FRACTIONATION AND CHARACTERIZATION OF SOLUBILIZED BIOPOLYMERS FROM ALKALINE PULPING LIQUORS

The conversion of lignocellulosic biomass to renewable liquid fuels or chemicals offers one approach to decrease dependence on fossil fuels. Attempts at commercializing the biochemical production of biofuels from lignocellulose has been hindered by the costs associated with pretreatment, enzyme production, and feedstock transportation. The infrastructure established by the forest products industry offers a way to decrease initial capital costs, and to generate new products and revenue from an industry showing declined profits. This work addresses two general themes of applying alkaline pulping chemistries to: (1) extract, separate, and recover chemically altered non-cellulosic biopolymers from woody biomass and (2) evaluate the impact that the removal of non-cellulosic biopolymers have on the yields of monomeric sugars by enzymatic hydrolysis. These general themes were addressed through three studies.

First, bench scale alkali extractions performed on a variety of hardwoods indicated that hemicellulose and lignin extractability was dependent on biomass species, which in turn were related to initial composition and properties of the cell walls. Ethanol precipitation could recover
the hemicellulose fraction and following precipitate bleaching the recovered material yielded 65-80% hemicellulose, depending on biomass source. Molecular weight characterization of the recovered hemicellulose by size-exclusion chromatography (SEC) indicated the presence of lignin and carbohydrates eluting at the 3-12 kDa range, and the application of novel reducing end quantification estimated the number average degree of polymerization would reach an asymptotic limit of 25 for switchgrass and 120 for silver birch. The high extraction yields of hemicellulose identified conditions that could be utilized to remove hemicellulose prior to chemical pulping or during alkaline pretreatments.

Lignin characterization was performed on fractions generated from a softwood kraft black liquor to determine the properties of solubilized lignin that resulted in their phase-partitioning behavior during a novel acidification process using CO₂. A bulk of the lignin precipitated between a pH of 11.6 to 10.0, with earlier fractions contaminated by higher levels of aliphatic extractives and polysaccharides. Lignin fractions were characterized for functional groups by ¹H and ¹³C NMR, molecular weight by gel-permeation chromatography (GPC), and lignin monomer generation by analytical pyrolysis-GC/MS. Select structural and chemical properties of the lignin fractions were correlated based on their linear dependencies to relate phase-partitioning behavior with respect to pH.

Lastly, alkaline pulping trials were conducted in a pressurized 10 L reactor vessel to determine hemicellulose and lignin dissolution during the course of a soda pulping process and to understand how pulping conditions may impact hydrolysis yields. Hemicellulose dissolution increased until the maximum temperature was reached (170°C) followed by a decrease in the polysaccharide content of the black liquor, an effect of polysaccharide degradation and re-
adsorption to the residual wood fibers. Lignin dissolution increased throughout the pulping trials, and at the most severe condition (1 hour at 170°C) only 10% of the lignin remained in the woody biomass. The alkaline pulping trials also produced a digestible substrate that generated high yields of monomeric sugars, over 80% for glucan and 60% for xylan, after enzymatic hydrolysis.