Kinetic Characterization for Pretreatment of Timber Varieties and Switchgrass using Diluted Acid Hydrolysis

Shu Chiang Yat, David Shonnard
Department of Chemical Engineering, Michigan Technological University, Houghton, MI 49931

In recent years, growing attention has been devoted to the use of lignocellulosic biomass as a feedstock to produce renewable carbohydrates as a source of energy products, including liquid alternatives to fossil fuels. The benefits of developing woody biomass to ethanol technology are to increase the long-term national energy security, reduce fossil energy consumption, lower greenhouse gas emissions, use renewable rather than depletable resources, and create local jobs. Currently, research is driven by the need to reduce the cost of biomass-ethanol production. One of the preferred methods is to thermochemically pretreat the biomass material and subsequently, enzymatically hydrolyze the pretreated material to fermentable sugars that can then be converted to ethanol using specialized microorganisms. The goals of pretreatment are to remove the hemicellulose fraction from other biomass components, reduce bioconversion time, enhance enzymatic conversion of the cellulose fraction, and, hopefully, obtain a higher ethanol yield. The primary goal of this research is to obtain kinetic detailed data for dilute acid hydrolysis for several timber species from the Upper Midwest region of the United States and switchgrass. These results will be used to identify optimum reaction conditions to maximize production of fermentable sugars and minimize production of non-fermentable byproducts.

The structural carbohydrate analysis of the biomass species used in this project was performed using the procedure proposed by National Renewable Energy Laboratory (NREL). Subsequently, dilute acid-catalyzed hydrolysis of biomass, including aspen, basswood, balsam, red maple, and switchgrass, was studied at various temperatures, acid concentrations, and particle sizes in a 1-L well-mixed batch reactor (Parr Instruments, Model 4571). 25g of biomass and 500mL of diluted acid solution were added into a 1-L glass liner, and then put into the reactor. During the experiment, 5 mL samples were taken starting at 100^{o}C at 3 min intervals until reaching the targeted temperature (160, 175, or 190^{o}C), followed by 4 samples after achieving the desired temperature. The collected samples were then cooled in an ice bath immediately to stop the reaction. The cooled samples were filtered using 0.2 μm MILLIPORE membrane filter to remove suspended solids. The filtered samples were then analyzed using High Performance Liquid Chromatography (HPLC) with a Bio-Rad Aminex HPX-87P column, and refractive index detection to measure monomeric and polymeric sugars plus degradation byproducts.

A first order reaction model was assumed and the kinetic parameters such as activation energy and pre-exponential factor from Arrhenius equation were obtained from a match between the model and experimental data.

On the experiment run, the temperature increases linearly after 40 minutes during experiments. Xylose and other sugars were formed from hemicellulose hydrolysis over this heat up period until a maximum concentration was reached at the targeted temperature. However, negligible amount of xylose byproducts and small concentrations of other soluble sugars, such as mannose, arabinose, and galactose were detected during this initial heat up period. Very little cellulose hydrolysis yielding glucose was observed during the initial heat up period. On the other hand, the xylose was degraded to furfural while maintaining the targeted

temperature in the longer period. Nevertheless, the glucose yield from cellulose was increased in the later time.

The kinetic coefficient governing the generation of xylose from hemicellulose and the generation of furfural from xylose presented a coherent dependence on both temperature and acid concentration. However, no effect was observed in the particle size results. There were three types of biomass used in this project; hardwood (aspen, basswood, and red maple), softwood (balsam), and herbaceous crop (switchgrass). The activation energies and the pre-exponential factors of the timber species and switchgrass were in a range of 49 and 180 kJ/mol and from 7.5×10^{4} to 2.6×10^{20} min^{-1}, respectively, for the xylose formation model. In addition, for the degradation model, the activation energies and the pre-exponential factors were ranged from 130 to 170 kJ/mol and from 6.8×10^{13} to 3.7×10^{17} min^{-1}, respectively. The results compare favorably with the literature values given by Ranganathan et al, 1985. Overall, up to 92 % of the xylose was able to generate from the dilute acid hydrolysis in this project.