

Carbohydrate stabilization extends the kinetic limits of chemical polysaccharide depolymerization

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Biomass-derived carbohydrates are important platform molecules for the production of renewable fuels and chemicals. The production of carbohydrates from lignocellulosic biomass requires the extraction of lignin and the cleavage of ether bonds in hemicellulose (mostly xylan) and cellulose chains while minimizing further degradation of the resulting carbohydrates.(1) Current methods lead to incomplete biomass depolymerization (producing only polysaccharides) and high process costs due to mineral acid recovery and enzyme production.(2) In inexpensive systems like pure water or dilute acid mixtures, carbohydrate monomer degradation rates exceed hemicellulose and especially cellulose depolymerization rates at most easily accessible temperatures, limiting sugar yields.

Here, we use a reversible stabilization of xylose and glucose by acetal formation with formaldehyde to alter this kinetic paradigm, preventing sugar dehydration to furans and their subsequent degradation. During a harsh organosolv pretreatment in the presence of formaldehyde and low water content, over 90% of xylan in beech wood was recovered as diformylxylose, stabilized xylose molecule, (compared to 16% xylose recovery without formaldehyde).(3) The subsequent depolymerization of cellulose led to carbohydrates yields over 70% and a final concentration of ~5wt%, whereas the same conditions without formaldehyde led to a yield of 28%.

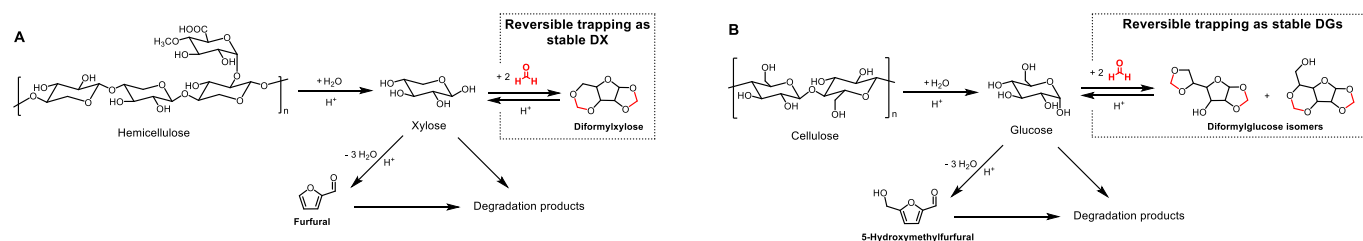


Figure 1 | Carbohydrates stabilization using formaldehyde. Prevention of polysaccharide degradation by reversibly forming (A) diformylxylose and (B) diformylglucose isomers by the addition of formaldehyde during acid-catalyzed biomass pretreatment and cellulose depolymerization

This approach could lead to new processes for depolymerizing and valorizing biomass derived-carbohydrates or their stabilized equivalents. For example, when diformylxylose was used as a starting reactant, similar furfural yields (65%) to those obtained with xylose via hydrogen transfer (1,2-hydride shift) were achieved without Lewis acid addition. Interestingly, no difference in the reaction kinetics was observed when a Lewis acid was added, which suggested that diformylxylose proceeded to furfural through a new mechanism. In light of these results, current efforts are focused on the utilization of these protected carbohydrates as new platform molecules to produce important building blocks such as furans and polyols. These new catalytic processes could help us understand in more depth the reactivity of stabilized carbohydrates and their potential applications within biorefineries.

1. J. S. Luterbacher *et al.*, Nonenzymatic Sugar Production from Biomass Using Biomass-Derived γ -Valerolactone. *Science*. **343**, 277–280 (2014).
2. L. Shuai, Y. M. Questell-Santiago, J. S. Luterbacher, A mild biomass pretreatment using γ -valerolactone for concentrated sugar production. *Green Chem.* **18**, 937–943 (2016).
3. Y. M. Questell-Santiago, R. Zambrano-Valera, M. T. Amiri, Carbohydrate stabilization extends the kinetic limits of chemical polysaccharide depolymerization. *Nature Chemistry* (2018), doi:10.1038/s41557-018-0134-4.