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Bonding Of Trifluoroacetic Acid with Cellulose

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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), hydrolysis*

I. Introduction

Cellulose is the most abundant polymer on Earth, which makes it also the most common organic compound. Annual cellulose synthesis by plants is close to 1012 tons. Plants contain approximately 33% cellulose whereas wood contains around 50 per cent and cotton contains 90%. Most of the cellulose is utilised as a raw material in paper production. This equates to approximately 108 tons of pulp produced annually. From this, only 4 million tons are used for further chemical processing annually. It is quite clear from these values that only a very small fraction of cellulose is used for the production of commodity materials and chemicals. This fact was the starting point of our research into understanding, designing, synthesising and finding new alternative applications for this well known but underused biomaterial.

Cellulose is a linear and fairly rigid homopolymer consisting of D-anhydroglucopyranose units (AGU). These units are linked together by β-(1→4) glycosidic bonds formed between C-1 and C-4 of adjacent glucose moieties. In the solid state, AGU units are rotated by 180° with respect to each other due to the constraints of β-linkage. Each of the AGU units has three hydroxyl (OH) groups at C-2, C-3 and C-6 positions. Terminal groups at the either end of the cellulose molecule are quite different in nature from each other. The C-1 OH at one end of the molecule is an aldehyde group with reducing activity. Aldehyde groups form a pyranose ring through an intramolecular hemiacetal form. In contrast, the C-4 OH on the other end of the chain is an alcoholborne OH constituent and thus is called the non-reducing end.

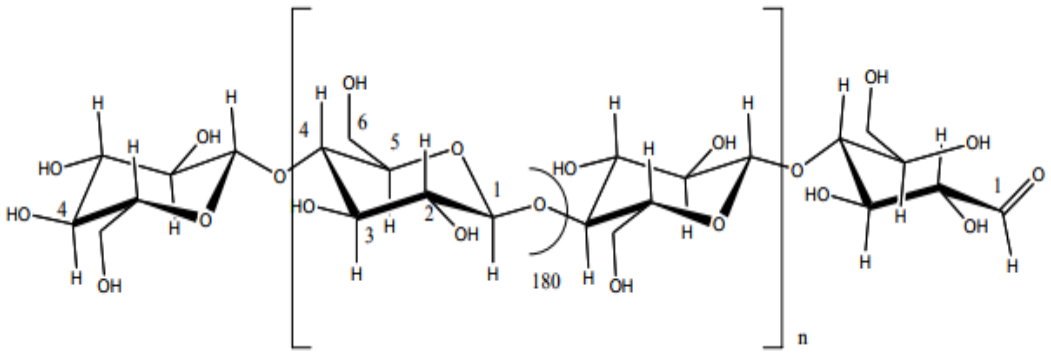


Figure 1: Molecular structure of cellulose representing the cellobiose unit as a repeating unit showing reducing (right) and non-reducing (left) end-groups

The chemical character and reactivity of cellulose is determined by the presence of three equatorially positioned OH groups in the AGU, one primary and two secondary groups. In addition, the β-glycosidic linkages of cellulose are susceptible to hydrolytic attack. The hydroxyl groups do not only play a role in the typical reactions of primary and secondary alcohols that are carried out on cellulose, but also play an important role in the solubility of cellulose.

There are two possible mechanisms by which the OH groups in the cellulose molecule form hydrogen bonds. One is by the interaction between suitably positioned OH groups in the same molecule (intramolecular). These are located between C2-OH and C6-OH groups and C3-OH with endocyclic oxygen.

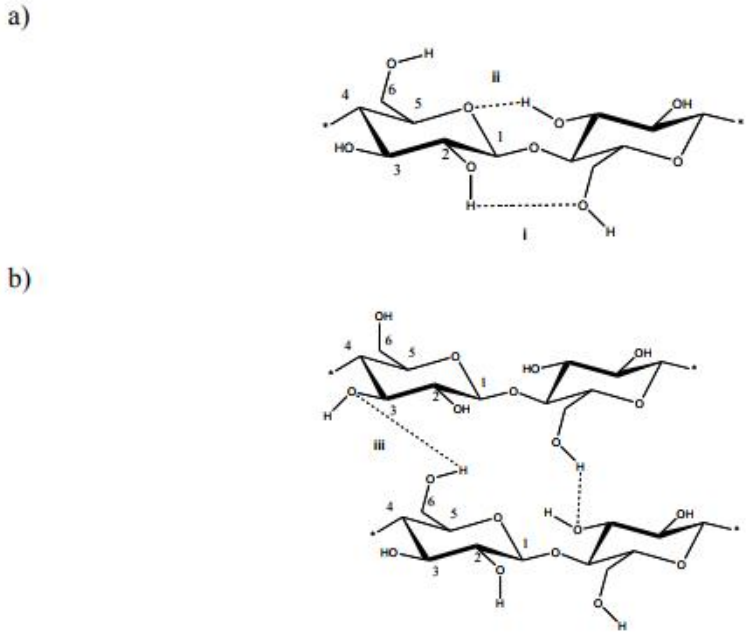


Figure 2. Cellulose structures showing a) the intramolecular hydrogen bonding between C2- OH and C6-OH (i), and C3-OH with endocyclic oxygen (ii); and b) the intermolecular hydrogen bonding between C3-OH and C6-OH (iii) (supramolecular structure).

Cellulose is regarded as a semi-flexible polymer. The relative stiffness and rigidity of the cellulose molecule is mainly due to the intramolecular hydrogen bonding. This property is reflected in its high viscosity in solution, a high tendency to crystallise, and its ability to form fibrillar strands. The chain stiffness property is further favored by the β-glucosidic linkage that bestows the linear form of the chain. The chair conformation of the pyranose ring also contributes to chain stiffness. This is in contrast to the α-glucosidic bonds of starch.

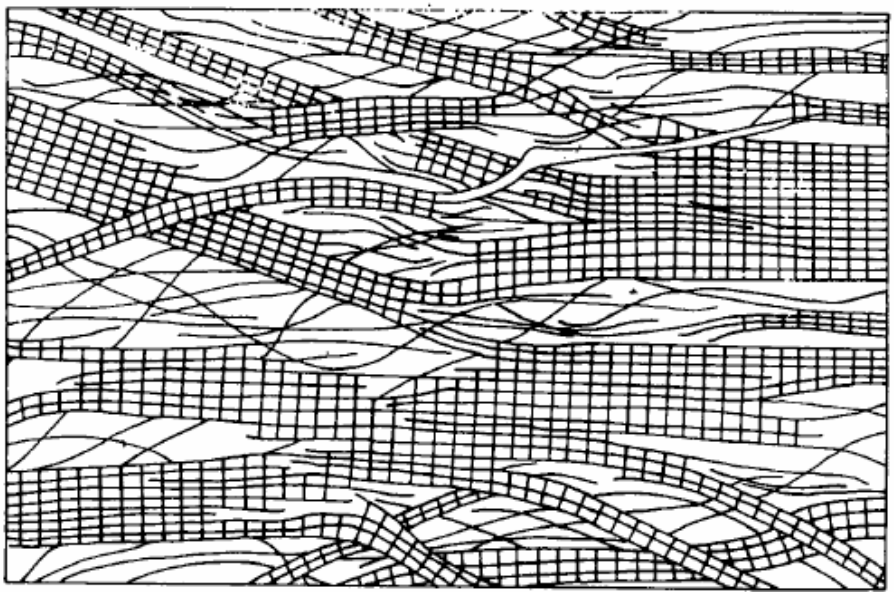


Figure 3. Fringed fibril model of the supramolecular structure of cellulose

II. Research Methodology

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.

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 H2SO4 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.

III. Results and discussions

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

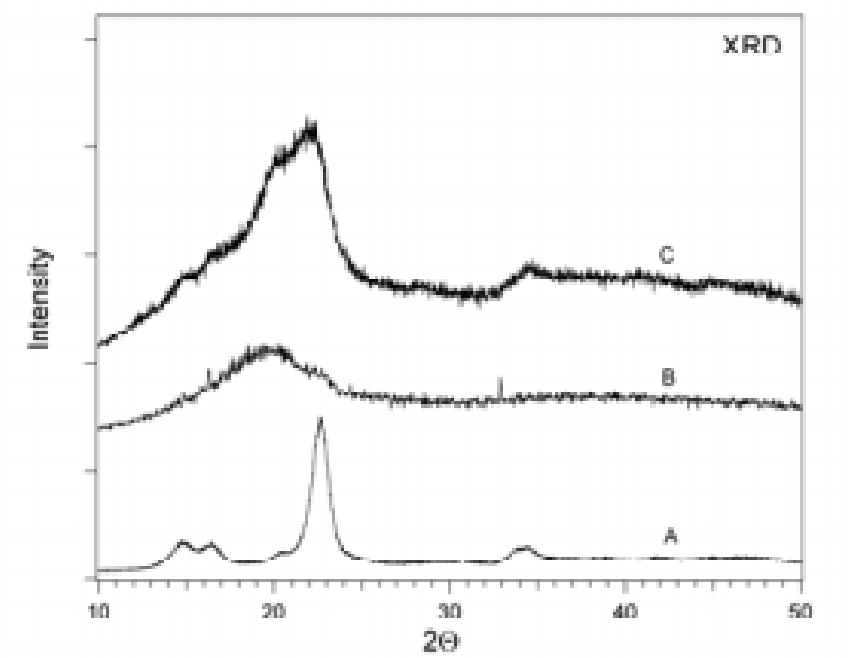
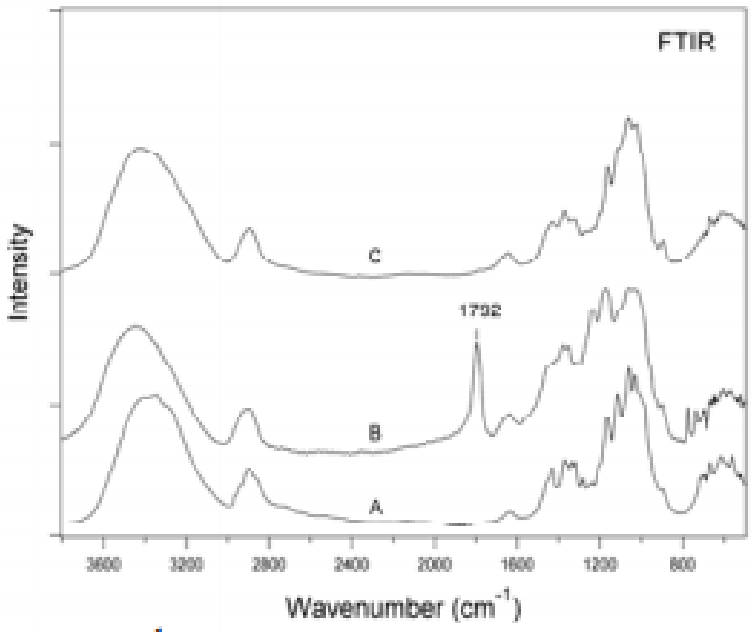


Figure 1 XRD patterns of A: untreated cellulose; B: cellulose_TFA ; C: cellulose_wash

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). 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 H2O at 150 °C for 30 minutes essentially no hydrolysis was observed.

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% H2SO4. 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.

IV. Conclusion

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.

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