Food Oils and Fats: Chemistry & Technology

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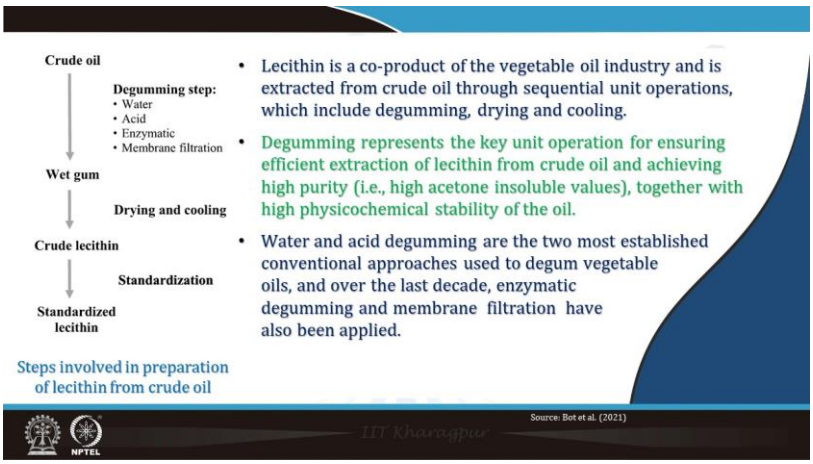
Module 11: By-products Utilisation & Valorisation of Oil Milling Industry Waste

Lecture 54: Lecithin Production

Hello everybody. Namaskar. Now, in today's lecture that is lecture 54, we will discuss lecithin production.

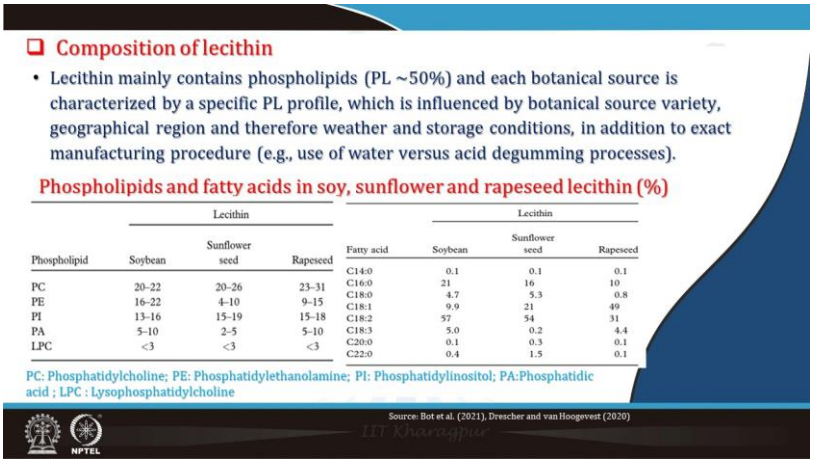
There, we will talk about structure and composition of lecithin, production process, quality analysis, modifications, and applications of lecithin.

You know lecithin is a generic term that is used for the description of a multi-component blend of phosphatidylcholine, phosphatidylethanolamine, phosphatidylserine, and phosphatidylinositol combined with other substances such as triglycerides, fatty acids, and carbohydrates. It is a structural and functional component of a diverse range of cell membranes for plants as well as for various terrestrial and marine animals. It is commonly used as an emulsifier in food, pharmaceutical, and cosmetic industries due to its ability to mix with both water and oil-based substances. Examples of lecithin which are available in the market include soy lecithin, sunflower lecithin, and so on.



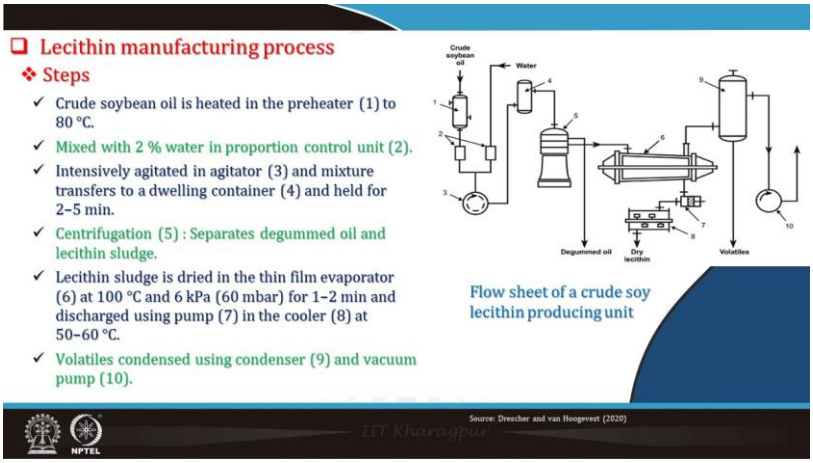
So, lecithin is basically a co-product of vegetable oil industry and is extracted from crude oil through sequential unit operations which include degumming, drying, and cooling. In the earlier classes, during refining process, we discussed what is degumming. So, from the degumming process, that is, the gums are extracted. So, degumming represents the key unit operation for ensuring efficient extraction of lecithin from crude oil and achieving high purity in the lecithin that is high acetone insoluble value together with high physicochemical stability of the oil. Water and acid degumming are the two most established conventional approaches used to degum vegetable oils, and over the last decade, enzymatic degumming and membrane filtration have also been applied. So, this

crude lecithin gum which is obtained, it is dried and cooled and then lecithin is obtained from that gums.

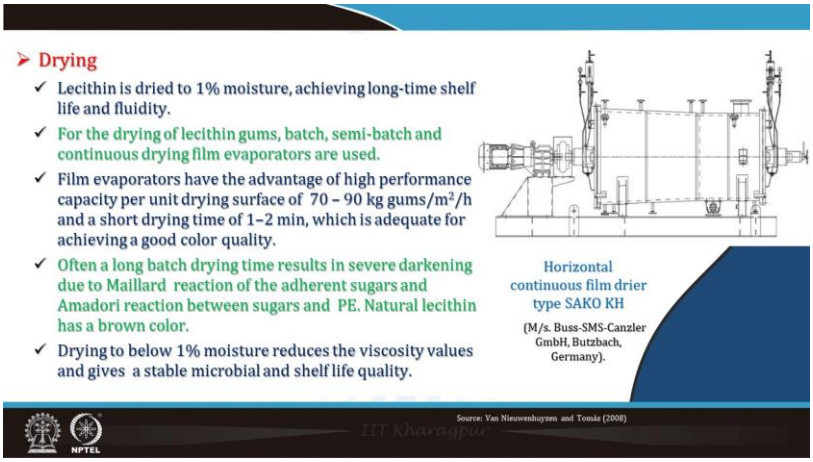


So, the composition of lecithin that is lecithin mainly contains phospholipid that is around 50 percent and each botanical source is characterized by a specific phospholipid profile which is influenced by botanical source variety, geographical region, and therefore weather and storage conditions, in addition to exact manufacturing procedure that is what is the use of the water or acid that is water versus acid degumming processes.

So, phospholipids and fatty acids in soya, sunflower, and rapeseed lecithin are given. For example, soybean lecithin contains about phosphatidylcholine in the range of 20 to 22 percent whereas, sunflower lecithin contains phosphatidylcholine in 20 to 26 percent. Rapeseed lecithin contains ranging from 23 to 31 percent phosphatidylcholine. Similarly, phosphatidyl ethanolamine also in the soya bean lecithin are maximum like about 16 to 22 percent, sunflower contains 4 to 10 percent and rapeseed contains 9 to 15 percent. Similarly, phosphatidylinositol is almost in the range of 13 to 18 percent in all three lecithins from three sources. Similarly, if you look at this fatty acid composition, you find that the C 18:2 that is linoleic acid in soya bean lecithin is 57 percent, sunflower seed lecithin it is 54 percent, and in rapeseed lecithin seed, lecithin is 31 percent. The C 18:1 that is the oleic acid. It contains about 10 percent in soybean lecithin, sunflower lecithin about 21 percent, and rapeseed lecithin 49 percent. So, these various lecithin from various sources vary in their phospholipid content as well as in their fatty acid composition.

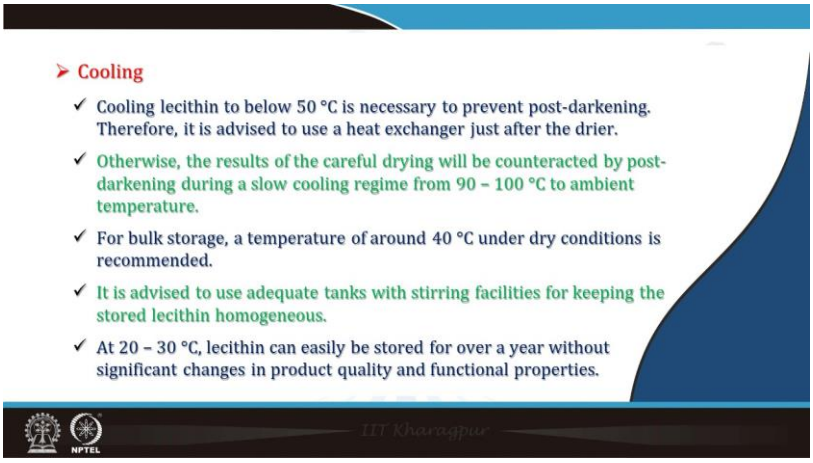


So, for the manufacture of lecithin, crude soybean oil is just a heated or soybean oil or any such oil which is used for lecithin production. It is heated in a preheater that is you can see, there is a setup to 80 degree Celsius, and then it is mixed with 2 percent water in proportion control unit, and it is intensively agitated using an agitator that is shown here at point 3 and mixture transfers to a dwelling container (4) and held for about 2 to 5 minutes in the dwelling container. The next step is the centrifugation, that is centrifugation separates the degummed oil and the lecithin sludge. The lecithin sludge is then dried in a film evaporator at around 100 degree Celsius and 6 kiloPascal that is 60 m bar for 1 to 2 minutes and discharged using a pump in the cooler unit at around 50 to 60 degree Celsius. The volatiles are condensed using condenser and vacuum pump.

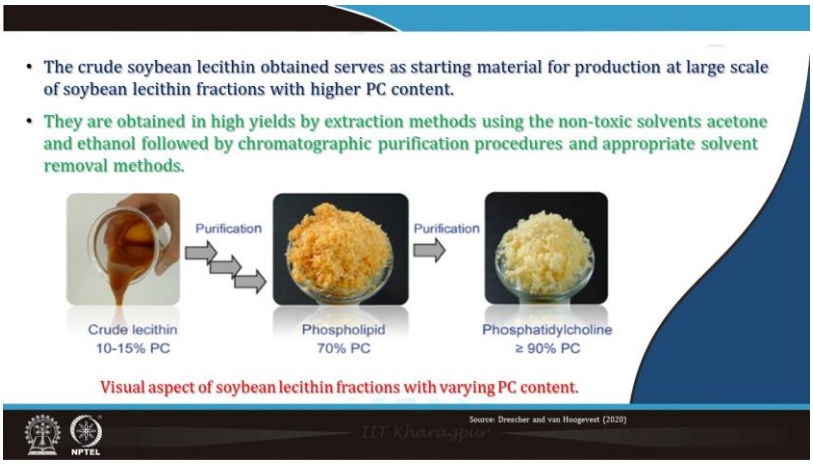


Drying of the lecithin is done and as far as possible maximum moisture is removed that is it is dried to around 1 percent moisture content achieving long shelf life and fluidity. For the drying of lecithin gums, batch, semi-batch, or continuous drying film evaporators are used. Film evaporators have the advantage of high-performance capacity per unit drying surface of about 70 to 90 kg gums per square meter per hour and a short drying time of about 1 to 2 minutes which is adequate for achieving a good color quality. Often a long batch drying time results in severe darkening due to the Maillard reaction and the adherent sugars and Amadori reactions between sugars and phosphatidyl ethanolamine.

Natural lecithin has a brown color. So, drying below 1 percent moisture reduces the viscosity values and gives a stable microbial and safe shelf life quality. Then cooling is another very important step in the lecithin production.

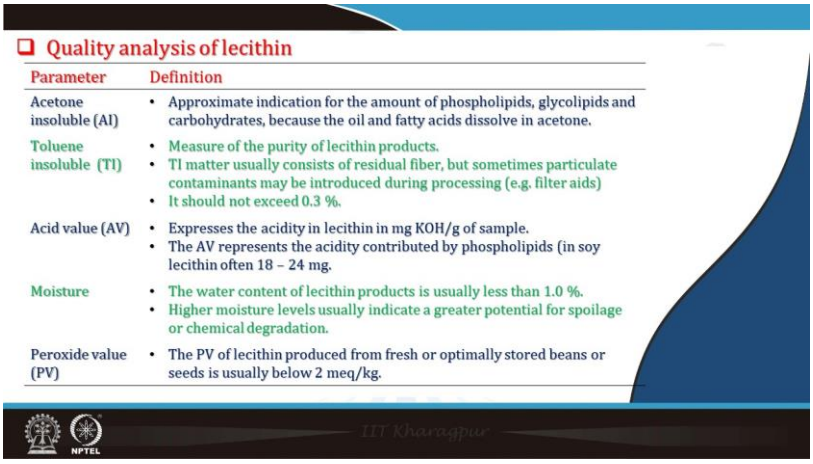


The lecithin is cooled below 50 degree Celsius, and it is necessary to prevent post-process darkening. Therefore, it is advised to use a heat exchanger just after the dryer. Otherwise, the results of the careful drying will be counteracted by the post-darkening during a slow cooling regime that is from 90 to 100 degree Celsius to ambient temperature. For bulk storage, a temperature of around 40 degree Celsius under dry conditions is recommended. It is advised to use adequate tanks with stirring facilities for keeping the stored lecithin homogeneous. At around 20 to 30 degree Celsius, lecithin can easily be stored for over a year without significant changes in product quality and functional properties.



The crude soybean lecithin obtained serves as a starting material for the production at large scale of soybean lecithin fractions with high phosphatidylcholine content. They are obtained in high yields by extraction methods using the non-toxic solvent acetone and ethanol followed by a chromatographic purification procedure and appropriate solvent removal method. You can see here, that is, crude lecithin about 10 to 15 percent how its

colour look like and then the phospholipid content is around 70 percent PC, that after purification you can see that the visual image picture is shown here in the figure. The same again lecithin after further purification that is where phosphatidylcholine is more than or equal to 90 percent, it becomes golden brown or delicate very attractive colour, it lecithin gives. So, the visual aspect of soybean lecithin, they vary with the phosphatidylcholine content in it.



As far as the quality analysis of lecithin is concerned let us talk about there are few parameters which are used to indicate the quality of lecithin.

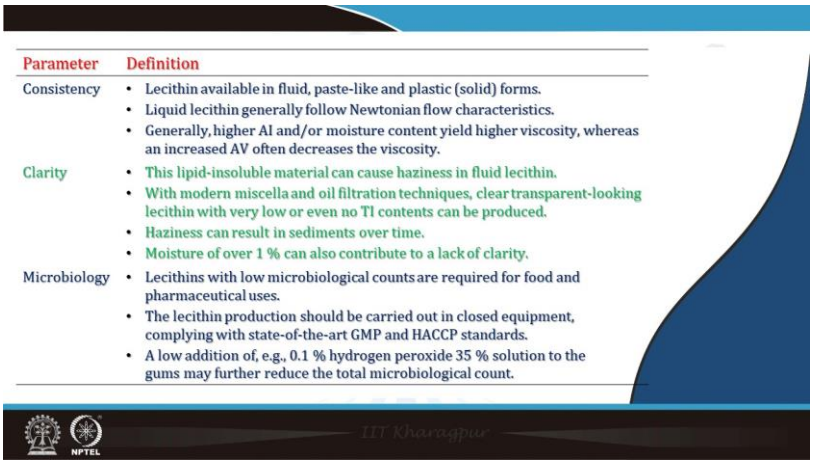
One is the acetone insoluble, popularly known as AI. An approximate indication for the amount of phospholipids, glycolipids, and carbohydrates because of the oil and fatty acid dissolve acetone. So, acetone insoluble indicate about approximate amount of the phospholipids. Toluene insoluble, they measure the purity of the lecithin product. The TI matter usually consists of residual fibre, but sometimes particulate containing contaminants may be introduced during processing like filter aids etc. and in any case, it should not exceed 0.3, i.e. TI should not exceed 0.3.

Acid value expresses the acidity of lecithin in milligram KOH per gram of sample and the average represents the acidity contributed by phospholipids (in soy lecithin often it is about 18 to 20 mg KOH per gram). The moisture content of the lecithin product is usually less than 1 percent. Higher moisture levels usually indicate a greater potential for spoilage or chemical degradation. Peroxide value of lecithin production from the fresh and optimally stored seeds is usually less than 2 meq per kg of the product.

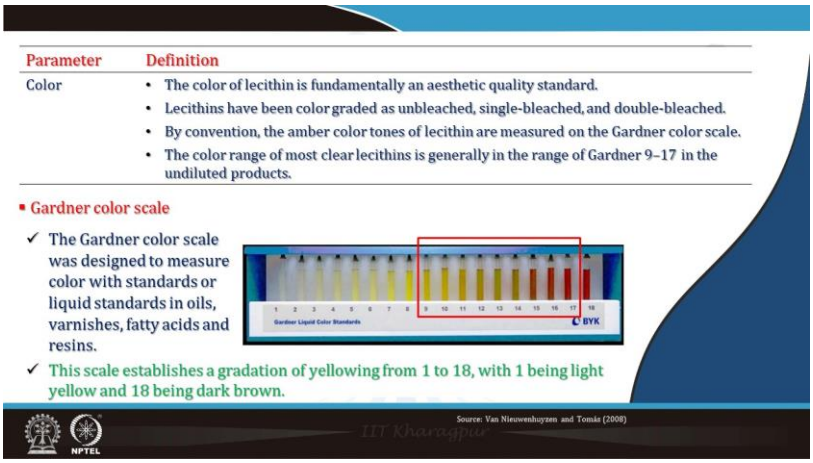
Then consistency lecithin available in fluid paste like and plastic forms liquid lecithin generally follow Newtonian flow characteristics and generally higher AI and or moisture content yields higher viscosity, whereas, an increased AV often decreases the viscosity.

Clarity that is lipid soluble material can cause haziness in the fluid lecithin. With modern miscella and oil filtration techniques, clear transparent-looking lecithin with very low or

even no TI contents can be produced. Haziness can result in sediments over the time. So, moisture of over 1 percent can also contribute to a lack of clarity

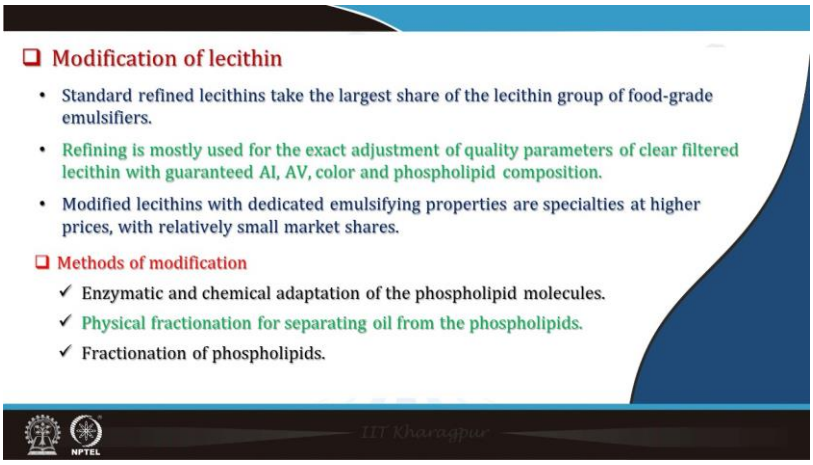


About microbiological quality, lecithin is generally low in microbiological counts, and it should be maintained low because they are required for food and pharmaceutical that is the one which has a lower microbiological content. The lecithin production should be carried out in closed equipment complying with the state of the art GMP and HACCP standards. A low addition of 0.1 percent hydrogen peroxide 35 percent solution to the gums may further reduce the microbiological quality or count in the lecithin.



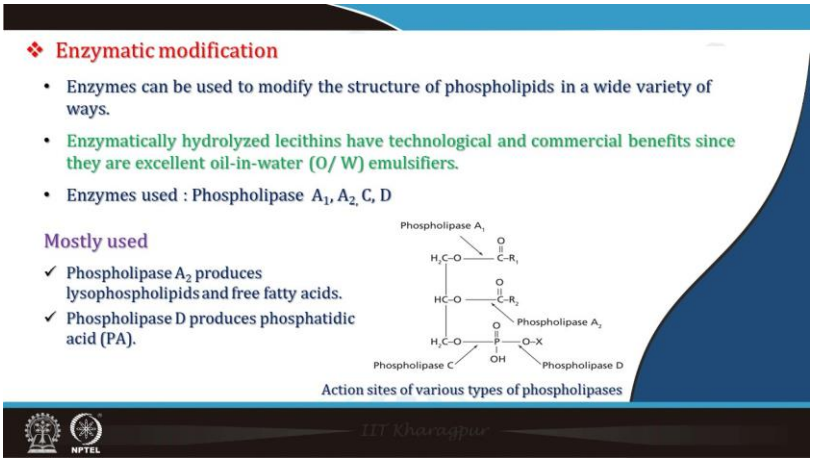
Then another is the color, it is a very important parameter as you have seen that how by changing the phosphatidylcholine content how the color of the lecithin is changed. So, the color of lecithin is fundamentally an aesthetic quality standard lecithin has been color graded as unbleached, single-bleached, and double-bleached. By convention, the amber color tones of lecithin are measured on the Gardner color scale. The color range of more clear lecithin is generally in the range of Gardner 9 to 17 in the undiluted products. As you can see here, that is what is the color in 9 to 17 in the gardener range. So, Gardner color scale was designed to measure color with standards or liquid standards in oil,

varnishes, fatty acids, and resins. This scale establishes a gradation of yellowing from 1 to 18, with 1 being the yellow light and 18 being dark brown in color



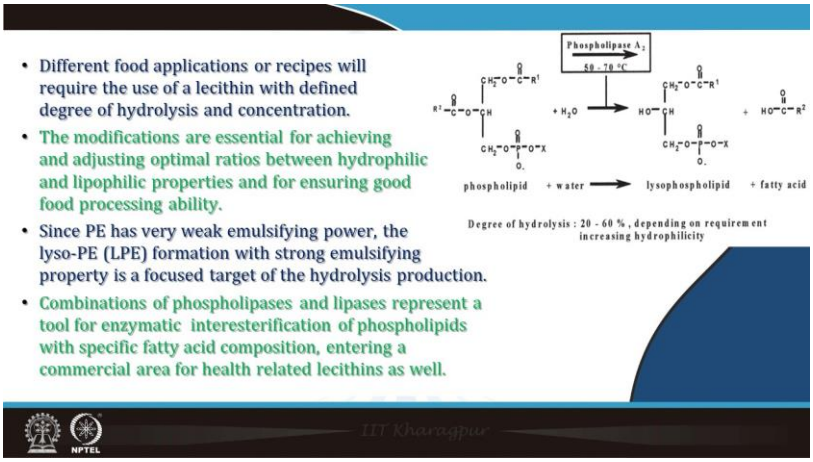
Then let us talk about there are certain technologies sometimes it is required to modify the lecithin to suit some specific process operations. Standard refined lecithin takes the largest share of the lecithin group of food-grade emulsifiers. So, refining is mostly used for the exact adjustment of the quality parameter of clear filtered lecithin with guaranteed values of AI, AV, color, and phospholipid composition. Modified lecithins with dedicated emulsifying properties are specialties at higher prices, with relatively small market shares.

So, the methods which are used for the modification of lecithin are enzymatic and chemical adaptation of the phospholipid molecules, then physical fractionation for separating oil from the phospholipids and the other method may be fractionation of phospholipids. So, let us talk about enzymatic modification.



You know that enzymes are used to modify the structure of phospholipids in a wide variety of ways. Enzymatically hydrolyzed lecithin have technological and commercial benefits since they are excellent oil-in-water emulsifiers. So, the enzymes which are used are phospholipase A_1, A_2, C, and D. Mostly used is the phospholipid A_2 which produces

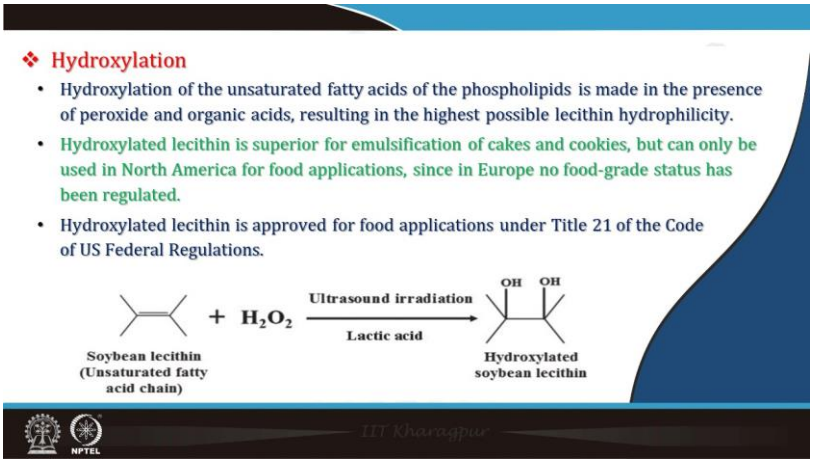
lysophospholipids and free fatty acids. Phospholipase D produces phosphatidic acid. You can see here that is this is the phospholipid particle, the phospholipase A1, it will be assigned at SN1 position. Phospholipase A2, it will be assigned SN2 position. Third i.e., phospholipase C, this esterlinkage between the fatty acid and phosphoric acid and phospholipase D that is it removes the choline from X. So, these are the various action sites of the various types of phospholipases. So, mostly it is the phospholipase A2 and phospholipase D. These are the one which is used to modify this.



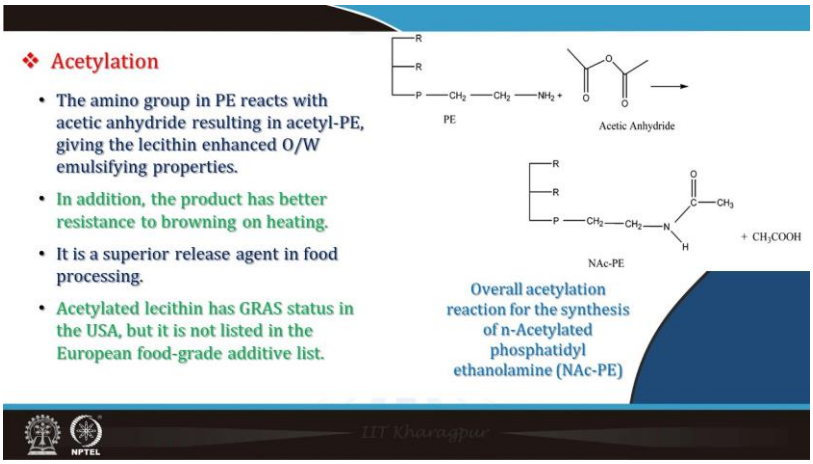
So, different food applications or recipes will require the use of lecithin with defined degree of hydrolysis and concentration. The modifications are essential for achieving and adjusting optimal ratios between hydrophilic and lipophilic properties and for ensuring good food processing ability. Since phosphatidyl ethanolamine has very weak emulsifying power, the lyso-PE formation with strong emulsifying properties is a focused target of hydrolyzed production or hydrolysis production. Combinations of phospholipases and lipases represent a tool for enzymatic interesterification of phospholipids with specific fatty acid composition, entering a commercial area for health-related lecithin as well.

And you can see here, that is the phospholipase A2 it acts at 50 to 70 degree Celsius, then phospholipids water and then this R1 it and HO R2 that is second group it it is broken as the lecithin is broken that ester linkage at SN2 position. And it gives lysophospholipids plus a fatty acid is released. The degree of hydrolysis may be around 20 to 60 percent depending on the requirement increase in hydrophilicity.

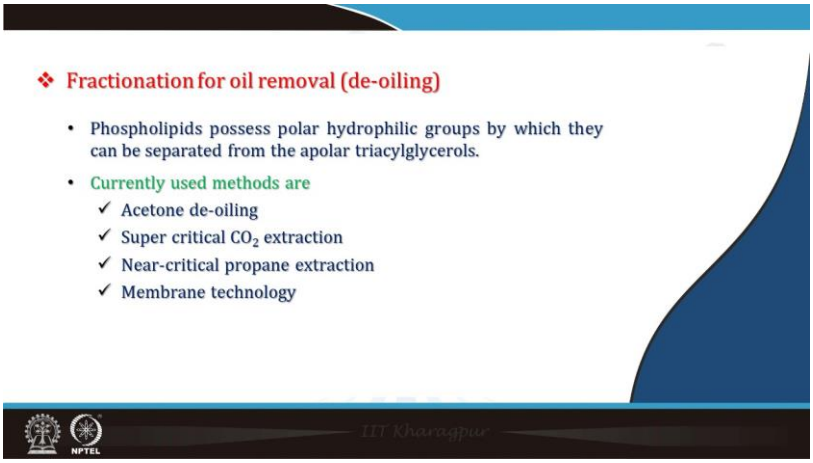
Hydroxylation, hydroxylation of the unsaturated fatty acid of the phospholipids is made in the presence of peroxide and organic acids, resulting in the highest possible lecithin hydrophilicity. Hydroxylated lecithin is superior for emulsification of cake and cookies, but can only be used in North America for food applications, since in Europe no food-grade status has been regulated. Hydroxylated lecithin is approved for food applications under Title 21 of the Code of US Federal Regulations.



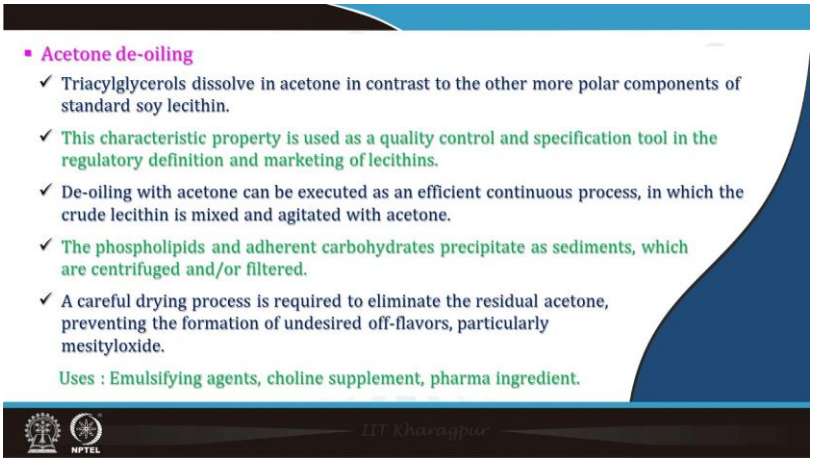
So, soybean lecithin (unsaturated fatty acid) plus H_2O_2 hydrogen peroxide under ultrasound irradiation and lactic acid, it gives hydroxylated soybean lecithin that is you can see how OH has come here.



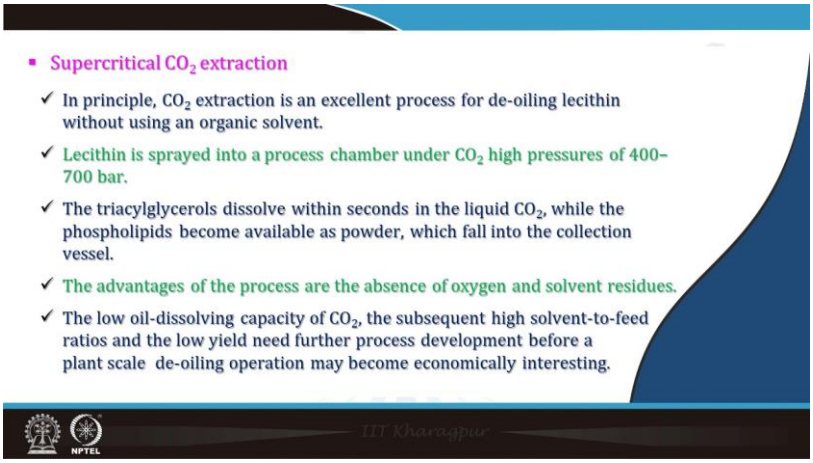
Then acetylation, there is an amino group in the phosphatidyl ethanolamine reacts with the acetic anhydride, resulting in acetyl PE that is an acetyl PE giving lecithin enhanced oil-in-water emulsifying properties. In addition, the product has better resistance to browning on heating. It is a superior release agent in food processing. Acetylated lecithin has GRAS status in the USA, but it is not listed in the European food-grade additive list. You can see the overall acetylation reaction for the synthesis of n-acetylated phosphatidyl ethanolamine that is phosphatidyl ethanolamine plus acetic anhydride and gives that general acetyl phosphatidyl ethanolamine plus acetic acetyl alcohol is liberated.



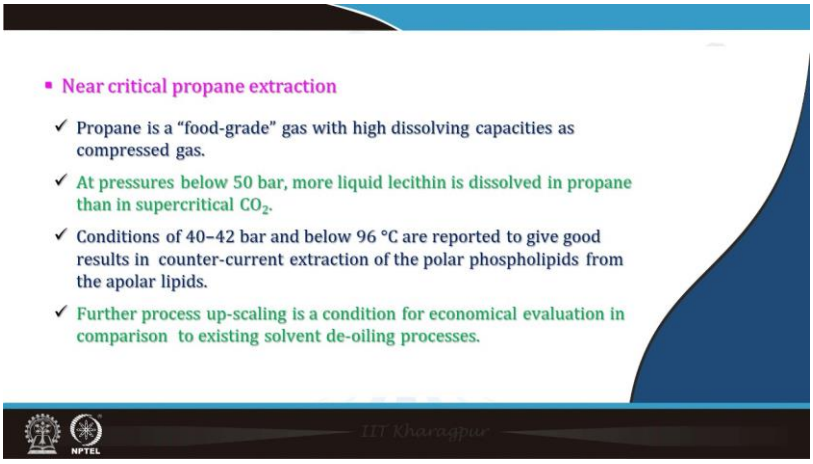
Fractionation for oil removal or de-oiling. Phospholipids possess polar hydrophilic groups by which they can be separated from the apolar triacylglycerols. So, currently used methods are acetone de-oiling, supercritical carbon dioxide extraction, near critical propane extraction, or membrane technology.



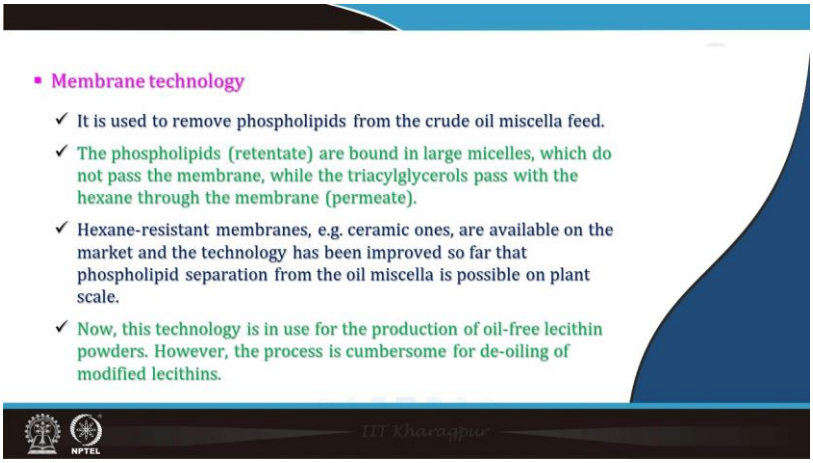
So, acetone de-oiling, a triacylglycerol dissolved in acetone in contrast to other more polar components of the standard soy lecithin. This characteristic property is used as a quality control and specification tool in the regulatory definition and marketing of lecithins. De-oiling with acetone can be executed as an efficient continuous process, in which the crude lecithin is mixed and agitated with acetone. The phospholipids and adherent carbohydrates precipitate as sediment, which can or are centrifuged and/or filtered and removed. A careful drying process is required to eliminate the residual acetone, preventing the formation of undesired off-flavors, particularly mesityloxide. So, the uses of this include emulsifying agents, choline supplements, or pharma ingredients.



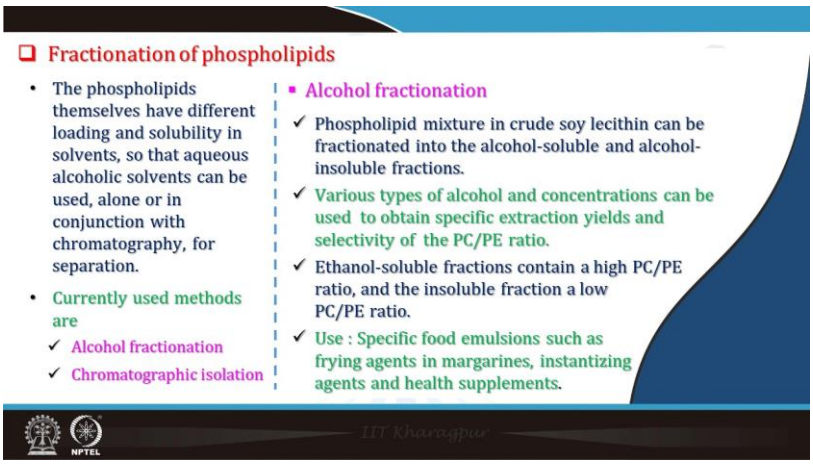
Supercritical carbon dioxide, in principle you know that carbon dioxide extraction is an excellent process for de-oiling lecithin without using any organic solvent. Lecithin is sprayed into a process chamber under CO_2 high pressures of around 400 to 700 bar is maintained. The triacylglycerols dissolve within seconds in the liquid carbon dioxide while the phospholipids become available as powder, which falls into the collection vessel. The advantage of the process is the absence of oxygen and solvent residues in the product. The low oil-dissolving capacity of carbon dioxide, the subsequent high solvent-to-feed ratio, and the low yield need further process development before a plant-scale de-oiling operation may become economically viable or economically interesting.



Near critical propane extraction, that is, you know propane is a food-grade gas with high dissolving capacities as compressed gas. At pressures below 50 bar, more liquid lecithin is dissolved in propane than in supercritical carbon dioxide. Conditions of around 40 to 42 bar and below 96 degree Celsius temperature are reported to give good results in counter-current extraction of the polar phospholipids from the apolar lipids. Further process up-scaling is a condition for economical evaluation in comparison to existing solvent de-oiling processes.



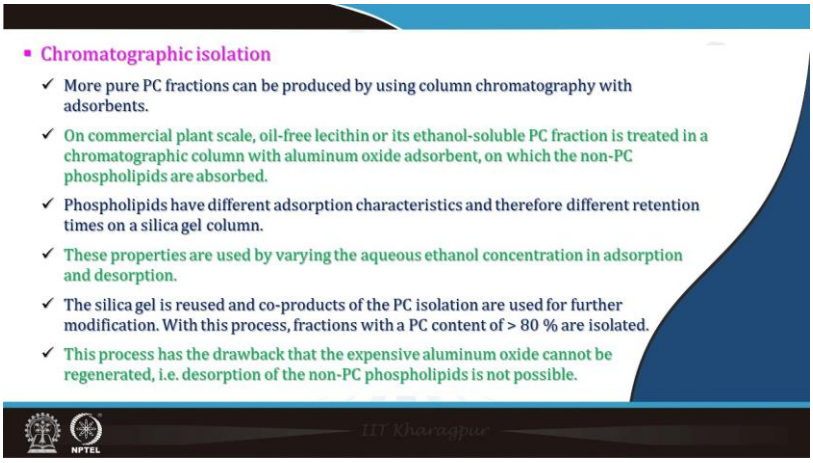
Then membrane technology, again we have discussed earlier. It is used to remove phospholipids from the crude oil miscella feed. The phospholipids are bound in the large micelles, which do not pass the membrane; they are retentate, while the triacylglycerol passes with hexane through the membrane. So, they become permeate. Hexane-resistant membranes such as ceramic ones are available on the market, and the technology has been improved so far that phospholipid separation from the oil miscella is possible on a plant scale. Now, this technology is in use for the production of oil-free lecithin powder. However, the process is cumbersome for de-oiling of modified lecithins.



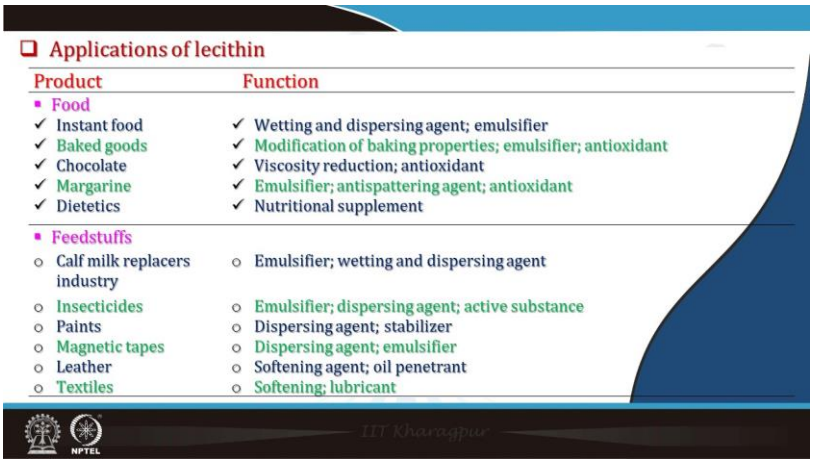
Then, fractionation of phospholipids. The phospholipids themselves have different loading and solubility in solvents, so that aqueous alcoholic solvent can be used, alone or in combination with chromatography, for separation. Currently used methods are alcohol fractionation and chromatographic isolation.

In alcohol fractionation, the phospholipid mixture in crude soy lecithin is fractionated into the alcohol-soluble and alcohol-insoluble fractions. Various types of alcohol and concentrations are used to obtain specific extraction yields and selectivity of the PC and PE ratio.

Ethanol soluble fractions contain a high PC to PE ratio, and the insoluble fraction gives a low PC to PE ratio. These are specific food emulsions such as frying agents in margarine, instantizing agents, and health supplements.



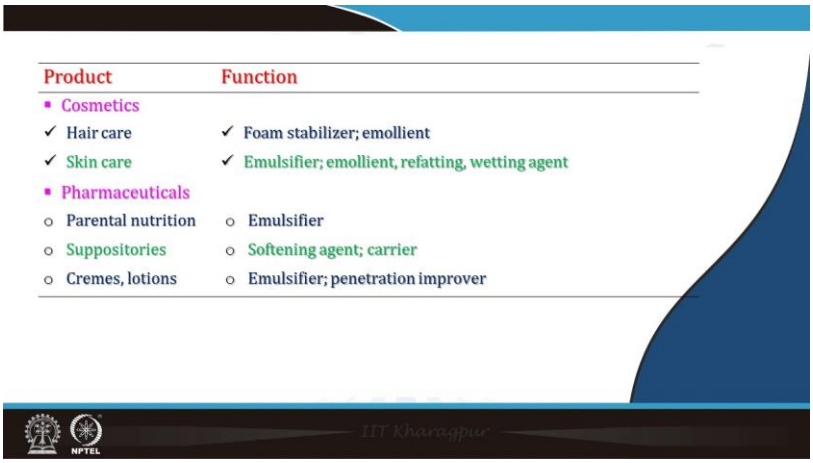
The chromatographic isolation that is more pure phosphatidylcholine fractions can be produced by using column chromatography with adsorbents. On commercial plant scale, oil-free lecithin or ethanol-soluble PC fraction is treated in a chromatographic column with aluminium oxide adsorbent, on which the non-PC phospholipids are absorbed. Phospholipids have different adsorption characteristics and, therefore, different retention times on a silica gel column. These properties are used by varying the aqueous ethanol concentration in adsorption and desorption. The silica gel is reused and co-products of the PC isolations are used for further modification. With this process, fractions with a phosphatidylcholine content of greater than 80 percent are isolated. This process has the drawback that the expensive aluminum oxide cannot be regenerated; that is, desorption of the non-PC phospholipids is not possible.



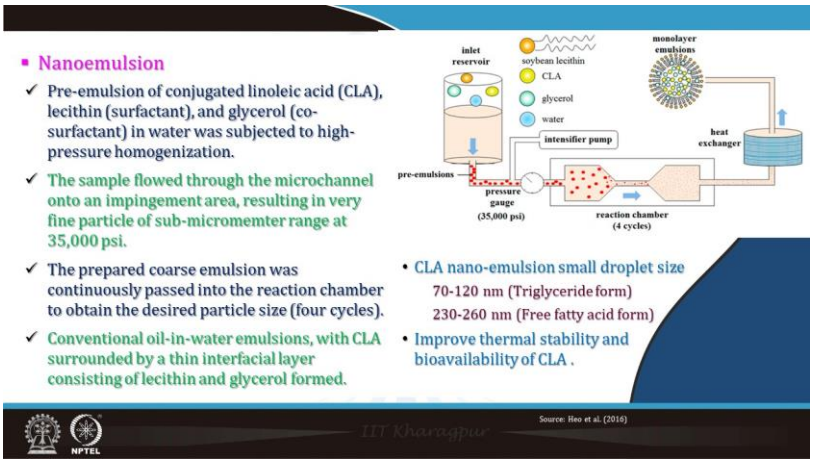
So, applications of lecithin are included in the food product. It is used in instant food as wetting and dispersing agent, as an emulsifier in baked goods. It is used for modification of baking properties, it is used as an emulsifier antioxidant in chocolate that is used for

viscosity reduction and antioxidant. In margarine, its function includes emulsifier, antispattering agent and antioxidants; and in dietetics, it is used as a nutritional supplement.

About feedstuffs, in the calf milk replacers industry, as an emulsifier and wetting and dispersing agent is used. In insecticides industry, this is used as an emulsifier, dispersing agent, and active substance. In magnetic tapes, also as well as in leather textile industry this is used as either dispersing agent, softening agent, oil penetrator, emulsifier, lubricant and so on.

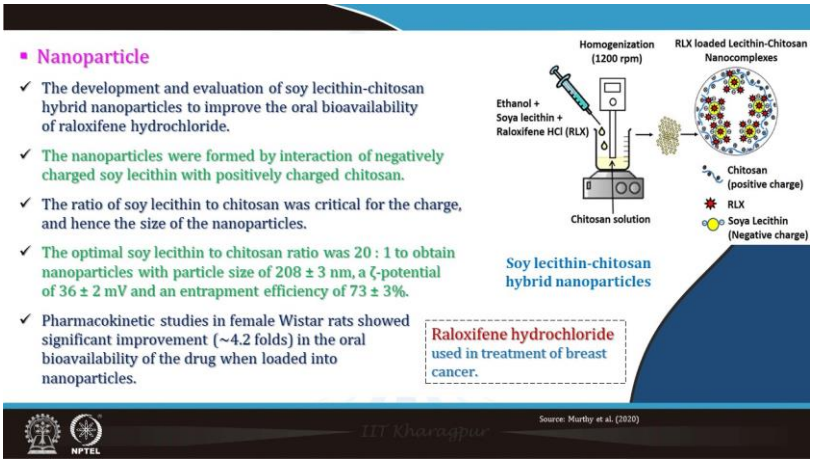


In cosmetics, that is used for hair care, skin care. In hair care, it is used as a foam stabilizer or emollient; in skin care, it is used as an emulsifier, emollient, refatting, and wetting agent. In pharmaceuticals, it is used in parental nutrition as an agent emulsifier; in suppositories, the softening agent, and carrier agent; in cremes and lotions, it is used as an emulsifier, penetration improver, and so on.



Nanoemulsion is the pre-emulsion of conjugated linoleic acid, lecithin, and glycerol in water that is subjected to high-pressure homogenization. The sample flowed through the microchannel onto an impingement area. You can see here that there are various that is soy lecithin, CLA, glycerol, and water. So, they are mixed into this emulsion; emulsion is

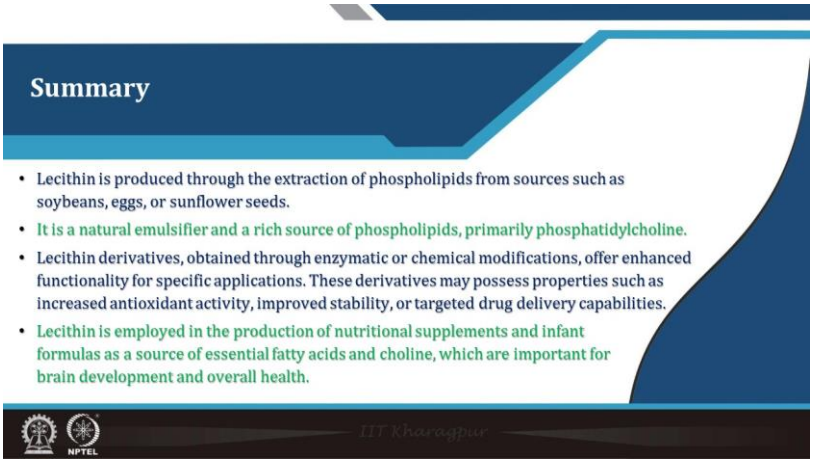
sent to this reaction chamber; these 4 cycles. These are the sub-micrometer range at 35000 psi. They verify that fine particles are formed here. Then the prepared coarse emulsions are continuously passed into the reaction chamber to obtain the desired particle size; that is four cycles. The conventional oil-in-water emulsions, with CLA surrounded by the thin interfacial layer consisting of lecithin and glycerol, are formed here. From the reaction, it goes to the heat exchanger and then monolayer emulsions are formed. CLA nano-emulsions, small droplets size like 70 to 120 nanometers, they are in triglyceride form and 230 to 260 nanometers are in free fatty acid form. So, they improve thermal stability and bioavailability of CLA.



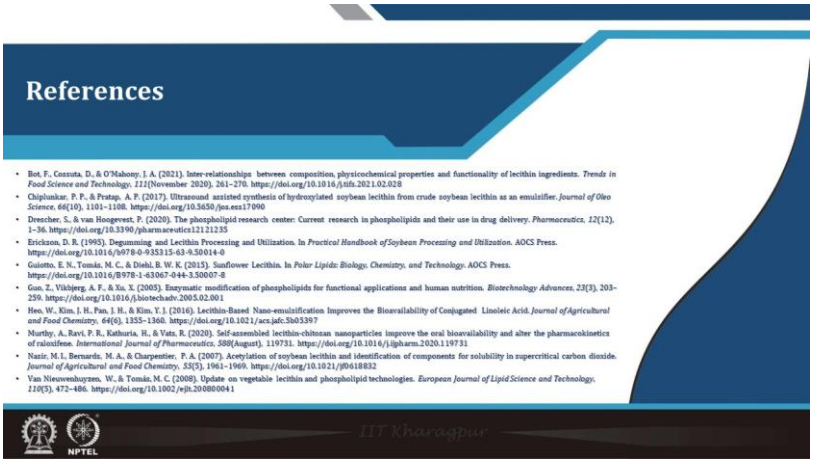
Nanoparticles; the development and evaluation of soy lecithin-chitosan hybrid nanoparticles to improve the oral bioavailability of raloxifene hydrochloride. The nanoparticles were formed by the interaction of negatively charged soy lecithin with positively charged chitosan. The ratio of soy lecithin to chitosan is critical for the charge, and hence the size of nanoparticles. The optimal soy lecithin to chitosan ratio was 20:1 to obtain nanoparticles with particle size range of 208 and a zeta potential of 36 plus minus 2 mV and an entrapment efficiency of 73 plus minus 3 percent.

So, pharmacokinetic studies in female Wistar rats showed significant improvement, maybe about 4.2 folds in the oral bioavailability of the drug when loaded into the nanoparticles. Normally, raloxifene hydrochloride is used in the treatment of breast cancer.

The process where soy lecithin-chitosan hybrid nanoparticle formation you can see here chitosan solution and then ethanol soy lecithin and raloxifene are injected into this, it is homogenized and then you get the powder. That is the formula this nanoparticles are obtained.



Finally, I will summarize this lecture by saying that lecithin is produced through the extraction of phospholipids from sources such as soybean, eggs, sunflower seeds etcetera. It is a natural emulsifier and rich source of phospholipids, primarily that is phosphatidylcholine. Lecithin derivatives obtained through enzymatic or chemical modifications offer enhanced functionality for specific applications. These derivatives may possess properties such as increased antioxidant activity, improved stability or targeted drug delivery capability. Lecithin is employed in the production of nutritional supplements and infant formulas as a source of essential fatty acids and choline, which are important for brain development and overall health.



So, these are your references.

This thank you very much for you. Thank you.