Frontiers in Biorefining

Biobased Products from Renewable Carbon

ABSTRACTS

Friday, October 22, 2010

Session 4B: Developing the Industrial Biorefinery

GREENING THE OLEFIN CHAIN: NEW TECHNOLOGY FOR THE CONVERSION OF RENEWABLE GLYCEROL TO COMMODITY AND SPECIALTY CHEMICALS

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New chemical technology will be required to make efficient use of renewable feedstocks in the conversion to existing chemical products. This paper will outline catalytic technology developed at The Dow Chemical Company to convert glycerol to epichlorohydrin by hydrochlorination (The GTE Process), and to convert glycerol to glyceryl ethers though alkylation with aldehydes and ketones (Reductive Etherification).

WHY BIOISOPRENE™? SITUATION ANALYSIS, OPEN INNOVATION, AND TECHNOLOGY DEVELOPMENT

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Genencor (Danisco USA Inc., Genencor Division), and The Goodyear Tire & Rubber Company are developing a revolutionary BioIsoprene™ product alternative for petroleum derived isoprene. Isoprene is a key chemical required to produce a diverse range of industrial products including a wide variety of specialty elastomers used in surgical gloves, motor mounts and fittings, rubber bands, golf balls, and shoes. Styrene-isoprene-styrene block copolymers form an essential part of hot-melt pressure-sensitive adhesive formulations, and *cis*-polyisoprene is used in tire manufacture. All of the world's isoprene is produced from petroleum-derived feedstocks and is subject to volatility in pricing and supply linked to oil. The development of BioIsoprene™ monomer could make the tire and rubber industry less dependent on petroleum through utilization of renewable feedstocks.

This paper describes our approach at developing a scalable and commercially relevant bioprocess for BioIsoprene™ production. Production titers of greater than 60 g/L are being achieved in a pre-pilot process. This process is a unique example of in-situ product removal, allowing the easy use of crude biomass hydrolysates. Analysis of the monomer has demonstrated that the BioIsoprene™ product is >99% pure prior to recovery and purification. Pre-pilot work with the developing process has lead to the manufacture of prototype passenger car tires demonstrating the functional process from start to finish.

FURANICS: VERSATILE MOLECULES APPLICABLE FOR BIOPOLYMERS AND BIOFUELS APPLICATIONS

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Avantium Chemistry (www.avantium.com) explores novel furan chemistry, focused on efficient and, compared to enzymatic bio-refinery processes, low cost conversion of C_6 sugars (i.e. glucose, mannose, galactose and fructose) and C_5 sugars (i.e. xylose and arabinose) into derivatives of the promising chemical key intermediate hydroxymethyl furfural (HMF) in the presence of a solid acid catalyst.

By applying its advanced high-throughput R&D technology, Avantium is developing a next generation biofuels, called "YXY Building Blocks", which can be produced on the basis of sugars and other, non-food, carbohydrates. Furanics are products derived from carbohydrates such as sugars. The company is developing chemical, catalytic routes to produce Furanics for a range of biofuel applications. Avantium targets to develop economically competitive molecules with advantageous qualities for both biopolymers as well as biofuels applications.

In the biopolymer area several value chains are evaluated including polyesters, polyamides and plasticizers. Furandicarboxylic acid based polyesters have PET-like properties including Molecular Mass and colour, interestinglysome properties such as the glass transition temperatures (Tg) were substantially improved. We showed that furan based polyesters can have similar or improved properties as conventional polymers such as PET and also that the production processes of bio-based polymers can be similar to conventional production processes

Recently, the company successfully conducted engine tests at the Advanced Engineering Engines Test Facility at DAF Trucks, the Netherlands to demonstrate the fuel potential of its novel biofuels. Using a regular Paccar PR 9.2 L, 183 kW diesel engine. Avantium is testing a range of blends of its novel biofuels (both C5 and C6 derived molecules) with regular diesel, with different concentrations (up to 30%) of Avantium's novel biofuel. The first tests were done with Ethyl Tetrahydrofurfuryl Ether (ETE). The European Standard Cycle (ESC) tests yielded positive results for all blends tested. No difference in engine operation was observed. Smoke and particulates as well as sulphur content decreased significantly with increasing ETE blending concentrations. Fuel consumption increases with increasing ETE amount, but is completely in line with the calculated lower energy content of ETE.

The excellent results of the biopolymer characterization and the biofuel engine tests support the proof of principle of our next generation YXY building blocks, and are a valuable milestone for our development program. The paper will present both biopolymer as well as biofuel test results.

APPLICATION OF SMALL-SPECIMEN RHEOLOGY AND ^{2}H QUADRUPOLAR INTERACTION IN BIOMASS ANALYSIS

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Efficient biomass utilization requires new analytical tools for better understanding of lignocellulosic organization, and thus also evaluating the effects of chemical and thermomechanical treatments required for biomass deconstruction. In this presentation, two such analytical techniques are discussed. First, the application of a novel submersion-torsion dynamic mechanical analysis (DMA) is demonstrated. This technique has distinct benefits and limitations with respect to more common stress modes, such as bending and tension. The second technique is a well known deuterium (^{2}H) solution-state NMR method for assessing matrix orientation; this is applied as a novel approach to probe the *in-situ* orientation of wood-polymers. Using a simple deuterated solvent, wood is equilibrated to a level below fiber saturation. This "bound solvent" exhibits sufficient mobility such that a liquid-state signal is observed from standard direct polarization. However orientation within the matrix imposes a motional bias and therefore residual quadrupolar couplings, which would otherwise average to zero under isotropic conditions. The degree of residual quadrupolar coupling (splitting in Hz from the isotropic signal) is directly related to the degree of matrix orientation (Figure1). The presentation will describe the analysis of solid wood using ethyleneglycol-D_4 and dimethylformamamide-D_1 as a function of grain orientation and temperature. Small specimen rheology and ^{2}H NMR show promise for analyzing morphological changes resulting from technologically relevant biomass treatments.

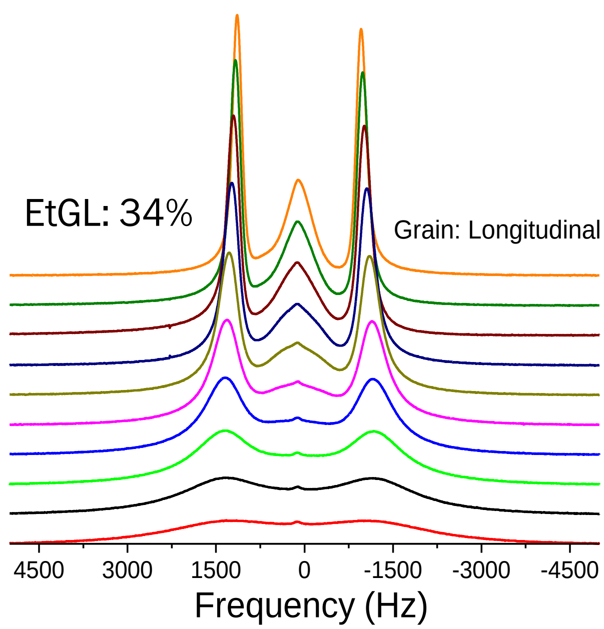

Figure 1. Isothermal ^{2}H Spectra of ethylene glycol-D4 in yellow-poplar wood at different temperatures. **Doublet:** aligned phase, **singlet:** isotropic phase.

NATUREWORKS INGEO™ BIOPOLYMERS

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NatureWorks began its journey as a project within Cargill to expand the market for corn wet-mill products. The project began in 1989 with the vision of fermenting corn derived sugars to lactic acid that would be used to make Ingeo™ Biopolymer. Over the years NatureWorks has produced material at pilot and commercial development scale facilities in Minnesota. Our current, state of the art facility, located in Blair NE is the largest biopolymer plant in the world. The Blair facility is a regional bio-refinery with over 60% of the feedstock coming from the 5 nearest surrounding counties. Nebraska ranks third among the top-five corn producing states in the US. The corn wet mill fractionates the corn kernel into four major components; hull and fiber, gluten meal, germ, and starch. Corn is approximately 60% starch by weight; a bushel of corn can be converted to 19 pounds of polymer resin. The Ingeo process can use any renewable fermentable sugar; currently corn sugars are lowest in cost. Ingeo Biopolymer is found in thermoforming, injection molding, fiber, and bottle applications across the globe. An integral part of the biorefinery concept is the use of renewable resources and beneficial impact on the environment. NatureWorks Ingeo Biopolymer has a favorable Eco-Profile compared to other petroleum based plastics. As currently produced, Ingeo Biopolymer has the lowest greenhouse gas emissions and uses the least non-renewable energy of any commercial plastic today.