



ABSTRACTS

Wednesday, October 20, 2010

Session 2B: Chemicals from Carbohydrates

ADVANCES IN LIGNOCELLULOSIC BIOREFINING: STRATEGIES FOR THE PRODUCTION AND APPLICATION OF γ -VALEROLACTONE

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Recent research in the field of biorefining has centered on the utility of building blocks, such as γ -valerolactone (GVL), to serve as sustainable intermediates for conversion of lignocellulosic biomass into valuable products. GVL can be used directly as a solvent or fuel additive, or it can provide an important starting material for a number of promising routes in the production of fuels and chemicals. In the past year, several GVL-based strategies for the production of chemicals—such as pentanoic acid, pentenoic acid, and 5-nonanone— and transportation fuels—such as valeric esters, nonane, and alkene oligomers— have been reported, and research on its use continues to develop. These promising applications for GVL and its stability in water solution make it appealing as a platform molecule that could impart flexibility to lignocellulosic based biorefineries. Presently, a major challenge impeding large scale production of GVL and valerolactone-based end products is the complexity of its preparation from cellulosic feedstocks and the difficulty of integrating sequential processes. Currently, GVL can be produced from levulinic acid, which is obtained from the acid catalyzed deconstruction of cellulose. However cost effective production of levulinic acid has not yet been established, because complex and energy intensive purification strategies to isolate levulinic acid from the mineral acid (commonly sulfuric acid) are necessary for downstream processes. Herein we present a reactive extraction strategy by producing levulinate esters as intermediates, using light alkenes derived from GVL, thereby eliminating the use of external solvents. The ester phase separates spontaneously from H_2SO_4 upon the addition of water, allowing for a straightforward recycle of H_2SO_4 for cellulose deconstruction. The ester products (butyl formate, butyl levulinate) can be then converted into GVL in a dual catalyst bed reactor, using Pd/C and Ru/C, analogous to the production of GVL from levulinic and formic acids, wherein the formic acid is used as a hydrogen source. Further, the ester products serve to diversify the biorefinery in that they can be used either in the production of high value specialty chemicals or used directly as fuel additives. This strategy may help to reduce the barrier impeding the large scale production of GVL—and sustainable fuels and chemicals—by facilitating both the purification of levulinic acid and the recovery of sulfuric acid without an additional requirement of raw materials (solvents) and downstream distillations.

SELF-ASSEMBLY OF BIOBASED BOLAAMPHIPHILES AS SOURCES OF NANOSTRUCTURAL MATERIALS

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Nanotechnology's impact for commerce and industry has been projected at over \$1 trillion within 20 years. However, controlled and predictable manufacture of new products at the nanoscale requires a fundamental shift in synthesis to include both stepwise formation of covalent bonds along with construction of multimolecular arrays based on noncovalent intermolecular forces. The recent interest in renewable carbon as a source of chemical building blocks provides an inexpensive supply of materials (carbohydrates, fatty acids) that possess the structural features necessary to support self-assembly. We will describe our investigation of glycal-based bolaamphiphiles as easily accessible and synthetically flexible probes of self-assembly. In aqueous solution, these compounds are transformed into nanoscale vesicles, tubes or helical ribbons, depending on the nature of the glycal headgroups and the length of alkyl chain joining the headgroups. We will report recent synthetic results, as well as molecular mechanics and molecular dynamics evaluation of small arrays of bolaamphiphiles.

NOVEL POLYSACCHARIDE DERIVATIVES FOR ADVANCED APPLICATIONS FROM BIOMASS

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Advances in polysaccharide synthesis techniques have enabled us to prepare derivatives from renewable biomass with increased selectivity, and with the ability to design novel materials with enhanced functional capabilities. As a result, we are now able to design polysaccharide-based materials with high performance in demanding applications, such as biomedical uses including drug delivery. We will discuss in this presentation the design and preparation of a new type of cellulose derivative, not accessible by conventional techniques. We will report on investigations of the structure-property relationships. We will also discuss the application of polysaccharide derivatives to an important problem in drug delivery, that is the enhancement of oral bioavailability of important flavonoid compounds, a class of highly bioactive natural materials present in various foodstuffs. These compounds have remarkable activity against a variety of ailments including cancer and heart disease, but have been impaired by their poor solubility and resulting low bioavailability. We will report on the preparation of molecular dispersions of flavonoids in polysaccharide derivative matrices and the impact of these amorphous systems on flavonoid solubility.

INTEGRATED BIOREFINERY DEVELOPMENT FOR CARBOHYDRATE PRODUCTION

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Abstract Not Available

PROCESS DEVELOPMENT FOR MANUFACTURING PROPYLENE CARBONATE AND POLY(PROPYLENE CARBONATE) FROM PROPYLENE OXIDE AND CARBON DIOXIDE

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Reusing existing CO₂ as a feedstock of carbon for producing chemicals such as cyclic propylene carbonate (PC) and poly(propylene carbonate) (PPC) has received much attention recently. Synthesis of cyclic carbonates and polycarbonates from CO₂ needs a reactive cyclic ether such as propylene oxide (PO) and an efficient and stable catalyst. PC is an important intermediate as a replacement of highly toxic phosgene as carbonylating agent in the production of isocyanates or polycarbonates. PC can be used in high energy cells and condensers, as a solvent and plasticizer for polymers as well as an absorbent in the removal of CO₂ and H₂S from natural gas and petroleum cracking gas. It is an aprotic polar solvent and used extensively as intermediate in the production of drugs and pesticides. It is frequently used as a high-permittivity component of electrolytes in lithium batteries, usually together with a low-viscosity solvent. The process for manufacturing PC uses ionic liquid-1-n-ethyl-3-methylimidazolium chloride (EMImCl) as catalyst. The reaction takes place at 212 °F and 114.7 psi in a stirred tank. Presently, the industrially important polycarbonate is synthesized from bisphenol A and diphenyl carbonate. Concerns about the use of bisphenol A in consumer products were regularly reported. Because of environmental and safety issues the development of feasible alternatives for manufacturing selected polycarbonates has been highly attractive. PPC has many potential applications in industry as binder resins, substitutes of thermoplastic polymers (e.g., polyethylene and polystyrene), and hydrolytically and/or biologically degradable polymers. The process for manufacturing PPC uses the (salen)CrIII complex as catalyst, where H₂salen = N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexenediimine. The reaction takes place at 850 psi and 86 °F. When the reaction is performed at elevated temperatures, propylene carbonate is the dominant product as a result of a backbiting mechanism. The manufacturing of PC requires 9990.2 lb/hr CO₂, while PPC requires 12762.8 lb/hr CO₂.

This study presents engineering and economic analyses of industrial scale processes to manufacture around 200 million lb/year pure cyclic propylene carbonate and around 200 million lb/year pure poly(propylene carbonate) (PPC) from CO₂, supplied by a bioethanol plant and purchased PO. The simulation package of Aspen Plus is used to design and simulate these processes with known kinetics data and catalysts to obtain the material and energy balances, the stream tables, list of the major equipment with operating conditions, and the utilities necessary. The economic analyses provided the discounted cash flow diagrams for the processes with net present value, payback period, and rate of return at the end of a 10-year of operation. As Figure 1 shows, when the selling price of PC is \$0.72/lb the

values of NPV, PBP, and ROR are $\$17.97 \times 10^6$, 3.5 years, and 33 %, respectively. Therefore, the process is feasible under the current economic data, available technology, and catalyst utilized. Figure 2 shows how the values of NPV, PBP, and ROR vary with the selling price of PPC. The selling price of PPC should be at least $\$0.97/\text{lb}$ or higher for the process to be feasible.

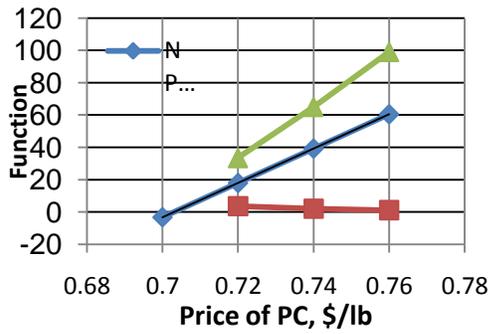


Figure 1. Change of NPV, PBP, and ROR with the selling price of PC.

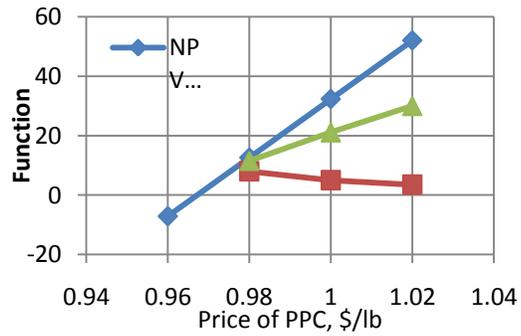


Figure 2. Change of NPV, PBP, and ROR with the price of PPC.

CO-PRODUCING ANIMAL FEED AND FUEL AT REGIONAL BIOMASS PROCESSING DEPOTS

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While there is great promise in second generation biofuels as a renewable alternative to petroleum, several concerns persist regarding the feasibility of a large scale bioeconomy, namely competition with food production, indirect land use change, logistical problems of supplying large refineries, and capturing economic value in rural areas. We propose a series of regional biomass processing depots (RBPDP) that can densify, store, and upgrade the value of biomass. Of particular interest is providing valuable animal feed alternatives or co-products to biofuel production, thereby enhancing the sustainability of the bioeconomy. We discuss two of these possibilities: producing a leaf protein concentrate from fresh green biomass, and using biomass pretreatment to increase the value of low-quality forages for cattle feed. The integration of these technologies with cellulosic biofuels is mutually beneficial, and can reduce or eliminate barriers to developing a substantial biofuel-based economy.

To demonstrate the potential of integrated food and fuel production, the theoretical maximum amount of biofuel produced on current cropland without affecting overall food production is considered. Current fiber, energy, and protein needs for human consumption, animal feed, and exports are met. This study suggests that over 50% of current US gasoline consumption can be displaced by biofuels grown on current cropland in the United States. The large volume of biofuel produced is due to intensive harvesting of corn land, which includes grain, stover, and cover crops. New animal feeding technologies also contribute to increased biofuel production. Likewise, greenhouse gas emissions are reduced by 670 Tg CO₂-eq/yr, which is over 10% of current U.S. emissions. These results are consistent across multiple sensitivity scenarios, as most of these scenarios result in ethanol production or GHG reduction within 20% of the values obtained under our base assumptions. Net soil organic carbon increases in this scenario; however, nitrate leaching is greater than if little to no biofuels are produced.