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From Sugar to Plastics

Editor's Note: The biggest story in materials this year is sustainability. Producers and users alike are looking for plastics made from feedstocks that are not as environmentally damaging as petroleum. While previous studies have shown various ways to chemically convert fructose and glucose into plastic intermediates and even fuels, these conversion processes are complicated and costly, and are only efficient for converting fructose. Glucose is a much more common sugar because it can be derived directly from starch and cellulose, both plentiful in plant material.

Like crude oil, basic sugars contain the building blocks for plastics and fuels, but the development of a conversion process for these renewable ingredients has faced stumbling blocks. New research, published in the June 15 issue of Science (2007, 316, 1597–1600), may remove those barriers by perfecting a transition step in the transformation process that produces 5-hydroxymethylfurfural, better known as HMF.

Made from petrochemicals, HMF is used in large quantities to create plastics and so-called fine chemicals, which are used in various specialty products. Now, Z. Conrad Zhang and colleagues at Pacific Northwest National Laboratory (PNNL) have found a way to use glucose and fructose to make HMF, which can then be used to produce anything from paints to biofuels. These two simple sugars could be harvested from plant cellulose or sugar beets, for example, and could serve as potential feedstocks that are much more sustainable than petrochemicals

The scientists report that they have cleared a major hurdle by using metal halides such as $CrCl_2$ in an ionic-liquid solvent to catalyze and then preserve the HMF produced from glucose and fructose. Their result comes through an unusual catalytic behavior: metal halides actually stabilized HMF once it had formed at catalytic concentrations, instead of enhancing further chemical reactions of the sugar feedstocks.

The team found that $CrCl_2$ as a catalyst with glucose produced HMF at yields approaching 70%. That high recovery rate could help push down costs, which have limited the use of biomass-based sugar stocks for industrial production of HMF. Current methods use acid catalysts to convert fructose or glucose, but the side reactions and byproducts for each sugar lead to problems with purification—and ultimately increase production costs. The PNNL team now intends to work on ways to make purer products.

The yield from fructose is similar to that reported in the past by other research groups, Zhang says. But he claims that his process is simpler, involving fewer steps, which would make it more cost-effective. Previous methods use an acidic catalyst, and the chemical reactions take place in a water-based solution, producing high levels of impurities. Instead of an aqueous solution, the PNL researchers use solvents known as ionic liquids, and they use metal chlorides as catalysts. The resulting chemical reaction gives nearly pure HMF, getting rid of the cost of purification, Zhang says.

After trying various metal chlorides, the researchers found that chromium chloride is the best catalyst for glucose. It gets the most HMF from glucose and works at temperatures of 80 °C for fructose and 100 °C for glucose.

The ultimate goal will be to build an economical reactor that can convert cellulosic biomass, such as grass and plant stalks, into HMF. Zhang says that his research team is already working on a method to utilize cellulose directly. However, he says, the first step will be to develop a commercial process for converting glucose into HMF, and that will take several years.

Another Major Commercial Development

Dow Chemical Co. is building a world-scale polyethylene plant in Brazil using sugarcane-based ethanol as the feedstock. Dow's partner is Crystalev, a major Brazilian ethanol producer. Expected to begin production in 2011, the facility will have a capacity of 350,000 metric tons annually.

This is a positive development on many fronts. Most importantly, sugarcane is a much more efficient source of biofeed stock than corn, which is used in North America. In fact, sugarcane is eight times more efficient as a feedstock than corn. Widespread use of corn as a plastic or fuel material also puts stress on global food supplies. It also makes no sense from an environmental perspective, given the amount of petroleum required to make ethanol.

On a molecular level, the new sugarcane-based material will be identical to current high-grade PE products made by Dow around the world from petroleum. In other words, it will be a drop-in replacement for applications including pipe, film, membranes and packaging. The new material will also be fully recyclable using current infrastructure. Dow also made pains to point out the new plant will not be built in a rainforest.

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