Supporting Information

Crystalline Cellulose under Pyrolysis Conditions: The Structure-Property Evolution via Reactive Molecular Dynamics Simulations

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(a) Cellulose equilibrium configurations from 500, 800, 1000, and 1200 K.

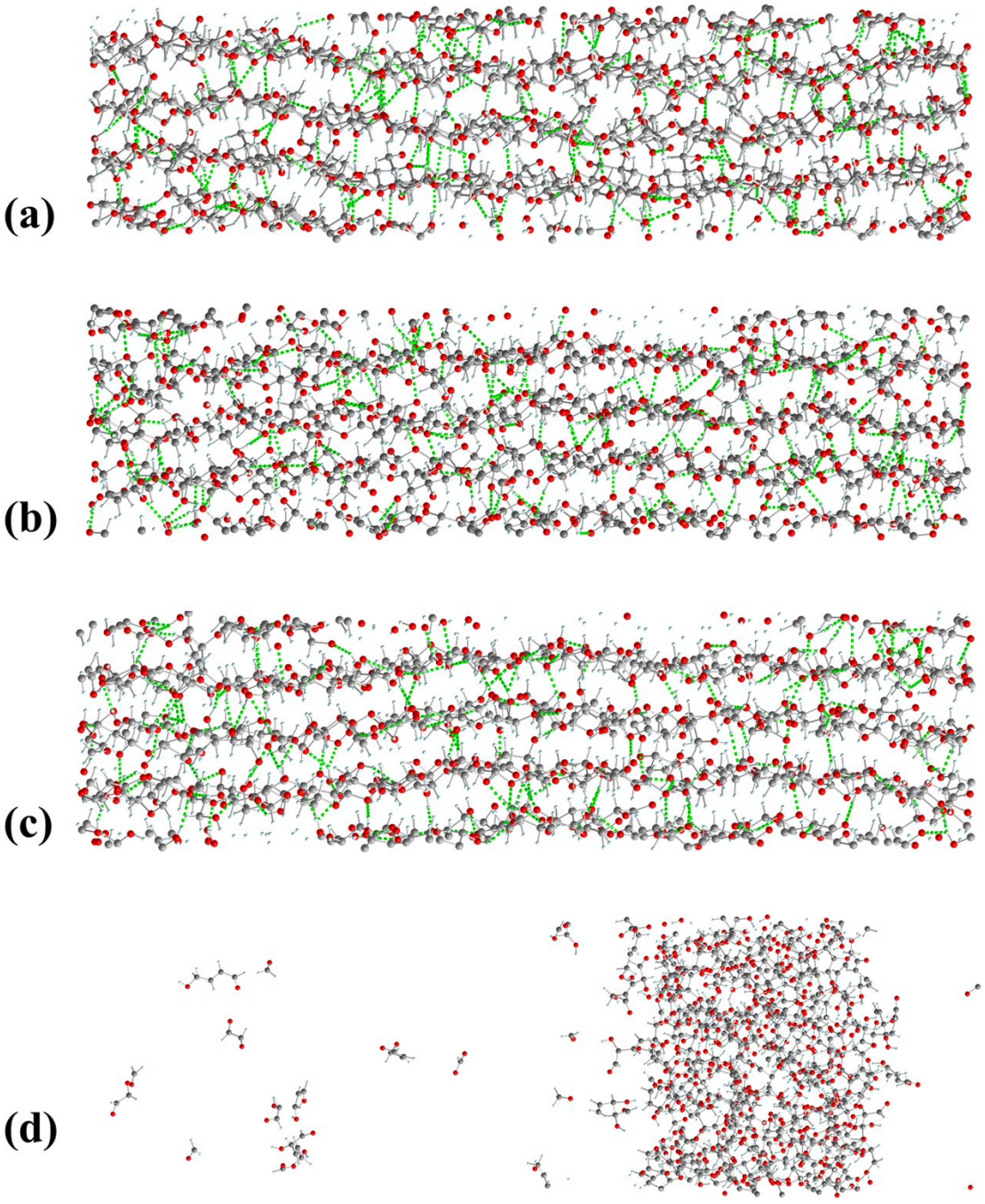

Figure S1. Cellulose equilibrium configurations at different temperatures: (a) 500 K; (b) 800 K; (c) 1000 K; (d) 1200 K. When the temperature is higher than 1200 K, the cellulose structure will decompose. The hydrogen bonding network is shown in green dashed lines.

Table S1. Comparison of unite cell parameters between experimental and simulation results.

Lattice size (Å)			Lattice angle (º)			Reference
a	b	c	α	β	γ	
7.784	8.201	10.380	90.0	90.0	96.5	293 K, Exp.[1]
7.786±0.016	8.203±0.017	10.382±0.062	90.0±0.01	90.0±0.01	90.88±0.74	300 K, RxMD of this work
7.861±0.038	8.282±0.040	10.482±0.152	90.0±0.69	90.0±0.76	89.28±0.72	500 K, RxMD of this work
7.876±0.029	8.298±0.031	10.503±0.116	90.0±19.64	90.0±18.34	86.02±0.54	800 K, RxMD of this work
7.908±0.021	8.332±0.022	10.546±0.084	90.0±13.60	90.0±6.98	83.82±2.17	1000 K, RxMD of this work
7.996±0.042	8.425±0.444	10.663±0.167	90.0±4.88	90.0±5.20	70.04±3.84	1100 K, RxMD of this work
8.47	8.11	10.51	90.0	90.0	90.0	300 K, Classical MD[2]
8.378±0.0002	8.168±0.0002	10.523±0.0002	89.97±0.02	89.97±0.02	90.92±0.03	300 K, Classical MD[4]
7.60	8.10	10.40	90.0	90.0	96.0	300 K, Classical MD[5]
7.60	8.74	10.46	90.4	92.3	103.5	300 K, Classical MD[6]
7.50	8.70	10.36	90.0	90.0	94.1	300 K, Classical MD[7]
8.03	8.13	10.39	90.0	90.0	97.5	300 K, Classical MD[8]

Reference:

1. Nishiyama, Y.; Langan, P.; Chanzy, H., Crystal Structure and Hydrogen-Bonding System in Cellulose Iβ from Synchrotron X-ray and Neutron Fiber Diffraction. *Journal of the American Chemical Society* **2002,** *124* (31), 9074-9082.

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3. Matthews, J. F.; Bergenstråhle, M.; Beckham, G. T.; Himmel, M. E.; Nimlos, M. R.; Brady, J. W.; Crowley, M. F., High-Temperature Behavior of Cellulose I. *The Journal of Physical Chemistry B* **2011,** *115* (10), 2155-2166.

4. Bergenstråhle, M.; Berglund, L. A.; Mazeau, K., Thermal Response in Crystalline Iβ Cellulose: A Molecular Dynamics Study. *The Journal of Physical Chemistry B* 2007, 111 (30), 9138-9145.

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6. Mazeau, K.; Heux, L., Molecular dynamics simulations of bulk native crystalline and amorphous structures of cellulose. *Journal of Physical Chemistry B* 2003, 107 (10), 2394-2403.

7. Viëtor, R. J.; Mazeau, K.; Lakin, M.; Pérez, S., A priori crystal structure prediction of native celluloses. *Biopolymers* **2000,** *54* (5), 342-354.
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(b) Calculated XRD results of cellulose at 500 K and 800 K

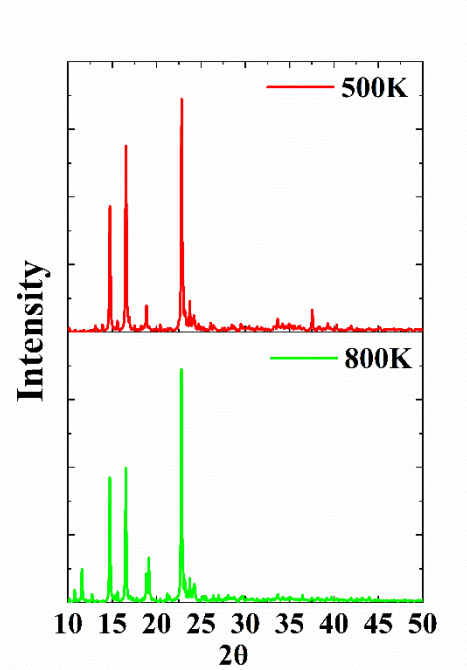

Figure S2. (a) XRD for cellulose structures at 500 K and 800 K.

(c) Cellulose Decomposition and Element Distribution Analysis at 1300 K

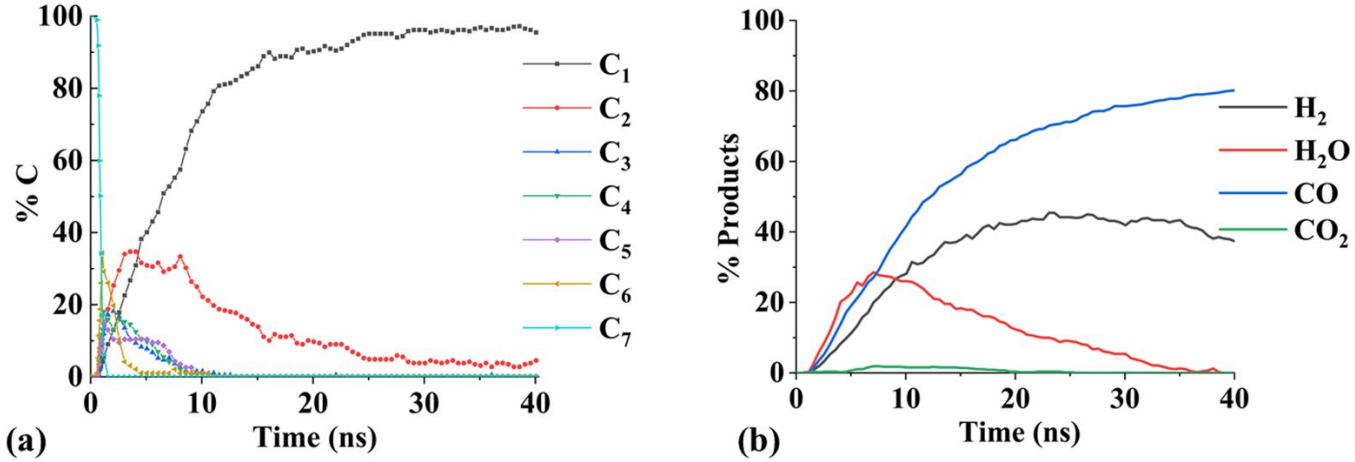

Figure S3. (a) Carbon distributions and (b) light gas-phase product distributions at 1300 K.

(d) Comparison of stress–strain diagram for different strain rates at 300 K

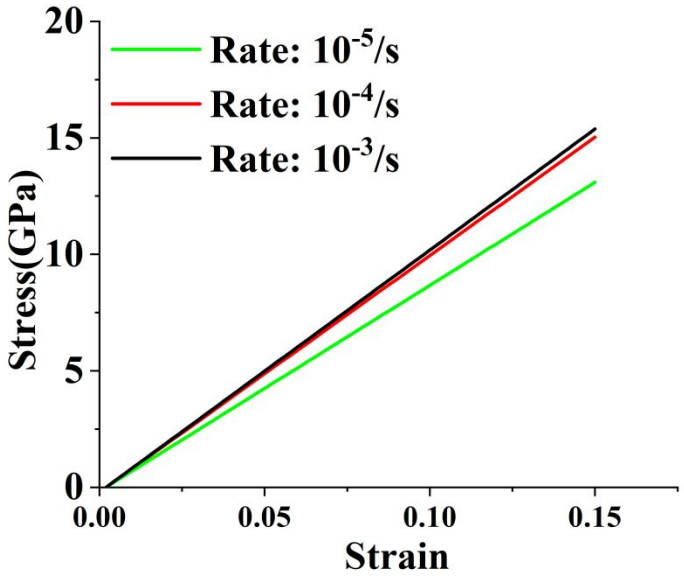

Figure S4. Comparison of stress–strain diagram for different strain rates at 300 K: strain rate of 10^{-3} /s is in black, strain rate of 10^{-4} /s is in red and train rate of 10^{-5} /s is in green, respectively.

(e) ReaxFF force field parameters used in this work.

Citation: Chenoweth, van Duin and Goddard, J Phys Chem A, 112, 1040-1053 (2008)

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 39       ! Number of general parameters
  50.0000 !p(boc1)
   9.5469 !p(boc2)
  26.5405 !p(coa2)
   1.5105 !p(trip4)
   6.6630 !p(trip3)
  70.0000 !kc2
   1.0588 !p(ovun6)
   4.6000 !p(trip2)
  12.1176 !p(ovun7)
  13.3056 !p(ovun8)
 -70.1292 !p(trip1)
   0.0000 !Lower Taper-radius (swa)
  10.0000 !Upper Taper-radius (swb)
   0.0000 !not used
  33.8667 !p(val7)
   6.0891 !p(lp1)
   1.0563 !p(val9)
   2.0384 !p(val10)
   6.1431 !not used
   6.9290 !p(pen2)
   0.3989 !p(pen3)
   3.9954 !p(pen4)
   0.0000 !not used
   5.7796 !p(tor2)
  10.0000 !p(tor3)
   1.9487 !p(tor4)
   0.0000 !not used
   2.1645 !p(cot2)
   1.5591 !p(vdW1)
   0.1000 !Cutoff for bond order*100 (cutoff)
   2.1365 !p(coa4)
   0.6991 !p(ovun4)
  50.0000 !p(ovun3)
   1.8512 !p(val8)
   0.0000 !not used
   0.0000 !not used
   0.0000 !not used
   0.0000 !not used
   2.6962 !p(coa3)
 3    ! Nr of atoms; atomID;ro(sigma); Val;atom mass;Rvdw;Dij;gamma;ro(pi);Val(e)
        alfa;gamma(w);Val(angle);p(ovun5);n.u.;chiEEM;etaEEM;n.u.
        ro(pipi);p(lp2);Heat increment;p(boc4);p(boc3);p(boc5),n.u.;n.u.
        p(ovun2);p(val3);n.u.;Val(boc);p(val5);n.u.;n.u.;n.u.
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C    1.3825   4.0000  12.0000   1.9133   0.1853   0.9000   1.1359   4.0000
     9.7602   2.1346   4.0000  33.2433  79.5548   5.8678   7.0000   0.0000
     1.2104   0.0000 199.0303   8.6991  34.7289  13.3894   0.8563   0.0000
    -2.8983   2.5000   1.0564   4.0000   2.9663   0.0000   0.0000   0.0000
H    0.7853   1.0000   1.0080   1.5904   0.0419   1.0206  -0.1000   1.0000
     9.3557   5.0518   1.0000   0.0000 121.1250   5.3200   7.4366   1.0000
    -0.1000   0.0000  62.4879   1.9771   3.3517   0.7571   1.0698   0.0000
   -15.7683   2.1488   1.0338   1.0000   2.8793   0.0000   0.0000   0.0000
O    1.2477   2.0000  15.9990   1.9236   0.0904   1.0503   1.0863   6.0000
    10.2127   7.7719   4.0000  36.9573 116.0768   8.5000   8.9989   2.0000
     0.9088   1.0003  60.8726  20.4140   3.3754   0.2702   0.9745   0.0000
    -3.6141   2.7025   1.0493   4.0000   2.9225   0.0000   0.0000   0.0000
 6     ! Nr of bonds; at1;at2;De(sigma);De(pi);De(pipi);p(be1);p(bo5);13corr;n.u.;p(bo6),p(ovun1)
                  p(be2);p(bo3);p(bo4);n.u.;p(bo1);p(bo2)
 1  1 156.5953 100.0397  80.0000  -0.8157  -0.4591   1.0000  37.7369   0.4235
       0.4527  -0.1000   9.2605   1.0000  -0.0750   6.8316   1.0000   0.0000
 1  2 170.2316   0.0000   0.0000  -0.5931   0.0000   1.0000   6.0000   0.7140
       5.2267   1.0000   0.0000   1.0000  -0.0500   6.8315   0.0000   0.0000
 2  2 156.0973   0.0000   0.0000  -0.1377   0.0000   1.0000   6.0000   0.8240
       2.9907   1.0000   0.0000   1.0000  -0.0593   4.8358   0.0000   0.0000
 1  3 160.4802 105.1693  23.3059  -0.3873  -0.1613   1.0000  10.8851   1.0000
       0.5341  -0.3174   7.0303   1.0000  -0.1463   5.2913   0.0000   0.0000
 3  3  60.1463 176.6202  51.1430  -0.2802  -0.1244   1.0000  29.6439   0.9114
       0.2441  -0.1239   7.6487   1.0000  -0.1302   6.2919   1.0000   0.0000
 2  3 180.4373   0.0000   0.0000  -0.8074   0.0000   1.0000   6.0000   0.5514
       1.2490   1.0000   0.0000   1.0000  -0.0657   5.0451   0.0000   0.0000
 3    ! Nr of off-diagonal terms. at1;at2;Dij;RvdW;alfa;ro(sigma);ro(pi);ro(pipi)
 1  2   0.1219   1.4000   9.8442   1.1203  -1.0000  -1.0000
 2  3   0.0344   1.6800  10.3247   0.9013  -1.0000  -1.0000
 1  3   0.1131   1.8523   9.8442   1.2775   1.1342   1.0621
18    ! Nr of angles. at1;at2;at3;Thetao,o;p(val1);p(val2);p(coa1);p(val7);p(pen1);p(val4)
 1  1  1  67.2326  22.0695   1.6286   0.0000   1.7959  15.4141   1.8089
 1  1  2  65.2527  14.3185   6.2977   0.0000   0.5645   0.0000   1.1530
 2  1  2  70.0840  25.3540   3.4508   0.0000   0.0050   0.0000   3.0000
 1  2  2   0.0000   0.0000   6.0000   0.0000   0.0000   0.0000   1.0400
 1  2  1   0.0000   3.4110   7.7350   0.0000   0.0000   0.0000   1.0400
 2  2  2   0.0000  27.9213   5.8635   0.0000   0.0000   0.0000   1.0400
 1  1  3  49.5561   7.3771   4.9568   0.0000   0.7533  15.9906   1.0010
 3  1  3  77.1171  39.8746   2.5403 -24.3902   1.7740 -42.9758   2.1240
 2  1  3  65.0000  14.2057   4.8649   0.0000   0.3504   0.0000   1.7185
 1  3  1  74.3994  44.7500   0.7982   0.0000   3.0000   0.0000   1.0528
 1  3  3  77.9854  36.6201   2.0201   0.0000   0.7434  67.0264   3.0000
 3  3  3  80.7324  30.4554   0.9953   0.0000   1.6310  50.0000   1.0783
 1  3  2  71.5018  21.7062   0.4735   0.0000   0.5186   0.0000   1.1793
 2  3  3  84.9468  23.3540   1.5057   0.0000   2.6374   0.0000   1.3023
 2  3  2  77.0645  10.4737   1.2895   0.0000   0.9924   0.0000   1.1043
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 1  2  3   0.0000  25.0000   3.0000   0.0000   1.0000   0.0000   1.0400
 3  2  3   0.0000   0.0148   6.0000   0.0000   0.0000   0.0000   1.0400
 2  2  3   0.0000   9.7025   6.0000   0.0000   0.0000   0.0000   1.0400
26    ! Nr of torsions. at1;at2;at3;at4;;V1;V2;V3;p(tor1);p(cot1);n.u;n.u.
 1  1  1  1  -0.2500  11.5822   0.1879  -4.7057  -2.2047   0.0000   0.0000
 1  1  1  2  -0.2500  31.2596   0.1709  -4.6391  -1.9002   0.0000   0.0000
 2  1  1  2  -0.1770  30.0252   0.4340  -5.0019  -2.0697   0.0000   0.0000
 1  1  1  3  -0.7098  22.2951   0.0060  -2.5000  -2.1688   0.0000   0.0000
 2  1  1  3  -0.3568  22.6472   0.6045  -4.0088  -1.0000   0.0000   0.0000
 3  1  1  3  -0.0528   6.8150   0.7498  -5.0913  -1.0000   0.0000   0.0000
 1  1  3  1   2.0007  25.5641  -0.0608  -2.6456  -1.1766   0.0000   0.0000
 1  1  3  2  -1.1953  42.1545  -1.0000  -8.0821  -1.0000   0.0000   0.0000
 2  1  3  1  -0.9284  34.3952   0.7285  -2.5440  -2.4641   0.0000   0.0000
 2  1  3  2  -2.5000  79.6980   1.0000  -3.5697  -2.7501   0.0000   0.0000
 1  1  3  3  -0.0179   5.0603  -0.1894  -2.5000  -2.0399   0.0000   0.0000
 2  1  3  3  -0.5583  80.0000   1.0000  -4.4000  -3.0000   0.0000   0.0000
 3  1  3  1  -2.5000  76.0427  -0.0141  -3.7586  -2.9000   0.0000   0.0000
 3  1  3  2   0.0345  78.9586  -0.6810  -4.1777  -3.0000   0.0000   0.0000
 3  1  3  3  -2.5000  66.3525   0.3986  -3.0293  -3.0000   0.0000   0.0000
 1  3  3  1   2.5000  -0.5332   1.0000  -3.5096  -2.9000   0.0000   0.0000
 1  3  3  2  -2.5000   3.3219   0.7180  -5.2021  -2.9330   0.0000   0.0000
 2  3  3  2   2.2500  -6.2288   1.0000  -2.6189  -1.0000   0.0000   0.0000
 1  3  3  3   0.0531 -17.3983   1.0000  -2.5000  -2.1584   0.0000   0.0000
 2  3  3  3   0.4723 -12.4144  -1.0000  -2.5000  -1.0000   0.0000   0.0000
 3  3  3  3  -2.5000 -25.0000   1.0000  -2.5000  -1.0000   0.0000   0.0000
 0  1  2  0   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
 0  2  2  0   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
 0  2  3  0   0.0000   0.1000   0.0200  -2.5415   0.0000   0.0000   0.0000
 0  1  1  0   0.0000  50.0000   0.3000  -4.0000  -2.0000   0.0000   0.0000
 0  3  3  0   0.5511  25.4150   1.1330  -5.1903  -1.0000   0.0000   0.0000
 1    ! Nr of hydrogen bonds. at1;at2;at3;r(hb);p(hb1);p(hb2);p(hb3)
 3  2  3   1.9682  -4.4628   1.7976   3.0000
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