Deciphering the Structural Complexity of *Populus* Secondary Cell Walls: Implications for Biomass Conversion Efficiency

Francis Burke

The BioSci Publisher, Richmond, British Columbia, Canada

Corresponding email: Francis.Burke@sophiapublisher.com


Received: 05 Jan., 2024
Accepted: 08 Feb., 2024
Published: 19 Feb., 2024

Copyright © 2024 Burke, This is an open access article published under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Preferred citation for this article:


The paper titled "Atomistic, macromolecular model of the *Populus* secondary cell wall informed by solid-state NMR" was published on January 3, 2024, in the open-access journal Science Advances, under the Science Publishing Group. The authors, Bennett Addison, Lintao Ba, Vivek Bharadwaj, Meagan F. Crowley, Anne E. Harman-Ware, Michael F. Crowley, Yannick J. Bomble, and Peter N. Ciesielski are from National Renewable Energy Laboratory and the Colorado School of Mines in Golden, CO, USA. The study presents an atomistic macromolecular model of the secondary cell wall (SCW) in *Populus* wood, focusing on the interactions and configurations of cellulose, hemicelluloses, and lignin. Utilizing solid-state nuclear magnetic resonance (ssNMR) measurements, the research investigates the structural configurations and intermolecular interactions within the SCW. This information is used to develop and refine molecular models through molecular dynamics (MD) simulations, enhancing the understanding of the SCW's architecture and informing biomass deconstruction strategies.

1 Interpretation of Experimental Data

The research highlights the spatial arrangement and interactions of cellulose, xylan, and lignin within the SCW. The 1D 1H-13C MultiCP-MAS ssNMR spectrum identifies distinct environments for cellulose and indicates the presence of acetylated xylan and lignin. Selective 1D MultiCP-DARR difference data quantify polymer-polymer contacts at the nanometer scale, showing how magnetization moves between carbon environments, providing crucial distance information for constructing accurate molecular models.

Figure 1 presents a comprehensive analysis of lignified *Populus* secondary cell walls (SCWs) using 1D 1H-13C MultiCP-MAS solid-state NMR (ssNMR). The spectrum delineates the chemical environments of the primary polymers: cellulose (gray), xylan (blue), and lignin (green), with specific regions assigned to their characteristic peaks. Cellulose's assignments include peaks for C1, C2, C3, C5, and C6 carbons. Xylan is highlighted by signals corresponding to acetylation and glucuronic acid residues. Lignin's spectrum reveals syringyl (S) and guaiacyl (G) units, identified through their aromatic and side-chain carbons, including the notable β-O-4 linkages. The black trace represents the raw data, while the red trace shows the fitted model, illustrating the accuracy of the spectral deconvolution informed by the combined 1D and 2D ssNMR data. This detailed spectral analysis aids in understanding the complex structural composition and interactions within *Populus* SCWs.

Figure 3 illustrates atomistic models of *Populus* secondary cell walls (SCWs) with various arrangements of cellulose, xylan, and lignin. The left panel shows several model variants, named based on the arrangement of hemicellulose and lignin. For instance, model "a" has all xylan bound to cellulose, while "b" models have 70% xylan bound to cellulose and 30% interspersed with lignin. The right panel presents a polar plot comparing the percentage of sink atoms within 1 nm of source atoms in these models against experimental ssNMR spin-diffusion data. The models vary in their alignment with experimental data, indicating different structural proximities within SCWs.
Figure 1 1D $^1$H-$^{13}$C MultiCP-MAS ssNMR provides a broad overview of lignified Populus SCWs
Note: General assignment regions are indicated for the predominant constituent polymers cellulose (gray), xylan (blue), and lignin (green), along with representative structures and their assignments indicated with color-coding. Chemical shift information and peak profiles extracted from a combined set of 1d and 2d ssNMR data were used to inform spectral deconvolution efforts used throughout this work; The raw data are shown in black, and the resultant fit is shown in red; a: Cellulose; Xn: Xylan; Ac: Acetyl; GalA: Galacturonic acid (pectin); GlcA: α-d-glucuronic acid; [4OMe] GlcA: (4-O-methyl)-α-d-glucuronic acid

Figure 3 Atomic SCW periodic model variants and comparison of their proximity analyses with ssNMR spin-diffusion experiments
Note: Left: Snapshots of several molecular model variants for the poplar ScW. The naming convention is as follows: the letter refers to the relative arrangement of hemicellulose and lignin, where “a” denotes a model with all xylan bound to cellulose, and no xylan interspersed with lignin; “b” denotes a model with 70% hemicellulose bound to cellulose, and the remaining 30% interspersed in the surrounding lignin-xylan matrix; “d” denotes a model with lignin-bound cellulose and with hemicellulose as the surrounding layer; “e” denotes a model with phase-separated hemicellulose and lignin both bound to cellulose at the top and bottom, respectively; “h” denotes a model with hemicellulose interspersed within the 18-chain elementary cellulose fibril leaving room for increased direct lignin-cellulose interaction. the number after the decimal denotes the number of 18-chain elementary fibrils in the model. b.8 and b.10 are larger systems constructed with 70% of xylan bound to cellulose, and the remaining 30% interspersed with lignin and consist of eight and ten 18-chain cellulose elementary fibrils, respectively. Right: Calculated percentage of sink atoms within 1 nm of source atoms in the model variants compared to that obtained from ssNMR spin-diffusion experiments depicted on a polar plot; The four dashed lines originating from the center indicate the four ssNMR magnetization metrics, with the experimental values indicated as black dots and the colors indicating the various models

Figure 4 depicts the atomistic model of lignocellulose assembly within Populus secondary cell walls (SCWs), aligning with ssNMR data. Panel A shows the molecular structures of lignin, xylan, and cellulose. Panel B illustrates their macromolecular assembly, where xylan on the cellulose surface adopts an extended configuration, pointing towards lignin. Panel C highlights the cellulose component, comprising two core bundles of four 18-chain elementary fibrils. Panel D focuses on hemicellulose, revealing a nearly complete sheath around cellulose, minimizing direct cellulose-lignin contact and some xylan isolated within core bundles. Panel E indicates that lignin primarily interacts with hemicellulose, with minimal direct contact with cellulose. This model underscores the spatial organization and interactions of these biopolymers, crucial for SCW integrity.
2 Insight of Research Findings
The study shows that the SCW's mechanical integrity and resistance to deconstruction arise from the complex interactions between cellulose, hemicelluloses, and lignin. The ssNMR data reveal subnanometer interactions, essential for understanding the SCW's structure. Molecular dynamics simulations support these findings, confirming the significance of initial polymer placement and suggesting minimal rearrangement over time.

3 Evaluation of the Research
The research successfully integrates ssNMR data with molecular dynamics simulations to provide a detailed macromolecular model of the SCW. The study's approach offers valuable insights into the structural arrangement of biopolymers, contributing to a better understanding of lignocellulosic biomass and its potential applications. However, limitations include the reliance on spectral deconvolution and the need for further investigation into different cell types and more mature wood samples.

4 Concluding Remarks
The study advances our understanding of the SCW architecture in Populus wood, highlighting the importance of polymer interactions at the nanometer scale. The integration of experimental and computational methods provides a robust framework for future research on plant cell wall structures and their applications in renewable energy and materials science.
Figure 5 Contrasting conformation of xylan polymers with different proximities to cellulose

Note: (A) Xylan bound to cellulose (orange) adopts conformations that enable acetate groups to consistently orient away from the cellulose surface. Unbound xylose (light blue) adopts a more random orientation of acetate groups. Exemplary xylan polymers are shown in licorice representation, with their acetate groups highlighted as spheres, and cellulose is shown as a white surface. (B) Unbound xylan $\phi + \psi$ distributions are not exclusively 31 and span a large range of values with a peak at ~1700. (C) For xylan chains with similarly oriented acetate groups, a wide distribution of canonical $\phi + \psi$ conformations is observed, although a peak ~1000 is prominent. (D) $\theta_2(O2-c5-c5-O2)$ values for the unbound xylan chain are widely distributed corresponding with the nonuniform acetate group orientations. (E) Bound xylan exhibits a narrow $\theta_2$ distribution centered at 00, which highlights the consistent orientation of acetate groups. Definition of canonical $\phi + \psi$ and $\theta_2(O2-c5-c5-O2)$ dihedral measurements is portrayed in (F) and (G), respectively.

5 Access the Full Text

Acknowledgement
I sincerely appreciate the open-access policy of Science Advances, which allows readers to freely share this valuable research. I would also like to thank the research team led by Yannick J. Bomble, and Peter N. Ciesielski for their outstanding work, which provides a valuable case for studies on plant cell wall architecture and its implications for renewable energy and materials science. Given that reviewers may have different perspectives on the interpretation of the data and results, I apologize if my analysis and evaluation differ from the authors' original intent. I look forward to further research to delve deeper into the complexities of this field.