

Stabilization of Carbohydrates with Formaldehyde during Integrated Biomass 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) Lowering acid use to improve process economics requires the use of higher temperatures and generally leads to significant sugar degradation and low yields, which is why these strategies have generally been difficult to implement.

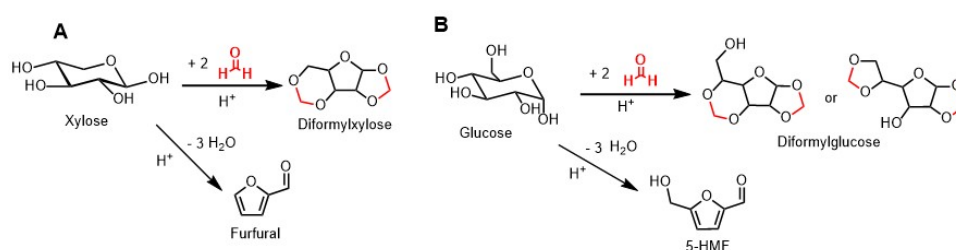


Figure 1. (A) Xylose conversion to diformylxylose and furfural (B) Glucose conversion to diformylglucose isomers and 5-hydroxymethylfurfural (5-HMF).

Recently, we have discovered that formaldehyde (FA) could be used to stabilize lignin and facilitate the conversion of extracted lignin to monomers at high yields (up to 97% of theoretical yield). (3) This method could also prevent xylan degradation by producing a stable xylose-derived molecule that we refer to as diformylxylose. In the current work, we study the stabilization of carbohydrates by the addition of FA during integrated biomass depolymerization. The low water content and the acidic environment in the biomass pretreatment allow FA to react with xylose, forming diformylxylose (Figure 1-A) at yields above 90% and minimizing xylose degradation into furfural. In comparison, reactions without FA lead to almost full xylose degradation into furfural with only 16% xylose recovery. Diformylxylose could be used as is or converted back to xylose at high yields in aqueous environments. A similar process is observed with glucose during cellulose acid depolymerization, forming diformylglucose (DG). The presence of FA led to the formation of two DG isomers from glucose by forming 1,3-dioxolane and 1,3-dioxane structures (Figure 1-B). As with DX, these structures stabilize glucose after depolymerization at conditions that were previously unfavorable due to carbohydrate degradation. Future efforts include the characterization of protected sugars and the removal of their protective groups.

[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] L. Shuai *et al.*, Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization. *Science*. **354**, 329–333 (2016).