**CHEMSYSTEMS**

**PERP PROGRAM**

# Report Abstract

## Glycerin Conversion to Propylene Glycol

## PERP06/07S4

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Nexant

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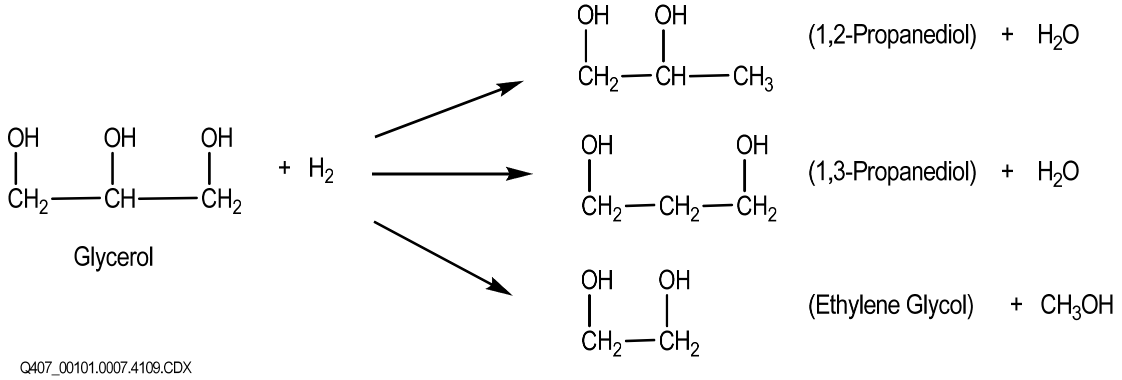
## 1 INTRODUCTION

The production of biodiesel in the form of fatty acid methyl esters (FAME) is expected to grow almost seven fold from one billion gallons per year in 2005 to about 6.6 billion gallons per year in 2015. Production growth in Western Europe is expected to flatten out, while robust growth will develop in North America and the rest of the world (primarily South-East Asia). While projected biodiesel production will remain small relative to global diesel fuel demand (still less than 1.5 percent in 2015), on the basis of the typical ratio of one pound of co-product glycerin per 10 pounds of biodiesel/FAME, there will be large quantities of glycerin available. This availability, coupled with a resulting low price for glycerin (particularly crude material), makes crude glycerin an attractive potential feedstock for a variety of derivative chemicals. This report provides an overview of related activities, and then focuses on glycerin conversion to propylene glycol where activity is keen.

## 2 CHEMISTRY

In the presence of metallic catalysts and hydrogen, glycerol can be hydrogenated to propylene glycol (1,2-propanediol), 1,3-propanediol, or ethylene glycol.




Various publications and patents present options for hydrogenating glycerol to propylene glycol. Catalyst systems examined include:

- Copper and zinc
- Sulfided ruthenium catalyst (at 2,175 psi and 240 to 270°C)
- Cobalt, copper, manganese, molybdenum, and an inorganic polyacid (achieving 95 percent PG yield at 3,625 psi and 250°C
- Homogeneous catalyst with tungsten and Group VIII transition metals at a pressure of 4,600 psi and 200°C
- Production of PG and 1,3-propanediol from vaporized glycerol solutions at 300°C in two stages

## 3 PLAYERS

At least seven entities are working to develop and/or commercialize glycerin to propylene glycol technology:

- Senergy/Suppes (University of Missouri)
- Cargill/Ashland
- Archer Daniels Midland (ADM)
- UOP/Pacific Northwest National Laboratory (PNNL)
- Virent Technologies (University of Wisconsin)
- Huntsman
- Dow Chemical

## 4 PRODUCT PURITY OF "RENEWABLE" PROPYLENE GLYCOL

A key concern in glycerin-to-PG processes is the suitability of the renewable propylene glycol produced for use in the various end uses, particularly personal care and food applications. The following summarizes the claims being made by several process developers:

- UOP claims that its simulation work indicates they can produce USP grade propylene glycol, and they intend to demonstrate this in a large-scale unit
- Cargill confirms that it is targeting personal care applications, and possibly also food applications
- Senergy Chemical (Suppes licensee) claims "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". Senergy claims they will be producing a near-USP-quality PG and they have plans to qualify their material for eventual sale into the USP market
- Davy claims "pharmaceutical grade material can be produced if required"

Of course, the proof will be by how well the marketplace will accept this form of propylene glycol. For industrial applications renewable propylene glycol should be readily accepted. However, for most personal care and pharmaceutical applications extensive testing of this material will be required before this material is qualified for use.

## 5 TECHNOLOGY DEVELOPMENT

### 5.1 Davy Process Technology – Gas Phase Process

Davy Process Technology (DPT) has developed a gas phase process for the hydrogenolysis of glycerin to propylene glycol in very good yields. In July, 2007 DPT announced the first license of this process to a joint venture between Cargill and Ashland. The Cargill/Ashland plant is expected to have an annual capacity of 65 thousand metric tons and to be built in a European location with start-up in early 2009. Cargill/Ashland expects the purity of the propylene glycol to be adequate for virtually any propylene glycol application.

Most previous work, as described in the patent literature, is based on the liquid phase hydrogenolysis of glycerin and suffered from poor conversions of glycerin and less than adequate selectivity to propylene glycol. DPT has now found that gas phase hydrogenolysis gives excellent glycerin conversion and very good selectivity to propylene glycol. The fact that such a conversion could be carried out in the gas phase is somewhat surprising considering the relatively low volatility of glycerin. Conventional wisdom would dictate that the high temperatures needed to volatilize the high boiling glycerin would lead to many side products as well as shortened catalyst activity. However, based on recent DPT patent disclosures, these fears were not realized.

Using a copper-based heterogeneous catalyst, selectivities of the DPT process are in the range of 93 to 96.5 percent. The major byproducts are ethylene glycol, hydroxypropanone, propanols, and ethanol.

### 5.2 UOP - Liquid Phase Process

In 2006 UOP announced the formation of a new Renewable Energy and Chemicals business unit focused on developing ways for UOP to leverage their know-how in conventional refining and chemical process technology into developing economic technologies for converting renewable feedstocks into fuels and chemicals.

In one of their first projects, UOP teamed with Pacific Northwest National Laboratory (PNNL) and have announced a catalyst breakthrough in the conversion of glycerin to propylene glycol. Currently UOP has a relationship with an operating company (unnamed at this time) to commercialize this process sometime in 2008.

While the overall chemistry is similar to the concept shown above for the DPT process, the UOP process is different in practice as it is a liquid phase process predicated on a base-promoted hydrogenolysis.

The highlights of the UOP process are listed below:

- Liquid phase process
- Conversion of glycerin is about 95.5 percent
- Selectivity of glycerin to propylene glycol is about 94.2 mole percent
- Crude 80 percent biodiesel glycerin containing up to 20 percent methanol and 2 percent fatty acids is suitable and is diluted with water to give a 40 percent aqueous glycerin feed
- Fatty acids are removed by acidulation to prevent catalyst fouling
- Distillation of crude glycerin is not required
- Propylene glycol purity is 99.6 percent

## 6 ECONOMICS

The cost of production for propylene glycol made from crude biodiesel-based glycerin is compared to conventional propylene oxide-based propylene glycol. The following cases are presented:

- Glycerin based with crude glycerin at $0.05/lb
- Glycerin based with crude glycerin at $0.17/lb
- Propylene oxide based with PO at cash cost of production
- Propylene oxide based with PO at full cost plus ten percent ROI

Even at the highest recent cost of crude biodiesel glycerin, the glycerin-based product has a cost advantage over conventionally produced propylene glycol. This is the obvious reason why this concept is receiving so much interest even from Dow Chemical, one of the world's largest producers of conventional propylene glycol.

However, these cost analyses are a snapshot in time and for a more complete analysis thought must be given to other cost scenarios such as a return or at least a partial return to a more "normal" oil price scenario. In the report we look at the sensitivity of propylene glycol costs as a function of both crude glycerin prices and propylene prices.

If propylene prices stay at these historic highs then the glycerin-based process has a distinct advantage. However, if oil prices abate, two factors will mitigate against the new glycerin-based processes. One is that propylene prices will fall and will cause the costs of PO-based propylene glycol to decrease as well. However, if oil prices abate, fuel prices will also fall and this will make biodiesel economics more difficult and production of biodiesel will decline. This in turn will cause biodiesel-based glycerin supply to decrease raising its price and further narrowing the cost gap or even surpass the costs of PO-based propylene glycol. These are the commercial risks inherent in any commercialization of a new process technology, but especially so with any new technology that is based on renewable resources and dependent on high oil prices to compete.

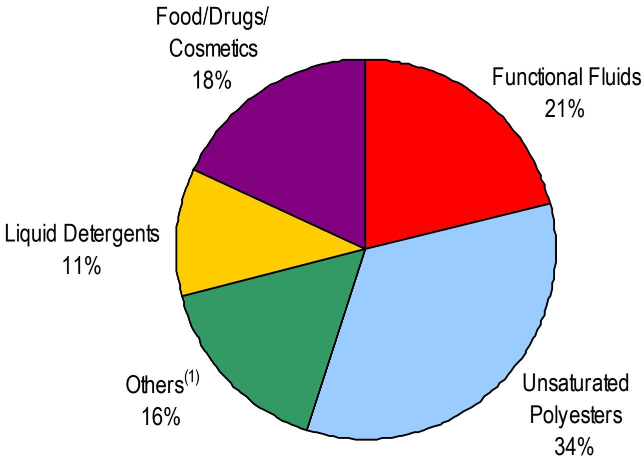
## 7 COMMERCIAL ANALYSIS

Propylene glycol has a broad spectrum of uses:

- Unsaturated polyesters
- Functional fluids
- Foods/drugs/cosmetics
- Liquid detergents
- Plasticizers, paints and coatings, tobacco humectant, pet foods, etc.

As can be seen in Figure 1, the largest market segment is unsaturated polyesters, which are resins used in fiberglass-reinforced structures and surface coatings. Fiberglass-reinforced structures are used in the construction (tub/shower units), marine (boat hulls), and transportation (sheets) industries. Dicyclopentadiene-based resins offer competition.

**Figure 1 Global Propylene Glycol Demand, 2006**




**Total = 1.5 Million Metric Tons/Year**

(1) Includes pet foods, plasticizers, paints and coatings, tobacco humectant, etc.

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Functional fluids, such as antifreeze and de-icing solutions, are the second-largest outlet for propylene glycol. In uses like aircraft de-icing and food industry coolant, propylene glycol is preferred over ethylene glycol due to its much lower toxicity.

Propylene glycol is an excellent solvent and extractant. Solvent applications include alkyd resins, printing inks, and coatings.

Propylene glycol finds broad use as a humectant in the pharmaceutical, cosmetic, animal food, and tobacco industries. Cosmetics include personal care products such as antiperspirants and deodorants. In these applications, propylene glycol functions to keep the moisture content of the materials in a narrow range, despite fluctuations in environmental humidity.

Non-ionic detergents utilizing propylene glycol find application in the petroleum production, sugar refining, and papermaking industries, as well as in toiletries and liquid detergents.

Miscellaneous uses for propylene glycol include plasticizers and hydraulic brake fluids.

United States, West European, and Japanese capacity and supply/demand/trade forecasts for propylene glycol out to 2012 are provided in the report.

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