Fermentative Upgrading of Xylose

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Abstract

Chemical pulp mills such as Kraft, soda, or sulfite mills are current examples of biorefineries that can convert lignocellulosic biomass into energy, pulp or cellulose derivatives, and tall oil. While existing viscose pulps use a hemicellulose extraction to generate soluble sugars for ethanol production, in general there still exists a large potential for other more profitable applications of the biomass (Fig. 1), i.e. the mill needs to present a widespread product portfolio.

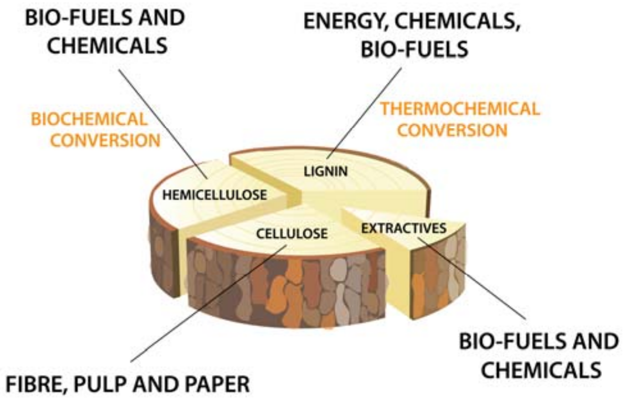

Figure 1. Multiple uses of wood components.

The biofuels under development from fermentation that will be discussed are the diesel fuel oxygenates dibutyl succinate and diethyl succinate to be used for reduced particulate emissions and fossil fuel replacement for diesel engines and butanol for Otto engines. It's important to stress that succinic acid, butanol and ethanol, needed for the production of the diesel additives and gasoline replacement will be produced from renewable resources and hence replacing products currently produced from non-renewable fossil sources. Since wood will be used, there will be no issue of competing with raw material used for food production. Besides biofuel production, succinic acid and butanol, can be used directly or further refined into numerous different products classified as green chemicals.

Fermentation products from xylose and hemicellulose

In contrast to cellulose, which is an unbranched polymer of the hexose D-glucose, hemicellulose is a branched polymer composed of both pentoses (D-xylose and L-arabinose), hexoses (D-mannose, D-galactose and D-glucose) and uronic acid. The hemicellulose fraction varies both in quantity and chemical structure depending on the lignocellulosic material. Hemicellulose from hardwood has usually a higher content of pentoses, and xylose is always the sugar monomer present in the largest amount. The polymeric carbohydrates can be hydrolyzed into monomeric sugars and subsequently fermented to the target product by a specific microorganism. So far there is more experience fermenting hexoses than pentoses. Succinic acid and butanol, described below, can be produced from five-carbon sugar and therefore these are of specific interest for a pulp mill based biorefinery concept. There are numerous applications of these fermentation products, as described below, but in this project, we are specially interested in their use as key intermediates in the production of diesel fuel additives.

Diesel fuel is an important transportation fuel throughout Europe due to the higher efficiency of diesel engines versus gasoline engines. Diesel engines have the disadvantage of producing significant particulate emissions that cause both environmental pollution and human health hazards. A well established approach to control particulate emissions is to add an oxygenate that leads to more complete combustion and less production of carbon particulates. Preliminary studies has indicated that the proposed oxygenates are effective in reduction of particulate emissions and can be produced from renewable resources. The European commission's goal is a 20 % usage of alternative fuels within road transport by 2020. The transport commission recommends a low blend of alternative fuels with already existing fuels. In this way, alternative fuels will be transitioned into the existing infrastructure and thereby avoiding the problem of constructing an entire new infrastructure to support the new fuels. The proposed oxygenates are both consistent with this strategy. As the proposed fuel oxygenate additives can be synthesized from biobased ethanol/butanol and succinic acid, this project offers a fully integrated approach for the development and deployment of a novel, biobased, non-toxic, diesel fuel oxygenate for the reduction of nitrogen oxides and particles. The environmental impact of the project is twofold; it will provide cleaner transportation fuel and at the same time reduce the amount of greenhouse gases emitted by partial replacement of a portion of the fossil fuel use in diesel fuel.

Diethyl succinate, as a primary diesel fuel oxygenate, it significantly reduces the amount of particles. The tests performed at LTU showed a 20% reduction in particles for a 5% diethyl succinate blend with Swedish MK 1 diesel fuel. The tests also showed a significant displacement in the particle size distribution from accumulation mode (large particles) to nuclei mode (fine particles). Subsequent to this discovery a patent application has been filed. For the production of diethyl succinate from biobased succinic acid and ethanol, we are proposing reactive distillation (RD). The overwhelming advantages of RD for equilibrium-controlled reactions such as esterification are; (1) elimination of equilibrium limitations for conversion by continuous removal of products from the reaction mixture, and (2) potential for integration of multiple process steps.

Dibutyl succinate is an ester that can be produced by the combination of butanol and succinic acid. While there is a strong synergy in the production of succinic acid and butanol because any carbon dioxide produced by the butanol fermentation can be consumed by the succinic acid fermentation, there is also a strong motivation for co-production to make dibutyl succinate. Dibutyl succinate has a wide range of uses as a solvent and chemical intermediate to replace petroleum, but, most importantly, recent studies have shown that dibutyl succinate is an effective diesel oxygenate/ extender for the reduction of particulate matter in diesel fuel combustion and also an effective additive to diesel fuel and biodiesel to improve cloud point and pour point properties. Dibutyl succinate is miscible with diesel fuel and no additional blending agents are necessary for its use in blends. This green alternative to fossil based fuel has great potential in at least the partial replacement of diesel fuel and improving its environmental footprint.

Succinic acid is considered as one of the most interesting chemicals to be produced in a biorefinery, as it can be further refined into different products covering a wide range of applications; biodegradable, glycol free, low corrosion deicing chemicals for airport runways; glycol free engine coolants; polybutylene succinate (PBS), a biodegradable polymer that can replace polyethylene and polypropylene; and non-toxic, environmentally safe solvents that can replace chlorinated and other solvent containing volatile compounds. Most of the potential applications of succinic acid are covered currently by fossil based maleic anhydride.

There is widespread interest in the fermentation production of succinic acid due to several economic analyses that point to its ability to compete on a cost basis with fossil fuel maleic anhydride. An increased market for biobased production of succinic acid is expected to come from the synthesis of biodegradable polymers and various green solvents. This position opens the opportunity to develop a second generation process that leapfrogs the current development and avoids the food-fuel (chemical) controversy and offers Sweden a competitive advantage by coupling it with Sweden's well established forest products industry.

Butanol is currently produced commercially from fossil fuels, but like succinic acid, this primary alcohol can also be produced by a so called ABE (Acetone, Butanol, Ethanol) fermentation using the anaerobic bacteria *Clostridium acetobutylicum* or *C. beijerinckii*. Production of biobutanol, using renewable biomass, has gained an increased interest, since butanol at 85% strength can be used directly in Otto engines as an alternative fuel, and in contrast to ethanol, without any change of current vehicle and engine technologies. As a fuel, butanol is as energy efficient as petrol. Butanol producing *C. acetobutylicum* can utilize all of the common sugars present in wood hemicellulose and cellulose hydrolyzates as feedstocks. In addition, polysaccharides such as sucrose can also be used as carbon source.

Summary

New strategies for production of biochemicals and biofuels are discussed. The ability to add value by fermentation offers a feasible value-added strategy.