GLYCEROL (CONTINUED)

MANUFACTURE

3. From Propylene via Acrolein

Raw material

<table>
<thead>
<tr>
<th>Basis</th>
<th>1000 kg glycerine (99%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene</td>
<td>832 kg</td>
</tr>
<tr>
<td>Oxygen</td>
<td>207 kg</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>90 kg</td>
</tr>
<tr>
<td>Hydrogen peroxide (100%)</td>
<td>440 kg</td>
</tr>
</tbody>
</table>

Reaction

\[
\begin{align*}
\text{H}_2\text{C}═\text{C}−\text{CH}_3 + \text{O}_2 &\rightarrow \text{H}_2\text{C}═\text{CH}−\text{CHO} + \text{H}_2\text{O} \\
\text{H}_2\text{C}═\text{CH}−\text{CHO} + \text{H}_3\text{C}−\text{C}−\text{CH}_3 &\rightarrow \text{H}_2\text{C}═\text{C}−\text{C}−\text{OH} + \text{H}_3\text{C}−\text{C}−\text{CH}_3 \\
\text{H}_2\text{C}═\text{CH}−\text{OH} + \text{H}_2\text{O}_2 &\rightarrow \text{CH}_2\text{OH} + \text{HOH} + \text{CH}_2\text{OH} \\
&\text{Glycerine}
\end{align*}
\]

Manufacture process

The vapour phase catalytic oxidation of propylene yields acrolein, which was further reacted with isopropanol to produce allyl alcohol and acetone. The allyl alcohol was then oxidized to glycerine with hydrogen peroxide.

Propylene and steam in about equal amounts (slight excess of steam) were mixed with oxygen (25% based on weight of propylene) and sent to a reactor. In the presence of a supported copper oxide catalyst, 20% of the
Propylene was oxidized to acrolein.

The reaction conditions are 350°C, 2 atm and 0.8 sec residence time. The acrolein was separated from unreacted propylene and tarry by-products by distillation. Acrolein yield is 85%.

The purified acrolein was reacted with isopropanol in the presence of a catalyst containing uncalcined magnesia and zinc oxide. The reaction was taken place at 400°C yielding a mixture of allyl alcohol and acetone. Yield of allyl alcohol is 77% based on acrolein charged. The allyl alcohol and acetone were separated by distillation.

Purified allyl alcohol was reacted with 2 molar solution of hydrogen...
peroxide which contains 0.3% of tungstic oxide. The reaction was carried out at 60 – 70°C for 2hrs, the resulting glycerine-water solution is sent to a still where high-purity glycerine was produced. The catalyst was recovered and recycled. Yield of glycerine based on allyl alcohol is 80 – 90%. The overall yield of glycerine based on propylene charged to the oxidation unit is about 50%.

4. From Sweet water

Raw material

Sweet water contains 12% glycerol. It is obtained as a by-product from soap and detergent manufacturing industries.

Manufacture process

Figure: Manufacture of glycerol from sweet water

Block diagram of manufacturing process

Diagram with process equipment

Animation
The sweet water containing about 12% glycerol was passed from flash chamber to decrease the temperature of the flow. The glycerine contains practically no salt was readily concentrated. To increase the concentration from 12% to 75% to 80% glycerol, the sweet water was charged to a triple effect evaporator. During evaporation no additional heat was required other than that present in the sweet water effluent from the hydrolyzer.

After concentration of the sweet water, the crude was settled for 48hr at elevated temperatures to reduce fatty impurities that could interfere with subsequent processing. Approximately 78% glycerol, 0.2% total fatty acids and 22% water were present in settled crude. Caustic was added to the still feed to saponify fatty impurities and reduce the possibility of co-distillation with the glycerol. After that, stream from still was heated in heat exchanger than entered into column where distillation of the settled crude was carried out at 200°C temperature and 8kPa pressure. The distilled glycerine was condensed in three stages at decreasing temperatures. The first stage yields the purest glycerine, usually 99% glycerol, which meets with CP specifications while lower grades of glycerine are collected in the second and third condensers. For final purification, glycerinewas treated with activated charcoal. Then charcoal can be removed by filtration or ion exchange method.

Engineering aspects

- **Synthetic versus natural product glycerol**

  Natural glycerol is currently being produced in India as soap plants having small capacity. Fat splitting plant only suggested where glycerol can be recovered in a large amount.

  Synthetic glycerol promotes the petrochemical industry and substitution of soap by detergent further leads to curtail natural glycerol supply. So ultimately it will stabilize the glycerol supply from both sources which creates attractive raw material for plastics.

- **Purification method for glycerol from soap manufacturing**

  The spent lyes from soap production often contain 8 – 15% glycerol. The grade of fats is responsible for the treatment required for the production of commercial quality glycerol. Caustic soda and hydrochloric acid was used to
remove the impurities from spent lye. The mineral or fatty acids were added into the spent lye, to reduce the pH as well free content of caustic. Soap was skimmed then an acid and coagulants were added. Filtration was carried out to recover the glycerol.

- **Purification method for glycerol from sweet water**

  Sweet water contains little mineral acids and salts and there so it required simple purification method compare to spent lye. To avoid the degradation of product, the sweet water has to be treated after splitting. The small amount of alkali was added to neutralize the liquor. This alkaline liquor was passed from the filter and evaporates it to 88% crude glycerol.

- **Qualities of glycerol**

  Generally glycerol is produced to satisfy the strict requirements, given by the United States Pharmacopeia (USP) and the soap and detergent association.

  Depend on their purity, the three main qualities of glycerol commercially available are as follows

  - Raw glycerol
  - Technical glycerol
  - Refined glycerol

  Raw glycerol containing 40 – 88 %wt of glycerol and rest is soaps and salts other impurities.

  Technical glycerol contains 97.0 %wt of glycerol. It is a high purity product, which is a free of soaps, salts and other impurities.

  Refined glycerol contains 99.7 wt% of glycerol. It is a pharmaceutical quality product which can be used in pharmaceuticals, foods, cosmetics.

**PROPERTIES**

- Molecular formula : \( \text{C}_3\text{H}_8\text{O}_3 \)
- Molecular weight : 92.09gm/mole
- Appearance : Colourless or pale yellow liquid
Odour: Odourless
Boiling point: 290°C
Melting point: 17°C, solidifies at much lower temperature
Vapour pressure: 0.0025mm at 50°C
Autoignition temperature: 370°C
Flash point: 160°C
Density: 1.261gm/cm³ at 20°C
Solubility: Miscible with water, alcohol and Immiscible with carbon tetrachloride, Carbondisulfide and oils

USES
- As a chemical in the manufacture of alkyd resins, cellophane
- As a solvent in drug and cosmetics
- As solvent, plasticizer, emollient, humectant, sweetener
- Used in manufacturing of nitroglycerol, liquid soaps, printing inks and copying inks
- As a lubricants, to preserve printing on cotton, for printing rollers
- As antifreeze in automobiles, gas meters, hydraulic jacks and in shock absorber fluids
- Also used in fermentation nutrients in the production of antibiotics