PERP Program
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Chem Systems' Process Evaluation/Research Planning program has published a new report, ***Glycerin (00/01S4)***.

Glycerin is one of several common names for the polyhydric alcohol that forms the backbone of natural oils and fats. Other names, glycerine, glycerol, trihydroxy propane and propane-1,2,3-triol, are also often used interchangeably. Glycerol is reserved for the pure chemical compound, propane-1,2,3-triol, which is the simplest trihydric alcohol.

The term glycerin (also spelled glycerine) generally applies to the several grades of purified commercial products that usually contain a minimum of 95 percent glycerol.
Glycerine has a number of applications:

- Solvent or vehicle for pharmaceutical products
- Humectant in cosmetics and tobacco
- Plasticizer for polymers
- Anti-freeze and heat transfer fluid
- Hydraulic fluid
- Intermediate in the production of explosives (e.g., nitroglycerine)
- Intermediate in the production of lubricants, polyurethanes, mono- and di-glycerides

Glycerol is produced from natural triglycerides found in fats and oils using three processes: saponification, hydrolysis, and ester interchange (methanolysis). It has also been synthesized commercially by several routes, each starting ostensibly with propylene. Routes via allyl alcohol have fallen into disuse. Now, only a single synthetic route through epichlorohydrin is practiced in the United States, and Dow is the sole U.S. producer.

Glycerol is obtained commercially from natural triglycerides as a co-product in the process of forming the following products:

Product	**Process**
Soap	Saponification
Fatty acids	Hydrolysis or “splitting”
Fatty acid methyl esters	Methanolysis

Glycerol and soap (the alkaline salts of fatty acids) are produced in the saponification process, in which fats and oils are treated with a boiling solution of caustic soda. In the hydrolysis process, fatty acids and glycerol are formed continuously in a countercurrent reactor where water and fats or oils meet at an elevated temperature and pressure. Natural glycerol is also produced by methanolysis of fats and oils, giving fatty acid methyl esters as the co-products. Sodium methoxide or other strongly alkaline substances catalyze the reaction.

Theoretical yields of glycerol from common fats and oils are in the range of 9 to 13 percent by weight of the starting material. However, practical plant yields, corrected for free fatty acids and upgrading yield losses, are typically about 0.5 percentage point lower. Certain fish oils and jojoba oil by comparison have only 2 to 5 percent available glycerol, because they are rich in waxy esters of fatty acids and fatty alcohols, both having chain lengths in the C_{14} to C_{18} range.

Synthetic glycerine can be produced from propylene via allyl chloride. Allyl chloride is manufactured by the non-catalytic chlorination of propylene in the vapor phase at high temperature. Allyl chloride is recovered and treated with hypochlorous acid to form the 1,2- and 1,3-dichlorohydrin. The latter are dehydrochlorinated to epichlorohydrin by reaction with calcium hydroxide or caustic soda, and epichlorohydrin is then hydrolyzed using a ten percent solution of sodium hydroxide to give glycerine.