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7th International Conference on
GREEN CHEMISTRY & TECHNOLOGY

June 18-20, 2018 | Dublin, Ireland

J Ind Environ Chem 2018, Volume 2 | DOI: 10.4066/2591-7331-C1-003

INVESTIGATING THE RECALCITRANCE OF BIORESOURCES FOR BIOFUELS

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After a 'slow-start,' we have seen the development of commercial cellulosic-ethanol plants on a global basis employing either the thermochemical or the biological technology platform. Despite these successes, numerous challenges remain which hinder broad acceptance of biofuels which for the biological platform include the recalcitrance of biomass and what to do with lignin. Research studies by our group and others have clearly shown that the recalcitrance of biomass is a multi-tiered effect due to the complex nature of the plant cell wall. On-going studies have shown that the natural variance of the plant-cell wall can influence recalcitrance and chemical pretreatments substantially altering the structure of the cell-wall components further reducing recalcitrance. Analysis of cellulose, hemicellulose and lignin from low and high recalcitrance biomass feedstocks including switchgrass and poplar, before and after chemical pretreatment, is one of the most promising methodologies to investigate and dissect the fundamental mechanisms of recalcitrance. Employing these protocols, we have shown that acidic and neutral pretreatments usually provide a biomass resource with increased crystallinity which is less reactive to cellulose and thereby not a beneficial component to reducing recalcitrance. The loss of hemicelluloses and changes in structure of lignin, during these pretreatments, certainly provides a more reactive biomass for biological deconstruction. Depending on the severity of the pretreatment, lignin undergoes a series of competing depolymerization reactions cleaving β-O-aryl ethers which can then undergo further condensation reactions. Likewise, the cleavage of ester linkages involving p-hydroxyl benzoic and other ester linkages, can decrease the affinity of cellulase to lignin and rupture LLC bonds which are beneficial to reducing recalcitrance. These changes in plant cell polymers also 'open-up' the cell wall structure which increase biomass accessibility and allows greater access to cellulose by cellulases. This presentation will examine how advanced NMR and GPC techniques can be used to investigate the changes in bulk cell wall chemistry and how ToF-SIMS can be used to monitor changes on the surface of biomass before and after pretreatment.