

195. Chemical Factors that Control Lignin Polymerization

Amandeep K. Sangha^{1,2*} (sanghaak@ornl.gov), Brian H. Davison,² Robert F. Standaert,^{2,3} Mark F. Davis,^{2,4} Jeremy C. Smith,^{1,2,3} Jerry M. Parks,^{1,2,3} and Paul Gilna² (BESC PI)

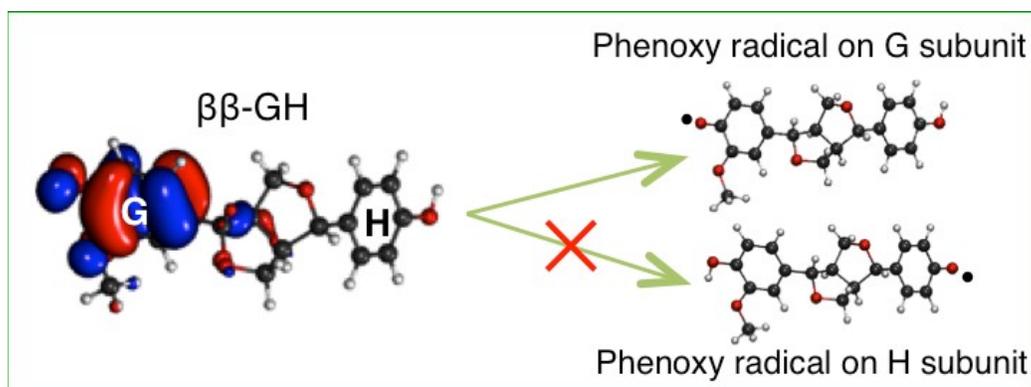
¹UT/ORNL Center for Molecular Biophysics; ²BioEnergy Science Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Biology and Soft Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ⁴Bioenergy Science Center, National Renewable Energy Laboratory, Golden, Colorado

<http://bioenergycenter.org>

Project Goals: The BioEnergy Science Center (BESC) is focused on the fundamental understanding and elimination of biomass recalcitrance. BESC's approach to improve accessibility to the sugars within biomass involves 1) designing plant cell walls for rapid deconstruction and 2) developing multi-talented microbes or converting plant biomass into biofuels in a single step (consolidated bioprocessing). BESC researchers provide enabling technologies in characterization, genomics, modeling and data management in order to 1) understand chemical and structural changes within biomass and 2) to provide insights into biomass formation and conversion.

Lignin structure, degree of polymerization and composition play an important role in biomass recalcitrance. Lignin formation involves the biosynthesis of monolignols, their transport to the cell wall lignification zone, peroxidase-mediated oxidation of lignin precursors, and finally radical coupling reactions to elongate growing lignin chains. We have performed quantum chemical calculations to investigate whether there might be chemical control of lignin polymerization.

We used density functional theory calculations to investigate the reactivity of various mono-, di- and trilignols comprising *p*-hydroxyphenyl (H) and guaiacyl (G) subunits linked through common β -O4, β - β and β -5 inter-unit bonds. We found that the composition of the highest occupied molecular orbital (HOMO) of neutral lignol oligomers plays a critical role in their oxidation: only lignol precursors with strong HOMO electron density on the phenolic oxygen can undergo facile oxidation to form radicals, which then participate in lignin chain elongation.



These results provide an explanation of why terminal H subunits and β -5 linkages involving either H or G subunits can stop chain elongation. The results also provide a coherent framework for understanding the propensity for growth or termination of different terminal subunits and inter-unit linkages in various lignin polymers.

The BioEnergy Science Center is a U.S. Department of Energy Bioenergy Research Center supported by the Office of Biological and Environmental Research in the DOE Office of Science.