



ABSTRACTS

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**Session 2A: From Pretreatment to
Fractionation**

PRETREATMENT FOR BIOBASED PRODUCTS

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Successful pretreatment is closely linked to the rates and extents of biocatalytic depolymerization of the structural carbohydrates in the plant cell walls. Pretreatment disrupts the close association of the cellulose and hemicellulose components associated with lignin in plant cell wall structures, thereby making the structural carbohydrates accessible to the action of enzymes or microorganisms. The exact nature of pretreatment depends on the type of products that are to be obtained from the biomass itself. Furthermore, the economic processing of lignocellulose to biofuels and bioproducts requires high concentrations of cellulosic slurries (>15 %) and conditions that minimize formation of sugar degradation products. The slurry itself must be readily pumpable for purposes of scale-up. This paper discusses pretreatment chemistry and the manner in which the plant cell wall structure may be altered to disrupt its physical structure while avoiding chemical changes that lead to aldehydes and other inhibitory degradation products. The role of pretreatment in fractionating sugars from biomass materials, and the interaction of enzymes with pretreated materials to form fermentable sugars, useful for bioproduct formation, will be addressed. The differences and benefits of different types of pretreatment – acid, base, and water – will also be compared.

Disclosure: Michael Ladisch is CTO of Mascoma Corporation.

HOW CAN WE IMPROVE THE DISSOLUTION AND RECOVERY OF BIOPOLYMERS FROM BIOMASS IN IONIC LIQUIDS SPECIFICALLY FOR BIOFUELS APPLICATIONS?

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We and others have demonstrated the dissolution and separation of the biopolymers in lignocellulosic biomass using ionic liquids (ILs) as solvents. In this presentation, we will discuss several aspects of this approach which might improve the biopolymer separation and energy efficiency of the process. Specifically we will address whether utilizing elevated temperatures (above the lignin glass transition temperature of 150 °C) at shorter times might be more effective than lower temperatures at longer times. In addition, we will discuss potential catalytic routes to help selectively cleave lignin from holocellulose to provide cleaner biopolymers requiring less subsequent processing. Finally we will discuss some aspects of IL recycle and reuse which must be addressed for the processes to become industrially viable.

WHICH FRACTIONATION PROCESS CAN OVERCOME TECHNO-ECONOMIC HURDLES OF A LIGNOCELLULOSIC BIOREFINERY?

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Lignocellulosics are considered as feed stock for transportation fuels and chemicals because they address two pressing global issues; climate change and “peak oil”. The collection and processing of wood at centralized facilities is already practiced by the forest products industry. Therefore, the production of renewable and carbon-neutral biofuels and chemicals besides traditional products such as paper, tissue, board and wood products also presents a great opportunity to the forest products industry to improve its profitability. Since the market for transportation fuels is an order of magnitude larger than the pulp market, these new products will have a lower price than pulp. Therefore at the present time the new products should be produced from the non-cellulose part of the wood chips or from additional biomass. To minimize capital and operating cost, the scale of the lignocellulosic biomass conversion should be maximized and closely integrated with pulp production. Also the biomass fractionation process must be omnivorous process and simple in order to minimize operating and capital costs.

The AVAP® process which uses SO₂-ethanol-water to fractionate lignocellulosics in hemicellulose sugars, degraded cellulose and sulfonated lignin may satisfy these requirements. The absence of a base (Mg, Na, etc) reduces the recovery of SO₂ and ethanol to simple absorption, distillation and washing unit operations. Also, the absence of bisulfite in the fractionation solution avoids degradation of the dissolved sugars. The presence of SO₂ eliminates troublesome lignin-based precipitates, hydrolyzes the hemicelluloses, and allows fractionation of a mixture of lignocellulosic biomass, including softwoods. At the same time the presence of ethanol leads to rapid impregnation of the biomass, thereby avoiding energy consuming size reduction unit operations and allowing high space velocity in the fractionation reactor. The science as well as some techno-economics of this promising omnivorous fractionation process will be discussed. Results to produce butanol from the conditioned hemicellulose fraction will be presented.

ADVANCED BIOFUELS – RESEARCH PROGRESS AT THE JOINT BIOENERGY INSTITUTE

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Today, carbon-rich fossil fuels, primarily oil, coal and natural gas, provide 85% of the energy consumed in the United States. Fossil fuel use increases CO₂ emissions, increasing the concentration of greenhouse gases and raising the risk of global warming. The high energy content of liquid hydrocarbon fuels makes them the preferred energy source for all modes of transportation. In the US alone, transportation consumes around 13.8 million barrels of oil per day and generates over 0.5 gigatons of carbon per year. This has spurred intense research into alternative, non-fossil energy sources.

The DOE-funded Joint BioEnergy Institute (JBEI) is a partnership between six leading research institutions (Lawrence Berkeley Lab, Sandia Labs, Lawrence Livermore Lab, UC-Berkeley, UC-Davis, and the Carnegie Institute for Science) that is focused on the production of infrastructure compatible biofuels derived from non-food lignocellulosic biomass. Biomass is a renewable resource that is potentially carbon-neutral. Plant-derived biomass contains cellulose, which is more difficult to convert to sugars. The development of cost-effective and energy-efficient processes to transform cellulose and hemicellulose in biomass into fuels is hampered by significant roadblocks, including the lack of specifically developed energy crops, the difficulty in separating biomass components, low activity of enzymes used to hydrolyze polysaccharides, and the inhibitory effect of fuels and processing byproducts on the organisms responsible for producing fuels from monomeric sugars. This presentation will highlight the research efforts underway at JBEI to overcome these obstacles.

ENZYMATIC BIOPROCESSING OF CELLULOSE IN NMMO

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Enzymatic conversion of cellulose was accomplished by dissolving cellulose in the lyocell solvent, N-methylmorpholine N-oxide near monohydrate (NMMO/H₂O), followed by gel formation caused by increased water content due to pH adjustment and enzyme addition. The initial dissolution and subsequent phase separation upon dilution is similar to the commercial Tencel® fiber production in which more than 99% of the solvent is recovered due to the essential lack of vapor pressure for NMMO/H₂O. Previous rheological studies by the presenting author indicate that lignin is not soluble in NMMO/H₂O and can be separated by simple filtration, whereas cellulose and hemicelluloses are soluble in NMMO/H₂O as well as in the ionic liquids tested: 1-ethyl-3-methylimidazolium acetate ([Emim]Ac), 1-ethyl-3-methylimidazolium diethyl phosphate ([Emim]DEP), and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). NMR, MRI and X-ray diffraction were used to characterize the formation of a gel phase for the cellulosic solutions and related diffusion characteristics after dilution with water. High cellulosic loading in the initial solvent (at least 15%w cellulose) and yields of reducing sugars (70-90% conversion) were accomplished by dissolution in a modified twin screw extruder. Hydrolysis was similar in both the extruder equipped with recycle and a subsequent reactor. The commercial enzyme mixtures (primarily Accelerase™1000 by Genencor) were more active in NMMO/H₂O than in the three ionic liquids tested or in aqueous systems with suspended cellulose. Initial reaction rates are much more rapid in the gel state than in suspension due to the accessibility of the cellulose by the enzymes. Analysis of variance of the data was performed using MATLAB and trendline analysis using Excel. At the 95% confidence level, conversion of cellulose to sugars after dissolving in NMMO/H₂O were dependent upon pH, cellulose concentrations and the general form of the cellulose (*i.e.*, suspended or regenerated). The conversion to sugars was higher in NMMO/H₂O than in the ionic liquids and higher than in suspended cellulose. The initial conversion rate in NMMO/H₂O was also higher than cellulose re-suspended after pretreatment with NMMO/H₂O. Most of the data was logarithmic at the 95% confidence level except at 60°C, high enzyme loading and high pH. The results at 60°C and HPLC results imply subsequent reactions following hydrolysis in NMMO/H₂O.

CHEMICALS AND PRODUCTS FROM THE INTEGRATED FOREST BIOREFINERIES

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The US Department of Energy has recently projected that more than 1.3 billion tons of biomass could be produced on a sustainable basis annually in US which could provide about 30% of the country's demand for transportation fuels. About a third of the biomass resources in US are wood-based which necessitates the development of Integrated Forest Biorefineries (IFBR). Due to the increasing off-shore competition, global movement and incentives for green fuels and chemicals, the North American pulp and paper industry needs to create additional revenues and diversify their products and markets to remain competitive. To achieve this, the pulp and paper mills need to evolve into IFBR. This presentation will provide an overview of the IFBR production platforms and potential chemicals and products that could be produced in the IFBR thereby addressing the IFBR research needs in the area of: 1) adding value prior to pulping; and 2) new values from residuals and spent liquors. In addition to the production of pulp and paper, the core business of the IFBR, there is a great opportunity to add new value-added co-products (e.g. biofuels, biochemicals and biomaterials) to improve the economics of the IFBR and provide flexibility to changing markets and prices. Potential products that could be obtained through both the biochemical and thermochemical conversion processes as well models of integrated technological schemes for the complex utilization of forest biomass for biofuels, biochemicals and market pulp will be presented and discussed. The main technological challenges that need to be overcome to maximize the IFBR value through integration of processing steps and utilization of waste streams for generation of high-value products will be summarized.