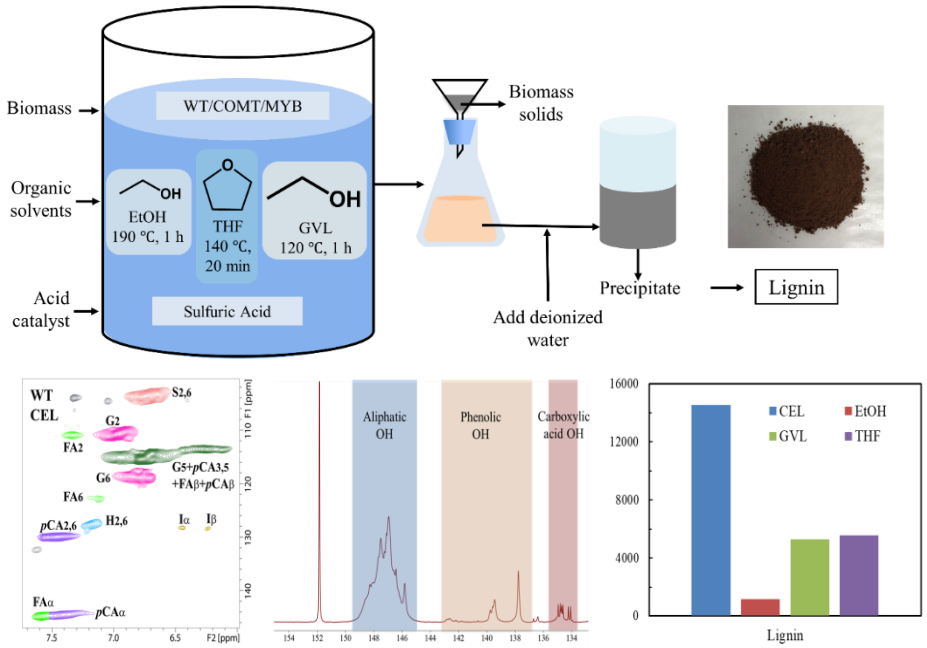
Different Solvent Pretreatments Result in Extracted Lignins with Altered Structures from Switchgrass



Top: Scheme of switchgrass pretreatment; Bottom: Characterization using HSQC, ^{31}P NMR and GPC

Scientific Achievement

We compared three organosolv pretreatments—ethanol (EtOH), tetrahydrofuran (THF), and γ–valerolactone (GVL)—for extraction of lignin from wild type and lignin-modified transgenic switchgrass, considering lignin utilization for high-value products.

Significance and Impact

This work examined the potential for combined genetic modification and organosolv pretreatments to decrease switchgrass recalcitrance. EtOH-lignin showed most significant change in molecular weights and inter-unit linkages, suitable for antioxidant applications. THF/GVL-lignin had higher molecular weights, inter-unit linkages and aliphatic hydroxyl contents, good for mono-aromatic compounds.

Research Details

- Lignin structural change during pretreatment process was studied using FTIR, HSQC, ^{31}P NMR, GPC and SAXS.
- Molecular dynamics simulations suggest a connection between the depolymerization of lignin and its ability to hydrogen bond with three organic solvents.

Liang et al., *ACS Sust Chem Eng* (2022). doi.org/10.1021/acssuschemeng.2c00948

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Liang article featured on cover of *ACS Sustainable Chemistry & Engineering*.

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"Chemical and Morphological Structure of Transgenic Switchgrass Organosolv Lignin Extracted by Ethanol, Tetrahydrofuran, and γ-Valerolactone Pretreatments"
Luna Liang, Yun-Yan Wang, Samarthya Bhagia, Vaidyanathan Sethuraman, Zhi Yang, Xianzhi Meng, Nathan Bryant, Loukas Petridis, Jeremy C. Smith, Sai Venkatesh Pingali, Nidia C. Gallego, Yunqiao Pu, Barbara R. Evans, Hugh M. O'Neill, Brian H. Davison, and Arthur J. Ragauskas
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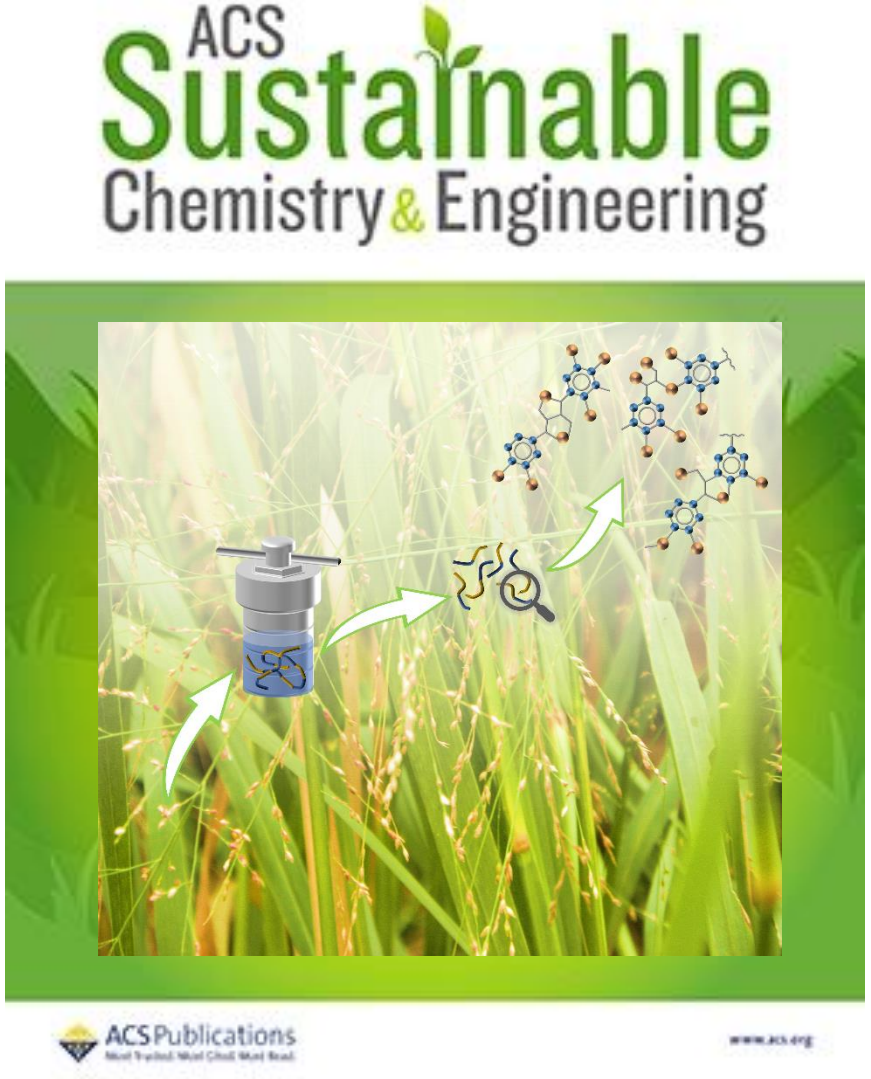
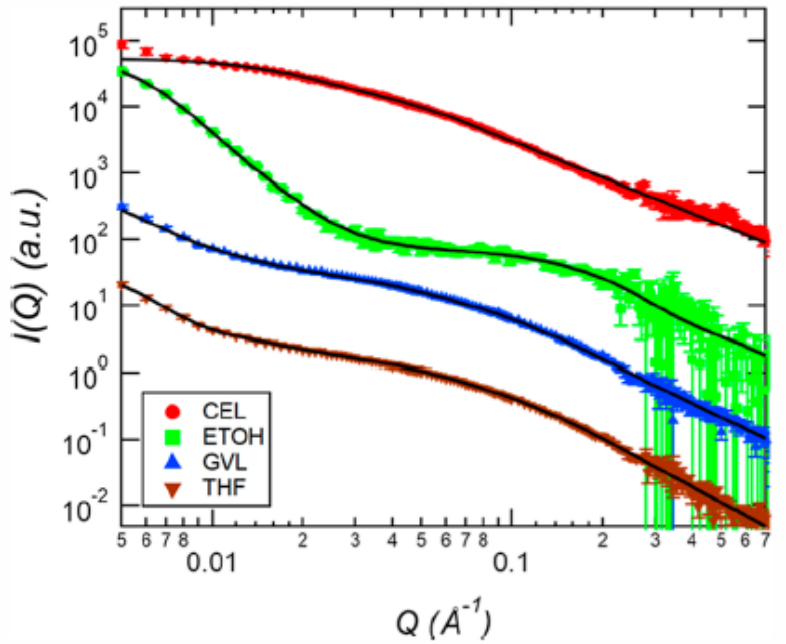
Caption (draft): Switchgrass is pretreated in various organic solvents under moderately elevated temperature, pressure and dilute acid. This extracts the lignin from the cellulose resulting in various lignin dimers and oligomers – suitable for further processing and valorization.



SAXS provides detailed extracted lignin structural information from Different Solvent Pretreatments from Switchgrass



SAXS profiles of recovered WT switchgrass lignin samples solubilized in 100% DMSO at 1.0 w/v % for the enzymatic-pretreated, CEL (red) and organosolv-pretreated, EtOH (green), GLV (blue), and THF (brown) with the unified fits as solid blank lines.

The recalcitrance of lignocellulosic biomass is a challenge in biological-based biorefinery systems due to the complex physicochemical structure of plant cell walls. Pretreatment and genetic modification are two approaches in biomass conversion that have succeeded in modifying the structure of lignocellulose to enable better enzymatic deconstruction. However, the structural differences among pretreatment-solubilized lignin isolated from switchgrass genotypes have not been extensively investigated.

Use of SAXS

- SAXS (at the BNL NSLS-II) provided detailed structural information about the extracted lignins. These included size (R_g) and lignin polymer arrangement (exponent P). These analyses complemented insights from NMR, GPC and molecular dynamics.
- We acknowledge the help of the BNL beam scientists to enable us to run a large number of samples in a short time.

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