Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

# Pyrolytic activation of cellulose: Energetics and condensed phase effects

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# Supporting Information

## Content

Two novel computational strategies are employed in this work to capture the finite temperature condensed phase and entropic effects in cellulose decomposition. System size is limited by the tools used in each strategy. Table S1 provides details on the two strategies, tools and corresponding system configurations.

*Table S1. Computational methods and System configurations*

| **Computational Strategy** | **Tools** | **Purpose** | **System (no. of molecules)** | |
|---|---|---|---|---|
| | | | **Solvent** | **Solute** |
| ConTS | Gromacs v 2018.7 | Finite temperature configuration | 7 cellobiose | 1 cellobiose |
| | VASP 5.4.1 | TS search (enthalpic barrier) | 7 cellobiose | 1 reacting cellobiose |
| Free-energy barrier correction | Gaussian 09 code | TS search (gas phase free-energy barrier) | | 1 reacting cellobiose |
| | Gromacs v 2018.7 (Thermodynamic Integration) | Finite temperature condensed phase interactions | 59 cellobiose | 1 Transition State |

## Condensed phase TS-Search method

Transition states for cellobiose breakdown via transglycosylation and ring contraction are calculated in finite temperature melt-phase environment. Images of the TS are provided in Figure S1. Unlike the finite temperature condensed phase calculations reported in this paper, the enthalpic barriers in the crystal structure (Figure S2) shows a minimum difference in the barriers of only 12.62 kJ/mol between the two mechanisms.

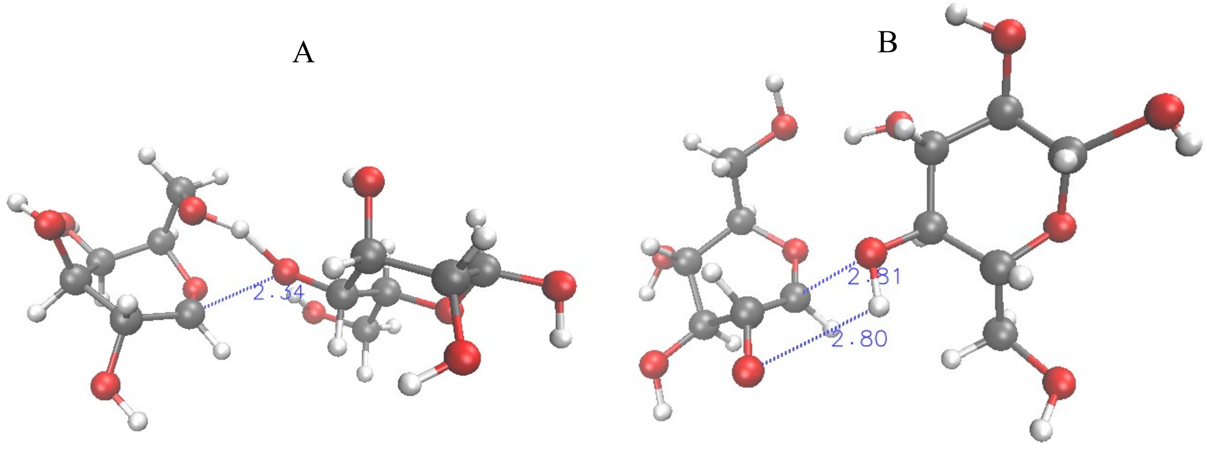


*Figure S1: DFT calculated transition states in condensed phase for (A) Transglycosylation (B) Ring contraction.*

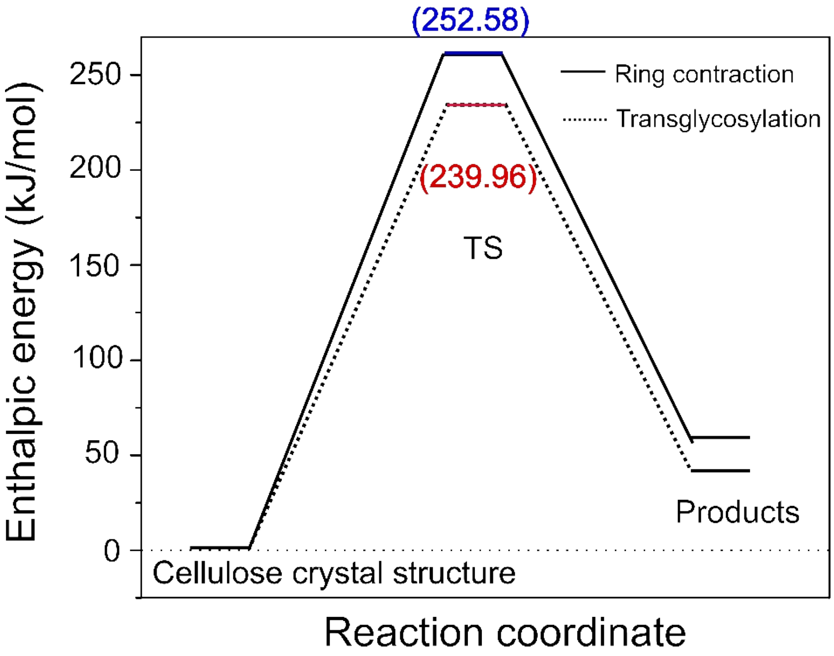


*Figure S2: DFT calculated transition state in crystal structure for (A) Transglycosylation (B) Ring contraction*

## Dispersion Correction

DFT calculations in the study were performed using PBE exchange correlation functional. Dispersion corrections were accounted for by performing DFT-D3 calculations using the Grimme method. As shown in Table S2, the corrections to the functional lead to negligible deviations from the original finite temperature barriers suggesting that the medium range non-covalent interactions have minimum effect of cellulose thermochemistry.

*Table S2: Comparison of finite temperature barriers calculated with and without dispersion corrections*

| **Mechanism** | **Temperature (K)** | **Enthalpic barrier (ΔH) (kJ/mol)** | **ΔH with VdW corrections (kJ/mol)** |
|---|---|---|---|
| Transglycosylation | 500 | 299.30 | 293.70 |
| | 1200 | 164.66 | 156.78 |
| Ring contraction | 500 | 399.73 | 394.56 |
| | 1200 | 294.22 | 288.50 |

## Condensed phase free-energy barrier corrections

### Interaction energy calculations (Thermodynamic Integration)

The interaction energy of the reactive solute molecule (reactant, TS, product) in the condensed phase is captured by calculating the relative solvation free energy using TI implementation in Gromacs 2018.7. The difference in the interaction between the reactant and TS ($\Delta G_R^{int} - \Delta G_{TS}^{int}$) gives the free energy correction to the gas phase barrier, as illustrated in Figure S3.

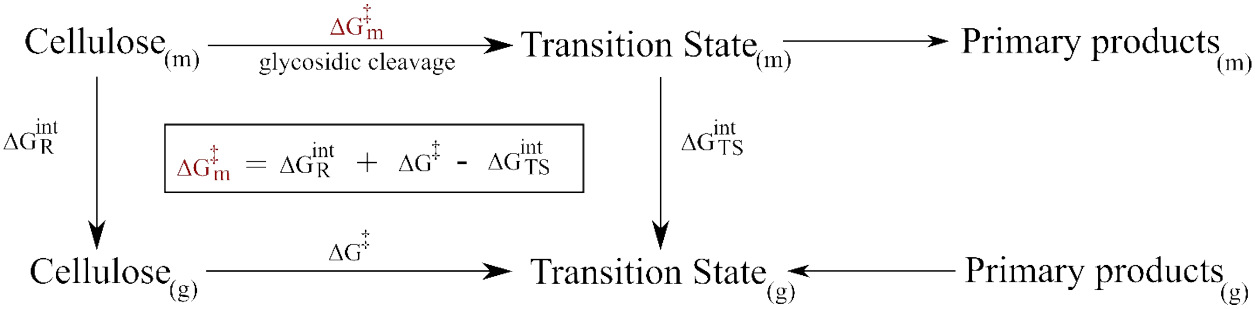
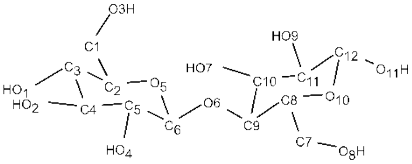


*Figure S3: Schematic showing the calculation of condensed phase corrections to gas phase free energy barriers.*

The non-bonded parameters of the reactant and transition state species used for the calculation of $\Delta G_R^{int}$ and $\Delta G_{TS}^{int}$ in Gromacs is provided in Table S3.

*Table S3: Non-bonding force-field parameters for cellobiose and its transitions states*

| **Molecule** | **Atom name** | **σ (nm)** | **ε (kJ mol)** |
|---|---|---|---|
|  | C1/C2/C3/C4/C5/C6/C7/C8/C9/C10/C11 | 0.350 | 0.276 |
| | H11/H12/H21/H31/H41/H51/H61/H71/H72/H81/H91/H101/H111/H121 | 0.250 | 0.126 |
| | HO2/HO3/HO4/HO6/HO7/HO8/HO9/HO11 | 0.000 | 0.000 |
| | O2/O3/O4/O6/O7/O8/O9/O11 | 0.312 | 0.711 |
| | O1/O5/O10 | 0.290 | 0.586 |

| **Atom name** | **Charge** | | |
|---|---|---|---|
| | **Cellobiose** | **TS - ring contraction** | **TS - transglycosylation** |
| C1 | 0.1132 | 0.081 | 0.1132 |

| | | | |
|---|---|---|---|
| C10 | 0.1545 | 0.1545 | 0.1545 |
| C11 | 0.151 | 0.151 | 0.151 |
| C12 | 0.1961 | 0.1961 | 0.1961 |
| C2 | 0.0795 | 0.0619 | 0.0795 |
| C3 | 0.1108 | 0.1557 | 0.1108 |
| C4 | 0.1343 | -0.1532 | 0.1343 |
| C5 | 0.1675 | 0.2375 | 0.1675 |
| C6 | 0.1978 | 0.191 | 0.0778 |
| C7 | 0.1148 | 0.1148 | 0.1148 |
| C8 | 0.0742 | 0.0742 | 0.0742 |
| C9 | 0.0079 | 0.0079 | 0.0079 |
| H101 | 0.1144 | 0.1144 | 0.1144 |
| H11 | 0.0921 | 0.1027 | 0.0921 |
| H111 | 0.1274 | 0.1274 | 0.1274 |
| H12 | 0.0921 | 0.1027 | 0.0921 |
| H121 | 0.0988 | 0.0988 | 0.0988 |
| H21 | 0.1264 | 0.1805 | 0.1264 |
| H31 | 0.1161 | 0.1362 | 0.1161 |
| H41 | 0.1126 | 0.105 | 0.1126 |
| H51 | 0.1324 | 0.136 | 0.1324 |
| H61 | 0.1046 | 0.2126 | 0.1046 |
| H71 | 0.0992 | 0.0992 | 0.0992 |
| H72 | 0.0992 | 0.0992 | 0.0992 |
| H81 | 0.124 | 0.124 | 0.124 |
| H91 | 0.1205 | 0.1205 | 0.1205 |
| HO1 | 0.4153 | 0.4399 | 0.4153 |
| HO11 | 0.4296 | 0.4296 | 0.4296 |
| HO2 | 0.4143 | 0.452 | 0.4143 |
| HO3 | 0.4147 | 0.4232 | 0.4047 |
| HO4 | 0.449 | 0.4047 | 0.449 |
| HO7 | 0.4402 | 0.4402 | 0.4402 |
| HO8 | 0.4246 | 0.4246 | 0.4246 |
| HO9 | 0.4246 | 0.4246 | 0.4246 |
| O1 | -0.6633 | -0.6936 | -0.6633 |
| O10 | -0.4105 | -0.4105 | -0.4105 |
| O11 | -0.5634 | -0.5634 | -0.5634 |
| O2 | -0.6679 | -0.5404 | -0.6679 |
| O3 | -0.6669 | -0.6693 | -0.5169 |
| O4 | -0.6802 | -0.6756 | -0.6802 |
| O5 | -0.4359 | -0.2858 | -0.4359 |
| O6 | -0.3606 | -0.6068 | -0.3806 |

| | | | |
|---|---|---|---|
| O7 | -0.6741 | -0.6741 | -0.6741 |
| O8 | -0.6942 | -0.6942 | -0.6942 |
| O9 | -0.6567 | -0.6567 | -0.6567 |