyst [6,7]. This process is based on three unique technical elements: (a) employing an extremely low acid (less than 0.1%) and high reaction temperature, (b) applying a counter-current moving bed scheme in the reactor design, and (c) utilizing the bed-shrinking phenomenon as a means to improve the reactor performance.

ELA reaction conditions are beyond the region normally explored in conventional acid hydrolysis processes. However, recent findings have proven that yields with yellow poplar feedstock using a bed-shrinking flow-through (BSFT) reactor in the vicinity of 90% are attainable under ELA conditions [7]. Accordingly, the current study conducted a two-stage BSFT reaction with hydrogen peroxide under ELA condition to improve the reactor performance. As a result, the process obtained a maximum glucose yield of over 63% from...
sugarcane bagasse. This data also suggests that the reaction mechanism may be quite different in this region compared to those found in conventional processes. As such, the current investigation was undertaken to provide further insights and kinetic data on the reactions taking place under ELA conditions.

**Materials and Methods**

**Materials**

The sugarcane bagasse feedstock was provided by BCI, Jennings, L.A. The chemical composition of a representative sample was 37.38% glucan, 17.89% xylan, and 21.74% Klasson lignin. The feedstock was milled to pass through a 2 mm screen before use. The composition of the pretreated yellow poplar was 56.05% glucan and 19.15% Klasson lignin. The pretreated conditions were 175°C/20 min. using hot water based on a bed-shrinking flow-through reactor under 20 mL/min flow rate.

**Batch Kinetic Experiments**

All the batch reactor experiments were performed using sealed tubular reactors. The reactors (13.5 cm² internal volume) were constructed out of Hastelloy C-276 tubing (0.5” [1.27 cm]) due to its strength at elevated temperatures, and corrosion resistance. Both ends of the reactor were capped with Swagelok end-caps to a size of 0.5” (1.27 cm) diameter x 6” (15.24 cm) in length. The reactors were packed with 0.8 g of the solid substrate and 6.4 mL of the acid solution to achieve a solid to liquid ratio of 1:8. The sulfuric acid concentrations were 0.07, 1.0, 2.0, and 3.0 wt.%. 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 the next oil bath set at the precise desired reaction temperature. The reactor temperature was monitored by a thermocouple inserted into the reactor. Reaction temperatures of 180, 190, 200, and 210°C were applied. After the desired reaction time, the reaction was quenched in an ice bath.

**Bed-Shrinking Flow-Through Kinetic Experiments**

The bed-shrinking flow-through (BSFT) reactor system developed by NREL is described in Figure 1. The main body of the reactor was Hastelloy C276 tubing (2” [5.08 cm]). The internal volume was 253 cm³. The Hastelloy C276 tubing (1/8” [1.6 mm] O.D. x 0.03” [0.8 mm] I.D.) was also used to connect the reactor with the other system components and for the preheating coil. The reactor, ancillary tubing, pump assembly, and collection system were all connected and pressurized to 400 psig with N₂ gas. The flow rate of the BSFT runs was maintained at 20 mL/min. The amount of initial biomass was 30 g. The reactor was equipped with an internal spring to compress the bed in the reactor as hydrolysis occurred. When the reaction reached the desired time, the flow was stopped and the reactor was quenched in cold water. Liquid samples were collected from the liquid holding tank for further composition analysis.

**Analytical methods**

The sugars were determined by HPLC using Bio-Rad Aminex, HPX-87P columns [8]. A refractive index detector was also used. The compositional analysis of all the biomass solid samples was carried out based on NREL standard methods [9]. The sugars in the liquid samples were determined after being subjected to a secondary acid hydrolysis. The conditions of the secondary hydrolysis were 4 wt.% sulfuric acid, 121°C, and 1 hr.

**Results and Discussion**

Low acid conditions have mostly been applied for hemicellulose hydrolysis primarily as a method of pretreatment for enzymatic hydrolysis. However, the past over several years, low acid conditions have been investigated from a different angle and with a different purpose, namely as a means of cellulose hydrolysis. As a result, the use of extremely low acid and hydrogen peroxide has produced enhanced results in that unusually high glucose yields have been achieved. The yields are particularly high when the experiments have been conducted with a bed-shrinking flow-through reactor.
The observed yields have been far above the level projected by known kinetics, often exceeding 60%.

**Batch Reaction**

The reaction kinetics under dilute acid are still far from being established. In the initial experiments, a series of batch runs were conducted using cane bagasse and pretreated bagasse with 0.07, 1.0, 2.0, and 3.0 wt.% sulfuric acid, at varying temperatures of 180, 190, 200, and 210°C. The reactions are summarized in Table 1. The results are shown in terms of the maximum glucose yield released in the liquid under various reaction conditions (Figure 2). The maximum yield of glucose obtained from the cane bagasse increased to about 34% when the acid concentration and reaction temperature were increased to 34% for 200°C, respectively. However, the maximum yields at 210°C were not higher than those at 210°C. This is contrary to the conventional concept of cellulose hydrolysis where higher yields are obtained at a higher temperature because the activation energy for hydrolysis is higher than that of the decomposition reaction.

The same batch experiments were also conducted using pre-treated bagasse as the feedstock. The overall reaction profiles for the maximum glucose yield were similar to those of the sugarcane bagasse (Figure 3). The yield of glucose released increased as the temperature and acid concentration were raised.

Although there was a similar tendency in the reaction profiles, the batch glucose yields obtained with the pretreated bagasse feedstocks were substantially higher than those obtained with the untreated feedstocks (sugarcane bagasse) for all reaction conditions, except for four point conditions; acid concentrations of 2.0, and 3.0 wt.% and temperatures of 200 and 210°C. A pretreated feedstock can be easily attacked by acid due to loosened lignocellulosic structure. For a hardwood substrate, like yellow poplar, the pre-treated biomass usually has a higher fraction of crystalline cellulose, since the easily hydrolysable glucan is removed during the pre-hydrolysis process. As such, the pretreatment (prehydrolysis) makes the feedstock more difficult to hydrolyze when it comes to acid hydrolysis. However, the sugarcane bagasse, an agricultural residue, produced contrary results. Although, the sugarcane bagasse did not have a lower fraction of crystalline cellulose than a hardwood biomass, the pretreatment process using a bed-shrinking flow-through reactor with hot water attained a lower fraction of K. lignin than that achieved when a percolation reactor with low acid.

**Bed-Shrinking Flow-Through Reaction**

A series of experiments were conducted using the NREL bed-shrinking flow-through (BSFT) reactor (See experimental section for description). The experiments were conducted under the same reaction conditions. The feedstocks were sugarcane bagasse and pre-treated bagasse. Five mL liquid samples were collected through the sampling port at each desired point in the reaction time, and the total maximum glucose yield obtained by integrating the glucose concentrations. The results of the sugarcane bagasse hydrolysis by the BSFT reactor are summarized in Figure 4 and Table 1.

The maximum glucose yield of 51.72% was obtained at a temperature of 200°C and acid concentration of 3.0 wt.%. Overall, the results were much higher than those with the batch reaction. The current authors previously conducted a modeling investigation to ascertain the positive effects of a bed-shrinking reactor.
As the reaction progresses, gradual depletion of biomass occurs, making the bed less dense. The spring-attached movable end then takes effect pressing the loose biomass particles maintaining the bulk packing density constant. However, the difference in the observed kinetics and performance data between the BSFT and the batch reactors was far above that predicted by the reactor theory in lieu of a solid-liquid contact pattern. For the acid concentration range of 1.0 to 3.0 wt.%, the maximum glucose yield of sugarcane bagasse increased substantially as the reaction temperature was increased. It was interesting finding to note the maximum yields in the reactions with a 0.07 wt.% acid concentration. Although 0.07 wt.% is an extremely low acid concentration, it was diluted over 10 times a concentration of 1.0 wt.%, the maximum yield with an acid concentration of 0.07 wt.% at all the applied reaction temperatures was almost the same as with 1.0 wt.%. It should also be noted that the simplistic approach of representing the acid hydrolysis of cellulose as a set of serial-parallel reaction patterns is grossly inadequate under ELA conditions.

**Bed-Shrinking Flow-Through Reaction with Pretreated Cane Bagasse**

An additional variation of the BSFT reaction was also investigated. In this case, pre-treated cane bagasse was applied as the feedstock for BSFT reaction under the same conditions as used for the original sugarcane bagasse, mentioned above. To prepare the pretreated cane bagasse, the BSFT reactor was used with hot water. The pretreated cane bagasse had a higher fraction of glucan and lower xylan and K. lignin than the original sugarcane bagasse. The results of BSFT the reaction with pretreated cane bagasse are summarized in Figure 5 and Table 1. The pattern of the released glucose yield was almost the same as the original sugarcane bagasse, yet the maximum yields were substantially higher than those of the original cane bagasse under all the reaction conditions. The maximum glucose yield was about 55% with an acid concentration of 3.0 wt.% at 190 and 200°C.

**Two-Stage Hydrolysis with Hydrogen Peroxide and Extremely Low Acid by BSFT**

Hydrogen peroxide is one of the few delignifying reagents that is environmentally benign. Currently, it is
Table 2. Composition of Pre-treated Bagasse Using BSFT with Hydrogen Peroxide

<table>
<thead>
<tr>
<th>Initial</th>
<th>Hydrogen peroxide concentration (wt.%)</th>
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<tbody>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Glucan</td>
<td>37.38</td>
</tr>
<tr>
<td>Xylan</td>
<td>17.89</td>
</tr>
<tr>
<td>K. Lignin</td>
<td>21.74</td>
</tr>
</tbody>
</table>

Table 3. Maximum Glucose Yield (%) From Two-stage Bed-shrinking Flow-through reaction.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Acid concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>180</td>
<td>54.47</td>
</tr>
<tr>
<td>190</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>58.63</td>
</tr>
<tr>
<td>210</td>
<td>63.53</td>
</tr>
<tr>
<td>220</td>
<td>63.25</td>
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widely used in the bleaching process in the pulp and paper industry. In the current study, hydrogen peroxide was applied to both delignifying and hemicellulose removal. For the first-stage, the BSFT reaction was conducted at 170°C for 20 min. with 0.5, 1.0, and 2.0 wt.-% hydrogen peroxide. The flow rate was maintained at 20 mL/min. The composition of the bagasse after the first-stage reaction is summarized in Table 2. Although the delignification using 2.0 wt.-% of the hydrogen peroxide was the best of the applied conditions, it broke the glucan more than the other. Therefore, 1.0 wt.-% of hydrogen peroxide was determined as the optimum pretreatment concentration for the first-stage. The second-stage was performed in the same BSFT reactor. In effect, the two-stage reaction involved a series reaction at two different temperatures and flow rates in one BSFT reactor. The two-stage BSFT reactions were conducted using 1.0 wt.-% of hydrogen peroxide and 0.07, 1.0, 2.0, and 3.0 wt.-% acid concentrations. The temperature was varied between 180 and 210°C. Table 3 and Figure 6 summarize the results. The maximum glucose yields were higher than those of the typical BSFT reaction for all the reaction conditions. The most astonishing point was the maximum yields under a 0.07 wt.-% acid concentration, which were higher than those with the other three acid concentrations (1.0, 2.0 and 3.0 wt.-%) for all the reaction conditions. The maximum yield of about 63% at 210 and 220°C was two times higher than that with the batch reaction. This phenomenon was very similar to previous results obtained with yellow poplar cellulose hydrolysis at a high temperature and extremely low acid concentration [7]. It was also evident that the hydrolysis rate for glucan

Figure 6. Maximum glucose yield for two-stage BSFT reaction with hydrogen peroxide and dilute acid.

(estimated from the initial slopes) was about three times higher with the BSFT than with the batch reactors. The reason for this difference is still a mystery, despite several theories. For a full understanding, the detailed reaction mechanism of this heterogeneous catalytic reaction needs to be verified.

References