Supporting Information

Effects of Xylan Side Chain Substitutions on Xylan-Cellulose Interactions and Implications for Thermal Pretreatment of Cellulosic Biomass

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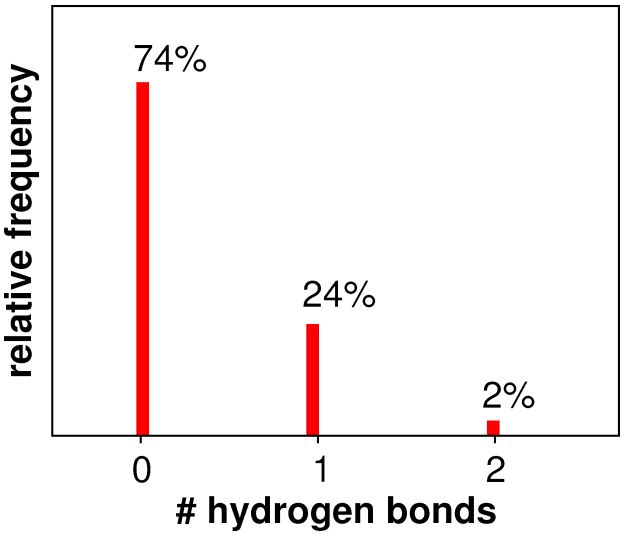

Figure S1. Frequency of GlcA-GlcA hydrogen bonds involving 4-OH groups. During most of the simulation time (74%) no hydrogen bond is formed.

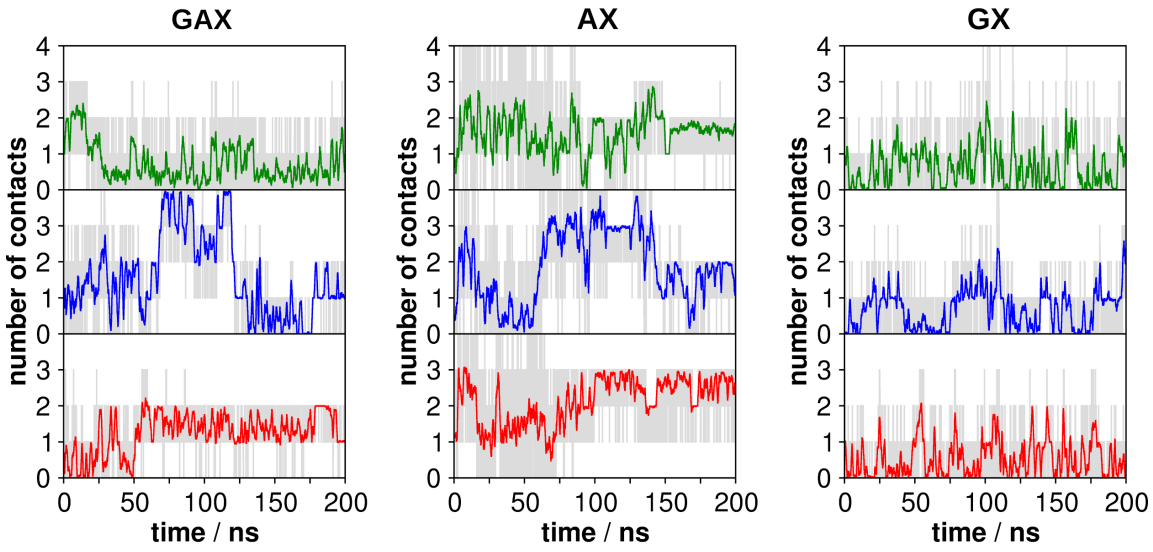

Figure S2. Interaction of GlcA and Ara substitutions with the cellulose surface. The graphics show the number of contacts between the substitutions and the cellulose surface. Since there are 4 substitutions in our xylan models, the number of contacts varies between 0 and 4. Different colors denote different independent MD simulations. Raw data are shown in gray and the colored curves are the smoothed raw data.

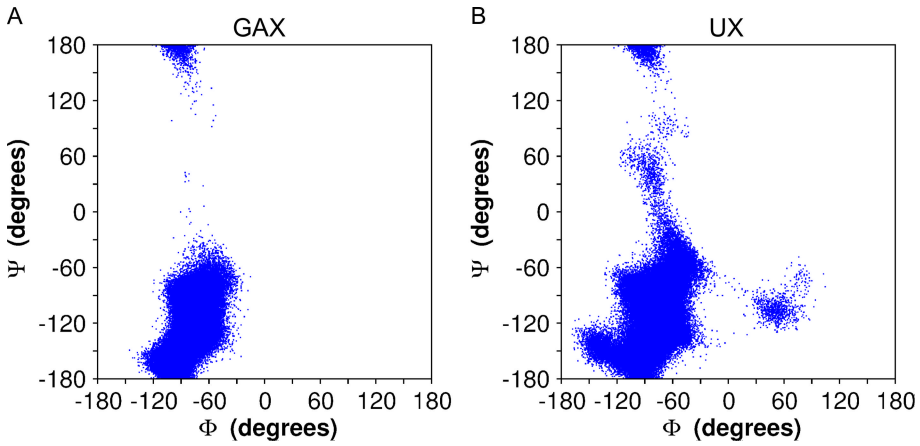

Figure S3. Distribution of glycosidic linkage dihedrals for GAX and UX bound to cellulose. Only the dihedrals adjacent to the α-1,2-GlcA substitutions where considered for GAX and the analogous dihedrals for UX. The results show that the substitutions reduce the backbone conformational flexibility.

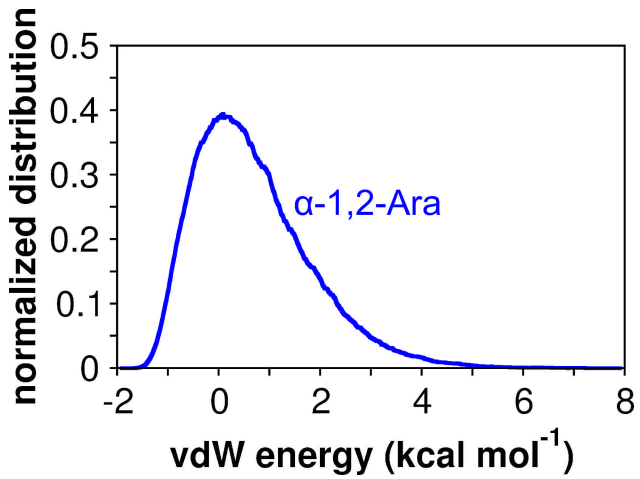

Figure S4. Normalized distribution of the van der Waals energy between the glycosidic oxygen and the α-1,2-Ara substitution.

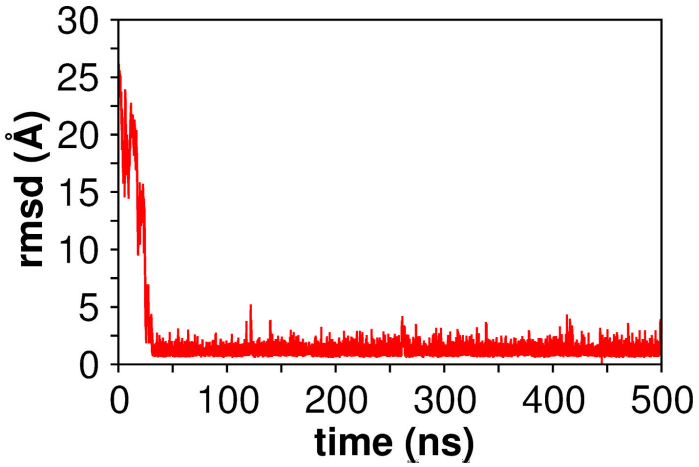

Figure S5. Rmsd of a single GAX chain on cellulose at high temperature, showing that binding to the hydrophobic face persists during the 500 ns of simulated time. The rmsd is calculated relative to the structure where xylan is ideally stretched on the hydrophobic surface.

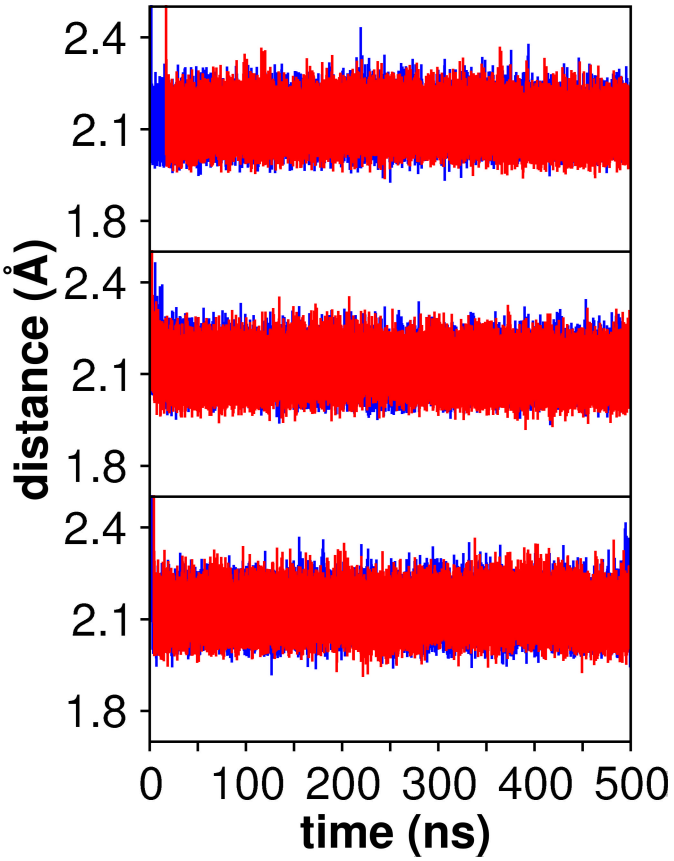

Figure S6. Distance between the two calcium ions (blue and red) and the GlcA substitutions at high temperature, in three independent simulations (different panels).