2012 Presidential Green Chemistry Challenge

Propylene Glycol from Renewable Sources

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Primary Sponsors

Battelle / Pacific Northwest National Laboratory
Mr. Alan Zacher (Principal Investigator)
P.O. Box 999, P8-60 / 902 Battelle Blvd
Richland, WA 99354
(509) 372-4545
alan.zacher@pnnl.gov

Archer Daniels Midland Company
Dr. Paul Bloom
4666 Faries Parkway
Decatur, IL 62526
(217) 451-2158
paul.bloom@adm.com

Contact Person

Ali Madison
Associate Communications Manager, Technology Deployment & Outreach
Battelle / Pacific Northwest National Laboratory
P.O. Box 999, K1-01 / 902 Battelle Blvd
Richland, WA 99354
(509) 375-3743
ali.madison@pnnl.gov

Contributors

Pacific Northwest National Laboratory Team: Mr. John Frye, Mr. Alan Zacher, Dr. James White (retired PNNL)

Archer Daniels Midland Company Research Team: Dr. Kevin Martin, Dr. Chris Hoffman, Dr. Todd Werpy, Mr. Joshua Terrian, Mr. Brad Zenthoefer, Dr. Gustavo Dassori, Dr. Paul D. Bloom, Mr. Kevin Adlaf

Archer Daniels Midland Company Production Team: Mr. Michael Kruley, Dr. Sundeep Vani, Mr. Kevin Moore, Mr. Brad Hunt, Mr. Chad Minks

Project title

Propylene Glycol from Renewable Sources, or PGRS

Most recent milestone

A new 100,000 metric ton per year Archer Daniels Midland Company production facility, built specifically to commercialize PGRS, was commissioned in April 2011. The facility is now producing propylene glycol that meets USP specifications entirely from renewable sources.

Award eligibility

The nominated technology is not eligible for either the Small Business or Academic awards categories.

EPA award focus area

Focus Area 1: The use of greener synthetic pathways

U.S. component

All research, development, and implementation of this technology occurred within the United States. Additionally, the industry partner who licensed the technology is based in the U.S., and the new production facility built by co-sponsor ADM to commercialize the technology is located near the company's headquarters in Decatur, Illinois.

Abstract

The PGRS process currently produces propylene glycol (PG) for the first time on a commercial scale entirely from renewable resources rather than from petroleum. The technical merit and economic competitiveness behind the PGRS technology has been demonstrated through ADM's commissioning and operation of a new 100,000 metric ton per year PG facility. This represents the first of its kind in the world, an operational commercial scale facility producing PG that meets U.S. Pharmacopeia (USP) specifications entirely from renewable resources rather than from petroleum. Other competing technologies directed towards making PG from renewables have been unable to produce this high quality material at full scale.

Propylene glycol is a commodity chemical used in everyday consumer products such as liquid detergents, hand sanitizers, pharmaceuticals, and cosmetics, as well as industrial products such as plastics, paint, antifreeze and aircraft de-icer. The largest use of PG is as a co-monomer in plastics, especially fiberglass resins. Until the introduction of this process, it has been commercially produced almost entirely from petroleum resources. In fact, this very useful organic compound is so widely used that more than two billion pounds of petroleum are consumed in its production each year worldwide. To help displace this consumption of petroleum—much of it imported from foreign sources—and to replace the toxic feedstock materials involved in its use, scientists at Pacific Northwest National Laboratory (PNNL) developed a catalytic process for producing PG from renewable sources. This safe, sustainable, cost-competitive, and commercially viable alternative converts plant-based, seed-oil-derived glycerol or plant sugar alcohols into PG, which can then be purified to meet a variety of market specifications. The glycerol can come from a variety of sources, including the crude glycerol byproduct from biodiesel production.

THE PROBLEM & THE PRODUCT

While the largest use of propylene glycol (PG) is in fiberglass resins, many liquid detergents, antifreeze, de-icers, paints, polyesters, cosmetics, personal care products, pharmaceuticals, plastics, and certain food additives—the things we use every day—are made using PG. Propylene glycol has traditionally been made through a variety of routes, but they all have one thing in common: they all start with petroleum, and involve the use of toxic materials. Until now, that is. With the revolutionary new propylene-glycol-from-renewable-sources—PGRS—catalytic process resulting from years of research and development at Pacific Northwest National Laboratory (PNNL)[1], these products can now be made just as cost effectively from renewable sources. Because the PGRS process relies on plant-based raw materials—which are safe, abundant, and low cost—rather than petroleum-derived propylene to produce PG, the production facilities can be both sustainable *and* economically competitive.

Compare this to existing processes, where PG is generated from propylene that is cracked from larger petroleum hydrocarbons, or alternatively, propane derived from natural gas production is dehydrogenated to propylene. The propylene is then converted into propylene oxide, a highly toxic chemical with an IDLH[2] estimated at 400ppm and classified by EPA as a Group B2 probable human carcinogen. Finally, ring opening of the epoxide yields PG. However, in the PGRS process, PG is not only produced from a renewable resource, but it also avoids the harmful intermediates and reactants that are used to produce it via the petroleum routes.

The annual global market for PG is currently about 3.5 billion pounds, with the U.S. market accounting for about one-third of this. Until now, this level of demand has been met with PG derived from approximately 2 to 2.5 billion pounds of petroleum annually.

THE CHEMISTRY

Originally patented in 2002, the PGRS process was developed for use with glycerol (glycerin) and other sugar alcohols that can be derived from processing a variety of crops, including corn and oilseed crops such as soybeans, Canola®, jatropha, and sunflowers, as well as from crop residues.

An excellent source of raw materials for the PGRS process is the glycerol byproduct from biodiesel production. For every 100 pounds of biodiesel produced, 10 pounds of glycerol are also formed. With the current U.S. market for biodiesel estimated at one to two billion pounds, the byproduct glycerol—100 to 200 million pounds—presents excellent opportunities for replacing petroleum-derived chemicals with renewable ones. The PGRS process can convert this byproduct glycerol into a more valuable commodity chemical, thereby adding significant value to the biodiesel production process.

The PGRS process relies on a carbon supported bi-functional metal catalyst used in combination with a soluble base co-catalyst. The reaction is conducted using an aqueous feed solution in a trickle bed reactor configuration under moderate hydrogen pressures (typically ~ 1200 psig). Hydrogen and aqueous feeds are fed co-currently in a down-flow manner. When glycerol is used as the feedstock to produce PG, reaction temperatures are somewhat milder to avoid carbon-carbon bond scission. Longer chain sugar alcohol compounds (such as sorbitol or xylitol) can also be used to produce PG and other products including ethylene glycol. Higher reaction

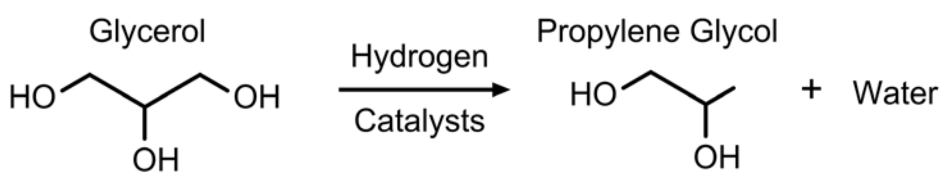
[1]Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy
[2]IDLH, or Immediately Dangerous to Life or Health, limits are essentially workplace exposure limits for hazardous chemicals

temperatures have usually been necessary in those cases because carbon-carbon bond scission is necessary to produce C3 products. PG yields of over 90% have been demonstrated with glycerol as the feedstock.

The overall reaction required to convert glycerol to PG can be represented by a simple dehydration reaction, removing a primary hydroxyl group and a proton, with formation of a carbon-carbon double bond, followed by rehydrogenation of the double bond. In the PGRS process, we believe the actual reaction mechanism proceeds via dehydrogenation of a primary alcohol group on the glycerol forming glyceraldehyde, followed by removal of a secondary hydrogen ion located alpha to the carbonyl by the base co-catalyst. This is followed by loss of the remaining primary hydroxyl group (which is thought to be facilitated by one component of the catalyst system).

The final two steps involve re-hydrogenation of the resultant carbon-carbon double bond and also conversion of the aldehyde group back to an alcohol. What is unique about the PGRS process, compared to other previously reported processes, is that PNNL researchers have discovered catalysts and process conditions that allow this multistep process to proceed in a single reactor that produces PG both in high selectivity and at high conversion. In order to obtain both high conversion and selectivity, the process needs to operate within a relatively narrow window of conditions. For example, if the hydrogen pressure is too low, large amounts of undesirable by-products are formed and only small amounts of PG are produced. Conversely, if the hydrogen pressure is too high, glycerol conversion is greatly reduced, but PG is the only product formed in significant quantity. Therefore, the key to the successful commercial viability of the process was finding the right balance of catalyst composition, feedstock purity, and reaction conditions that resulted in high, single-pass yields of PG.

While this is essentially simple chemistry, the innovation of the PGRS process is the discovery and refinement of robust carbon supported bi-functional metal catalysts that can perform this chemistry with high selectivity, allowing the chemistry to become highly efficient and cost competitive. Though other routes for converting glycerol to PG have been developed, tested, and even piloted, to date no other bio-based process is sufficiently cost effective to be commercialized on an industrial scale, which is demonstrated by the historical exclusivity of industrial scale PG-from-petroleum routes.



When using glycerol as a feed, the PGRS catalysts are well over 90% selective, converting the majority of the glycerol to PG. The small amounts of byproducts formed are recovered and purified to obtain additional value; the waters of reaction are also recovered and reused.

The catalyst is also broadly applicable to other feeds to produce PG and other lower polyols from larger sugar alcohols such as sorbitol and xylitol. With adjustments to the catalyst and the process, the catalyst can perform both dehydroxylation and hydrogenolysis of the secondary carbon-carbon bonds when converting 5-carbon and 6-carbon sugar alcohols. The process more selectively cleaves the 3rd and 4th carbon-carbon bond in sorbitol, resulting in significant amounts of PG and glycerol, which will also eventually be converted to more PG. There is also a tendency to cleave the bond between the 2nd and 3rd carbons, resulting in byproduct ethylene glycol that can be separated and sold as a valuable coproduct. When using 5-carbon sugar alcohols such as xylitol or arabinitol, the process is most selective to a mixture of PG and ethylene glycol.

The following is a list of patents related to the development of this technology, all of which are owned by Battelle and exclusively licensed to Archer Daniels Midland Company (ADM):

- **US Patent No. 6,841,085** "Hydrogenolysis of 6-carbon sugars and other organic compounds"
- **US Patent No. 6,677,385** "Hydrogenolysis of 5-carbon sugars, sugar alcohols and compositions for reactions involving hydrogen"
- **US Patent No. 6,479,713** "Hydrogenolysis of 5-carbon sugars, sugar alcohols, and other methods and compositions for reactions involving hydrogen"
- **US Patent No. 7,038,094** "Hydrogenolysis of 5-carbon sugars, sugar alcohols, and methods of making propylene glycol"
- **US Patent No. 6,570,043** "Converting sugars to sugar alcohols by aqueous phase catalytic hydrogenation"
- **US Patent No. 6,235,797** "Ruthenium on rutile catalyst, catalytic system, and method for aqueous phase hydrogenations"
- **US Patent No. 6,982,328** "Methods of producing compounds from plant materials"
- **US Patent No. 7,652,131** "Methods of producing compounds from plant materials"
- Foreign equivalents are pending in Europe

The following are a couple selected peer reviewed publications on PGRS:

- "New Catalysts for the Hydrogenolysis of Glycerol and Sugar Alcohols," published in *Catalysis of Organic Reactions: Twenty-second Conference.* 2008.
- "Catalytic Hydrogenolysis of 5-Carbon Sugar Alcohols," published in *Catalysis of Organic Reactions: Twenty-second Conference*. 2008.

THE BENEFITS and DRAWBACKS

Using glycerol-derived PG in place of petroleum-derived PG has several benefits, including:

- replacing toxic petrochemical feedstocks with benign natural material that is abundant, low cost, and also safer to transport and store
- making a significant contribution to reducing U.S. petroleum consumption, and ultimately, our nation's dependence on foreign oil
- representing a critical step toward a reduction of greenhouse gas emissions from chemical manufacturing.

Most pivotal to this discussion is that PGRS is indeed commercially viable. In 2009, Archer Daniels Midland Company (ADM)—which exclusively licensed the PGRS process from Battelle in 2006 following extensive research collaboration—initially took the process down the road to commercialization

Archer Daniels Midland Company
ADM is one of the largest agricultural processors in the world—a global leader in turning crops into products that serve the vital needs of a growing population.

by developing a commercial process that included upstream and downstream process development, reactor design and engineering and commercial scale up of the novel catalyst technology based on PNNL patents.

Motivated by the success of research efforts in demonstrating commercially viable production of bio-based PG—at prices competitive with those of the petroleum-derived alternative—ADM then constructed a full-scale renewable glycols facility in Decatur, Illinois (shown at right). The recently completed facility began operating in April 2011. Using the PGRS process and a special ADM-developed separations process, ADM is using the facility to convert renewable resources into PG meeting both USP and industrial specifications for products we depend on every day. The facility will produce up to 100,000 metric tons of PGRS each year, capable of meeting approximately 20 percent of annual U.S. demand for PG.

Now marketed as Evolution Chemicals™ Propylene Glycol, ADM's new product based on the PGRS process meets the American Society for Testing and Materials (ASTM) standards for 100% bio-based renewable carbon content, enabling customers to uniquely market and label their end-use products. The USDA's BioPreferred®[3] program, for example, will help consumers, businesses, and governments easily identify bio-based products, and also act as a marketing tool for product manufacturers and vendors.

A life cycle analysis study performed by ADM on the PGRS process—and reviewed and endorsed by Michigan State University Professors Bruce E. Dale and Seungdo Kim—shows a reduction of up to 61% in greenhouse gases compared to the propylene oxide route to PG. This enables ADM's customers to make progress toward meeting corporate sustainability goals as well as reduces the carbon footprint of chemical manufacturing facilities producing PG.

As with any industrial scale process, there are limitations associated with the PGRS process. Clearly, the one that stands out is that the process is not 100% selective to propylene glycol. Coproducts produced in this process must be separated from the PG produced from this process. This is also required for petroleum derived PG. In traditional petroleum derived PG, byproducts are mostly PG dimers and trimers which are separated from PG by distillation. When glycerol is used as the feedstock, the PGRS process produces a small amount of ethylene glycol byproduct, which also must be removed through distillation. However, when larger 5-6 carbon polyols are used as the feedstock, more ethylene glycol can be produced. Ethylene glycol is a key raw material for antifreeze and a monomer in polyethyleneterephthalate (PET). Many companies that use PET for packaging are actively pursuing new sources of renewable-based ethylene glycol to use in their applications. Most notably, Coca-Cola has announced their Plant Bottle™ that uses a renewable-based ethylene glycol.

ADM's expertise and innovation in chemistry, engineering and catalysis played a significant role in the successful commercialization of this process. ADM developed a commercial catalyst

[3]The purpose of this program is to promote the increased purchase and use of biobased products in an effort to reduce petroleum consumption, increase usage of renewable resources, better manage the carbon cycle, and contribute to reducing adverse environmental and health impacts. www.biopreferred.gov.

based on the PNNL technology, completed reactor engineering and construction, and developed a novel separations process designed specifically for this chemistry that can produce PG that meets industrial or U.S. Pharmacopeia/European Pharmacopeia (USP/EP) specifications. This results in a USP-PG that is acceptable in pharmaceutical, cosmetic, and food applications on a global basis. The resultant USP/EP PG product is also both Kosher and Halal certified.

TECHNOLOGY COMPARISON

What separates the PGRS process from other technologies for renewable PG is real, industrial scale impact. Because the theory is quite simple, there have been many other proposed processes for producing renewable PG. Some of these technologies go back to 1958 in U.S. patent 2,852,570 by Conradin et al, and even further back to 1935 in U.S. patent 2,004,135 by Rothrock et al. In addition, like the PGRS process patented in 2002, other advanced processes for PG from glycerol have been developed and patented in the last 15 years.

Many press releases have been issued about these new technologies promising the construction of industrial scale renewable PG plants that could finally reduce our dependence on petroleum derived PG. These facilities were promised to begin production in the last 6 years, but to the best of PNNL's and ADM's knowledge, there are no press releases claiming success. One group in China, Global Biochem, has produced biobased PG from carbohydrates, but has not announced a PG product that meets USP, EP or JP specifications.

Among competing technologies, the technical superiority and economic competitiveness of the PGRS process has been demonstrated in that it is apparently the first to finally break the barrier of an industrial scale process for renewable derived PG, which is finally beginning to displace some of our dependence on petroleum derived PG.

Comparing the published reports of modern renewable glycerol-to-PG processes to the PGRS process, there are a wide variety of different catalysts, intermediates, process conditions, reactor technologies, solvents, and separation systems. Many of these publications date back to 2000 and earlier. While some of these differences could be analyzed and compared, the sponsors believe that the metric by which a technology should be judged is whether it has measurable, positive impact on our lives.

Our nation is committed to developing alternatives to expensive imported petroleum and is taking steps on many fronts to accomplish this. While there are valuable ideas embodied in many of the competing PG technologies, to date, the PGRS process is the only one that has been demonstrated to have real impact in reducing our dependence on petroleum derived PG. It has been commercialized by a well-established industrial giant with the means to penetrate, influence, and lead the transformation of national—and international—markets. That is why the sponsors believe that the PGRS process should be considered for the prestigious honor of the Presidential Green Chemistry Award.

SUMMARY – Reviewing the Big Picture

Approximately 2 to 2.5 billion pounds of petroleum are consumed each year to meet current world-wide demand for PG. Used to manufacture chemicals needed to produce everyday industrial and consumer products that can be found in every household in America—and around the developed world—PG has historically only been produced using this non-renewable resource, inhibiting our national energy independence. While the developers of many competing technologies have made promises to address this challenge, the PGRS process offers a commercially proven, cost-effective way to make PG from renewable resources and offers an alternative to petroleum derived PG today. That is impact.

More and more consumers are choosing products that offer a lower carbon footprint, and many corporations are developing sustainability programs. The PGRS process offers the chemical industry and consumers a real, tangible opportunity to produce and choose products that reflect their desire to improve sustainability.

From a business and operations standpoint, the PGRS process employs a highly selective and efficient catalytic process that meets the requirements and demands of a commercial chemical process. This is combined with the process and separations developed by ADM to produce a final product that meets or exceeds customer specifications. And there is no better evidence of its significance and viability in the commercial marketplace than actual, industrial scale commercial production of renewable derived PG in 2011 that actively displaces our dependence on petroleum derived PG.

The benefits of the breakthrough PGRS process are significant and carry real impact to the national—and global—environment. The need to reduce fossil fuel consumption is well understood and more widely embraced than ever. The PGRS process represents a significant step toward actually fulfilling that need. Producing renewable chemicals to replace petroleum-derived chemicals, the new process also helps complement and build upon the significant worldwide investment to develop renewable fuels to replace petroleum-derived fuels.

There are big-picture, short-term benefits for many, including:

- ***Consumer product manufacturers.*** Makers of products that employ propylene glycol during manufacture can reduce their carbon footprint today with product from the PGRS process while remaining competitive in their respective markets.
- ***The United States and other countries.*** Countries around the world with national interests surrounding alternative energy and materials will benefit from the introduction of a viable alternative to petroleum use—on a scale large enough to have meaningful results and tangible impact today.
- ***Humankind.*** People will reap the benefits of a cleaner environment, and will have more options as consumers to do their part through the many products they choose.

And while these short-term wins are highly significant on their own, and help create the habits now that will be necessary to our future, there are also inherent broad, long-term benefits. By shifting the way in which we steward our natural resources, we will benefit the health, well-being, and thinking of future generations and contribute to the increased energy security and independence of our country.

In summary, the sponsors believe the PGRS process should be considered for the Presidential Green Chemistry Award because in 2011 it has demonstrated a real, industrial scale impact in displacing a petroleum derived chemical with a renewable one. Products you can purchase today may already contain PGRS derived renewable PG, and their numbers will continue to significantly increase.