A new route to improved glucose yields in cellulose hydrolysis

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Abstract

An unusual inverse temperature-dependent pathway was discovered for cellulose decrystallization in trifluoroacetic acid (TFA). Cellulose was completely decrystallized by TFA at 0 °C in less than 2 hours, a result not achieved in 48 hours at 25°C in the same medium. The majority of TFA used in cellulose decrystallization was recycled via a vacuum process. A small remaining amount of TFA was diluted with water to make a 0.5% TFA solution and used as a catalyst for hydrolysis. After one minute at 185 °C under batch conditions, the glucose yield reached 63.5% without production of levulinic acid. In comparison, only 15.0% glucose yield was obtained in the hydrolysis of untreated cellulose by 0.5% H_2SO_4 under the same conditions. Further improvement of glucose yield is possible by optimizing reaction conditions. Alternatively, the remaining TFA can be completely removed by water while keeping the regenerated cellulose in a highly amorphous state. This regenerated cellulose is much more reactive than untreated cellulose in hydrolysis reactions. The lower temperatures and shorter reaction times with this activated cellulose makes it possible to reduce operating costs and decrease byproduct yields such as HMF and levulinic acid.

Keywords: Cellulose; trifluoroacetic acid; TFA; crystallinity; decrystallization; glucose; hydrolysis; amorphous; XRD; FTIR.

1. Introduction

Cellulose is the most abundant renewable resource available for the production of fuels and industrial chemicals. The crystal structure and hydrogen bonding in cellulose greatly limit access by reactants and catalysts to the β-1,4-glycosidic bonds. Water, for example, is almost completely excluded from the crystalline regions in cellulose. [1, 2] This limitation is one reason that hydrolysis of cellulose is much slower than starch. Cellulose decrystallization remains a major bottleneck in cellulose conversion by chemical and biological processes.

The acid-catalyzed hydrolysis of cellulosic materials was industrialized almost a century ago. [3] Although high sugar yields can be obtained in concentrated acid hydrolysis processes, the high cost to recover the acid makes this economically unviable. In dilute acid hydrolysis processes glucose yields have been limited to below 60%. [4-6] Glucose yield must be improved to make the dilute acid process more economically viable. Glucose degradation [7] and cellulose modification [8-9] are two factors that limit glucose yields in dilute acid hydrolysis. Pre-activation, by transforming crystalline cellulose to amorphous cellulose (decrystallization), allows mild conditions to be used in hydrolysis and thus reduces glucose degradation and inhibitory cellulose modifications during reactions.

Sulfuric acid is widely used in both concentrated and dilute acid hydrolysis processes. The process to recover sulfuric acid after hydrolysis is tedious. Trifluroacetic acid (TFA) is a volatile acid and can be potentially recycled after hydrolysis by distillation. However, concentrated TFA has to be used to obtain high glucose yields in cellulose hydrolysis. [10-13] For example using diluted TFA (2N), less than 3% of cellulose was hydrolyzed after 75 minutes at 120 °C. [14] Using concentrated TFA allows for dissolution of the cellulose and provides a process that is nearly homogeneous. Diluting TFA, by adding water, causes the loss of its dissolving capability and results in a heterogeneous process.

In this paper, we used concentrated TFA to quickly decrystallize cellulose at 0 °C and recycled the majority of TFA via vacuum evaporation. The residual TFA was diluted to 0.5 % and used as a catalyst for cellulose hydrolysis. Alternatively, this residual TFA was removed by washing the cellulose with water to prepare a highly amorphous cellulose sample. This pre-activated amorphous cellulose was compared with untreated cellulose in dilute acid hydrolysis using 0.5 % H_2SO_4.

2. Materials and methods

2.1 Sample preparation

Cellulose (cotton linters, product no. C6663) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich. Cellulose and trifluoroacetic acid (1:15 mass ratio) were mixed at 0 °C for 2 hours in a sealed flask. After treatment, the sample was exposed to a vacuum (30 mtorr) at room temperature for 2 hours and at 105 °C for 12 hours. The sample was named as cellulose_TFA. By comparing the cellulose mass before and after treatment, it was determined that the residual TFA in the sample was 12 wt%. A portion of this sample was washed by water for 12 hours, filtered and dried at 105 °C for 24

hours. The water-washed sample was named cellulose_wash. X-ray Diffraction (XRD) measurements and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the two TFA treated samples and an untreated cellulose sample.

2.2 X-ray diffraction method (XRD)

XRD measurements were performed on a Philips PW3040/00 X'Pert MPD system. The diffracted intensity of Cu Kα radiation (wavelength of 0.1542 nm, under a condition of 50 kV and 40 mA) was measured in a 2θ range between 10 ° and 50 °.

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

KBr pellets of samples were prepared by mixing (2-4 mg) cellulose sample with 200-250 mg KBr (spectroscopic grade) with an alumina mortar. The 13 mm diameter pellets were prepared in a standard tool under a pressure of 1360 atm. IR-spectra were recorded using a Nicolet 740 FTIR spectrometer with a DTGS detector at 4 cm^{-1} resolution. N_2 gas flow was used as background for each spectrum and 64 scans were taken per sample.

2.4 Hydrolysis tests

Hydrolysis tests were performed in parallel using a high-throughput batch reactor (Symyx heated orbitol shaker system with 24-well plates). In our experiments, 50 mg samples including untreated cellulose, cellulose_TFA, and cellulose_wash were loaded into separate vials. Water (1.200 ml) was added to the vial that was pre-loaded with cellulose_TFA and 1.200 ml 0.5 H_2SO_4 was loaded to each remaining vials. The vials were sealed and fixed on an aluminum plate, then installed into a Symyx reactor. The reactions were carried out for one minute at 185. The reaction was stirred using orbitol shaking at 700 RPM. After the reactions were completed, they were cooled to room temperature. The products in each vial were analyzed by HPLC.

2.5 HPLC Analysis of Liquid Products

Liquid products were analyzed by HPLC using a Bio-Rad Aminex HPX-87H column. A refractive index detector was used for analysis. The effluent used was 0.005 M H_2SO_4. Values in the paper are reported as molar yields.

3. Results and discussions

3.1 cellulose sample characterizations

Figure 1 shows cellulose XRD patterns for three cellulose samples: untreated, cellulose_TFA, and cellulose_wash.

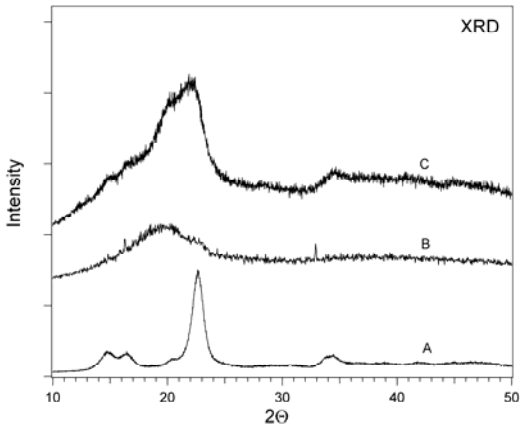
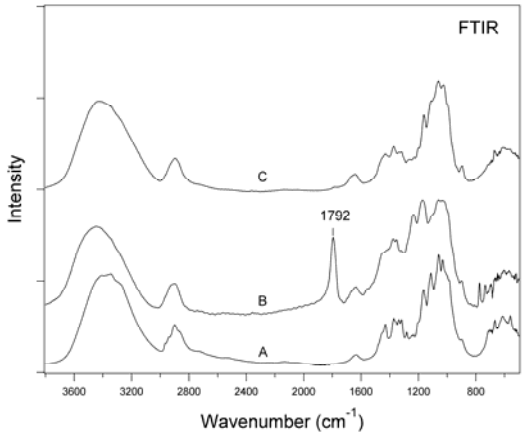


Figure 1 XRD patterns of A: untreated cellulose; B: cellulose_TFA ; C: cellulose_wash.

The strongest peak for untreated cellulose, at 2θ = 22.6°, originates from the cellulose crystalline plane 002. [15, 16] This peak was completely eliminated in the sample of cellulose_TFA. The XRD results suggest that cellulose was essentially completely decrystallized by TFA at 0 °C in less than 2 hours. In other experiments, not shown, we observed that cellulose decrystallization was not completed for 48 hours at 25°C in the same medium. A small amount of crystalline cellulose may exist in the sample of cellulose_wash, a result of the process used to remove the residual TFA. Our results indicate that cellulose was highly activated in the cellulose_TFA and cellulose_wash samples and we attribute this to the low crystallinity of the samples.

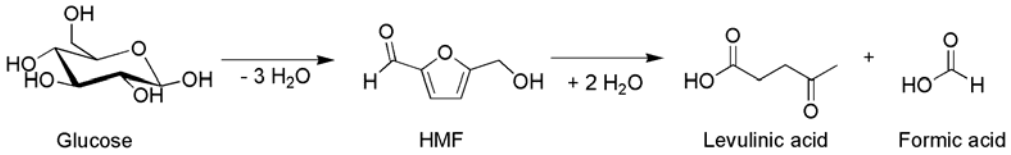
Figure 2 shows cellulose FTIR spectra of an untreated sample, cellulose_TFA, and cellulose_wash.



The vibration peak at 1792 cm^{-1} in the sample of cellulose_TFA corresponds to that of the carbonyl group in cellulose trifluoroacetate (1790 cm^{-1}). [17, 18]. This peak was extremely tiny in the sample of cellulose_wash. The area of the peak was around 0.03% of that in cellulose_TFA, which means that the residual TFA was almost completely removed through washing with water and drying. When a sample of cellulose_wash was treated in pure H_2O at 150 °C for 30 minutes essentially no hydrolysis was observed.

3.2 Hydrolysis tests

In cellulose hydrolysis tests, cellobiose, glucose and glucose degradation products, including hydroxymethylfurfuraldehyde (HMF), levulinic acid, formic acid, and acetic acid were detected in liquid product solutions by HPLC. To better understand the cellulose hydrolysis process, glucose, HMF and levulinic acid yields (C_5+C_6) were summed to provide the overall cellulose conversion. The glucose degradation pathway to HMF and levulinic acid is shown in scheme 1.



Scheme 1

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The hydrolysis reaction test was carried out at 185 °C using a short residence time (one minute). Levulinic acid was not produced in this test. The yield of glucose, HMF and total C_5+C_6 product (in this case C_6 products) are plotted in Figure 3. The glucose yield reached 63.5% for cellulose_TFA while only 15.0% glucose yield was obtained with untreated cellulose.

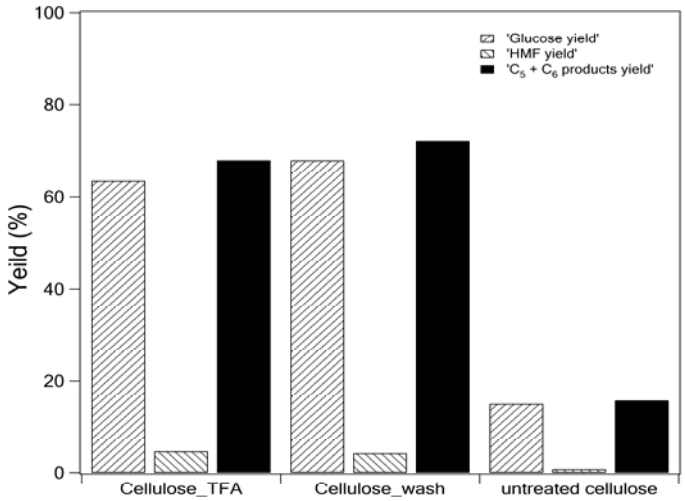

Figure 3 The yield of glucose, HMF and total C_5 and C_6 product from the hydrolysis of cellulose samples at 185 °C for one minute

Cellulose decrystallization can significantly decrease the reaction temperature and shorten the reaction time for hydrolysis reaction, which is very important in suppressing glucose degradation reactions. The high glucose yield from cellulose_TFA indicates that the residual TFA can act as hydrolysis catalyst even when diluted to 0.5%. The glucose yield from cellulose_TFA is almost comparable with that from the hydrolysis of cellulose_wash by 0.5% H_2SO_4. It suggests that both TFA and sulfuric acid are effective catalyst at this concentration once cellulose is pre-activated by decrystallization. Further improvement in glucose yield in the TFA process could be made through optimization of process conditions. For example, traditional dilute acid process uses high temperature

(~215 °C) and low residence time (~3 min). [19] A process based on cellulose_TFA could use residual TFA as a catalyst and may produce higher glucose yield and be operated at lower temperatures. This process would also be compatible with the traditional dilute process. Cellulose_wash maintains a very high amorphous structure after removing TFA by water-washing. The high reactivity of this pre-activated cellulose can also be expected in enzyme hydrolysis process.

4. Summary

Cellulose was quickly decrystallized in TFA at 0 °C. Most of the TFA used in the decrystallization process was recycled by a vacuum evaporation. The residual TFA in cellulose sample was diluted to 0.5% TFA solution and used as a catalyst for cellulose hydrolysis. The glucose yield reached 63.5% in 1 minute at 185 °C under batch reaction conditions. This yield is four times higher than that obtained from untreated cellulose by 0.5% H_2SO_4 under the same condition. The glucose yield could be further improved by optimizing reaction conditions.

The residual TFA in the treated cellulose can be removed by water. After drying the cellulose retained its highly amorphous structure. This regenerated cellulose is much more reactive than untreated cellulose in hydrolysis reactions. High glucose yields could also be expected from the hydrolysis of this regenerated cellulose using enzyme processes.

5. Acknowledgements

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