

MANUFACTURING PROCESSES

Glycerol is obtained as a by-product in the conversion of fats and oils to fatty acids or fatty acid methyl esters. This type of glycerol is known as native or natural glycerol, in contrast to synthetic glycerol from propene. Other methods of production, eg. Fermentation of sugar or hydrogenation of carbohydrates is not industrially important.

1) GLYCEROL FROM FATS AND OILS:

Although a component of all plants and animal fats and oils, glycerol does not exist in the free form but as fatty acids esters; all three hydroxyl groups are usually esterified. Such esters are called triglyceride. The glycerol content of fats and oils varies between 8 and 14%, depending on the proportion of free acid and the chain length distribution of the fatty acids esters. To obtain glycerol, fats and oils must be split.

a) FATS SPLITTING:

From fat splitting or hydrolysis without added alkali, of fats and oils. This is a method for preparing fatty acids, which are then in some cases reduced to the corresponding fatty alcohols. The glycerin is then obtained in the sweet water. Crude glycerin recovered from this is termed as saponification crude. The main sources of natural glycerol are now high pressure splitting and transesterification. Glycerol from the neutral saponification of oils is encountered only in small quantities.

b) HIGH PRESSURE SPLITTING:

Splitting under pressure has been known since 1845. Continuous process reactors are now used. water and fat are fed into a splitting column in countercurrent fashion at 5-6 Mpa and 250°C 260°C, leading to a 15% solution of glycerol in water known as sweetwater. This glycerol is marketed as 88% saponification Crude or hydrolysis glycerol.

c) TRANSESTERIFICATION:

Natural crude glycerol of same quality can be obtained from the continuous transesterification of oils and fats to their methyl esters.

d) SAPONIFICATION:

The splitting of fats by saponification of neutral oil is a traditional method: caustic alkali or alkali carbonates are used, as in the production of soap. The use of calcium hydroxide in the form of milk of lime is also possible.

GLYCEROL SYNTHESIS:

Until 1949 all glycerin was obtained from the glycerides in the form of fats and oils, but from that time on production of synthetic glycerin increased until, in 1965 it accounted for about 60% of the market. The first glycerol process put on stream in 1948, followed the discovery that propylene could be converted to glycerol by several routes, the synthesis of glycerol from propylene became possible.

Three processes are known for the production of glycerol from propene, involving the following intermediate stages:

- 1) Ally chloride-epichlorohydrin
- 2) Acrolein-allyl alcohol-glycidol
- 3) Propene oxide-allyl alcohol-glycidol

2) PRODUCTION FROM ALLYL CHLORIDE:

The first synthetic glycerol was produced in 1943 by I.G.Farben in Oppau and Hydebreck and in 1948 by Shell in Houston, Texas. The allyl chloride produced is oxidized with hypochlorite to dichlorohydrin, which is then converted without isolation to epichlorohydrin by ring closure with calcium or sodium hydroxide. Hydrolysis to glycerol is carried out with sodium hydroxide or sodium carbonate. Epichlorohydrin is hydrolyzed at 80-200°C with a 10-15% aqueous solution of sodium hydroxide or sodium carbonate at atmospheric or overpressure. The yield of dilute (10-25%) glycerol solution is >98%. The solution contains 5-10% sodium chloride and less than 2% of other impurities. Glycerol is finally treated further to remove colored impurities and odorous material, this can be performed for example with activated carbon.

3) PRODUCTION FROM PROPENE OXIDE:

Preparation from propene oxide does not use chlorine. Propene is epoxidized to propene oxide, which is then isomerized to allyl alcohol by the propyl process. A second epoxidization is carried out with peracetic acid, and the resulting glycidol is hydrolyzed to glycerol.

4) FERMENTATION FROM SUGAR

The formation of glycerol by fermentation of alcohol was discovered in 1858 by Pasteur. Industrial use became possible once the mechanism was understood; the fermentation could be interrupted at the glyceraldehyde 3-phosphate stage with sodium carbonate or with alkali or alkaline earth sulfites. After reduction to glycerol phosphate, glycerol is obtained in yield up to 25% by hydrolysis. The process is economically unimportant.

5) HYDROGENATION OF CARBOHYDRATES

Hydrogenation of natural polyalcohols such as cellulose, starch, or sugar leads to mixture of glycols, which can be separated by distillation. Catalyst used in high temperature includes nickel, cobalt, copper, chromium and tungsten as well as oxides of some of the lanthanides. The crude glycerin produced is poor in quality and requires drastic, expensive refining methods.

6) OTHER NON-COMMERCIAL PROCESS

- a) Photo production of glycerol along with other biomass is possible by means of solar energy and algae.
- b) Another synthetic process involves the catalytic hydrogenation of carbon monoxide.
- c) A process based on the manufacture of synthetic glycerol from invert molasses via sorbitol has been suspended since 1969.

PROCESS DESCRIPTION:

It has been shown that when fats and fatty oils are hydrolyzed with water or saponified with alkalis in the presence of water to form fatty acids in one case and soap in the other, glycerin is always formed. In the making of soap and glycerin by alkaline saponification of fats, the glycerin is commonly recovered in solution in the soap lyes. Many of these lyes when removed from the soap pan contain excess alkali which must be removed before the glycerin can be properly recovered. Neutralization with acid would be extremely wasteful. The lye is therefore boiled with fatty matter, usually in separate kettles, until substantially all the excess alkali reacts to make more soap, after which it is sent to the glycerin department for treatment and recovery of glycerin. The spent lye removed directly from the different changes may average around 4 to 7% of glycerin.

Purifying the solution:

Soap lyes are given chemical and physical treatments that are calculated to remove as much of the objectionable impurities as possible while clarifying them at the same time. Most or all of the caustic alkali should have been removed in the soap-boiling department, but the solution will contain a small fraction of a percent of sodium carbonate and a small amount of soluble soap. The lye may be advantageously brought almost to neutrality with a small quantity of mineral acids such as sulfuric or hydrochloric acid. It can then be stirred and heated or boiled with some dissolved metallic salt, which makes insoluble precipitates with soap, and with carbonated alkalis. The addition of these reagents is performed under chemical control so that sufficient is employed to remove the last alkalinity and to precipitate any soap present as insoluble soaps, but there will be none of the unused precipitate left. These materials form gelatinous precipitates either with alkali or with soluble soaps, so that after the precipitate has been removed by filtration in the filter press, the lye is clarified as well as nearly neutral.

Evaporation of the solution:

The lye is now evaporated preferably in vacuum evaporators. With the removal of water, the glycerin and salt concentration gradually increases until the salt saturation point is reached, after which salt begins to separate. Further evaporation should be performed in apparatus provided for salt removal. This can be done continuously by the continuous removal of a portion of the settlings from the conical bottom of the evaporator or intermittently by providing the evaporator with a salt drum beneath with a valve between the evaporator and drum so the salt contents may be removed at intervals.

Treatment of soap lyes with sulfuric acid and ferric or aluminum sulfate results in the formation of sodium sulfate which finds its way into the recovered salt and back to the soap pans. Sodium sulfate is not so good for graining soap and lye washes as sodium chloride. Although the employment of hydrochloric acid and ferric chloride for soap lyes for glycerin recovery is somewhat more expensive than sulfuric acid and sulfates, the advantages obtained may outweigh the difference in the cost.

In evaporating glycerin lyes there is very little actual volatilization of glycerin in the early stages. In the final stages, in bringing the concentrate upto crude glycerin, there is an amount of volatilization of glycerin which though appreciable need not be large. In spite of the fact that very little glycerin need be lost by volatilization in concentrating glycerin lyes to soap lye crude, there may be considerable losses in this operation due to excessive entrainment and poor separation of entrained material from the vapors.

Glycerin evaporators:

Glycerin evaporators are commonly heated by steam in tube calandrias within the lower portion of the evaporators. Diminished pressure is maintained by condensing the vapors with cold water in a barometric column. Non-condensable gases are removed from the top of the barometric head either with a wet vacuum pump or an auxiliary steam exhauster. Many different types of evaporators may be used but whatever the type, it should be such that the heating surfaces will not become coated with salt. It is highly important that means shall be provided to reduce entrainment. For this reason it is customary to introduce one or another of various types of "catch-alls" between the evaporator and condenser.

The various types of crude glycerin, whether from aqueous hydrolysis with or without catalyzers, or from soap lyes, are not pure enough for most uses. In order to obtain good grades of refined glycerin's the crude glycerin must be distilled.

Refining of glycerin:

Glycerin boils at 290°C at atmospheric pressure. It is generally stated that glycerin boiling at this temperature is accompanied by decomposition. This is probably not correct or at any rate the decomposition is inappreciable if air is effectively excluded and if local overheating is avoided and if a good excess of steam is present at all times.

There is such a wide difference in the boiling points of water and glycerin difference of about 190°C at atmospheric pressure, that separation of water vapor from glycerin has long been practiced by fractional condensation.

Glycerin distillation with open steam at atmospheric pressure is at high temperature and if a concentrated condensate is collected, any vapor not condensed necessarily contains a large percentage of glycerin so that only a poor separation is made, and any attempt to recover all the glycerin necessitates the condensation of all the direct steam employed along with at least a substantial portion of the glycerin.

It is probable that the greatest improvement in glycerin refinement came from the joint use of direct jet steam and diminished pressure in conjunction with indirect steam heating of all the still contents. Distillation with direct steam at diminished pressure gave greatly improved results both in the quality of distillation and in the ease and thoroughness of separation.