Food Oils and Fats: Chemistry & Technology

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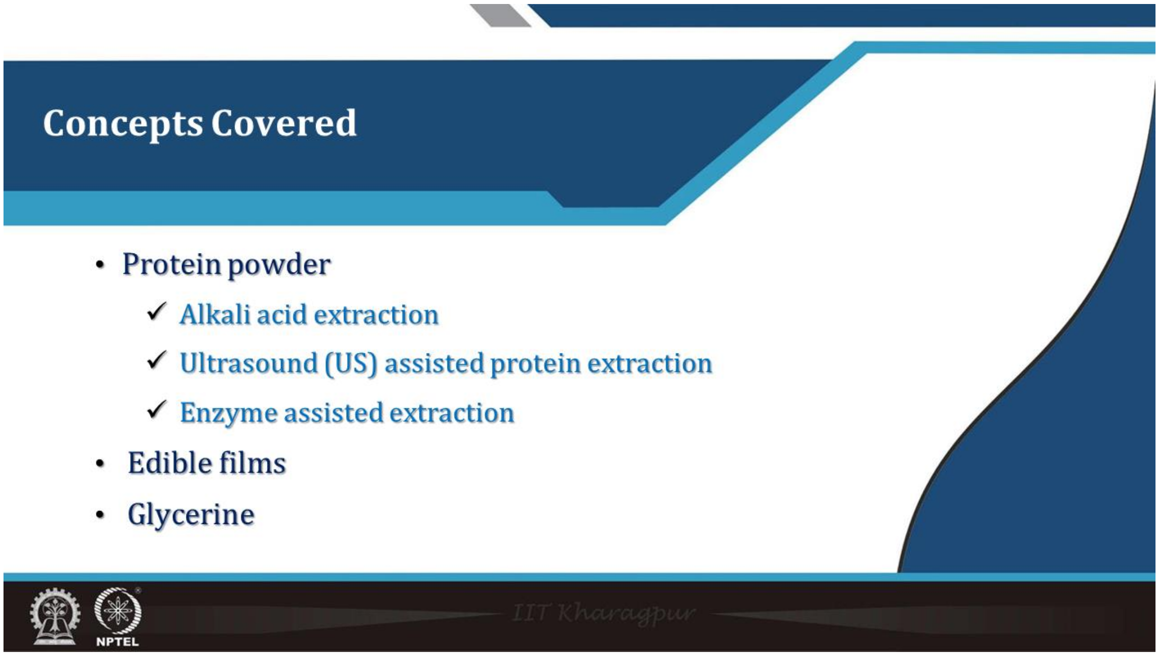
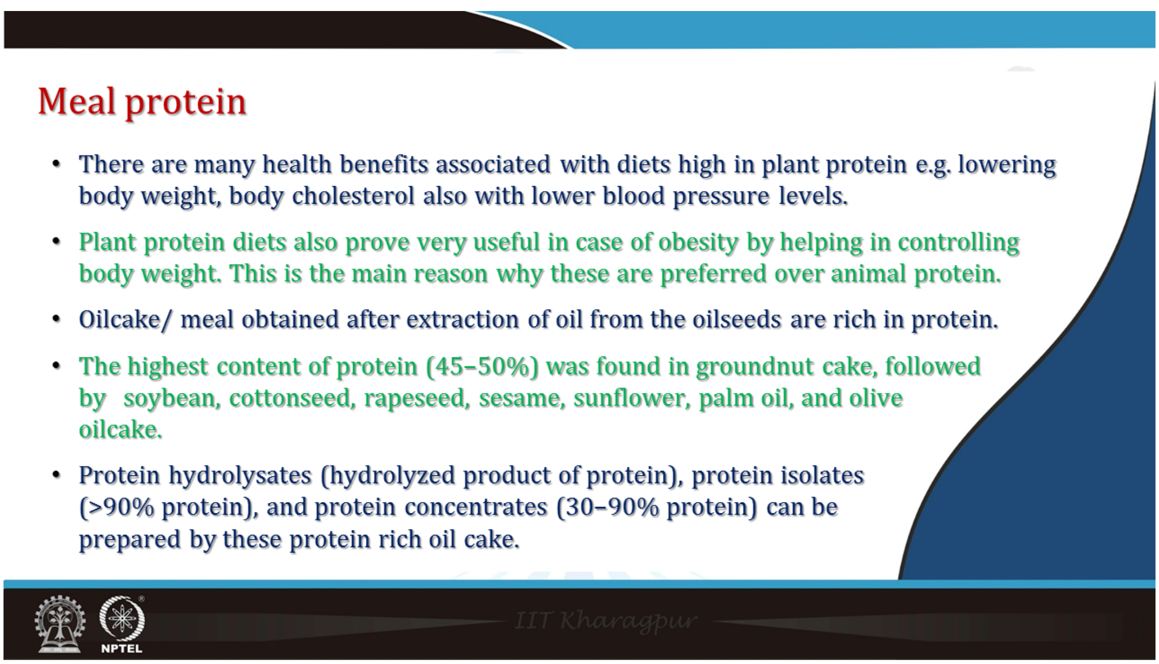
Module 11: By-product Utilization & Valorization of Oil Milling Industry Waste

Lecture 52 : By-products Utilization– Part I

Hello everyone! Namaskar! Now, in this lecture 52, we will discuss utilization of byproducts. In the earlier class, we studied what are the various byproducts and what is their usefulness.



Now, in this lecture, we will talk about some of the conversion of these byproducts into different materials which can be used for food purposes as well as non-food purposes. And we will take three important products, one is the protein powder.

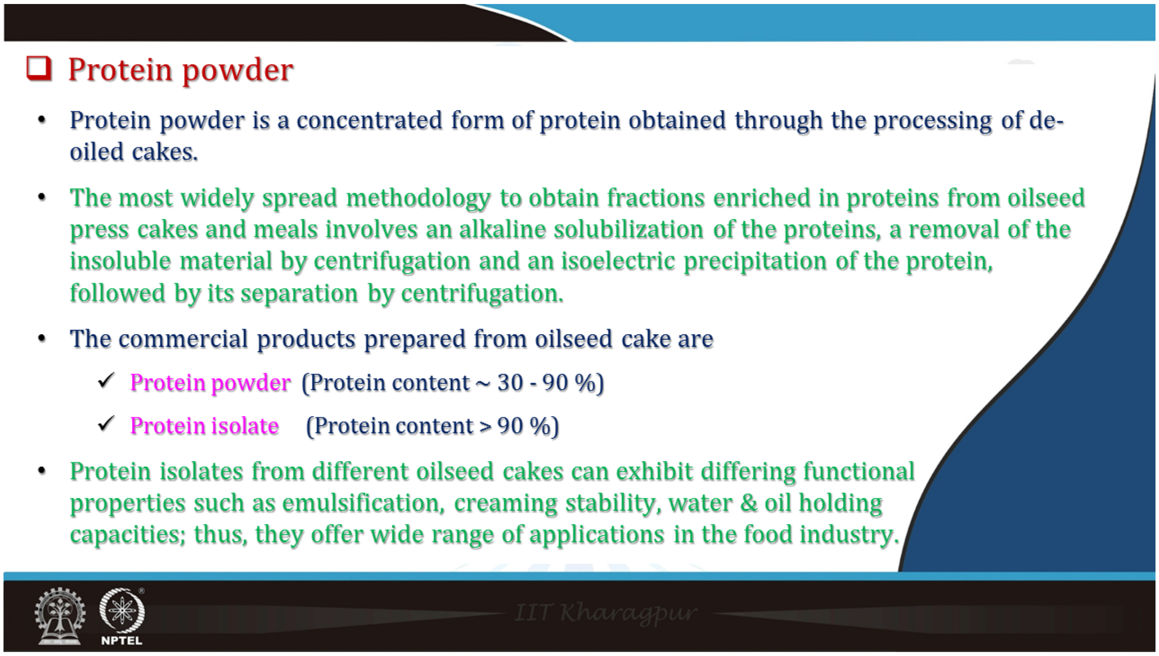


So, how this de-oiled meal can be converted into a good food grade protein powder that is by different extraction method, alkali extraction, ultrasound assisted extraction or enzyme assisted extraction. And then these can be used for making generating edible films and glycerin is the one product which you see that is a fatty acid distillate, glycerin.

So, the manufacture of preparation of these three major products from the byproducts of oil milling industry will discuss. So, let us see de-oiled cake which you obtain which is also known as meal. So, they are having many health benefits associated with the diet high in plant protein, ok. For example, lowering the body weight, body cholesterol also they lower the blood pressure or regulate the blood pressure.

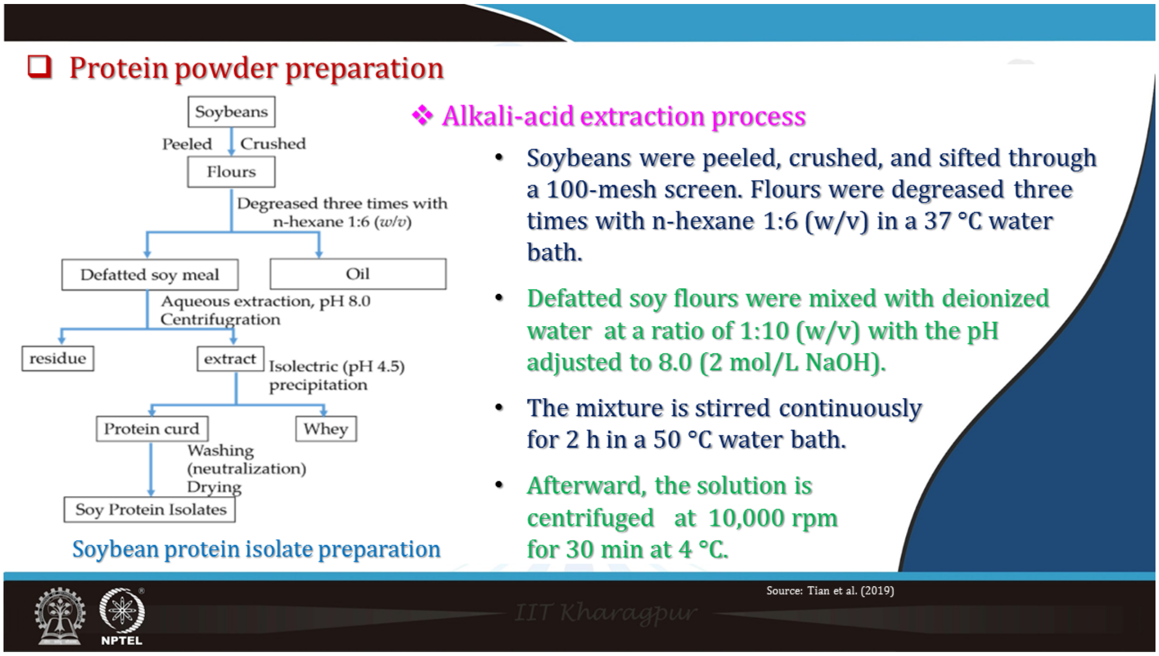
So, the meal containing that is food which contains high protein content it has very good advantages. So, plant protein diets also prove very useful in case of obesity by helping in controlling body weight. This is the main reason why these are preferred over animal proteins. So, oil seed cake or oil seed meal, de-oiled meal obtained after the extraction of oil from the oilseed. They are rich in protein content we discussed in the earlier class. So, the highest content of protein may be as high as 45 to 50 percent in the groundnut followed by soybean, cotton seed, rapeseed, sesame, sunflower, palm oil, olive oil cake, etcetera.

They are all having very good quantity of the protein not only good quantity, but also they have very good quality proteins. So, this protein hydrolysate it like hydrolyzed product of protein, protein isolate which has more than 90 percent protein and protein concentrate which has protein content ranging from 30 percent to 90 percent, they can be prepared by these protein rich oil cake.



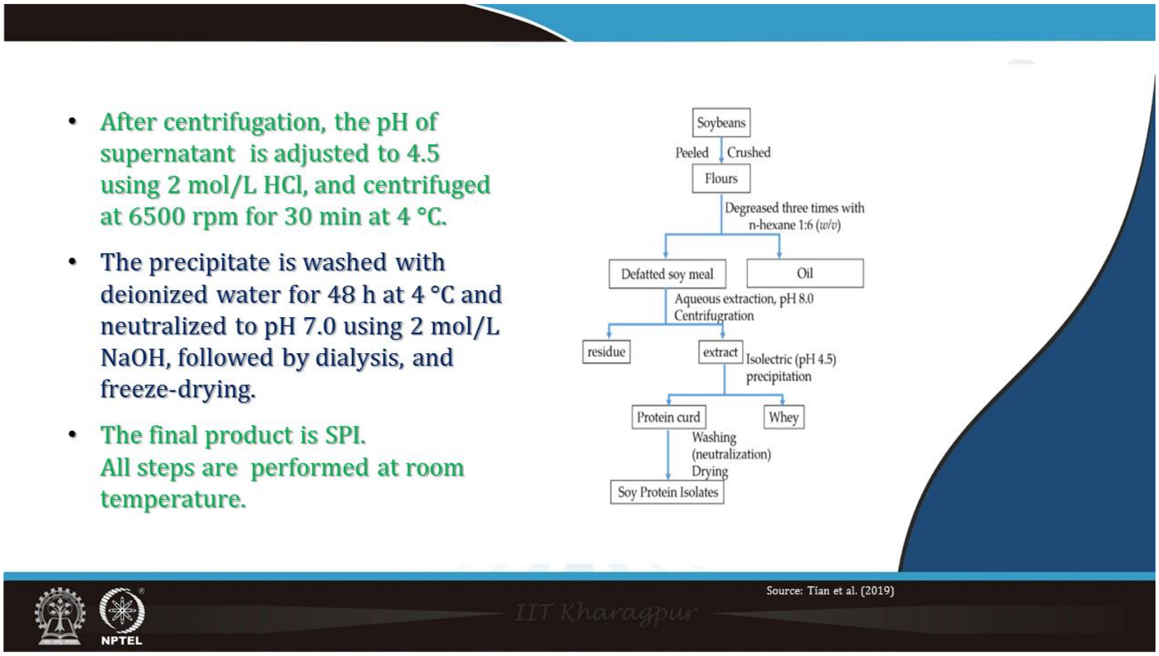
So, that protein can be isolated or it can be purified and concentrated. So, protein powder basically is a concentrated form of protein obtained through the processing of de-oiled cake. The most widely used or spread methodology to obtain fractions enriched in protein from oilseeds pressed cake and meals have an alkaline solubilization of the protein, a removal of the insoluble material by centrifugation and an isoelectric precipitation of the protein, followed by its separation by centrifugation.

So, this is the way by which these proteins can be obtained they can be. And then these commercial products prepared from oilseed cakes pressed oil cake are that is a protein powder, that is, which contain protein to 30 to 90 percent and then obviously, protein isolate which has protein more than 90 percent. So, isolates from different oilseed cakes that is protein isolates can exhibit differing functional properties, such as emulsification, cream instability, water and oil holding capacities and thus they offer wide range of applications in food industry, ok.

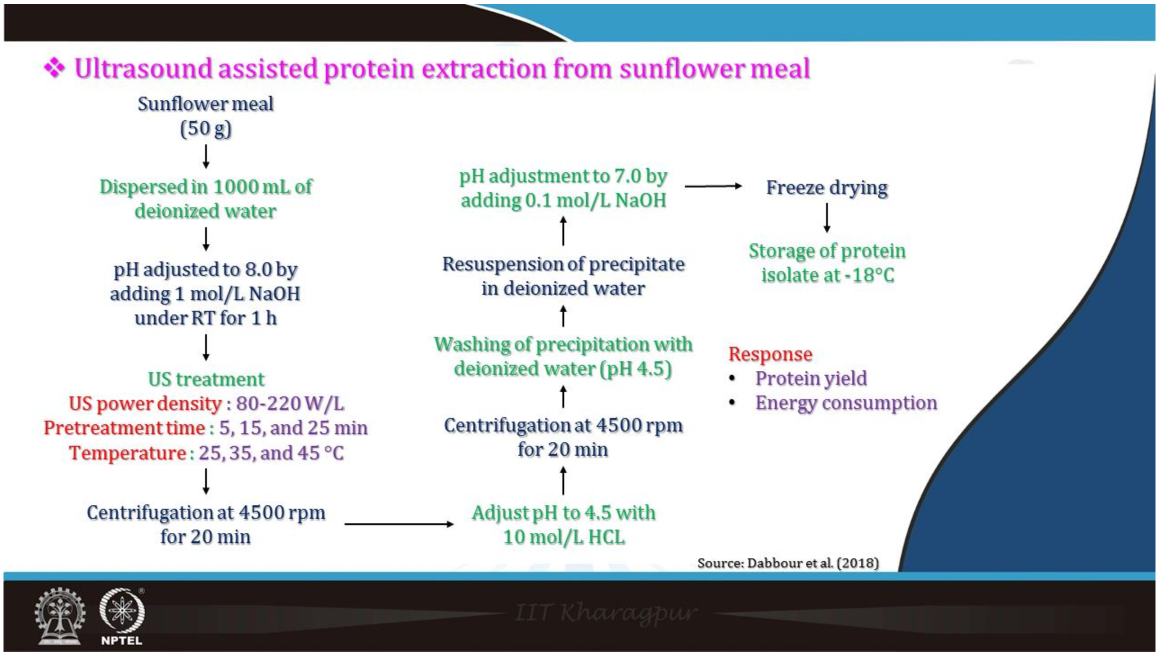


So, let us see protein powder preparation. The flow chart is shown here, ok. And what is the alkali acid extraction process is more commonly used where soybeans obviously, where peeled, crushed and sifted through 100-mesh screen and the flours are degreased three times with n-hexane, that is, 1 is to 6 weight by volume in a 37 degrees Celsius water, ok.

So, you get the oil and from this process that is defatted soybean meal is obtained. So, that is, by standard method. So, this defatted soybean meals, what is done, this is mixed with the deionized water at a ratio of 1 is to 10 weight by volume with the pH adjusted to 8, pH is adjusted 8, and for this even 2 mole per liter of NaOH is used. So, the mixture is stirred continuously for 2 hours at 50 degree Celsius in a water bath, ok. And this, afterward the solution is centrifuged at 10000 rpm for 30 minutes at 4 degree Celsius to get the soy protein isolates, ok.

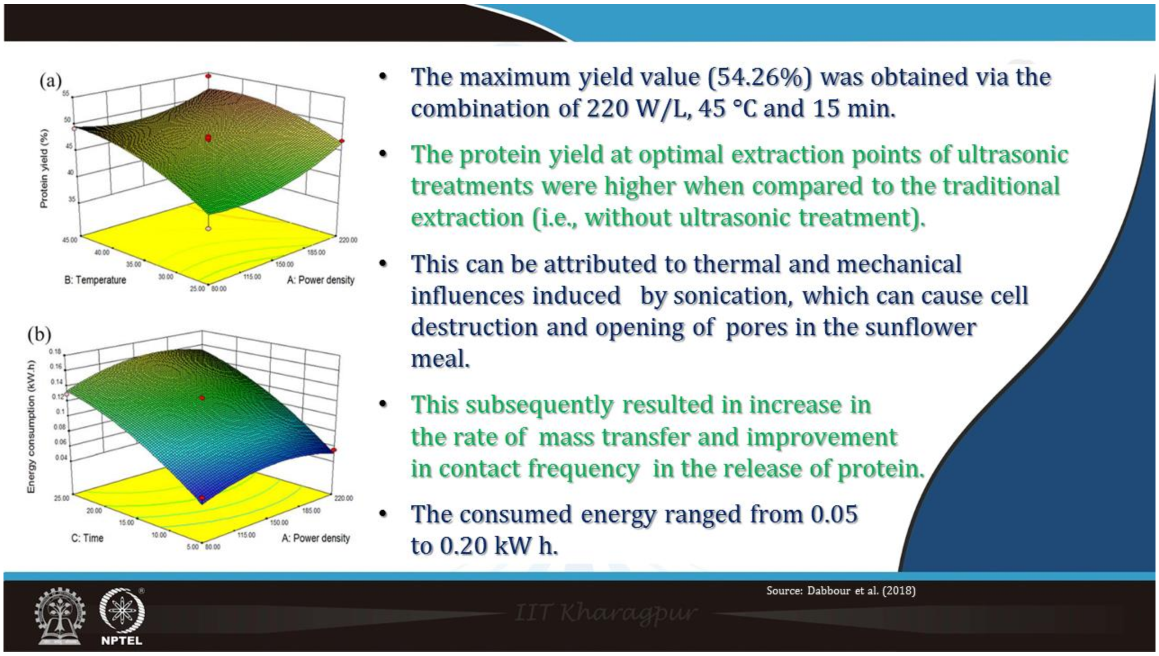


So, after centrifuging, the pH of the supernatant is adjusted to 4.5 using 2 mole per liter of NaOH at a ratio and centrifuged at 6500 rpm for 30 minutes at 4 degree Celsius, ok. Then, this, the precipitate, which obtained after this centrifugation is washed with deionized water for about 48 hours at 4 degree Celsius and neutralized to pH 7 using 2 mole per liter of NaOH followed by dialysis and freeze drying. So, after freeze drying you get the final product that is a soy protein isolate and it is in the form of powder. All steps are performed obviously, at room temperature ok.

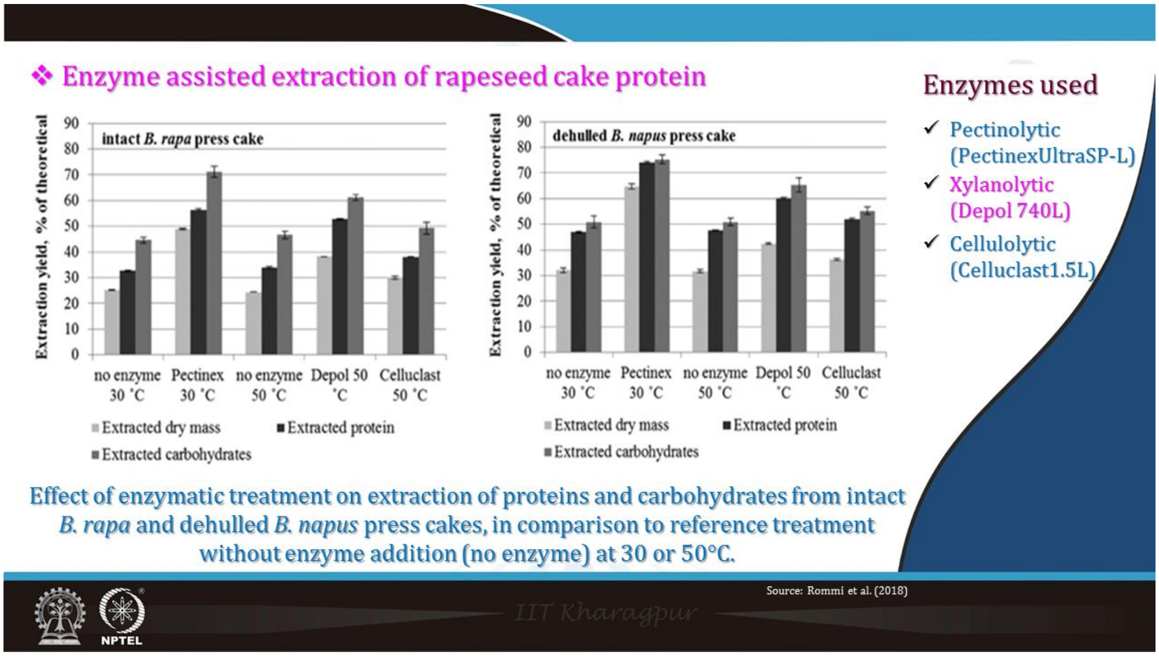


Then, the other method is the ultrasound assisted protein extraction from sunflower meal, you get around 50 gram of sunflower meal, it is dispersed in 1000 liter of deionized water, then pH is adjusted to 8 by adding 1 mole per liter of sodium hydroxide under RT for 1 hour retention time for 1 hour, ok. And then it is given a ultrasonification treatment, that is, a power density is 80 to 220 Watt per liter, pretreatment time is 5, 15 and 25 minutes in different experiments are given and temperature were varied from 25 to 35 to 45 degree Celsius, ok.

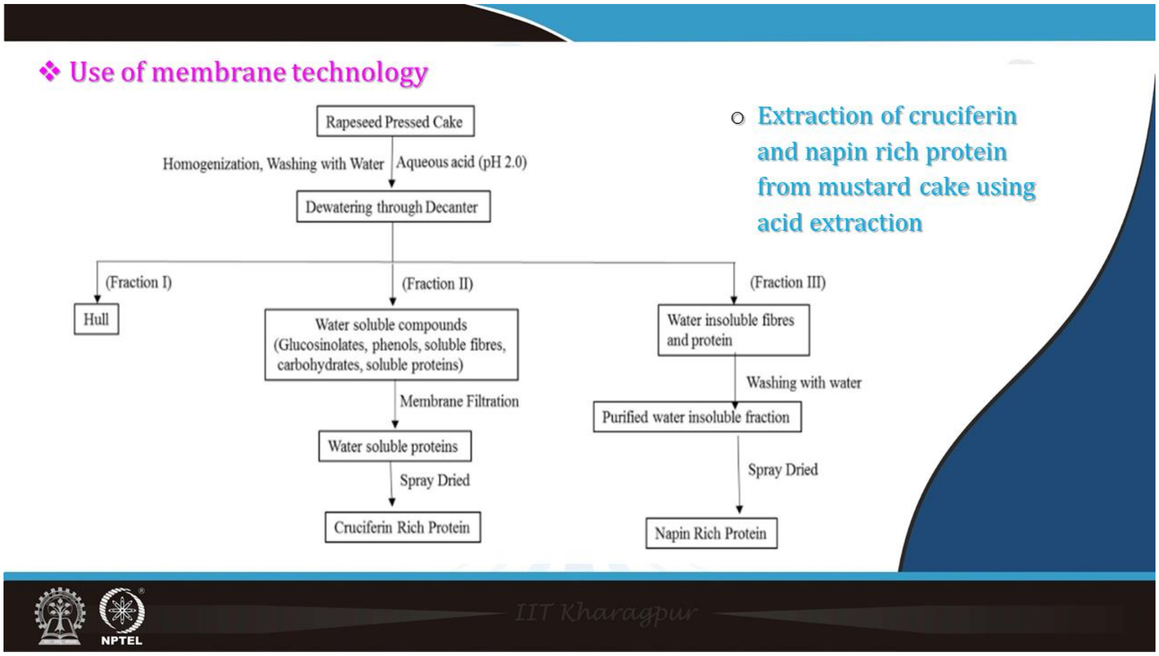
And the centrifugation. It was followed by centrifugation and 4500 rpm per 20 minutes, then pH is adjusted to 4.5 with 10 mole per liter HCl, then it is further centrifuged at 4500 rpm for 20 minutes. Then finally, the washing of precipitate with deionized water. The pH is 4.5, and resuspension of precipitate in deionized water followed by pH adjustment to 7 by adding 0.1 mole per liter NaOH. Then, this precipitate is obtained, the freeze dried, and then you get the protein isolate powder. At minus eighteen degree Celsius, it may be stored up, ok. So, this was the process, that is, usually described by Dabbour et al in 2018, they conducted experiment, and the responses they related protein yield as well as energy consumption.



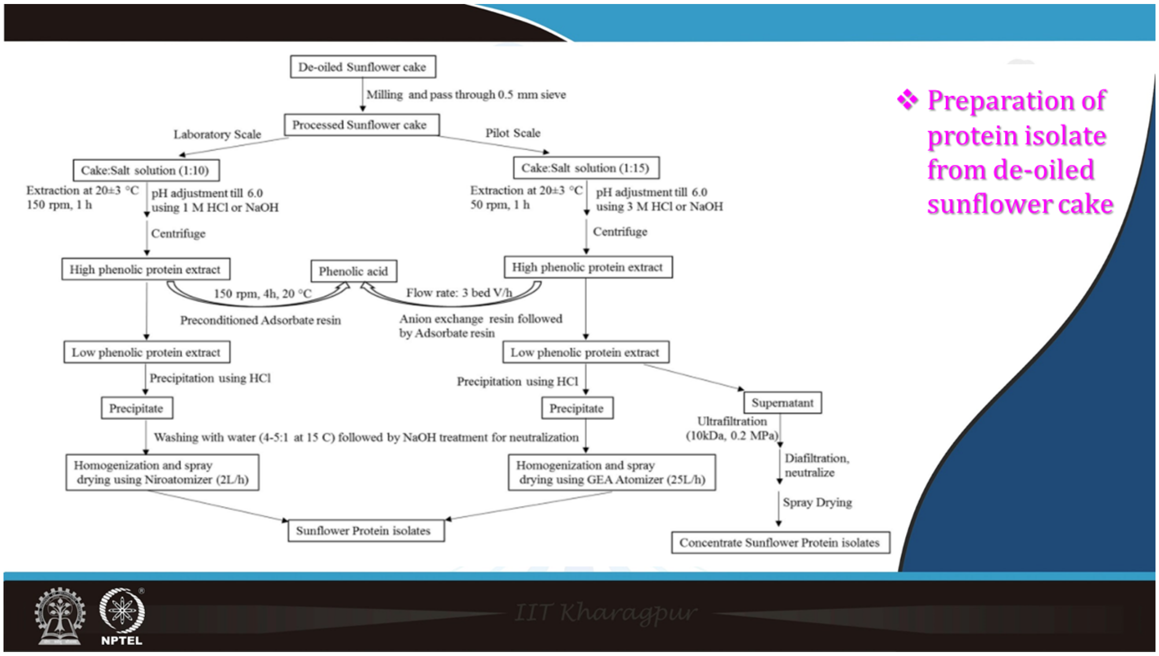
And their results showed, that is, the maximum yield value, that is, 55 percent approximately was obtained by the combination of 220 Watt per liter, 45 degree Celsius and 15 minutes retention time. The protein yield at optimal extraction point of ultrasonic treatment were higher when compared to the traditional extraction, that is, without ultrasonic treatment, ok. And this case can be attributed to thermal and mechanical influences induced by sonication, which can cause cell disruption and opening of the pores in the sunflower meal. And this subsequently resulted in increase in the rate of mass transfer and improvement in the contact frequency in the release of protein, ok. And the consumed energy during the process was about 0.05 to 0.2 kilowatt hour, ok.



Then enzyme assisted extraction of a rapeseed meal, you can see, that is, enzymes were used. Pectinolytic, xylanolytic as well as cellulolytic enzymes are given here. They were used and these two diagram, diagram, bar diagram. So, that is the effect of enzyme treatment on extraction of protein and carbohydrate from intact *B. rapa* and dehulled *B. napus* pressed cake in comparison to the reference treatment. That is, reference means where there was no enzyme treatment; and these experiments were at 30 degree Celsius and 50 degree Celsius. And you can see, in all the methods, the amount of extraction, that is, yield, extraction yield increased with the both temperature as well as when the enzymes were used; and you can see in both the cases, that is, the extraction yield increased.



Then, the membrane technology was used, that is, extraction of cruciferin and napin rich protein from mustard cake using acid extraction, ok. Then, in this, the rapeseed pressed cake is taken, homogenized, washed with water, and of course, acid pH 2 is maintained. Then, it is dewatered through decanter and then obtained in different fraction, that is, first fraction is the fraction 1 is the hull and fraction 3 is the water insoluble fibres and protein. It is washed with water, purified water insoluble fraction and spray dried finally, which gives you napin rich protein. Whereas the second fraction which is obtained; it contains water soluble component like glucosinolates, thiols, soluble fibers, carbohydrate and soluble proteins, ok. This is subjected to membrane filtration, that is, UF and MF membranes of particular particle sizes, specific pore sizes are used; and this is used to separate the water soluble proteins, then, which is finally, spray dried and gives the cruciferin rich protein. So, this method, cruciferin rich protein and napin rich protein is obtained from the mustard cake, ok.

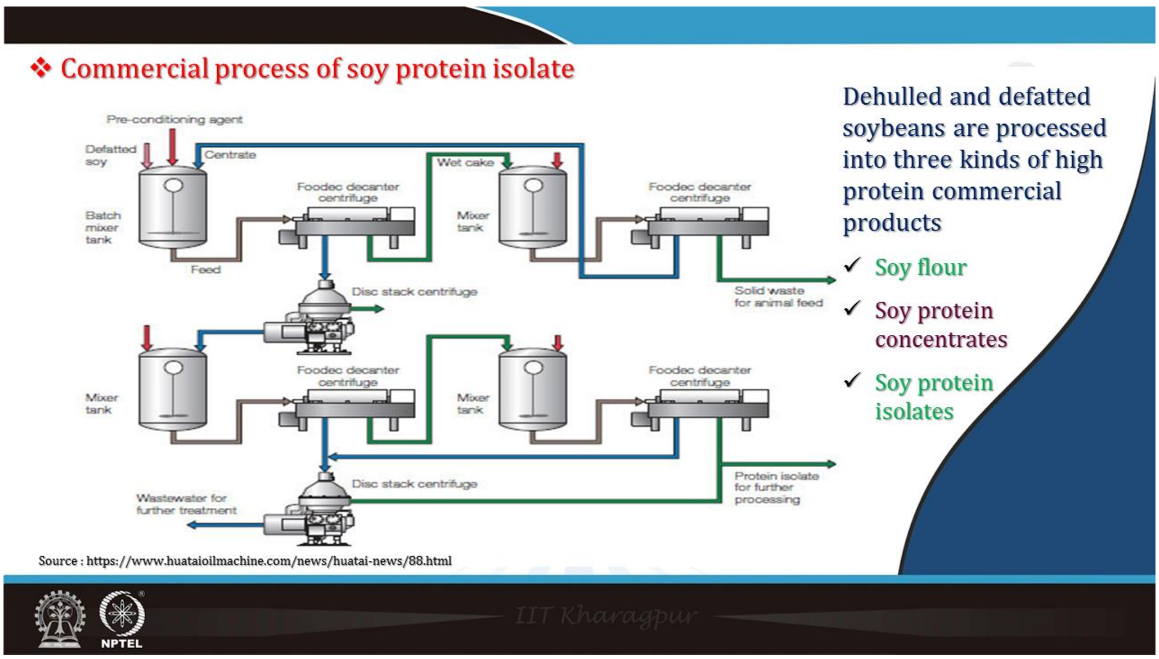


This is a diagram for the preparation of protein isolate from de-oiled sunflower cake. So, process flow chart is given here. The de-oiled sunflower cake is used; it is milled and passed through 0.5 mm sieve. Then the processed sunflower cake which is obtained after milling ok, then it is subjected to two process: one is the same process, but one is the laboratory scale and other is the pilot scale.

In the laboratory scale, this pressed cake, there is the de-oiled pressed cake or powder cake, it is dissolved into cake and salt solution 1 is to 10. Whereas, in the pilot scale, the cake and salt solution is maintained 1 is to 15, ok. In the laboratory scale, both in this case, their extraction time is around 1 hour, they are centrifuged at 150 rpm and 20 plus minus 3 degree Celsius, pH is adjusted till 6 using 1 Molar HCl or NOH in both the cases, ok. Whereas, the in the pilot scale, the rpm is about 50 and extraction time is 1 hour, another extraction rate is; temperature is same. So, by both the process, you get high phenolic protein extract; and this high phenolic protein extract in the laboratory scale, it is further centrifuged that at 150 rpm for 4 hours at 20 degree Celsius, ok.

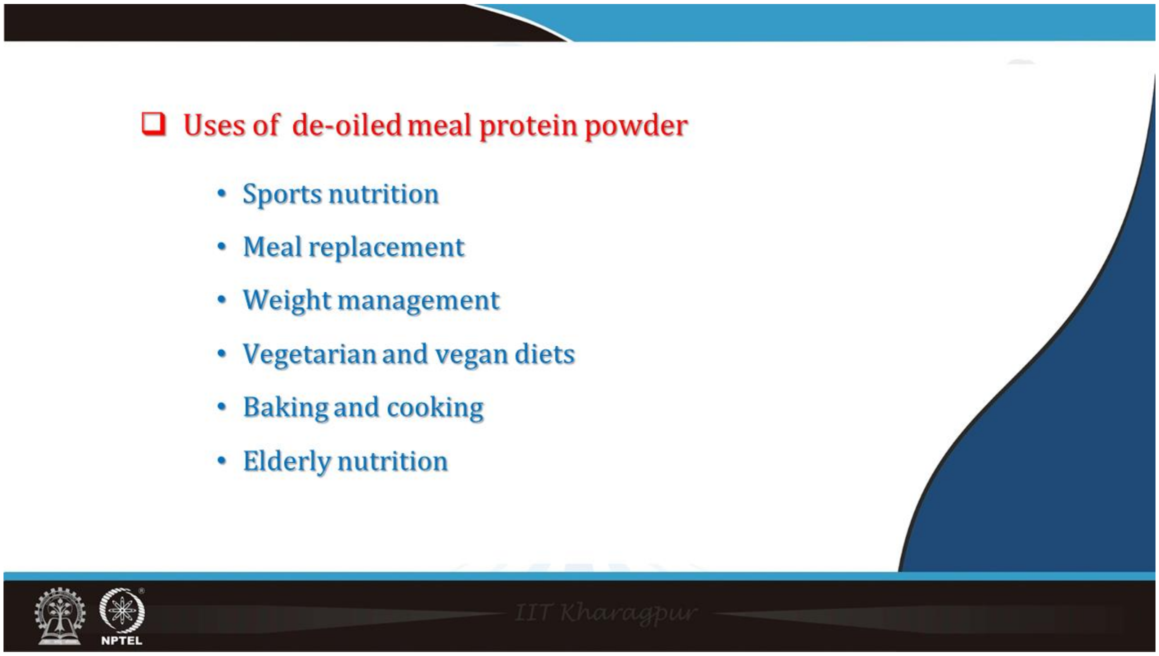
And in pilot scale it is a set with a 3 bed V per hour; it is flow rate; then, it is, there is preconditioned adsorbate resin, you get phenolic acid. And the remaining other, they pass through low protein, low phenolic protein after the extraction of the phenolic whatever you get, low phenolic protein extract from both the setups, that is, laboratory as well as pilot scale. They are precipitated, subjected to precipitation using HCl, the precipitate is obtained, and this is then washed with water, that is, 4 to 5:1 at 15 degree Celsius followed by NaOH treatment for neutralization. And then, it is subjected to homogenization and spray drying using Niroatomizer the 2 litre per hour whereas, in the pilot scale is used drying using GEA atomizer using 25 litre per hour, and then it gives sunflower protein isolates.

After then, low phenolic protein extended the pilot scale after precipitation, then the supernatant, which is obtained, it is ultrafiltered using 10 kilo Dalton membrane and 0.2 MegaPascal pressure; and then diafiltration neutralize and spray dried, it gives concentrate sunflower protein isolates. So, sunflower protein isolate and sunflower protein concentrated sunflower protein isolate, these are the obtained by using this process.

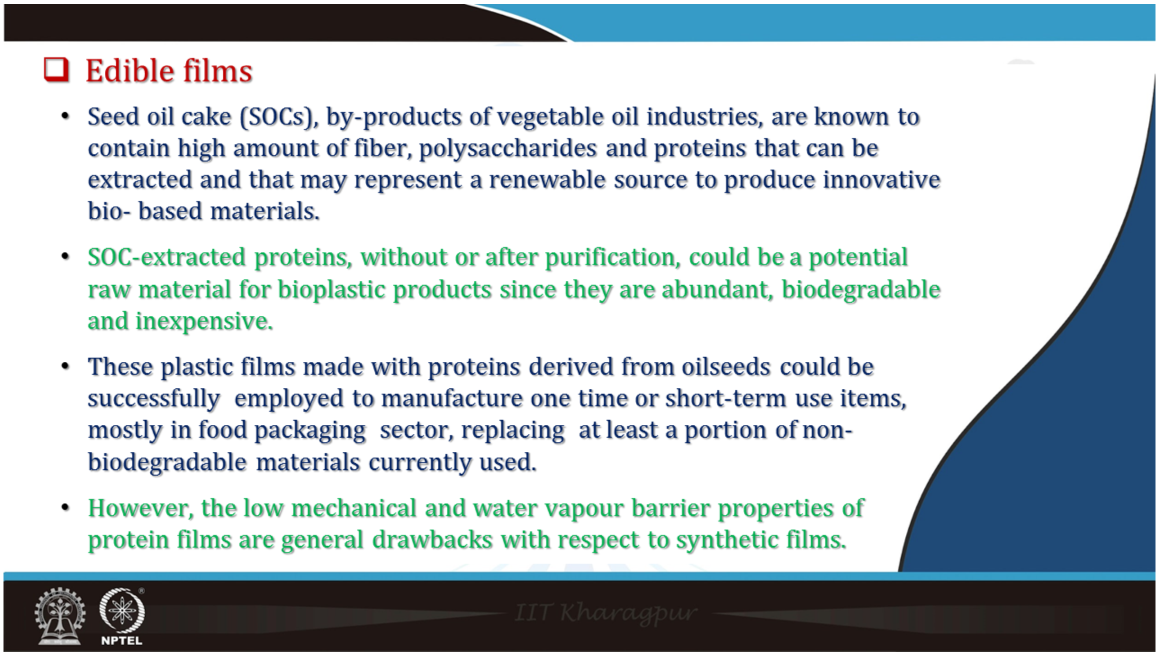


Here, again the, it is a commercial process flow chart for the preparation of, way of protein isolate is shown here, that is, how, that is, schematic presentation is shown, ok. That is the preconditioning agent, defatted and then concentrate, this line blue line, green red lines are shown. This mixture and dehulled and defatted.

Soyabeans are processed into 3 kinds of high protein commercial products, like soya flour, soya protein concentrates, and soya protein isolates; these are standard process they used, ok.

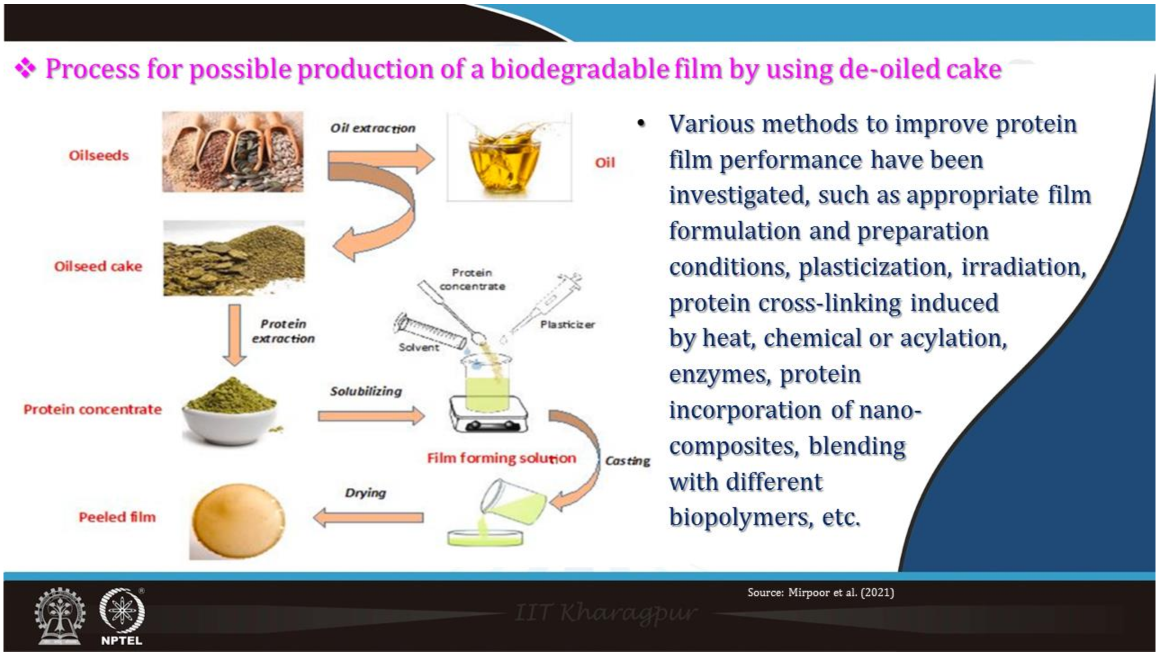


Then the. As far as the uses of these de-oiled cakes are, they can be used like, in earlier, that is, in the sports nutrition because these protein powder they have very good quality protein, that is, quantity as well as quality as they can be used in the formulation of various food, that is, the high protein food, which is required by the sport persons, etcetera. Then can be used for meal replacement, even for formulation of the food for weight management. Then, this can be used for making, even for texturization, for making protein meat, or other diets for vegan people. They can be used as an ingredient in bakery products, confectionery products, in cooking formulation, mixes, etcetera as well as even, that is, the elderly nutrition, that is, food for elderly people, for diabetic people, for other persons, that is the, for making, formulating protein rich food, you can have high protein, low carb diet, can be used prepared by, used by, prepared by using these ingredients.

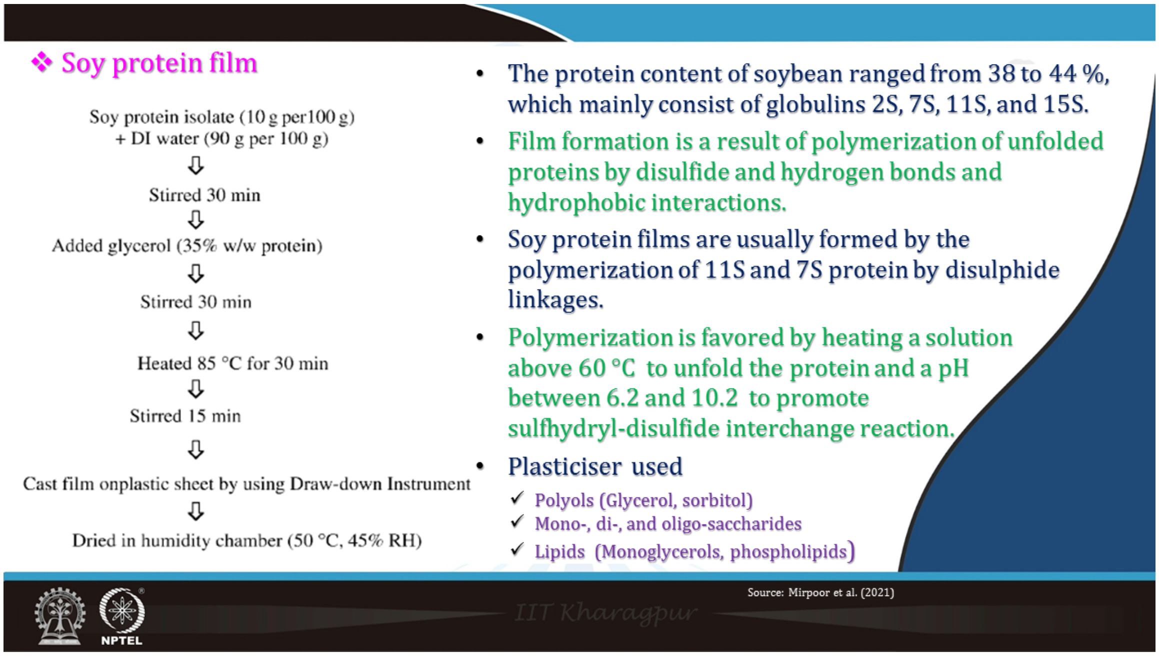


Then let us talk about edible films, that is, seed oil cake, byproduct of vegetable oil industries are known to contain high amount of fiber, polysaccharides and protein that can be extracted and they may be, that may be represent a renewable source to produce innovative bio based materials.

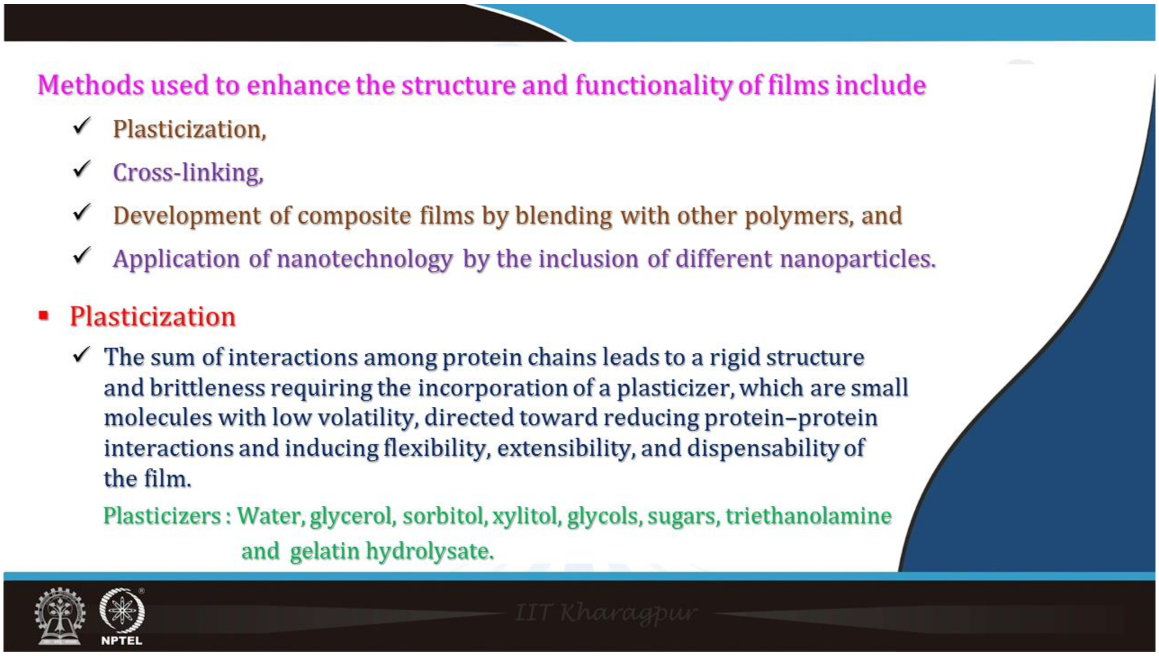
There is seed oil cake extract proteins without or after purification can be a potential raw material for bioplastic product since they are abundant, biodegradable and inexpensive. These plastic films make with the protein derived from oil seed could be successfully employed to manufacture one time or short term use items, mostly in food packaging sector, replacing at least a portion of the non-biodegradable materials currently used. However, the low mechanical and water vapour barrier properties of the protein films are general drawbacks with respect to synthetic films.



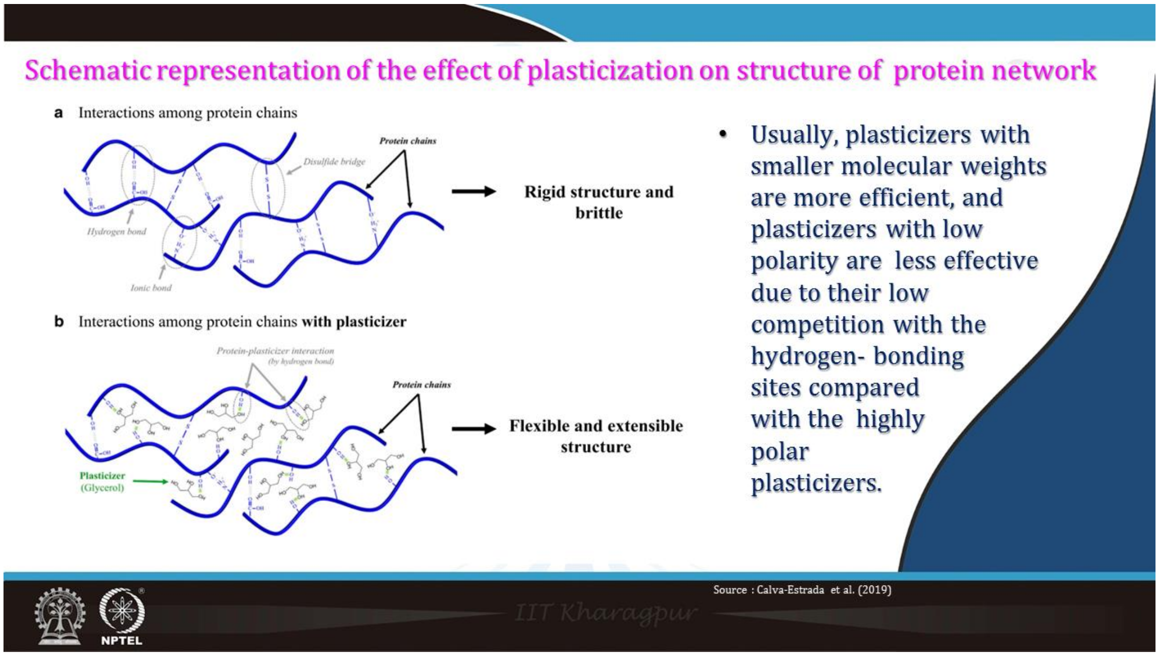
So, here, it is the process of possible production of a biodegradable film by using the seed oil cake. And there are various methods which used to improve protein film performance and these have been investigated, such as the appropriate film formulation and preparation conditions, plasticization, irradiation, protein crosslinking induced by heat, chemical or acylation, enzyme, protein incorporation of nanocomposite, blending with different biopolymers, etcetera. So, from oil seed cake, that is, protein, after protein extraction, then protein concentrate, which is obtained. It can be used various protein concentrates, solvent, plasticizers, etcetera, plasticizers, and then, this solution, and this solution can be film forming solution is made, and this solution can, that is, the peeled film can be formed, it is casted into a specific film, and then, it is peeled.



So, using a standard method like you see here, that soy protein film, that is, the protein content of soybean cake or meal range from around 38 to 44 percent, which mainly consist of globulin 2S, 7S, 11S and 15S. So, film formation is a result of polymerization of unfolded proteins by disulfide and hydrogen, sulfide bonds and hydrophobic interactions. So, soy protein films are usually formed by the polymerization of 11S and 7S protein by disulfide linkages. So, polymerization is favored by heating a solution above 60 degree Celsius, ok, that is, around heated 85 degree Celsius for 30 minutes, and to unfold the protein; and a pH between 6.2 and 10.2 to promote the sulfhydryl disulfide interchange reaction. You can see here, that is, protein isolate, 10 gram plus deionized water, 90 gram per 100 gram, it is stirred for 30 minutes. Then, glycerol is added at 35 weight by weight percentage, stirred for 30 minute, heated at 85 degree Celsius for 30 minute, again stirred for 15 minute, and then the film is casted, that is, cast film on plastic sheet by using Draw-down instrument, etcetera, and then dried in humidity chamber of at around 50 degree Celsius, humidity may be 45 percent, low humid air. So, this, the film is obtained, ok. So, normally, plasticizers, which are used, may be polyols like glycerol and sorbitol, etcetera, mono, di and oligosaccharides, and lipids, sometime monoglycerides, phospholipids, etcetera can be used.

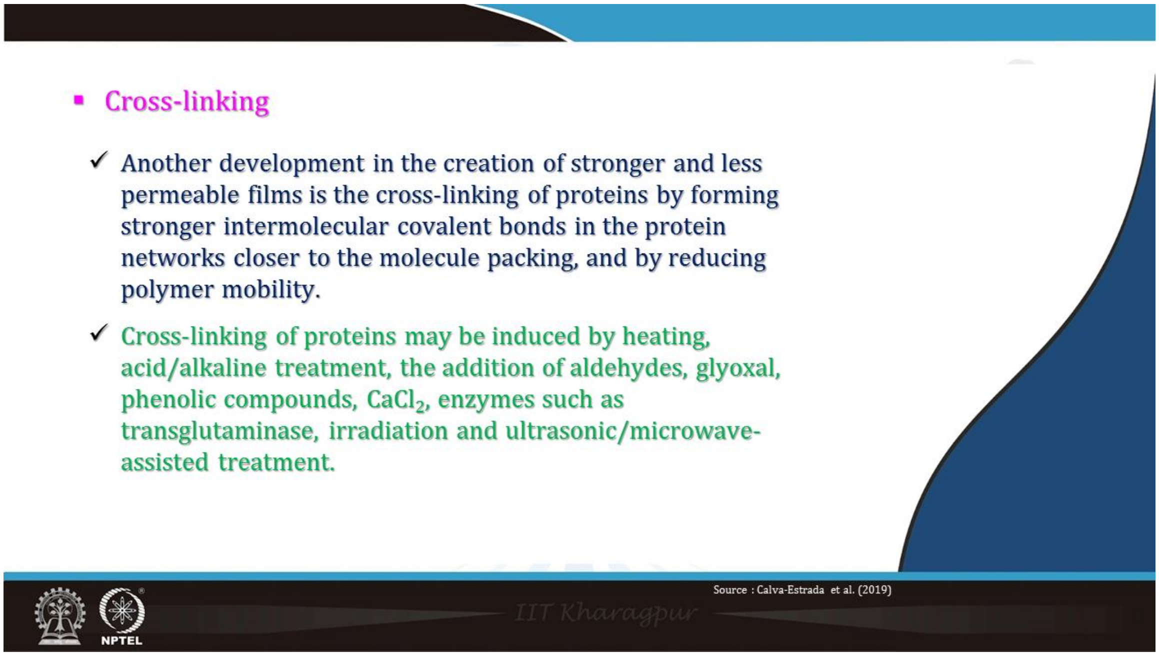


So, methods normally which are used to enhance the structure and functionality of films include plasticization, cross linking, development of composite film by blending with other polymers, and application of nanotechnology by the inclusion of different conditions. So, plasticization that is the sum of interactions among protein chains lead to a rigid structure and brittleness requiring the incorporation of a plasticizer, which are small molecules with low volatility. Then they are directed towards reducing protein-protein interactions and inducing flexibility, extensibility, and dispensability of the film. And various plasticizers which are water, glycerol, sorbitol, etcetera.

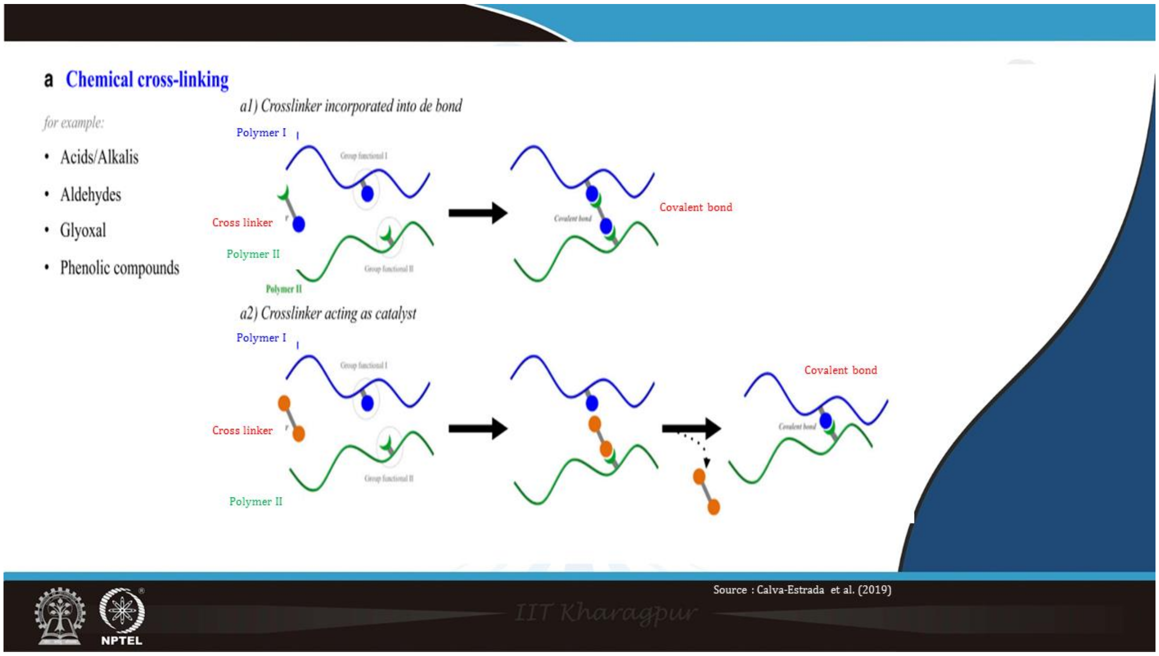


So, here you can see schematic representation of the effect of plasticization, that is, the structure of protein, that is, how it is, that is, a double bond it keeps a rigid structure, that is, protein chains, how they can interact, is shown and then interaction among the protein chain with plasticizer, it gives a flexible and extensible structure. Then only protein-protein chain interact, it gives a rigid structure, but plasticizer is made, it introduces plasticity, which makes it flexibility, flexible structure is obtained.

Usually plasticizers with small molecular weight are more efficient, and plasticizers with low molecular polarity are less effective due to their low competition with the hydrogen bonding sites compared with the highly polar plasticizers.

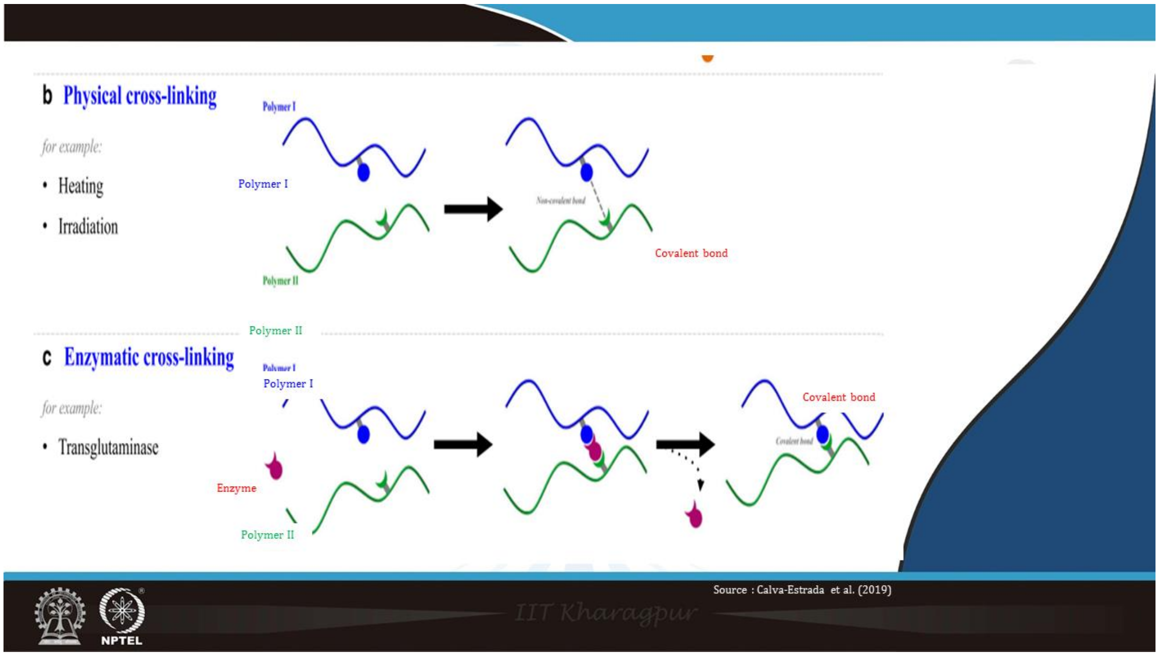


Then, cross linking, that is, another development in the creation of stronger and less permeable film is the cross linking of protein by forming stronger intermolecular covalent bonds in the protein network closer to the molecular packing, and by reducing the polymer mobility. The cross linking of protein may be induced by heating, acid treatment, alkali treatment or by addition of aldehyde, glyoxal, phenolic compounds, calcium chloride or enzymes such as, transglutaminase, irradiation and ultrasonic or microwave assisted treatments.



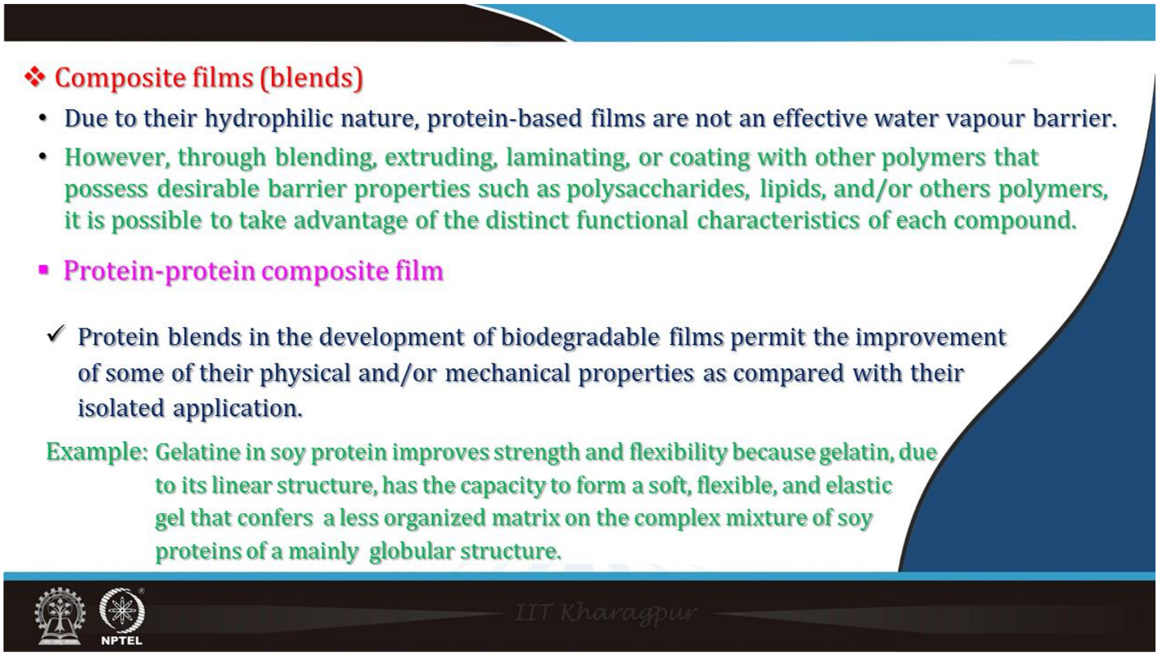
Here you see, that various chemical cross linking, how it is done, various chemical like acid, alkali, aldehyde, etcetera. This is polymer 1 and polymer 2 and the cross linking is obtained, may be covalent bonding.

Then, there is a cross linker acting as a catalyst here. In this case, there is a cross linker, it does not form any bonding etcetera, but rather it has a catalyst and then after cross linker is separated, it can be from the reaction. It does not take part in reaction, but it increases that catalyzes the reaction. So, again, covalent bond is formed between various groups.

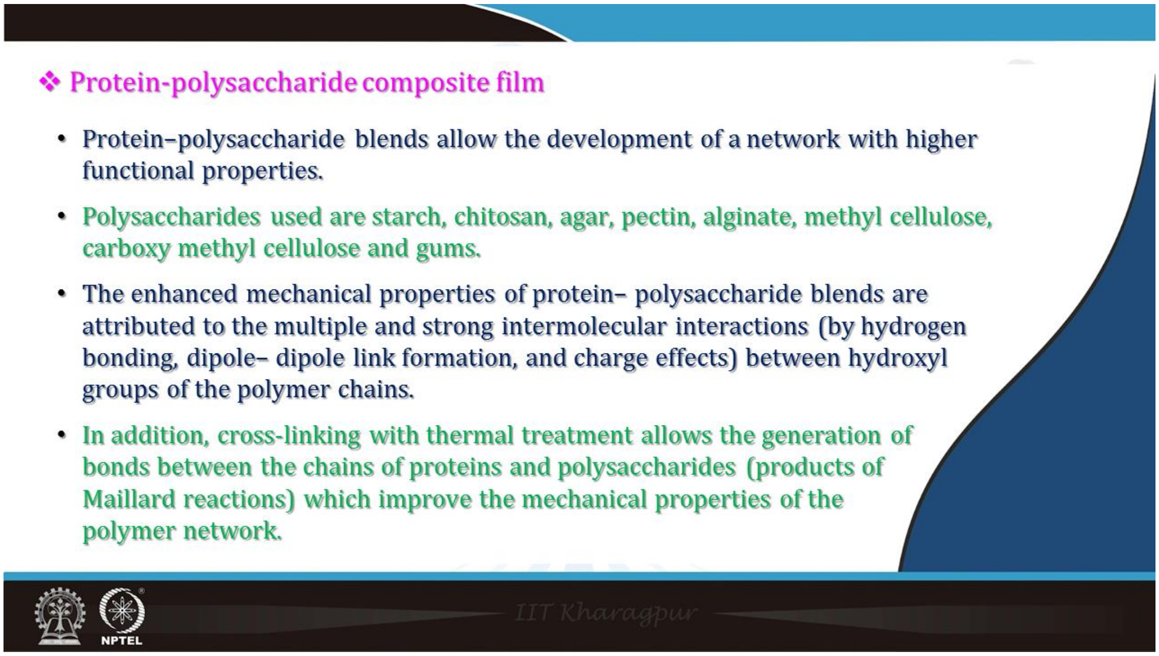


Similarly, here, physical cross linking like heating and irradiation or enzymatic cross linking, enzyme transglutaminase, it is shown here, that is, ok.

How pictorial it is shown in this, how the cross linking covalent bonds, etcetera are formed then, ok. Then let us talk about another: the composite films. The composite films are blends, that is, the another, due to their hydrophilic nature. Protein based films are not an effective water vapour barrier, ok. However, through blending, extruding, laminating or coating with other polymers that possess desirable barrier properties, such as polysaccharide, lipids and other polymers, it is possible to take advantage of the distinct functional characteristics of each component.

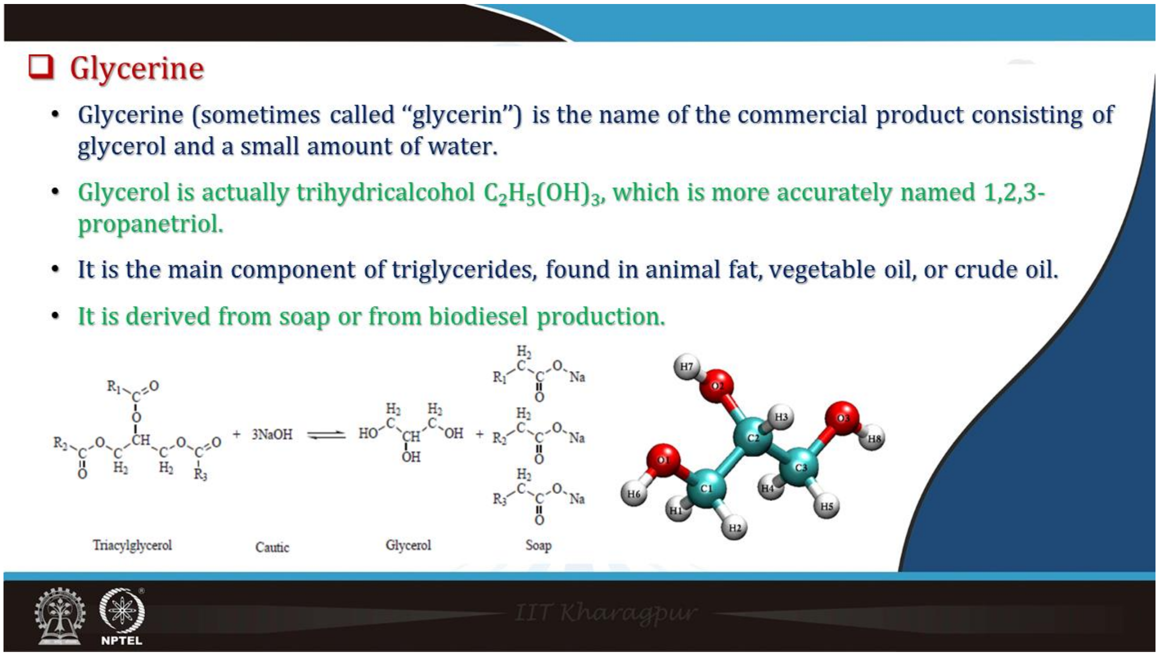


So, there may be composite film like protein-protein composite film, where protein blends in the development of biodegradable film permit the improvement of some of their physical and or mechanical properties as compared with the isolated applications. For example, gelatine in soy protein improves strength and flexibility because gelatin, due to its linear structure, has the capacity to form a soft, flexible and elastic gel that conform a less organized matrix and the complex mixture of soy protein of a mainly globular structure, ok.

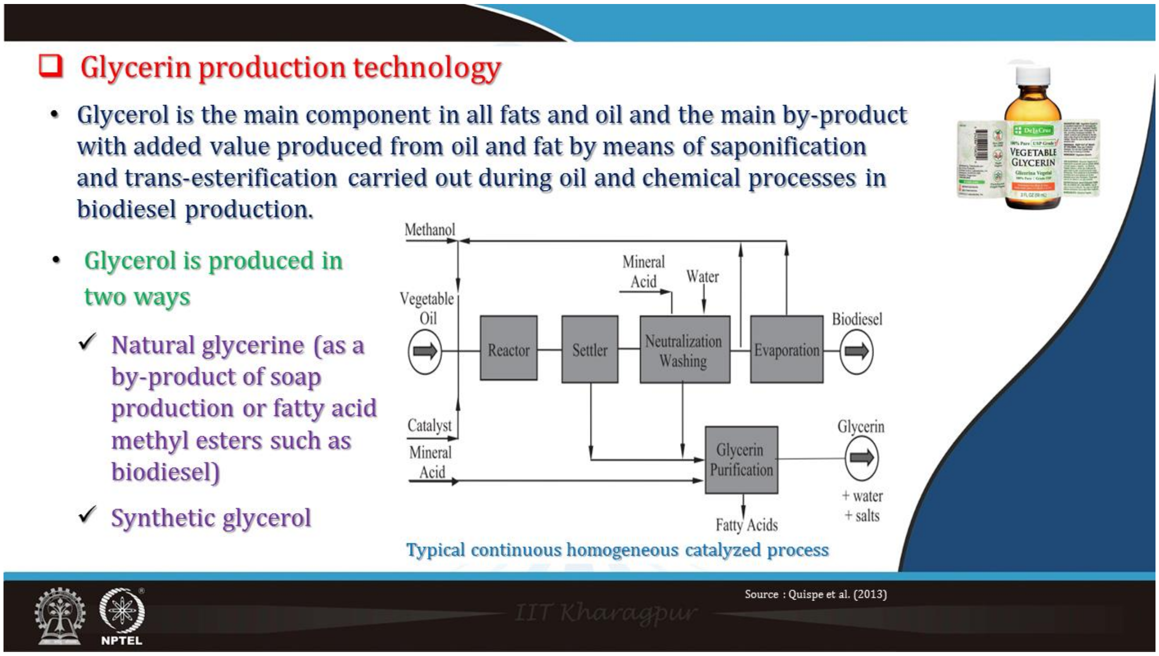


Then, protein-polysaccharide composite film, then protein-polysaccharide blends allow the development of a network with higher functional properties. Polysaccharides used are starch, chitosan, agar, pectin, alginate, methyl cellulose, carboxy methyl cellulose, gums, etcetera. The enhanced mechanical properties of protein-polysaccharide blends are attributed to the multiple and strong intermolecular interactions by, that is, the and then interactions may be by hydrogen bonding, dipole-dipole link formation or charge effects, etcetera will be there; and these are between hydroxyl group and the polymer chains. In addition, cross linking with thermal treatments allows the generation of bonds between the chains of protein and polysaccharides which improve the mechanical properties of the polymer network.

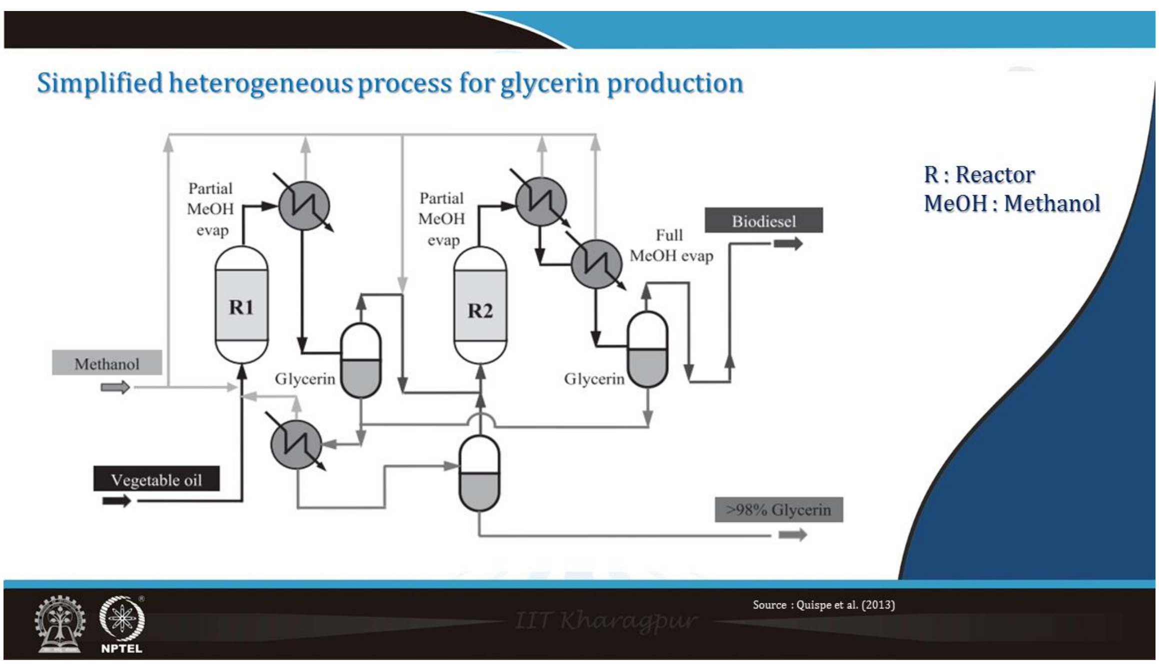
Then, there may be protein-lipid composite films. The moisture barrier properties of protein-based film can be improved through the inclusion of lipids in their formulation, which favor protein-protein interactions in the film matrix and therefore, improve their mechanical properties as the lipids, which are normally used, may be fats, waxes, oils, fatty acids, etcetera. Then, nanocomposite films. They are biopolymers matrix reinforced with nanoparticles loads or fillers having a dimension smaller than 100 nanometer, which improve their mechanical, thermal, and barrier property. For example, the incorporation of nanomulsions, nanoliposomes, and or nanoparticles in the protein-based films significantly improves its barrier and other mechanical properties, etcetera.



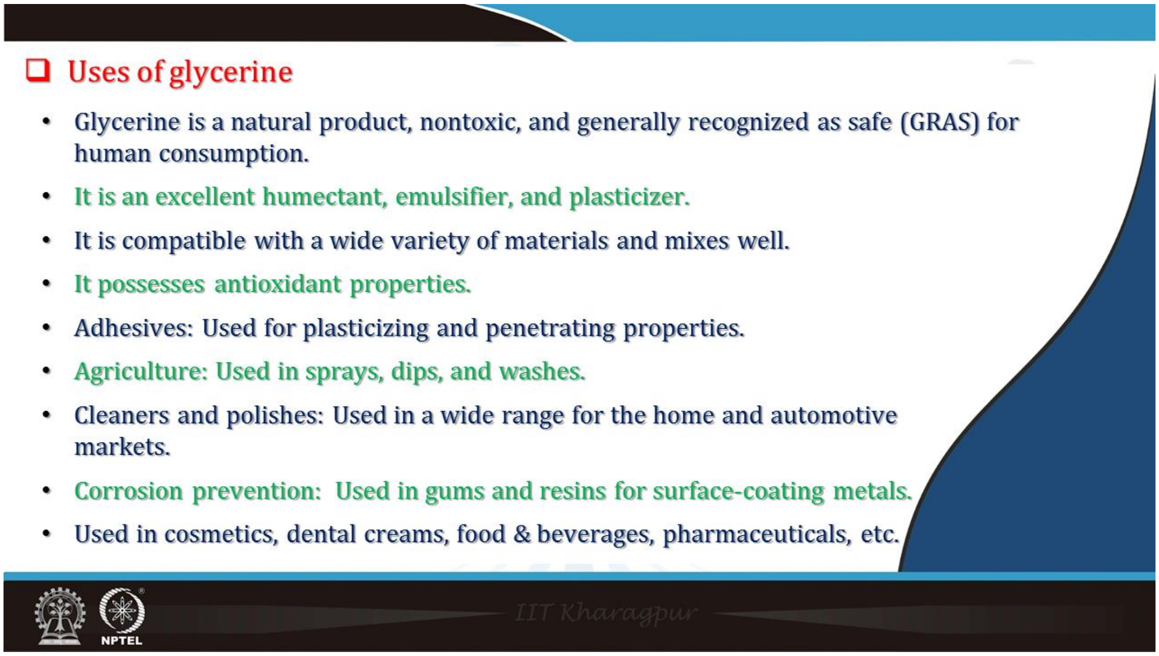
Then the another important product is the glycerine, as we discussed. The glycerine, sometime also called as is the glycerin, is the name of the commercial product consisting of glycerol and a small amount of water. So, glycerol is actually, it is triacylglycerol which is more accurately named 1,2,3-propanetriol. It is the main component of triaglycerides, found in animal fat, vegetable oil, or crude oil. And it is derived from the soap or even from biodiesel production. So, this glycerol production technology, you can see, it is the main component of all fats and oils and the main byproduct with added value obtained from oil and fat by means of saponification and transesterification carried out during oil and chemical process or in biodiesel production.



Glycerol is produced in two ways. One is the natural glycerine, that is, as a byproduct of soap production or fatty acid methyl ester, such as biodiesel; and then synthetic glycerol, ok. So, that is methanol, vegetable oils, ok. It can be treated in reactor, settler in the neutralization washing, and after that, it can be obtained, that is, by catalyst or mineral acid. Glycerol purification you can give fatty acids and glycerin is obtained, ok.



This is a simplified heterogeneous process for glycerin production. Here you have R 1 and R 2 reaction, and in this, it is treated with the methanol and gets biodiesel as well as more than 98 percent of glycerin is, it is basically vegetable oil, as you can see, and methanol under specific conditions, they are allowed, reacted with, treated with different reactors, ok.



Then, this glycerin can be used, it is a natural product, non-toxic and generally recognized as safe for human consumption. It is an excellent humectant, emulsifier, and plasticizer. It is compatible with a wide variety of materials and it mixes well in those materials. It possesses antioxidant properties. It can be used as adhesives, that is, for plasticizing and penetrating properties. It can be used in agriculture, that is, used as sprays, dips, washes, etcetera. It is used in the cleaners and polishers, that is, used as a wide range of home and automotive markets. It is used for corrosion prevention, gums, resins, surface coating material and used in cosmetics, dental creams, food and beverages, pharmaceuticals. So lot of the glycerin has very important commercial applications, and it is one major byproduct of, which can be processed.

So you can see that in the lecture, that is, about 25-30 minutes now, we have a good idea that development of high value products from oil seed cake contributes to the efficient utilization of resources and minimizes the waste in the oil seed processing industry. Protein extraction from oilseed cake can result in protein powders, isolates, or concentrates that are used as dietary supplement, food ingredients or sport nutrition. Edible films offer economic advantage in reducing food waste, enhancing product quality and providing innovative packaging solutions. Glycerin, an important byproduct of biodiesel production from edible oil exhibits a wide range of applications encompassing food, agriculture, cosmetic, pharmaceutical, medical, and more, making it a versatile and valuable compound. So, this is way, at least I have shown you just, but there are lot of applications you will find in the literature, and that really adds value to the industry and it makes the oil milling industry economically viable industry. Because.

These are the references which are used. This.

Thank you very much for your patience here. Thank you.