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# **Title**

Supramolecular self-assembled chaos: polyphenolic lignin's barrier to cost-effective lignocellulosic biofuels

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Supramolecular self-assembled chaos: polyphenolic lignin's barrier to cost-effective lignocellulosic biofuels.

Achyuthan KE, Achyuthan AM, Adams PD, Dirk SM, Harper JC, Simmons BA, Singh AK.

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### Abstract

Phenylpropanoid metabolism yields a mixture of monolignols that undergo chaotic, non-enzymatic reactions such as free radical polymerization and spontaneous self-assembly in order to form the polyphenolic lignin which is a barrier to cost-effective lignocellulosic biofuels. Post-synthesis lignin integration into the plant cell wall is unclear, including how the hydrophobic lignin incorporates into the wall in an initially hydrophilic milieu. Self-assembly, self-organization and aggregation give rise to a complex, 3D network of lignin that displays randomly branched topology and fractal properties. Attempts at isolating lignin, analogous to archaeology, are instantly destructive and non-representative of in planta. Lack of plant ligninases or enzymes that hydrolyze specific bonds in lignin-carbohydrate complexes (LCCs) also frustrate a better grasp of lignin. Supramolecular self-assembly, nanomechanical properties of lignin-lignin, lignin-polysaccharide interactions and association-dissociation kinetics affect biomass deconstruction and thereby cost-effective biofuels production.

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