Food Oils and Fats: Chemistry and Technology

Professor H N Mishra

Agricultural and Food Engineering Department

Indian Institute of Technology Kharagpur

Module 07: Modifications of Oils and Fats

Lecture 31: Hydrogenation

NPTEL ONLINE CERTIFICATION COURSES

Food Oils and Fats: Chemistry & Technology

Professor H N Mishra

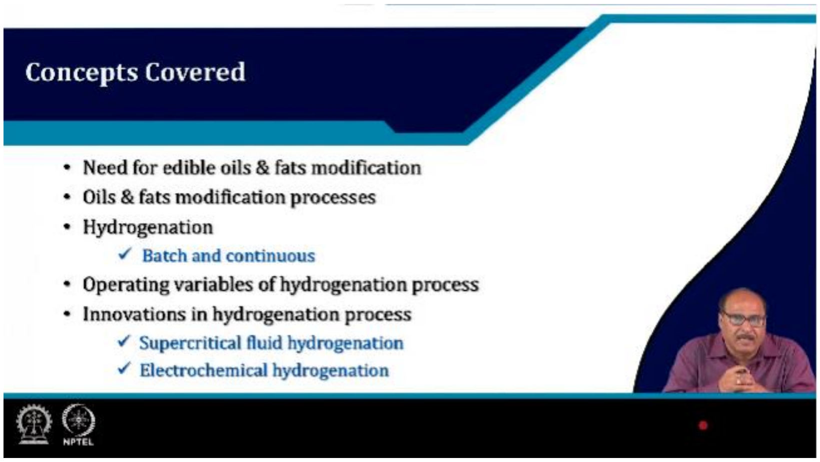
Agricultural and Food Engineering Department

Indian Institute of Technology Kharagpur

Module 7 : Modifications of Oils and Fats

Lecture 31 : Hydrogenation

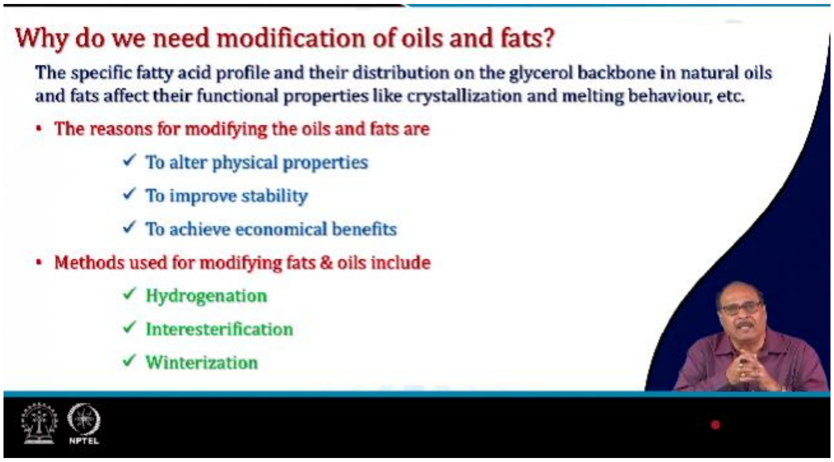
Hello everybody, Namaskar. Now, we are in the 7th module of the course and this 7th module that is 5 lectures of this module will be devoted on Modifications of Food, Oils and Fats. And today's lecture, lecture number 31 will be devoted on Hydrogenation.



Concepts Covered

- Need for edible oils & fats modification
- Oils & fats modification processes
- Hydrogenation
  - ✓ Batch and continuous
- Operating variables of hydrogenation process
- Innovations in hydrogenation process
  - ✓ Supercritical fluid hydrogenation
  - ✓ Electrochemical hydrogenation

The concept which I will discuss in this lecture include what is the need of edible oils and fat modification, why do we modify fats and oils and then what are the various processes that are used to modify fats and oils and hydrogenation is one among them. So, we will start with the hydrogenation process, what is the concept of the hydrogenation, how it is done both batch and continuous process, then operating variables for the hydrogen process and innovations in the hydrogenation process is a recent development that is super critical fluid hydrogenation and electrochemical hydrogenation process.

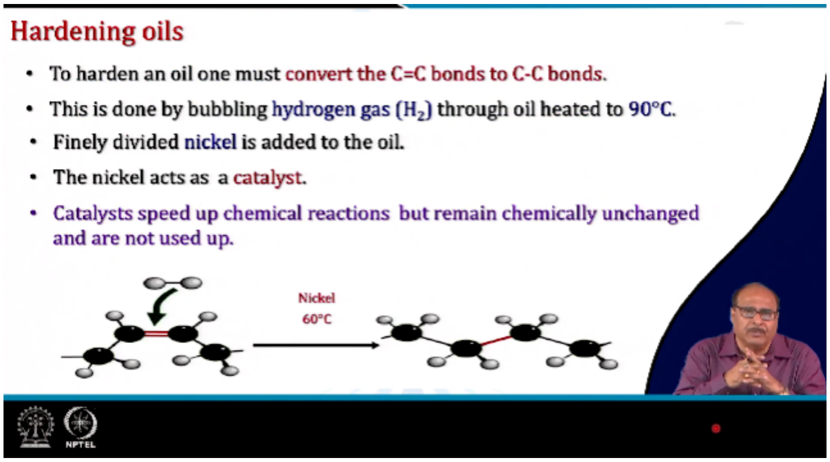


Why do we need modification of oils and fats?

The specific fatty acid profile and their distribution on the glycerol backbone in natural oils and fats affect their functional properties like crystallization and melting behaviour, etc.

- The reasons for modifying the oils and fats are
    - ✓ To alter physical properties
    - ✓ To improve stability
    - ✓ To achieve economical benefits
- Methods used for modifying fats & oils include
    - ✓ Hydrogenation
    - ✓ Interesterification
    - ✓ Winterization

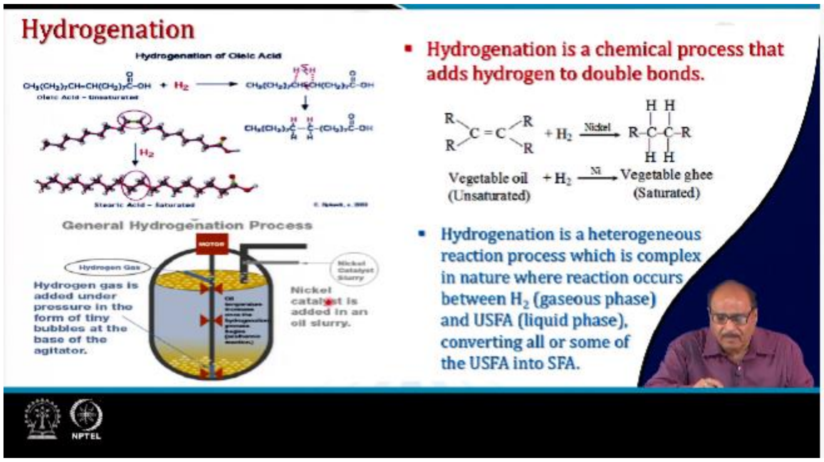
So, let us see first why do we need modifications of food, oils and fats. You know that these oils and fats they are extracted from their sources in natural food, oils and fats, then they contain their triglyceride and in the triglyceride means that is glycerol and 3 fatty acids molecule are attached and these are all ordered i.e. these are the mixture of mixed triglycerides. So, various that we have discussed in detail in earlier classes. So, what it generally observed this the specific fatty acid profile and their distribution on the glycerol backbone in natural oils and fat they affect their functional properties like their crystallization, their melting behavior, their specific heat all the properties etc are influenced that also we discussed in the earlier classes. So, it may so happen that a particular oil or fat by the virtue of its triglyceride that is 3 fatty acids in nature and its arrangement on the glycerol backbone, it may not be suitable for a particular operation. It may not have certain particular characteristics which desired in that particular operation of the food process. So, this is done by the modification that is accordingly these triglycerides are modified to suit the particular operations. To alter the physical properties that these particularly fatty acid positions, their unsaturated may be converted into saturated R1, R2, R3 where a position may be interchanged. So, it is by interchanging these by modifying these fatty acids on the glycerol backbone or their nature, it may improve the physical properties of the oil, it may improve the stability of the triglyceride as well as it is done to achieve economic benefits. So, these are the 3 major reasons for modifying oils and fats and modified oil or fat may be tailored way to suit a particular physical operations, particular chemical operation in a particular product for particular specific product manufacturing or for introducing a specific characteristics in the product. So, this is the main purpose of the modification of oils and fats. So, the what are the processes now which are used to modify oils and fats? Normally 3 process are there which is used by the industry and these include hydrogenation, interesterification and then winterization are also called as crystallization. So, these are the 3 major oil and fats modification process. Now, we will take up all these one by one in this at their various detailed process for the operations etc.



Hardening oils

- To harden an oil one must convert the C=C bonds to C-C bonds.
- This is done by bubbling hydrogen gas (H_2) through oil heated to 90°C.
- Finely divided nickel is added to the oil.
- The nickel acts as a catalyst.
- Catalysts speed up chemical reactions but remain chemically unchanged and are not used up.

So, first we will start with the hydrogenation process that is the hardening oils you know that you must have seen that is vanaspati, there is some vegetable oils in the earlier classes we discussed that is the it is basically because of the presence of unsaturated fatty acids that plant oils are liquid at room temperature. But these fats are the animal fats or other products which they are solid at room temperature they contain those mostly saturated fatty acids. So, the main process to make a liquid oil into a solid fat we must convert double bond unsaturated bonds carbon-carbon linkage to saturated that is C into C single bond carbon-carbon linkage. And this is done by bubbling the hydrogenation gas through it because you see if you see the recall our earlier class where we did the complete structure of this there are two. So, if in the double bond position further hydrogen is added then this bond is really converted into saturated one and the unsaturated fatty acid will be converted into saturated fatty acids and accordingly liquid fat liquid oil will be converted into solid fat. So, that is the hardening oil sequence. So, this is done by bubbling the hydrogen gas through oil heated to 90°C and the normally nickel is used as a catalyst and this catalyst speed of the chemical reactions, but they remain chemically unchanged and they are not used up in the process. So, they can be finally, removed. So, that is the hardening oil.



Hydrogenation

- Hydrogenation is a chemical process that adds hydrogen to double bonds.

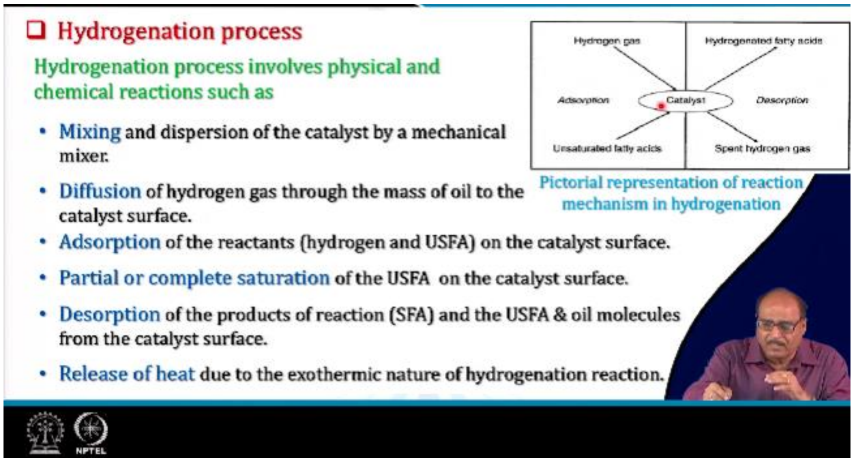
$$\text{Vegetable oil (Unsaturated)} + H_2 \xrightarrow{Ni} \text{Vegetable ghee (Saturated)}$$

- Hydrogenation is a heterogeneous reaction process which is complex in nature where reaction occurs between H_2 (gaseous phase) and USFA (liquid phase), converting all or some of the USFA into SFA.

Hydrogen gas is added under pressure in the form of tiny bubbles at the base of the agitator.

Nickel catalyst is added in an oil slurry.

This process of hardening the oil is known as hydrogenation. So, hydrogenation is now you can say that it is a chemical process that adds hydrogen to the double bond. You can see here these are the unsaturated composition here and then in the presence of nickel hydrogen is added and double bond is converted into single bond. So, unsaturated vegetable oil is it becomes vegetable key. That the further it is the you see that is oleic acid you know that oleic acid that is a stearic acid or palmitic acid, oleic acid, linoleic acid, linolenic acid. So, that is C18 acids which are this stearic acid there is no double bond single bond. Then it one saturated one unsaturation bond becomes oleic two unsaturation becomes linoleic three unsaturated bonds becomes linolenic acid. So, in a control condition finally, whether if linolenic acid is desaturated it will become linoleic acid, linoleic acid is desaturated it will become oleic acid and oleic acid primarily partly. It is the schematic representation of a hydrogenation setup it is basically a vessel where all the arrangements I will tell you later also where all the arrangements for stimulate, hardening, catalyst addition, for heating, cooling all this thing and for giving the proper reaction. So, that the saturation of the oil is done. So, all these arrangements are provided. So, under control condition hydrogen gas is added into the heated oil in the vessel there is a motor is provided which mixes the catalyst as well as hydrogen properly and provides the proper medium for the reaction and environment for the reaction for the conversion of the oil. So, it is a basically a heterogeneous reaction process which is complex in nature where reaction occurs between hydrogen, gaseous phase and the unsaturated fatty acid which is liquid phase and converting either all or some of the unsaturated fatty acids into saturated fatty acids.



❑ **Hydrogenation process**

Hydrogenation process involves physical and chemical reactions such as

- **Mixing** and dispersion of the catalyst by a mechanical mixer.
- **Diffusion** of hydrogen gas through the mass of oil to the catalyst surface.
- **Adsorption** of the reactants (hydrogen and USFA) on the catalyst surface.
- **Partial or complete saturation** of the USFA on the catalyst surface.
- **Desorption** of the products of reaction (SFA) and the USFA & oil molecules from the catalyst surface.
- **Release of heat** due to the exothermic nature of hydrogenation reaction.

Pictorial representation of reaction mechanism in hydrogenation

Then again a pictorial representation of the reaction mechanism in hydrogenation process you can see there is a catalyst. So, hydrogen gas is the adsorbed on the catalyst surface then unsaturated fatty acids also rear and then it gives the adsorption and finally, the hydrogenated fatty acids are given out by the desorption process and spent hydrogen gas. So, it involves adsorption and then desorption phenomena. That is the process hydrogenation involves mixing and dispersion of the catalyst by a mechanical mixture, then diffusion of hydrogen gas through the means of oil to the catalyst surface, then adsorption of the reactants that is hydrogen and unsaturated fatty acids on the catalyst surface, then partial and complete saturation of the unsaturated fatty acids on the catalyst surface, then desorption of the catalyst a product reaction that is saturated fatty acid and the unsaturated fatty acids and oil molecules from the catalyst surface and finally, release of heat due to exothermic nature of hydrogenation reactions. So, this is basically typical sequence of the hydrogenation process.

❖ **Purpose of hydrogenation**

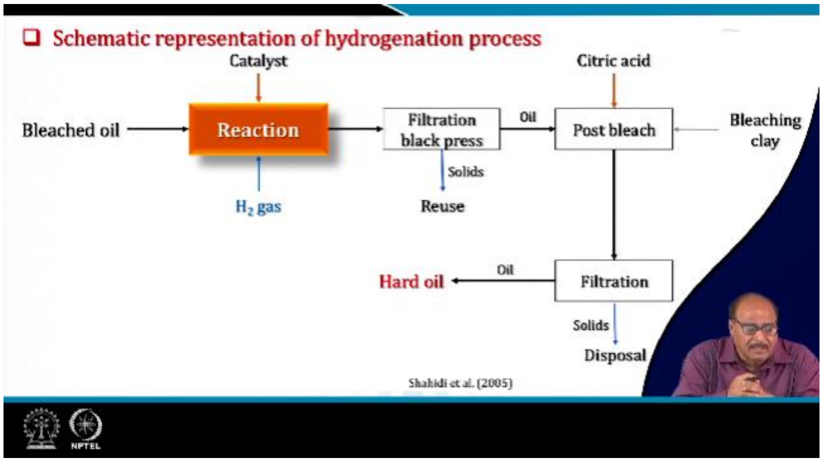
- To change naturally occurring fats and oils into physical forms with the consistency and handling characteristics required for functionality.
- To increase oxidative stability.

❖ **Effects of hydrogenation**

- ✓ The USFA become more saturated.
- ✓ The iodine value of the oil decreases.
- ✓ The melting point of the oil increases.
- ✓ The oxidative stability of the oil improves.
- ✓ A multitude of side reactions take place, including the formation of certain alcohols and acids.
- ✓ Isomerization of some of the polyunsaturated fatty acids takes place.

- **The products of hydrogenation are a very complex mixture because of the simultaneous reactions that occur.**
  - ✓ Saturation of double bonds,
  - ✓ Cis-/trans-isomerization of double bonds, and
  - ✓ Shifts of double-bond locations, usually to the lower energy conjugated state.

And the products of hydrogenation are very complex mixture because of the semi continuous or simultaneous reactions that occur. There may be saturation of all double bonds or partially saturation of double bond depending upon the conditions, there may be formation of *cis trans* isomers that is *cis trans* isomerization of double bond and there may be shift of double bond locations usually to lower energy conjugated states. So, the purpose of hydrogenation is basically as I told you to change the naturally occurring fats and oils into physical forms with the consistency and handling characteristics which is required for their specific functionality even there is a selective hydrogenation which I will come little later that you by the process of selective hydrogenation by proper control of conditions one can prepare a solid fat of a particular specific characteristics, specific consistency, specific degree of unsaturation etc. So, the effects of hydrogenation obviously, if the unsaturated fatty acids become more saturated the iodine value of the oil decreases, the melting point of the oil increases, the oxidative stability of the oil improves and a multitude of side reactions take place including the formation of certain alcohol and acids.



- **Schematic representation of hydrogenation process**

Catalyst

Citric acid

Bleached oil

Reaction

Filtration black press

Oil

Post bleach

Bleaching clay

Solids

H_2 gas

Reuse

Hard oil

Oil

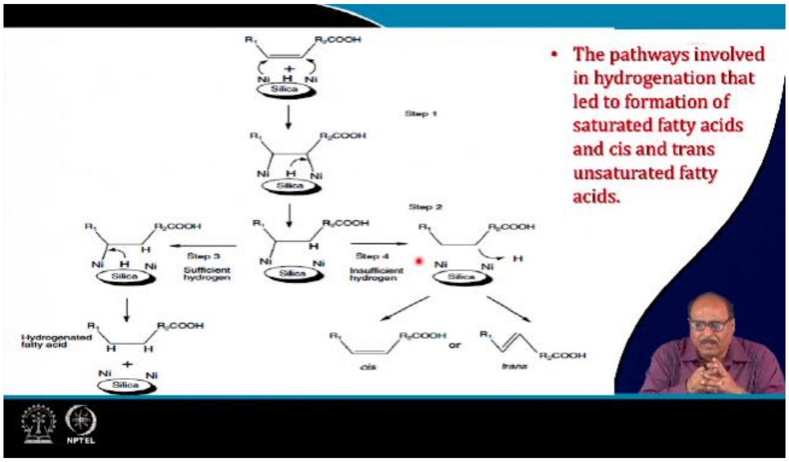
Filtration

Solids

Disposal

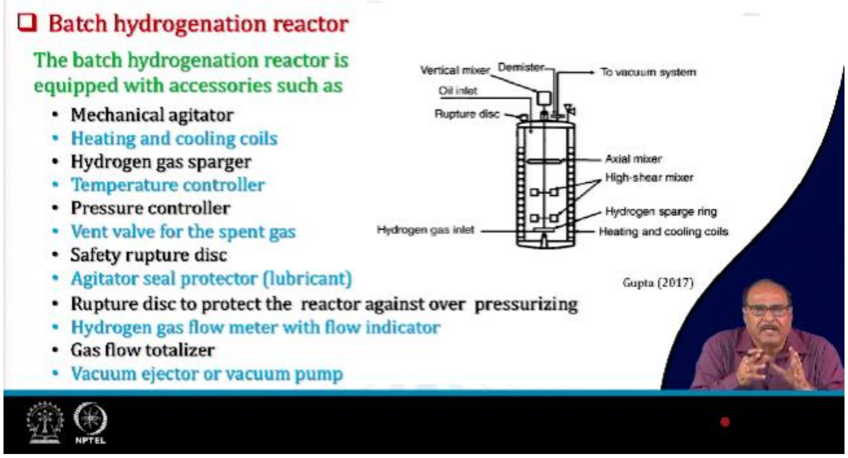
Shahidi et al. (2005)

So, this is the schematic of the hydrogenation process. So, the bleached oil then here it is the catalysts are added the reaction hydrogen gas and then filtration black press solids are that is they are used the catalyst is removed and then oil is obtained. So, the post bleaching citric acid is added post bleaching clay and then filtration and hard oil. So, that is the here reaction is hydrogenation reaction then after that bleaching is done then finally, it is filtered whatever properly filter you get the hard oil or vanaspati.



- The pathways involved in hydrogenation that led to formation of saturated fatty acids and cis and trans unsaturated fatty acids.

This is a schematic representation and the pathways which are involved in the hydrogenation related chemistry of the hydrogenation process that is that lead to the formation of saturated fatty acids and *cis trans* isomers unsaturated fatty acids are shown here you can see there is a double bond. So, the nickel the surface you are taking the hydrogenation catalyst and then in the first step you see how hydrogen is coming here and in getting adsorbed and the nickel. Then you get this here hydrogen that is it has come here and nickel catalyst then in the step 3 then again next this hydrogen the another hydrogen molecule again it is replacing here. It becomes hydrogen and hydrogen it is added. So, hydrogen is added in this and double bond which were there it becomes single bond it becomes saturated hydrogenated fatty acid and other alternatively this side depending upon the process which are made selectivity and all those things that is you see if there is an insufficient hydrogen then there is only one hydrogen there it may more neutral and here it is see that it may be *cis or trans* even this hydrogen may be cis or transformation forms may be formed. So, that is depending upon how the oxygen sufficient hydrogen supply or insufficient hydrogen supply or other conditions prevailing in the system temperature and all those things it may be fully hydrogenated partially hydrogenated or even some cis forms may be converted into transforms and all these combinations and permutations may take place.



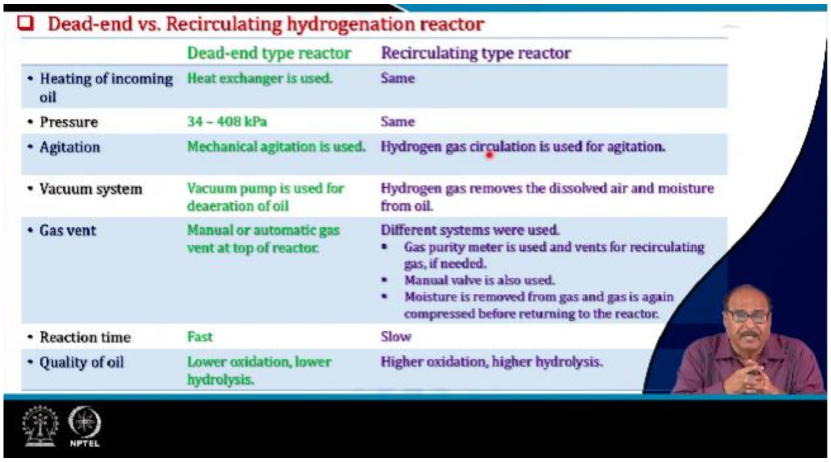
❑ Batch hydrogenation reactor

The batch hydrogenation reactor is equipped with accessories such as

- Mechanical agitator
- Heating and cooling coils
- Hydrogen gas sparger
- Temperature controller
- Pressure controller
- Vent valve for the spent gas
- Safety rupture disc
- Agitator seal protector (lubricant)
- Rupture disc to protect the reactor against over pressurizing
- Hydrogen gas flow meter with flow indicator
- Gas flow totalizer
- Vacuum ejector or vacuum pump

Gupta (2017)

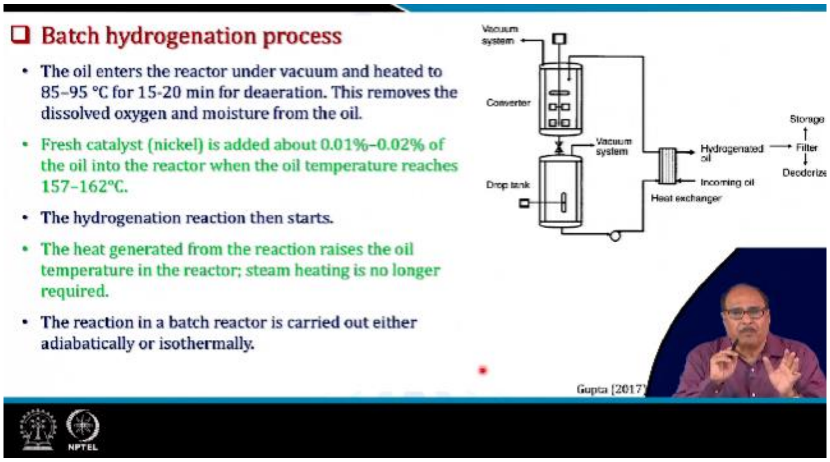
So, this is the batch hydrogenator reactor and just schematic it is provided with the all the setups and accessories to conduct the hydrogenation process. So, it includes a mechanical agitator, it has the coils for heating and cooling of the oil then it is system for hydrogen gas is sparging hydrogen gas is sparger then temperature controller pressure controller vent valve for the spent gases safety rupture discs agitator or seal protector, then rupture disc to protect the reactor against over pressurizing hydrogen gas flow meter with flow indicator gas flow totalizer and vacuum ejector or vacuum pump. So, these are all these the accessories are arrangements provided into the reaction vessels to control the properly do the hydrogenation process in a batch system.



Dead-end vs. Recirculating hydrogenation reactor

	Dead-end type reactor	Recirculating type reactor
• Heating of incoming oil	Heat exchanger is used.	Same
• Pressure	34 – 408 kPa	Same
• Agitation	Mechanical agitation is used.	Hydrogen gas circulation is used for agitation.
• Vacuum system	Vacuum pump is used for deaeration of oil	Hydrogen gas removes the dissolved air and moisture from oil.
• Gas vent	Manual or automatic gas vent at top of reactor.	Different systems were used. ▪ Gas purity meter is used and vents for recirculating gas, if needed. ▪ Manual valve is also used. ▪ Moisture is removed from gas and gas is again compressed before returning to the reactor.
• Reaction time	Fast	Slow
• Quality of oil	Lower oxidation, lower hydrolysis.	Higher oxidation, higher hydrolysis.

So, dead end or recirculating hydrogenation reaction a comparison. In a dead end type of reactor, heating of the incoming oil is through heat exchanger and in the recirculating type also the same heat exchangers are used. And the pressure in both the cases may be 34 to 408kPa, but agitation in the dead end type reactor it is a mechanical agitation whereas, in the recirculating type reactor hydrogen gas circulation is used for agitation. In the vacuum system the vacuum pump is used for deaeration of oil in the dead end type reactor whereas, the hydrogen gas which is it removes the dissolved air and moisture from the oil. Then as far as the gas vent that is in the dead end type reactor manual or automatic gas vent traps of the reactor are there whereas, in the case of recirculating type reactor different systems are used that gas purity meter is used and vents for the recirculatory gas if needed ok. Oil vent is also used and moisture is removed from gas and gas is again compressed before returning to the reactor. The reaction time is fast in dead end type reactor whereas, it is slow in a recirculating type reactor and the quality of the product oil it is lower oxidation lower hydrolysis in the case of dead end type reactor whereas, higher end type recirculatory type reactor it gives higher oxidation and higher hydrolysis.

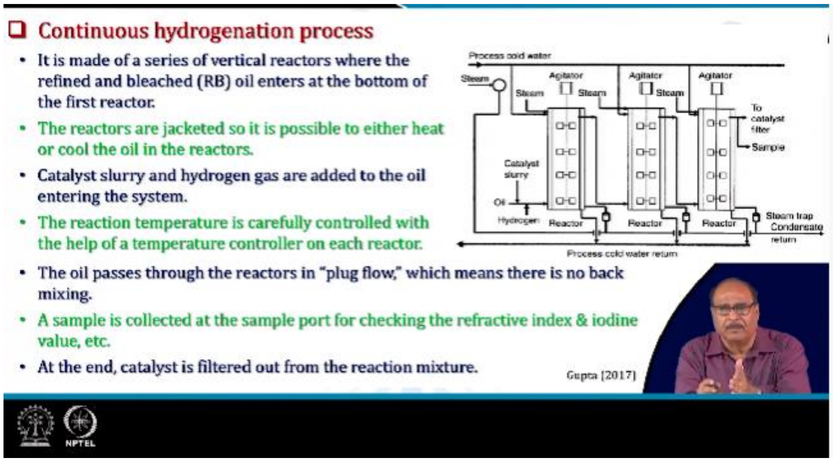


Batch hydrogenation process

- The oil enters the reactor under vacuum and heated to 85–95 °C for 15-20 min for deaeration. This removes the dissolved oxygen and moisture from the oil.
- Fresh catalyst (nickel) is added about 0.01%–0.02% of the oil into the reactor when the oil temperature reaches 157–162°C.
- The hydrogenation reaction then starts.
- The heat generated from the reaction raises the oil temperature in the reactor; steam heating is no longer required.
- The reaction in a batch reactor is carried out either adiabatically or isothermally.

Gupta (2017)

So, as far as the batch process of hydrogenation is concerned you see here that is the oil enters the reactor under vacuum and it is heated to a temperature of 95 to 85 to 95°C for about 15 to 20 minute for deaeration that is this heating of the oil it removes the dissolved oxygen and moisture from the oil. So, that is the first step. Then the fresh catalyst there is a catalyst mixing tank in which that a small quantity of oil is taken and it is the nickel is used as a catalyst. So, nickel is which all because it is a nickel is highly pyrochemical if it comes in open atmosphere it catch its fire. So, the same oil in which it is to be which is to be hydrogenated a small quantity of that oil is taken and concentrated solution of nickel is made and this nickel solution finally, is introduced with the third piping system into the reactor when the oil temperature has reached to 157 to 162°C. The oil is heated and separately the nickel is being mixed in the catalyst and at the same time this oil is also being heated to that. And once it has come to around 160°C temperature then the catalyst is brought to the with the proper port that is provided in the system it brought to the reaction medium and the case would be taken that finally, overall that is the rate of the nickel that is added is 0.01 to 0.02% So, that should be taken care of. So, the hydrogenation reaction then starts hydrogen gas is introduced once at this temperature nickel is added then hydrogen gas is introduced then heat generated from the reaction raises the temperature of the reactor further and then this exothermic reaction is necessary that is steam supply there are the automatic control were provided in the equipment then the steam supplies automatically sort of because it is not required anymore because it is exothermic reaction and the heat generated from the reaction is sufficient to maintain the temperature of the oil to maintain the reaction. The reaction in the batch reactor is carried out either adiabatically or isothermally and once complete because there are the equipment provided with this in the arrangement to take the sample out and the sample intermittently they are taking out and they are analyzed for their reflective index or as a iodine value to know the what is the final level of saturation and then accordingly the need of the process the hydrogen supplies cut off the material is cooled down then it is sent to the filters where the these catalyst which were added they are properly removed they are filtered and the hydrogenated oil is sent for further process. There are two three policy filters are provided that is the catalyst should be completely removed and the chamber is also provided some system for the taking out the volatile vapors from the there.

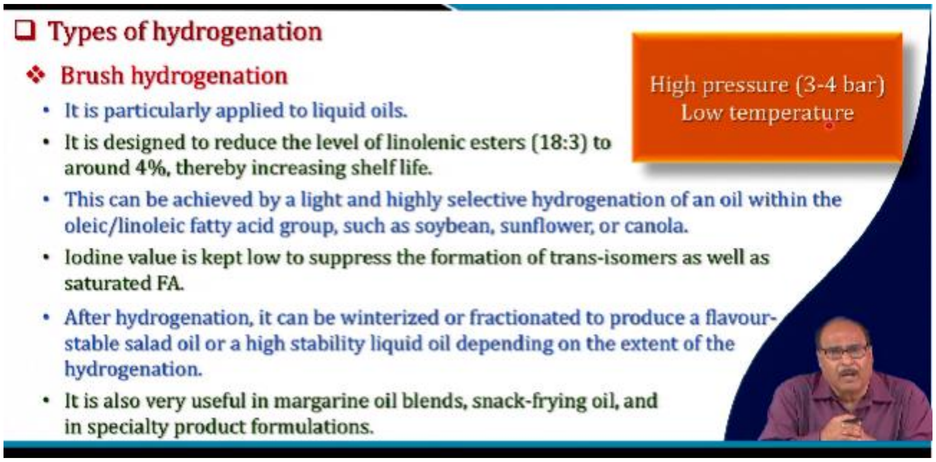


Continuous hydrogenation process

- It is made of a series of vertical reactors where the refined and bleached (RB) oil enters at the bottom of the first reactor.
- The reactors are jacketed so it is possible to either heat or cool the oil in the reactors.
- Catalyst slurry and hydrogen gas are added to the oil entering the system.
- The reaction temperature is carefully controlled with the help of a temperature controller on each reactor.
- The oil passes through the reactors in "plug flow," which means there is no back mixing.
- A sample is collected at the sample port for checking the refractive index & iodine value, etc.
- At the end, catalyst is filtered out from the reaction mixture.

Gupta (2017)

So, this is this was your batch process in a continuous hydrogenation process that you can say definitely different batch equipment similar equipment arranged in a series alright. So, there is an oil and catalyst slurry and oil they are they enter into the one reactor then from that they exit and that becomes entry to the second reactor then come of the second reactor will come an entry for the second third reactor and so on. And each individual reactors are provided with all the accessory and arrangement as we as I showed you which is provided in the batch reactors. So, this is basically it is a made in a series of vertical reactors where the refined and bleached oil enters at the bottom of the first reactor the reactors are jacketed. So, it is possible to either heat or cool oil in the reaction then in individual reactor you can control the entry that the temperature pressure as per the requirement. Catalyst slurry and hydrogen are added to the oil entering the system the reaction temperature is carefully controlled with the help of a temperature controller on each reactor the oil passes through the reactors in plug flow which means there is no mixing. The sample is collected at the sample port for checking the reflective index and iodine value and at the end catalyst is filtered out from the reaction mixture.



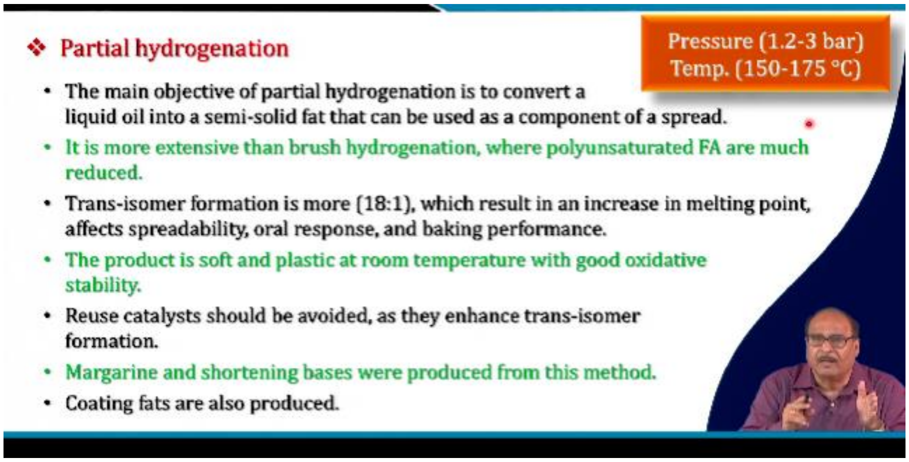
Types of hydrogenation

Brush hydrogenation

- It is particularly applied to liquid oils.
- It is designed to reduce the level of linolenic esters (18:3) to around 4%, thereby increasing shelf life.
- This can be achieved by a light and highly selective hydrogenation of an oil within the oleic/linoleic fatty acid group, such as soybean, sunflower, or canola.
- Iodine value is kept low to suppress the formation of trans-isomers as well as saturated FA.
- After hydrogenation, it can be winterized or fractionated to produce a flavour-stable salad oil or a high stability liquid oil depending on the extent of the hydrogenation.
- It is also very useful in margarine oil blends, snack-frying oil, and in specialty product formulations.

High pressure (3-4 bar)
Low temperature

Then the type of hydrogenation process that is there are hydrogen reaction there is a brush hydrogenation. Brush hydrogenation is a high pressure about 3 to 4 bar and low temperature and this is particularly applied to liquid oil. It is designed to reduce the low level of linolenic esters that is 83 to around 4 percent by increasing the shelf life of the oil. This can be achieved by a light and highly selective hydrogenation of an oil within the oleic linolenic fatty acid group such as soybean, sunflower, canola oil etcetera which has a high amount of PUFA polyunsaturated fatty acid. Iodine value is kept low to suppress the formation of trans isomers as well as saturated fatty acids. After hydrogenation it can be winterized or fractionated to produce a flavor stable solid oil or a high stability liquid depending on the extent of the hydrogenation. It is also useful very useful in the margarine oil blends, snack frying oils and in specialty product formulations.

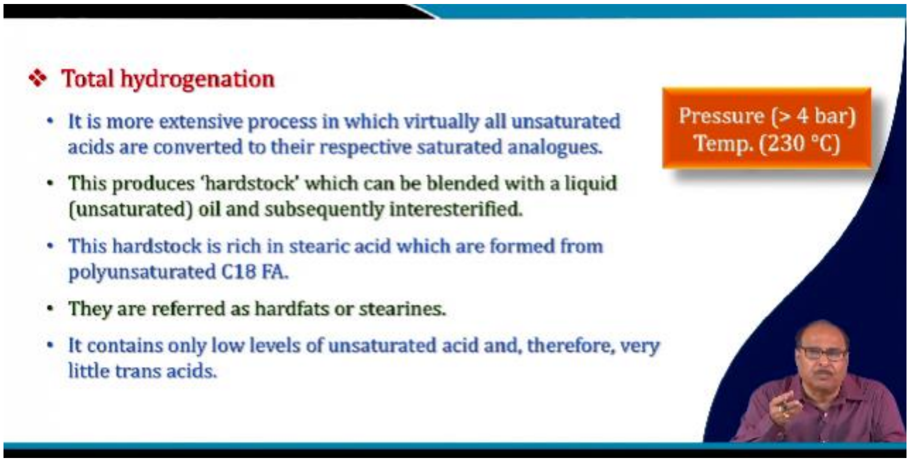


❖ Partial hydrogenation

Pressure (1.2-3 bar)
Temp. (150-175 °C)

- The main objective of partial hydrogenation is to convert a liquid oil into a semi-solid fat that can be used as a component of a spread.
- It is more extensive than brush hydrogenation, where polyunsaturated FA are much reduced.
- Trans-isomer formation is more (18:1), which result in an increase in melting point, affects spreadability, oral response, and baking performance.
- The product is soft and plastic at room temperature with good oxidative stability.
- Reuse catalysts should be avoided, as they enhance trans-isomer formation.
- Margarine and shortening bases were produced from this method.
- Coating fats are also produced.

Then next is the partial hydrogenation. So, in the partial hydrogenation process temperature is around 150 to 175°C and pressure is maintained to 1.2 to 3 bar in the reaction medium. So, the main objective of partial hydrogenation is to convert a liquid oil into a semi solid fat that can be used as a component of a spread that is here partial hydrogenation not very hard not a complete hydrogenation. It is more extensive than the brush hydrogenation where polyunsaturated fatty acids are much reduced. Trans isomer formation is more active to one which results in an increase in the melting point affect the spread ability, overall response and breaking performance. The product is soft and plastic at room temperature with good oxidative stability. Used catalyst should be avoided as they enhance trans isomer formation. So, in the partial hydrogenation at least as far as possible the catalyst should not be reused ok. Then margarine and shortening bases were produced from this method using this method and even coating fats are applying coating into various foods. They are also produced using this partial hydrogenation method.

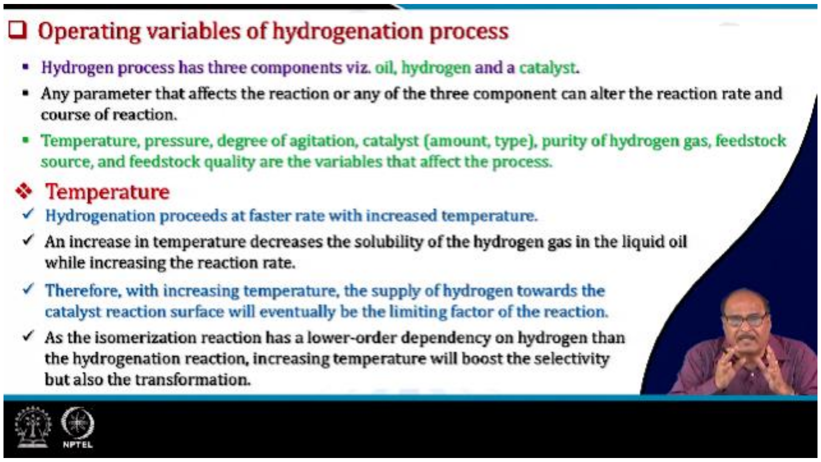


❖ Total hydrogenation

- It is more extensive process in which virtually all unsaturated acids are converted to their respective saturated analogues.
- This produces 'hardstock' which can be blended with a liquid (unsaturated) oil and subsequently interesterified.
- This hardstock is rich in stearic acid which are formed from polyunsaturated C18 FA.
- They are referred as hardfats or stearines.
- It contains only low levels of unsaturated acid and, therefore, very little trans acids.

Pressure (> 4 bar)
Temp. (230 °C)

Then total hydrogenation total hydrogenation at the name itself indicates it is more extensive process in which virtually all unsaturated fatty acids are converted into their respective saturated analogs that is the oil becomes a very hard fat. The pressure is normally more than 4 bar in this case and temperature is above 230°C or so. This product that is hard stock which can be blended with a liquid unsaturated oil subsequently inter esterified. This hard stock is rich in stearic acid which are formed from polyunsaturated like C18 fatty acids. They are referred as hardfats or stearin. It contains only low levels of unsaturated fatty acids therefore, very little trans fats.



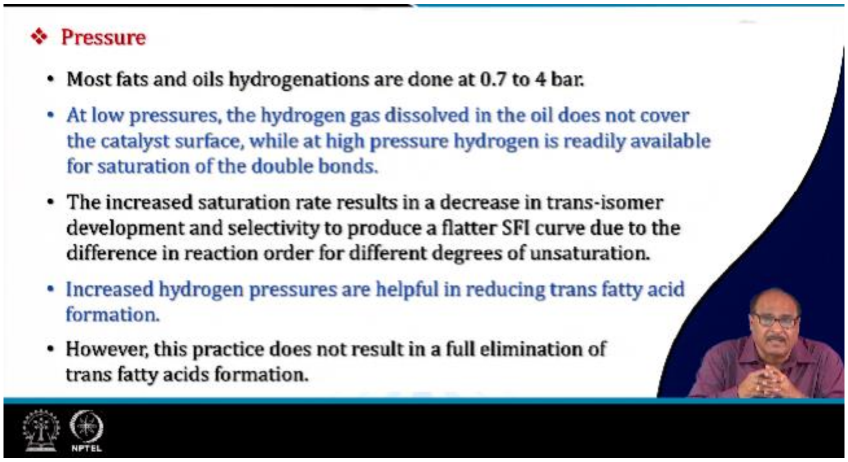
❑ Operating variables of hydrogenation process

- Hydrogen process has three components viz. oil, hydrogen and a catalyst.
- Any parameter that affects the reaction or any of the three component can alter the reaction rate and course of reaction.
- Temperature, pressure, degree of agitation, catalyst (amount, type), purity of hydrogen gas, feedstock source, and feedstock quality are the variables that affect the process.

❖ Temperature

- ✓ Hydrogenation proceeds at faster rate with increased temperature.
- ✓ An increase in temperature decreases the solubility of the hydrogen gas in the liquid oil while increasing the reaction rate.
- ✓ Therefore, with increasing temperature, the supply of hydrogen towards the catalyst reaction surface will eventually be the limiting factor of the reaction.
- ✓ As the isomerization reaction has a lower-order dependency on hydrogen than the hydrogenation reaction, increasing temperature will boost the selectivity but also the transformation.

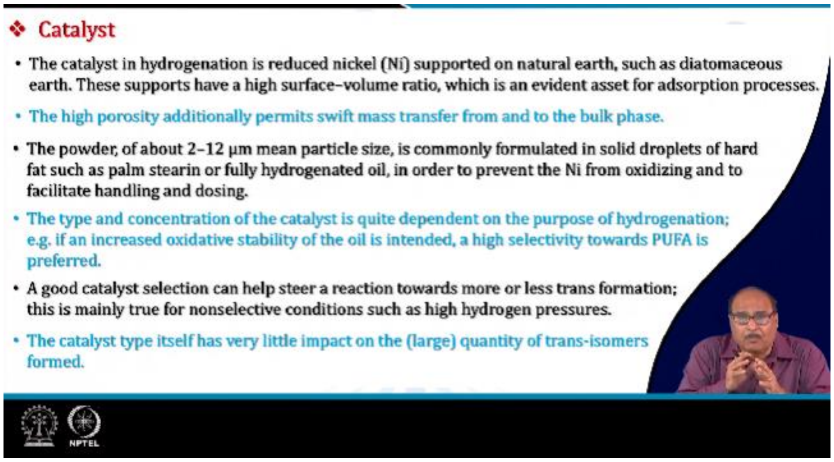
So, the operating variables which are important in this process are there is hydrogen process they have the three components basically you see that one is the oil, then hydrogen gas and catalyst. So, these proper characteristics of all these must be properly maintained in order to get the proper result proper quality hydrogenated fat. So, the temperature, pressure, degree of agitation, catalyst that is both amount and type, purity of hydrogen, feed stock source and feed stock quality are the variables that affect the hydrogenation process. So, now, first the temperature hydrogenation proceeds at a faster rate with increased temperature and increase in temperature decreases the solubility of hydrogen gas in the liquid oil while increasing the certain reaction rate. Therefore, with increasing temperature the supply of hydrogen towards the catalyst reaction surface will eventually be the limiting factor of the reaction. As the isomerization reaction has a lower order dependency on hydrogen than the hydrogenation reaction, increasing temperature will boost the selectivity, but also the transformation.



❖ **Pressure**

- Most fats and oils hydrogenations are done at 0.7 to 4 bar.
- At low pressures, the hydrogen gas dissolved in the oil does not cover the catalyst surface, while at high pressure hydrogen is readily available for saturation of the double bonds.
- The increased saturation rate results in a decrease in trans-isomer development and selectivity to produce a flatter SFI curve due to the difference in reaction order for different degrees of unsaturation.
- Increased hydrogen pressures are helpful in reducing trans fatty acid formation.
- However, this practice does not result in a full elimination of trans fatty acids formation.

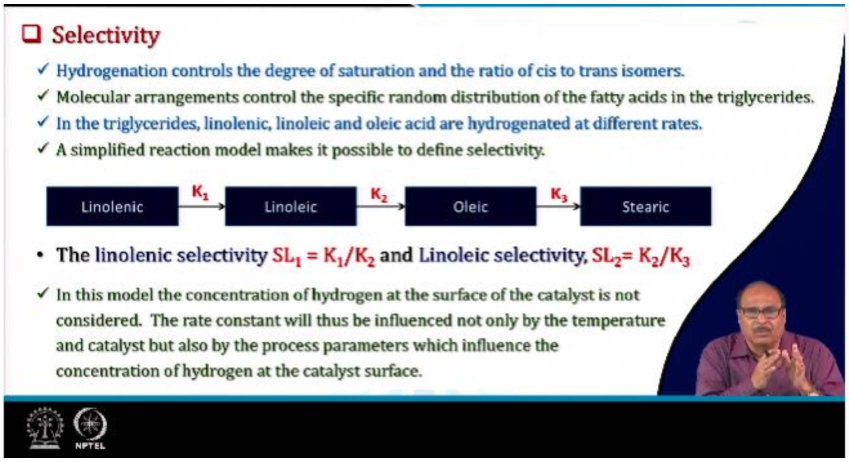
Then the pressure is another variable most fats are and oils hydrogenations are done at 0.7 to 4 bar pressure. At low pressure the hydrogen gas dissolved in the oil does not cover the catalyst surface while at high pressure hydrogen is readily available for saturation of the double bonds. The increased saturation rate results in a decrease in the trans-isomer development and selectivity to produce the flatter saturated fatty acid SFI curve. Sulfur is a very important factor due to the difference in reaction order for different degrees of unsaturation. So, increased hydrogen pressure is helpful in reducing trans fatty acid formation. However, this picture practice does not result a full elimination of trans fatty acid formation, but the obviously, if pressure is maintained lower level the transfer to acid formation is eliminated or at least lower down.



❖ **Catalyst**

- The catalyst in hydrogenation is reduced nickel (Ni) supported on natural earth, such as diatomaceous earth. These supports have a high surface–volume ratio, which is an evident asset for adsorption processes.
- The high porosity additionally permits swift mass transfer from and to the bulk phase.
- The powder, of about 2–12 μm mean particle size, is commonly formulated in solid droplets of hard fat such as palm stearin or fully hydrogenated oil, in order to prevent the Ni from oxidizing and to facilitate handling and dosing.
- The type and concentration of the catalyst is quite dependent on the purpose of hydrogenation; e.g. if an increased oxidative stability of the oil is intended, a high selectivity towards PUFA is preferred.
- A good catalyst selection can help steer a reaction towards more or less trans formation; this is mainly true for nonselective conditions such as high hydrogen pressures.
- The catalyst type itself has very little impact on the (large) quantity of trans-isomers formed.

The catalyst in the hydrogenation is reduced nickel supported on natural earth such as diatomaceous earth etc. These supports have a high surface volume ratio which is an evident asset of the adsorption process. The high porosity additionally permits swift mass transfer from and to the bulk phase. So, the powder of about 2 to 12 μm mean particle diameter is commonly formulated in solid droplets of hard fat such as palm styrene or fully hydrogenated oil in order to prevent the nickel from oxidizing and to facilitate handling and dosing. The type and concentration of catalyst is quite dependent on the purpose of hydrogenation. For example, if an increased oxidative stability of the oil is intended a high selectivity towards the towards the polyunsaturated fatty acid preferred. A good catalyst selection can help over a reaction period towards more or less transformation and this is mainly true for nonselective condition such as high hydrogen pressure. The catalyst type itself has very little impact on the large quantity or trans isomer form. So, this again should be properly controlled.



❑ Selectivity

- ✓ Hydrogenation controls the degree of saturation and the ratio of cis to trans isomers.
- ✓ Molecular arrangements control the specific random distribution of the fatty acids in the triglycerides.
- ✓ In the triglycerides, linolenic, linoleic and oleic acid are hydrogenated at different rates.
- ✓ A simplified reaction model makes it possible to define selectivity.

$$\text{Linolenic} \xrightarrow{K_1} \text{Linoleic} \xrightarrow{K_2} \text{Oleic} \xrightarrow{K_3} \text{Stearic}$$

- The linolenic selectivity $SL_1 = K_1/K_2$ and Linoleic selectivity, $SL_2 = K_2/K_3$

- ✓ In this model the concentration of hydrogen at the surface of the catalyst is not considered. The rate constant will thus be influenced not only by the temperature and catalyst but also by the process parameters which influence the concentration of hydrogen at the catalyst surface.

Now, let us talk about selectivity that is you know the hydrogenation controls the degree of saturation and the ratio of *cis* to *trans* isomers and that is very important as far as the final product characteristics and its usefulness in various process operations is concerned. So, this should be properly conducted molecular arrangement of the on the triglyceride bag bowl it control the specific random distribution of fatty acids in the triglyceride. In the triglyceride linolenic, linoleic and oleic acid are the hydrogenated at different rate obviously, because of their number of more unsaturated fatty acid or polyunsaturated fatty acid they saturate or hydrogenate at a faster rate than do the less unsaturated fatty acid. That is unsaturated monounsaturated fatty acid they normally desaturate or hydrogenate at a slower rate. And this a simplified reaction model making it possible to define selectivity as shown here. And if you see that linolenic is a getting saturated then linoleic converted to linoleic and its rate of hydrogenation is K1, then linoleic to oleic rate of conversion is K2 and oleic finally, it is converting into stearic acid which is saturated fatty acid and if its rate is at K3.

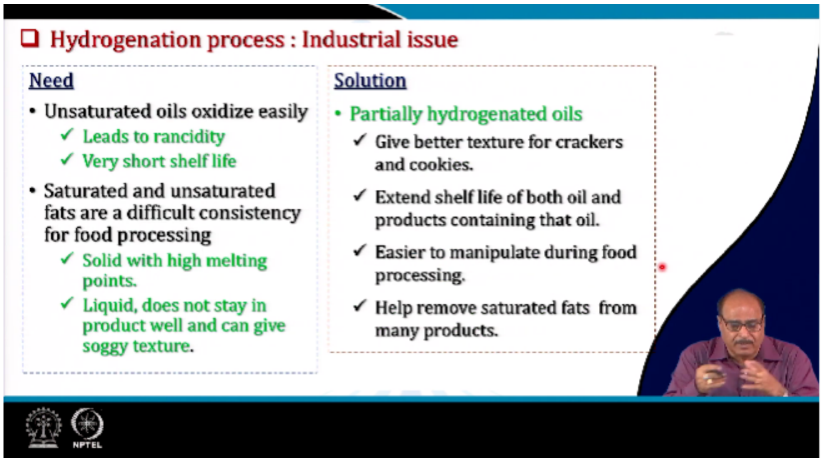
And linolenic selectivity

$$SL_1 = \frac{K_1}{K_2}$$

linoleic selectivity

$$SL_2 = \frac{K_2}{K_3}$$

So, that is how the selectivity is defined, but this model in this model the concentration of hydrogen at the surface of the catalyst is not considered. The rate constant will therefore, be influenced not only by the temperature and catalyst, but also by the process parameter which influence the concentration of hydrogen at the catalyst surface. So, this also should be so, the considered while designing the models for selectivity while developing choosing the models for selectivity.



❑ Hydrogenation process : Industrial issue

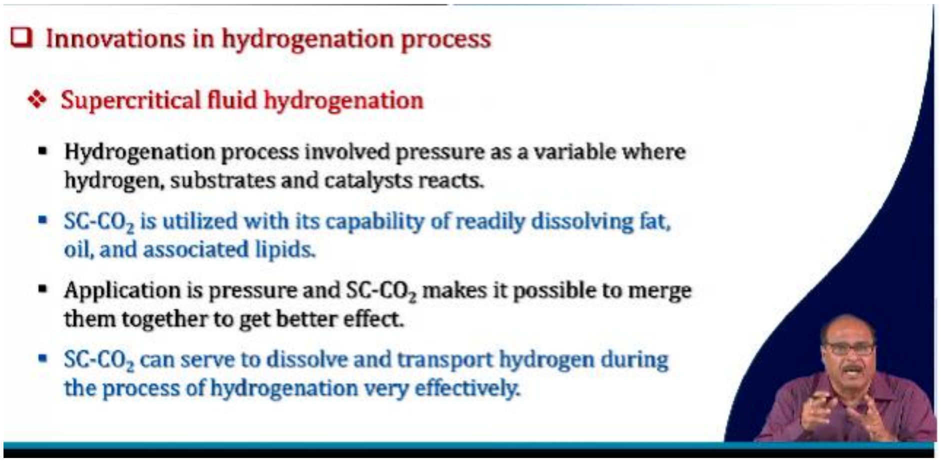
Need

- Unsaturated oils oxidize easily
  - ✓ Leads to rancidity
  - ✓ Very short shelf life
- Saturated and unsaturated fats are a difficult consistency for food processing
  - ✓ Solid with high melting points.
  - ✓ Liquid, does not stay in product well and can give soggy texture.

Solution

- Partially hydrogenated oils
  - ✓ Give better texture for crackers and cookies.
  - ✓ Extend shelf life of both oil and products containing that oil.
  - ✓ Easier to manipulate during food processing.
  - ✓ Help remove saturated fats from many products.

So far there is unsaturated oil oxidizes quickly leads to rancidity it has a very short supply, but the saturated and unsaturated fats are difficult consistency for food processing solid fats are with high melting points liquid does not stay in product well and can give a soggy texture etcetera these are some of the problem associated. So, which are the industrial issue. So, what is the solution? You have partially hydrogenated oil shooting to specific applications. So, these partially hydrogenated oil can give better texture for crackers and cookies they extend the shelf life of both oil and products are containing the oils they are easier to manipulate during food processing and help remove saturated fats from many products.

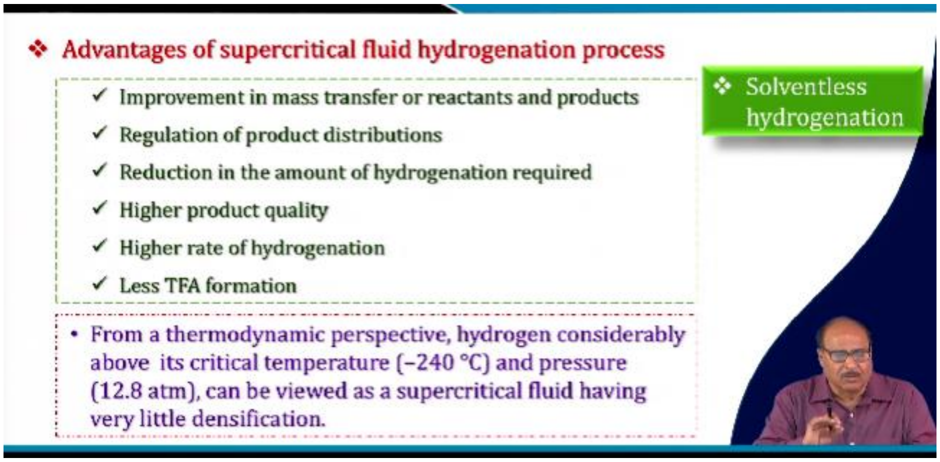


❑ Innovations in hydrogenation process

❖ Supercritical fluid hydrogenation

- Hydrogenation process involved pressure as a variable where hydrogen, substrates and catalysts reacts.
- SC-CO_2 is utilized with its capability of readily dissolving fat, oil, and associated lipids.
- Application is pressure and SC-CO_2 makes it possible to merge them together to get better effect.
- SC-CO_2 can serve to dissolve and transport hydrogen during the process of hydrogenation very effectively.

Then innovations in the hydrogenation process, they are super critical fluid hydrogenation the hydrogenation process involves pressure as a variable where hydrogen substrates and catalyst reacts. Now, the super critical carbon dioxide is utilized with its capacity for readily dissolving fat oil and associated lipids. So, application of application is pressure and super critical carbon dioxide make it possible to merge them together to get better effects. So, super critical carbon dioxide can serve to dissolve and transfer the hydrogen during the process of hydrogenation very effectively.



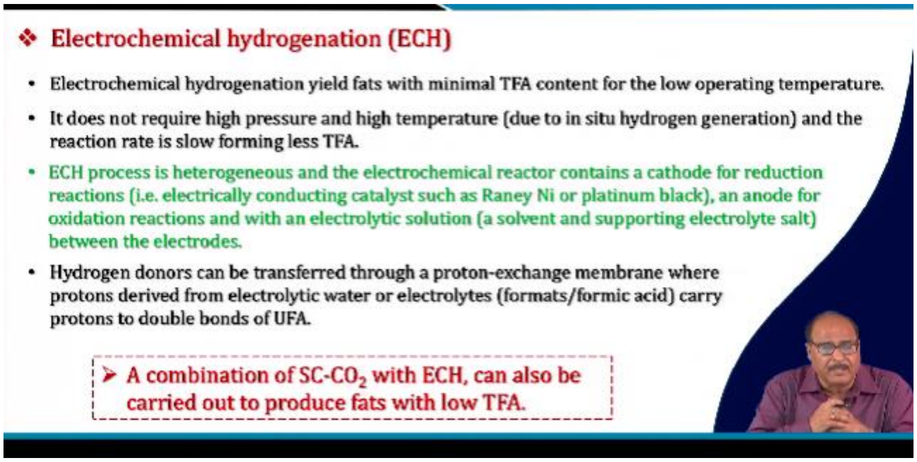
❖ Advantages of supercritical fluid hydrogenation process

- ✓ Improvement in mass transfer or reactants and products
- ✓ Regulation of product distributions
- ✓ Reduction in the amount of hydrogenation required
- ✓ Higher product quality
- ✓ Higher rate of hydrogenation
- ✓ Less TFA formation

❖ Solventless hydrogenation

- From a thermodynamic perspective, hydrogen considerably above its critical temperature (−240 °C) and pressure (12.8 atm), can be viewed as a supercritical fluid having very little densification.

So, the advantages of super critical fluid hydrogenation process that is it is a solvent less hydrogenation, it improves mass transfer or reactants and products regulations of product distributors, reduction in amount of hydrogenation required, higher product quality, higher rate of hydrogenation and less trans fatty acid formation. So, from a thermodynamic perspective hydrogenation considerably above its critical temperature that is minus 240 to 240°C and pressure 12.8 atmosphere can be viewed as a super critical fluid having very little densification.

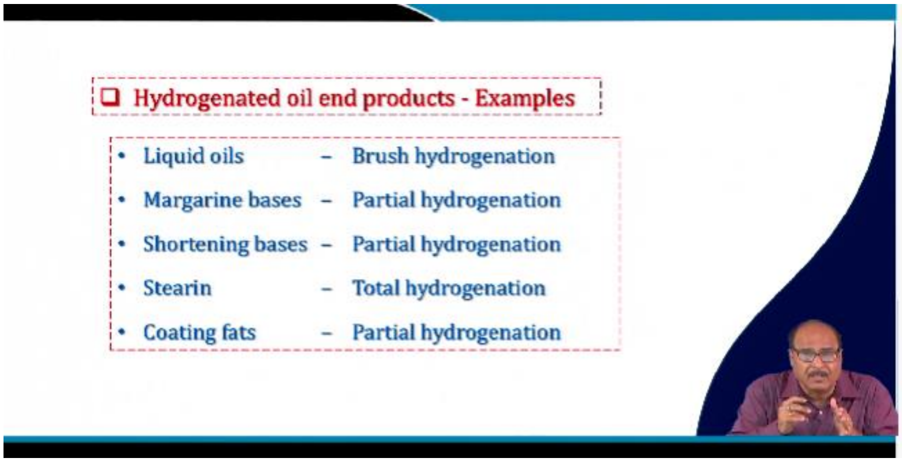


❖ **Electrochemical hydrogenation (ECH)**

- Electrochemical hydrogenation yield fats with minimal TFA content for the low operating temperature.
- It does not require high pressure and high temperature (due to in situ hydrogen generation) and the reaction rate is slow forming less TFA.
- ECH process is heterogeneous and the electrochemical reactor contains a cathode for reduction reactions (i.e. electrically conducting catalyst such as Raney Ni or platinum black), an anode for oxidation reactions and with an electrolytic solution (a solvent and supporting electrolyte salt) between the electrodes.
- Hydrogen donors can be transferred through a proton-exchange membrane where protons derived from electrolytic water or electrolytes (formats/formic acid) carry protons to double bonds of UFA.

➢ A combination of SC-CO_2 with ECH, can also be carried out to produce fats with low TFA.

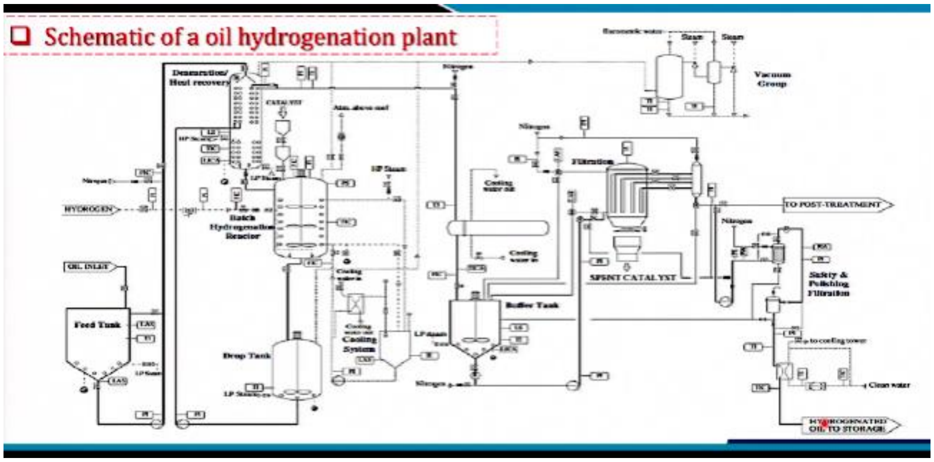
Then electrochemical hydrogenation (ECH) electrochemical hydrogenation yields fat with minimum trans fatty acids content for the low operating temperature. It does not require high pressure and high temperature due to in situ hydrogen generation and the reaction rate is slow forming less trans fatty acids. ECH process is a heterogeneous and the electrochemical reactor contains a cathode for reduction reactions ok. And anode for oxidation reaction with the electrolytic solution and these are between the electrodes. So, hydrogen donors can be transformed through a proton exchange membrane where protein derived from electrolytic water or electrolysis carry protons to the double bonds of unsaturated fatty acids. So, a combination of super critical carbon dioxide with ECH can also be carried out to produce fats with low trans fatty acids.



❑ **Hydrogenated oil end products - Examples**

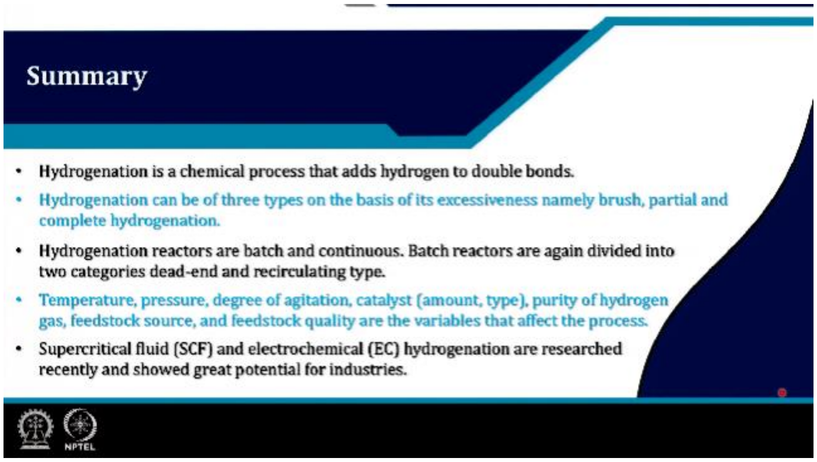
- Liquid oils – Brush hydrogenation
- Margarine bases – Partial hydrogenation
- Shortening bases – Partial hydrogenation
- Stearin – Total hydrogenation
- Coating fats – Partial hydrogenation

So, the hydrogenated oil end product the examples are like liquid oil thereby made by gross hydration, margarine bases by partial hydrogenation, shortening bases by partial hydrogenation again, stearin by total stearin that is complete hydrogenation by total hydrogenation and coating fats are normally by partial hydrogenation. So, depending upon what with the characteristic required in the end product various hydrogenation can be done.



❑ Schematic of a oil hydrogenation plant

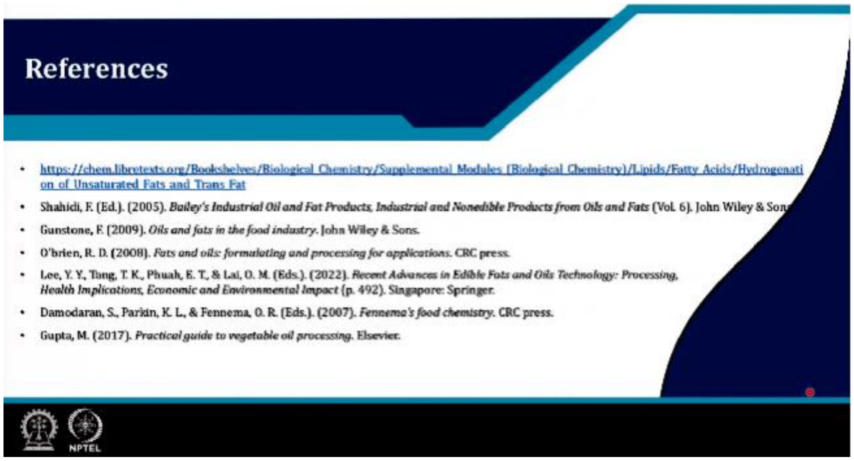
So, this is a complete setup for the schematic for the hydrogen, hydrogen from typical hydrogenation plant and all the that is oil inlet and the treating with the reaction, steam generation continuous process that is the batch hydrogenation reactions are provided in top tank, buffer tank, then spent catalyst filtration section catalyst is and then hydrogenation oil to the storage this is given.



Summary

- Hydrogenation is a chemical process that adds hydrogen to double bonds.
- Hydrogenation can be of three types on the basis of its excessiveness namely brush, partial and complete hydrogenation.
- Hydrogenation reactors are batch and continuous. Batch reactors are again divided into two categories dead-end and recirculating type.
- Temperature, pressure, degree of agitation, catalyst (amount, type), purity of hydrogen gas, feedstock source, and feedstock quality are the variables that affect the process.
- Supercritical fluid (SCF) and electrochemical (EC) hydrogenation are researched recently and showed great potential for industries.

So, I would summarize this lecture finally, by saying that hydrogen, hydrogenation is a chemical process that adds hydrogen to double bonds. Hydrogenation can be of three types on the basis of the effectiveness namely brush, partial and complete hydrogenation. Hydrogenation reactors are batched and continuous both. Batch reactors are again divided into two categories that is dead end and recirculating type, temperature, pressure, degree of agitation, catalyst both a mountain type, purity of hydrogenation, gas feedstock, source and feedstock quality are the variables that affect the process. Supercritical fluid and electrochemical hydrogenation are researched recently and showed great potential for the industries and that should be tested.



References

- https://chem.libretexts.org/Bookshelves/Biological_Chemistry/Supplemental_Modules_(Biological_Chemistry)/Lipids/Fatty_Acids/Hydrogenation_of_Unsaturated_Fats_and_Trans_Fat
- Shahidi, F. (Ed.). (2005). *Bailey's Industrial Oil and Fat Products, Industrial and Nonedible Products from Oils and Fats* (Vol. 6). John Wiley & Son
- Gunstone, F. (2009). *Oils and fats in the food industry*. John Wiley & Sons.
- O'brien, R. D. (2008). *Fats and oils: formulating and processing for applications*. CRC press.
- Lee, Y. Y., Tang, T. K., Phuah, E. T., & Lai, O. M. (Eds.). (2022). *Recent Advances in Edible Fats and Oils Technology: Processing, Health Implications, Economic and Environmental Impact* (p. 492). Singapore: Springer.
- Damodaran, S., Parkin, K. L., & Fennema, O. R. (Eds.). (2007). *Fennema's food chemistry*. CRC press.
- Gupta, M. (2017). *Practical guide to vegetable oil processing*. Elsevier.

And these are the references which is these used in this lecture only. Thank you very much for your patience hearing. Thank you.