Chemical Process Intensification
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Lecture 30
Supercritical Extraction for Process Intensification

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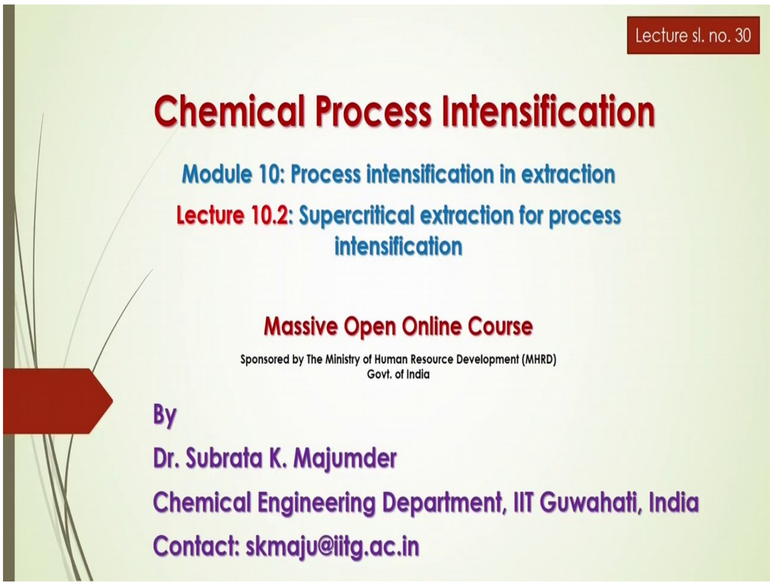

Welcome to massive open online course on Chemical Process Intensification, so were are discussing about process intensification in extraction under module 10 and in this module today we will discuss more about the process intensification in extraction and in this lecture we will discuss supercritical extraction for process intensification.

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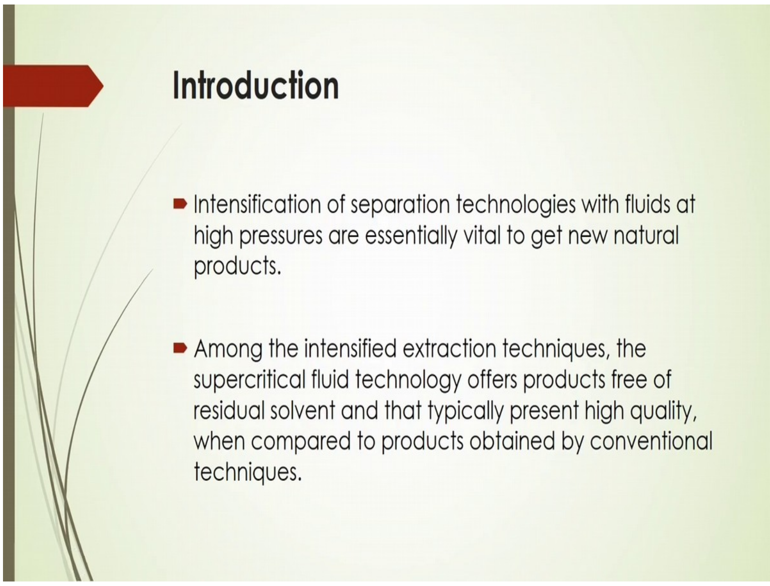

Now, you know that the intensification of separation technologies with fluids at high pressure are essentially vital to get new natural products in greenery way and also with you know more efficient way and also that whatever products is coming based on this intensification of supercritical extraction. We can have products of free residual solvent and that typically present high-quality when compared to products that obtain by conventional techniques.

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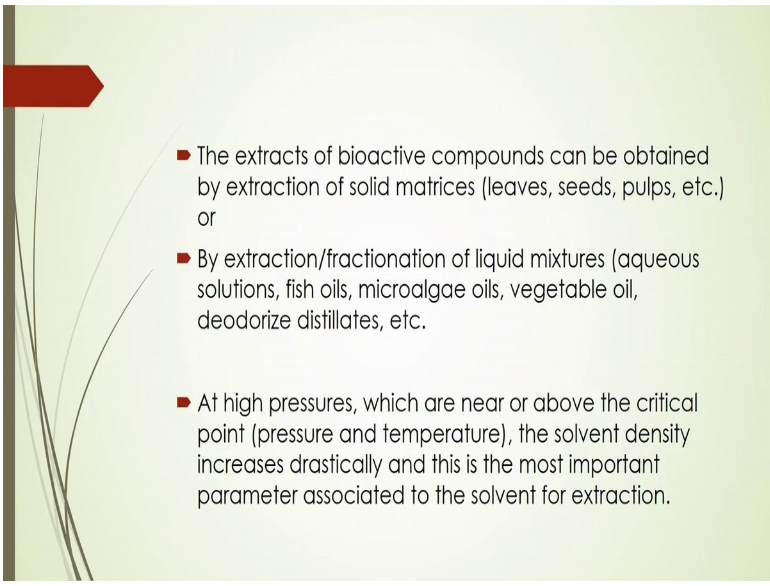

And the extracts of that bioactive compounds can be obtained by extraction of solid matrix leaves, seeds, pulps, et cetera or by extraction or fractionation of liquid mixture aqueous solutions, fish oils, microalgae oils, vegetable oil, deodorize distillates, etc. Also at high pressure we are near or above the critical point the solvent density increases drastically at this supercritical conditions and this is the most important parameter associated to the solvent for extraction.

In the previous lecture we have already discussed the basics of extraction process as well as various aspects of intensification, so we are not going to discuss again here that basic principles of extraction, only we will discuss about that supercritical extraction by solvent of that super critically conditions.

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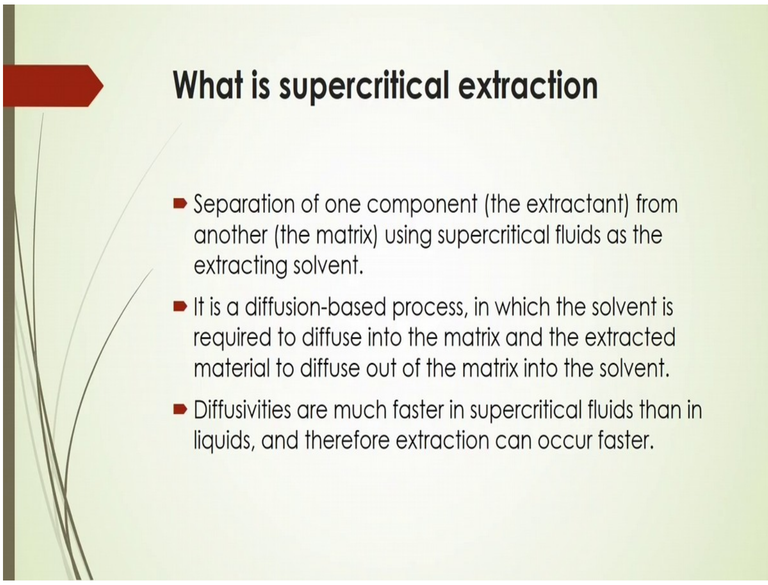

Now, what is that supercritical extraction? Now, as per definition we can say that the separation of one component, the extractant from another the matrix using supercritical fluids as the extracting solvent. It is a diffusion based process actually in which the solvent is required to diffuse into the matrix and the extracted material to diffuse out of the matrix into the solvent.

And the diffusivities are much faster in you know supercritical fluids than in liquids and also because of that this extraction based on this supercritical conditions will be you know faster. So basically this diffusion based process, how you can intensify the diffusion, so that you can get more extraction in this particular high pressure systems.

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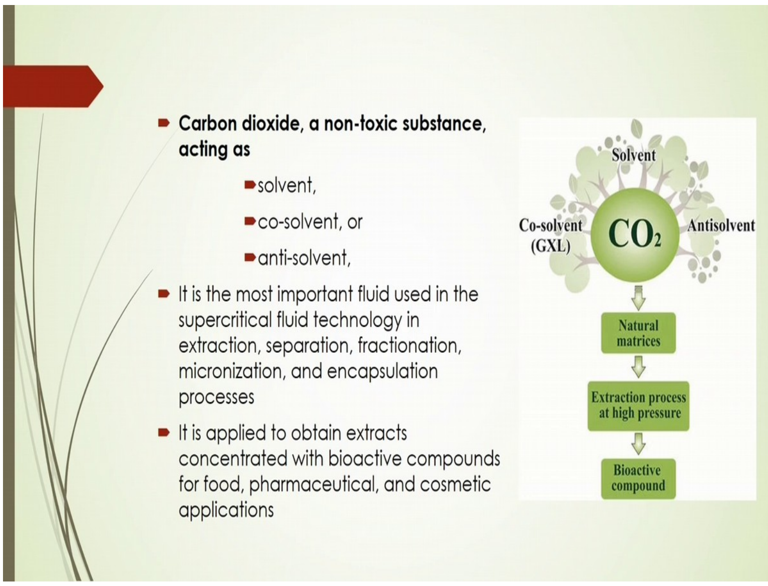

Now very important point here that what are the solvents that you can use for that extraction process under this supercritical conditions. Now, carbon dioxide you know that at its supercritical conditions will be acting as a solvent which will be non-toxic in properties and also it will be acting as solvent, co-solvent or anti-solvent also and it is the most important fluid used in the supercritical fluid technology in extraction even you know that separation, fractionation, micronization and encapsulation processes and it is actually applied to obtain extracts that is concentrated with bioactive compounds for food, pharmaceuticals and also cosmetics application.

Now, you will see that we can say that this is the carbon dioxide can be acted as a co-solvent, even solvent and anti-solvent and from use of this carbon dioxide as a solvent you can produce that natural matrix and where through which that this you can separate the salutes by this carbon dioxide solvent and in that case whenever passing through that natural matrix it will go to the extraction process at high pressure and also after that, at this high-pressure that through this you know natural matrix this suppression of the salutes will be there and whatever compounds will be coming that will be called as bioactive compounds at its higher you know operating conditions of pressure and temperature.

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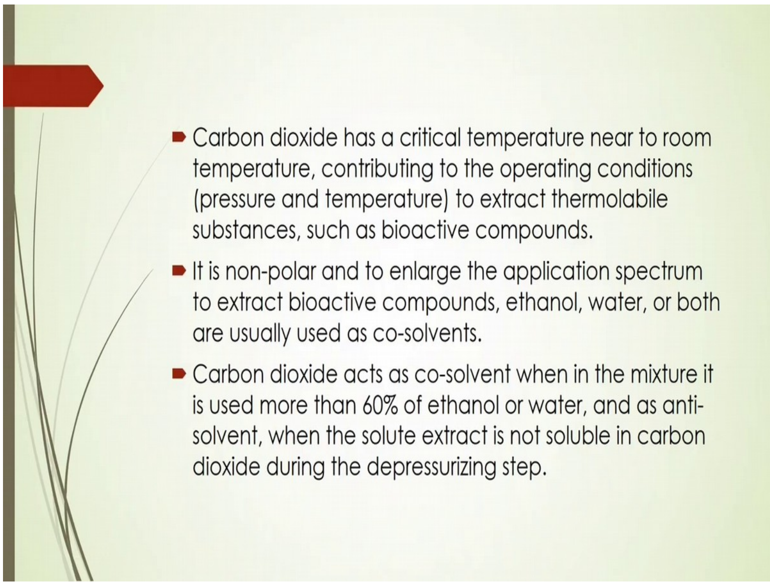

Now, if you say that carbon dioxide of course has a critical temperature near to room temperature, but here pressure will be little bit higher in that case contributing to the operating conditions to extract you know thermolabile substances and also you can say that it will be as bioactive compounds and also this carbon dioxide acts as a co-solvent when in the mixture, it will use more than 60 percent of ethanol or water and also it can be used as an anti-solvent when the solute extract is not soluble in carbon dioxide during the depressurising step and it is nonpolar and also to enlarge the applications spectrum to extract bioactive compounds ethanol, water or both are usually used as co-solvent there.

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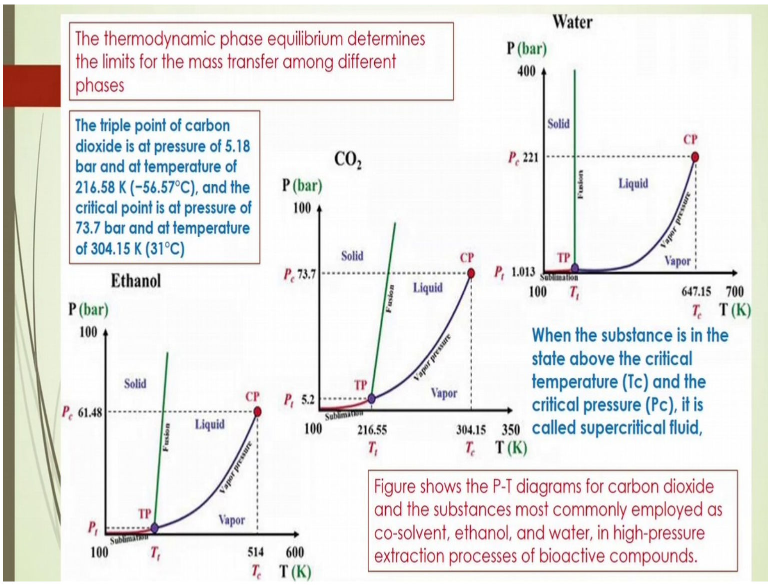

So this is actually the condition at which you can get the supercritical solvent of carbon dioxide, in this case the thermodynamics phase equilibrium that will determines the limit for the mass transfer among different phases. Here in this slides we are showing that different phase equilibrium condition of ethanol, carbon dioxide and water whereas ethanol you will see that here at this diagram Pc P versus temperature that means here this is the critical condition at which that this ethanol can be actually a liquid as well as vapour and also above that it will be solid and sometimes above this critical condition it will be considered as a you know a supercritical fluid.

So as ethanol you can say that at 61.48 pressure and also that temperature of 514 Kelvin it will be the point of condition or you can say that the condition of pressure and temperature and which is representing the critical point of this ethanol and you will see that if you increase the pressure from its triple point at here and if you increase the pressure and also increase the temperature you will see that how the equilibrium conditions are there and when this ethanol will be remaining as liquid and where and at which condition it will be as a vapour there.

And also above this you know that triple point you will see that there will be you know that some equilibrium condition of fusion where that solid may be converted to liquid or liquid may be converted to solids there at this you know equilibrium pressure and temperature whereas similarly that carbon dioxide is little bit higher you know that pressure and also the temperature is also at lower relative to that ethanol for getting that supercritical condition and here also you will see that triple point will be that different from this ethanol.

So, this is the gas it will be actually converting to the solid, liquid and also supercritical fluids at different operating condition of you know thermodynamic condition of pressure and temperature. So above this critical point you have to do remember this, when this carbon dioxide gas get the supercritical condition beyond of this pressure and also temperature and water also you will see that this is the triple point where that gas liquid solid you know will be at this point will be same in that case and beyond this points this is the liquid condition and this is the vapour and this is the solid conditions and critical conditions that a critical pressure will be as you know that 221 bar, whereas this critical temperature will be you know that 647.15 Kelvin.

So beyond this pressure and temperature the water will be acting as that supercritical conditions, so this figure is actually show the pressure temperature diagrams for the carbon dioxide, ethanol and water and the substances most commonly employed as co-solvent, ethanol and water in high-pressure extraction processes of a bio active compounds and also you will see that you have to remember that triple point of carbon dioxide is of pressure of 5.18 bar and at temperature of 216.58 Kelvin it is around 56.57 degrees centigrade that is a negative and the critical point is at pressure of 73.7 bar and temperature of 304.15 Kelvin.

So this is the condition at which you can get the you know that transition of this supercritical to the critical and then triple point condition and also the changes of phase from liquid to solid, solid to you know liquid or liquid to vapour and vapour to liquid like this, so when the substance is in the state above the critical temperature and the critical pressure it is called supercritical fluid.

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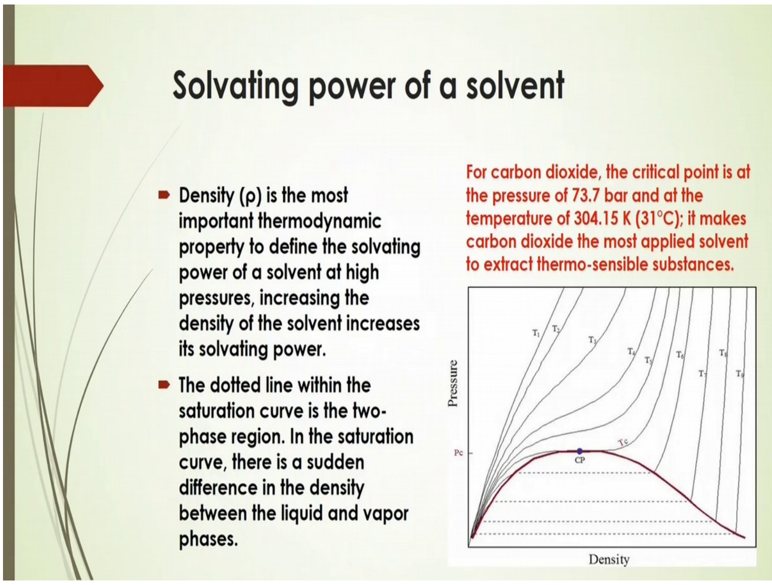

Now, why that carbon dioxide to be actually acting as a intensified extraction process as a solvent at this supercritical condition because you know that you will see that at the supercritical condition the properties of that carbon dioxide or other fluids will be changing. In that case the density is the most important thermodynamic property to define the solving power of a solvent at high-pressure because in that case the solvating power of the solvent will be changing at this supercritical condition.

Now increasing the density of the solvent increases its solvating power in the supercritical condition and in the figure you will see the dotted line, we are shown that within the saturation curve is the two-phase region. In saturation curve, there is a you know this is called saturation curve and there is a certain difference in the density between the liquid and vapour there at different temperature.

So at different temperature if you increase that pressure you will see that density according will be changing at different temperature, so for carbon dioxide you will that critical point is at the pressure of 73.7 bar and at the temperature of you know 304.1 k in this case it makes carbon dioxide the most applied solvent to extract the thermo sensitive materials. So density is one of the important thermodynamic property to define the solvating power of the solvent for the extraction process at this high pressure.

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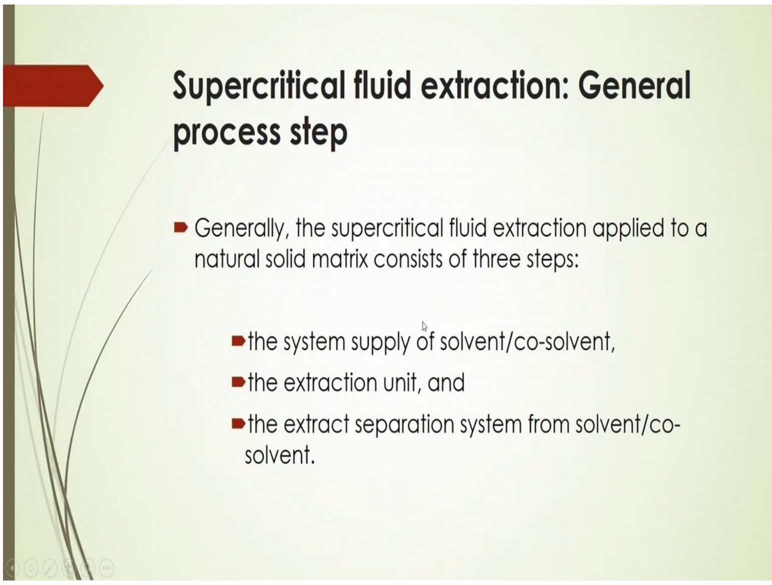

Now, what are the general process step of this supercritical fluid extraction? Generally the super critical fluid extraction applied to a natural solid matrix that consist of three steps like the system supply of solvent or co-solvent, the extraction unit and the extract separation system from solvent or co-solvent.

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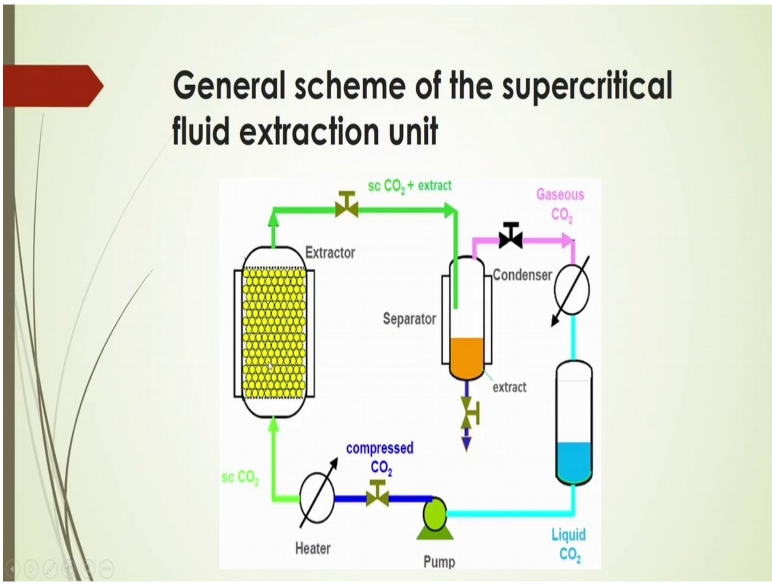

And this is the general schematic diagram for the supercritical fluid extraction unit, you will see this is the extractor here and in this extractor the carbon dioxide will come you know after compressing as supercritical condition and this supercritical condition, this carbon dioxide gas go to the extractor and then from the extractor this supercritical carbon dioxide with extractor entity will come and after that it will pass through the separator where that extractor and will be separated from that carbon dioxide and that carbon dioxide will again will be you know that condense and will get as a liquid carbon dioxide and after that it will be pumping and compressed at it supercritical condition again it is to be sent to the extractor for the extraction of the solute, so this is the basic you know schematic diagram of that supercritical extraction unit by using that solvent of carbon dioxide.

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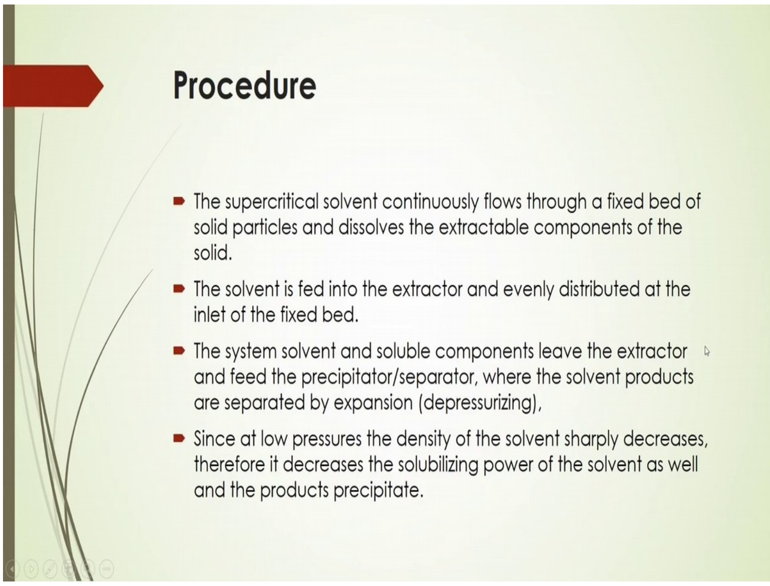

Now the supercritical solvent continuously flows through a fixed bed of the solid particles and dissolves the extractable components of the solid and the solvent is then feed into the extractor and evenly you know distributed at the inlet of the fixed bed and the system solvent and the soluble components leave the extractor and feed the precipitator or separator where solvent products are separated by expansion.

So this is called depressurising condition and you will see that at low pressures you know the density of the solvent of course will be decreasing sharply and because of that it decreases the solubilising power of the solvent as well and also the products precipitation. So based on this you know that changing of density with respect to pressure that you know changing of that solubilising power that is tends to decrease and also because of that there will be precipitation of the products and based on which you that separation will be there.

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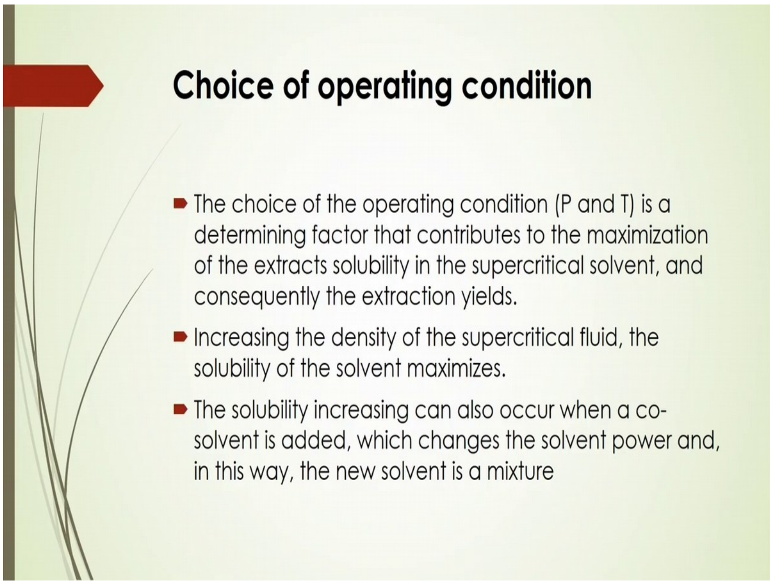

Now, choice of operating condition how you will choose that operating condition for the particular extraction process. And in this case the choice of the operating condition actually mainly a factor that contributes to the maximisation of the extracts solubility in the supercritical solvent and also it will give you that consequently the extraction yields. If you increase the density you will see that supercritical fluid, the solubility of the solvent will be you know maximised and in that case the solubility increasing can also occur when a co-solvent is added which changes the solvent power and this way the new solvent is a mixture it will and act and it will enhance that the separation efficiency.

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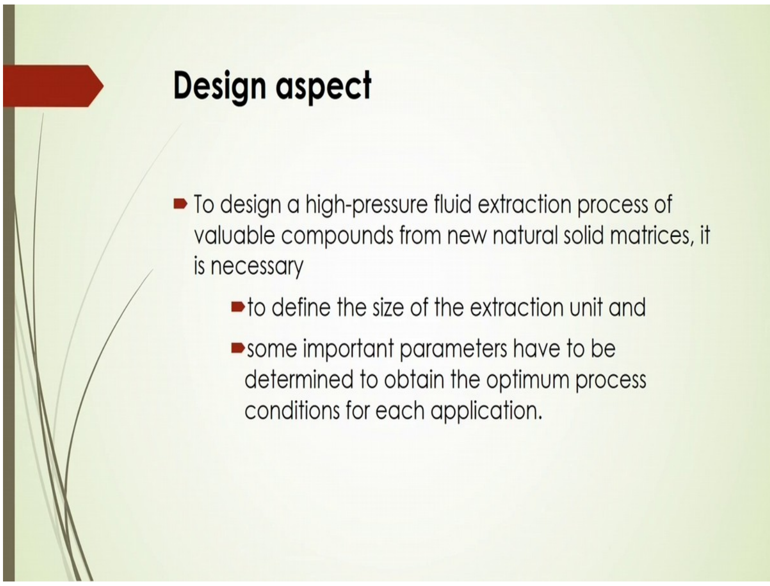

And how to design of those you know that extraction column in this case to design a high-pressure fluid extraction process of valuable compounds from new natural solid matrix, it is of course necessary to define the size of the extraction unit and some important parameters that is to be determined to obtain the optimum process condition for each application, so you have to depend the system in such a way that you know that size of the extraction unit should be you know minimized and also you know parameter like you know mass transfer, even solubility criteria, even packing materials and also if what is the channels and also flooding conditions is there or not so everything should be considered for the optimisation of this design unit there.

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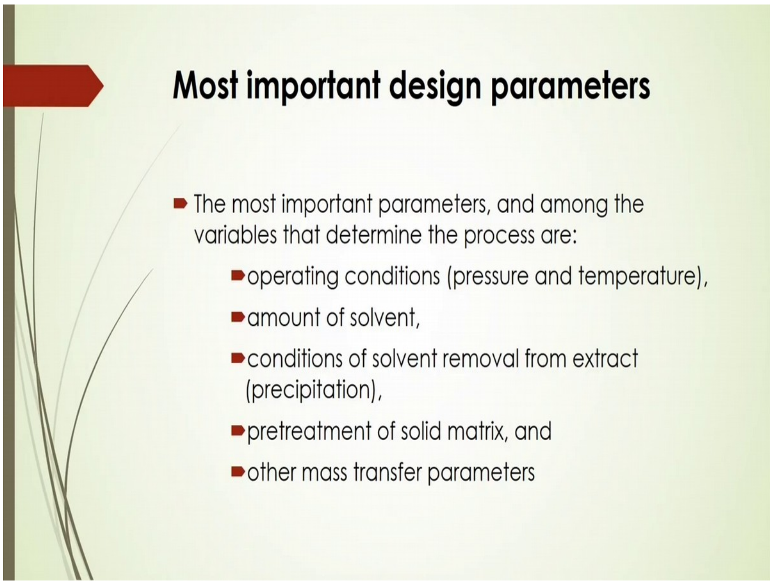

And most important design parameters for this extraction process actually are the operating condition that is pressure and temperature, amount of solvent, conditions of solvent that will be removed from extractant and also the pre-treatment of the solid matrix and other mass transfer parameters, so these are to be actually considered as a design parameters.

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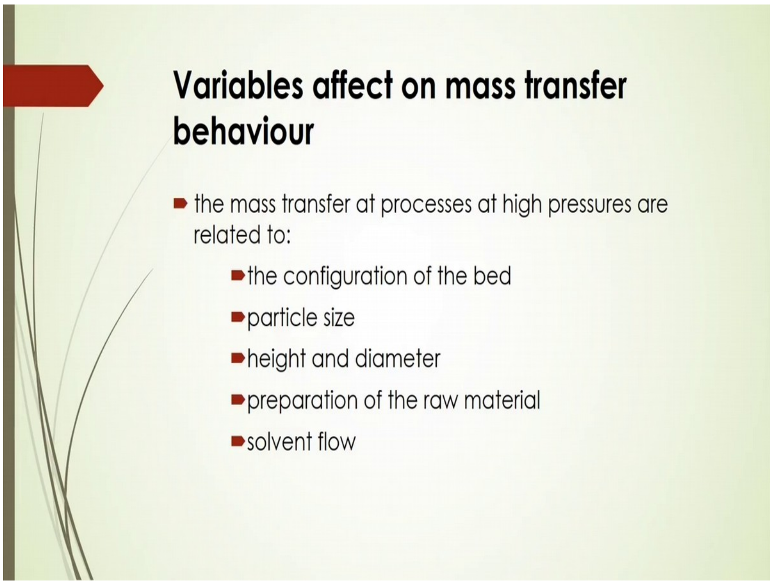

Now, what are the actually different variables that on the mass transfer behaviour in this supercritical extraction process because you know that ultimately the pressure and temperature is the one important factor for this mass transfer process and since you are going to increase that you know mass transfer phenomena based on that pressure and temperature, but there are some other hydro dynamic characteristics also you have to think about because that solvent whatever you are actually allow to pass through that you know packing materials of that you know extraction device that how actually that you know solvent will be distributing inside the bed, that distribution parameters also important to actually enhanced that mass transfer process that is called the extraction process and also you know that configuration of the bed also that is important sometimes you know that the packing materials it will be you know staggered, sometimes that packet material stays or sometimes that packing material may be you know at that certain structure.

So that also can be considered to effect on that mass transfer behaviour and also based on that you know study you can also assess that whether that intensification of the process is possible or not and also particle size is also important because based on that particle size you will see that mass transfer will be happened over the surface of the particles and it may enhanced the contact between that solvent and the solute and also liquid and liquid they are inside the bed by you know that well distribution by this packing materials.

So particle size sometimes it will be you know that a factor for mass transfer behaviour and height and diameter of course very important that if you increase the height and diameter accordingly that you know that you will see that mass transfer phenomena will be there because all these mass transfer coefficient we know that depends on that mainly you know three or four types of you know variables like one is called dynamic variable that is flow rate of the fluid and distribution of the fluid and then you can say that geometrical variables where you can consider the particle size, even you know that channelling or special configuration of bed and height and diameter.

And also another important factor is that what type of solvent you are using? If you use different solvents like those have different you know physical properties accordingly at supercritical condition, those physical properties will be changing at its super critical conditions.

So those physical property change also it may effect on that mass transfer characteristics and also you know that this mass transfer behaviour will change also if the materials or salutes are getting the precipitated or not at its supercritical conditions during the extraction process or not that is very important because that depends on you know that how that solubility will be assessed there and solvation power or the solutes there and then of course that solvent flow that is one dynamic variables.

Another important variable that is called thermodynamic variable of course this is pressure and temperature. So these are the variables like you know that dynamic variable, geometric variable, physical properties as variables and the thermodynamic variable these four types of variables are mainly important for changing of this mass transfer behaviour.

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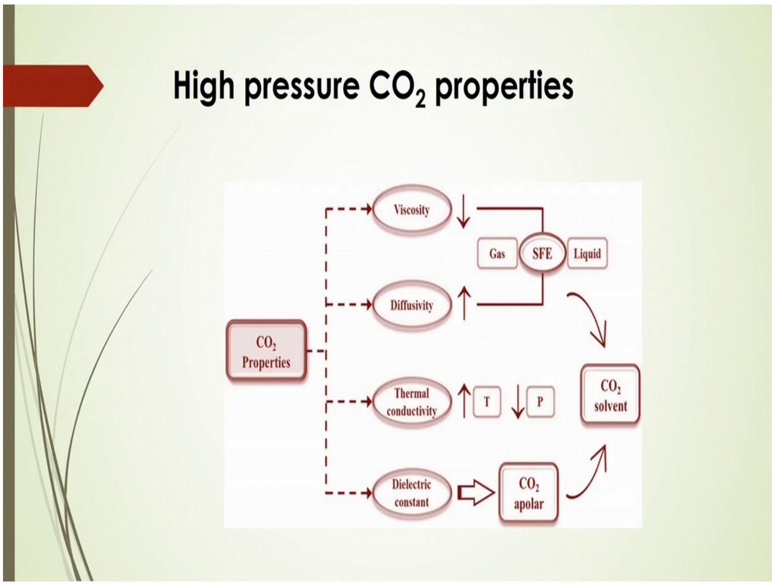

Now, what is that high-pressure carbon dioxide properties that actually effect on the mass transfer characteristics of this supercritical extraction? In this case viscosity is one of the important factor and it is actually decreasing with you know that high-pressure and also you know that diffusivity is also increased by you know that decreasing that pressure and also you can say that the viscosity is decreasing with decrease in the pressure and thermal conductivity that is you know that increases with temperature, but pressure is decreasing in that case and dielectric constant also is one of the important physical property at this supercritical conditions.

So at this dielectric constant this will give you that carbon dioxide is polar or nonpolar and then carbon dioxide a polar and then it will be acting as a carbon dioxide as a solvent and then it will be used as supercritical extraction by considering it as a solvent.

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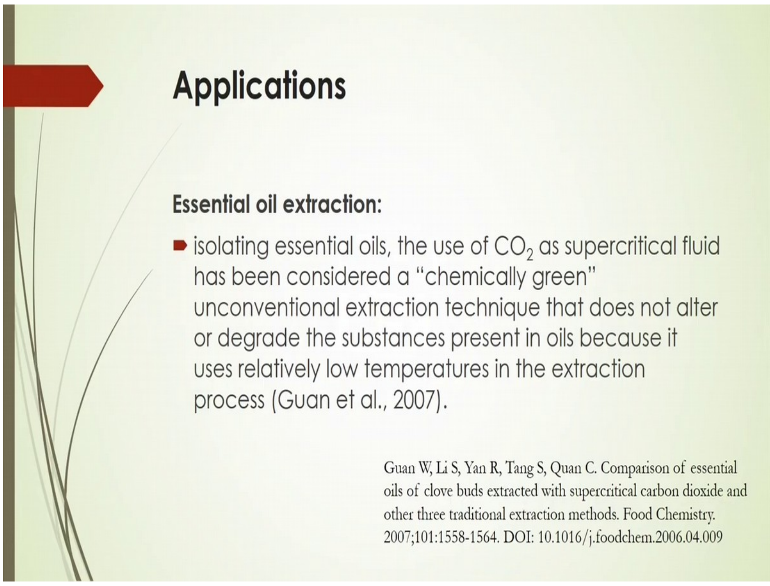

Now, let us consider some applications of this you know supercritical extraction like if you want to extract that some essential oil, so in that case isolating essential oils, the use of carbon dioxide as supercritical fluid is generally considered as a chemically green solvent and it is unconventional extraction techniques that does not alter or degrade the substances present in oils because it uses relatively low temperatures in the extraction process. So carbon dioxide as a solvent at its supercritical condition will be acting as a you know that green solvent which is more you know that intensification for this extraction process.

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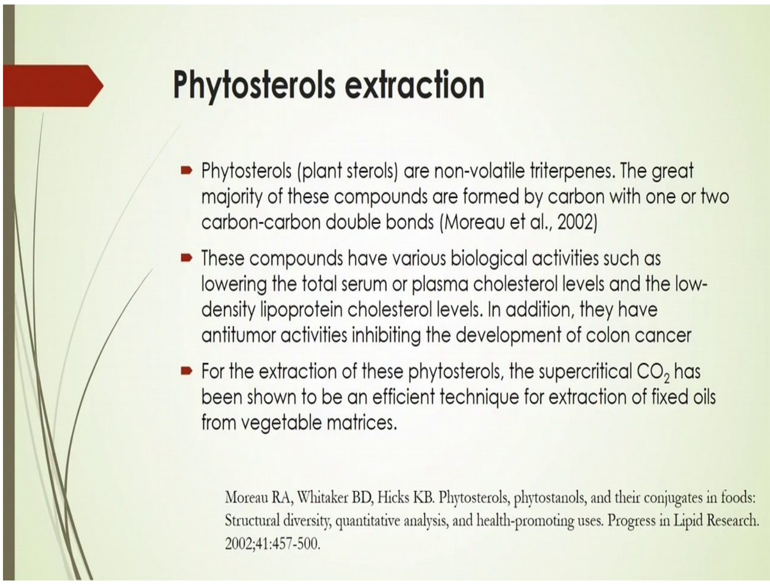

And another application is called phytosterols extraction, in this case the plant sterols that is called phytosterols are non-volatile triterpenes, in that case great majority of these compounds are formed by carbon with one or two carbon-carbon double bonds according to Moreau et at. 2002 and these compounds have various biological activities such as lowering the total serum or plasma cholesterol leaves and the low density lipoprotein and cholesterol levels and also they have anti-tumour activities inhibiting capacity and also the development of colon cancer by you know that is anti-tumour activity inhibiting the development of colon cancer and that is why this phytosterols are very important which is to be extracted by this supercritical extraction in efficient way and also green process.

And for the extraction of this phytosterols the supercritical carbon dioxide has been shown to be an efficient technique for extraction of the fixed audience from this vegetable matrix.

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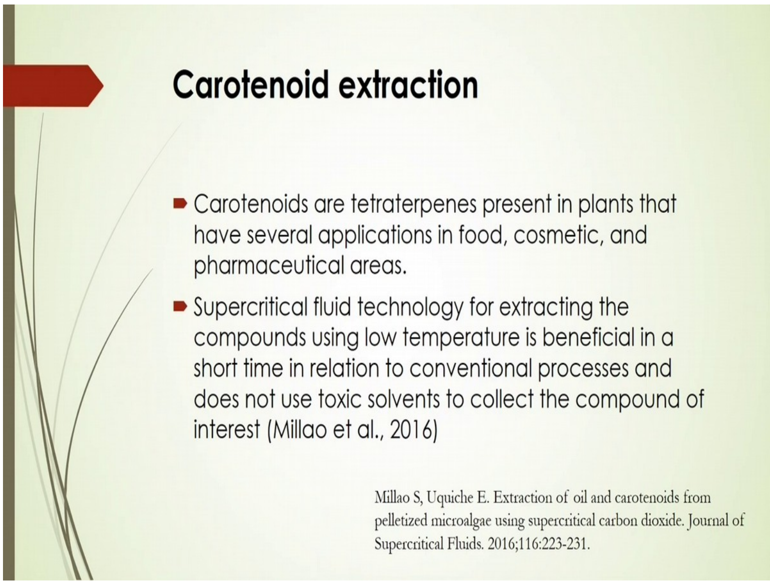

Another important materials, it is called carotenoid extraction it is very useful compound present in plants that have several applications in food, cosmetic and pharmaceutical areas. In this case this supercritical extraction process is used to you know extract this compound and it is very beneficial in a short time in relation to the conventional process and also in this case it is not required to use some toxic solvents to collect those compound of interest as reported by Millao et al. 2016, so supercritical extraction is the greenery process of extraction by which you can extract this carotenoid extraction, carotenoid substance without using some other toxic solvent.

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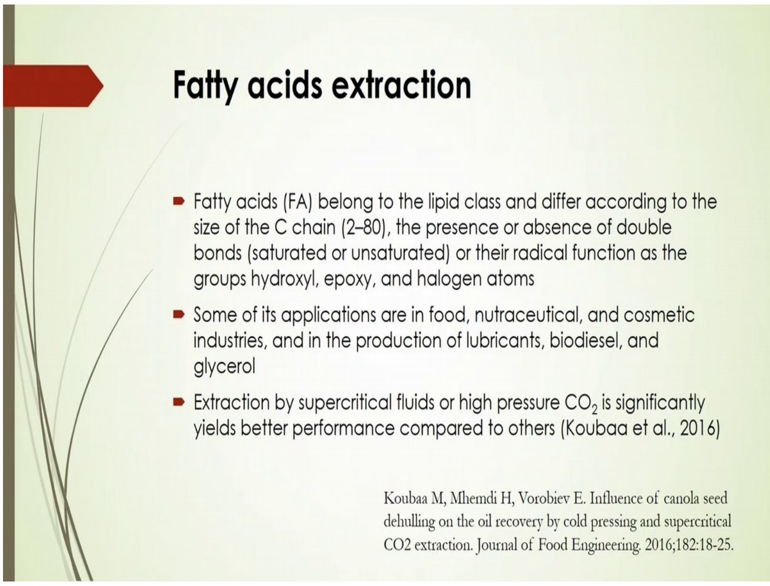

Now fatty acid extraction, you will see that fatty acids generally you know belong to the lipid class and differ according to the size of the carbon chain which is in range of 2 to 80 and the presence or absence of double bonds or their radical function as the groups hydroxyl, epoxy and halogen atoms. In this case you know that this fatty acids extraction by conventional solvents is not so easy and it is time consuming as well as that more energy consumption, more you know it is not also economic and it is not eco-friendly.

So that is why you know extraction by supercritical fluids or high-pressure carbon dioxide is significantly used as a better you know techniques to get better yields and performance compared the other conventional processes and in that case it is actually you know also giving that you know high performance of the mass transfer during that extraction process to get this fatty acids without using some other toxic or solvents.

So Koubaa et al. 2016 they have reported that you know canola seed dehulling on the oil recovery by cold processing and supercritical carbon dioxide extraction that this type of extraction even in fatty acid extraction it is very useful, so that is why process intensification by the supercritical extraction is coming based on this you know greenery development or sustainable development or by Green synthesis you can say.

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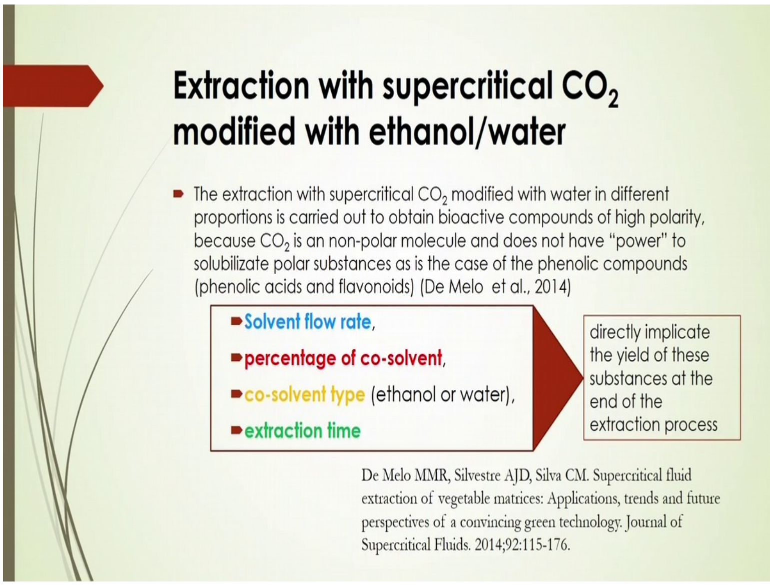

Extraction with supercritical carbon dioxide modified with ethanol or water mixture in that case the extraction with supercritical carbon dioxide modified with water in different proportions that is carried out to obtain bioactive compounds of high polarity because this carbon dioxide is an nonpolar molecules and does not have power to stabilise polar substances as is the case of the phenolic compounds.

So phenolic acids and flavonoids are you know that phenolic compound and in this case this carbon dioxide as a supercritical solvent we can say that we are or you can use to get more yield of this you know that extraction with this ethanol or water. And in that case mainly it depends on that yield of this substances at end of the extraction process mainly you know depends on that solvent flow rate, percentage of co-solvent what you are using, even co-solvent type whether it is ethanol or water, even also that extraction time. So these are the factors which actually to be considered during this extraction of this supercritical carbon dioxide with ethanol or water.

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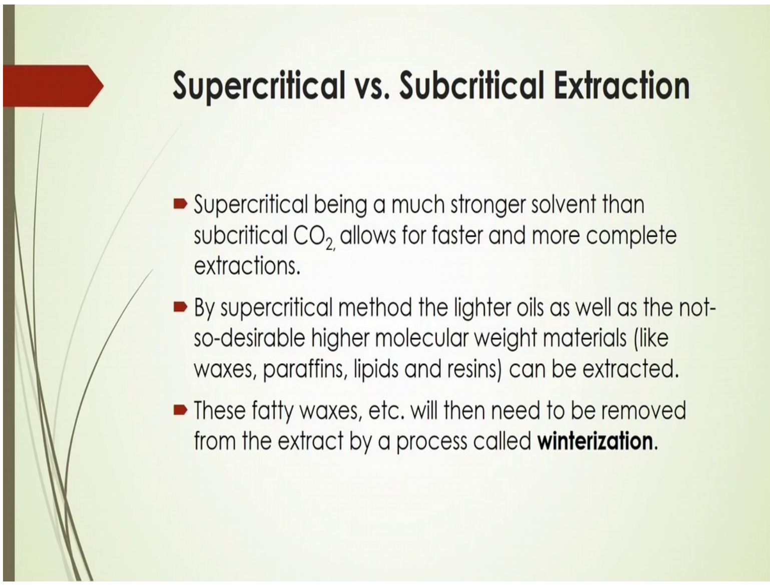

Now, we are talking about that supercritical extraction, but what about the sub-critical extraction, what is the comparison of this super critical extraction compared to that subcritical extraction? Now supercritical extraction also that it is much stronger solvent than you know subcritical carbon dioxide which we will allow for faster and more complete extractions there.

And by supercritical methods the lighter oils as well as the not so describable higher molecular weight, materials like waxes, paraffins, lipids and resins can be extracted there and this fatty waxes, et cetera will then need to be removed from the extract by a process that is called winterization.

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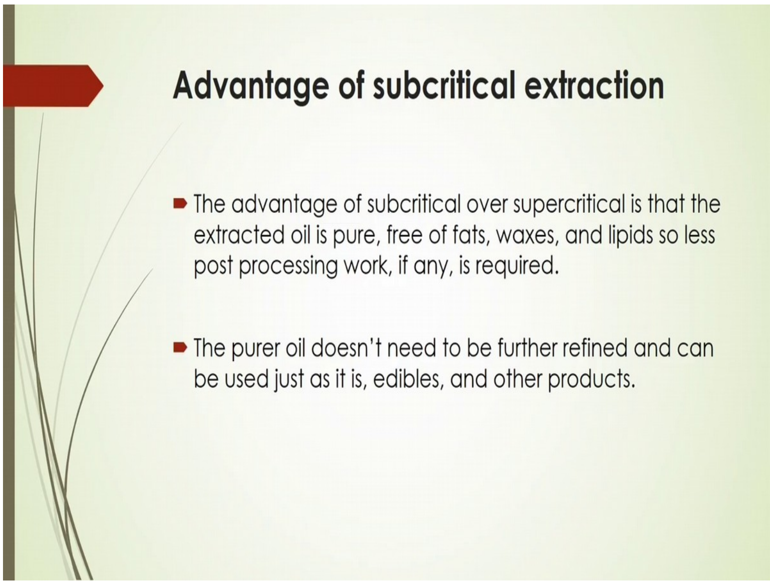

And the advantage of that subcritical over supercritical is that the extracted oil is pure, free of fat, waxes and lipid, so less post processing work, if any, is required. And in that case purer oil does not need to be further refined and can be used just as it is edible and other products there.

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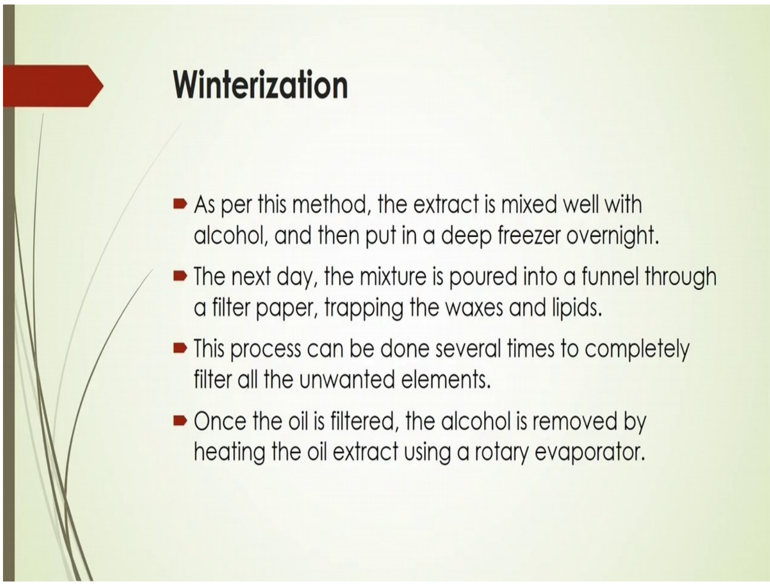

Winterisation, in that case after getting the products after supercritical extraction you have to again separate those extracted materials thereby winterisation and based on this winterisation method the extractor is mixed well with some alcohol and then put in a deep freezer overnight and after that the mixture is poured into a funnel through a you know filter paper trapping the waxes and lipids and then this process can be done several times to completely filter all the unwanted materials. Once the oil is filtered, the alcohol is then removed by heating the oil extract using a rotary evaporator or some by other means.

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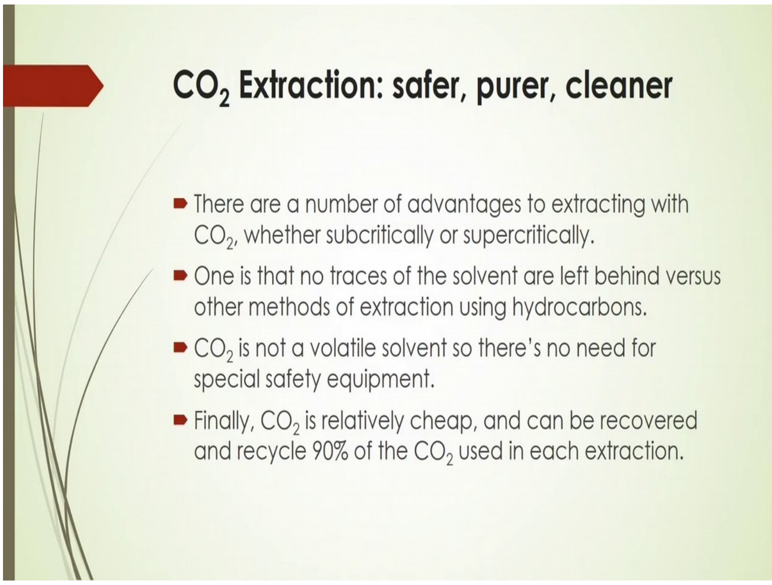

And so we have discussed that different aspects of carbon dioxide extraction at its supercritical condition in a greenery way so that we can get more yield, more performance, even intensification of the extraction process based on this and also some processes may be you know the more advantageous in sup critical conditions, but some you know the materials which will be more you know favourable at its supercritical condition though there will be a high energy consumptions, but you can get it that more safer way even more purer way and cleaner way, so there are number of advantages to extracting with carbon dioxide whether this subcritically or supercritically.

Now, one is that no traces of the solvent are you know left behind versus other methods of extraction using hydrocarbons. So carbon dioxide is mostly useful solvent at its supercritical conditions which will give you that non-toxic way of yield of that extraction. Now, again that carbon dioxide is not a volatile solvent, so there is no need for special safety equipment and also it is you can say that relatively cheaper and also it can be recovered and recycle almost 90 percent of the carbon dioxide which is used in each extraction process.

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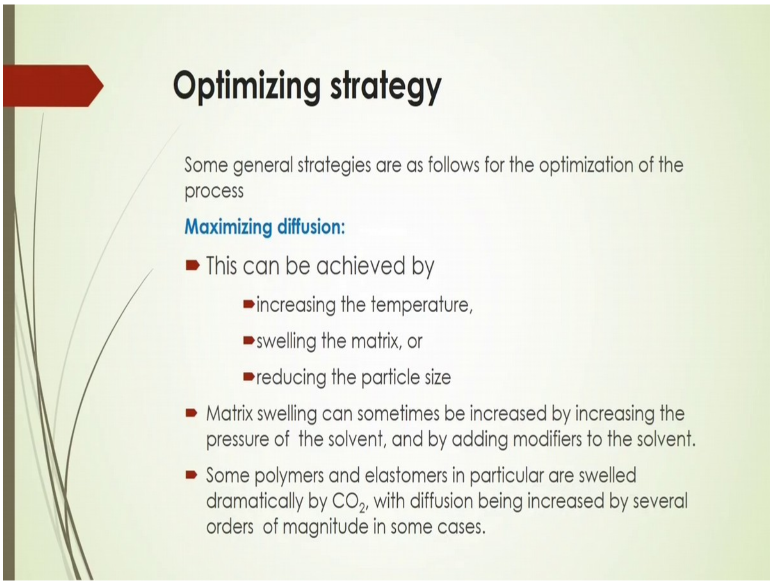

Now, you have to think about that optimisation of this supercritical extraction by carbon dioxide gas, in that case you have to know some strategy for that what should be that you know maximising condition of that extraction process. So some general strategies are as follows for the optimisation of the process like you know maximising diffusion, how it can be done this can be actually done by increasing the temperature, swelling the matrix or reducing the particle size.

In that case the matrix swelling can sometimes be increased by increasing the pressure of the solvent and by adding you know modifiers to the solvent, so some polymers and you know elastomers in particular are swelled dramatically by carbon dioxide with diffusion which is being increased by several orders of magnitude in some cases. So that is why you can maximise that diffusion based on this aspect of this swelling effect and also the particle size effect and also that increase or decrease of the temperature there.

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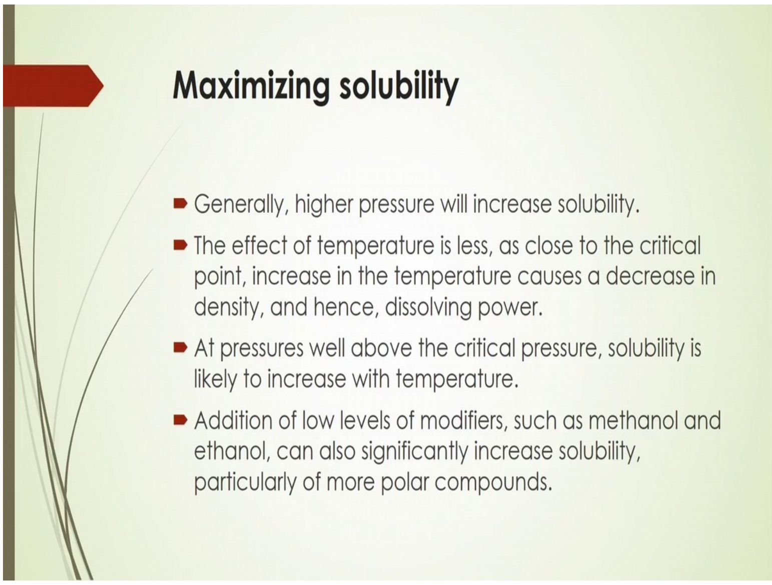

You can also maximise the solubility generally high pressure will increase that solubility and at pressure well above the critical pressure solubility is likely to increase with temperature and addition of low levels of modifier such as methanol and ethanol can also significantly increase the solubility particularly of more polar compound, so in that case you have to consider those things that how to increase that you know solvation power and also how the temperature will effect on that solvation power at its critical condition, so effect of temperature is less as close to the critical point that actually increasing in the temperature causes a decrease in density and hence the dissolving power there.

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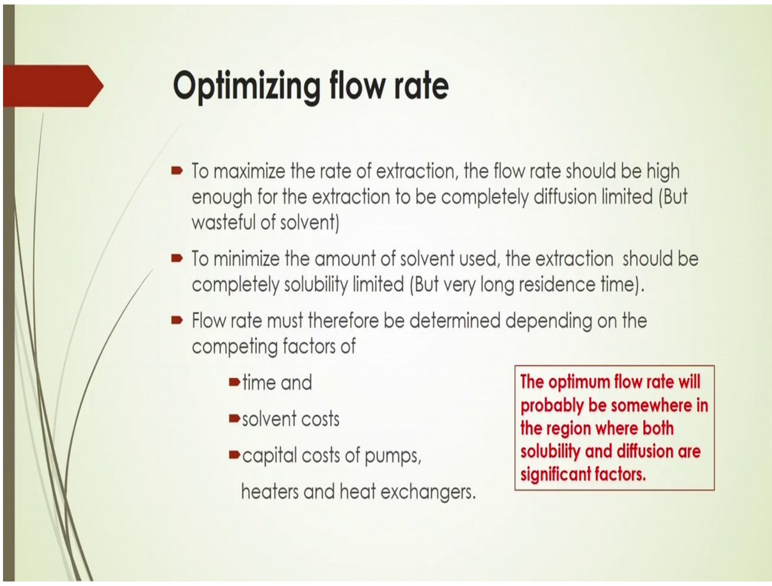

And you can also design that system based on the optimisation of the flow rate there, to maximise that rate of extraction the flow rate you know should be high enough for the extraction to be completely diffusion limited where you can say that wasteful of solvent is the main concern and to minimise that amount of solvent used, the extraction should be completely solubility limited, but very long residence time there it is one important shortcomings, but flow rate must therefore, be determine depending on the competing factors of time, solvent cost, capital cost of pumps, heaters and heat exchanger, so the optimum flow rate will probably be somewhere in the region where both solubility and diffusion are significant factors.

So these are the factors that you have to consider during you know design of that system and also case to case you have to take care of those optimising condition to get that better yield of extraction process and its intensification way.

So we have discussed you know several aspects of that supercritical extraction, how it can be done with carbon dioxide to make it solvent and then extraction and then how it will be you know that separating and what will be the general you know schematic of that supercritical extraction that we have discussed and how it can be so, this is one of the important aspect of process intensification in extraction.

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So I will suggest you to go further about process intensification in extraction through this you know references and we will discuss more about the process intensification in the successive lectures and with you know other modules like membrane technology how it can be used in chemical engineering process as a process intensification. So thank you for giving attention for this lecture.