BioFuels from Lignin and Novel Biodiesel Analysis (2009)

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The forest biorefinery concept involves converting a pulp mill into a multi-purpose biofuels, biomaterials, and biopower production facility in which these products are produced in an environmentally compatible and sustainable manner. A key challenge in this process is the recovery of lignin from process streams such that it can be utilized in a variety of innovative green chemistry processes.

The first part of this thesis presents a study based on green prospects for the paper industries current (black liquor) and future (ethanol organosolv) lignin rich solutions. The first study examines the fundamental chemical structure of LignoBoost derived lignin recovered from Kraft pulping streams using an acid precipitation/washing methodology. Functional group analysis and molecular weight profiles were determined by nuclear magnetic resonance (NMR) and size exclusion chromatography. These findings gave valuable insight into the physical properties and the determining chemical properties of this currently underutilized, renewable bioresource. A known chemical structure and composition provided valuable data to optimize a subsequent controlled catalytic deoxygenation and liquefaction step for high yield biooil production.

The second study is based on the future second generation bioethanol production process, where ethanol produced from lignocellulosic materials will bring about the co-production of significant amounts of under-utilized lignin. The study examines the potential of conventional heterogeneous and novel homogeneous catalysts for the selective cleavage of the aryl-O-aryl and aryl-O-aliphatic linkages of ethanol organosolv lignin to convert it from a low grade fuel to potential fuel precursors or other value added chemicals. The experimental data demonstrated that aryl-O-aryl and aryl-O-aliphatic linkages could be cleaved and the hydrogenated lignin had a decrease in oxygen functionality and the formation of products with lower oxygen content.

The second part of this thesis reports the development and optimization of a novel qualitative method for the determination of the various types of hydroxyl groups present in biodiesel production streams. In the first study, the use of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) as a phosphitylation reagent for quantitative 31P-NMR analysis of the hydroxyl groups in biodiesel process samples has been developed. Subsequently a characteristic chemical shifts library is developed with model compounds to provide quantitative data on the concentration of alcohol, free glycerol, partially hydrolyzed triglycerides and free fatty acids in a rapid manner.

The last part of this thesis depicts the results of an industrial trial based on the novel biodiesel analytical method developed earlier. Due to optimized sample preparation and signal acquisition, the novel TMDP/31P–NMR method can handle samples through the whole production line regardless of process step or feedstock used, becoming a novel research tool for process step optimization and for the characterization of biodiesel and its processing components.