*
_____

(jskim84@kyonggi.ac.kr[*])

ELA (Extremely Low Acid) hydrolysis of Lignocellulosic Biomass

Jun Seok Kim[*]
Department of Chemical Engineering, Kyonggi University, Suwon, Korea
(jskim84@kyonggi.ac.kr[*])

INTRODUCTION

Biomass treatment using acid based treatment has much longer history than the enzymatic process. Acid-catalyzed wood saccharification had been in operation in Germany as early as 1940s . In recent years, however, treatment of lignocellulosic biomass with dilute sulfuric acid has been primarily used as a means of pretreatment for enzymatic hydrolysis of cellulose. The conventional dilute-acid based cellulose hydrolysis has been an unpopular concept ever since it is known to pose an inherent technical problem. Despite the diminished interest in acid technology, a number of different reactor configurations have been proposed and investigated such as plug-flow reactor, percolation reactor, progressive batch/percolation reactor, counter-current, and co-current reactors. Our laboratory, in coordination with a research team at NREL, has been working on the development of a novel biomass saccharification process on extremely low acid (ELA) catalyst. This process is built upon three unique technical elements: (a) employing extremely low acid (less than 0.1%) and high reaction temperature, (b) applying counter-current moving bed scheme in the reactor design, and (c) utilizing the bed-shrinking phenomena as a means to improve the reactor performance. The ELA reaction conditions are beyond the region normally explored in the conventional acid hydrolysis processes. Recent findings have proven that the yields with yellow poplar feedstock using bed-shrinking flow-through (BSFT) reactor in the vicinity of 90% are attainable under the ELA conditions. In this study, two-stage BSFT reaction with hydrogen peroxide and ELA was conducted to improve the reactor performance. This process obtained over 63% of the maximum glucose yield from sugarcane bagasse. This data also suggest that the reaction mechanism may be quite different in this region from those found in the conventional processes. This investigation is undertaken to provide further insights and kinetic data on the reactions taking place under the ELA conditions.

MATERIALS AND METHODS

Material

Sugarcane bagasse feedstock was provided by BCI, Jennings,LA. The chemical composition of a representative sample was 37.38% glucan, 17.89% xylan, and 21.74% Klason lignin. It was milled to pass through a 2 mm screen before use. The composition of prehydrolyzed yellow poplar was 56.05% glucan and 19.15% Klason lignin. The prehydrolysis conditions was 175 ^{o}C / 20min. using hot water by bed-shrinking flow-through reactor under 20 mL/min of flow rate.

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]) because of its strength at elevated temperatures, and corrosion resistance. Both ends of the reactor were capped with Swagelok end-caps into a size of 0.5 in. (1.27cm) diameter x 6 in. (15.24 cm) length. The reactors were packed with 0.8 g solid substrate and 6.4 mL acid solution to achieve a solid to liquid ratio of 1:8. The sulfuric acid concentration was 0.07, 1.0, 2.0, and 3.0 wt.% . The reaction

temperatures were controlled in oil baths. The reactors were first submerged into oil bath set at 50°C above the desired reaction temperature for rapid preheating. The reactors were then quickly transferred into 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 NREL The main body of the reactor is Hastelloy C276 tubing (2 in. [5.08cm]). The internal volume was 253 cm^3. The Hastelloy C276 tubing (1/8 in. [1.6mm] O.D. x 0.03 in. [0.8mm] I.D.) was used to connect the reactor with other components of system as well as for 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 BSFT runs was kept at 20 mL/min. The amount of initial biomass was 30 g. The reactor is equipped with an internal spring to compress the bed in the reactor as hydrolysis occurs. When the reaction reached desired time, the flow was stopped and the reactor was quenched in cold water. The liquid sample was collected from liquid holding tank for further composition analysis.

RESULTS AND DISCUSSION

The low acid conditions have been applied mostly for hemicelluose 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, namely as a means of cellulose hydrolysis. This work by extremely low acid and hydrogen peroxide has produced enhanced results in that unusually high glucose yields have been achieved. Yields were particularly high when the experiments were conducted with a bed-shrinking flow-through reactor. The observed yields are far above the level projected by the known kinetics often exceeding 60%.

Batch Reaction

The reaction kinetics under dilute acid is far from being established. In the initial experiments, we have conducted a series of batch runs for cane bagasse and pre-treated bagasse using 0.07, 1.0, 2.0, and 3.0 wt.% sulfuric acid, at varying temperatures of 180, 190, 200, and 210 ^{o}C. The maximum yield of glucose obtained from the cane bagasse increased as reaction temperature and acid concentration were increased up to about 34 % for 200 ^{o}C. However, the maximum yields at 210 ^{o}C are not increased than those of 210 ^{o}C. It is contrary to the conventional concept of cellulose hydrolysis where higher yields are obtained at higher temperature because the activation energy for hydrolysis is higher than that of decomposition reaction. Although there was a similar tendency in the reaction profiles, the batch glucose yields obtained with pre-treated bagasse feedstocks are substantially higher than those of the untreated feedstocks (sugarcane bagasse) for all reaction conditions except for four point conditions, acid concentration of 2.0, and 3.0 wt.% and temperatures of 200, and 210 ^{o}C . Pre-treated feedstock can be easily attacked by acid cause of loosen lignocellulosic structure. For the hardwood substrate as like yellow poplar, the pre-treated biomass usually has higher fraction of crystalline cellulose since the easily hydrolysable glucan is removed during the pre-hydrolysis process. The prehydrolysis therefore makes the feedstock more difficult to hydrolyze when it comes to acid hydrolysis. For sugarcane bagasse, agricultural residue, however, there have contrary results. In this work, the sugarcane bagasse has not lower fraction of crystalline cellulose than that of hardwood biomass, but also pre-treated process using bed-shrinking flow-through reactor by hot water attained lower fraction of K. lignin than that of using percolation reactor by low acid.

Bed-Shrinking Flow-Throw Reaction

A series of experiments were conducted using the NREL invented bed-shrinking flow-through (BSFT) reactor (See experimental section for description). The experiments were conducted at the same reaction conditions. The feedstocks were sugarcane bagasse and pre-treated bagasse. The 5 mL of liquid samples are collected through the sampling port at each desired point in the reaction time, and total maximum glucose yield obtained by integration of glucose concentrations. The results we

have obtained that the maximum glucose yield of 51.72% at temperature of 200°C and acid concentration of 3.0 wt. %.   These results have much higher yield than those of batch reaction. We have previously conducted a modeling investigation that ascertains the positive effect of bed-shrinking reactor. However, the difference of observed kinetics and performance data between the BSFT and the batch reactors is far above that predictable by the reactor theory in lieu of the solid-liquid contact pattern. For the acid concentration range of 1.0 to 3.0 wt. %, the maximum glucose yields of sugarcane bagasse increased substantially as reaction temperature was increased. There is interested finding that the maximum yield in reactions of 0.07 wt.% acid concentration. Although 0.07 wt.% of acid concentration, extremely low acid, is diluted over 10 times to 1.0 wt.%, the maximum yield under 0.07 wt.% of acid concentration at all range of applied reaction temperatures almost caught up that of 1.0 wt.%. One should also realize the simplistic approach of representing the acid hydrolysis of cellulose as one set of serial-parallel reaction pattern is grossly inadequate under the ELA conditions.

Bed-Shrinking Flow-Throw Reaction with Pre-treated Cane Bagasse

An additional variation of of BSFT reaction was investigated. In this case, pre-treated cane bagasse was applied as a feedstock for BSFT reaction under same conditions of original sugarcane bagasse mentioned above. For prepare the pre-treated cane bagasse , BSFT reactor was used with hot water. Pre-treated cane bagasse has higer fraction of glucan , lower xylan and K. lignin than those of original sugarcane bagasse. The pattern of released glucose yield was almost same as original sugarcane bagasse but maximum yields were substantially higher than those of original cane bagasse at each reaction condition. The maximum glucose yield is about 55% under acid concentration of 3.0 wt.% at 190, and 200 ^{o}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 widely used in the bleaching process of pulp and paper industry. In this case, hydrogen peroxide was applied to not only delignifying but also hemicellulose removal properly.

For the first-stage, the BSFT reaction was conducted at 170 ^{o}C during 20 min. with 0.5, 1.0, and 2.0 wt. % hydrogen peroxide. Although the delignificaton using 2.0 wt.% hydrogen peroxide is the best of applied conditions, it could break the glucan much more than other. Therefore, 1.0 wt.% of hydrogen concentration was optimum to pretreatment for the first-stage. After the first-stage, the second-stage was performed in same BSFT reactor. Actually, two-stage reaction has a series reaction at two different temperatures and flow rates in one BSFT reactor. Two-stage BSFT reactions were conducted using 1.0 wt.% of hydrogen peroxide and 0.07, 1.0, 2.0, and 3.0 wt.% of acid concentration. The temperature was varied over the range of 180-210 ^{o}C. The most astonishing point is that the maximum yields under 0.07 wt.% of acid concentration. Those yields are higher than other three acid concentration (1.0, 2.0, and 3.0 wt.%) at each reaction condition. The maximum yield about 63% at 210, and 220 ^{o}C are two times higher than that of batch reaction respectively. This phenomenon is the almost same as what we have previously investigated about yellow poplar cellulose hydrolysis under high temperature and extremely low acid concentration. It is clearly seen that the hydrolysis rate for glucan (estimated from the initial slopes) is about three times higher with the BSFT than with the batch reactors. What causes this difference still remains as a mystery. For it to be fully understood, the detailed reaction mechanism of this heterogeneous catalytic reaction must be verified.

Acknowledgment

REFERENCES

1. Cahelar, D.R., Lee, Y.Y., and Chambers, R.P. (1979) Biotechnol. Bioeng., 25, 3-17
2. Song, S.K., and Lee, Y.Y. (1983) Chem. Eng. Commun., 17, 23-30
3. Torget, R.W., Kim, J.S., and Lee, Y.Y. (2000) Ind. Eng. Chem. Res., 39, 2817-2825

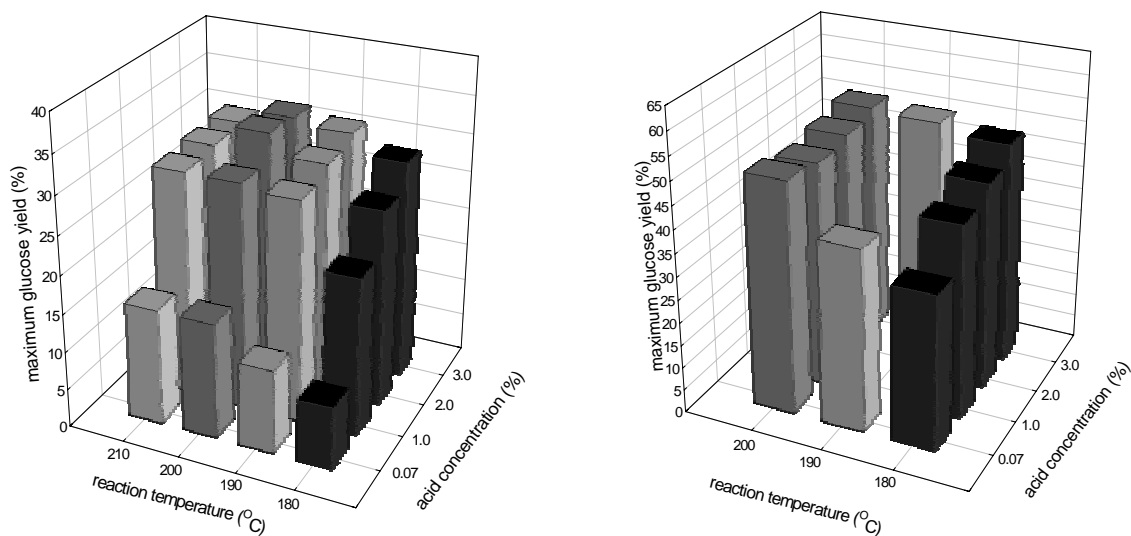4. Chen, R.W., Wu, Z.W., and Lee, Y.Y. (1998) Appl. Biochem. Biotechnol., 70/72, 37-49

Fig. Maximum glucose Yield of batch reaction for pre-treated (left) and BSFT reaction for untreated bagasse (right).
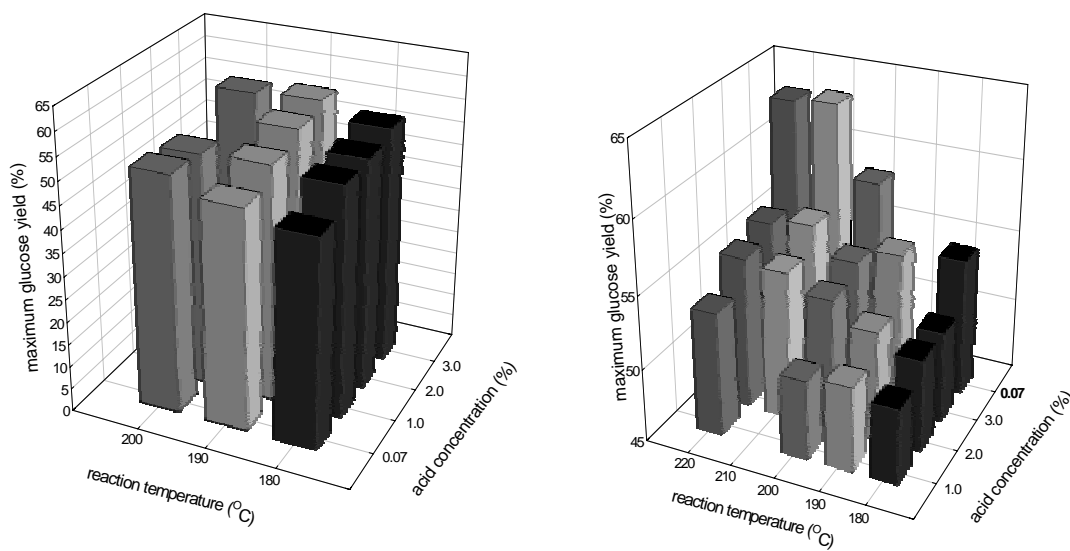
Fig. Maximum glucose Yield of BSFT reaction (left) and two-stage BSFT reaction with hydrogen peroxide (right).