Suzanne Shelley,
Contributing Editor

A Renewable Route to Propylene Glycol

Rapid expansion in biodiesel production has spurred a bumper crop of competing processes to turn byproduct glycerin into propylene glycol.

Price and supply stability are the hallmarks of a desirable feedstock for the production of chemicals and plastics. In the days of yore, petroleum and natural gas enjoyed such defining characteristics, but this is no longer the case. Add to that the numerous environmental implications associated with using fossil fuels and their derivatives, and it's no surprise that alternative feedstocks — those based on renewable agricultural and forest materials — have become the apple of nearly every chemical and plastics producer's eye.

Many such companies have been working for years to move promising, lab-based technologies that convert renewable feedstocks into value-added commodity and specialty products into commercial-scale production. The widespread production of eco-friendly transportation fuels, such as biodiesel from vegetable oils (*e.g.,* soybean, rapeseed or palm oil), represents some of the most recent commercial successes in the quest to pioneer bio-based routes for producing fuels that are not dependent on petroleum, natural gas or other hydrocarbon-derived feedstocks.

The rapid expansion in biodiesel production has created a perhaps-unexpected opportunity for the chemical industry to move one particular biobased production route onto the fast lane for commercialization. Specifically, at least a half-dozen chemical producers are seeking to bank on the sudden glut of glycerin — the main byproduct of biodiesel production — as an inexpensive, sustainable, environmentally benign alternative to conventional petroleum-derived feedstocks for the production of propylene glycol (1,2-propanediol; PG).

Over the past few months, Dow, Huntsman, Ashland, Cargill, Archer Daniels Midland (ADM), Senergy Chemical, Virent and others, have either announced plans or broken ground on new plant construction to commercialize process routes designed to convert biodiesel-derived glycerin into PG. A variety of glycerin-to-PG commercialization efforts are underway — most of which are slated to come online by 2008.

Traditionally produced from petroleum-derived propylene oxide, PG is a widely used commodity chemical that plays a significant role in the manufacture of a broad array of industrial and consumer products, including unsaturated polyester resins, plasticizers and thermoset plastics, antifreeze products, heat-transfer and coolant fluids, aircraft and runway de-icing products, solvents, hydraulic fluids, liquid detergents, paints, lubricants, cosmetics and other personal-care products. Today, industry estimates put global demand for PG between 2.6 and 3.5 billion lb/yr.

Biodiesel production — driving innovation

Biodiesel is produced by reacting vegetable oils or animal fats with an alcohol, such as methanol or ethanol, in the presence of a catalyst, to yield methyl esters (biodiesel) and byproduct glycerin. According to the National Biodiesel Board (Jefferson City, MO; www.biodiesel.org), the U.S. industry trade group, this bio-sourced diesel product burns more cleanly than its fossil-fuel-derived counterpart, and it can be blended in any amount with traditional diesel, or used on its own, in existing diesel engines with little or no modifications. Biodiesel is not only biodegradable and non-toxic, but it is also essentially free of sulfur and aromatics, the group says (box, next page).

As a result, biodiesel capacity in the U.S. has more than quadrupled in recent years. For instance, Joe Jobe, CEO of the National Biodiesel Board, stated in testimony on May 3 before the U.S. House Small Business Committee, that in 2004, there were just 22 plants in the U.S. that were producing roughly 157 million gal/yr of biodiesel. Today, 148 plants are producing biodiesel at a rate of 1.4 billion gal/yr. In addition, the National Biodiesel Board reports that new capacity and capacity expansions that have been announced in the U.S. to date — should they all come to fruition — are expected to result in another 1.7 billion gal/yr of biodiesel over the next two years.

During the transesterification of feedstock vegetable oils, every nine pounds of diesel yields one pound of glycerin (or 1.25 lb of glycerin is produced for every gallon of biodiesel). U.S. demand for glycerin, which is a key ingredient in soaps, hand lotions and other products, is currently about 600 million lb/yr. However, market analysts project that the anticipated surge in biodiesel production will yield an additional 1 billion lb of glycerin over the next two years — essentially flooding the market.

Converting glycerin into PG

While the actual production economics associated with producing PG from biodiesel-derived glycerin remain to be seen, once the pending fleet of facilities comes online, the use of glycerin as a feedstock could reduce the cost of PG by as much as $0.40/gal, according to Galen Suppes, a professor of chemical engineering at the Univ. of Missouri, Columbia (www.missouri.edu). Suppes has developed a patented process for converting biodiesel-derived glycerin into PG, which was awarded the U.S. Environmental Protection Agency's 2006 Presidential Green Chemistry Award.

Suppes' process was also recently licensed to Senergy Chemical (Gig Harbor, WA; www.senergychem.com), and is said to have a variety of demonstrable performance advantages over other processes that are being pursued by other chemical producers. The technology uses hydrogen as a co-reagent to perform a hydrogenolysis conversion of glycerin, in the presence of a copper-chromite catalyst. In the course of the reaction, the process first removes a water molecule from the glycerin, and then adds a hydrogen molecule. This yields two products — acetol and propylene glycol — as well as a water byproduct (figure).

"Our highly selective process has multiple advantages over other published technologies," says Suppes. "These include temperatures lower than the conventional 500°F, and pressures considerably lower than the conventional 2,170 psi. Both of these advantages help to reduce capital and operating costs." In addition, the process "has higher yields — in excess of 90% to produce a mixture of acetol and propylene glycol, whereas other published processes tend to have a PG yield around 80% — and very low conversion to unwanted ethylene glycol — typically less than 1.5%, while most competing processes yield PG with 10% ethylene glycol content," he notes

According to Suppes, ethylene glycol is not only undesirable because of its toxicity, but each pound of ethylene glycol produced also yields another 0.5 lb of unwanted byproducts. Meanwhile, the use of a catalyst based on copper and chromium "helps to reduce costs compared to competing processes that rely on precious-metal catalysts," he says.

In January, Senergy Chemical ran a commercial trial of the process in Houston, TX, and is now constructing

BIODIESEL: SORTING FACT FROM FICTION

As demand for renewable fuels continues to rise, biodiesel promises to occupy an increasingly bigger portion of the proverbial barrel. In addition to its favorable environmental profile, biodiesel has some other positive performance attributes, such as increased cetane, high fuel lubricity, high oxygen content and the highest Btu content of any alternative fuel, which makes it a "preferred blending stock to produce ultraclean diesel," says the National Biodiesel Board.

A recent U.S. Dept. of Energy (DOE; Washington, DC; www.doe.gov) study showed that the production and use of biodiesel, compared to petroleum diesel, resulted in a 78.5% reduction in carbon dioxide emissions. Moreover, biodiesel has a positive energy balance. According to DOE, for every unit of energy needed to produce a gallon of biodiesel, 3.24 units of energy are produced.

Biodiesel can be blended at any level with petroleum diesel to create a biodiesel blend, and can be used in compression-ignition (diesel) engines with little or no engine modifications. Biodiesel blends are denoted as BXX, with the XX representing the percentage of biodiesel in the blend. Today, most biodiesel sold in the U.S. is B20 (a blend of 20% biodiesel and 80% petrodiesel fuel).

Fuel-grade biodiesel must be produced in compliance with strict industry specifications (ASTM D6751) to ensure proper performance. And today, it is the only alternative fuel to have fully completed the Tier I and Tier II health-effects testing requirements of the 1990 Clean Air Act Amendments, according to the Biodiesel Board.

One potential downside is that pure biodiesel (B100) has a solvent effect, which can cause it to release deposits accumulated on tank walls and pipes from previous diesel fuel use. High-biodiesel blends can lead to the release of deposits, which may clog filters initially, so the Board recommends that precautions be taken to replace fuel filters frequently until such build-up is eliminated. The group says that this issue is less prevalent with B20 blends, and there is no evidence that lower-level blends (such as B2) have experienced filter pluggage.

This solvency effect can also soften and degrade certain types of incompatible elastomers and natural rubber compounds over time (*i.e.,* those used for certain fuel hoses and fuel pump seals), although this effect is lessened as the biodiesel blend level is reduced. The Board notes that extensive experience with B20 has found that no changes to gaskets or hoses are necessary, and that many OEMs have switched to components that are more compatible with biodiesel.

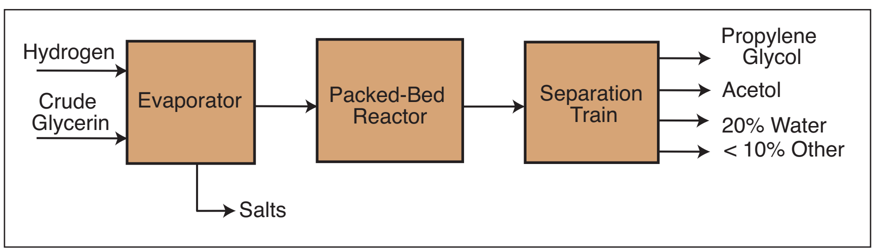

Figure. The ability to convert glycerin into propylene glycol is helping a growing list of chemical companies to produce more environmentally benign PG, while reducing their dependence on the conventional feedstock, petroleum-derived propylene oxide. Source: Dr. Galen Suppes, University of Missouri-Columbia.

its first 65-million lb/yr (7.5-million gal/yr) facility in the Southeast U.S. to produce PG from biodiesel-derived glycerin, says the president of Senergy Chemical, Mark Tegen. "We are not experiencing the purity problems that some other chemical companies have announced with respect to their soon-to-be-developed glycerin-to-PG processes," he continues. "We will be producing a near-USP-quality grade of PG and we have plans to qualify our material for eventual sale into the USP market."

Dow Chemical Co. (Midland, MI; www.dow.com) claims to be the world's largest producer and marketer of propylene glycol with total 2007 global production capacity for PG at 705 kiloton/yr (kta; the equivalent of 157 million gal/yr) — a 140-kta increase over 2006. The firm has introduced a glycerin-derived PG product dubbed "propylene glycol renewable" (PGR). The company's Dow Haltermann Custom Processing (DHCP) business unit is currently conducting pilot PGR trials with customers, and expects to have limited commercial-scale quantities available later this year. Full-scale commercial production of PGR is slated to begin at DHCP's Houston facility, which already produces biodiesel.

According to the company, one particular environmental benefit of Dow's process is that the production of PGR consumes "considerably less fresh water" than the conventional, petroleum-based route for producing PG (although the company declined to be more specific). In general, Tegen says the renewable route to PG "is a very clean process, which generates no appreciable emissions other than salts and water."

Dow's efforts to produce a bio-based PG product are being driven in part by pressures coming up through the refinery-to-retail supply chain, as strong demand for propylene glycol is shadowed by parallel interest in sustainable products among its customers. "There's strong global demand for PG, and unplanned outages, along with planned turnarounds, are continuing to add tightness to the supply in the market," says Mady Bricco, global product director, propylene oxide and propylene glycol for Dow. "Manufacturers in several downstream industries are demanding the ability to provide more sustainable products to their customers. Using PGR will enable customers to exercise their commitment to technologies that consume less fossil fuel and other finite resources," she continues.

Nonetheless, to maintain its competitive advantage in the face of dynamic market conditions, Dow is happy to straddle the fence between its newer bio-based PGR and its traditional hydrocarbon-based PG. "PGR pricing is independent of the volatility associated with hydrocarbon and energy costs," says Bricco. "However, our conventional propylene glycol offering helps to liberate Dow from any potential variability in seed oil and glycerin costs," she adds.

Huntsman Corp. (The Woodlands, TX; www.huntsman.com), which currently produces 145 million lb/yr of conventional PG at its Port Neches, TX, facility, has also entered the ring to produce PG from biodiesel-derived glycerin. The company is currently scaling up a proprietary glycerin-to-PG process at its development facility in Conroe, TX, and expects to begin production in 2008 (pending further scale-up and transfer of the process to its larger-scale commercial plant). Eventual capacity is slated to be 100 million lb/yr. "

The projected oversupply of glycerin resulting from biodiesel production was a key element in our decision to develop this technology," says David Hester, Huntsman's global business development director for performance products. "Having a glycerin-based technology as an alternative to the PO-based route will not only ensure a sustainable process, but will provide us with a hedge against higher oil prices," he adds.

According to the company, Huntsman's process first involves the cleanup of the crude glycerin, which is then hydrogenated to 1,2-propylene glycol in a reaction that is "high in conversion and highly selective to PG," (the firm declined to provide specific conversion rates or yields). Distillation is then used to to purify the PG.

In May, Ashland (Covington, KY; www.ashland.com) and Cargill (Minneapolis, MN; www.cargill.com) announced the formation of a joint venture that will be devoted solely to the development and production of chemicals made from renewable resources. Its first venture will be the production of PG from biodiesel-derived glycerin. The joint venture is planning a 65,000-metric ton/yr plant, which will use both licensed and proprietary (Cargill) technologies, at a yet-to be-finalized location in Europe. Startup is anticipated for mid-2008.

Meanwhile, last November, Virent Energy Systems, Inc. (Madison, WI; www.virent.com), developer of the patented BioForming technology platform for converting biomass into renewable fuels and chemicals, was awarded a $2-million grant from the U.S. Dept. of Agriculture (USDA; Washington, DC; www.usda.gov) and the U.S. Dept. of Energy (DOE; Washington, DC; www.doe.gov) to further its capabilities to convert glycerin from biodiesel production into PG. The grant was awarded as part of the joint USDA-DOE Biomass Research and Development Initiative. Working in conjunction with Future Fuel Chemical Co. — formerly a subsidiary of Eastman Chemical Co., which will supply the glycerin and help design and test the first prototype system at its Batesville, AR, biodiesel plant — Virent is working to optimize its yields of propylene glycol using glycerin of variable qualities.

UOP LLC (Des Plaines, IL; www.uop.com) is also getting involved, having established a new business unit — Renewable Energy and Chemicals — last December to pursue promising technologies for converting renewable feedstocks into value-added chemicals and plastics. Through this initiative, the company will continue to expand its existing efforts to produce biodiesel from vegetable oils, and to pursue technology to convert biodiesel-derived glycerin into propylene glycol, says company spokesperson Susan Gross, who notes that it is premature to comment on any scaleup plans at this time. [UOP has been working with the U.S. Dept. of Energy's Pacific Northwest National Laboratory (PNNL; Richland, WA; www.pnnl.gov) since 2004.]

Back in 2005, Archer Daniels Midland (ADM; Decatur, IL; www.admworld.com), announced plans to build its own glycerin-to-PG process, at a polyols facility that will produce both PG and ethylene glycol, at an as-yet-undisclosed location. ADM also declined to comment further on its process technology at this time.

"As with most commodities, the overwhelming majority of the cost is associated with the raw materials(s). Because crude glycerin is currently abundant and cheap, this process technology will remain competitive as long as that remains the case," says Tegen of Synergy Chemicals. "It uses a combination of conventional technology and equipment with some novel process concepts, and generates expected capital expenditures that are substantially less than conventional propylene oxide to propylene glycol processes."

Rapid growth in biodiesel production — and that industry's pending surplus of byproduct glycerin — has provided the chemical industry with the shot in the arm needed to move several promising, competing processes for producing lucrative, bio-based PG from the drawing board to commercial-scale viability. Over the next few months, these sustainable technologies will allow the chemical industry to provide a more environmentally benign version of the widely used commodity chemical PG, while reducing its dependence on costly, environmentally undesirable petroleum-based feedstocks. CEP

Using Corn Instead of Glycerin to Produce Propanediols

In addition to their glycerin-based route for producing PG, Suppes and his colleagues at the Univ. of Missouri have also developed a suitable technology for producing propylene glycol (1,2-propanediol; PG) using corn as the feedstock, instead of glycerin. "Should the use of ethylene glycol, which is toxic, ever be banned for use in antifreeze products, the demand for propylene glycol will be sufficiently high to create a significant market for the widespread production of corn-derived propylene glycol," says Suppes. "Because feedstocks based on corn sugars are more expensive than glycerin, there is not much incentive to produce corn-derived PG at this time," he continues .

Last month, DuPont officially christened its $100-million facility in Loudon, TN, which is using a proprietary fermentation process to produce 1,3-propanediol from corn sugar instead of petroleum-based feedstocks. Source: DuPont.

However, when it comes to another propanediol — 1,3-propanediol (PDO, a premium-price intermediate used in the production of polymers) — DuPont Tate & Lyle Bio Products LLC (Wilmington, DE; www.dupont.com) has just started up a $100-million plant in Loudon, TN, to produce a bio-based form of 1,3-propanediol (dubbed Bio-PDO), using corn sugar as the starting material. The facility uses a proprietary fermentation process to produce Bio-PDO from corn, making it the first plant in the world to manufacture this new bio-based product, according to the company.

The production of Bio-PDO consumes 10% less energy and reduces greenhouse gas emissions by 20% on a per-pound basis, compared to conventional petroleum-based PDO, says the company. In particular, production of 100 million lb of Bio-PDO will save the energy equivalent of 15 million gal/yr of gasoline, enough to fuel 27,000 cars annually. "The corn fields of today will be the oil fields of the future," says Tate & Lyle chief executive Iain Ferguson. The process has received the American Chemical Society's (Washington, DC; www.acs. org) 2007 Heroes of Chemistry Award.

Today, Bio-PDO is a key ingredient for the production of DuPont's Sorona polymer product line, which is used during the production of carpet fiber, apparel, automotive, home furnishings, packaging and engineering thermoplastic resins. While Sorona polymers have been traditionally produced from petrochemical feedstocks, the manufacture of Sorona using up to 40% Bio-PDO began this year. Bio-PDO can also be used in cosmetics, liquid detergents and industrial applications such as antifreeze and other formulations that use glycols.

Whether or not corn-derived Bio-PDO will ultimately displace glycerin-derived PG will likely depend on cost. "In many end-use applications, PDO could be used in place of PG, but generally it is not, because it is more expensive," says Suppes. Similarly, Hester of Huntsman adds: "Bio-PDO could become a competitor to bio-based PG in certain applications, [but only those] where the functional differences result in a price-performance advantage."

As for the production route, the Bio-PDO process uses a biotechnology route based on fermentation to convert corn sugar into 1,3-propanediol. "However, in the case of converting glycerin to PG, enzymes cannot compete with traditional catalysts for producing PG," Suppes notes.