

Acid Hydrolysis of Cellulose in Zinc Chloride Solution

N. J. CAO, Q. XU, AND L. F. CHEN*

*Department of Food Science, Purdue University,
West Lafayette, IN 47907*

ABSTRACT

The efficient conversion of cellulosic materials to ethanol has been hindered by the low yield of sugars, the high energy consumption in pretreatment processes, and the difficulty of recycling the pretreatment agents. Zinc chloride may provide an alternative for pretreating biomass prior to the hydrolysis of cellulose. The formation of a zinc-cellulose complex during the pretreatment of cellulose improves the yield of glucose in both the enzymatic and acid hydrolysis of cellulose. Low-temperature acid hydrolysis of cellulose in zinc chloride solution is carried out in two stages, a liquefaction stage and a saccharification stage. Because of the formation of zinc-cellulose complex in the first stage, the required amount of acid in the second stage has been decreased significantly. In 67% zinc chloride solution, a 99.5% yield of soluble sugars has been obtained at 70°C and 0.5M acid concentration. The ratio of zinc chloride to cellulose has been reduced from 4.5 to 1.5, and the yield of soluble sugars is kept above 80%. The rate of hydrolysis is affected by the ratio of zinc chloride to cellulose, acid concentration, and temperature.

Index Entries: Cellulose; acid hydrolysis; zinc-cellulose complex; zinc chloride

INTRODUCTION

The hydrolysis of cellulose can be achieved with either acids or enzymes, but this process is economically unfavorable (1-3)). Because of their small molecular size, many acids can easily penetrate the crystalline structure of cellulose to achieve a pseudo-first-order sequential reaction at

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

relatively high temperatures (4,5). The major drawback of high-temperature acid hydrolysis comes from the simultaneous rapid decomposition of glucose (6). The products of the degradation inhibit the fermentation process of microorganisms. Acid hydrolysis of cellulose at low temperature is limited by the penetration rate of proton into the cellulose lattice. Therefore, pretreatment process that loosens up the cellulose crystalline structure is the key to enhancing the yield of glucose in the low-temperature process.

Cellulose fibers can be considered as the aggregation of elementary fibrils. For ideal hydrolysis, the individual fibrils of cellulose are completely separated via the destruction of their internal hydrogen bonding (7), and the individual glycoside bonds are exposed to the catalyst. This condition can only be met in a cellulose solution. In the solution, a relationship exists between the dissolved cellulose molecules and the solvent in forming water-soluble, stable, and chelated complexes that separate cellulose fibril to its individual cellulose molecules (8,9).

Zinc chloride is known to be an effective swelling agent of cellulose (10). In the 60–70% (w/w) concentration range, zinc chloride can also dissolve native cellulose and reduce the crystallinity of cotton. It has been reported that cellulose dissolved in the zinc chloride solution had a high hydrolysis rate, as well as high glucose yield and high final glucose concentration (11–13). Recently, we have found that low-DP-insoluble zinc-cellulose complexes can be prepared from native cellulose at 70°C with a ratio of zinc chloride to cellulose of 1.5 (w/w), and these complexes can be hydrolyzed effectively to glucose by enzymes (40 IU/g cellulose, 50°C, pH 4.8) and produced 14% (w/v) of glucose solution within 12 h at a yield > 93% (11).

The objective of this work is to improve the economics of acid hydrolysis of cellulose via the formation of zinc-cellulose complexes that can be carried out at a low temperature. For developing an economical process, the reduction of zinc-to-cellulose ratio is the most important factor. For this purpose, the rate of hydrolysis and yield of glucose were investigated as a function of the ratio of zinc chloride to cellulose, acid concentration, and temperature.

MATERIALS AND METHODS

Materials

Avicel pH 101 (Microcrystalline cellulose) was purchased from FMC (Newark, DE). Technical-grade zinc chloride was obtained from Ashland Chemical Company. Glucose, cellulose, and other chemicals were purchased from Sigma Chemical Company (St. Louis, MO).

Methods

Acid Hydrolysis of Cellulose in Zinc Chloride Solution

A 75% solution of zinc chloride (solution I) was prepared by dissolving 92 g solid zinc chloride in 30 mL water. An amount of cellulose was mixed with water to form cellulose slurry (50% w/w). Solution I was poured into cellulose slurry with thorough mixing at 70°C to form a cellulose solution (solution II, final concentration of zinc chloride ranged from 35 to 67% w/w). The required amount of hydrochloric acid was then added into solution II to start the acid hydrolysis process. Samples were withdrawn from the solution periodically and were added to anhydrous ethanol. When there was no cellulose precipitate formed in the ethanol solution, it implied the end of hydrolysis process. The sugar concentration in the sample was determined by HPLC. The zinc ions in the samples was maintained below 20 ppm by precipitating zinc ions with a saturated sodium carbonate solution. The glucose yield was calculated by glucose weight released by hydrolysis divided by the sum of cellulose weight multiplying cofactor 1.1.

Disappearance of Glucose in Zinc Chloride Solution

Glucose was dissolved in 67% (w/w) zinc chloride to form a 10% (w/v) glucose solution. An aqueous glucose solution containing 0.5N HCl was used as a control. The glucose solution was warmed at different temperatures (50–100°C) for 2 h and transferred into an ice bath for a rapid cooling. The glucose concentration in the solution was analyzed with a Glucose Analyzer (Beckman Instruments, Inc., Fullerton, CA) to calculate the disappearance of glucose.

Analytical Methods

The glucose concentration was measured with a Beckman Glucose Analyzer. Soluble sugars in hydrolysate were measured by HPLC (Waters 712 WISP system) with column ORH-801 (Interaction Chemicals, Inc.). Zinc content was determined with an atomic absorption spectrophotometer (2380, Perkin-Elmer).

RESULTS AND DISCUSSION

It is expected that cellulose hydrolysis proceeds faster in a liquid state than in the solid or colloid state. At a high concentration, the Hammett acidity of zinc chloride solution is near -2.0 . Under these conditions, the alcohol group of the anhydrous glucose is protonated, and cellulose can be easily dissolved and partially hydrolyzed at an elevated temperature. Like the hydrolysis of cellulose in solid state, cellulose in solution also can

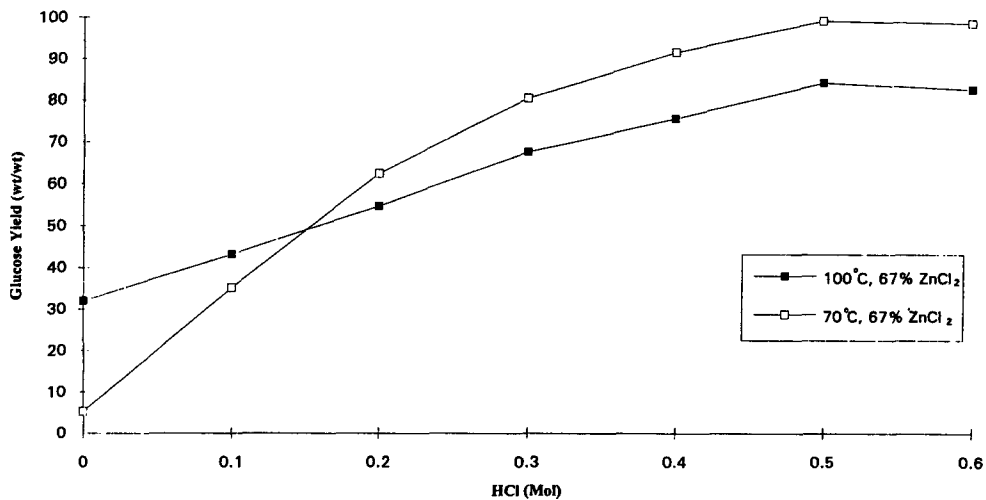


Fig. 1. Effect of acid concentration on glucose yield. Concentration of zinc chloride solution was 67% (w/w); the ratio of ZnCl₂ to cellulose was 18.0 (w/w); hydrolysis time was 2 h.

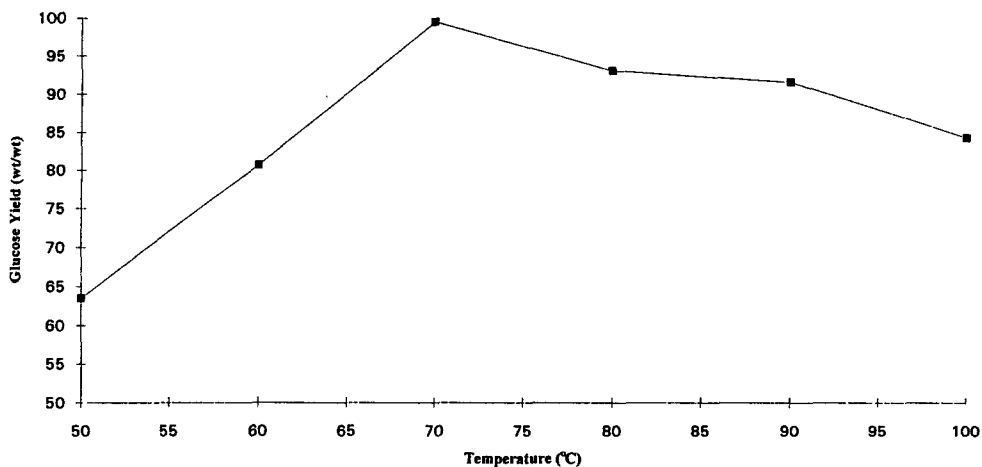


Fig. 2. Effect of temperature on glucose yield in zinc chloride solution. At different temperatures, 10.0 g cellulose were hydrolyzed in 67% zinc chloride for 2 h. 0.5M HCl was added in zinc chloride solution. The ratio of ZnCl₂ to Avicel was 18.0 (w/w).

be hydrolyzed by diluted acid to produce glucose. Figure 1 shows that above 0.5N acid concentrations, the maximal yield of glucose can be achieved in the experimental temperature range following the zinc chloride pretreatment of cellulose. When the reaction temperature is increased, both the rates of hydrolysis and degradation are simultaneously increased. The optimum temperature is approx 70°C (Fig. 2). Zinc chloride accelerates the hydrolysis of glycoside bonds by forming complexes with cellulose and decreases the concentration of hydrochloric acid required for pro-

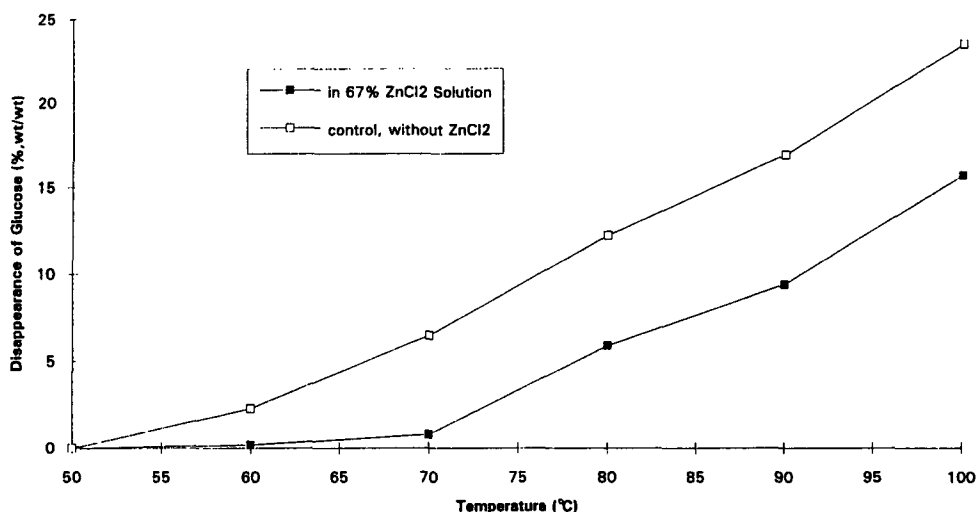


Fig. 3. Effect of concentrated zinc chloride on disappearance of glucose. At different temperatures, 10% (w/v) glucose solution was heated for 2 h. The residual glucose was detected with a glucose analyzer; the disappearance yield was calculated.

ceeding hydrolysis of cellulose. This phenomenon is also seen in the enzyme hydrolysis (11). It is important to note that cellulose cannot be efficiently hydrolyzed by zinc chloride solution without the presence of the additional acid.

In solution state, all the glycoside bonds of the cellulose molecules were exposed to the catalyst, and cellulose was converted to glucose quantitatively without a measurable amount of degradation at 70°C. Compared with Saeman and Fagan's results (14,15), the hydrolysis of solid cellulose in 3-5% dilute acid solution was temperature-dependent, and the hydrolysis took more than 24 h to complete with <50% glucose yield. When cellulose is pretreated with concentrated sulfuric acid, the cellulose become water-soluble. The soluble cellulose can be hydrolyzed by refluxing it in a dilute acid solution. The time for complete hydrolysis of the soluble cellulose is more than 3.0 h at reflux temperature. The above comparisons indicates that zinc-cellulose complexes can be hydrolyzed faster than solid cellulose and soluble cellulose. The rate of cellulose hydrolysis is controlled by acid concentration and temperature.

In zinc-cellulose solution, zinc chloride not only catalyzes the hydrolysis, but also drastically reduces the glucose degradation in the heating process by the forming of zinc-carbohydrate complex (Fig. 3). The rate of glucose degradation in 67% zinc chloride solution is 10% less than that in control at 100°C after heating for 2 h; the initial temperature of glucose degradation rose to 70°C. Combined with the data in Fig. 2, we can find that at this temperature, the process can obtain a higher soluble sugar yield and <1% disappearance of glucose.

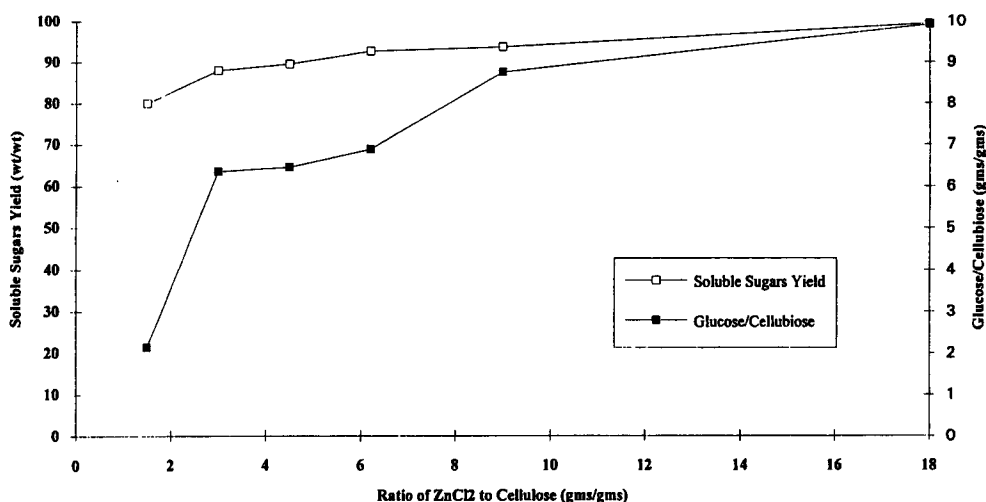


Fig. 4. Ratio of zinc chloride to cellulose and glucose yield. At 70°C, cellulose was hydrolyzed in a different ratio of zinc chloride to cellulose in the presence of 0.5M HCl.

For economical consideration, the concentration of zinc chloride and ratio of zinc chloride to cellulose are important factors. In zinc chloride solutions with the concentration ranging from 64 to 72%, cellulose can be rapidly liquefied in a few minutes to form cellulose solution (10). We have found that the maximum amount of cellulose dissolved in the zinc chloride solution depended on the molecular weight of cellulose. In a 70% (w/w) zinc chloride solution, the cellulose solubility was about 1 g of cellulose for each 2 mL of zinc chloride solution. The ratio of zinc chloride to cellulose in this mixture was 4.5 (12,16). By controlling the cellulose molecular weight with acid hydrolysis, the ratio of zinc chloride to cellulose can be decreased from 18 to 1.5 (Figs. 4 and 5), and the soluble sugar yield was gradually decreased from 99.5 to 80%. The decrease of soluble sugar yield was owing to the limited solubility of zinc-cellulose complex, the higher concentration of glucose that may repolymerize, and the slow degradation of glucose over a long hydrolysis time. When the ratio of zinc chloride to cellulose was above 9, >90% of the soluble sugars was glucose; if the ratio was between 6.2 and 3.0, the glucose percentage in the hydrolysate was kept at 85–87%. When the ratio was below 3.0, the concentration of cellulose rose sharply. Although the ratio of zinc chloride to cellulose was finally decreased step by step to 1.5, the cellulose hydrolysis was limited by lower water activity. Within 18 h of hydrolysis time, the maximum yield of soluble sugar was 80%, of which 53% was glucose (Figs. 4 and 5). Under this condition, the concentration of zinc chloride in cellulose solution was below 40% (w/w), and the carbohydrate concentration was about 30% (w/v). In order to obtain higher yield of glucose, therefore, a suitable water activity must be maintained.

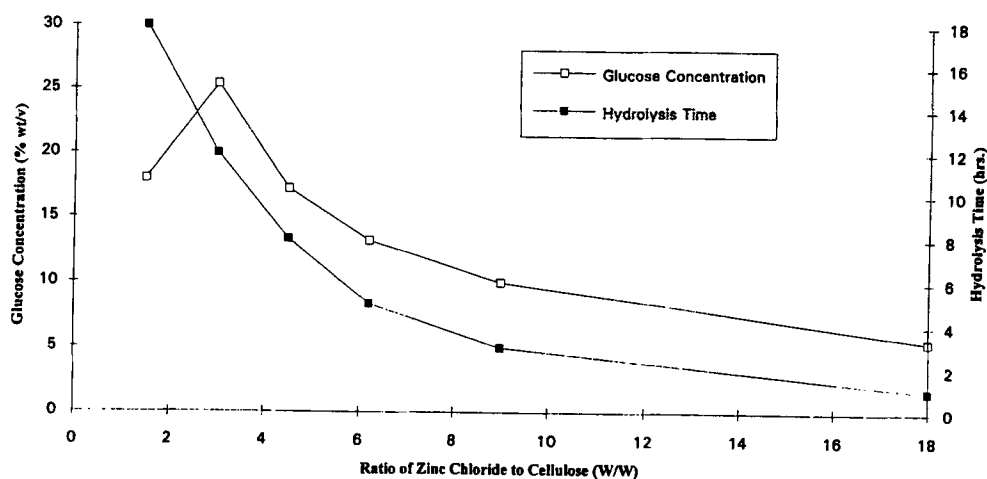


Fig. 5. Maximum concentration of glucose and hydrolysis time in different ratio of zinc chloride to cellulose. The condition of hydrolysis was the same as Fig. 4.

CONCLUSIONS

Concentrated zinc chloride solution is able to dissolve cellulose by the formation of a zinc-cellulose complex. In acid solution, these zinc-cellulose complexes in the solution can be hydrolyzed more easily than the solid cellulose and soluble cellulose from concentrated sulfuric acid. The hydrolysis can be carried out at a low ratio of zinc chloride to cellulose to increase the economic feasibility of the process.

REFERENCES

1. Walker, L. P. and Wilson, D. B. (1991), *Bioresource Technol.* **3**.
2. Zacchi, G., Skoog, K., and Hahn-Hagerdal, B. (1989), *Biotechnol. Bioeng.* **32**, 460.
3. Brenne, W. and Rugg, B. (1985), *Report of the Environmental Protection Agency EPA/600/S2-85/137*.
4. Wenzl, H. F. J. (1970); in *The Chemical Technology of Wood Academic*, New York, p. 157.
5. Schwald, W. and Bobleter, O. (1989), *J. Carbohydr. Chem.* **8**, 565.
6. Mok, W. Shu-Lai, and Antal, M. J., Jr. (1992), *Ind. Eng. Chem. Res.* **31**, 94.
7. Abatzoglou, N., Bouchard, J., and Chornet, E. (1986), *The Can. J. Chemical Eng.* **64**, 781.
8. Nikitin, N. I. (1966), *The Chemistry of Cellulose and Wood*, Israel Program for Scientific Translation, p. 74.
9. Chen, L. F. and Gong, C. S. (1982), *Biotechnol. Bioeng. Symp.* **12**, 57.

10. Patil, N. B., Dweltz, N. E., and Radhakrishnan, T. (1965), *Textile Res. J.* **35**, 517.
11. Cao, N. J., Xu, Q., Chen, C. S., Gong, C. S., and Chen, L. F. (1994), *Appl. Biochem. Biotechnol.* **45/46**, 521.
12. Chen, L. F. and Yang, C. M. (1985), US Patent 4,525,210, June 25.
13. Cao, N. J., Chen, C. S., Xu, Q., Gong, C. S., and Chen, L. F. (1992), *Fourteen Symposium on Biotechnology for Fuels and Chemicals*.
14. Saeman, J. (1945), *Ind. Eng. Chem.* **37**, 43.
15. Fagan, R. D., Grethlein, H. E., et al. (1971), *Environ. Sci. Technol.* **5**, 545.
16. Chen, L. F., Yang, C. M., and Clark, N. J. (1984), US Patent 4,452,640, June 5.