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### Inverse temperature effect on cellulose decrystallization and hydrolysis

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### Introduction

Cellulose is the most abundant renewable carbon source in the biosphere. Nature cellulose contains a large portion of crystalline cellulose, which is not accessible to most solvents, reactants and catalysts. Cellulose decrystallization can eliminate this barrier and provide an efficient pathway for the utilization of cellulose in producing industrial chemicals based on renewable sources.

Liquid ammonia is a widely used swelling agent, albeit at a rather low temperature (below -30 °C, which requires high pressure operation) for cellulose decrystallization in industry. It is desirable to use a volatile swelling agent or solvent that can decrystallize cellulose and can be recycled under milder conditions. Trifluoroacetic acid (TFA), as a volatile liquid between -15 °C and 78 °C, offers a more convenient operating temperature window than liquid ammonia. It has been reported that TFA swells cellulose at room temperature for an extended period, but the dissolution process is driven by trifluoroacetylation through esterification. [1] The resulting product is a partially trifluoroacetylated cellulose.

In this paper, we reveal a new route to rapidly decrystallize cellulose using TFA without esterification or morphology change on the cellulose macrofiber. As a result of this novel pre-treatment, improved glucose yield was obtained from dilute acid hydrolysis.

### Materials and methods

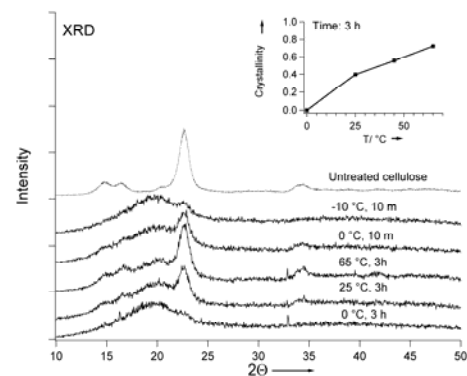
Cellulose (cotton linters, product no. C6663) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich. Cellulose and trifluoroacetic acid (1:15 mass ratio) were mixed at 0 °C for 2 hours in a sealed flask. After treatment, the sample was exposed to a vacuum (30 mtorr) at room temperature for 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.

Hydrolysis tests were performed in parallel using a high-throughput batch reactor. 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<sub>2</sub>SO<sub>4</sub> was loaded to each remaining vials. The vials were sealed and fixed on an aluminum plate, then installed into a Synyx reactor. The reactions were carried out for one minute at 185. The reaction was stirred using orbital shaking at 700 RPM. After the reactions were completed, they were cooled to room temperature. The products in each vial were analyzed by HPLC.

### Results and Discussion

Figure 1 shows cellulose XRD patterns for an untreated cellulose and that treated by TFA for 3 hours (0, 25 and 65 °C) and 10 minutes (0 and -10 °C). The strongest peak, at 2θ =

22.6°, originates from the cellulose crystalline plane [002]. [2] The intensity of this peak was dependent on the temperature at which crystalline cellulose was treated by TFA. Surprisingly, decreasing TFA treatment temperature accelerates the disappearance of this crystalline peak. After cellulose was treated at 0 °C for 3 h, this crystalline peak completely disappeared. Cellulose decrystallization can be further accelerated by decreasing decrystallization temperature to -10 °C, as shown in figure 1 (XRD patterns for 10- minute decrystallization at 0 and -10 °C). The area of the [002] peak was normalized to that of untreated cellulose and was used to define the relative crystallinity of cellulose samples. The results are shown in the insert. An inverse temperature effect on cellulose decrystallization in TFA is clearly revealed in the insert. The same effect was also observed for other crystalline cellulose peaks. Apparently, TFA treatment at low temperature reduces the long-range order in the crystalline cellulose at a rate that accelerates with decreasing TFA treatment temperature. Further studies show that it took only 100 minutes to completely decrystallize cellulose at 0 °C in TFA, a result not achieved in 48 hours at 25°C in the same medium.



FTIR and NMR analyses of TFA treated samples indicate that no trifluoroacetylation reaction took place after TFA treatment at 0°C. TFA dimer was the prevailing species found at this low temperature. However, trifluoroacetate ester was formed at higher temperatures.

The hydrolysis reaction test showed that Levulinic acid was not produced in this test. The glucose yield reached 63.5% for cellulose\_TFA while only 15.0% glucose yield was obtained with untreated cellulose. Therefore, amorphous cellulose obtained from TFA treatment greatly enhance the rate of hydrolysis to glucose.

### Significance

This paper reveals a new route to improved glucose yield, following pretreatment of crystalline cellulose with TFA dimer molecules. The TFA dimer rapidly decrystallizes cellulose at 0°C or below, yielding amorphous cellulose which can be readily hydrolyzed by conventional hydrolysis medium at high rate.