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> **Lecture – 34 Modified Fats**



# Modification of oils and fats

The oils and fats when extracted from various sources after refining etc., they may not be present in their desired form or functionality to suit a specific food operation or specific use. These fats and oils are usually modified using appropriate procedures in order to improve their functional properties like crystallization, melting behaviour and other properties so as to make them suitable for specific operations or use.

By modifying the fat, their physical properties are actually altered and their stability is improved, so that maximum economical benefits can be obtained out of fats and oils. Commonly used methods for modifications of oils and fats include hydrogenation, interesterification and winterization.



#### **Hydrogenation:**

Hydrogenation is a heterogeneous reaction process which is complex in nature where different reactions occur between hydrogen which is gaseous phase and unsaturated fatty acids i.e. the liquid phase. These reactions between the gaseous phase and the liquid phase convert either all of or some of the unsaturated fatty acids into saturated fatty acid. The valancy of the carbon is not saturated, there will be 2 or 3 or more double bond in the chain of the fatty acid (see Fig.). So, here in the hydrogenation process these double bonds or unsaturation is converted into saturation. By the introduction of hydrogen into the molecule in the presence of nickel under suitable or appropriate conditions, double bond is converted into a single bond. The unsaturated vegetable oil or unsaturated fatty acid is converted into saturated fat or ghee and the same thing here is shown in the case of molecular formula.

Linolenic acid has about three double bonds in its structure. If this linolenic acid is saturated once, one double bond is converted into linoleic acid, and if the linoleic acid is again saturated, its one double bond is converted into single bond and it will be converted into oleic acid and the oleic acid after saturation will be converted into stearic acid. So, in this process unsaturated oil or fat is converted into a saturated fat or oil.



The hydrogenation process involves multiple 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 unsaturated fatty acids) on the catalyst surface.
- Partial or complete saturation of the USFA on the catalyst surface.
- Desorption of the products of the reaction  $(SFA)$  and the USFA  $\&$  oil molecules from the catalyst surface
- Release of heat due to the exothermic nature of the hydrogenation reaction.

So, these are the different stages or different reactions which take place during the hydrogenation process, the same thing has been shown here in this diagram pictorially.



The purpose of hydrogenation is actually to change naturally occurring fats and oils into physical forms with the consistency and handling characteristics required for the desired functionality. Another important function is to improve its oxidative stability, because unsaturated fats and oils generally are more prone to oxidation. So, by converting unsaturated oils into saturated fat, they are made more stable to oxidation i.e. the oxidation can be prevented.

### **Effects of hydrogenation**

- $\checkmark$  The USFA become more saturated.
- $\checkmark$  The iodine value of the oil decreases Iodine value is the measure or the degree of unsaturation. So, more the unsaturated fat higher will be the iodine value.
- $\checkmark$  The melting point of the oil increases.
- $\checkmark$  The oxidative stability of the oil improves.
- $\checkmark$  A multitude of side reactions take place, including the formation of certain alcohols and acids.
- $\checkmark$  Isomerization of some of the polyunsaturated fatty acids takes place.

Though, the products of hydrogenations are very complex mixture, because of the simultaneous reactions that occur in the system depending upon the temperature, pressure, catalyst, etc. The saturation of double bonds, cis-trans isomerisation of the double bond and shift of double-bond locations usually to the lower energy conjugated sides are involved.



The equipment used in the hydrogenation process is basically a reaction vessel 'hydrogenator'. The reaction vessel is equipped with all sorts of necessary instrumentation and other facilities for making the reaction to take place i.e. for addition of the hydrogen and providing suitable temperature and pressure.



### **Batch hydrogenation reactor**

It 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



The equipment is filled to its desired capacity. The oil first is heated to around 85 to 95 ºC for 15 to 20 min and then through the input assembly, is introduced into the reaction vessel. And, then fresh catalyst (nickel) is added at a rate of 0.01 to 0.02 % of the oil into the reactor, when the oil temperature has been reached to around 155 - 160 ºC. So, the hydrogenation reaction then proceeds. Heat generated from the reaction raises the oil temperature in the reactor and the steam supply automatically cuts off when the temperature comes to the desired level. The reaction in a batch reactor is carried out either adiabatically or isothermally.



#### **Continuous hydrogenation process**

Three such reactor vessels are arranged in parallels and all these vessels are provided with the suitable arrangement for the continuous flow of the oil. In the first system, catalyst and oil are fed into the reaction vessels and then hydrogen gas is introduced.

From the first vessel, it passes through the second vessel and then goes to the third vessel. In each vessel, required temperature and pressure etc. is maintained and finally, when it comes to the last vessel after the hydrogenation process is complete, the product is taken out. It is then sent to the filtration unit for the removal of added catalyst from the mixture and then oil or fat is allowed to cool down to solidify.

And, in fact, the removal of the catalyst is very important and the filter which is provided in the system should be perfect to remove almost all the catalyst from the oil otherwise, it will be problematic. Once after the reaction, the effectiveness of catalyst gets little reduced so, it can be further activated and one catalyst can be used three or four times.

The end of the saturation process both in the continuous process as well as in the batch process is determined by doing certain tests. In fact, the samples are taken out at regular intervals and analysed for different tests like iodine value, refractive index, etc.

The hydrogenator equipment are provided at the top with some vent or valve etc. so that head space gases etc. which are generated during the reaction should be allowed at continuous interval to go out of the system to maintain the proper reaction rate.

#### **Operating variables of hydrogenation process**

- $\Box$  Pressure
- 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.



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### **Temperature**

- The reaction increases substantially with increasing temperature, so hydrogen atoms near the absorbed double bond will react faster with the double bond.
- Under these conditions, the reaction interface is virtually instantly depleted of hydrogen.
- 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 trans formation. So, a proper balance between the temperature and pressure and suitable selection of the catalysts etc. should be maintained in the reaction system.
- In recent years, the trend has been mainly to lower the operation temperatures, resulting in a significant trans reduction but also a lower capacity.

#### **Q** 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, 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 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. **SWAV2**

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- The powder, 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. Nickel is a paraphobic material; it violately burns if comes in direct contact with air. So, generally nickel is kept in some dissolvent some sort of oil to avoid contact.
- 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 non-selective conditions such ad high hydrogen pressures.
- The catalyst type itself has very little impact on the (large) quantity of trans isomers formed. The proper activity of the catalyst will facilitate the reaction at a proper rate which may encourage less convergence of cis into trans, but so, it need to be properly.



### **Selectivity**

By having appropriate selectivity and choosing the process parameters, the hydrogenated fat or saturated fat of desired consistency can be obtained.

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

In fact, this selectivity is defined under the normal conditions, that is a highly unsaturated fat like polyunsaturated fat, they undergo convergence into saturated fat at a high rate than those with the less unsaturated fatty acid. There is more polyunsaturated fatty acid hydrogenate at a faster rate than less polyunsaturated fatty acid and that is the selectivity.

In fact, in the triglyceride linolenic, linoleic and oleic acid because they have a different saturation, unsaturation level so, they get hydrogenated at different rates. That is if the rate of hydrogenation of linolenic to linoleic if we say that  $K_1$ , that is the rate of convergence from linoleic to oleic if  $K_2$  and rate of convergence of oleic to stearic if it is  $K_3$ , then linolenic selectivity  $SL_1$  will be equal to  $K_1/K_2$ ;  $K_1/K_2$  is the convergence of linolenic to linoleic and finally, linoleic to oleic and the linoleic selectivity will be  $SL<sub>2</sub>$ will be  $K_2/K_3$ .

However, in this model the concentration of hydrogen at the surface of 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. By having appropriate selectivity, we can get the fat or saturated fat of desired consistency for desired operations i.e. more or less soft fat with having proper functional characteristics.



### **Hydrogenation process : Industrial issue**

### **Need**

Industry needs the proper stability and functionality of the oil.

Unsaturated oils oxidize easily

 $\checkmark$  Leads to rancidity

 $\checkmark$  Very short shelf life

Saturated and unsaturated fats are a difficult consistency for food processing

- $\checkmark$  Solid with high melting points.
- $\checkmark$  Liquid, does not stay in product well and can give soggy texture.

#### **Solution**

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

### **Interesterification (IE)**

- Interesterification refers to the fats and oils reaction in which the fatty acids of triglycerides exchange positions from one glyceride to another, thereby altering the chemical composition as well as physical properties of the fats.
- Efficient way for changing and controlling the melting properties of oils and fats.
- Rearrangement process which does not change the degree of unsaturation or the isomeric state of the fatty acids as they transfer in their entirety from one position to another.
- Under some conditions, the fatty acids are distributed in a more random manner than they were present originally.
- Based on the catalysts, this method is divided into chemical & enzymatic interesterification processes.



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In the chemical interesterification process in fact, in the triglyceride (see Fig.) the first position is the  $R_1$  second position is the  $R_2$  and third position is the  $R_3$ . By the appropriate selection of catalyst and having proper conditions in the reaction vessel, they can be interchanged. So, the  $R_2$  which was in the second position comes to the first position. Thus, it is basically the interchange between the fatty acids group.



# **Effect of Interesterification**

Interesterification is used to modify fats such as:

- Change the overall melting profile.
- Improve the compatibility of the triglycerides in solid state.
- Improve the plasticity of the resulting solid by changing the crystallization properties.
- Combine the properties of mixed oils and fats.
- IE can also be used to produce a waxy translucent for coating purposes.
- IE blends soft oils with hard fats to a desired functionality and consistency.
- By combining IE and other modification processes, many products such as shortenings, margarines, and vegetable ghee with low trans fat or no trans fat at all can be formulated.
- Satisfactory quality of confectionery fats can be produced.

### **Chemical interesterification** • The interesterification process works through the use of a variety of chemicals as the catalyst. • Chemical interesterification has been used to modify oils and fats into functional products for many decades.

- It leads to a random distribution of fatty acids on the glycerol backbone.
- Chemical interesterification requires high temperature and pressure which degrade the oils and fats and introduce impurities.
- Loss of valuable minor-components such as tocopherols.
- High oil losses (up to 10 %).
- Risky operation because of catalyst.



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### **Catalyst for chemical IE**

Acids, bases and their corresponding salts and metals are used for the IE which can be subdivided into high and low temperature groups.

- High temperature catalysts
	- $\checkmark$  Include metal salts such as chloride, carbonates, oxides, nitrates and acetates of zinc, lead, iron, tin and cobalt.
- Low temperature catalysts
	- $\checkmark$  Includes alkylates (methylate and ethylate) of Na and Na/K alloy.
- $\checkmark$  Alkylates of Na are simple to use and inexpensive; only small quantities are required and they are active at low temperature  $< 50^{\circ}$ C.



# **IE Process parameters**

The quality of the product at the end should be controlled by controlling the oil quality.

# **Oil quality**

- Should be free from contaminants; minor components or contaminants will also consume the catalyst to a considerable degree.
- Should be free from moisture; affects the 'pure reaction' and consume the classic catalysts, such as sodium methylate, in the proportion of 1 : 20.
- FFA content will also deactivate the catalyst, albeit less extremely, and often a bit of caustic soda is added prior to the reaction.
- Also, oxidation parameters such as the peroxide value will lower the catalyst efficiency and thereby increase the cost of achieving full randomization.

#### $\Box$  Catalyst

- In the light of the interesterification reaction, the active catalyst species needs to be an electron donor.
- Pure alkali metals such as Na or K were ideal for such reactions, and in small scale operations these proved successful.
- . However, for larger operations alkoxides (sodium methoxide or sodium methylate) are the principal catalyst, because of their high reaction rate at rather low temperatures.
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#### **Commercial plant for the interesterification process**

The actual reaction system is like a hydrogenator reactor provided with all necessary instrumentation and other facilities to maintain the temperature, pressure and to facilitate the entry of oil and catalyst. They are provided with de-acidification, deodorization or bleaching facilities. The bleached and neutralized ion is put to the reaction vessel where the catalyst is sent and then the proper temperature pressure conditions are maintained within the vessel to get the desired interesterification reaction process.

#### **Enzymatic interesterification**

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- The Interesterification process with the use of a biologically derived enzyme is known as enzymatic interesterification (EIE).
- The demand of this method increases because of increasing trend to avoid chemicals in food processing.
- Lower capital investment cost as compared to the chemical process.

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### **Types of enzymatic interesterification**

- **Nonspecific enzymatic**
- $\checkmark$  Used for the production of commodity fats to modify the overall melting properties, increasing compatibility within the solid phase and enhancing the plasticity of the final product.
- **Specific enzymatic**
- $\checkmark$  Used to produce tailor-made products as cocoa butter equivalents, anti-bloom agents, breast milk substitutes, and low calorie fats.



### **Continuous multi column enzymatic interesterification system**

In this reaction setup, there are reaction vessel and oil feed tank i.e. preheated oil utilized and refined oil is passed through these packed bed reactors.

It is a four column reactor comprising of

- A temperature-controlled SS feed tank of 150 kg capacity.
- Four temperature-controlled enzyme columns each packed with 10 kg enzyme.
- A temperature-controlled SS product tank of 150 kg capacity.

The temperature and other conditions inside the reaction vessels are maintained by hot water circulation system at which the reaction is allowed to proceed. At the end of the reaction, the catalyst is removed by using appropriate filtration and then this interesterified oil is obtained.

#### **Winterization**

- Winterization is a thermo-mechanical separation process where component triglycerides of fats and oils are crystallized from a melt.
- The two-component fractional crystallization is accomplished with partial solidification and separation of the higher melting triglyceride components.
- In this process, the fat is melted and heated to eliminate any crystal memory.
- The molten fat is cooled down under controlled agitation and cooling conditions to produce crystals nuclei formed by the higher melting triglycerides.
- Then, nuclei will grow to form crystals of the desired size.

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- When the crystallisation has progressed far enough, the slurry is separated.

In fact, this process allows to get the winterization as well as tempering processes are allowed to get the fat of desired polymer confirmations as well as desired characteristics for suitable particular process operations.



Apparently this process looks very simple, but in practice this physical process is complicated by the fact that the formation of the nuclei depends upon foreign particles, agitation, temperature, the triglyceride composition and the type of the pre treatment followed by the fat.



### **Fat crystallization occurs in two steps**

The crystallization actually occurs in two steps; one is the nucleation and then the crystal growth. Rate of nucleation depends upon the triglyceride composition of the oil being winterized, the cooling rate of the oil, the temperature of the nucleation and the mechanical power input or agitation. The crystal growth depends upon the crystallization temperature, time and mechanical input or agitation.

Another important term here is the solvent fractionation. In fact, it is the term used to describe a process for the crystallization of a desired fraction from a mixture of triglyceride dissolved in a suitable solvent. Fractions may be selectively crystallized at different temperatures after which the fractions are separated and the solvents are removed. Solvent fractionation is practiced commercially to produce hard butters speciality oils and some salad oils from which a wide array of edible oils.

Using solid solvent fractionation, different solvents can be used to fractionate different or specific triglyceride and then these specific triglyceride are further modified to have desired characteristic and properties to suit particular food process operations.

The different processes are introduced by which different vegetable oils and fats can be modified to improve their functionalities, their usability in different food products and food processes and of course, improve their sensory, organoleptic and other characteristics.