Once A Fossil Fuel Product, Now From A Renewable Resource

Pacific Northwest Natl Lab



"Propylene glycol has been used in a broad range of consumer products for decades, from foodstuffs to antifreezes," says Alan Zacher, a chemical engineer at the Pacific Northwest National Laboratory (PNNL) in Richland, Wash. "As a compound derived from petroleum products, it's so widely used that more than 900,000 metric tons of petroleum resources are consumed in its worldwide production each year."

In the mid 1990s, Zacher was part of a PNNL team exploring ways to produce propylene glycol (PG) from a renewable biomass source — the simple corn sugar sorbitol — in an intensive research partnership with several private organizations. Sorbitol is one of a number of plant-based sugars — compounds like glucose, xylose and glycerol (also known as glycerin) — that were candidates for developing PG compounds.

If a substance found in both foods and antifreeze sounds off-putting, whether from petroleum or bioalternatives, be assured that there are two types of propylene glycol — PG-I, the industrial grade, and USP, a grade tailored for human use and in line with U.S. Food and Drug Administration standards. USP stands for U.S. Pharmacopoeia, a compendium of

government standards."As a consequence of this work," Zacher notes, "our industrial partner, Archer Daniels Midland [ADM], opened a new plant in Decatur, Ill., last year to produce PG-I and USP PG from a byproduct of biodiesel fuel, a renewable product itself.

"This is important," he says. "Biobased PG has the potential to play a big role in reducing our level of oil consumption."

Advancing Energy Capacity, Lowering Greenhouse Emissions, Corn

One of 10 U.S. Department of Energy National Laboratories, PNNL engages in research and development for the Departments of Energy and Homeland Security, the National Nuclear Security Administration and other government and private organizations. Its mission includes the pursuit of new technologies for increasing American energy capacity, lowering dependence on imported oil and reducing the environmental impact of energy use.

"The PG project grew out of discussions with NCGA, the National Corn Growers Association," notes Eric C. Lund, Ph.D., technology commercialization manager at PNNL. "They were interested in looking for new commercial outlets for corn. Since they don't have their own research capabilities, they approached us.

"PNNL has long-standing research programs directed toward producing chemicals from renewable sources," he says. "We were intrigued by the possibilities, so we entered into a partnership with them." Subsequently, ADM joined the project.

He adds: "This has been a textbook example of the advantages of well-designed public/private partnerships for public benefit."

Seeking a Catalyst

Notes organic chemist Paul Bloom, Ph.D., business director of industrial chemicals at ADM, "The concept itself of creating propylene glycol from renewable sources is not that new. Scientists at the University of Wisconsin demonstrated its feasibility as early as the 1930s, but they couldn't produce it in a way that was economical for commercial production." ADM's Evolution Chemicals Division has been looking for ways to produce biobased PG for at least 20 years, he adds, but the catalysts — the agents for producing it economically and up to quality standards — had never been identified.

That was the challenge facing Zacher and his colleagues at PNNL — research chemist John Frye, Jr., and project manager Todd Werpy, Ph.D. In addition to NCGA support, funding for this phase was provided through grants from the U.S. Department of Energy Office of Biomass Programs.

"John is some kind of creative genius," Zacher says. "You give him a problem, and he gets really quiet for a long while. Then he gets this look in his eyes and starts weaving a compelling story with a direction and catalysts we should pursue. Then we'd go from there. The two-fold breakthrough was finding catalysts for taking both sorbitol and glycerol to propylene glycol."

> *The central issue is getting a catalyst to cut only the right places in molecules that make up simple sugar variations like sucrose, sorbitol, dextrose and glycerol.*

They're all fairly similar — in Zacher's description: "Carbon atoms in a row, with an oxygen hanging off of most of them."

Selective Simple Chemistry

"Converting glycerol into PG is simple chemistry," Zacher says. "You snip off only a single OH group. But you have to do it selectively to make the process efficient and economical. The trick is finding the right catalyst — a finely tuned pair of chemical scissors to cut only the right bonds. The result is propylene glycol, water and a few byproducts."

The right catalyst is essential because other catalysts and processes can make PG, but not cheaply enough to make commercial production feasible. The conversion process also produces a few byproducts, such as ethylene glycol, so the next step is to filter out those compounds to create pure PG.

"The PNNL team came up with a novel set of catalysts that enormously improved the capabilities to do this," Bloom says. "That was the key. From there, we used their findings to scale up a technology for commercial production."

The Biodiesel Factor

Preceding the development of biobased PG was the broad effort in the 1990s to replace petroleum products with fuels from renewable sources, such as ethanol as a supplement for gasoline. A prime target was a biobased replacement for diesel fuel. Because diesel yields better mileage than comparable gasoline engines, it has long been popular for long-distance transportation — more than 90 percent of freight is shipped in diesel-powered trucks, trains and boats.

Its popularity presented an opening for development of biodiesel alternatives produced from soy and other oily plant and animal sources. According to the National Biodiesel Board, an industry trade group, some 112 million gallons of biodiesel were sold in the United States in 2005; with some 150 biodiesel plants in operation in 2011, the figure was 1.1 billion gallons.

And, biodiesel production has a byproduct — the sweet, colorless, syrup-like liquid called glycerol.

"The early 2000s led to a 'glut' of glycerol research," Zacher notes. "People thought biodiesel would saturate the glycerol market. A 'free' feedstock makes every idea look economical, but it turned out that glycerol was never going to be free. Only economically sensible ideas would prevail."

Flexible Feedstocks

The PNNL/ADM team did better. PNNL's initial focus was a catalyst that would make PG from sorbitol, but it turned out it could make PG out of glycerol as well. ADM joined the project, both in research and funding, with an immediate goal of developing a formula that would enable commercialization. They ended up working on the glycerol byproduct from biodiesel.

"The ADM team participated in additional collaborative work to improve the technology," Lund notes, "and once they felt it would be commercially deployable, we entered into a licensing agreement with the company in 2006 granting them rights to manufacture propylene glycol."

Adds Bloom: “We went with glycerol as our initial starting point but we approached the research targeting a number of potential sources, including corn sugars. Our goal for the long-term is to be able to work with flexible feedstocks — not just glycerol but also multiple carbohydrates including sucrose, dextrose, carbohydrates, corn stover and other cellulosic feedstocks.”

Measurable Contributions

ADM’s new Decatur facility opened in phases. The plant began production of glycerol in 2009, limited production of industrial-grade PG in 2010, continuous PG-I production in March 2011 and USP production in November 2011. The new plant has an annual production capacity of 100,000 metric tons.

“This product and process follows the principles of green chemistry,” Bloom says. “It not only reduces the demand for petroleum feedstocks, our independently reviewed Lifecycle Analysis indicates that it has a 61 percent greenhouse gas reduction compared to petroleum-based PG.” He notes that ADM propylene glycol meets American Society for Testing and Materials standards for 100 percent biobased renewable carbon content and meets the standards for the U.S.D.A. BioPreferred program.

“To our knowledge,” he says, “this is the first facility in the world manufacturing biobased propylene glycol that meets industry specifications for USP.”

In March 2012, Zacher was named PNNL’s Inventor of the Year for 2011, a recognition of his contributions, including more than 20 U.S. patents, plus another 20 overseas. All but one have been for renewable products and solvents. Zacher, Frye and Werpy have also all been named Battelle Distinguished Inventors, a recognition awarded by Battelle, the organization that manages PNNL for the Department of Energy.

“My approach is a love of problem-solving, overcoming challenges,” Zacher says. “As a scientist and engineer, I start from other people’s ideas, great ideas and figure out how to make them work.

“And,” he adds, “I’ve always wanted to be able to drive by a plant and say, ‘That’s something I’ve had a part in.’”

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