

Conversion of sugars to hydrocarbons via depolymerization and decarboxylation of polyhydroxyalkanoates

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There are many potential chemical intermediates that can be made by fermentation of sugars, and a variety of chemicals that could be made by growing organisms such as fungi on biomass. Virtually all of these intermediates require some form of chemical transformation before they are ready to be used as infrastructure-compatible (drop-in) transportation fuels. Based on a survey of the potential products that can be made from biomass components by chemical and biological routes and the feasibility of transforming them into hydrocarbon fuels it is obvious that there are two main transformations that need to occur, deoxygenation and carbon chain extension. The potential routes for decreasing the oxygen content of biomass intermediates include dehydration, hydrodeoxygenation and decarboxylation. We are developing chemical transformation routes to efficiently convert biomass-derived intermediates into fuel products that are compatible with the existing fuel distribution infrastructure, which fit within the specifications for gasoline, jet or diesel fuels.

A potential route that is being examined is the conversion of polyhydroxyalkanoates (PHA) to alkenes that would be intermediates to hydrocarbon fuels. This route appears promising as there are several microorganisms, which incorporate high levels of PHA (up to 80% of dry cell mass) as a form of energy storage molecule to be metabolized when other energy sources are not available. Thermal breakdown of PHA proceeds via an intermediate carboxylic acid, which can then be decarboxylated to an alkene. Oligomerization of alkenes by well known commercial technologies would permit production of a range of hydrocarbon fuels from sugar intermediates. Polyhydroxybutyrate (PHB) can be produced in *Cupriavidus necator* (formerly known as *Ralstonia eutropha*) on a variety of carbon sources including glucose, fructose and glycerol with PHB accumulation reaching 75% of dry cell mass. We have demonstrated the thermal breakdown of polyhydroxybutyrate to 2-butenic acid (crotonic acid, CA) and demonstrated thermal decarboxylation of CA to propene at yields approaching 70% at 400°C in 15 min. Combining the breakdown and decarboxylation steps we have demonstrated that PHB can be directly converted to propene and carbon dioxide under similar conditions and in similar yields. PHB containing cell mass from *Cupriavidus necator* has also been directly converted to propene and carbon dioxide without prior separation of PHB from the cell mass. Current research is aimed at finding catalysts that would permit lower temperature decarboxylation and higher propene yields.