

Biodiesel One-Day Course

From Field to Fuel

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Coeur d' Alene, Idaho

Glycerin Production and Utilization

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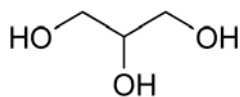
Liberty Process
Technologies

Glycerin General Information

What is Glycerin?

- A colorless, odorless, hygroscopic and sweet tasting viscous liquid¹
- A three carbon alcohol
- The backbone of the triglyceride molecule

1. Definition from Wikipedia



Names for Glycerin

- Glycerol
- Glycerine
- 1,2,3 –propanetriol
- propane-1,2,3-triol
- trihydroxy propane
- glyceryl alcohol

Glycerin Properties

- | | |
|-------------------------|-----------------|
| – Melting point | -17.8 °C |
| – Boiling point (1 atm) | 290 °C |
| – Density (25 °C) | 1.262 g/ml |
| – Flashpoint (open cup) | 176 °C |
| – Solubility | water, ethanol |
| – Toxicity | 20 mL/kg (oral) |

Sources of Glycerin

- Natural
 - Soap production (soap lye)
 - Fat splitting (sweet water)
 - Methyl ester production
- Synthetic

History

- Discovered in 1779 by Scheele
- First major source – spent lye from soap making process
- Primary source for last 20 years – sweet water from fat splitting (fatty acid production)

Highly Functional

- Glycerol contains one secondary and two primary alcohol groups per molecule
- Reacts with organic and inorganic acids to form aldehydes, esters, ethers and many derivatives
- The presence of multiple alcohol groups facilitates the formation of polymers and coatings
 - Polyesters, polyethers
 - Alkyd resins

Important Characteristics

- Non-toxic
- Water soluble
- Viscous
- Hygroscopic
- Acts as both a solvent and reactant
- Useful in the development of green products and processing technologies

Non-toxic

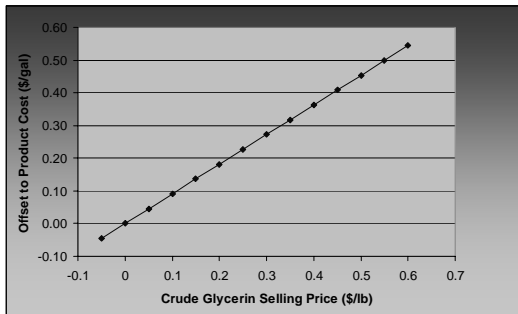
- Biocompatible
 - Synthesized by plants and animals
 - Glycerol is metabolized to pyruvate
- Safe in topical formulations
 - Ingredient in personal care products
- Approved for food and pharmaceutical applications (GRAS)

Glycerin in "Green" Products

- Biodegradable co-polymers of glycerol and lactic acid
 - Polyesters, polycarbonates
- Development of glycerol ethers as oxygenated fuel additives to improve combustion

Glycerin Production

Impact of Crude Glycerin Price on Biodiesel Cost



Glycerin Production

- Sourced from fats and oils processing
 - Saponification (soap making)
 - Hydrolysis (fat splitting)
 - Transesterification (biodiesel)
- Product categories
 - Crude: 75 – 90% glycerol
 - Refined
 - Kosher

Types of Refined Glycerin

- 99.5% Technical Grade
- 96% USP (Vegetable-based)
- 99.5% USP (Tallow-based)
- 99.5% USP (Vegetable-based)
- 99.5% USP/FCC - Kosher
- 99.7% USP/FCC - Kosher

Glycerin - U.S. Production

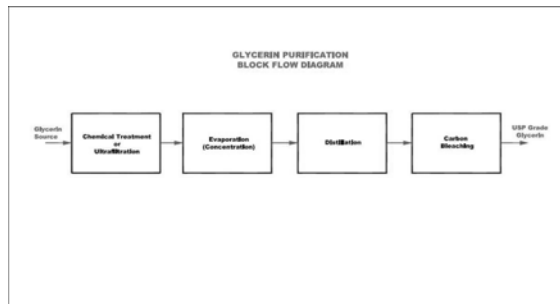
PRODUCER	CAPACITY*
Cognis, Cincinnati, Ohio	65
Colgate-Palmolive, Jeffersonville, Ind.	20
Crompton, Mapleton, Ill.	20
Crompton, Memphis, Tenn.	30
Dial, Montgomery, Ill.	30
Dow, Freeport, Tex.	140
Lever, Hammond, Ind.	25
Lonza, Painesville, Ohio	20
Marietta American, Olive Branch, Miss.	2
Procter & Gamble, Ivorydale, Ohio	150
Starchem, Fostoria, Tex.	20
Uniqema, Chicago, Ill.	35
Total	557

*Millions of pounds per year of refined glycerine.

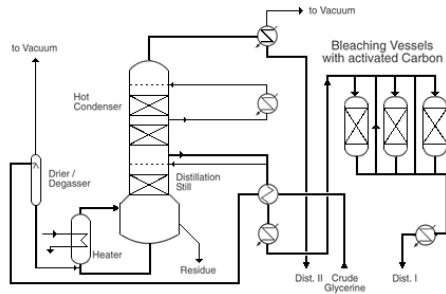
Crude Glycerin from Biodiesel Processing

- Glycerol content – 40 to 90%
- Water content – 8 to >50%
- Methanol content – should be less than 0.5%
- Salt content – 0 to 10%

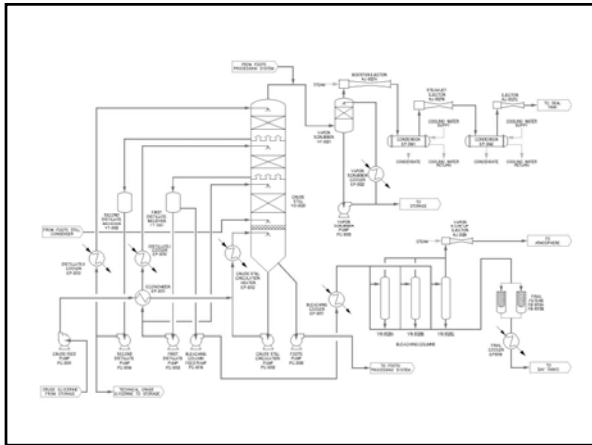
Glycerin Purification

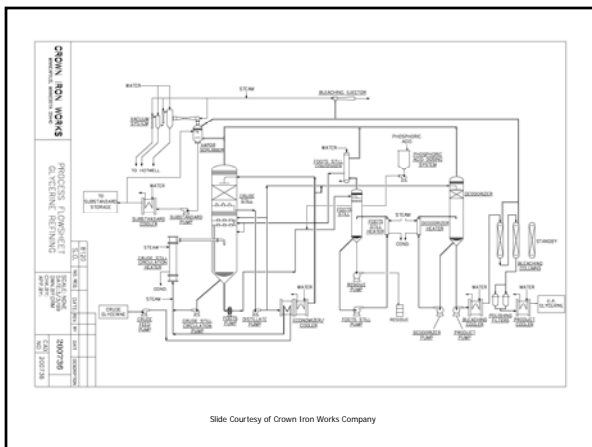


Glycerine Distillation Process



Slide Courtesy of Lurgi





Slide Courtesy of Crown Iron Works Company

Refined Glycerin – Important Quality Parameters

- Purity
- Color
- Odor
- Fatty Acids and Esters
- Chlorides

Chemical Derivatives from Glycerin

Specialty Chemicals

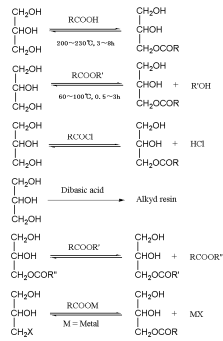
- Glycerol provides a C3 building block for complex structures
- Glycerol is easily modified by reacting -OH functional groups
- Can produce water soluble, nontoxic, nonflammable products

Pathways for Glycerol Modification

- Esterification
- Etherification
- Oxidation
- Reduction
- Amination
- Halogenation
- Phosphorylation
- Nitration
- Sulfaction

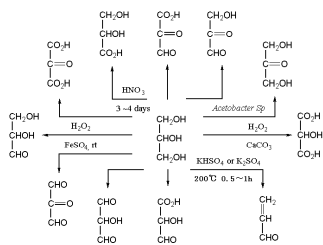
Glycerol Derivatives

- Esterification



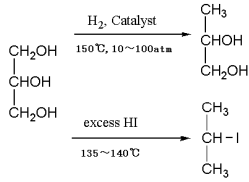
Glycerol Derivatives

- Oxidation



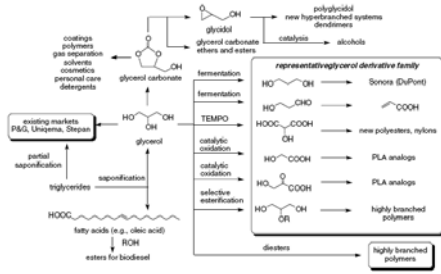
Glycerol Derivatives

- Reduction



Glycerol Derivatives

Families of Possible Glycerol Reactions (source: Biomass oil analysis: research needs and recommendations)



Glycerin Utilization

Glycerin Applications

- Adhesives
- Cements
- Ceramics
- Cleansers
- Hydraulic fluids
- Lubricants
- Polishes

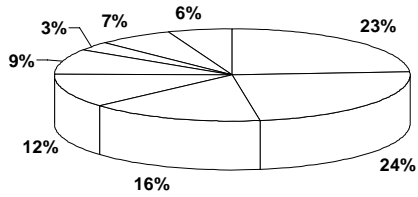
Glycerin Applications (cont'd)

- Solvent
- Fermentation substrate
- Sweetener
- Plasticizer
- Antifreeze
- Wood preservative

Glycerin Utilization by Industry

- Cosmetics
- Explosives
- Food
- Pharmaceutical
- Polymer
- Printing

Glycerin Utilization by Industry



- Food products
- Personal care
- Oral care
- Tobacco
- Polyether polyols
- Alkyd Resins
- Drugs
- Misc.

Glycerin Applications (cont'd)

- **Drugs;**
- Used in medical and pharmaceutical preparations, mainly as a means of improving smoothness, providing lubrication and as a humectant. Also may be used to lower intracranial and intraocular pressures.
- Laxative suppositories, and cough syrups

Glycerin Applications (cont'd)

- **Personal care;**
- Used in toothpaste, mouthwashes, skin care products, hair care products and soaps
- Serves as an emollient, humectant, solvent and lubricant in personal care products
- Competes with sorbitol although glycerin has better taste and higher solubility.
- A component of glycerin soap

Glycerin Applications (cont'd)

• **Foods and beverages;**

- Serves as humectant, solvent and sweetener, may help preserve foods.
- Solvent for flavors (such as vanilla) and food coloring.
- Humectant and softening agent in candy, cakes and casings for meats and cheeses.
- Manufacture of mono- and di-glycerides for use as emulsifiers
- Used in manufacture of polyglycerol esters going into shortenings and margarine.
- Used as filler in low-fat food products (i.e., cookies).
- Glycerin has approximately 27 food calories per teaspoon and is 60% as sweet as table sugar.

Glycerin Applications (cont'd)

• **Polyether polyols;**

- One of the major raw materials for the manufacture of polyols for flexible foams, and to a lesser extent rigid polyurethane foams
- Glycerin is the initiator to which propylene oxide/ethylene oxide is added

Glycerin Applications (cont'd)

• **Alkyd resins (plastics) and cellophane;**

- Used in surface coatings and paints
- Used as a softener and plasticizer to impart flexibility, pliability and toughness
- Uses include meat casings, collagen casings (medical applications) and nonmeat packaging
- Plasticizer in cellophane.

Glycerin Applications (cont'd)

• **Other applications;**

- Manufacture of paper as a plasticizer, Nitroglycerin, humectant and lubricant
- Humectant for pet foods to retain moisture and enhance palatability
- Used in lubricating, sizing and softening of yarn and fabric
- Used in de-/anti-icing fluids, as in vitrification of blood cells for storage in liquid nitrogen
- Patent applications have been filed for detergent softeners and surfactants based on glycerin (i.e., alkyl glyceryl ethers) instead of quaternary ammonium compounds.

Glycerin Applications (cont'd)

• **Other applications**

- Can be added to solutions of water and soap to increase that solution's ability to generate soap bubbles that will last a long time
- Use as antifreeze in cryogenic processes
- Used in fog machine fluids
- Used in hookah tobacco mixtures (called "ma'assel" or "shisha" tobacco), often along with molasses and/or honey

Strategies to Increase Glycerin Utilization

- Expand existing markets

- Develop new markets
 - Identify new applications
 - Develop new products

Glycerin Consumption

U.S. DEMAND

1999: 427 million pounds;
2000: 453 million pounds;
2004: 494 million pounds,

GROWTH

Historical (1995 - 2004): 1.9 percent per year;
Future: ?????

PRICE

Historical (1995 - 2000): High, \$1.08 per pound, list, refd.,
USP, CP, non-kosher, 99.7 percent, tanks, dlvd.;

Low, \$0.60, same basis. Current: \$0.60, same basis.

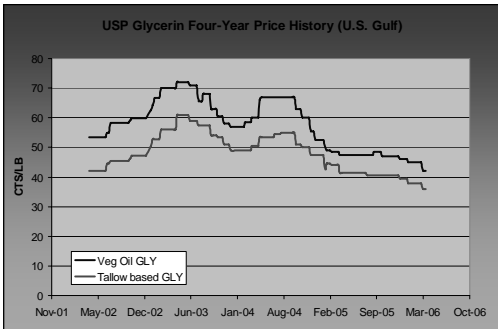
Glycerin Market - Strengths

- Market growth is 3.5 percent annually (aging "baby boom" generation consumes more skin care cream).
- Strong growth in sun screen lotions.
- Good solubility and taste give glycerin an edge on sorbitol in toothpastes and mouthwash
- The best performing sector, is food (continuing trend towards lower fat content in foods). 4 percent annual growth

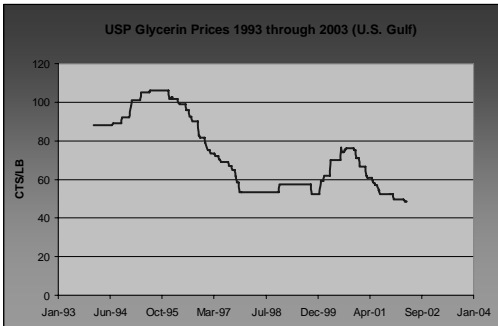
Glycerin Market - Weakness

- There is a significant increase of crude glycerin from biodiesel production
- Glycerin use in polyether polyols and alkyd resins is shrinking at 1 percent and 1.5 percent annually.

Glycerin Prices



Glycerin Prices



Glycerin: Replacement for Petrochemical Feedstocks

- Renewable
- Domestically produced
- Easily derivatized
- Nontoxic
- Nonflammable
- Available in high purity

Areas for Product Development

- Biomedical applications
- Coatings and polymers
- Specialty and fine chemicals

Summary

- Glycerin is an important byproduct of biodiesel production that impacts plant profitability
- Glycerin is nontoxic, biodegradable, and biocompatible
- Glycerin is a versatile substrate that may be converted into numerous biobased products
- New uses for glycerin are needed to help stabilize product pricing
