

Organic Chemical Technology
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Lecture - 07
Soaps and Glycerin Manufacture

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is soaps and glycerin manufacture. In this lecture and coming couple of lecture we are going to discuss about soaps and detergent industries. Soaps are natural product industry outputs whereas the detergents are the synthetic products.

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Soaps and Detergents

- Soap was never actually discovered but instead gradually evolved from crude mixtures of alkaline and fatty materials
- Soaps were believed to be physical mixtures of alkaline and fatty materials until 18th century, but subsequently realized soaps were formed actually by chemical reactions
- Soaps and detergents are used for self cleanliness of human beings and their surroundings
- They are also used for industrial surface active applications
- Their principle action is based on colloidal chemistry
- Dirty/stain is pulled away from the surface to be cleaned by the surface chemistry || *
- Success of any cleaning agent is to supply compounds with both hydrophobic and hydrophilic groups
- These groups appreciably decrease surface tension and increase wettability respectively * *

Soaps why they are natural product industry outputs because the soaps are obtained by the reaction between long chain fatty glycerides or long chain fatty acids plus you know

sodium hydroxide or potassium hydroxide. So, when you do the reaction between these two or the reaction between the glycerides and then whatever the sodium hydroxide or potassium hydroxide if you take that reaction itself is known as the saponification reaction.

So, since the source for the soaps manufacture is long chain fatty acids or long chain fatty glycerides. So, these glycerides are products of a natural product industries like oil industries, oils and fat industries as in previous week we have seen how to extract oils etc. from different types of sources like you know vegetable seeds etc. So, in those lectures we realize that the oils, vegetable oils whatever are there they are nothing but the mixtures of different types of long chain fatty glycerides or long chain fatty alcohols etc.

So since the soaps are also being produced from the constituents of the oil industry. So these soaps are also considered as a natural product industries whereas the detergents are synthetic chemicals. In the soaps manufacture we also get glycerin as co-product that is the reason in this particular lecture we will be concentrating on the manufacturing of soaps and glycerin at industrial scale. How the soaps and glycerin are being produced in the chemical plants that is what we are going to discuss primarily in this lecture. However, before going into the details of such manufacturing processes, we will be having a kind of introduction about the soaps and detergents industries.

Soaps were never actually discovered but instead gradually evolved from crude mixtures of alkaline and fatty materials and then in the ancient days up to 18th century or before that it was believed that soaps are a physical mixture of alkaline and fatty materials. However, later it has been realized that they are actually forming by the chemical reactions between fatty materials and alkaline materials. Soaps and detergents are used for self cleanliness of human beings and their surroundings as well. There are also different types of industrial applications are there that we are going to discuss anyway. Similarly, soaps and detergents are used for industrial surface active applications.

In some of the industrial applications, it is required to lower the surface tension wherever such kind of requirements are there, often either soaps or detergents used. Primarily detergents are being used but however soaps are also being used for such kind of applications. Why primarily detergents are used because detergents lower the surface

tension to much lower level compared to the soaps. Their principle action is based on the colloidal chemistry. Let us say you have a stain or dirt on a surface and then you wanted to remove it.

Then when you apply the surface active materials like soaps and detergents, what will happen? The surface active components of these soaps and detergents will be pulling away the dirt or stain from the surface to be cleaned and then principle is the surface chemistry mechanism. So, this is important to understand. The success of any cleaning agent is to supply compounds with both hydrophobic and then hydrophilic groups as well. These groups oppressively decrease surface tension and increase wettability respectively. Both are required not just the decreasing surface tension but also increasing wettability is also required so that to have the efficient cleaning of the surfaces.

So, these are provided by hydrophobic and then hydrophilic groups of soaps and detergents respectively. Now, we see applications of soaps and detergents. These soaps and detergents not only used for the cleanliness of the human beings and their surroundings but also used for several industrial applications wherever it is required to reduce the surface tension or increase the wettability.

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Applications of soaps and detergents

- Textile manufacture
- Sanitation industry
- Food processing
- Shaving soaps
- Synthetic rubber and plastic emulsion polymerization
- Paints – water emulsion formulations
- Paper – application of sizing
- Oil production – drilling fluid oils
- Inks – water in oil emulsions
- Agriculture – emulsifying agents for sprays
- Construction – waterproofing cements by formation of insoluble soaps; bituminous emulsions

Some of such industrial applications are listed below here. In the textile manufacture, they are very often used. Sanitation industry also they are used. Food processing industries, shaving soaps industries they are used and then they are also used in synthetic rubber and plastic emulsion polymerization purpose as well. In paints as water emulsion formulations purpose also these are used. In paper application of sizing in oil production industries as drilling fluid also these are used or along with the drilling fluids these are used. In inks industry water in oil emulsions purpose also these surfactants or surface active components of the soaps and detergents are being used. In agriculture industry often it is essential to have emulsifying agents for the sprays of different types of fertilizers. So, there also these are in general used. In construction industries waterproofing cements by formation of insoluble soaps, bituminous emulsions, etc. for that purpose also these are used.

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Classification of cleansing compounds

- Classified as soaps and detergents

- Soaps:

- Compounds of type $R \cdot \text{COO} \cdot M$
- M is an alkali element (Na or K)
- Fatty acid radical is $R \cdot \text{COO} \cdot$
- This radical may be representing oleic, stearic, palmitic, lauric and myristic
- These present in soaps as mixtures based on glyceride raw materials

Now, classification of cleansing compounds that we have already seen that soaps and detergents are two classifications. Now, we see individually a few basic concepts about soaps and detergents then we move on to their manufacturing process. Soaps they are compounds of type $R \cdot \text{COO} \cdot M$. So whatever $R-1 \cdot \text{COO} \cdot \text{CH}_2$, $R-2 \cdot \text{COO} \cdot \text{CH}$, $R-3 \cdot \text{COO} \cdot \text{CH}_2$ these kind of compounds that we have seen that glycerides in the oil components they are usually taken as raw material and then they are reacted with alkali like NaOH or KOH. This here M is represented by either N, Na or K sodium or potassium, then you get the components of certain something like $R \cdot \text{COO} \cdot M$. So, these are nothing but the soaps and then such kind of reactions are known as the saponification reactions. Details of such reactions anyway we are going to discuss. Here M is an alkali element like sodium or potassium. Fatty acid radical is nothing but $R \cdot \text{COO} \cdot$. This radical may be representing oleic, steric, palmitic, lauric, myristic, etc. like you know $\text{C}_{17} \text{H}_{33} \text{COO}$, $\text{C}_{17} \text{H}_{31} \text{COO}$, $\text{C}_{17} \text{H}_{29} \text{COO}$. These things are nothing but such kind of radicals. They are having names or something like this as shown here. These details are also we have seen

in the chapter on oils and fats industry. These represent in soaps as mixtures based on glyceride raw materials.

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Detergents

- Detergents are synthetic organic chemicals
- These promote better “surface tension lowering” than soaps
- However, use of detergents increased to the point of creating problems in
 - Municipal sewage plants due to excessive foaming and
 - Inability to reduce organic content of the sewage effluent
- These problems exist because biodegradation of detergent compounds becomes tough to achieve which is an important factor to consider
- Detergent compounds which can be oxidized to simple end-products are known as biologically soft syndets
- These syndets are preferred in detergent compounding *
- Detergents can be anionic, cationic, non-ionic and amphoteric

Coming to the detergents, detergents are synthetic organic chemicals. Though soaps are natural chemicals, detergents are organic chemicals we are discussing together because their characteristics as well as their applications more or less similar. These promote better surface tension lowering than soaps. They reduce surface tension much lower level to the much lower level compared to the soaps. That is the reason they are better compared to the soaps. However, there are also some kind of problems are associated with this.

Use of detergents increase to the point of creating problems especially let us say if you take an example of municipal sewage plants, there is excessive foaming is there in municipal sewage plants because of a presence of detergents in the large quantities. Also, their inability to reduce organic content of the sewage effluent naturally. Actually organic contents are something like C₁₇, H₃₃, COO or C₁₇, H₃₁, COO, etc. These kind of things what happens, they are very difficult to remove biologically or they are not easily

biodegradable. So, these 2 problems are very essential to consider before treating the municipal sewage sludge.

These problems exist because biodegradation of detergent compounds becomes tough to achieve which is an important factor to consider. Thus, detergent compounds which can be oxidized to simple end products are known as biologically soft syndets. These syndets are preferred in detergent compounding in general because they are biologically degradable. They can be easily oxidized to simple end products. So, such kind of compounds you try to have in the detergents so that there will not be any problem of biodegradation.

If you have a compound which is very difficult to biodegrade, then obviously the treatment of municipal sewage sludge is going to be difficult because all these detergent wastage, liquid, etc., after washing clothes, etc., from the household, they are all going as a municipal sewage sludge. So then if these are present in the larger quantities, then what happens? Excessive foaming will take place. If the excessive foaming is there, then you cannot handle the sewage sludge properly.

So, if you have compounds which can be biologically oxidized or easily oxidized to simple end products, which are biologically soft syndets, then it is going to be very advantage or easier for the municipal sewage to be treated as well. These syndets are preferred in detergent compounding because of such reasons. Detergents can be anionic, cationic, nonionic and amphoteric. So, this is only the introduction about the detergents. We are

going to discuss more about detergent in the subsequent lecture, which is completely dedicated on detergents.

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Methods of soap production

- Two types:
 - Batch saponification process *
 - Continuous hydrolysis and saponification process * → * Fatty acids *
* Sapon *
* By mass *

Batch saponification processes:

- These processes are oldest types of soap manufacture
- In these processes, two options are possible
- (a) acid hydrolysis of glycerides followed by alkali addition || *
- (b) Direct saponification using strong caustic

But now we move on to the methods of soap production which is the primary objective of today's lecture. Methods of soap production, there are two types are there. One is the batch of saponification process. Whatever the reaction between long-chain fatty acids and then alkali are there, you know that reactions are nothing but saponification reactions. Those reactions occur in the batch process.

They are oldest type of processes. Such processes are known as the batch saponification processes. However, in the newer ones, continuous hydrolysis and saponification process also taking place. In the continuous hydrolysis, what you try to do? You try to do the fat splitting so that to get the fatty acids and then do the reaction of fatty acid with NaOH or KOH that is saponification reaction to get the soaps. This is the newer one and this is having several advantages because in this process, what are we having? We are having not only

the soap, but also fatty acids and then glycerin also you are having as a product. So, the distribution of the product, what percentage of these components you required, you know that is also important. So, distribution of the product is going to be easier in the case of continuous hydrolysis and saponification process. So, the details we are going to see anyway. Batch saponification processes. These processes are oldest types of soap manufacture.

In these processes, two options are available. First is the acid hydrolysis of glycerides followed by alkali addition. Second one is the direct saponification using strong caustic. Either of the approaches were followed in the batch saponification process. However, nowadays, mostly continuous hydrolysis followed by saponification processes are being installed because of their advantages.

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Continuous hydrolysis and saponification process:

- **This method has following advantages over batch processes**
 - Flexibility in control of product distribution [fatty acid glycerin soap]
 - Higher glyceride yields (> 80%)
 - Less off-colour production during short-time hydrolysis step
 - Requires less space and manpower
- **Thus, this method is preferred over batch methods and accordingly continuous process discussed in details**

Continuous hydrolysis and saponification process. This method has following advantage over batch process something like flexibility in control of product distribution, you know how much yield of fatty acid is required, how much yield of glycerin is required, how much yield of soaps required, all these you can control easily. Flexibility is there in the

continuous hydrolysis and saponification process. Also higher glyceride yields are possible. Then in the hydrolysis step if you do for the short time there is a possible that off color would be there.

So, that off coloring would be less or less off color production during short time hydrolysis step is the other advantage in the continuous hydrolysis and saponification process as well requires less space and manpower obviously because it is a continuous process. Thus, this method is preferred over batch methods and accordingly we are going to discuss about this continuous process for fatty acids production, soap production and glycerin production.

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Continuous process for fatty acids, soap and glycerine

- **Chemical reactions: two important reactions**
- (a) **Fat splitting reaction**

$$(R \cdot COO)_3 \cdot C_3H_5 \text{ (triglyceride)} + 3H_2O \rightarrow 3R \cdot COO \cdot H \text{ (fatty acid)} + C_3H_5(OH)_3 \text{ (glycerol)}$$

Handwritten notes: 250°C, 40-45 atm
- (b) **Saponification reaction**

$$R \cdot COO \cdot H + M \cdot OH \rightarrow R \cdot COO \cdot M \text{ (soap)} + H_2O$$

Handwritten note: BP ~ 270°C

So, we see the conventional way the process like you know chemical reactions, raw materials, basis quantitative requirements, flowchart followed by the description of the process we are going to discuss. So, let us start with the chemical reactions as I already mentioned two important reactions are taking place in continuous hydrolysis and saponification processes. So, first one is the hydrolysis that is nothing but fat splitting reaction.

Here what happens is triglycerides react with water at high temperature something like 250, 230 to 250 degrees centigrade and about 40 to 45 atmosphere. So, when you interact this triglycerides and then hot water at high pressure counter currently then what happens

you get the fatty acids and then glycerol mixture. Boiling point of the glycerol is approximately around 290 degrees centigrade but your operating temperature is less than 250 degrees centigrade what happens so this glycerol settles as the bottom product so that bottom product is having impurities also along with the glycerin. So, those impurities are separated as the from the bottom of the reactor whereas from the top of the reactor you get the fatty acids which may be having excessive steam also because you are doing this reaction at high temperature and high pressure. So, then after removing that excessive steam by passing it through a flash tank then you can get the pure fatty acids those pure fatty acids you can further do the vacuum distillation further to improve its purity. Once you have the sufficient purity of the fatty acids then what you do you do the saponification reaction where this fatty acid react with the NaOH or KOH to get RCOOM soap along with the water.

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- **Raw materials:**
 - Fatty constituents such as refined tallow, recovered and refined grease, coconut and palm oils, etc.
 - Fat splitting metal oxide catalysts such as ZnO
 - Alkali for saponification
 - Builder type additives such as rosin
- In India, caustic soda and vegetable oil are used as raw materials for production of toilet soaps as use of animal tallow is not allowed
- Other important constituents are distilled fatty acids derived from vegetable oils such as palm oil or other solvent extracted oils and minor oils
- Required raw materials (such as vegetable oils and their derivatives) demand-supply gap is met through imports, if required

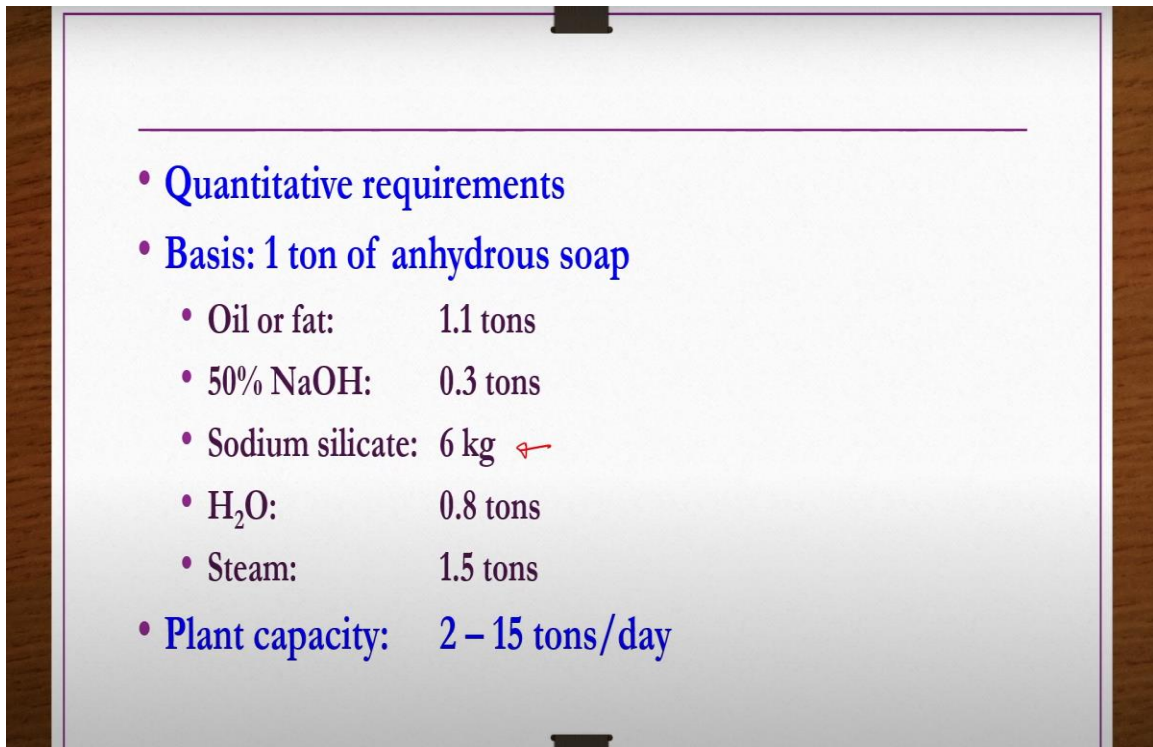
Raw materials obviously the oils which are having fatty constituents such as refined tallow recovered and refined grease coconut and palm oil etc. anything you can take in which fatty

constituents are there. But however you should also take concentration economics availability all these factors should be considered because these fatty constituents are available in so many types of vegetable oils and then animal fats etc. as we have seen in the previous chapter on oils and fats industries.

Anyone can be used but you should see the economics and then accordingly you should select economics as well as the availability of such raw materials. Then this fat splitting reaction does not occur without metal oxide catalyst such as ZnO so that should also be one raw material. Then after this reaction whatever fatty acids are there they would be reacting with alkali. So, alkali for the saponification process that is again required and then builder type additives such as rosin, sodium silicate etc. may also be required. In India caustic soda and vegetable oil are used as raw material for production of toilet soaps as animal tallow is not allowed in India for the manufacturing of the soaps. Other important constituents are distilled fatty acids derived from vegetable oil such as palm oil or other solvent extracted oils and minor oils that we have discussed in the previous chapter on oils and fats industry they can also be used as per the requirement. In the flow sheet we are going to discuss how the other things are also being used otherwise primarily these are the raw materials in fact first three only. Fourth one is also not compulsory is as per the requirement consumer requirement the fourth one is there. Required raw materials such as

vegetable oils and their derivatives if any demand supply gap is there that should be made through imports if at all required.

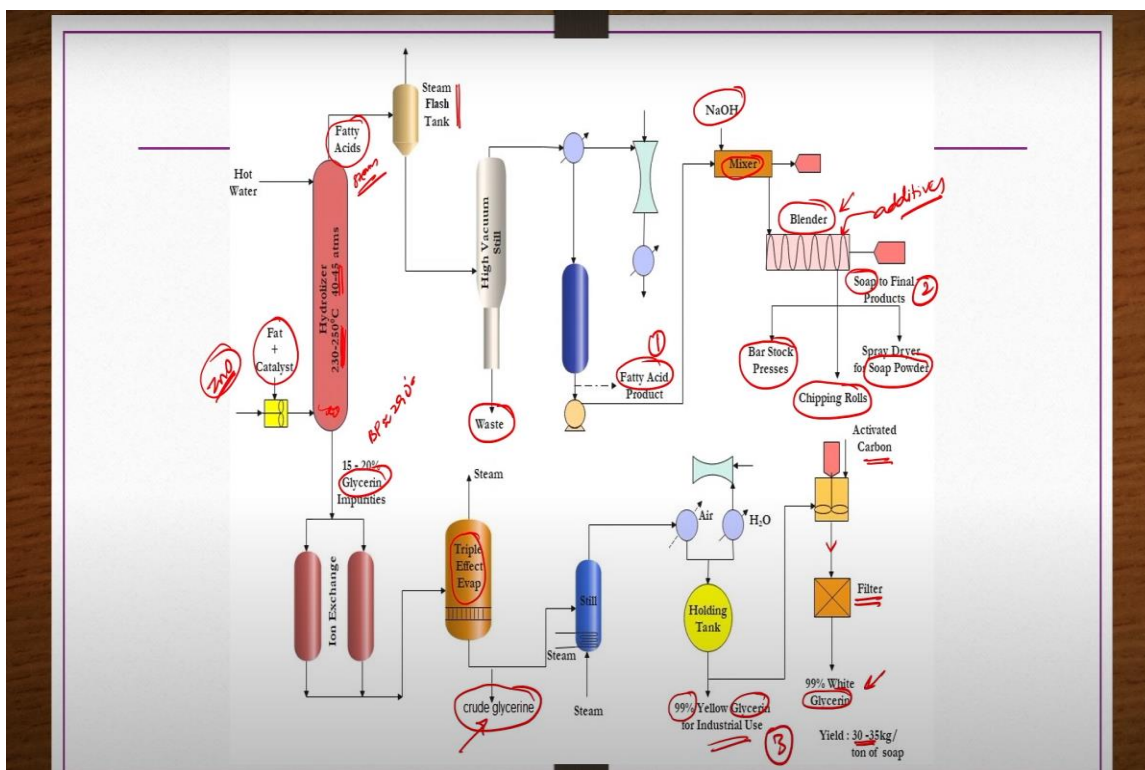
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- **Quantitative requirements**
- **Basis: 1 ton of anhydrous soap**
 - Oil or fat: 1.1 tons
 - 50% NaOH: 0.3 tons
 - Sodium silicate: 6 kg →
 - H₂O: 0.8 tons
 - Steam: 1.5 tons
- **Plant capacity: 2 – 15 tons/day**

Quantitative requirements if you want to produce 1 ton of anhydrous soap then oil or fat you required 1.1 tons and then 50 percent NaOH 0.3 tons sodium silicate 6 kgs H₂O water 0.8 tons steam 1.5 tons plant capacity 2 to 15 tons per day. This sodium silicate is very good filler economical one and then antioxidant agent as well it also improves the harness of the product. So, for that purpose also it is used.

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Flow chart of the process is supplied here. So, now let us see how the soap manufacturing is being carried out industrially. At chemical plants how the soaps are being produced that can be understood from this flow chart not only soaps but also glycerin as well as the fatty acid. So, the starting step of the process is the hydrolysis reactor or hydrolyzer to this reactor fat and catalyst something like a metal oxide like ZnO along with the fat are supplied to the bottom of the reactor that is hydrolyzer to this reactor from the top hot water at 230 to 250 degree centigrade is supplied and then pressure is maintained between 40 to 45 atmosphere. So that this fat and catalyst mixture interact with hot water counter currently. Then the splitting of fat takes place in the presence of this catalyst along with the hot water. So then when the splitting of fat takes place what you get you get the fatty acids and then glycerin. This glycerin as mentioned its boiling point is roughly 290 degree centigrade your operating temperature is less than 250 degree centigrade.

So, then obviously glycerin would be settling as a bottom product whereas the fatty acids which are more volatile having low boiling point they will be evaporating from the top as a top product. So this fatty acids may be containing the steam as well. So that steam is reduced or removed by passing through this top product by passing this top product through

steam flash tank and then you remove the steam from here. Then whatever the remaining fatty acids mixture is there that is vacuum distilled in a high vacuum or still to remove the waste if at all present and then pure fatty acids are taken to the storage tank. So it can be taken as a product if you are targeting the fatty acids.

If you wanted to make soap also this fatty acid is mixed in a high speed mixture in which sodium hydroxide is being added continuously. So that the saponification reaction between fatty acid and NaOH takes place and then soap formation occurs. If at all saponification is not complete so then what we do this solution whatever coming from the mixture is passed through a blender which is having the low speed creak and wear kind of thing. So that to make sure the remaining degree of saponification can also takes place by this process or when it passes through the blender most of the saponification is completed and then you get the soap as a final product. To this blender you can also add the additives that is also the other purpose of this blender not only just to make sure the complete the degree of saponification but also to add additives something like sodium silicate that will improve the hardness of the product etc. such kind of advantages are there. So this soap as per your requirement you can make as bars or you can make as powder or you can make as chipping rolls. So this is the second product first one is the fatty acid second one is the soap. From the bottom of the hydrolyzer you get the glycerin with impurities glycerin is only 15 to 20 percent here. So that mixture you pass through series of cation and anion exchanges so that to remove color and then impurities to some extent. Then the material that has come out from the ion exchanges after removing the impurities and then color to some extent it is passed through triple effect evaporator so that to concentrate the glycerin percentage.

So from here you get the crude glycerin if you are intended for using as industrial application. So then you check if that crude glycerin having sufficient purity or not and then you can stop the process here itself. Otherwise if you are planning it for the human consumption purpose then what you have to do this crude glycerin you have to do the vacuum distillation and then whatever the distillate is there that is nothing but the pure glycerin 99 percent. But it is yellow in color so it can be used only for the industrial purpose after removing that yellow color that can be used for the human consumption whatever the white glycerin that you get. How you can get this yellow glycerin you pass through an

adsorption column where activated carbon is there. So this activated carbon will be adsorbing the yellow color from the glycerin and then you get the pure glycerin. So that pure glycerin that may be carrying some amount of activated carbon particles as well. So then that mixture you pass through filter phase so that to remove such particles and then you get 99 percent white glycerin. Yield is approximately 30 to 35 kg per ton of the soap. So this glycerin is the third product.

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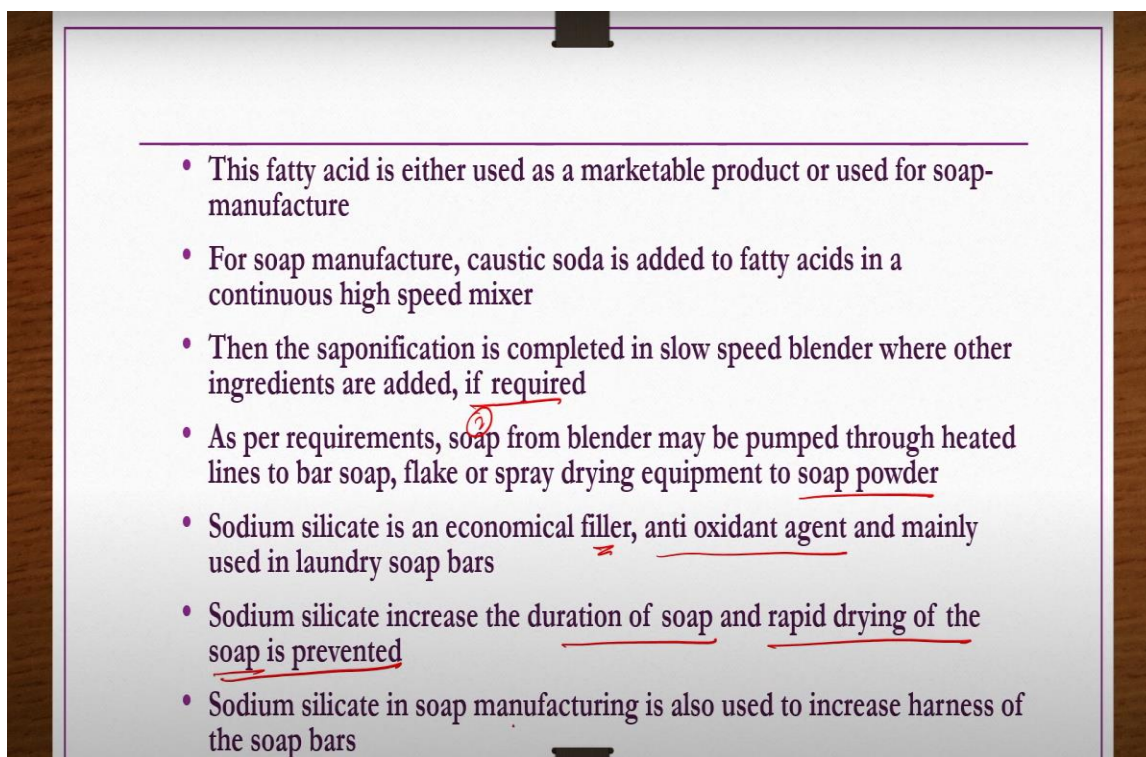
• Process description

- To the bottom of hydrolysis tower, glycerides and catalyst are supplied
- In this tower, high pressure water at 230-250°C is passed counter-currently to the glycerides
- This counter current interaction between glycerides and high pressure water leads to fat splitting reaction
- This fat splitting reaction occurs with 15 – 20% glycerine solution and removed from bottom of the tower
- Whereas the fatty acids are passed overhead to a flash tank to remove excess steam
- Then these crude fatty acids are vacuum distilled
- Condensate of distillation is collected in distillate receiver
- This condensate is nothing but purified fatty acid

So whatever the steps that we discussed in the flow chart the same steps are provided here for the repetition as well as the understanding point of view. To the bottom of hydrolysis tower glycerides and catalyst are supplied in this tower. High pressure water at 230 to 250 degree centigrade is passed counter currently to the glycerides. This counter current interaction between glycerides and then high pressure water leads to fat splitting reaction. This fat splitting reaction occurs with 15 to 20 percent glycerin solution and removed from the bottom of the tower. Whereas the fatty acids are passed overhead to a flash tank to

remove excess steam. Excess steam are possible along with the fatty acids because of the fat splitting reaction occurring at high temperature and high pressure using the hot water. Then this crude fatty acids are vacuum distilled. Condensate of distillation is collected in a distillate receiver. This condensate is nothing but purified fatty acid that is one of the product.

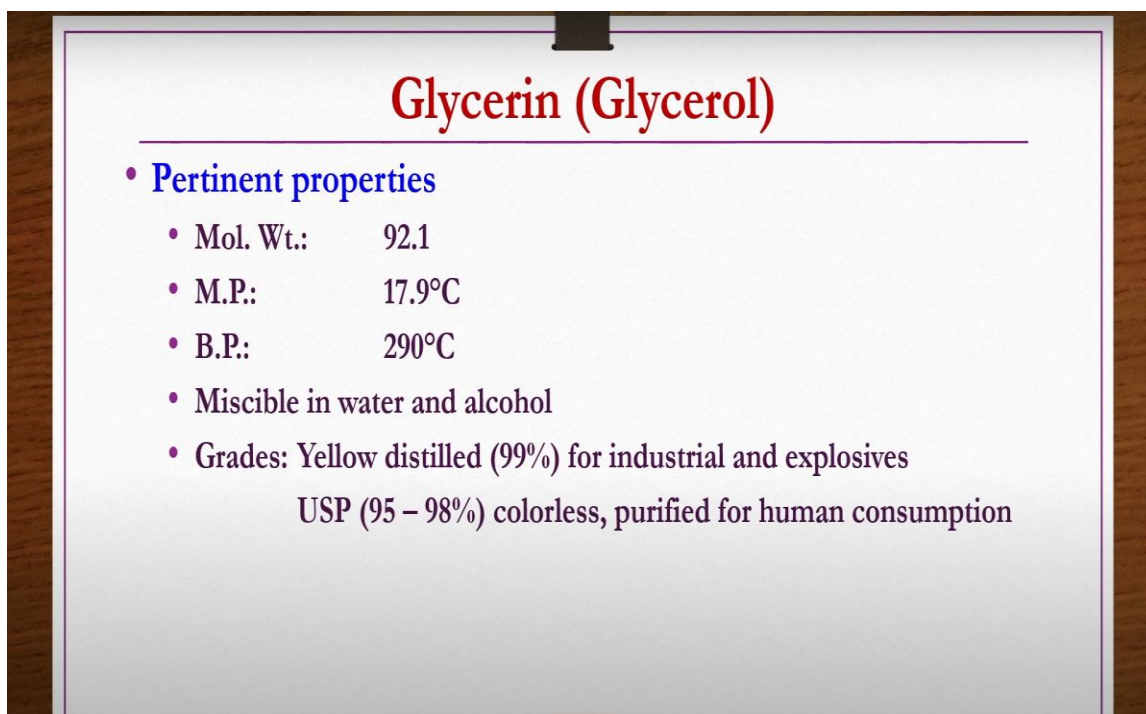
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- This fatty acid is either used as a marketable product or used for soap-manufacture
 - For soap manufacture, caustic soda is added to fatty acids in a continuous high speed mixer
 - Then the saponification is completed in slow speed blender where other ingredients are added, if required
 - As per requirements, soap from blender may be pumped through heated lines to bar soap, flake or spray drying equipment to soap powder
 - Sodium silicate is an economical filler, anti oxidant agent and mainly used in laundry soap bars
 - Sodium silicate increase the duration of soap and rapid drying of the soap is prevented
 - Sodium silicate in soap manufacturing is also used to increase harness of the soap bars

Now this fatty acid is either used as a marketable product or used for soap manufacture. For soap manufacture caustic soda is added to fatty acids in a continuous high speed mixer. Then the saponification is completed in slow speed blender where other ingredients are also added if required. As per requirements, soap from blender may be pumped through heated lines to bar soap, flake or spray drying equipment to soap powder etc as per the consumer requirement. Sodium silicate may be added as an ingredient in the blender because it is an economic filler. It is antioxidant agent and mainly used in laundry soap bars manufacture. Sodium silicate increase the duration of soap and rapid drying of soap is prevented. If it is rapidly drying what happens? The soap bar may be having the cracking.

If the cracking is there that may not be pleasing to the customer and then there may not be market for it. So, it has to be slow and then for the slowing down the drying also the sodium silicate is used. Sodium silicate in soap manufacturing is also used to increase hardness of the soap bars.

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Glycerin (Glycerol)

- **Pertinent properties**
 - Mol. Wt.: 92.1
 - M.P.: 17.9°C
 - B.P.: 290°C
 - Miscible in water and alcohol
 - Grades: Yellow distilled (99%) for industrial and explosives
USP (95 – 98%) colorless, purified for human consumption

Now we discuss about glycerin or also known as glycerol. Pertinent properties of glycerin if you see, molecular weight is 92.1, melting point is 17.9 degrees centigrade, boiling point is 290 degrees centigrade. It is miscible in water and alcohol. Yellow distill 99 percent is one of the grade which is used for industrial applications and in explosives whereas, USP 95 to 98 percent colorless purified glycerin is used for human consumption.

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Industrial applications of glycerine

- Industrial applications of glycerine are based on
 - Its physical properties of moistening and lubrication
 - Chemical reactivity of its OH groups
- Some of the industrial applications include:
 - Alkyl resins and plastics: 35%
 - Tobacco humidification: 15%
 - Cellophane plasticizer 12%
 - Explosives 10%
 - Food and pharmaceuticals 10%

Industrial applications of glycerin, glycerin having industrial applications because of two important reasons. One is the physical reason that is its moistening and then lubrication ability because of such physical properties it is having several industrial applications. As well its reactivity because of its OH groups also one of the reason that you know it is having several industrial applications. Some of them are mentioned here like for the manufacture of alcohol resins and plastics it is used. For tobacco humidification also it is used, cellophane plasticizer also it is used, explosives purpose also used and then even in the food and pharmaceuticals also it is used.

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Methods of production

- **Classification of processes**
 - Natural product triglyceride hydrolysis (in soap manufacture process)
 - Synthetic glycerine from propylene (petrochemical processing)
 - Allyl chloride route
 - Acrolein route: it produces acetone co-product

Now methods of the production, there are two methods of the production as I already mentioned. One is the natural product method, another one is the synthetic chemical approach. So, natural product method just now we have seen in the case of soap manufacture flowcharts, the same process is followed. However, synthetic processes are there those things we are going to see anyway. Classification of processes, natural product triglyceride hydrolysis as we discussed in the soap manufacture process there itself we have discussed this one. Synthetic glycerin from propylene petrochemical processing that is through allyl chloride route, acrolein route in which acetone is also obtained as a co-product.

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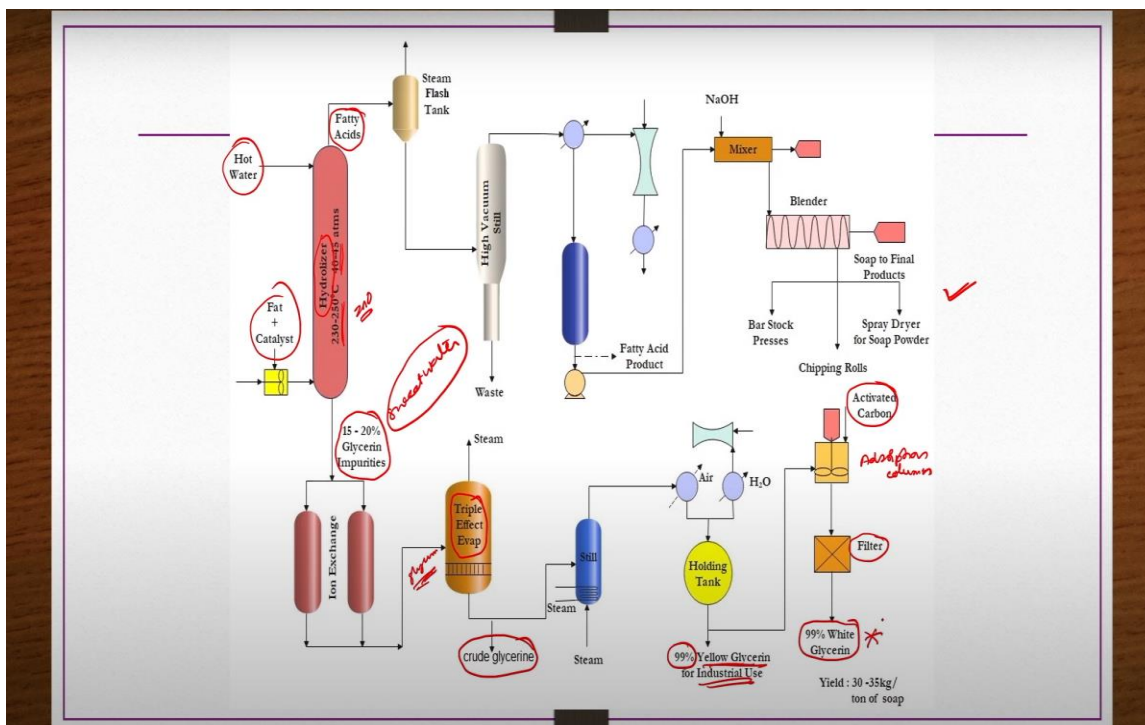
Natural product triglyceride hydrolysis

- It is also a process where by-product glycerine obtained from soap manufacturing (same flowsheet discussed under soap manufacture)
- Dilute glycerine (sweetwater) is obtained as by-product in hydrolysis of fatty acids using hot water and metal oxide catalyst for soap production purpose
- This dilute glycerine is passed through successive beds of anion and cation exchange resins to remove colour and dissolved salts to some extent
- Then liquid effluent is concentrated by triple effect evaporation followed by vacuum distillation to produce industrial grade (99%) yellow glycerine
- Finally, a purification step is performed using activated carbon to obtain water-white USP glycerine

Now we discussed natural product triglyceride hydrolysis process to get the glycerin. It is also a process where byproduct glycerin obtained from soap manufacturing just discussed. Dilute glycerin whatever the 15 to 20 percent glycerin along with the impurities is there that is nothing but sweet water or it is also known as the sweet water that is dilute glycerin is obtained as byproduct in hydrolysis of fat acids using hot water and metal oxide catalyst for soap production purpose. Wherever that fat splitting reaction is occurring using the hot water in the presence of a metal oxide catalyst, then you as a product you get fatty acids as well as the glycerin 15 to 20 percent glycerin along with the impurities whatever the 15 to 20 percent glycerin along with the impurities is there that is nothing but the dilute glycerin it is also known as the sweet water. This dilute glycerin is passed through successive beds of anion and cation exchange resins to remove color and dissolve salts to some extent if at all present. Then liquid effluent is concentrated by triple effect evaporation followed by vacuum distillation to produce industrial grade 99 percent pure yellow glycerin. This yellow color can be removed by performing or passing it through activated carbon chamber

or absorption column so that you get water white USP glycerin. This activated carbon that is present in the absorption column will be absorbing the yellow color and then you will be getting the water white pure glycerin which is suitable for the human consumption whereas this yellow glycerin is suitable for the industrial applications.

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Now the flow chart that we have already seen this is the same flow chart that we used for the soap manufacture because from the fats you are also getting the fatty acid soaps along with the glycerin. So, here in this process to repeat the primary reactor is hydrolyzer or hydrolysis reactor in which fat splitting reaction is taking place at 230 to 250 degrees centigrade and 40 to 45 atmosphere in the presence of metal oxide catalyst something like ZnO. To this reactor if you supply fat and catalyst to the bottom of the reactor and from the top of the reactor if you supply the hot water they will interact each other counter currently so that the fat splitting reaction will take place. Then because of high volatility fatty acids would be collected from the top along with the excess steam then these fatty acids are passed through flash tank to remove excess steam followed by the vacuum distillation to purify the fatty acids followed by the reaction of the fatty acids with the alkali

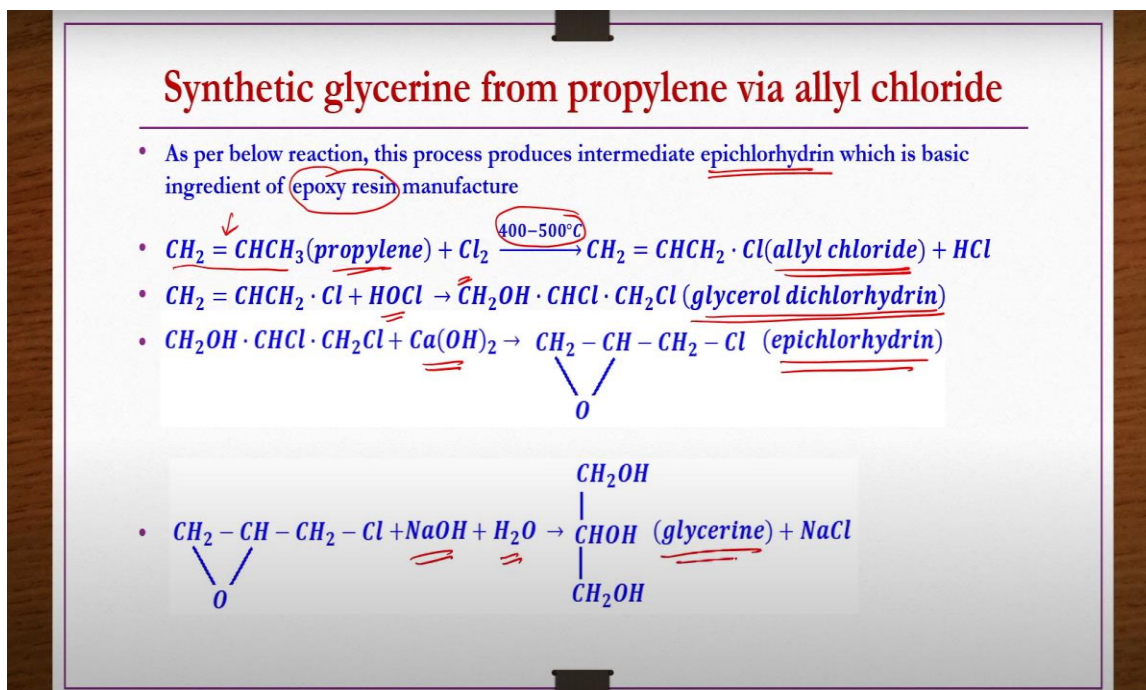
to get the soaps. This process we have already seen whereas bottom of this hydrolysis reactor what you get? You get the glycerin around 15 to 20 percent along with the impurities.

So, this dilute solution is also known as the sweet water. So, this sweet water is passed through series of cation and anion exchange resins so that to remove color and then some amount of salts if at all they are present. After removing the color and salts then what you do? The effluent you take to triple effective evaporator to which steam is supplied to provide the required energy for the evaporation of the solution. Whatever the solution that glycerin solution you are getting sweet water solution after removal of impurities and then colors etc. that has to be passed through triple effective evaporator.

It is shown one only there are 3 evaporators are there. So, all these 3 evaporators energy has to be supplied so that whatever the dilute glycerin solution is there it can start boiling and an evaporation takes place and then impurities go off you can have the pure glycerin. So, how do you obtain or achieve that heating requirement for this triple effective evaporation to take place that you do using the steam. Whatever the crude glycerin is there that you can take it as a product if you are happy with its purity otherwise that crude glycerin would be vacuum distilled and then whatever the distillate you receive in the receiver that is nothing but the pure yellow glycerin 99% pure yellow glycerin. So, this yellow glycerin you cannot use for the human consumption but you can use it for industrial applications. So, many applications as we already listed out then if you pass it through an adsorption column in which packing of the column is done using the activated carbons.

So, through this bed it is actually in the form of packed bed through this packed bed through this packed absorption bed when you pass through this 99% pure yellow green glycerin. So, then yellow color would be absorbed by the activated carbon and then pure white glycerin or colorless glycerin you get as a product. However, this may also contain some amount of activated carbon. So, what you do you pass it through a filter press where the activated carbon particle if at all they are present in the pure glycerin they will be removed. So, this final white glycerin whatever is there that is suitable for the human consumption. So, that is what about natural product glycerin or natural synthesis process of glycerin production.

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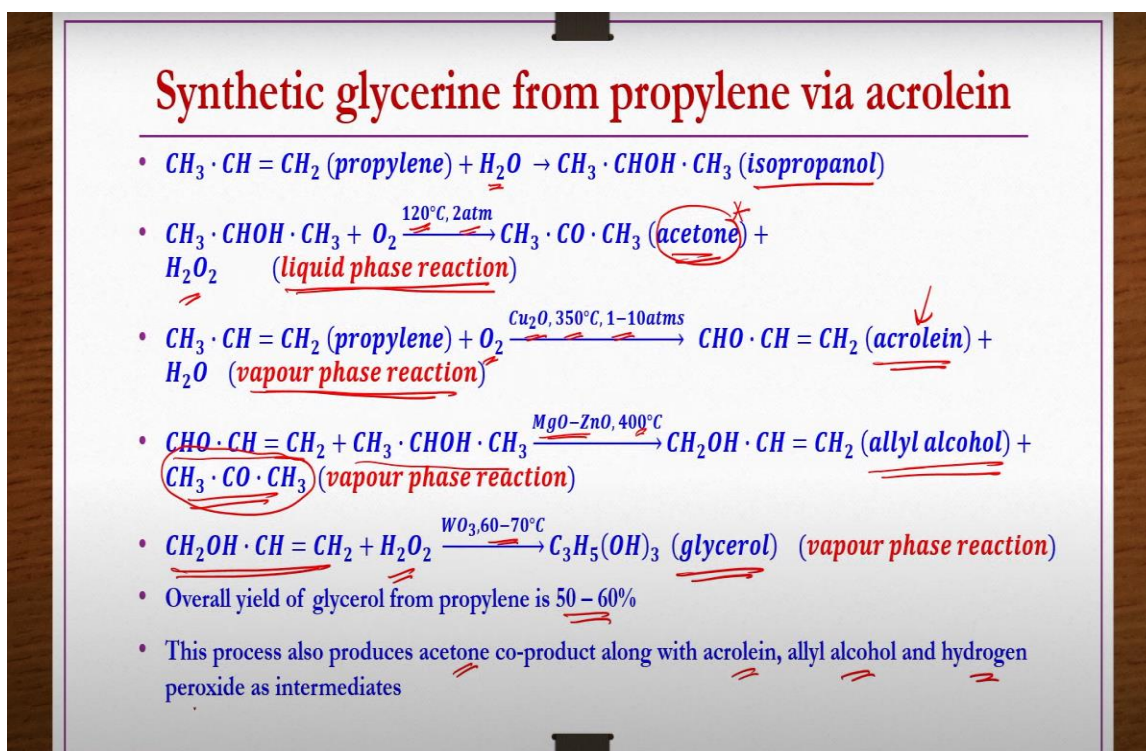


Now, we talk about synthetic glycerin production from propylene via allyl chloride route there are different routes are there we are going to see the reactions of 2 routes only other ones we have shown as a pictorial representation only. So, here what happens reactions we are going to see in this reaction you get intermediate epichlorhydrin as well which is basic ingredient in many of the epoxy resins manufacture. So, not only required glycerin but also you are getting some other you know byproducts or coproducts which are useful from the industrial applications point of view.

First here what happens whatever the propylene is there that is $\text{CH}_2 \text{ CH CH}_3$ is a propylene. So, then specifically double bond we are showing here this propylene undergoes chlorination at high temperatures of 400 to 500 degrees centigrade to get so called allyl chloride, this can also be used as one of the product. Then this allyl chloride would further react with hypochlorite solution to get glycerol dichlorhydrin. So, this glycerol dichlorhydrin will further react with calcium hydroxide to get so called epichlorhydrin which is a important intermediate or byproduct of the process. This epichlorhydrin if you further react with sodium hydroxide in water, then you get the glycerin $\text{C}_3\text{H}_5\text{OH}$ thrice

plus NaCl salt also. So, in the synthetic process so many steps purification steps are required however, we are talking only through reactions.

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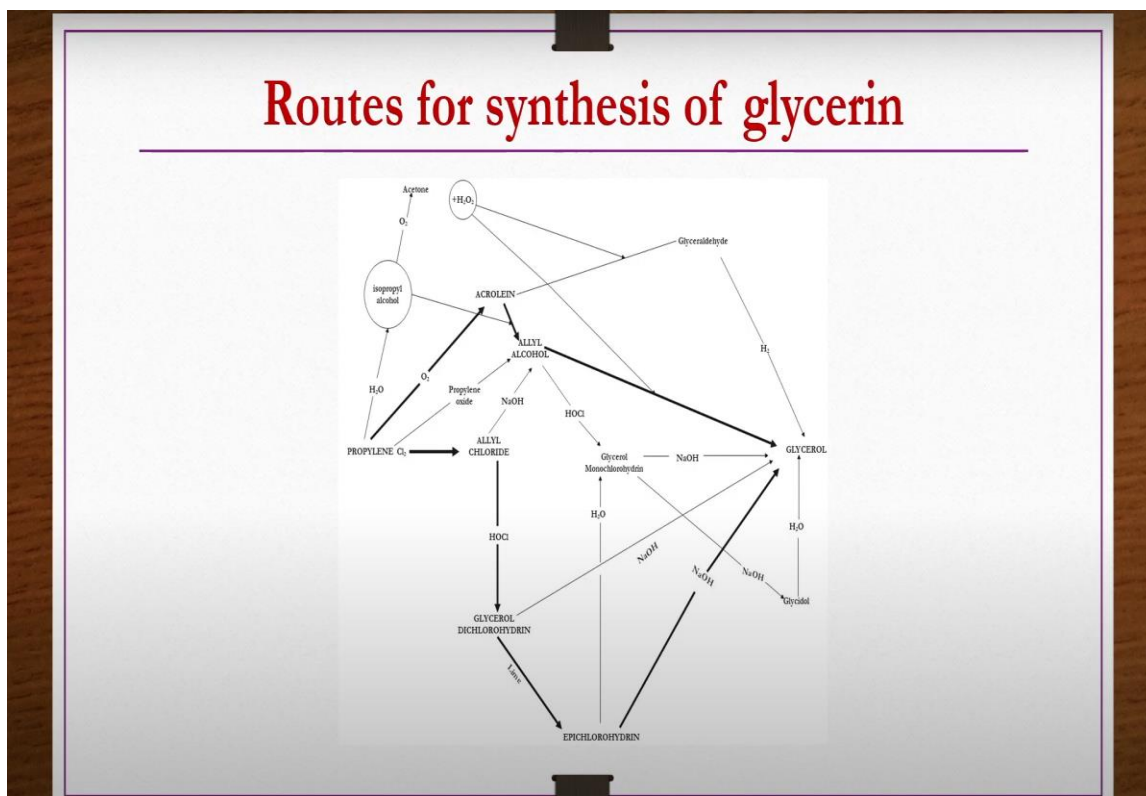
Then synthetic glycerin from propylene but via acrolein route acrolein also one of the important coproduct. So, here propylene reacts with water to give the isopropanol. This isopropanol gets oxidized at 120 degrees centigrade and 2 atmosphere pressure conditions to give the acetone. So, then acetone is one of the important coproduct rather saying byproduct you can say as a coproduct because acetone is having huge market.

Along with the acetone you also get hydrogen peroxide. This reaction is a liquid phase reaction. Now this propylene may also get oxidized using oxygen in the presence of cuprous oxide catalyst at 350 degrees centigrade and 1 to 10 atmosphere to give acrolein which is one of the important intermediate of the process. Along with the acrolein you also get the water vapors. This reaction is a vapor phase reaction. Now this acrolein plus isopropanol reacts together in the presence of metal oxide catalyst like MgO, ZnO or their mixture at 400 degrees centigrade to get allyl alcohol as the product along with the acetone.

So, here also we are getting acetone that is the reason I said acetone as a coproduct rather calling it as a byproduct.

Large amount of acetone is produced in this process. So, that you can consider as a coproduct after purification. Then finally what happens? This allyl alcohol whatever is there that reacts with hydrogen peroxide in the presence of WO_3 catalyst at 60 to 70 degrees centigrade to give glycerol which is nothing but $\text{C}_3\text{H}_7\text{CO OH}_3$ that is $\text{CH}_2\text{OH CH OH CH}_2\text{OH}$. So, now here how many products are there? One is the acetone another one is acrolein and then even this allyl alcohol is also one of the product. The overall yield of glycerin from propylene is around 50 to 60 percent. This process also produces acetone as coproduct along with acrolein, allyl alcohol and hydrogen peroxide as intermediates. These are the two synthetic routes we have discussed but there are other possible synthetic routes as well.

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So, some of them are pictorially shown here.

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Natural vs. synthetic product glycerol

- In India, majorly natural product glycerine is being produced
- Soap plants have such small capacity that central fat-splitting plants have been suggested wherein
 - Glycerine can be recovered economically via large capacity throughput and
 - Fatty acids shipped to small soap manufacturers
- However, synthetic glycerine may be produced successfully by promotion of petrochemical industries
- Furthermore, substitution of soap by detergents shall further curtail natural glycerine supplies
- By this substitution, net results will be stabilized glycerine from both sources which can be an attractive raw material for chemical speciality products such as plastics

Natural versus synthetic product glycerol. In India majorly natural product glycerin is being produced because most of the oils and fats are you know vegetable oils based. That is the reason you know mostly you get natural product glycerin in India. So, plants have such small capacity that central fat splitting plants have been suggested wherein glycerin can be recovered economically via large capacity throughput and whatever the fatty acids are there, they may be shipped to small soap manufacturers. However, synthetic glycerin may be produced successfully by promotion of petrochemical industries. Actually, petrochemical industries are already in a good stage but however, how much are they prioritizing the glycerin production that is what it means to. Further substitution of soap by detergent shall curtail natural glycerin supplies as well. So, net result would be stabilized

glycerin from both sources which can be an attractive raw material for production of several specialty chemicals such as plastics etc.

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