# Organic Chemical Technology
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## Lecture - 06
## Processing of Oils and Waxes

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is processing of oils and waxes. Before going into the details of today's lecture, we will have a recapitulation of what we have discussed in last couple of lectures. We started with oils and fats industries or manufacture of different types of oils and then fats. In the oils we started with edible and essential oils. So, these edible oils are nothing but in general long chain fatty esters, sometimes acids etc. So, and then their derivatives also sometimes like you know, long chain fatty alcohols may also be present. These are used not only for food purpose or edible purpose, they are also increasingly being used for the industrial purpose, different types of edible oils are also being used for the industrial purpose something like you know soaps, paints, varnishes etc. Whereas essential oils are nothing but some types of aromatic components which are you know primarily used in cosmetics, pharmaceuticals etc. these kind of industries these are being used.

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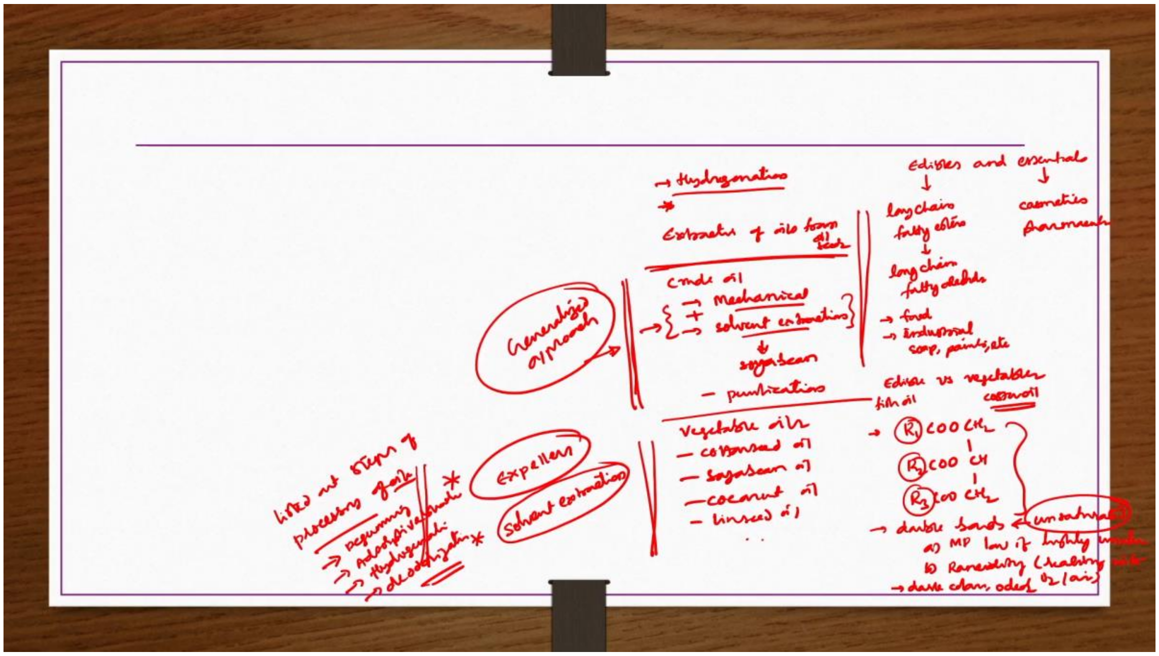

→ Hydrogenation
→
Extraction of oils from oil seeds
Crude oil
→ { → mechanical + → solvent extraction }
↓
soyabean
– purification
Vegetable oils
– cottonseed oil
– soyabean oil
– coconut oil
– linseed oil
. .
Edibles and essentials
↓ long chain fatty esters
↓ long chain fatty alcohols
→ food
→ industrial soap, paints, etc
↓ cosmetics pharmaceuticals
Edible vs vegetables
fish oil
castor oil
→ $R_1COOCH_2$
$R_2COOCH$
$R_3COOCH_2$
→ double bonds ← unsaturated
a) MP low if highly unsatu
b) Rancidity (reacting with $O_2$/air)
→ dark colour, odour
Generalized approach
listed out steps of processing of oils
→ Degumming
→ Adsorptive bleaching
→ Hydrogenation
→ deodorization
* Expellers
* Solvent extraction

Primarily our concentration was on edible oils, vegetable oils, right. So, these edible oils versus vegetable oils also we have seen actually not all edible oils are vegetable oils because something like you know fish oil etc. they are also edible oils but they are not vegetable oils, right. So, likewise not all vegetable oils are edible oils, something like you know, castor oil etc. vegetable oils but we do not use for the edible purpose, right. Then we started on the composition of these edible oils. These are something like you know R1 COO CH2, R2 COO CH2, R3 COO CH2 such kind of you know glycerides or you know or mixtures of such kind of glycerides would be there in the these edible oils, right. So, these are nothing but mixtures of different types of fatty acids, okay. So now in these chemical structures if you see this R1, R2, R3 are not necessarily be you know same they would be different from one to other in general, right and they will be including double bonds. Because of these double bonds almost all vegetable oils are edible oils are unsaturated oils, right. So, if they are unsaturated so then what are the problems? The problem is that you know the melting point would be low if highly unsaturated that is what we discussed. Also, rancidity increases that is reactivity with oxygen or air increases that we do not want. What happens if the rancidity increases it leads to some kind of dark color order to the oil. So, you do not feel comfortable to consuming such kind of oils. So, then what you do these unsaturated oils has to be saturated, right. How do you saturate them by using hydrogenation processes. Then we have discussed about extraction of oils from seeds, from oil seeds. Most of the oil seeds are you know, especially for vegetable oils, oil seeds are utilized for the extraction of these oils. So, crude oil we can get by mechanical methods as well as the solvent extraction methods. Primarily, people earlier were using mechanical methods. Later on solvent extraction method was developed for some kind of oils like soya bean oil etc. because their content oil content in soya bean seeds is very less, less than 40 percent or something like that. Under such conditions mechanical method would not able to recover or extract entire oil contents. Then the solvent extraction has been found and then people realize that the solvent extraction has been good for other oil extraction also. Then later on people started using these two in combination also rather one individual. So, all the options were there. So, then this oil extraction generalized approach we have seen mechanical and then solvent extraction process then we also seen the steps of purification, how to do the purification of such oils those things also we have seen, right. Then we started discussing on specific to certain types of vegetable oils. These particular details we discussed generalized one irrespective of what kind of oil you are going to extract. So, generalized approach we discussed but later on we have discussed specific to certain type of vegetable oils like you know cotton seed oil, soya bean oil, coconut oil, linseed oil etc. these kind of things also we have seen. So, in addition to these specific to specific type of oils we have also seen details of working principles of expellers because expellers are very essential in mechanical methods of oil extraction from the oil seeds. So, schematically we have seen their working principles etc. Then what we have done in the solvent extraction, solvent extraction step is very essential. So, specific to soya bean oil we have discussed how solvent extraction is being incorporated industrially in especially in the oil industries that is what we have seen. Then also we have listed out steps of processing of oils. There are certain steps like you know there are certain steps like degumming or steam reforming or steam refining and then adsorbed tube leaching and then hydrogenation followed by finally deodorization or decolorization both occurs in one particular things. So, these things we have seen in last couple of lectures especially associated or dedicated to the oils and fats industries.

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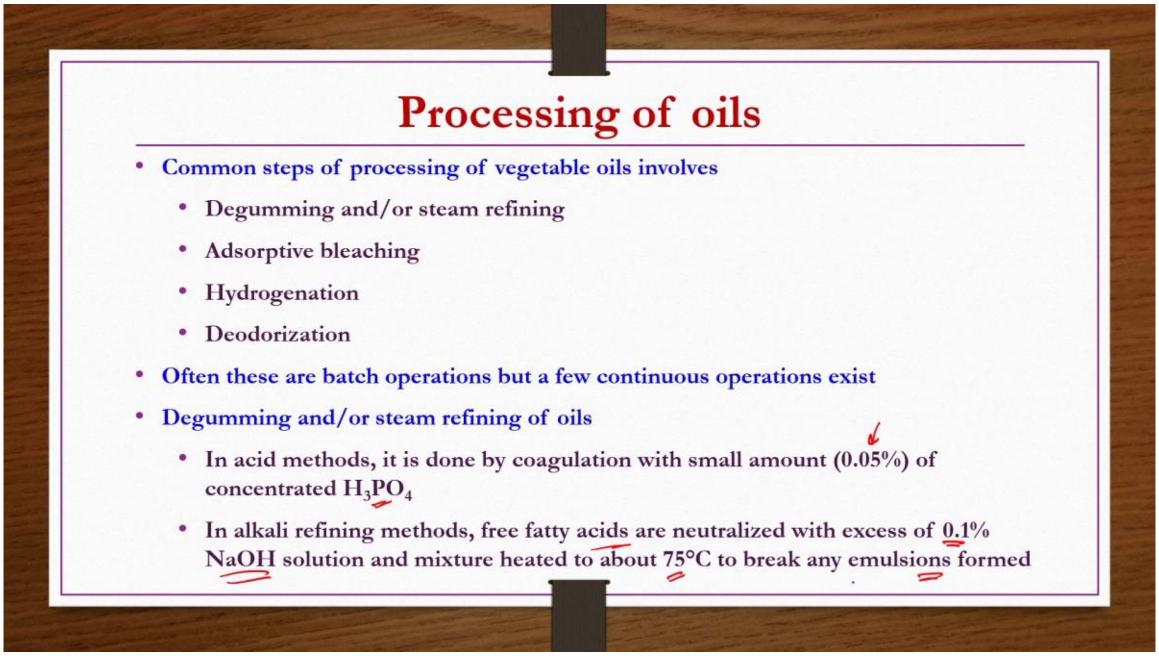

## Processing of oils

- Common steps of processing of vegetable oils involves
  - Degumming and/or steam refining
  - Adsorptive bleaching
  - Hydrogenation
  - Deodorization
- Often these are batch operations but a few continuous operations exist
- Degumming and/or steam refining of oils
  - In acid methods, it is done by coagulation with small amount (0.05%) of concentrated $H_3PO_4$
  - In alkali refining methods, free fatty acids are neutralized with excess of 0.1% NaOH solution and mixture heated to about 75°C to break any emulsions formed

Now, in this lecture we are going to discuss in detail about processing of oil. We have seen until now extraction of oil but that crude oil is not suitable for edible purpose especially. Though crude oil may be directly used to some kind of industrial applications but edible oil they are not suitable. So, then we have to do the required processing. So, those processing details in detail with flow sheet reactions etc. all those things we are going to discuss in this present lecture. Processing of oils it includes several steps something like degumming, steam refining, adsorbed tube leaching, hydrogenation and deodorization. Most of these processes occur in batch mode because of certain limitations. Those limitations we are going to discuss in hydrogenation step anyway. So, but however there are a few plans or exceptions where continuous processing of oils is also existing. So, we see both batch mode as well as the continuous mode how these kind of you know oil processing has been done at the industry level. Let us start with degumming steam refining of oils. In the degumming first usually coagulation is done with some amount of concentrated phosphoric acid and then it is very less amount 0.05 percent almost negligible amount of concentrated phosphoric acid is taken so that to coagulate the gums whatever are present. Then free fatty acids are neutralized with excess of 0.1 percent NaOH solution and then mixture is heated about 75 degree centigrade so that to break if at all any emulsions are formed.

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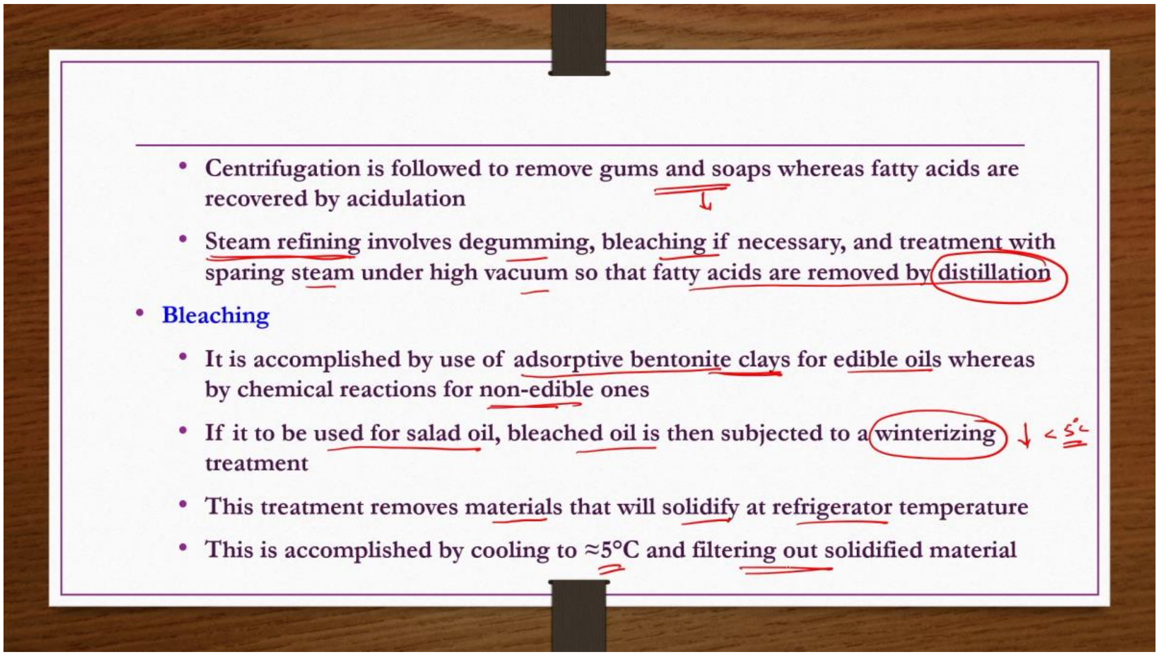

- Centrifugation is followed to remove gums and soaps whereas fatty acids are recovered by acidulation
- Steam refining involves degumming, bleaching if necessary, and treatment with sparing steam under high vacuum so that fatty acids are removed by distillation

- **Bleaching**
  - It is accomplished by use of adsorptive bentonite clays for edible oils whereas by chemical reactions for non-edible ones
  - If it to be used for salad oil, bleached oil is then subjected to a winterizing treatment ↓ < 5°c
  - This treatment removes materials that will solidify at refrigerator temperature
  - This is accomplished by cooling to ≈5°C and filtering out solidified material

Then centrifugation is followed to remove gums and soaps and those gums and soaps are taken as foods and then transferred to the soap manufacturing industries whereas the fatty acids are recovered by acidulation process. Steam refining involves degumming, bleaching if necessary and treatment with sparing steam under high vacuum so that fatty acids are removed by distillation primarily in this steam refining approach distillation is taking place. So, by distillation and then for the distillation purpose you are using steam actually whatever the heating requirement is there that you are providing by steam and then vacuum. So, this vacuum distillation causes the free fatty acids to be removed from the foods like gums and soaps etc. Then bleaching it is accomplished by use of adsorptive bentonite clays for edible oils whereas for non-edible oils it is possible by chemical reactions. If it to be used for salad oil then bleached oil is then subjected to winterizing treatment where winterizing in the sense you reduce the temperature to very low temperature something like 0 to 5 degree centigrade something like that. So, that whatever the impurities are there they will be solidified and then those solidified impurities would be filtered out. This treatment removes materials that will solidify at refrigerator temperature. This is accomplished by cooling to 5 degree centigrade approximately or even less sometimes and then finally filtering out the solidified material.

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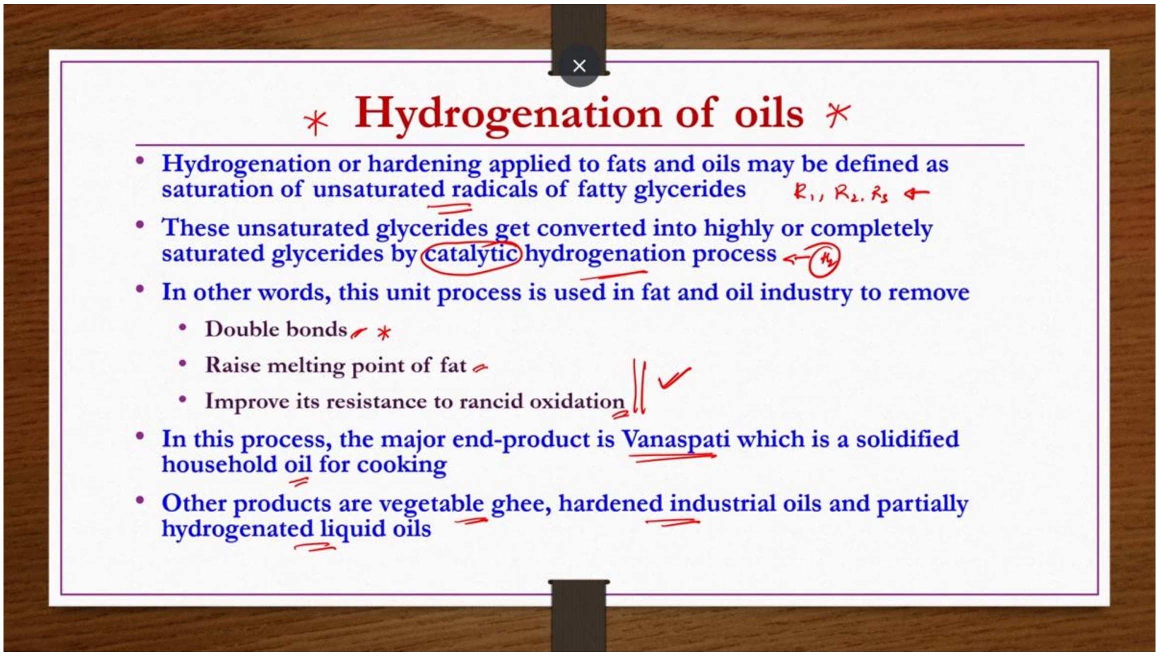

# * Hydrogenation of oils *

- Hydrogenation or hardening applied to fats and oils may be defined as saturation of unsaturated radicals of fatty glycerides $R_1, R_2, R_3$ ←
- These unsaturated glycerides get converted into highly or completely saturated glycerides by catalytic hydrogenation process ← $H_2$
- In other words, this unit process is used in fat and oil industry to remove
  - Double bonds *
  - Raise melting point of fat
  - Improve its resistance to rancid oxidation ✓
- In this process, the major end-product is Vanaspati which is a solidified household oil for cooking
- Other products are vegetable ghee, hardened industrial oils and partially hydrogenated liquid oils

Now, we see the third and most important step of processing of oils that is hydrogenation of oils. Hydrogenation of oils why it is required as we have already discussed in previous couple of lectures. The crushed oil crushed crude oil whatever or extracted crude oil whatever you are having that is primarily unsaturated one. So, that is double bonds are there. So, because of this one the melting point of oils and fats is in general low and then reactivity with oxygen is high both of them are not good for edible oils. How it is possible? It is possible by reducing the double bonds either partially or completely and that can be done by the hydrogenation. So, if there are no double bonds then melting point would be approximately 69 degree centigrade. If there are 3 double bonds let us say then melting point decreases to minus 4 or minus 5 degree centigrade something like that. That is that much severe is the effect of this unsaturation. Also rancidity if there are no double bonds then nil reactivity with oxygen is nil. But if you have 3 double bonds then reactivity with oxygen is extremely high. So, these are the primary problems associated with the unsaturated crude oil. But if you do the hydrogenation then you know the unsaturation would decrease partially or even completely depending on the operating conditions and depending on the oil, depending on the catalyst etc. those other factors are definitely be there. But only process to reduce this double bonds is the hydrogenation that is the reason it is most important and essential part of the processing of oils or purification of oils. So, hydrogenation or hardening it is also known as the hardening applied to fats and oils may be defined as saturation of unsaturated radicals of fatty glycerides whatever R1, R2, R3 etc that we have discussed or shown previous slides. You know they are nothing but the unsaturated radicals of fatty glycerides. So they are containing double bonds and then hydrogenation is nothing but making them saturated by removing the double bonds. These unsaturated glycerides get converted into highly or completely saturated glycerides by catalytic hydrogenation process. This process hydrogenation occur only in the presence of catalyst. It does not occur if there is no catalyst. It may be occurring but the required temperature pressure conditions may be very severe and then using a very high temperature pressure conditions is very dangerous especially when you are using hydrogen. Hydrogenation is occurring using the hydrogen. What we are going in this process basically chemistry point of view if you see whatever the glycerides are there those glycerides you are reacting with the hydrogen in the presence of catalyst at certain temperature and pressure. So that those unsaturated radicals get converted into the saturated radicals. In other words, this unit process is used in fat and oil industry to remove double bonds. If you remove the double bonds obviously melting point of the fat increases and then it improves resistance to rancid oxidation as well. So if you fulfill this condition obviously these two conditions would be fulfilled. These three things are happening in the hydrogenation of oils process. In this process major end product is Vanaspati which is a solidified household oil for cooking. Other products are vegetable ghee, hardened industrial oils and partially hydrogenated liquid oils as well. Now we see in detail about this hydrogenation process like you know raw materials, reaction, process flowchart, engineering problems etc. All those things we are going to discuss because it is very essential from the final products point of view.

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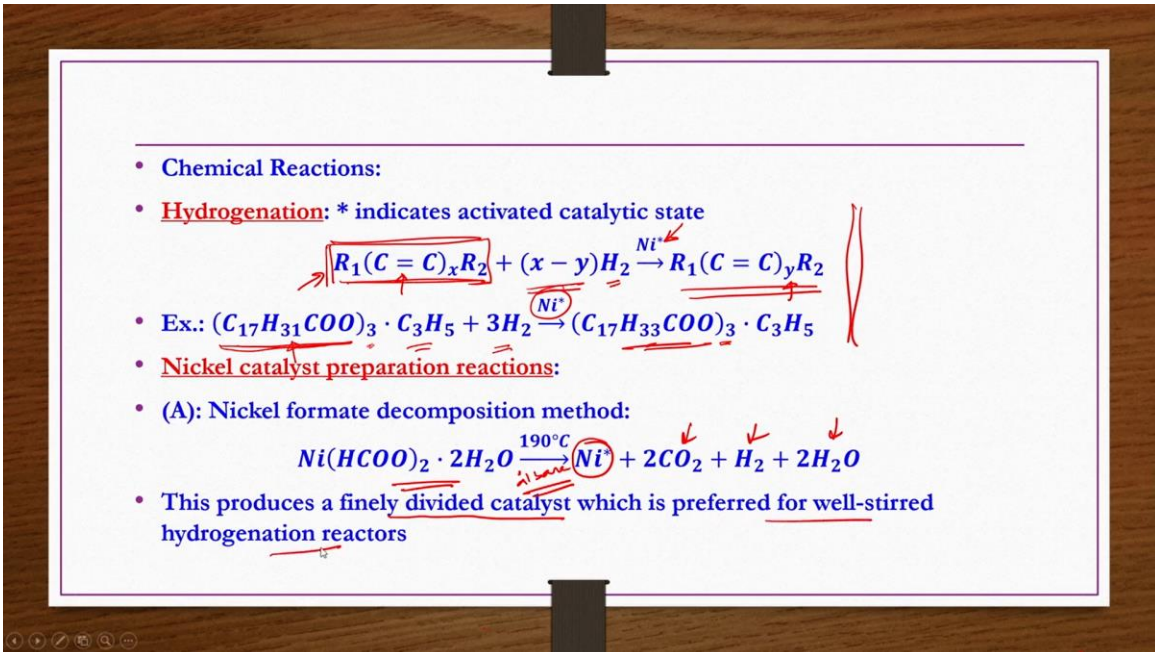

- **Chemical Reactions:**
- **Hydrogenation: * indicates activated catalytic state**

$$\boxed{R_1(C=C)_xR_2} + (x-y)H_2 \xrightarrow{Ni^*} R_1(C=C)_yR_2$$

- **Ex.: $(C_{17}H_{31}COO)_3 \cdot C_3H_5 + 3H_2 \xrightarrow{Ni^*} (C_{17}H_{33}COO)_3 \cdot C_3H_5$**
- **Nickel catalyst preparation reactions:**
- **(A): Nickel formate decomposition method:**

$$Ni(HCOO)_2 \cdot 2H_2O \xrightarrow{190°C} Ni^* + 2CO_2 + H_2 + 2H_2O$$

- **This produces a finely divided catalyst which is preferred for well-stirred hydrogenation reactors**

Chemical reactions, hydrogenation reaction first we see. In the reaction we have star that indicate activated catalytic state. Whatever the unsaturated glycerides are there, so that is represented by this one generalized one. R1 something like you know we have written like this R1 COO CH2 and then R2 COO CH and then R3 COO CH2. These are connected. So now these are represented general way in something like this. So this is the generalized representation of a glyceroids. X is the number that indicates number of double bonds that are present. This is not equal symbol, it is a double bond symbol. You should consider it as a double bond symbol and then you are reacting with x minus y moles of $H_2$. If you take 1 mole of a glyceride then you are reacting with x minus y moles of hydrogen in the presence of nickel catalyst. Then you are getting glyceride only but here number of double bonds decreased. Earlier it is x, here in this reaction x minus y what does it mean? You are using hydrogen. Hydrogen is essential that means x is greater than y. So from the x number of double bonds it is being reduced to y number of double bonds. Like that sequence of reaction may be progressing and then it is possible that there may not be any double bonds also but that depends on the degree of hydrogenation, temperature, pressure, catalyst, etc. So, it is a very generalized one. Now we take an example. Let us say radical whatever is there, oleic radical it is this one $C_{17}H_{31}COO_3$ and then 3, $3H_5$. This is one glyceride. So, it react with 3 moles of $H_2$ in the presence of a nickel catalyst. Then here now here what you have? 31 that means it must be having at least 2 double bonds. 2 and then this is 3 times or there is 6 double bonds would be there here. So that after this treatment what you are getting? You are getting only 3 double bonds. Out of 6 you are getting only 3 double bonds. So if it is 35, H number of H atoms is 35 that means there are no double bonds. If H atoms like it is you have to see something like alkanes generalized principle. Hn, $C_nH_{2n}$ plus 2 is alkane. If n is 17, so $C_{17}H_{36}$ supposed to be it should be but $C_{17}H_{35}$ and then this COO is also there. So that is the reason it is 35. Then it is it should be taken as like you know only single bonds are there and it is completely saturated one. But alkanes are there H, $C_nH_{2n}$ is the principle. So let us say $C_{17}$ then $H_{34}$ and then this what we have $C_{17}H_{33}$ is there because the COO is also there. So then 1H is being replaced by that one. So now here this indicates that there is 1 double bond, 1 double bond is there here. And then how many such things are there? Radicals are there, 3 are there. So overall total 3 double bonds are there in the product here. Whereas in the reactants 6 double bonds were there. So, by doing this hydrogenation reaction you have partially reduced the unsaturation. Likewise, sequence of the reactions you can continue and then you can reduce almost all you know double bonds and then you may even have completely saturated fats. Now this is about hydrogenation reaction in general but it requires catalyst since we are using here reactions associated or reaction that are being carried out using the nickel catalyst. We see preparation of a nickel catalyst only reactions part we see not the manufacturing or preparation part. Let us say if you wanted to prepare a nickel catalyst from the nickel formate decomposition the reaction is that nickel formate if you heat it to the 190 degrees centigrade in the oil base, this is oil base reaction. Then what happens? The carbon dioxide, hydrogen and then water vapor would be released and then you get activated nickel catalyst have sufficiently high surface area. This produced finely divided catalyst which is preferred for well-stayed hydrogenation reactors.

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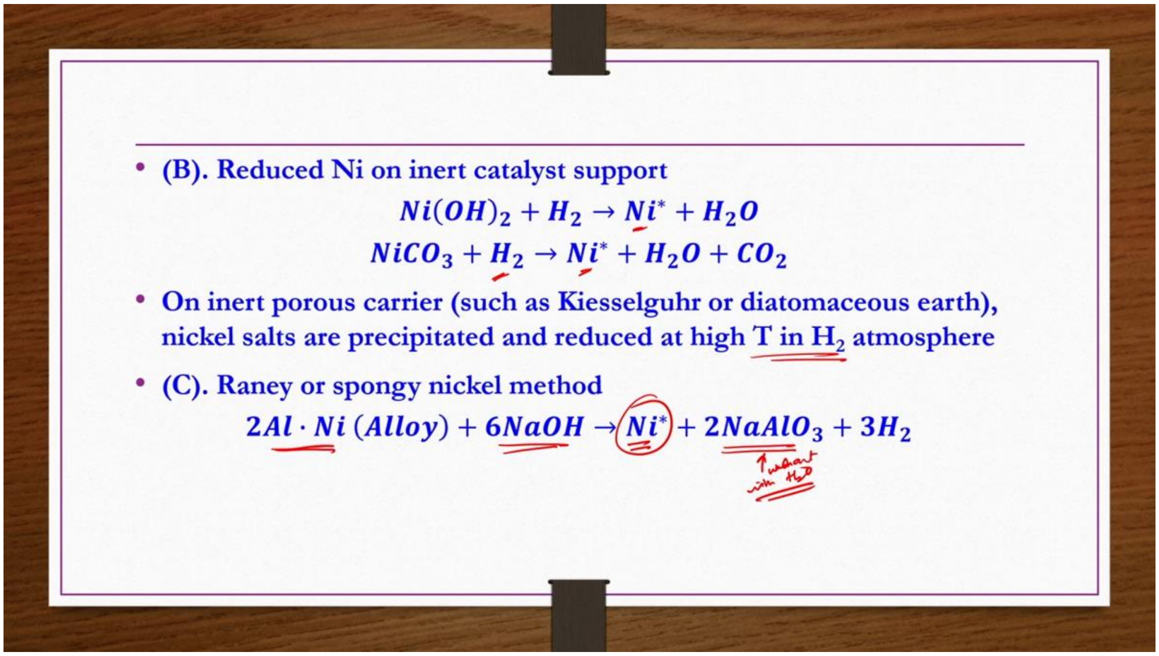

- **(B). Reduced Ni on inert catalyst support**

$$Ni(OH)_2 + H_2 \rightarrow \underline{Ni}^* + H_2O$$

$$NiCO_3 + \underline{H}_2 \rightarrow \underline{Ni}^* + H_2O + CO_2$$

- **On inert porous carrier (such as Kiesselguhr or diatomaceous earth), nickel salts are precipitated and reduced at high $\underline{\text{T in H}_2}$ atmosphere**
- **(C). Raney or spongy nickel method**

$$\underline{2Al \cdot Ni}\ (Alloy) + 6\underline{NaOH} \rightarrow \boxed{Ni^*} + 2\underline{NaAlO_3} + 3H_2$$

washout with $H_2O$

So next one is the reduced nickel on inert catalyst support. Here in general nickel salts in general are being impregnated on the inert catalyst supports and then they are reacted in the presence of hydrogen atmosphere at certain high temperature then you will get the nickel catalyst. So on inert porous carriers such as Kiesselguhr or diatomaceous earth, nickel salts are precipitated and reduced at high temperatures in hydrogen atmosphere. Next one is Raney or Spongy nickel method. Here what you have alumina nickel alloy and then if you react it with sodium hydroxide then you get nickel catalyst and then sodium aluminates may also form. These aluminates you can wash out with water. So, then you can get the spongy nickel catalyst.

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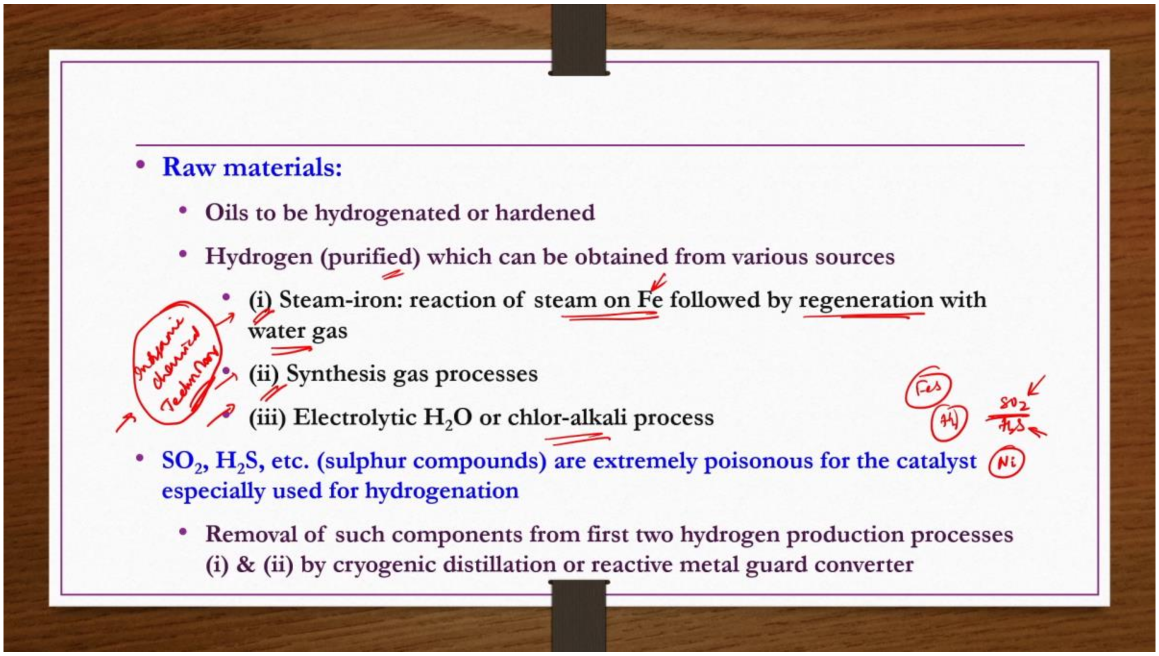

- **Raw materials:**
  - Oils to be hydrogenated or hardened
  - Hydrogen (purified) which can be obtained from various sources
    - (i) Steam-iron: reaction of steam on Fe followed by regeneration with water gas
    - (ii) Synthesis gas processes
    - (iii) Electrolytic $H_2O$ or chlor-alkali process
- **$SO_2$, $H_2S$, etc. (sulphur compounds) are extremely poisonous for the catalyst especially used for hydrogenation**
  - Removal of such components from first two hydrogen production processes (i) & (ii) by cryogenic distillation or reactive metal guard converter

Inorganic chemical Technology

FeS

$H_2$

$\frac{SO_2}{H_2S}$

Ni

Now the raw materials for the hydrogenation of oils obviously two important raw materials. One is the crude oil that you are trying to do the hydrogenation or you wanted to improve its saturation or decrease its unsaturation. Another one is how are you doing? You are doing by using hydrogen plus catalyst also you are using. So those are only primarily raw materials. So primary raw materials oils to be hydrogenated or hardened then hydrogen purified one which can be obtained from various sources. Actually, hydrogen is very explosive. It is very dangerous to hold or store in particular plants unless it is being consumed within short span of the time. So, in general in the plants wherever the hydrogen is required what industrialist or the people working in the plants they do? They try to produce that hydrogen in situ there in the plant itself and then immediately they try to use it. So different methods are there. Those are something like steam iron method where reaction of the steam on iron followed by regeneration with water gas reactions are there. Then synthesis gas processes then electrolytic H2O or chlor-alkali processes. All these methods we have already discussed in some other course like inorganic chemical technology. So, this course is also completed and then available on the MOOCs portal. So, all these details of manufacturing and purification of hydrogen by all 3 different methods are available in this course in organic chemical technology. Since it is not part of this course we are not going to discuss in detail about these things. In general what happens in these first 2 steps? There is a possibility of impurities like SO2, H2S such kind of impurities are possible that depends on the resource. Let us say iron you in general you take FeS or Fe2S3 something like these kind of components you take. So then obviously there is a possibility of SO2 or H2S formation along with the H2. So then purification is required. Why required? Because these SO2 or H2S or any sulphated components in general are very poisonous to catalyst which are being used for the hydrogenation. So they can also be removed anyway. How they are used or removed in general? They are removed by the cryogenic distillation or reactive metal guard converter.

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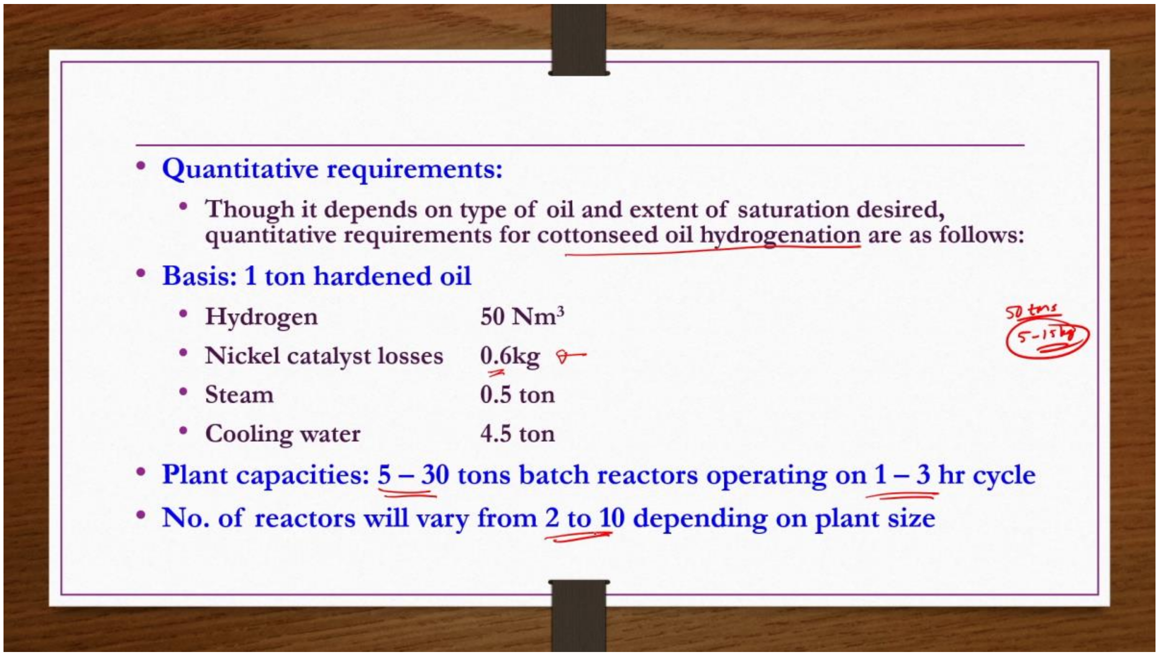

- **Quantitative requirements:**
  - Though it depends on type of oil and extent of saturation desired, quantitative requirements for cottonseed oil hydrogenation are as follows:
- **Basis: 1 ton hardened oil**

| | |
|---|---|
| Hydrogen | 50 Nm$^3$ |
| Nickel catalyst losses | 0.6kg |
| Steam | 0.5 ton |
| Cooling water | 4.5 ton |

- **Plant capacities: 5 – 30 tons batch reactors operating on 1 – 3 hr cycle**
- **No. of reactors will vary from 2 to 10 depending on plant size**

50 tons
5-15kg

Now quantitative requirements as I have been telling hydrogenation is nothing but the reducing the unsaturation or increasing the degree of saturation in the oils and that depends on the type of the oil and then catalyst and then what conditions are you operating etc. So those kind of things are there. So, because of that reason exactly quantitative requirements is difficult to mention but however with respect to cotton seed oil hydrogenation requirements, quantitative requirements are presented here. Let us say if you want to get 1 ton of hardened oil or hydrogenated oil if you target 1 ton then hydrogen 50 normal cubic meters required, nickel catalyst losses 0.6 kgs. Actually, nickel catalyst we are going to discuss in the flow chart anyway. What happens after the hydrogenation the slurry is filtered out in the filter press and then whatever the slurry is there that is nothing but the catalyst rich phase. That rich catalyst rich phase again we put back in the hydrogenation reactor. So, in this process there is a loss of catalyst there. So rather giving the quantity required for the hydrogenation how much quantity of nickel required so losses are provided here. Let us say if you have 50 tons plant then approximately 5 to 15 kg of catalyst is in general required. Steam 0.5 tons, cooling water 4.5 tons and then plant capacity is usually 5 to 30 tons batch reactors operating on 1 to 3 hour cycle. Number of reactors may vary from 2 to 10 depending on the plant size as well.

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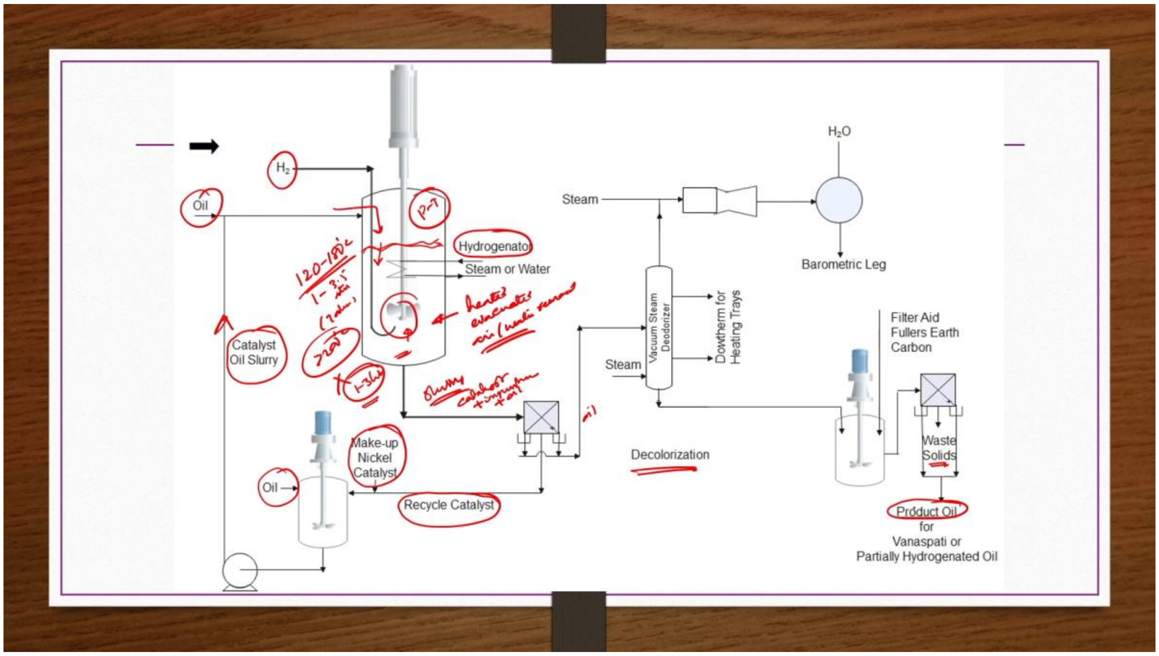

So, flow chart is shown here hydrogenation process. Here what happens you have a hydrogenator or the hydrogenation reactor this is that one. To this reactor you take the oil and then you heat it and then apply the vacuum to drive off or remove the air, water kind of thing removal takes place by this heating and applying by vacuum. Heating and applying vacuum will lead to removal of air and water from the oil if at all it is present in the crude oil. So then to this reactor what you try to supply you supply catalyst oil slurry from here and then hydrogen gas pure hydrogen gas from the top. This hydrogen is supplied to the bottom of the reactor so that you know one can use the turbines and then mix properly so that to disperse the oxygen to the entire volume of the oil. Let us say oil is occupied up to this volume so then it should not be released only at the top so that only the oil that is at the top is in interaction with the H2 but it should be in interaction with the entire volume so for that purpose the H2 is provided at the bottom. So, this catalyst slurry how are you making you take the oil and then catalyst in one batch mode container which is provided with the mixer as well. So, this oil and catalyst you mix and then supply to the reactor. So, after the reaction what happens you know the slurry usually you get after the hydrogenation has been done. That would be having catalyst plus impurities plus you know hydrogenated oil. This hydrogenation usually takes place between 120 to 180 degrees centigrade and then 1 to 3.5 atmosphere only at the max it goes to 7 atmosphere in general. This again depends on what is your final product whether Vanaspati or ghee or whatever you are trying to get so based on these conditions will vary. So those things we are going to see anyway. Also the H2 selectivity in the reaction also depends on this pressure temperature relation. So however it is not preferred to go for higher temperature more than 200 degrees centigrade is not preferred why because at the high temperature pyrolysis of oils may take place plus catalyst poisoning or you know sintering of the catalyst may also take place. If not poisoning sintering of the catalyst would definitely be taking place at higher temperature. So you do not prefer to go for higher temperatures. So after the hydrogenation reaction this reaction usually takes place for 1 to 3 hours depending on the degree of saturation is required and then type of oil and then what type of catalyst are using in general that is also make difference. So because of such conditions like you know you need long residence time that is also one of the reason that most of the hydrogenation processes are batch processes. So, this slurry after you know reaction that would be passed through a filter press where the clear oil or hydrogenated oil is separated as filtrate whereas the slurry or cake is nothing but the catalyst rich phase which is primarily catalyst only that would be recycled to the mixer where oil and catalyst are being you know mixed. If required to this container make up catalyst also provided. Whereas the filtrate oil whatever is there it has to be undergo next step of processing that is deodorizing or decolorization. So that is done in vacuum steam deodorizer followed by adsorption using fuller's earth carbon etc. So once these steps are done so the whatever the final liquid oil or you know fat that is there that would be again passed through a filter press to remove if at all there are any solids and then product oil finished oil that is collected for vanaspati or partially hydrogenated oil as per the condition that you have maintained.

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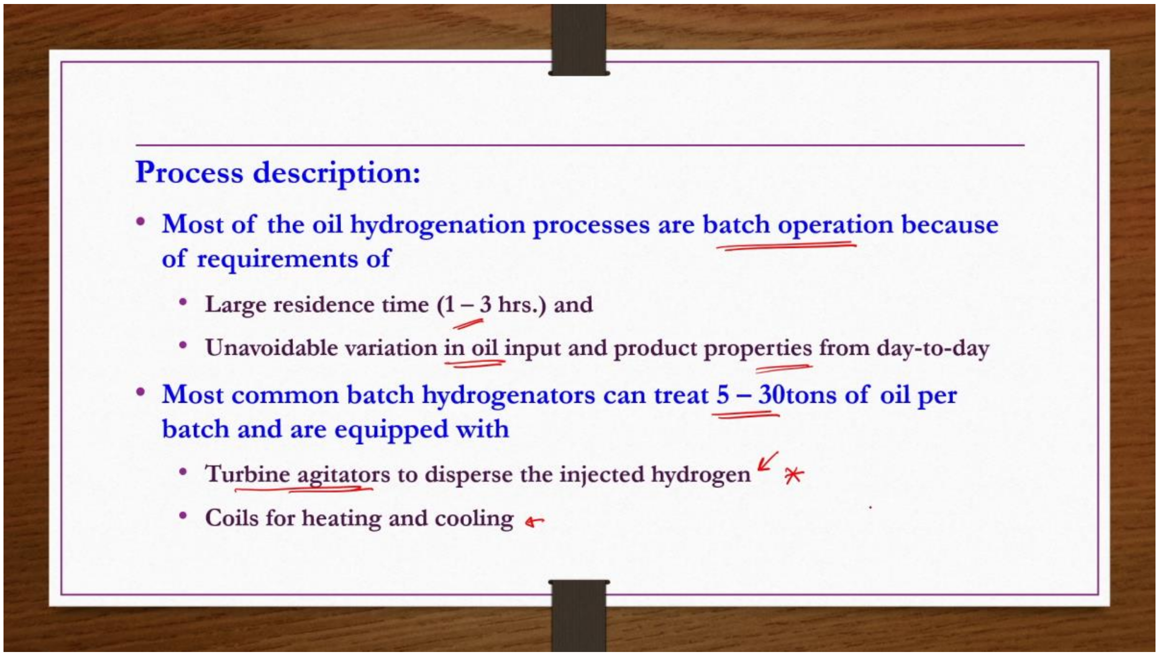

**Process description:**

- Most of the oil hydrogenation processes are batch operation because of requirements of
  - Large residence time (1 – 3 hrs.) and
  - Unavoidable variation in oil input and product properties from day-to-day
- Most common batch hydrogenators can treat 5 – 30tons of oil per batch and are equipped with
  - Turbine agitators to disperse the injected hydrogen
  - Coils for heating and cooling

So, whatever we have seen in the flowchart in the previous slide the same thing we are going to discuss here as a text. Most of the oil hydrogenation processes are batch operations because of a large residence time 1-3 hours when you have such large residence time it is not possible to do continuous. However, if you still wanted to do the continuous process then the size of the reactor should be very high and then flow of the material that should be as low as possible. But one has to see the final economics as well in that case. Then unavoidable variation in oil input and product properties from day to day. Whatever the oil that you get in general it may not be having the same properties every day and then you may not be aiming to do the same product. One day you may be planning for the vanaspati another day the plant may be required to make the ghee variations etc. So then product also variations may be there. So because of such reasons people prefer for batch operations. Most common batch hydrogenators can treat 5 to 30 tons of oil per batch and are often equipped with turbine agitators to disperse the injected hydrogen. It is very essential because this hydrogen has to be in contact with the entire volume of the crude oil. It is not only the top one. So that is the reason hydrogen is injected at the bottom and then turbine agitators are also provided so that to disperse it to the entire volume of the oil that is being hydrogenated. Then coils for heating and cooling also provide. So heating is required but also in this reaction you know whatever the delta H is there that is mildly exothermic that we are going to see under the thermodynamics and kinetics of the process. So, because of that one sometimes cooling is also required.

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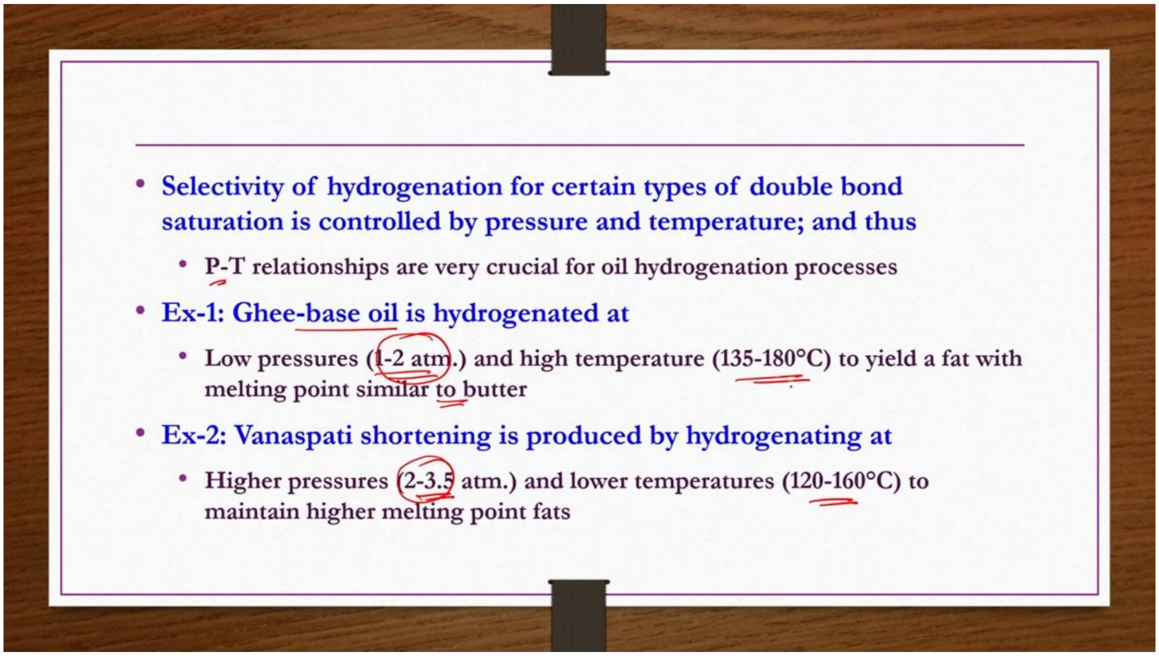

- **Selectivity of hydrogenation for certain types of double bond saturation is controlled by pressure and temperature; and thus**
  - P-T relationships are very crucial for oil hydrogenation processes
- **Ex-1: Ghee-base oil is hydrogenated at**
  - Low pressures (1-2 atm.) and high temperature (135-180°C) to yield a fat with melting point similar to butter
- **Ex-2: Vanaspati shortening is produced by hydrogenating at**
  - Higher pressures (2-3.5 atm.) and lower temperatures (120-160°C) to maintain higher melting point fats

Then selectivity of hydrogen for certain types of double bond saturation is controlled by pressure and temperature. Thus, pressure temperature relationships are crucial for oil hydrogenation process. How it is important? For example, if you are planning ghee based oil is to be hydrogenated at low pressures and then high temperatures to yield a fat with melting point similar to butter will be produced. Likewise, if Vanaspati shortening is produced by hydrogenating at high pressures and low temperatures to maintain higher melting points of fats you know these kind of variations would be there. So low pressure like you know it is low pressure only 3.5 atmosphere is also not very high pressure but within the range of conditions that are being operated or that are being required in the process. So these conditions are you know 3.5 atmosphere is considered as high. Similarly, the temperature also 180 is not too high temperature but if you go beyond 200 degree centigrade then pyrolysis would take place that is the reason the temperature upper limit of the temperature is restricted up to 180 degree centigrade only.

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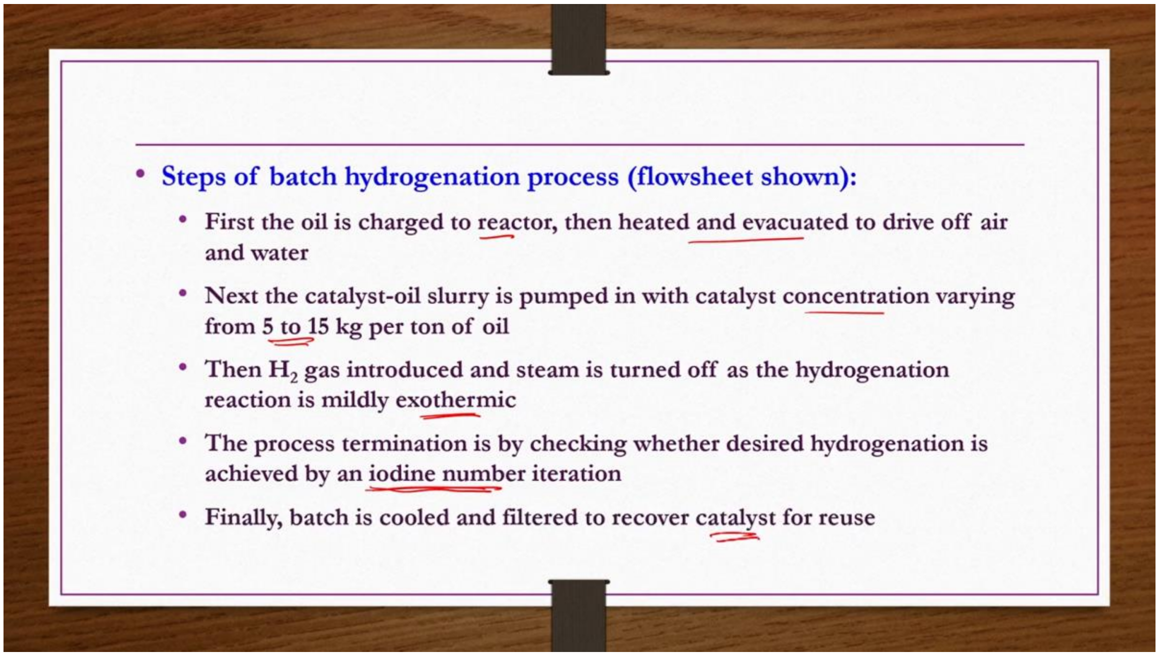

- Steps of batch hydrogenation process (flowsheet shown):
  - First the oil is charged to reactor, then heated and evacuated to drive off air and water
  - Next the catalyst-oil slurry is pumped in with catalyst concentration varying from 5 to 15 kg per ton of oil
  - Then $H_2$ gas introduced and steam is turned off as the hydrogenation reaction is mildly exothermic
  - The process termination is by checking whether desired hydrogenation is achieved by an iodine number iteration
  - Finally, batch is cooled and filtered to recover catalyst for reuse

Steps of batch hydrogenation process if you list out again that we have already seen in the flow sheet. First the oil is charged to the reactor then heated and evacuated to dry off air and then moisture if at all present. Next the catalyst oil slurry is pumped in with catalyst concentration varying between 5 to 15 kg per ton of oil. Then hydrogen gas introduced and steam is turned off as the hydrogenation reaction is mildly exothermic. The process termination has to be checked how do you check you continuously keep measuring the iodine number. So, if it is as per the requirement of the oil so then you can assume that the you know you should stop the hydrogenation process and then subsequent deodoration you should start. Finally, batch is cooled and filtered to recover catalyst for reuse.

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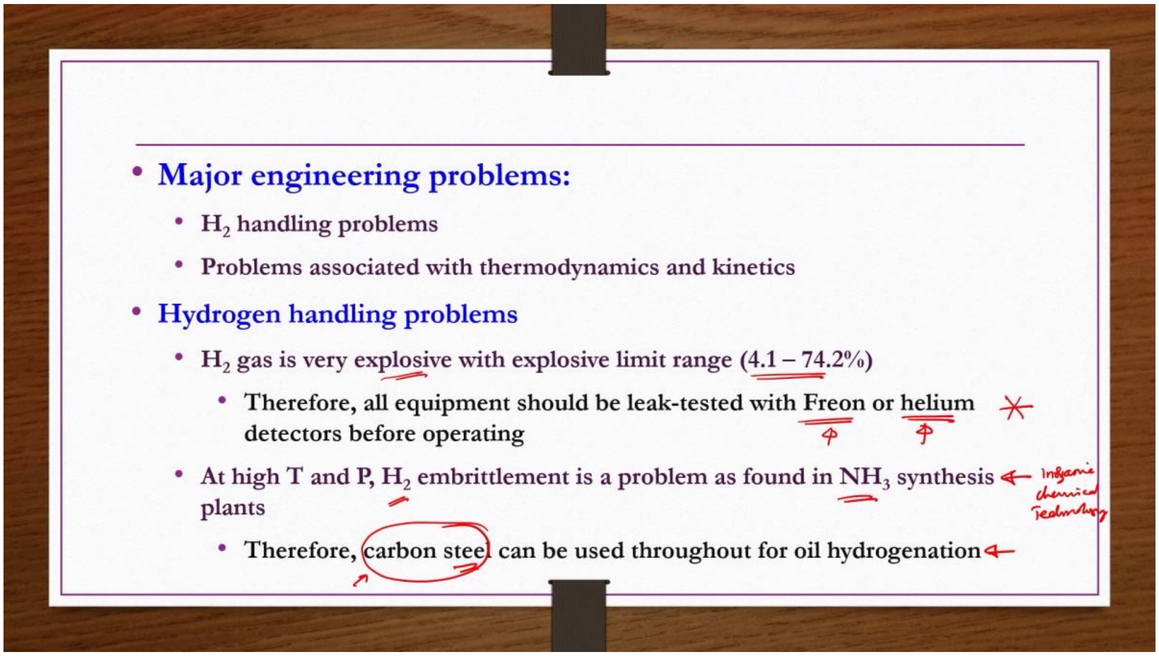

- **Major engineering problems:**
  - $H_2$ handling problems
  - Problems associated with thermodynamics and kinetics
- **Hydrogen handling problems**
  - $H_2$ gas is very explosive with explosive limit range (4.1 – 74.2%)
    - Therefore, all equipment should be leak-tested with Freon or helium detectors before operating
  - At high T and P, $H_2$ embrittlement is a problem as found in $NH_3$ synthesis plants
    - Therefore, carbon steel can be used throughout for oil hydrogenation

Inorganic chemical Technology

So now we will discuss major engineering problems of this hydrogenation of oils process. One is the hydrogen handling problem because hydrogen is very explosive if you do not handle properly explosions may take place. So, it has to be handled carefully also wherever there is a hydrogen requirement and then pressure or temperatures are applied. So, then material of construction also becomes very essential so that to avoid the cracking of the reactor during the hydrogenation process. So, such kind of problems are possible with hydrogen handling whereas problems associated with the thermodynamics and kinetics. Whereas different rate steps are there so which is controlling which is limiting all those things one has to have the clear idea so then there may be some problems associated with the thermodynamics and kinetics as well. So we are going to see steps associated or the other additional information associated with these problems. Let us start with hydrogen handling problems. Hydrogen gas is very explosive with explosive limit range of 4.1 to 74.2 percent. Therefore, all equipment should be leak test with Freon or helium detectors before operating. So this is very very essential. This leak testing is very very essential. At high temperature and pressure hydrogen embrittlement is a big problem as found in general in ammonia synthesis plants. So, these problems are also we have discussed in our other course in organic chemical technology. So, we are not repeating them here again. Therefore, carbon steel can be used throughout for the oil hydrogenation or hydrogenation reactor whatever is there that should be manufactured or material of construction should be carbon steel for hydrogenation reactor. In addition the entire other processes also one can use carbon steel for the hydrogenation process.

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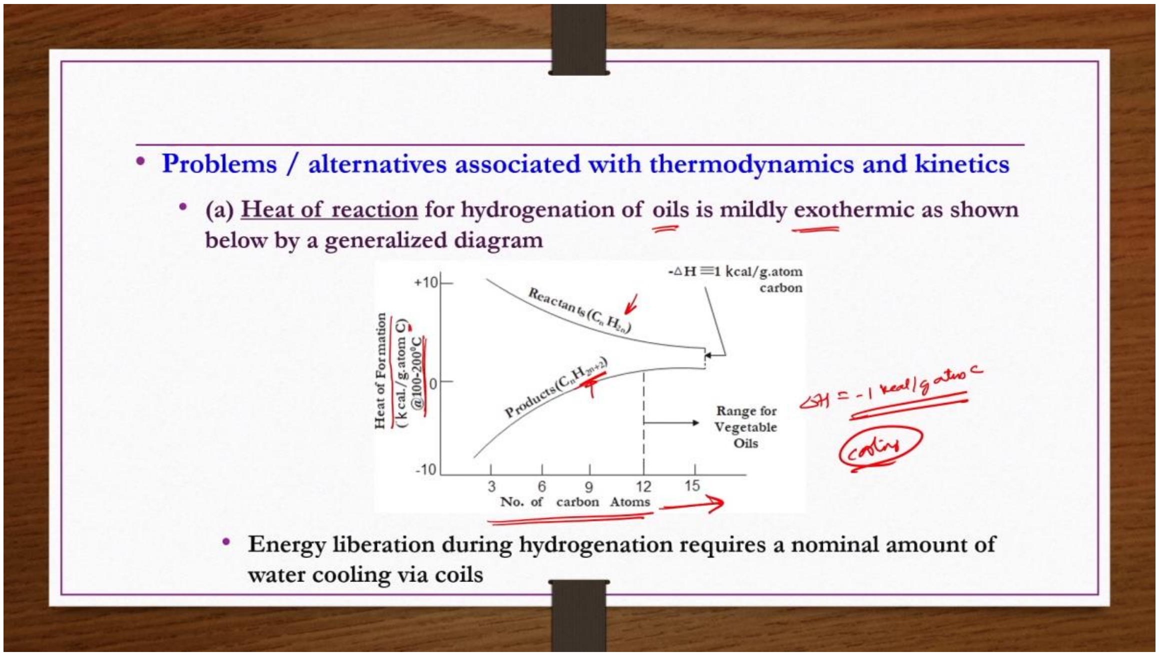

- **Problems / alternatives associated with thermodynamics and kinetics**
  - (a) Heat of reaction for hydrogenation of oils is mildly exothermic as shown below by a generalized diagram
  - Energy liberation during hydrogenation requires a nominal amount of water cooling via coils

Now problems or alternatives associated with the thermodynamics and kinetics of hydrogenation of oils would be discussed. So first one is the heat of reaction for hydrogenation of oils. It is mildly exothermic. Let us say if you see here per atom of carbon the heat of formation in kilocalorie per gram by varying the temperature of hydrogenation between 100 to 200 degrees centigrade then enthalpy of the reactants is decreasing with increasing the carbon atoms whereas the enthalpy of the products increasing with increasing the number of carbon atoms. See now here CnH2n is there that means there are double bonds are there. Here in the products CnH2n plus 2 is there so that means you know hydrogenation has been taken place and then it is a completely saturated one. And then how many carbon atoms that you should take in general for most of the vegetable oils you know range for carbon atoms is 12 or more than that one. So then you have to take this side difference of delta H. Now delta H product that is enthalpy of the product minus enthalpy of the reactants if you do that is coming minus 1 kilocalorie per gram per atom of the carbon. So, it is only mildly exothermic so certain cooling requirements would definitely be there or the reactor has to be jacketed so that cooling of the reactor may take place. Energy liberation during hydrogenation requires a nominal amount of water cooling via coils. Coils or jacketed columns are used in general.

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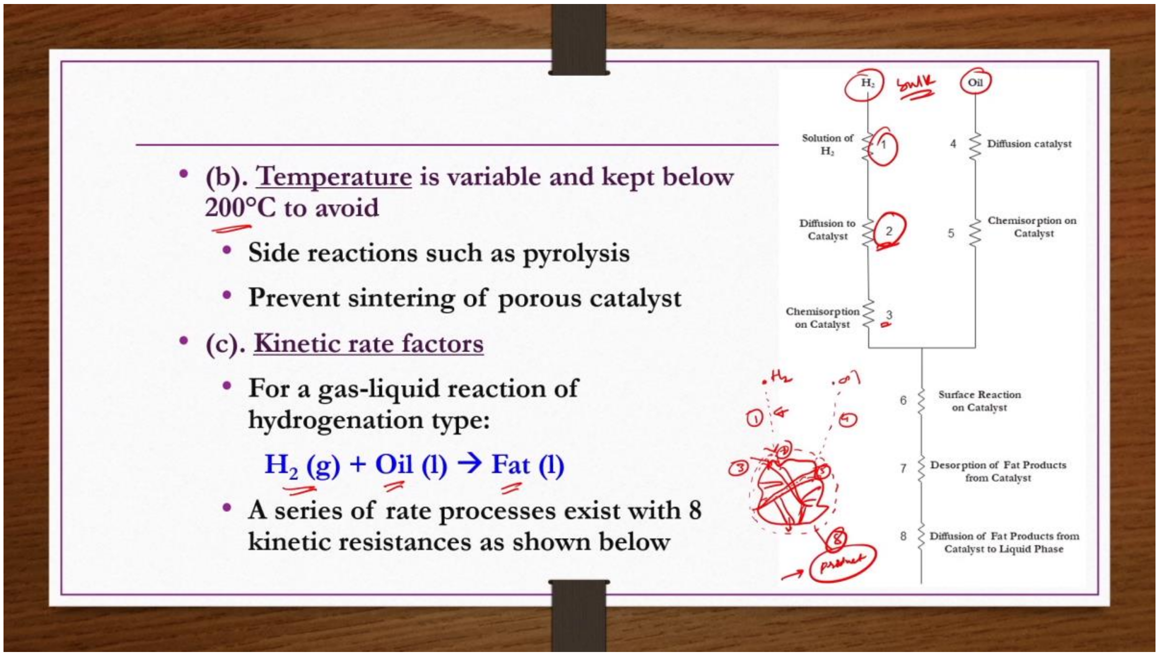

- (b). Temperature is variable and kept below 200°C to avoid
  - Side reactions such as pyrolysis
  - Prevent sintering of porous catalyst
- (c). Kinetic rate factors
  - For a gas-liquid reaction of hydrogenation type:

    $H_2 (g) + Oil (l) \rightarrow Fat (l)$
  - A series of rate processes exist with 8 kinetic resistances as shown below

The next parameter to be considered is the temperature and it has to be kept below 200 degrees centigrade why because of the possibility of pyrolysis of oil as well as the sintering of the catalyst because of these 2 reasons the temperature has to be less than 200 degrees centigrade and then kinetic rate factors several steps are there for a gas liquid reaction of hydrogenation type as we have discussed in general. You know let us say you have hydrogen and oil gas liquid reacting respectively and then fat liquid is forming. So a series of rate processes exist with 8 kinetic resistance as shown here. So here what you have before reaching the catalyst surface there is a H2 and then oil bulk storages are there. From the bulk hydrogen storage solution of H2 getting H2 solution is the first kinetic resistance and then that one getting diffused onto the catalyst surface is the second kinetic resistance and then chemisorption of hydrogen on catalyst surface is the third resistance. So, let us say you have the catalyst particle something like this, pores are there some of them are connected some of them are not connected something like this. So, in the bulk you have the H2. Now this H2 has to come on to the closer to the surface actually this catalyst surface may be you know covered with some kind of films of the products or something like that or sometimes reactants also. So, this H2 has to come up to the film level so then there is one step one kinetic resistance is there and then from here to reaching to the surface of the catalyst by diffusion that is the second step. And then this H2 getting chemically adsorbed onto the catalyst surface is the third step. So, three steps are there three kinetic resistance are there. Same is true for the oil also from the bulk then reaching up to the film that is let us say in labeling 4 and then from the film to the catalyst surface that is diffusion of oil to the catalyst surface is 4 and then chemically being adsorbed onto the catalyst surface is the fifth one. Then on the surface of the catalyst the reaction is take place when both H2 and then oil reach the catalyst surface then this catalytic heterogeneous reaction takes place between hydrogen and oil. So that takes that reaction takes place on the surface of the reaction or as well as the inside the pores. So, whatever the reaction takes place so that leads to the formation of the products and then products would be diffused back to the surface. So desorption of the product should also be taking place desorption of the product should take place and then diffusion of the product from the surface to the bulk product storage. So, this is the step number 8. How this diffusion is taking place that is because of the concentration difference. Initially the concentration of the product was 0 everywhere they are formed inside the catalyst force as well as the surface of the catalyst. So then concentration of the products is higher compared to the bulk reason. So, because of the concentration difference the product from the catalyst surface as well as the from interior of the catalyst they will come to the bulk location into the bulk fluid stream. So, this occurs because of the concentration difference. These are the 8 steps are there so out of this the step number 1 and 2 are the rate limiting steps because they require higher energy to occur these 2 steps.

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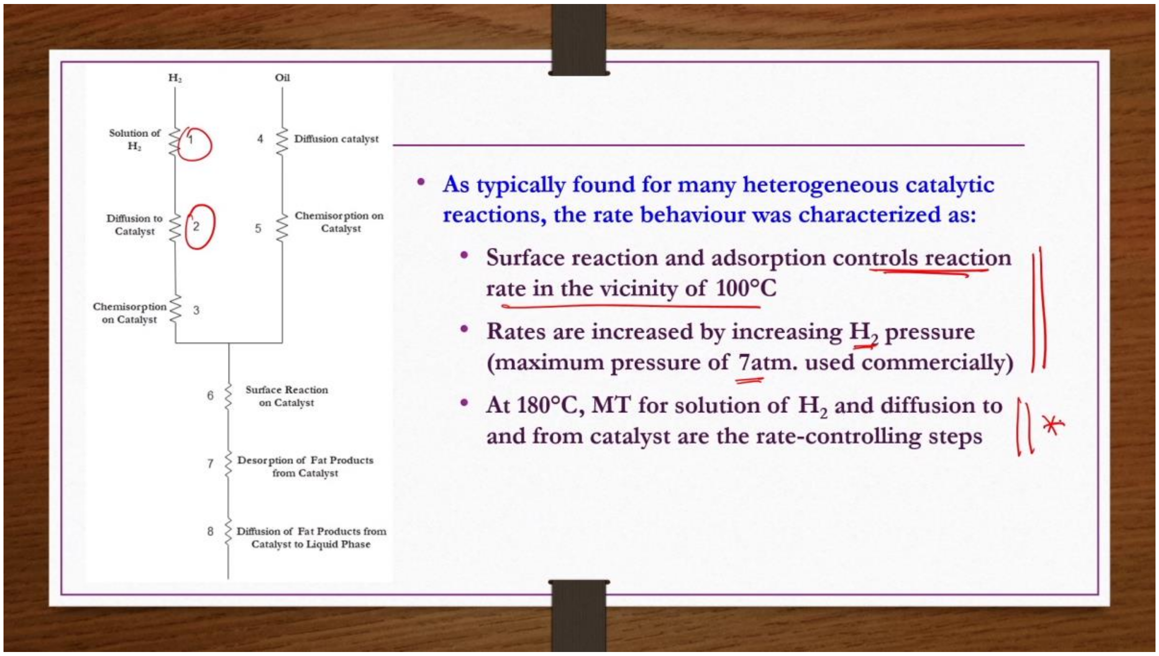

- As typically found for many heterogeneous catalytic reactions, the rate behaviour was characterized as:
  - Surface reaction and adsorption controls reaction rate in the vicinity of 100°C
  - Rates are increased by increasing $H_2$ pressure (maximum pressure of 7atm. used commercially)
  - At 180°C, MT for solution of $H_2$ and diffusion to and from catalyst are the rate-controlling steps

The same is shown here again as typically found for many heterogeneous catalytic reactions the rate behavior was characterized as surface reaction and adsorption controls reaction rate in the vicinity of 100 degree centigrade and then rates are increased by increasing H2 pressure maximum up to 7 atmosphere used commercially. So, these are the observations from the realistic conditions. So, one has to do the experiments and then one has to find out these conditions. They are not by some mathematical or theoretical calculations. At 180 degree centigrade mass transfer for solution of H2 and diffusion to and from catalyst are the rate controlling steps because of higher energy requirement for these steps. So that is all about the hydrogenation of oils. So once the hydrogenation of oil is done so mostly you know saturation degree has increased or unsaturation degree has decreased.

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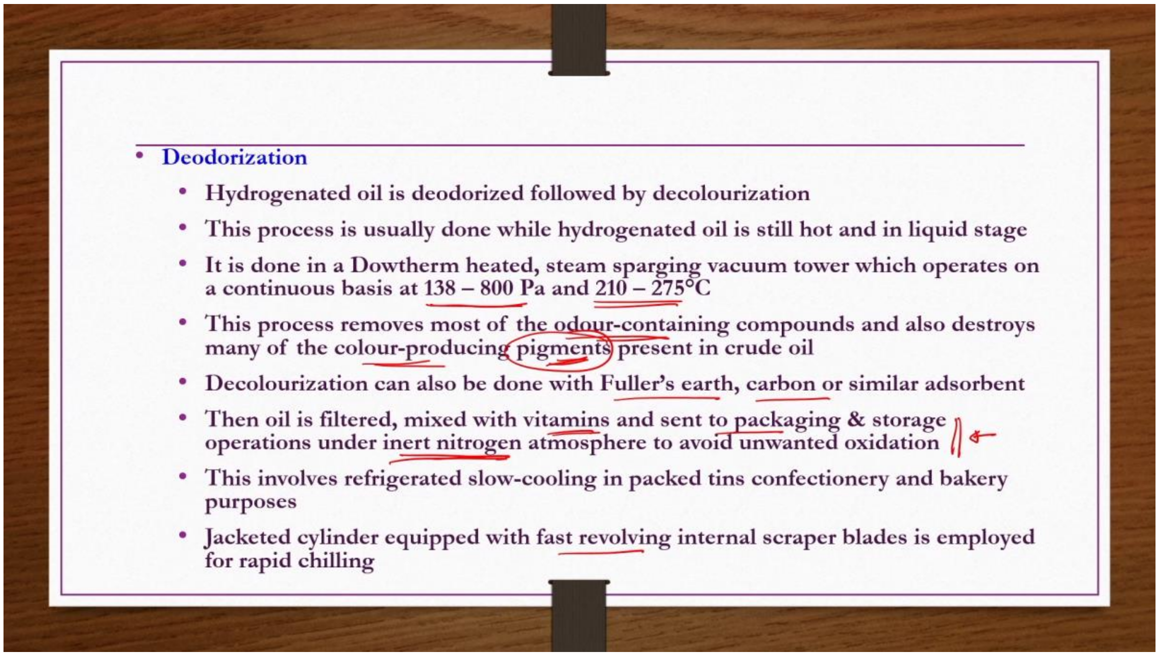

- **Deodorization**
  - Hydrogenated oil is deodorized followed by decolourization
  - This process is usually done while hydrogenated oil is still hot and in liquid stage
  - It is done in a Dowtherm heated, steam sparging vacuum tower which operates on a continuous basis at 138 – 800 Pa and 210 – 275°C
  - This process removes most of the odour-containing compounds and also destroys many of the colour-producing pigments present in crude oil
  - Decolourization can also be done with Fuller's earth, carbon or similar adsorbent
  - Then oil is filtered, mixed with vitamins and sent to packaging & storage operations under inert nitrogen atmosphere to avoid unwanted oxidation
  - This involves refrigerated slow-cooling in packed tins confectionery and bakery purposes
  - Jacketed cylinder equipped with fast revolving internal scraper blades is employed for rapid chilling

Still after that also you may need to do some kind of a processing that is deodorization or decolorization that we see now. Hydrogenated oil is deodorized followed by decolorization. This process is usually done while hydrogenated oil is still hot and in liquid stage. It is done in a Dowtherm heated steam sparging vacuum tower which operates on a continuous basis at 138 to 800 Pascal and 210 to 275 degree centigrade. This process removes most of the ordour-containing compounds and also destroys many of the color producing pigments present in the crude oil or hydrogenated oil. Even after the hydrogenation some of the pigments may be present in general. That is the reason we are doing this deodorization and decolorization process because the colors are basically incurred because of the presence of the pigments. Decolorization can also be done with Fuller's earth carbon or similar absorbents as well. Then the oil is filtered mixed with vitamins if required and then sent to packaging and storage operations but under inert nitrogen atmosphere to avoid unwanted oxidation. Though that may not be taking place, if still oxidation is taking place that means your hydrogenation reaction is not successful. If the hydrogenation reaction has been successfully done then the oil or fat is completely saturated and then its reactivity with the oxygen or air is nil. So but still if the complete hydrogenation may not be taking some time so then under such conditions it is better to avoid oxidation of the such product oil. So, for that you required an inert nitrogen atmosphere storage conditions. This involves refrigerated slow cooling in packed tins, confectionery and bakery purpose. Jacketed cylinder equipped with fast revolving internal scraper blades is employed for rapid chilling as well. So that is all about the processing of oils in the batch mode. Let us say if you wanted to discuss continuous processing of edible oils we discussed through flow chart.

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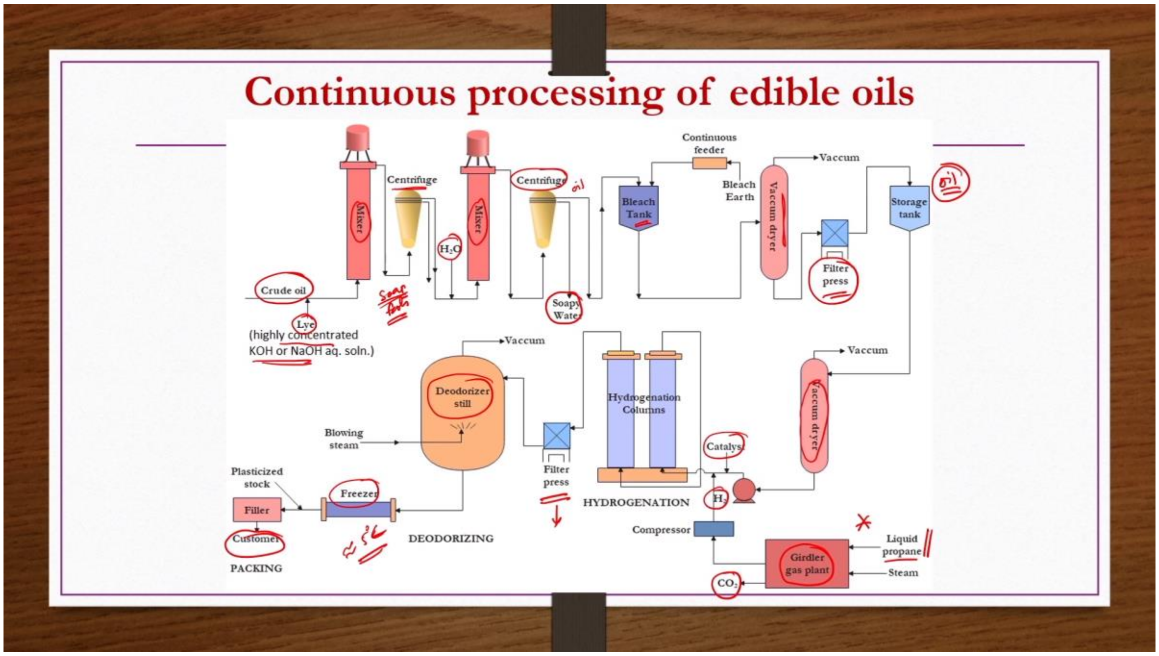

Continuous processing of edible oils

So here what we have? We have a crude oil which is nothing but the oil that has been extracted from the vegetable seeds directly whatever the oil that you get after the extraction that is nothing but crude oil. This oil along with the lye which is nothing but highly concentrated KOH or NaOH aqueous solution they are mixed in a mixer. What is the purpose of this one? This purpose is to remove the soaps or foods. So, by reacting with NaOH this crude oil in a mixer then what happens whatever the foods are there or the soaps are there they would be coagulating and they can be separated at. How they would be separated? They would be separated using the centrifuge. If still some amount of soaps are remaining then what you do? You mix the clear liquid from the or clear oil from the centrifuge which is not completely oil. Still if you believe that there are some soaps then what you have to do? You have to add or mix with water and then once again you have to do the centrifugation. So that soapy water would be collected as the one phase whereas the oil would be collected as the other phase in the centrifuge. How it occurs in the centrifuge that we are going to see in the next slide anyway. Then this oil free from the foods and then soapy water etcetera would be taken to the bleach tank where bleaching is done. Then vacuum drying and then filter press processes are followed so that to avoid or remove any contaminants or impurities solid impurities are still present or if any moisture is there that would also be removed by the vacuum dryer. If at all impurities because of the bleaching reactions are there or still some foods are there or small amount of seeds are present, crushed seeds are present they will all be removed by the filter press process. Then the clear oil is taken to the storage tank which is still not hydrogenated. It is only food removal and then bleaching has been done and then moisture removal has been done by the vacuum dryers but it is not been hydrogenated. Before doing the hydrogenation we have to do all these steps. So, then this oil if you are doing immediately the hydrogenation so then this vacuum dryer may not be required. If you are doing after couple of weeks or couple of months so then there is a possibility that moisture may be captured and then that has to be removed by the vacuum dryer after removing the moisture by the vacuum dryer. Oil is taken to the hydrogenation column along with the required catalyst and then hydrogen. See here hydrogen is produced at the plant site by reacting liquid propane with the steam that is in a Girdler gas plant. So by this reaction what happens you get hydrogen and then $CO_2$. You remove $CO_2$ or do this operation of this gases mixture get the $H_2$ that $H_2$ you directly supply to the hydrogenation columns. So, this now there is no danger of storing of hydrogen because hydrogen is explosive. So, this is more better. Now this hydrogenation reaction may be taking place in one reactor two reactors or up to ten reactor depends on the capacity. After the hydrogenation whatever the final liquid is there so that you pass through the filter press so that to recover the catalyst and then reuse them and then filtrate you take to the deodorization still. So this filtrate oil which is hydrogenated already if it is still required deodorization or decolorization subsequently you do the same thing and then you take it to a freezer. Let us say if at all some kind of solidifying material or their impurities are there which may be solidified at the low temperature approximately 5 degrees centigrade or something less than that one. So that oil you pass through the freezer after deodorization you pass it through the freezer and then do the filtration to remove the solidified material and then final product you take to the packaging etc. So this is continuous processing of edible oils.

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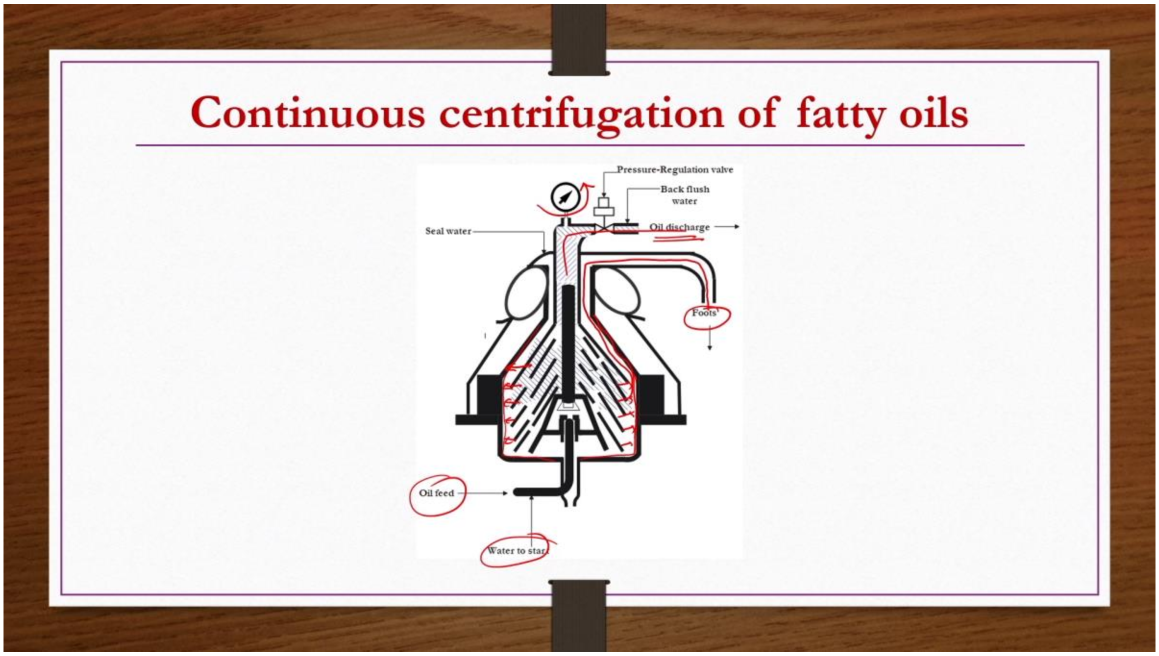

Continuous centrifugation of fatty oils

Now the centrifugation is very much important step in the continuous processing of edible oils that we have seen. So continuous centrifugation of fatty oils is shown here. So centrifugation that is it is nothing but a centrifugation bowl. So this is the centrifugation bowl which is having a inlet at the bottom from which you can give the oil feed if required water is also given to start. So, then this bowl what happens it is having provision to rotate when it rotates because of the centrifugation forces the heavier foods etc. would be thrown towards the wall and then lighter oil would be remaining towards the center of the column. So that oil is discharged from the top this way. Whereas the heavier foods are collected from here this part and then they are discarded as foods or after the collection as foods they will be transported to the soap manufacturing industries for making soaps because foods are a good ingredients for the soap making. So, this is a working principle of centrifugation process continuous centrifugation process.

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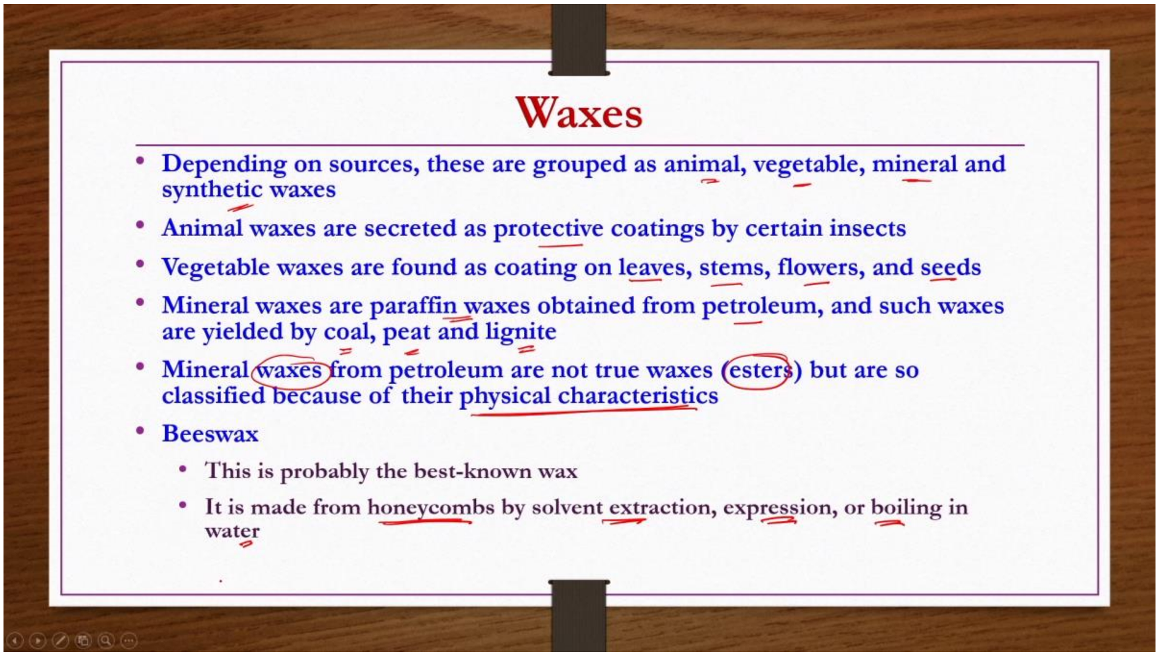

## Waxes

- Depending on sources, these are grouped as animal, vegetable, mineral and synthetic waxes
- Animal waxes are secreted as protective coatings by certain insects
- Vegetable waxes are found as coating on leaves, stems, flowers, and seeds
- Mineral waxes are paraffin waxes obtained from petroleum, and such waxes are yielded by coal, peat and lignite
- Mineral waxes from petroleum are not true waxes (esters) but are so classified because of their physical characteristics
- Beeswax
  - This is probably the best-known wax
  - It is made from honeycombs by solvent extraction, expression, or boiling in water

So with this we complete extraction of oils as well as the processing of oils. Now we get into the details of waxes. Depending on the source from where are we getting these waxes this can be classified as animal waxes, vegetable waxes, mineral waxes and synthetic waxes. Animal waxes are secreted as protective coatings by certain insects. Vegetable waxes are found as coatings on leaves, stems, flowers and seeds. So, we do some kind of physicochemical processes to extract them. Whereas the mineral waxes are paraffin waxes obtained from petroleum industries and such waxes are yielded by coal, peat and then lignite as well. Mineral waxes are in general esters but still we consider them as waxes because of their physical characteristics. Their physical characteristics are much closer to the waxes that is the reason these esters you know which we are getting from the petroleum industries they are also considered as waxes. So now what we do we take a few types of common waxes and then conclude today's lecture. Beeswax, this is probably the best known wax how we get? We get it from the honeycombs by solvent extraction followed by the expression or by boiling in water. In most of the candles this beeswax is in general present.

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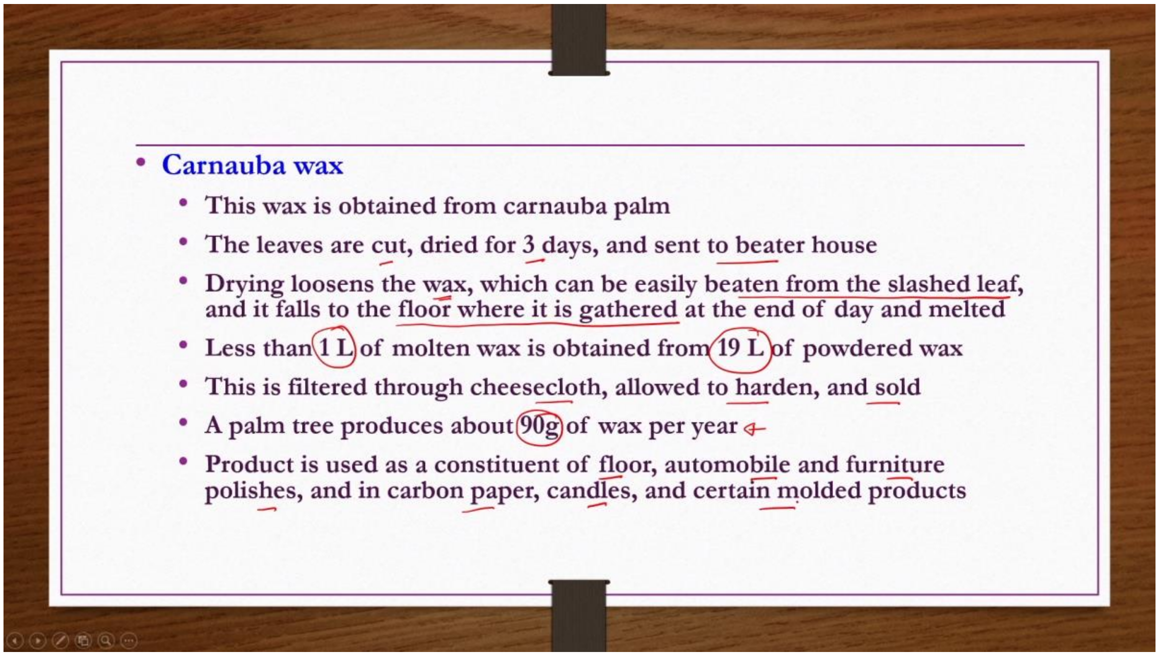

- **Carnauba wax**
  - This wax is obtained from carnauba palm
  - The leaves are cut, dried for 3 days, and sent to beater house
  - Drying loosens the wax, which can be easily beaten from the slashed leaf, and it falls to the floor where it is gathered at the end of day and melted
  - Less than ① L of molten wax is obtained from 19 L of powdered wax
  - This is filtered through cheesecloth, allowed to harden, and sold
  - A palm tree produces about 90g of wax per year
  - Product is used as a constituent of floor, automobile and furniture polishes, and in carbon paper, candles, and certain molded products

Then next one is Carnauba wax. This wax is obtained from Carnauba palm. The leaves are cut dried for 3 days and sent to beater house, a kind of mixing by hot water or individually mixing or beating them into fragmentation. Drying loses the wax which can be easily beaten in from the slashed leaf and it falls on the floor where it is gathered at the end of the day and melted. Less than 1 liter of molten wax is obtained from 19 liters of powdered wax in general. This is filtered through cheesecloth allowed to harden and sold.

A palm tree produces only about 90 grams of wax per year naturally if you go by the natural process. Whereas you take its leaves and then do the cutting drying process and then beating process etc. Then you can extract larger amount of wax in less time. Product is used as a constituent of floor, automobile and furniture polishes and in carbon paper, candles and certain molded products as well.

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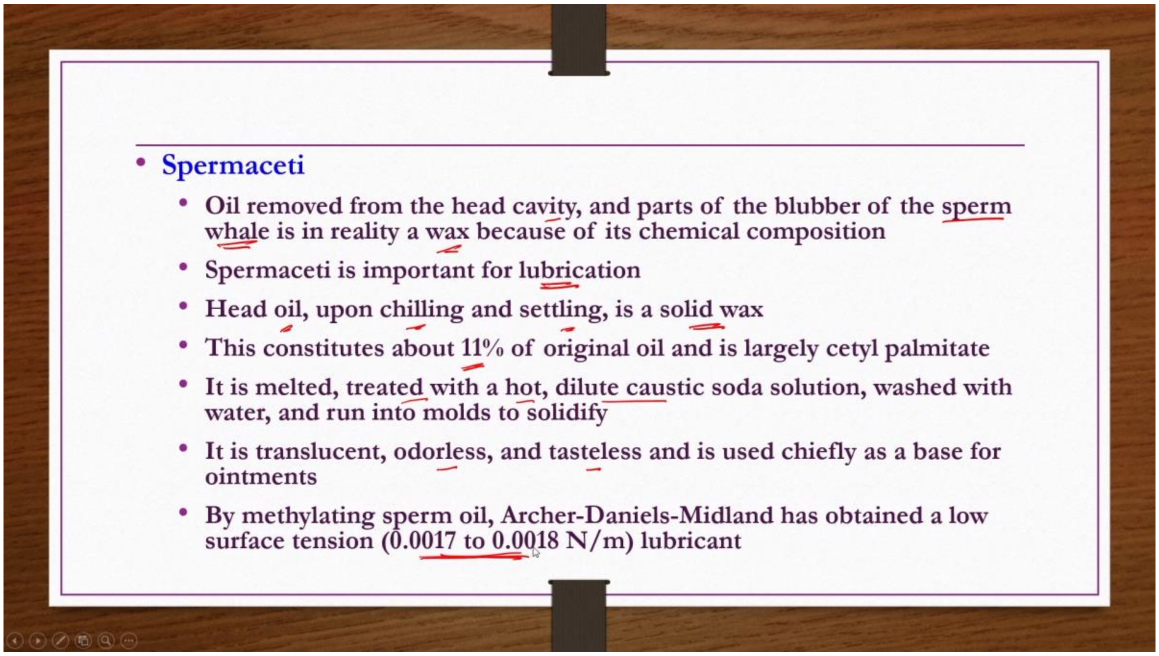

- **Spermaceti**
  - Oil removed from the head cavity, and parts of the blubber of the sperm whale is in reality a wax because of its chemical composition
  - Spermaceti is important for lubrication
  - Head oil, upon chilling and settling, is a solid wax
  - This constitutes about 11% of original oil and is largely cetyl palmitate
  - It is melted, treated with a hot, dilute caustic soda solution, washed with water, and run into molds to solidify
  - It is translucent, odorless, and tasteless and is used chiefly as a base for ointments
  - By methylating sperm oil, Archer-Daniels-Midland has obtained a low surface tension (0.0017 to 0.0018 N/m) lubricant

Next one is Spermaceti. Oil removed from the head cavity and parts of the blubber of the sperm whale is in reality is a wax because of its chemical composition. It is important for lubrication purpose. Head oil upon chilling and settling you get solid wax from the head oil. This constitutes about 11 percent of original oil and is largely cetyl palmitate. It is melted, treated with hot, dilute caustic soda solution, washed with water and run into molds to solidify. It is translucent, odorless and tasteless and is used chiefly as a base and is used primarily as a base for ointments. By methylating sperm oil, one can get lubricants of very small surface tension values.

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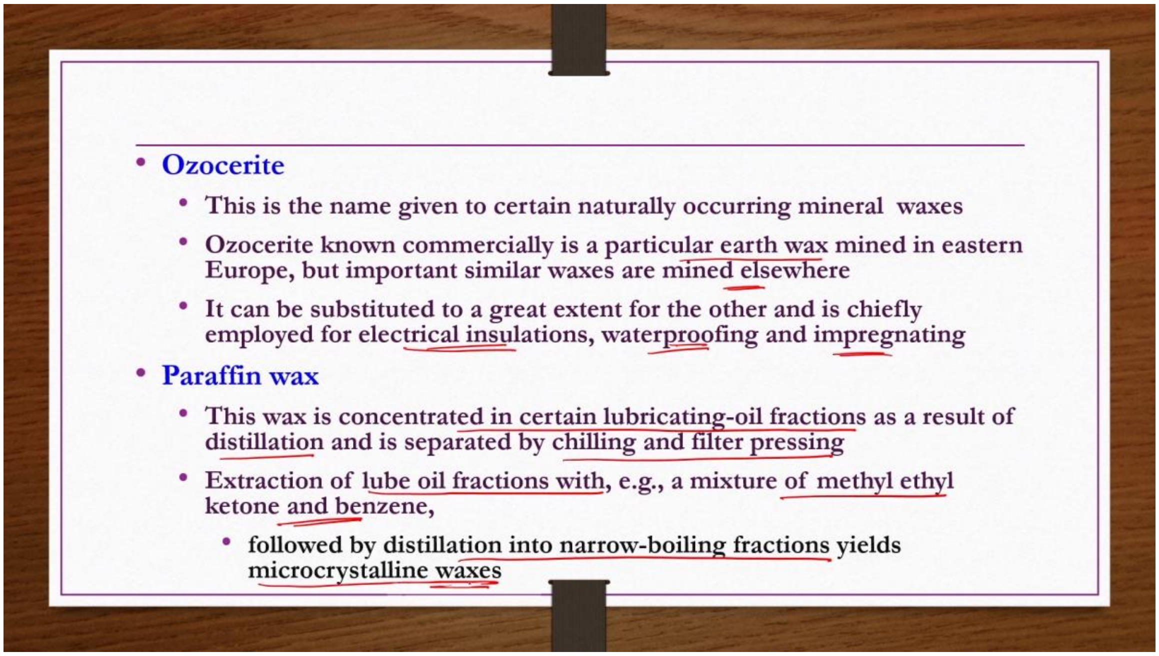

- **Ozocerite**
  - This is the name given to certain naturally occurring mineral waxes
  - Ozocerite known commercially is a particular earth wax mined in eastern Europe, but important similar waxes are mined elsewhere
  - It can be substituted to a great extent for the other and is chiefly employed for electrical insulations, waterproofing and impregnating
- **Paraffin wax**
  - This wax is concentrated in certain lubricating-oil fractions as a result of distillation and is separated by chilling and filter pressing
  - Extraction of lube oil fractions with, e.g., a mixture of methyl ethyl ketone and benzene,
    - followed by distillation into narrow-boiling fractions yields microcrystalline waxes

Next is Ozocerite. This is the name given to certain naturally occurring mineral waxes. Ozocerite known commercially is a particular earth wax mined in Eastern Europe but important similar waxes are also mined elsewhere in United States of America. It can be substituted to a great extent for the other and is primarily employed for electrical insulations, waterproofing and impregnating. Next one is the Paraffin wax. This wax is concentrated in certain lubricating oil fractions as a result of distillation and is separated by chilling and filtering process. Extraction of lube oil fractions with using a mixture of methyl, ethyl, ketone and benzene followed by distillation into narrow boiling fractions yield microcrystalline waxes.

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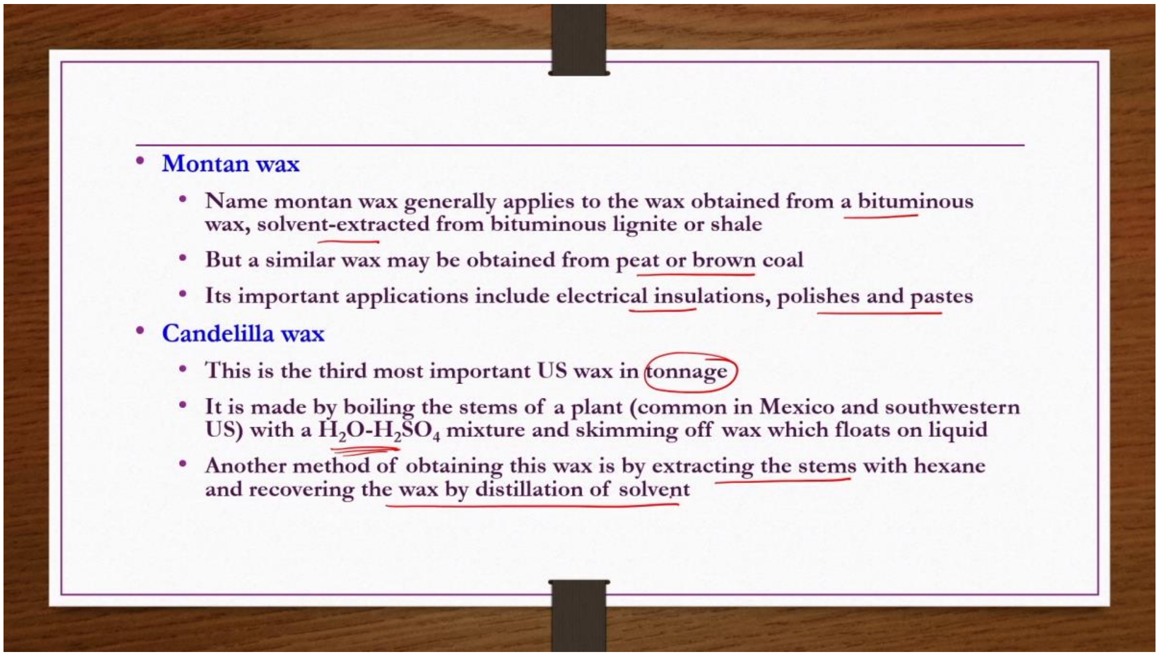

- **Montan wax**
  - Name montan wax generally applies to the wax obtained from a bituminous wax, solvent-extracted from bituminous lignite or shale
  - But a similar wax may be obtained from peat or brown coal
  - Its important applications include electrical insulations, polishes and pastes
- **Candelilla wax**
  - This is the third most important US wax in tonnage
  - It is made by boiling the stems of a plant (common in Mexico and southwestern US) with a $H_2O$-$H_2SO_4$ mixture and skimming off wax which floats on liquid
  - Another method of obtaining this wax is by extracting the stems with hexane and recovering the wax by distillation of solvent

Montan wax, the name is given generally to the wax obtained from a bituminous wax, solvent extracted from bituminous lignite or shale but similar wax may be obtained from peat or brown coal as well. Its important applications include electrical insulation, polishes and paste. Candelilla wax, this is the third most important wax in the United States especially in terms of the tonnage of the production. It is made by boiling the stems of plant with H2SO4 and then water mixture and skimming of the wax which floats on the liquid because of low density. Another method of obtaining this wax is by extracting the stems with hexane and recovering the wax by distillation of solvent.

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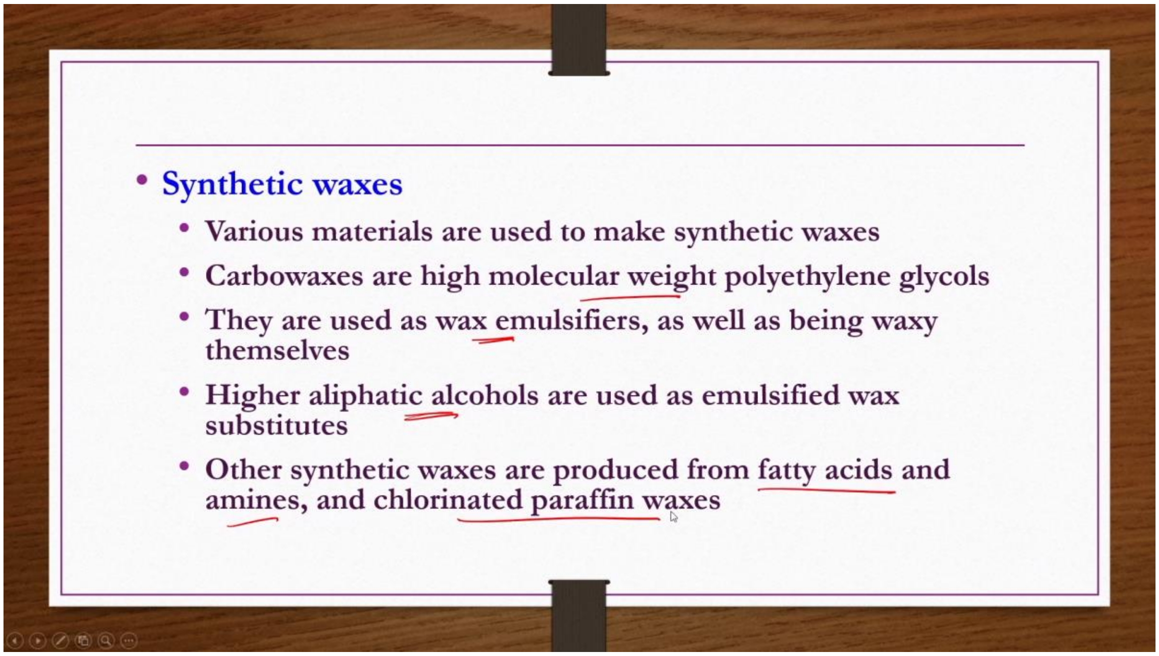

- **Synthetic waxes**
  - Various materials are used to make synthetic waxes
  - Carbowaxes are high molecular weight polyethylene glycols
  - They are used as wax emulsifiers, as well as being waxy themselves
  - Higher aliphatic alcohols are used as emulsified wax substitutes
  - Other synthetic waxes are produced from fatty acids and amines, and chlorinated paraffin waxes

Finally, synthetic waxes, various materials are used to make synthetic waxes. Carbowaxes are high molecular weight polyethylene glycols. They are used as wax emulsifiers as well as being waxy themselves. Higher aliphatic alcohols are used as emulsified wax substitutes. Other synthetic wax are produced from fatty acids and amines and chlorinated paraffin waxes as well.

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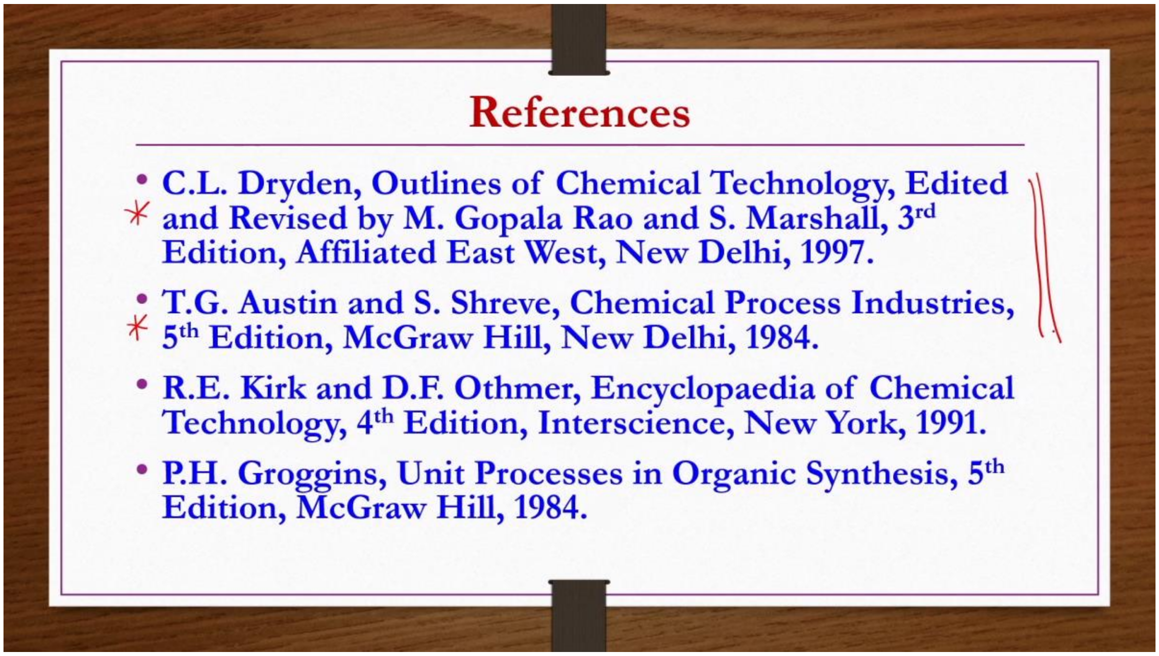

## References

- C.L. Dryden, Outlines of Chemical Technology, Edited and Revised by M. Gopala Rao and S. Marshall, 3rd Edition, Affiliated East West, New Delhi, 1997.
- T.G. Austin and S. Shreve, Chemical Process Industries, 5th Edition, McGraw Hill, New Delhi, 1984.
- R.E. Kirk and D.F. Othmer, Encyclopaedia of Chemical Technology, 4th Edition, Interscience, New York, 1991.
- P.H. Groggins, Unit Processes in Organic Synthesis, 5th Edition, McGraw Hill, 1984.

The references for today's lecture are provided here. Outlines of Chemical Technology by Dryden edited and revised by Gopala Rao and Marshall Sittig, third edition. Chemical Process Industries by Austin and Shreve, fifth edition. Encyclopedia of Chemical Technology, Kirk and Othmer, fourth edition. Unit Processes in Organic Synthesis by Groggins, fifth edition. However, the entire lecture slides that are presented in today's lecture are collected from these two reference books. Thank you.