

## FRACTIONATION AND CHARACTERIZATION OF LIGNIN STREAMS FROM ENGINEERED SWITCHGRASS

*Enshi Liu<sup>1</sup>, Lalitendu Das<sup>1</sup>, Bingyu Zhao<sup>2, 4</sup>, Mark Crocker<sup>3, 4</sup>, Jian Shi<sup>1, \*</sup>*

*<sup>1</sup>Biosystems and Agricultural Engineering, University of Kentucky, Lexington, KY 40546*

*<sup>2</sup>Department of Horticulture, Virginia Tech, Blacksburg, VA 24061*

*<sup>3</sup>Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511*

*<sup>4</sup>Department of Chemistry, University of Kentucky, Lexington, KY 40506*

*Email: j.shi@uky.edu*

Development of biomass feedstocks with desirable traits for cost effective conversion is one of the main focus areas in biofuels research. Pretreatment is a crucial step for making biomass feedstocks more amenable to biological conversion by unlocking sugars for fermentation. Nevertheless, as suggested by techno-economic analyses, the success of a lignocellulose-based biorefinery largely relies on the utilization of lignin to generate value-added products, i.e. fuels and chemicals. The fate of lignin and its structural/compositional changes during pretreatment have received increasing attention of late; however, the effect of genetic modification on the fractionation, depolymerization and catalytic upgrading of lignin from engineered plants is not well understood. This study aims to fractionate and characterize the lignin streams from wild-type and engineered switchgrass species (with low/high lignin content and high S or G lignin content) using three different pretreatment methods, i.e. dilute acid, ammonia hydroxide, and ionic liquid (cholinium lysinate). The molecular weight of the lignin fractions recovered from the liquid and solids streams after pretreatment and enzymatic hydrolysis was determined by gel permeation chromatography (GPC), while the cleavage of inter-unit lignin linkages was tracked by  $H^1C^{13}$  HSQC NMR, results being compared with lignin in untreated switchgrass. Analytical-scale pyrolysis of lignin streams was carried out in a pyrolysis-GC/MS instrument to characterize the lignin pyrolysates and provide information about lignin structure and composition. Results from this study provide a better understanding of how lignin engineering of switchgrass influences lignin fractionation and upgrading during conversion processes based on different pretreatment technologies.