Supporting Information for

Mechanistic Insights into the Formation and Deconstruction of Phenyl Glycoside Linkages in Lignocellulosic Biomass

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Figure S.1 shows the relative electronic energy as a function of distance between the C_1 location on xylose and the oxygen at the C_4 location on lignin, with the energy of the complex separated by 2.97 Angstroms taken as reference. The distance between the C_1 location on xylose and the oxygen at the C_4 location on lignin will be referred to as the reaction coordinate. As shown in Figure S.1 when the reaction coordinate is at 2.97 Angstroms, the system is at a minimum and this will be referred to as the reactant complex. Incrementally decreasing (scanning) the distance of the reaction coordinate results in a small barrier, ∼3 kJ/mol at a reaction coordinate distance of ∼2.6 Angstroms. Further, scanning the distance of the reaction coordinate results in a continuous decrease in energy, towards a product complex. Taking the approximate product structure on the left hand side of the scanned plot, i.e., the structure with a reaction coordinate of ∼2.1 Angstrom and a relative energy of ∼ -9 kJ/mol, and implementing geometry optimization with no constraints reveals a distance of ∼1.5 Angstroms in the reaction coordinate, suggesting a carbon-oxygen bond forms. In other words, the product complex corresponds to a phenyl glycoside (PG) linkage forming. Although the barrier of ∼3 kJ/mol is computed in electronic energy, given the minimal magnitude of the barrier, it is assumed the free energy barrier is reasonably approximated by ∼3 kJ/mol as well.

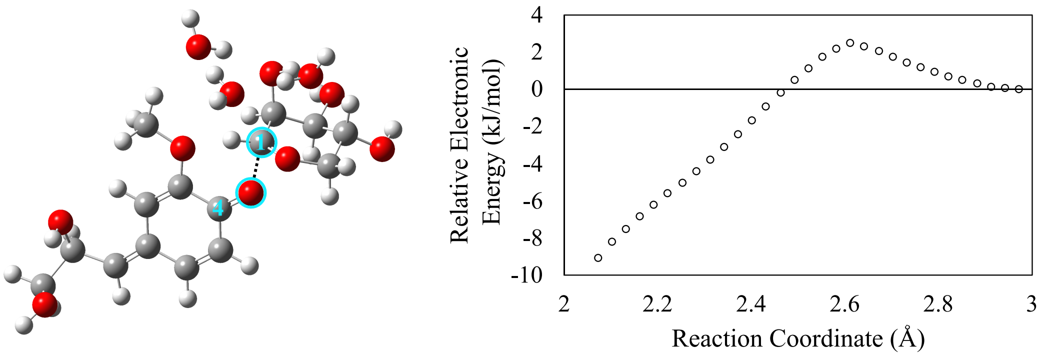

Figure S.1: The relative electronic energy as a function of distance between the C_1 location on xylose and the oxygen at the C_4 location on lignin (reaction coordinate) with the energy of the complex separated by 2.97 Angstroms taken as reference. Energies reported are at a M06-2x/6-311++G(d,p) level of theory

During biomass deconstruction, elevated temperatures are often employed [1, 2], as a result, evaluating the reaction energetics as a function of temperature is necessary to bring the computational results closer to experimental conditions. Figure S.2 and Figure S.3 shows the activation and reaction free energies, respectively, for cleaving the mannose and xylose PG LCC linkage ($C_1 - O_1$ and $O_1 - C_{4'}$) as well as the competing hemicellulose degradation pathways ($C_2 - OH$ and $C_3 - OH$), as a function of temperature. The circles denote the computationally computed values at 298K. The lines represent the predicted free energies as a function of temperature, and were calculated by assuming enthalpic and entropic contributions were constant at the values computed at 298K. Therefore, the predicted reaction energetics were determined by incorporating the absolute temperature, i.e., $\Delta G = \Delta H - T\Delta S$. Such an approach has demonstrated good accuracy in predicting the temperature dependence of biomass deconstruction reaction energetics [3].

As observed in Figure S.2, the free energy barriers demonstrate an inverse correlation with temperature, i.e., as the temperature is increased the activation energies decrease. Such a result is anticipated for the majority of dissociation reaction. Moreover, the activation barriers of each deconstruction reaction show similar slopes. As observed in Figure S.3, the reaction free energy of every pathway shows an inverse correlation with temperature, indicating as the temperature increases, the reaction energies will become more favorable, characteristic of most dissociation reactions. The $O_1 - C_{4'}$ bond breaking is endergonic and demonstrates a minimal temperature dependence, indicating no feasible temperature will be attainable that will result in the $O_1 - C_{4'}$ bond breaking becoming exergonic. The $C_2 - OH$ bond breaking with mannose is endergonic until ~420K, where the reaction becomes exergonic. The $C_2 - OH$ bond breaking with xylose as well as $C_3 - OH$ and $C_1 - O_1$ bond breaking for mannose and xylose are exergonic for the entire temperature range explored. As described in the main paper, cleaving the PG linkage, $C_1 - O_1$ bond breaking, is exergonic and possesses minimal activation barriers, <95 kJ/mol, indicating such a pathway will be the first deconstruction pathway accessible in acid catalyzed deconstruction of PG linkages. Such a conclusion remains consistent even when considering the reaction energetic's temperature dependence.

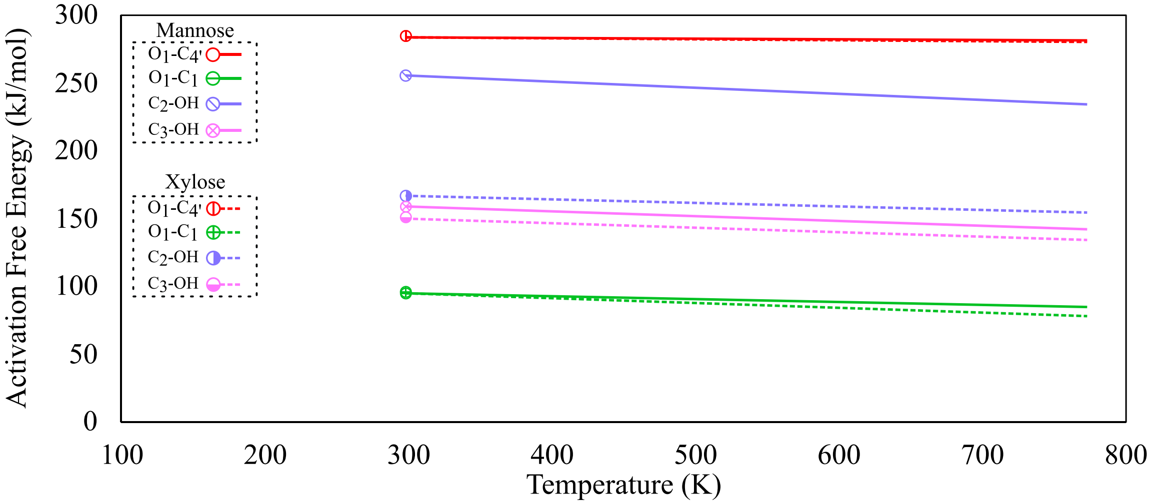

Figure S.2: The free energy barriers for the deconstruction pathways of a phenyl glycoside (PG) LCC linkage as a function of temperature. The circles denote the computationally computed activation barriers at 298K, while the lines are calculated assuming the enthalpic and entropic contributions are constant with the values computed at 298K.

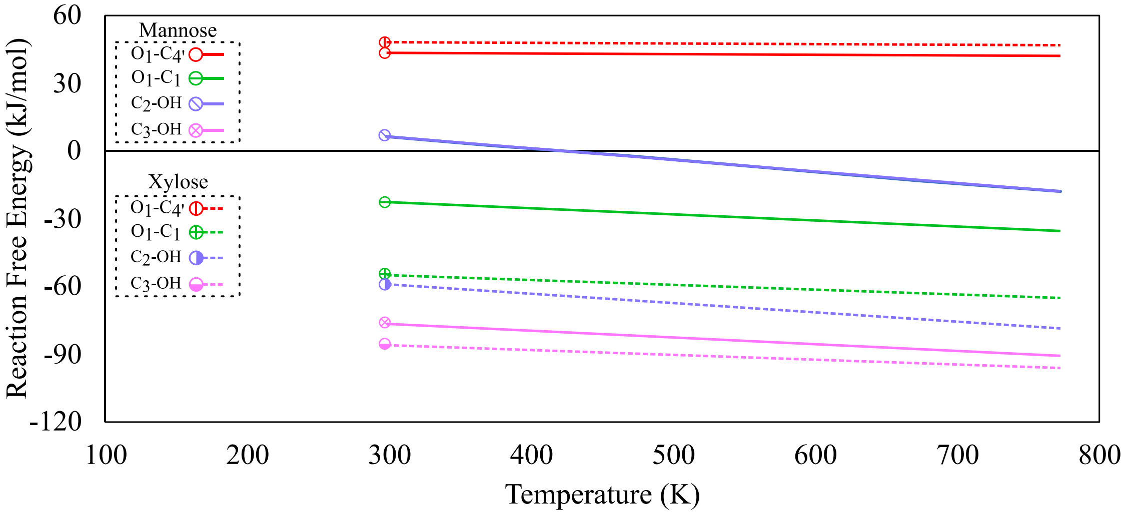

Figure S.3: The reaction free energies for the deconstruction pathways of a PG LCC linkage as a function of temperature. The circles denote the computationally computed reaction energies at 298K, while the lines are calculated assuming the enthalpic and entropic contributions are constant with the values computed at 298K.

References

[1] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Lee, M. Holtzapple, and M. Ladisch, “Features of promising technologies for pretreatment of lignocellulosic biomass,” *Bioresource technology*, vol. 96, no. 6, pp. 673–686, 2005.

[2] V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, and D. B. Levin, “Biomass pretreatment: fundamentals toward application,” *Biotechnology advances*, vol. 29, no. 6, pp. 675–685, 2011.

[3] S. Beck and S. H. Mushrif, “Reaction pathways and energetics of the deconstruction of lignin carbohydrate complexes (lccs) in lignocellulosic biomass,” *Sustainable Energy & Fuels*, 2024.