SUPPLEMENTARY INFORMATION

Rapid Dissolution of Lignocellulosic Biomass in Ionic Liquids Using Temperatures above the Glass Transition of Lignin

Weiying Li[†[a,b]], Ning Sun[†[a]], Breena Stoner[[a]‡], Xinyu Jiang[[a]※], Xingmei Lu[[a]§] and Robin D. Rogers*[[a]]

NMR analysis for IL decomposition. To determine whether IL decomposed under the processing conditions, [C_2mim]OAc was heated at 185 ^oC for 10 min or 110 ^oC for 16 h and analyzed by NMR using a Bruker Avance 500 MHz NMR spectrometer. ^1H NMR spectra were collected with 128 scans at 500.13 MHz. The results are shown in Figure S1 and indicate some decomposition of the IL after heating.

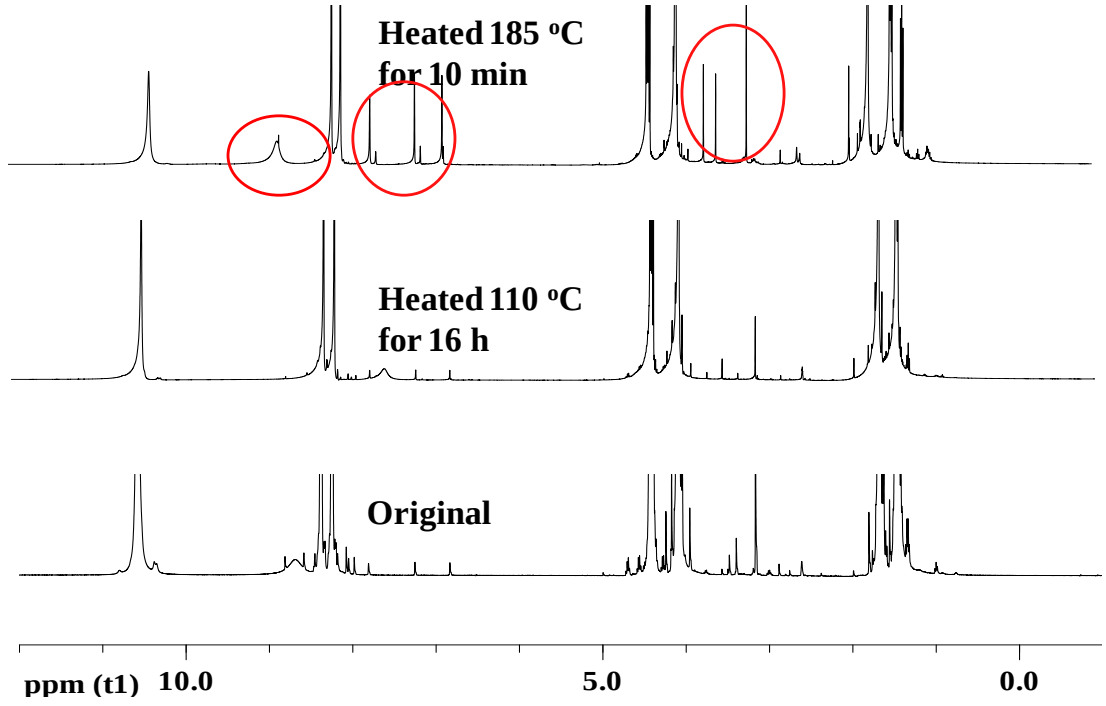
FTIR analysis for regenerated MCC. To determine whether cellulose was acetylated in [C_2mim]OAc after heating, 0.5 g MCC was dissolved in [C_2mim]OAc under different heating conditions: 90 ^oC for 10 min, 110 ^oC for 16 h, and 185 ^oC for 10 min. After dissolution, the solution was regenerated in 100 mL DI water at room

[a] Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA. Email: rdrogers@as.ua.edu
[b] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China.
† W. Li and N. Sun made equal contributions to this paper.
‡ Current address: Department of Chemistry, University of Central Florida, Orlando, FL 32816, USA.
※ Current address: School of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China.
§ Current address: Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100080, China.

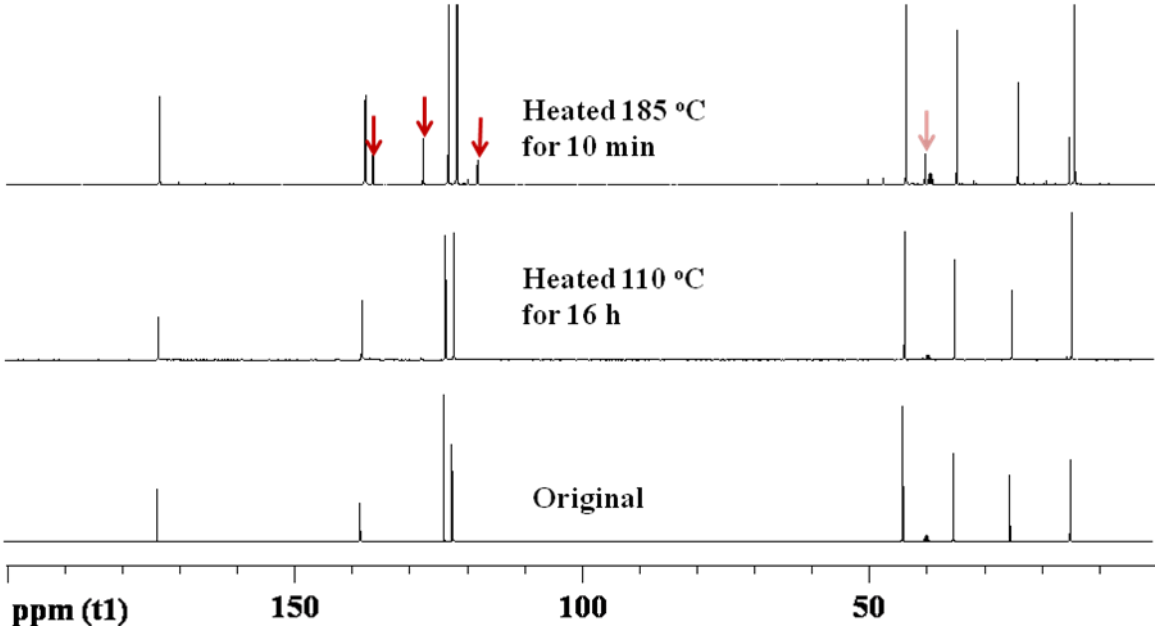
temperature with magnetic stirring. The mixture was then centrifuged and the regenerated MCC was further washed with 2 x 100 mL DI, and finally separated using vacuum filtration through a ceramic funnel with nylon filter paper. The regenerated MCC was dried in an oven at 90 ^{o}C overnight. FT-IR spectra of the regenerated MCC were collected using a Perkin-Elmer Spectrum 100 FT-IR spectrometer (Waltham, MA) equipped with an attenuated total reflectance (ATR) cell with 4 scans at 2 cm^{-1} resolution. The results are shown in Figure S2 and indicate some acetylation of MCC after heating at higher temperature.

Cellulose content determination. 2 g dried biomass samples (≤0.25 mm) were weighed and transferred to a 100 mL round bottomed flask. DI water (75 mL), glacial acetic acid (0.5 mL), and sodium chlorite (0.6 g) were added successively. A 25 mL Erlenmeyer flask was inverted in the neck of the reaction flask and the flask was placed on an oil bath at 75 ^{o}C. The flask was heated for 1 h with magnetic stirring. Then, without cooling, additional glacial acetic acid (0.5 mL) was added, followed by sodium chlorite (0.6 g). The heating was continued at 75 ^{o}C for an hour. At the end of the second and third hours, the additions of acetic acid and sodium chlorite were repeated, the acid always being added first. At the end of the fourth hour of chloriting, the flask was placed in an ice bath until the contents have cooled below 5 ^{o}C. The holocellulose was filtered on a nylon filter paper, washed with distilled water to pH 7, then washed with acetone, and dried in oven overnight. Dried holocellulose was weighed, and transferred to a 50 mL beaker. 5% NaOH

solution (w/w, liquid to solid ratio 30:1) was added. The beaker was placed in an oil bath, heated for 4 h at 60 ^{o}C with magnetic stirring. Then, without cooling, the mixture was filtered using a nylon filter paper. The residue was then transferred to a 50 mL beaker, and stirred with 17% NaOH solution (w/w, liquid to solid ratio 30:1) at room temperature for 45 min. Then, the mixture was filtered. The cellulose was then washed with 17% NaOH solution, 10% acetic acid, distilled water and acetone successively, and dried at 50 ^{o}C in a vacuum oven for 12 h.



a)



b)

Figure S1. ^{1}H(a) and ^{13}C (b) NMR of top: [C_2mim]OAc heated at 185 ^{o}C for 10 min, middle: [C_2mim]OAc heated at 110 ^{o}C for 16 h, bottom: original [C_2mim]OAc. The extra peaks are from 1-methylimidazole.

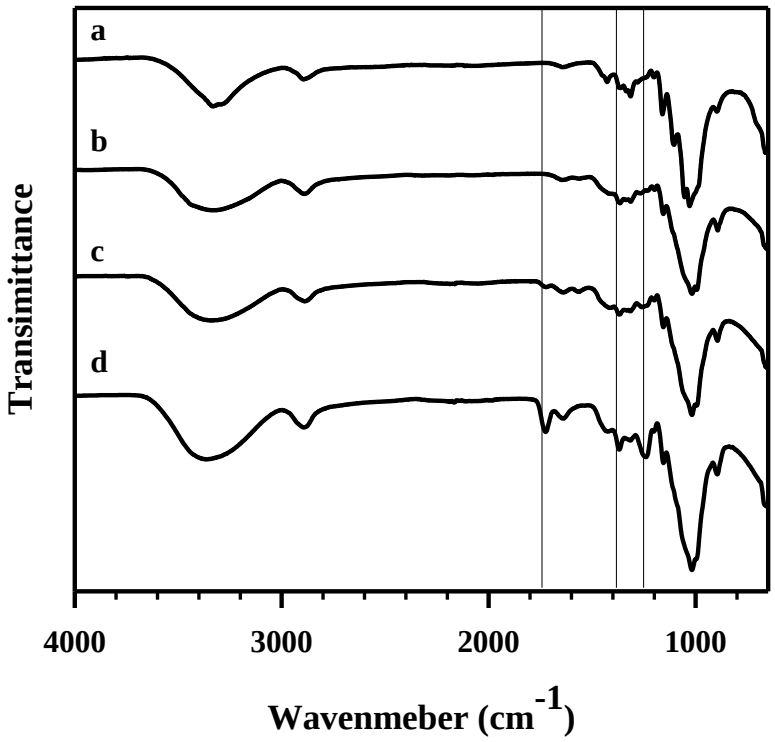


Figure S2. FT-IR spectra for a) MCC, b) regenerated MCC after dissolution in [C_2mim]OAc at 90 ^{o}C for 10 min, c) regenerated MCC after dissolution in [C_2mim]OAc at 110 ^{o}C for 16 h, d) regenerated MCC after dissolution in [C_2mim]OAc at 185 ^{o}C for 10 min indicating some acetylation. Vertical solid lines mark peaks of acetylated MCC.

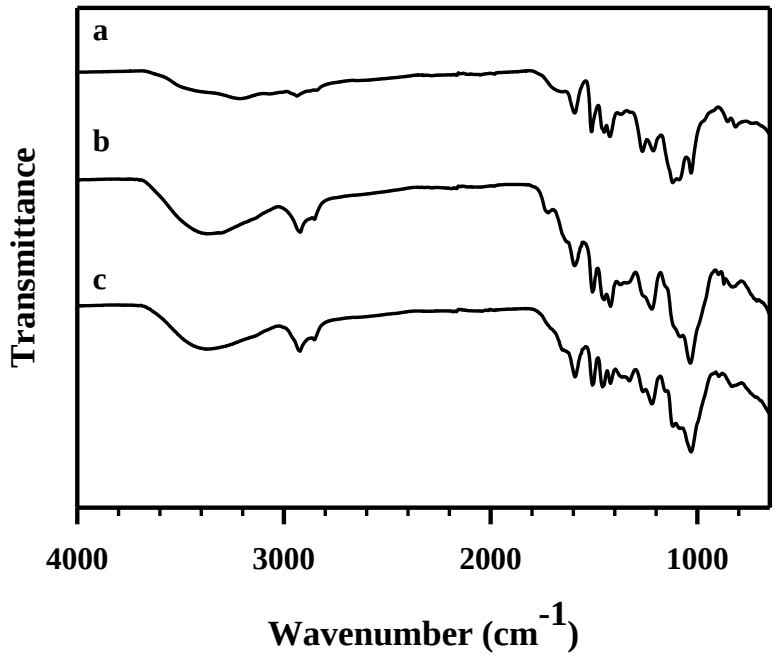


Figure S3. FT-IR spectra for a) Indulin AT, b) recovered lignin from the 185 ^{o}C, 10 min run, and c) recovered lignin from the 110 ^{o}C, 16 h run showing that the recovered lignins from either higher temperature or lower temperature methods have similar structures.