BIOdiesel Tech NOTES

Issue TN #35 (July 2018)

Biodiesel Education Program, University of Idaho
Sponsored by USDA under the Farm Bill

POTENTIAL USES OF CRUDE GLYCEROL FROM BIODIESEL PRODUCTION

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Glycerol is the by-product of biodiesel production. By the rule of thumb, for each gallon of biodiesel produced, roughly 0.07 gal of crude glycerol accompanies. Based on the U.S. biodiesel production of 2.5 billion gal in 2017, about 160 million gal of crude glycerol were generated.

Historically, glycerol production from vegetable oils for traditional applications, such as food, pharmaceuticals, and human care products, was very much steady at an annual rate of 450 million lb (43 million gal) before 2007. This traditional glycerol-producing industry has now been heavily affected by the surplus crude glycerol from the biodiesel industry.

Glycerol is a sugar alcohol and soluble in water. It is colorless, odorless, hygroscopic, and sweet-tasting viscous liquid. High purity glycerol is a very important industrial feedstock. Traditionally, its applications are found in food, drugs, cosmetics and other personal care products, packing materials, and tobacco products.

Glycerol, when used in combination with other chemicals, yields many useful products. For example, glycerol and ethylene glycol together can be used as a solvent for alkaline treatment of polyester fabrics, as a dielectric medium for compact pulse power systems, and as a medium in electro-deposition of indium-antimony alloys from chloride tartrate solutions.

The crude glycerol from biodiesel production has low value due to the impurities that are carried over from the transesterification of various feedstock and/or the chemicals added during processing (see our **TechNote #06** for more details). Finding new applications of low-grade glycerol is a major topic of concern for the biodiesel industry. Finding a value-added use for glycerol can offset the production cost of biodiesel.

Refined to a High Purity

As mentioned above, high purity glycerol has many established markets for industrial applications. Once refined, glycerol is a valuable product to sell.

The refining of the crude glycerol to a high purity for industrial uses are generally through filtration, chemical treatment, and fractional vacuum distillation to yield various commercial grades. Vacuum fractionation is needed because of the high boiling temperature (>290°C or 554°F) and, especially, the tendency of glycerol decomposition around its boiling temperature. Further purifications, such as bleaching, de-odoring, and ion exchange, may be needed to remove trace impurities for special applications.

However, the economy of such refining will depend on the production scale and/or the availability of glycerol refining facilities and is typically beyond small- and even medium-sized producers' budgetary affordability. This is mainly because the process of fractional vacuum distillation requires a major capital investment upfront and a considerable operating cost, on top of the requirement of highly skillful operators.

Value-added Uses of Large Quantities

Once purified to the required purities, glycerol can be used for more value-added products. Examples include 1,3-propanediol (1,3-PD), succinic acid, dihydroxyacetones, polyglycerols, glyceric acids, and

Table 1. Basic properties of pure glycerol.

Chemical name	Propane-1,2,3-triol
Trivial names	Glycerol, glycerin, glycerine
Chemical structure	CH_2-CH-CH_2 | | | OH OH OH
Chemical formula	$C_3H_8O_3$
Molecular weight	92.09 g/mol
Density	1,261 kg/m³ (10.5 lb/gal)
Boiling point (decompose)	290–297°C (554-566°F)
Melting point	17.9°C (64.2°F)
Flash point	188-199°C (370-390°F)
Auto-ignition temperature	370°C (698°F)

others. All of these are raw materials for commodity products.

Propanediol is a valuable chemical raw material for producing composites, adhesives, laminates, powder and UV-cured coatings, moldings, novel aliphatic polyesters, co-polyesters, solvents, anti-freeze, and others. One of the most successful applications has been in the formulation of the polymer of Sorona (by Dupont) or Corterra (by Shell) (chemical name polytrimethylene terephthalate or PTT), which is the raw material for making carpets of domestic and industrial grades. Propanediol can be converted from glycerol via biological/fermentation processes and by chemical/catalytic processes.

Succinic acid is a very important industrial material and has enormous global demand. Succinic acid can be produced by biological/ fermentation processes from glycerol. It serves as the basic building block for some polyesters and resins that have industrial application. Succinic acid is also used to produce 1,4-butanediol (BDO). BDO is an important raw material for the industries of automotive and electronics to produce various functional parts, including connectors, insulators, gearshift knobs and reinforcing beams. Produced to the required purity grade, succinic acid is also used as a flavoring agent for food and beverage industries.

Dihydroxyacetone (DHA) is another example that can be obtained from glycerol. DHA a simple three-carbon sugar, non-toxic in nature. DHA can be produced by biological processes (either anaerobic or aerobic) from glycerol. It has been used in the cosmetic industry as a tanning agent. US FDA approved DHA as a cosmetic ingredient in 1970s. A small quantity of DHA is also used in wine during sugar fermentation, which has the anti-microbial activity in wine.

Glyceric acid (GA) is a natural three-carbon sugar acid obtained from the oxidation of glycerol. The esters of GA are known as glycerates, which are a family of chemicals for a wide spectrum of applications. GA has a great potential to be a building block for cosmetics and pharmaceuticals .

Other value-added applications of glycerol have also been explored. Examples include poly-glycerol esters, hyperbranched polyesters, and polyhydroxy-alkonates. **Poly-glycerol esters** find their utilization as antifogging and antistatic additives, lubricants, or plasticizers. **Hyperbranched polyesters** can be obtained by reacting glycerol and adipic acid in the presence of a tin catalyst, and have a wide range of industrial applications. **Polyhydroxyalkonates** (PHA) is another chemical that researchers have explored and synthesized by mixed culture fermentation of glycerol. PHA is used to produce polymers that have the characteristics of flexible and strong, perfect for making packaging material. Most importantly, PHA from glycerol is considered as a “green chemical”, i.e., it is biodegradable.

Other uses of crude glycerol without further processing include direct- and/or co-combustion in boilers for heat and power, co-gasification of glycerol with other biomass for syngas (a mixture of CO and H_2), steam reforming for hydrogen production, etc.

Other Applications of Small Quantities

Small and/or medium-sized biodiesel producers typically do not generate large enough quantities of crude glycerol to justify the cost of a refining facility and/or downstream processing facilities. Alternative ways have been explored as means for crude glycerol utilization and disposal.

Crude glycerol can be a substrate of carbon source in fermentations for alcohols (e.g., ethanol and butanol) and hydrogen, and for biogas if co-digested with other waste streams such as animal manure or sewage sludge.

Crude glycerol is also used as an effective substrate for boosting the microbial activities in wastewater treatment facilities in the case of spike increases of wastewater volumes in communities.

Another attempt of crude glycerol utilization is as a feed additive for livestock. It was claimed by many researchers that crude glycerol is a suitable energy source for pigs and laying hens. Adding crude glycerol to animal feed in a controlled quantity does not have negative effects on animals (Silva et al., 2014). Similar research has been conducted for ruminant animals. PURE glycerol is FDA approved for use in animal feed (FDA, 21 C.F.R. 582.1320). However, it is not the author’s knowledge that if the CRUDE glycerol from biodiesel production can be used directly as a livestock feed additive in the U.S. per FDA regulations.

Use of crude glycerol as a dust depressor for dust control is said effective. Pure glycerol is non-toxic and biodegradable. Once spread onto dirt roads, glycerol can be biologically degraded to an insignificant level within a few weeks. However, crude glycerol directly from biodiesel production contains impurities. There is a concern that, once crude glycerol is widely used as a dust depressor, the impurities in crude biodiesel may potentially cause issues to human health and/or the environment, which is unclear to the author.