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Biorefinery Product Opportunities from Glycerol

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Introduction

Plant triglycerides from oil crops give the integrated biorefinery a hydrocarbon-based source of renewable carbon for the production of fuels and chemicals. Biodiesel is formed when triglycerides (or a wide variety of other naturally occurring hydrocarbons) are subjected to transesterification with methanol using a strongly basic catalyst such as sodium or potassium hydroxide. The reaction forms a mixture of fatty acid methyl esters (biodiesel), and aqueous glycerol (glycerine)² as a coproduct in a 90/10 wt% ratio (Claude, 1999).³ The ease of this reaction, coupled with a \$1.00/gallon tax credit for biodiesel blenders, has stimulated significant recent growth for the industry. About 580 million gallons of biodiesel were produced in 2007, as compared with 100 million gallons as recently as 2005 (National Biodiesel Board, 2007). Biodiesel is fully compatible with existing diesel engines, and offers several environmental and performance benefits (Fukuda, Kondo, and Noda, 2001; Lotero *et al*, 2005; and Hill *et al*, 2006). In the context of the integrated biorefinery, biodiesel becomes one member of a family of compounds manufactured by an oleochemical operating unit also producing fatty acids, glycerol, meal and protein (Figure 1).

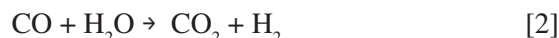
Recent research has focused on converting the glycerol coproduct into fuels and high value chemicals as a means to offset the production cost of biodiesel, which is significantly higher than nonrenewable diesel. In the biorefinery model, glycerol coproducts have a positive, synergistic effect on biodiesel production. Tyson *et al* have reported that inclusion of coproducts in biodiesel production could potentially lower the effective biodiesel cost from \$2.50/gal to slightly over \$1.00/gal (Tyson, *et al*, 2004). Conversely, failure to

find new uses for glycerol may serve to limit the growth of the biodiesel industry as surplus glycerol accumulates.

A number of promising new technologies have started to emerge from current research as potential candidates for conversion of inexpensive glycerol into both fuel and chemicals (Pagliaro *et al*, 2007; Johnson and Taconi, 2007; and Behr *et al*, 2008).⁴ This paper briefly overviews several new opportunities.

Glycerol in Fuel Applications

The nation's fuel supply is potentially an immense sink for consuming surplus glycerol. Glycerol's high polarity and water solubility preclude its direct addition to fuel supplies, but gasification and steam reforming have been examined as means to produce syngas (CO/H₂) or hydrogen from glycerol via equations 1 and 2 (Soares, Simonetti, and Dumesic, 2006).



These processes are great equalizers of biomass feedstocks, as conditions can generally be found to deconstruct a huge number of different organic materials into hydrogen for fuel applications or syngas for well-known Fischer-Tropsch processes. The primary challenge to these processes is their cost relative to producing the same materials from coal or natural gas.

Syngas and hydrogen formation can be coupled with downstream conversions expanding gasification to include chemical and power production (Simonetti *et al*, 2007). By incorporating several fundamental process steps (reforming, catalytic upgrading, Fischer-Tropsch synthesis, combustion, etc.) with syngas production, glycerol can also be positioned as a primary biorefinery feedstock for chemicals, fuels and

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² Although the terms are frequently interchanged, this paper will use the term *glycerol* to describe the pure compound, 1,2,3-trihydroxypropane, and *glycerine* to describe an aqueous solution containing glycerol as the primary component.

³ Note that other sources indicate up to 14 wt% of glycerol (Garcia, Besson, and Gallezot, 1997).

⁴ The number of citations in Web of Science for the term "biodiesel" has increased from 46 in 2000 to 494 in 2007. The subset of those papers describing relevant research on glycerol has increased from three papers in 2000 to 68 in 2007.

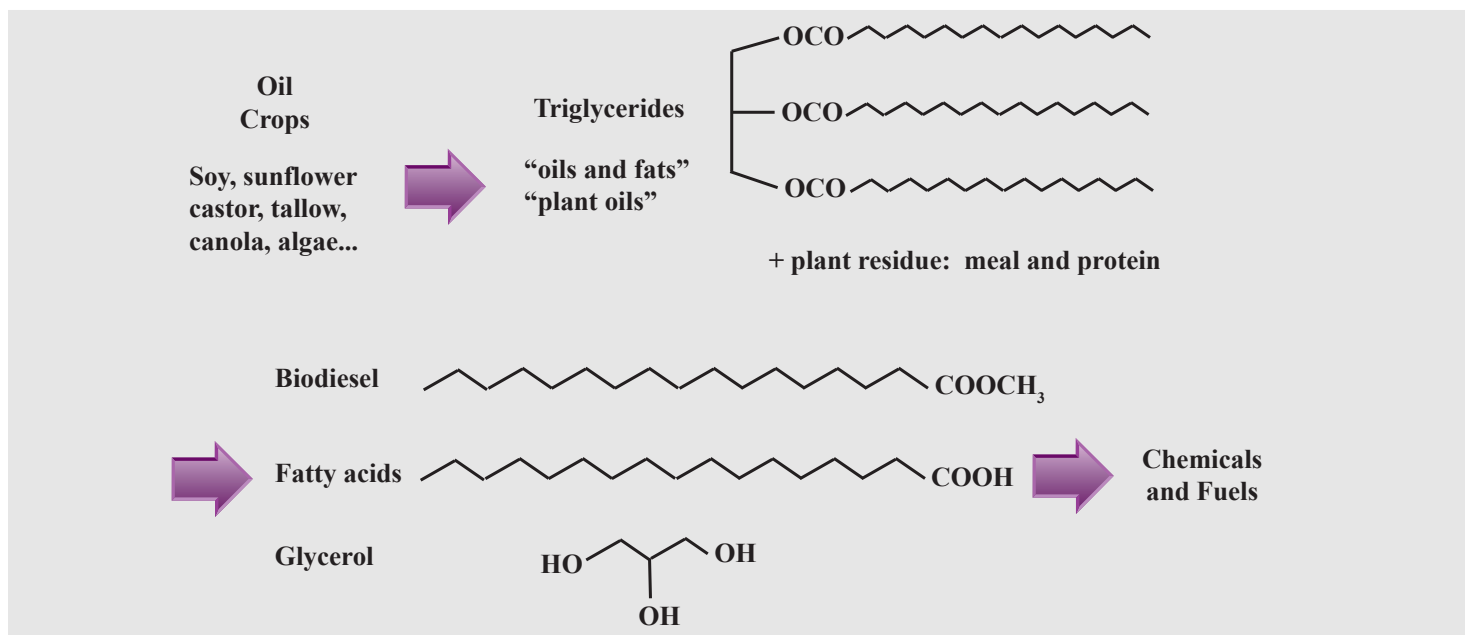


Figure 1. The Oleochemical Operating Unit of the Integrated Biorefinery

power, depending on the conversion technology employed. Glycerol can also be used as a starting material for production of fuel additives. Fuel oxygenates also address a large market opportunity for surplus glycerol. *t*-Butyl ethers and glycerol acetate esters are recognized as diesel (or gasoline) oxygenates because of their high octane value and ability to improve cold flow properties (Wessendorf, 1995; Klepacova, Mravec, and Bajus, 2005; and Karinen and Krause, 2006). Processes suitable for scaleup to pilot levels have been described (Behr and Obendorf, 2003; Melero *et al*, 2007).

Glycerol as a Primary Chemical Building Block for the Biorefinery

An effective consumption of glycerol will result from its use as a chemical building block. The historically high price of glycerol (\$0.50 – 0.90/lb) has limited the economic viability of processes requiring chemical modification of its structure. Accordingly, glycerol has normally been used “as-is” after isolation and purification. As the price of glycerol drops and its availability rises, glycerol ceases to become a simple additive for a fragmented list of small volume products, and assumes a position as the starting point for the production of large volume materials. The polyfunctional structure of glycerol suggests a number of processes that can be carried out.

a. Reduction Processes

Catalytic hydrogenolysis converts glycerol into a family of derivatives currently produced by the chemical industry, including ethylene glycol, propylene glycol, acetol and lactic acid (Maris *et al*, 2007) (Figure 2). Of particular interest is Suppes’ report of a selective, high yield hydrogenolysis of glycerol leading to propylene glycol (Dasari *et al*, 2005). Over 1 billion pounds of propylene glycol is produced annu-

ally, and serves as a replacement for ethylene glycol in antifreeze, as a polymer component and a number of smaller volume applications. The process also offers product control. By altering the conditions, acetol can be made as the primary product in >90% selectivity (Chiu *et al*, 2006). This process is currently being examined as a new commercial route for propylene glycol production.

b. Oxidation Processes

Catalytic oxidation converts glycerol into several structurally interesting materials, often in high yield (Figure 3) (Gallezot, 1997; Garcia, Besson, and Gallezot, 1995; Kimura *et al*, 1993; Kimura, 1993; Carrettin *et al*, 2002; Ketchie, Murayama, and Davis, 2007; and Ciriminna and Pagliaro, 2004). The product composition of these conversions is controlled through choice of catalyst, oxidant, and reaction pH. In contrast to glycerol reduction, the compounds most easily prepared by oxidation do not currently address large volume chemical markets. But as the cost of glycerol drops, products resulting from oxidation will experience a parallel drop in production cost, making the available structures of greater interest to industry. For example, Gallezot has described heterogeneously catalyzed aerobic processes that lead to glycerol derivatives of increasing oxidation state. More recent work has examined selective oxidation as a route to convert glycerol into acrylic acid, which would provide a link between a renewable starting material and another recognized high volume industrial chemical.⁵

⁵ J. Dubois, French Patent FR 2897059 to Arkema, 2007.

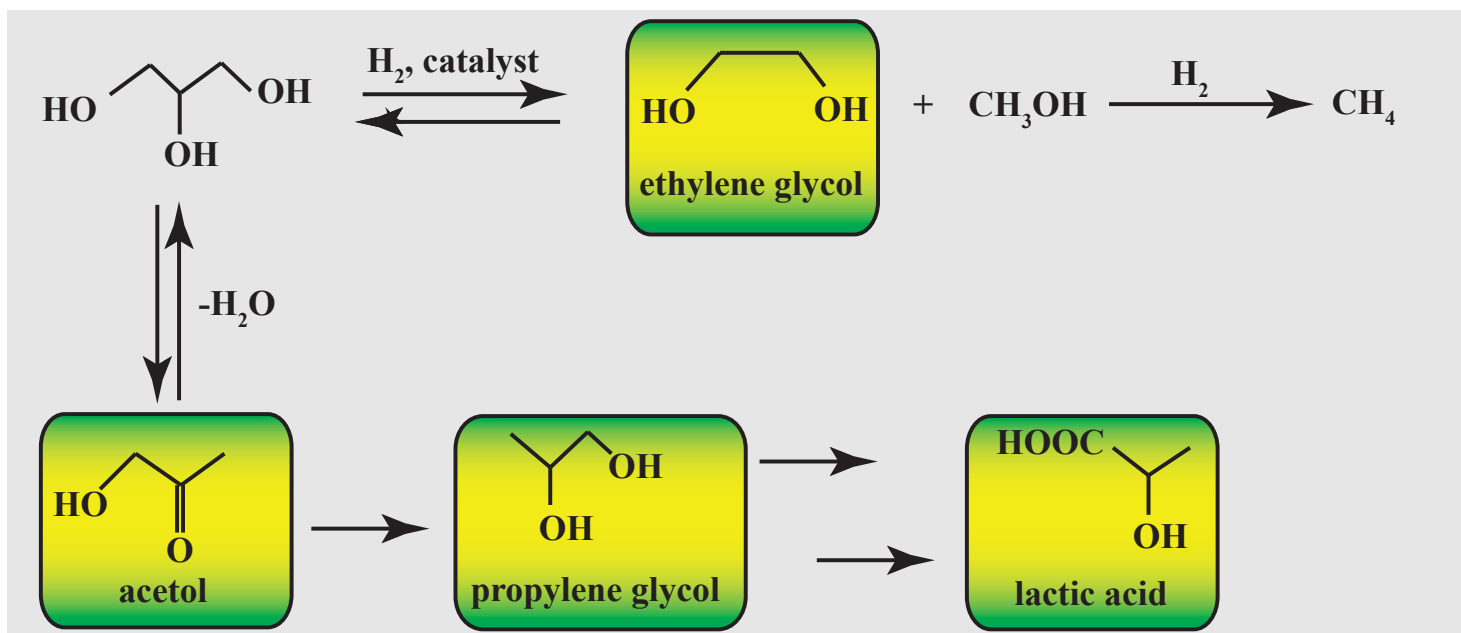


Figure 2. Glycerol Reduction Products

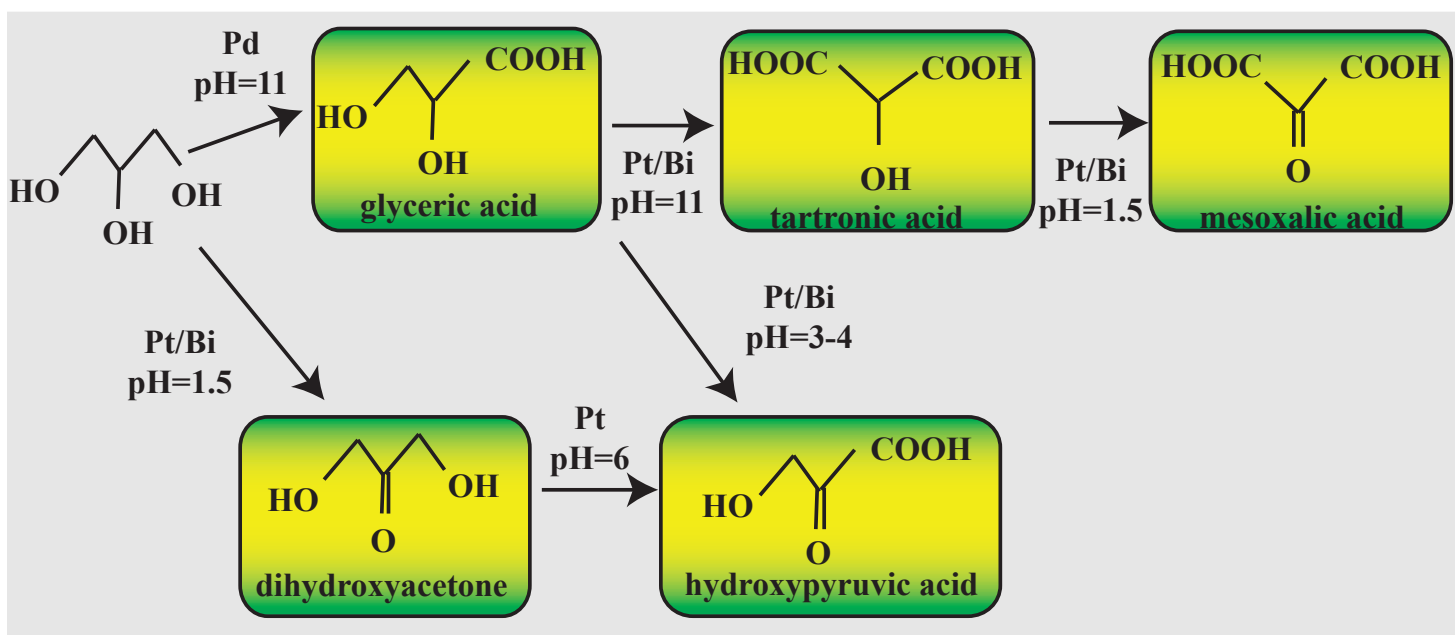


Figure 3. Glycerol Oxidation Processes

c. Dehydration Processes

Catalytic and thermal dehydration of glycerol is used to produce a third family of chemical derivatives (Figure 4), and links to several large volume products. Within this family of compounds, acrolein has received the most recent attention, primarily because of its possible use as a precursor to acrylic acid, a high volume chemical with an annual production of 2.6×10^9 lb. Several processes have been reported for this conversion (Watanabe *et al*, 2007; Ott, Bicker, and Vogel, 2006; Chai *et al*, 2007; and Tsukuda *et al*, 2007).

d. Polymerization Processes

Glycerol has traditionally played a role in the production of several types of commercial polymers. Selective etherification reactions convert glycerol into polyglycerol esters, which have been used as biodegradable surfactants and lubricants (Clacens, Pouilloux, and Barault, 2002; Kunieda *et al*, 2002)⁶ and as replacements for conventional poly (oxoethylene) nonionic surfactants. Polyglycerol and polyglycerol methacrylates are used as treatments for wood to improve its stability (Morlat *et al*, 2001).

⁶ A. Behler and B. Fabry, Eur Pat EP 1106675, 2001.

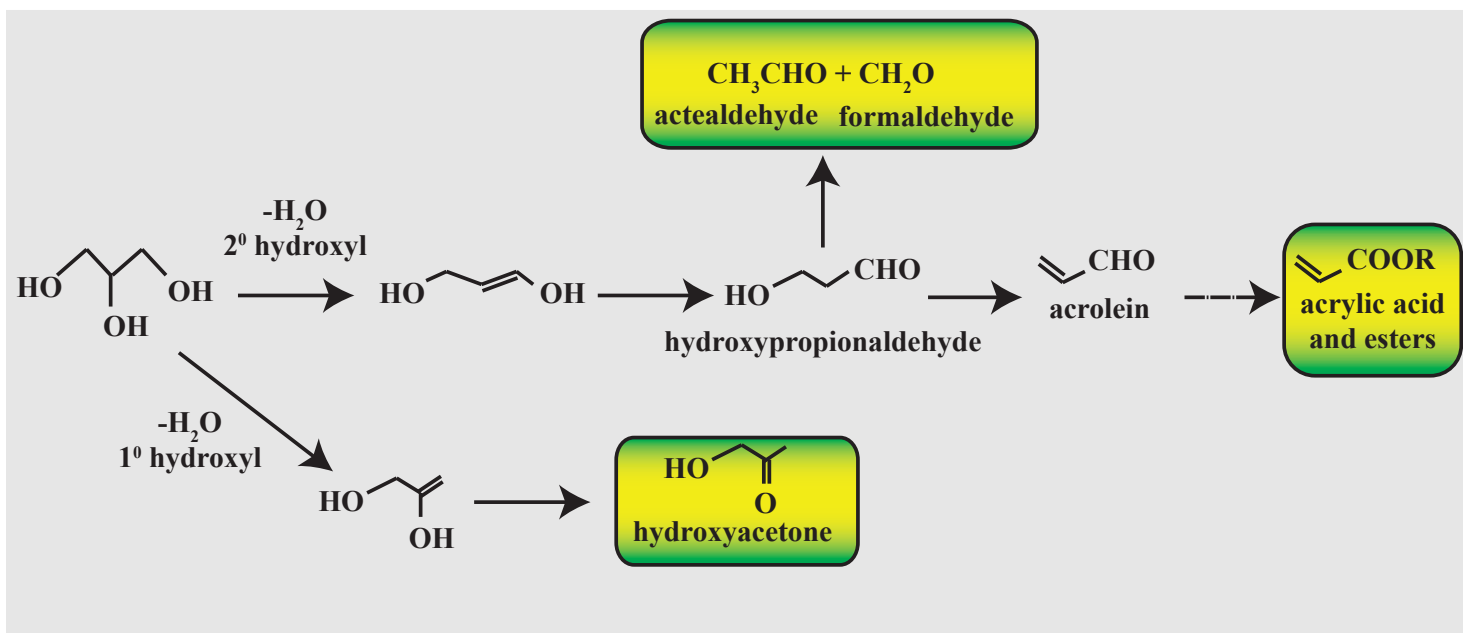


Figure 4. Dehydration Processes for Glycerol

More recently, glycerol's multifunctional structure has been used to prepare highly branched polymers (Arvanitoyannis *et al*, 1995). Branched polymers exhibit a wide range of new properties that could be exploited in useful marketplace products. Many of these could be high value applications, such as use in sensors, personal care products, or organic conductors. However, the volume of such materials will be fairly low, thus, while they might help the profitability of the oleochemical operating unit, they would not be able to offer a significant consumption of large amounts of glycerol. Other applications in large volume markets have been suggested, and branched polymers could find utility as polyester polyols, surfactants, coatings and alkyd resins, new solvents, and polyurethanes (Table 1).

Table 1. Size of Various Market Segments Related to the Use of Branched Polymers

Market Segment	Market Size (10 ⁶ lb)	Year
Polyether polyols	7600	2001
Polyester polyols	460	2001
Surfactants	1700 ^a	2000
Alkyd resins & coatings	1700	2000
Polyurethane foam	3400	2001
Polyurethane elastomers	430	1997

^adetergents only

e. Biochemical Processes

Glycerol is a feedstock in biochemical transformations, with the majority of current research focused on its conversion to 1,3-propanediol (1,3-PDO). 1,3-PDO is one of the components of DuPont's Sorona (1,3 PDO and terephthalic

acid), a polymer being investigated for use in textiles and carpeting, and the basis of a commercial production facility in Loudon, TN. The current biochemical production of 1,3-PDO, developed by Genencor and DuPont⁷, ferments corn-derived glucose using transgenic *E. coli*. However, glycerol can also be biochemically converted into 1,3-PDO (Cameron *et al*, 1998). Glucose-based processes give high 1,3-PDO concentrations (>125 g/L), but their yield (g 1,3-PDO/g glucose) is relatively low (30-40%). In contrast, the theoretical yield from glycerol is 67%. Fermentation of glycerol is being investigated with several organisms, including transgenic *Clostridium acetobutylicum* (Gonzalez-Pajuelo *et al*, 2006), *Klebsiella pneumoniae* (Mu *et al*, 2006)), and *Clostridium butyricum*. The latter is suggested to be an economical source of 1,3-PDO at a glycerol cost of \$0.14/lb (Gonzalez-Pajuelo, Andrade, and Vasconcelos, 2004). Cameron has described engineering *E. coli* for a biochemical production of the structurally similar propylene glycol (1,2-PDO) from glycerol (Altaras and Cameron, 1999). This process proceeds through dihydroxyacetone as a metabolic intermediate, implying that proper choice of organism could lead to either 1,2- or 1,3-PDO from glycerol, since one of the first intermediates in 1,3-PDO production is also dihydroxyacetone (Cameron *et al*, 1998).

Several organisms ferment glycerol to 3-hydroxypropionaldehyde (3-HPA) (Doleyres, *et al*, 2005). Although research on 3-HPA is still exploratory, it is an interesting chemical intermediate as the proposed central component of a network of several high volume biorefinery products, including 1,3-PDO (Figure 5). HPA exhibits considerable product inhibition because of its toxicity (Zheng *et al*, 2006).

⁷ L. Laffend, V. Nagarajan, and C. Nakamura, US Patent 5,686,276, 1997.

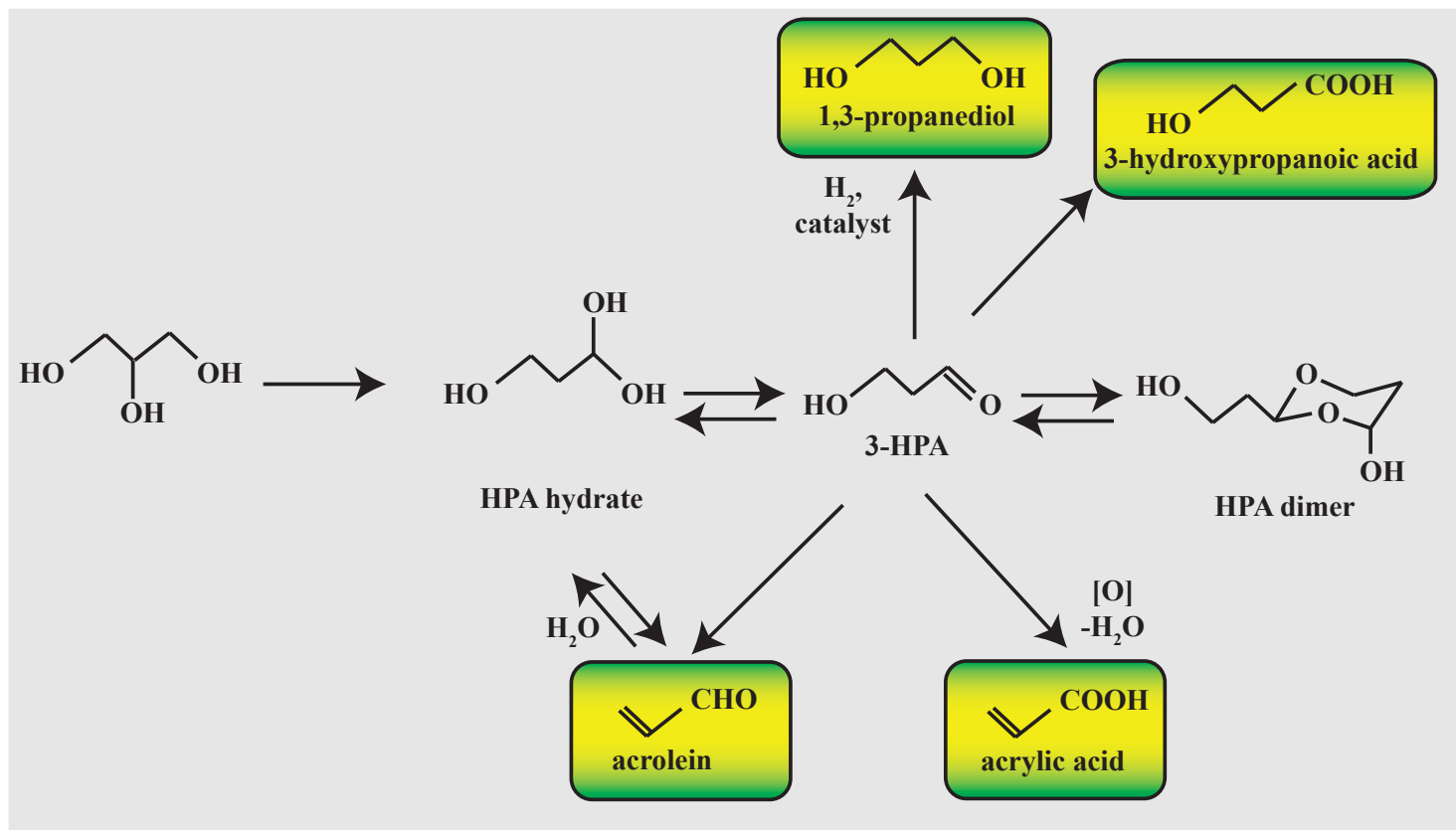


Figure 5. Conversion of Glycerol to 3-HPA and Related Derivatives

However, interest in 3-HPA as a chemical intermediate has led to processes that mediate its toxic effects, including product removal during fermentation (Rueti *et al*, 2007), or fermentation with different organisms (Vancauwenberge, Slininger, and Bothast, 1990). In aqueous solution, *Lactobacillus reuteri* exhibits significantly higher tolerance toward 3-HPA than other organisms and converts glycerol to reuterin, a natural antimicrobial that is an equilibrium mixture of 3-HPA, 3-HPA hydrate, and the 3-HPA dimer. The antimicrobial properties of reuterin have been extensively exploited in the food industry, for example, by inhibiting growth of *Listeria* or *E. coli* in meat and dairy products.

Inexpensive glycerol could allow 3-HPA to serve as a precursor to several important industrial chemicals. A potential large-scale use of 3-HPA is in the production of 1,3-PDO by combining the high yield of 3-HPA from *L. reuteri* or other processes with conventional catalytic hydrogenation (Besson *et al*, 2003).⁸ A direct, one-pot approach is possible, as 3-HPA hydrogenations in aqueous solution have been reported.⁹ The eventual choice between glycerol and glucose-based processes for PDO production will be made based on the relative economic performance.

Alternatively, 3-HPA is a precursor to acrolein and acrylic acid. Heating of aqueous 3-HPA solutions leads to the formation of acrolein, and conversely, acrolein hydration forms HPA hydrate. 3-HP is also a precursor to 3-hydroxypropanoic acid, which has been observed in low concentrations from a number of biosynthetic and enzymatic conversions of glycerol (van Maris *et al*, 2004).¹⁰ Catalytic dehydrations of 3-hydroxypropionic acid can be used to form acrylic acid and acrylate esters.¹¹ However, no commercial processes based on this technology have been developed (Vollenweider, 2004).

f. Other Glycerol Derivatives

Glycerol carbonate. Glycerol carbonate (Figure 6) is a relatively new material in the chemical industry, but one that could offer some interesting opportunities, as it can be prepared directly and in high yield from glycerol.

Glycerol carbonate has been investigated as a novel component of gas separation membranes, polyurethane foams¹²

⁸ G. Komplin and J. Smegal, PCT Patent WO 2007121219 to Shell International, 2007; N. Matsuoka and T. Kadota, Patent JP 2004182622 to Asahi, 2004.

⁹ G. Komplin, J. Powell, and P. Weider, US Patent Application 20050414, 2005.

¹⁰ M. Mukoyama and T. Toratani, Japan Patent JP 2007082476 to Nippon Shokubai Company, 2007; D. Cameron, World Patent WO 2000US23878 to Wisconsin Alumni Research Foundation, 2001.

¹¹ A. Zacher, J. Holladay, M. Lilga, J. White, D. Muzatko, R. Orth, P. Tsobanakis, X. Meng, and T. Abraham, PCT WO 2007106100 to Battelle Memorial Institute, 2007.

¹² D. Randall and R. De Vos, Eur Pat. EP 419114 to Imperial Chemical Industries PLC, UK 1991.

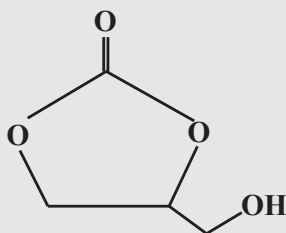


Figure 6. Structure of Glycerol Carbonate

as a surfactant component¹³ as a new solvent for several types of materials, as a component in coatings, as a potential component of the paint industry, acting as a nonvolatile reactive solvent, as a source of new hyperbranched polymers (Rokicki *et al*, 2005), and as a component of detergents. Dimethyl carbonate is being positioned as a green replacement for phosgene in the production of polycarbonates and polyurethanes. Inexpensive glycerol carbonate could serve as a source of new polymeric materials for this industry.

Glycerol carbonate can be prepared by simple processes, such as the direct reaction of glycerol with urea at 120° in diethylene glycol for 24h¹⁴ or the treatment of glycerol with ethylene or propylene carbonate.¹⁵ Direct production of glycerol carbonate from glycerol and carbon dioxide under supercritical conditions or in the presence of tin or cerium catalysts has also been reported (Vieville, *et al*, 1999; Aresta *et al*, 2006).¹⁶ Recently, glycerol carbonate has been synthesized

in very high yield by the reaction of glycerol and dimethyl carbonate in the presence of an immobilized lipase from *Candida antarctica* (Kim *et al*, 2007).

Epichlorohydrin. Recent work has examined the use of glycerol as a starting material for the production of epichlorohydrin, a high value chemical intermediate with production levels of nearly 1 billion lb/yr. Traditional routes to epichlorohydrin start by hydroxychlorination of propylene, and proceed through 1,3-dichloro-2-propanol as an intermediate (Figure 7) (Weissermel and Arpe, 2003). However, this process also forms the 1,2-dichloro isomer, which is considerably less reactive. Glycerol, in contrast, selectively forms the 1,3-isomer, and thus, low cost glycerol could be a viable alternative for the production of epichlorohydrin. Recent work has examined the kinetics and mechanism of this reaction (Tesser *et al*, 2007).

Conclusions

The growth of today's biodiesel industry has resulted in the development of a parallel glut of glycerol. While glycerol is potentially a structurally well-defined three carbon chemical intermediate, its traditional high cost has resulted in a lack of technology for conversion into other chemical compounds. As the cost of glycerol drops, new processes incorporating additional conversion steps will become economically viable, allowing glycerol to be used as a platform for a wide variety of new biobased industrial chemicals and fuels.

¹³ M. Weuthen and U. Hees, Ger. Patent DE 4335947 to Henkel K.-G.a.A., Germany 1995.

¹⁴ M. Okutsu and T. Kitsuki, World Patent WO 0050415 to Kao Corp, Japan 2000; M. Okutsu, Japan Patent JP 2007039347 to Kao Corp.

¹⁵ Z. Mouloungui, J. Yoo, C. Gachen, A. Gaset, and G. Vermeersch, European Patent EP 739888 to Organisation Nationale Interprofessionnelle Des Oleagineux-Onidol, Fr. 1996.

¹⁶ K. Tomishige, Japan Patent JP 2008001659 to Tsukuba University, 2008.

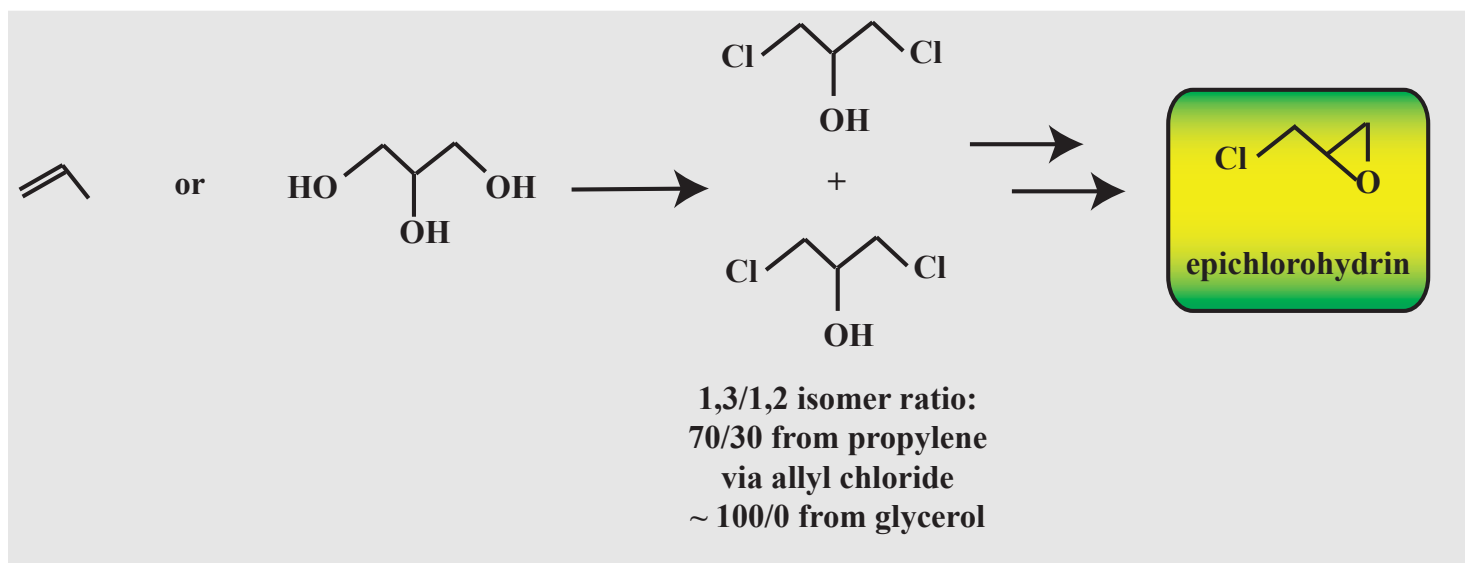


Figure 7. Conversion of 3-Carbon Building Blocks to Epichlorohydrin

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