
# ABSTRACTS

## Thursday, October 21, 2010

## Session 3A: Catalysis in the Biorefinery

# ONE STEP CATALYTIC CONVERSION OF BIOMASS-DERIVED CARBOHYDRATES TO CHEMICALS AND TRANSPORTATION FUELS

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With diminishing reserves of fossil fuel, the production of liquid fuels and value-added chemicals directly from biomass is of great current interest. Carbohydrates, such as mono and polysaccharides and cellulose, typically constitute 50-80% of plant biomass. Existing technologies to biomass-derived products are typically energy intensive multi-step processes. We will demonstrate that biomass-derived carbohydrates such as fructose, glucose, and even cellulose can be catalytically converted to 2,5-dimethyltetrahydrofuran (DMTHF) in one step in relatively good yields under mild conditions. DMTHF is superior to ethanol and has many of the desirable properties currently found in typical petroleum-derived transportation fuels. Using a different catalytic reaction condition, 5-methylfurfural (MF) can also be obtained with relatively high selectivity from carbohydrates. MF is an useful intermediate for the production of drugs, agricultural chemicals, and perfumes. The scope and mechanism of these catalytic transformations will be discussed.

# BIOTECHNOLOGICAL PRODUCTION OF LONG CHAIN α,ω-DICARBOXYLIC ACIDS AND EPOXY-DERIVATES FROM PLANT OIL

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An important field in sustainable industrial chemistry is the development of new applications for plant fats and oils. One of the most promising applications is the usage of bifunctional derivatives like dicarboxylic acids (DCA), epoxidized triacylgycerides (ETAG) and epoxidized fatty acids (EFA) as precursors for bioplastics polymer building blocks. In contrast to conventional plastics, bioplastics are polymers derived from renewable biomass sources.

The majority of industrial DCA, ETAG and EFA production for polyamide (PA), polyester (PE) and epoxy resins synthesis is still done *via* chemical synthesis out of fossil recourses under harsh reaction conditions. Biotechnology provides novel biochemical approaches for long-chain DCA, ETAG and EFA synthesis that can provide an eco-efficient process alternative.

Long-chain DCA can be produced *via* biotransformation for instance using different yeasts. For this a metabolic pathway called ω-oxidation is required. Fatty acids are oxidized at their terminal methyl group in three enzymatic steps. By blocking the degradation of DCA, achieved by inhibiting the β-oxidation pathway an enrichment of DCA in the supernatant of the culture is possible.

Best known DCA producer is the pathogenic strain *Candida tropicalis*. Within fermentation processes we screened different substrates and optimized the biotransformation of oleic acid into the corresponding 1,18-octadecenedioic acid in 30 L- scale. The process is divided into two main phases: an optimized cell growth phase with different fed batch strategies to avoid crabtree effects and a production phase which requires pH changes and limiting amounts of C- and N-sources. We achieved biomass concentrations up to 40 g DW/L, DCA conversion rates of 0,44 g/(L h) and a maximum DCA concentration of 100 g/L.

In parallel we study and optimize different further non-pathogenic fungal strains with a high performance in DCA production according to their genetically homology and functional gene expression of the ω-oxidation pathway.

Unsaturated triacyglyderides and fatty acids can be epoxidized enzymatically *via* epoxidases, monooxidases and lipases. We studied the performance of commercially available enzymes as well as novel discovered enzymes with different fatty acids and plant oils. We were able to demonstrate up 100 % conversion of different substrates to ETAG and EFA within a time scale of a few hours.

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# CATALYSIS FOR BIORENEWABLE CHEMICALS: CREATING A GENERALIZED PRODUCTION PARADIGM

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A truly sustainable chemical industry will require the utilization of renewable carbon feedstocks. The use of biobased feedstocks, which would be available in a biorefinery, is beginning to receive an unprecedented amount of attention due to its particular promise. However, the prevailing approach for developing biorenewable chemicals to replace petrochemicals relies primarily on targeting catalytic conversions to one or two chemicals at a time. This serial approach is inherently expensive and time consuming. Since biorenewable chemicals must compete against a highly efficient petrochemical production system based primarily on conversions of ethylene, propylene and benzene, there is a need to create a generalized framework in which a range of biorenewable chemicals can be produced from a common technological conversion platform. One such generalized production framework, being developed by *CBiRC,* depends on the creation of a common metabolic pathway leading to intermediate chemicals that are subsequently converted to chemical products using chemical catalysts. Discussed will be catalytic chemistry approach being developed by *CBiRC* for producing chemicals in a biorefinery.

# PRODUCTION OF RENEWABLE AROMATIC CHEMICALS USING VIRENT'S CATALYTIC BIOFORMING® PROCESS

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Organic chemicals are used globally as feedstocks for the production of a wide variety of goods including plastics, fertilizers, synthetic fabrics, detergents, and dyes. Since over 90% of the organic chemicals produced worldwide are derived from petroleum, developing renewable replacements for these organic chemicals will lower global demand for petroleum, reduce pricing volatility, and address environmental concerns. Carbohydrates are the most widely distributed, naturally occurring organic compounds on Earth, and hold considerable potential to replace petroleum as the source for organic chemicals. Virent's BioForming process unlocks this potential by enabling the economic production of organic chemicals from biomass derived carbohydrates using aqueous phase reforming, a novel heterogeneous catalytic pathway currently being scaled and commercialized. Virent's technology employs a solid state catalyst system, similar to those used in conventional oil refineries, to produce premium hydrocarbon products from carbohydrates, including a broad range of organic chemicals that are used for the production of plastics, synthetic fabrics, and solvents. The organic chemicals produced by the BioForming process are recognizable platform chemicals and match petroleum derived organic chemicals in composition and offer superior environmental performance. The BioForming process can transform a broad range of renewable carbohydrates, including oligomeric and monomeric hexoses and pentoses. This presentation will provide a brief introduction to Virent's BioForming process, summarize recent data collected from Virent's pilot plants and discuss the progress of Virent's commercialization efforts. In addition, the market opportunities and challenges associated with the commercialization of renewable chemicals from biomass will be covered.

**RHENIUM-CATALYZED DEOXYDEHYDRATION OF POLYOLS BY SULFITE**

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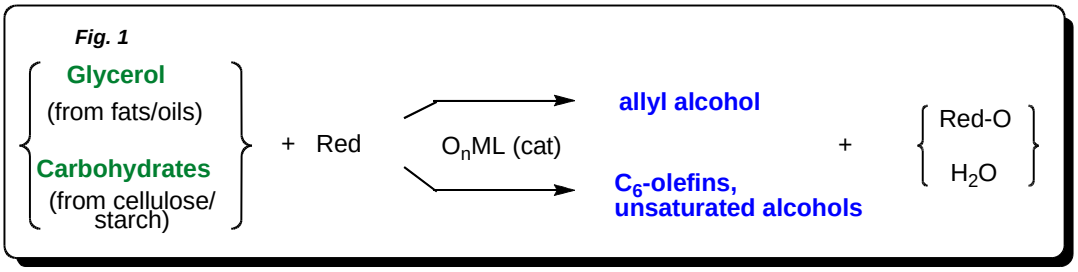
To access many chemicals and most potential fuels from oxygen-rich biomass resources, e.g. cellulose, monosaccharides and glycerol, selective partial or complete hydroxyl group removal via dehydration and/or reduction (deoxygenation) is needed. The long term, practical objective of our project is to develop catalytic processes for the *deoxydehydration* (DODH) of biomass-derived carbohydrates and polyols to produce unsaturated alcohols and hydrocarbons of value as chemicals and fuels (Fig. 1).




We have found that methyltrioxorhenium ($MeReO_3$) and perrhenate salts ($Z^+ReO_4^-$) catalyze the DODH of glycols and the deoxygenation of epoxides to olefins in moderate to good yields with sulfite as the reductant. The scope, efficiency and preliminary mechanistic studies of these reactions will be described.