Novel Separation Processes
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Lecture No. # 41
Supercritical Fluid Extraction

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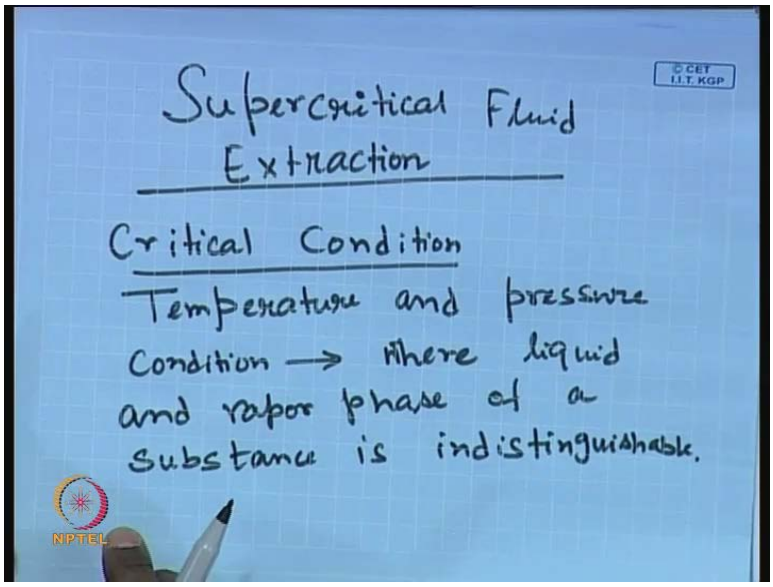

Now, we in this class will start with the another novel separation process, that is quite important and getting an much importance nowadays and this super critical fluid extraction and this is the last topic of our course. Now, this is the emerging separation process and to understand, the basic principles of super critical fluid extraction your to just look into, what is called critical condition. Critical condition is a condition, a set of certain temperature and pressure condition. It is a set of temperature and pressure condition where you cannot distinguish between the liquid phase and the vapor phase of the particular substance. Where liquid and vapor phase of a substance becomes indistinguishable.

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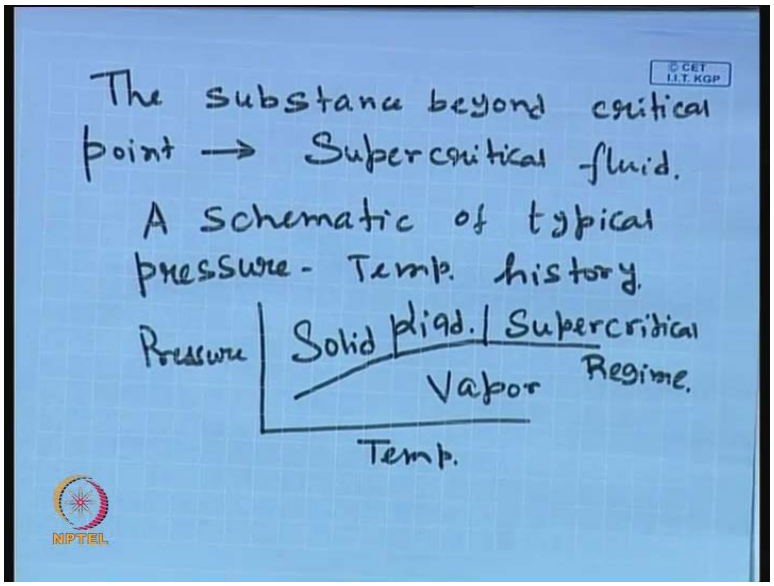

So, at the particular and any the substance beyond the critical condition is known as the super critical fluid, the substance beyond the critical condition, beyond critical points is known as the super critical fluid. Now, I will just give a schematic you know a schematic of typical pressure, temperature history of substance, this is the pressure, this is temperature, this the solute phase and then you can you can have the liquid phase and beyond this critical condition, will be having the super critical region. So, here you have a vapor phase and you have a solid phase. Here will be having a liquid phase and this is the critical condition and you cannot distinguish between the liquid and vapor phase beyond in the super critical region. The physical and the thermal properties have you know some of the changes of the properties are very important in the super critical fluid region.

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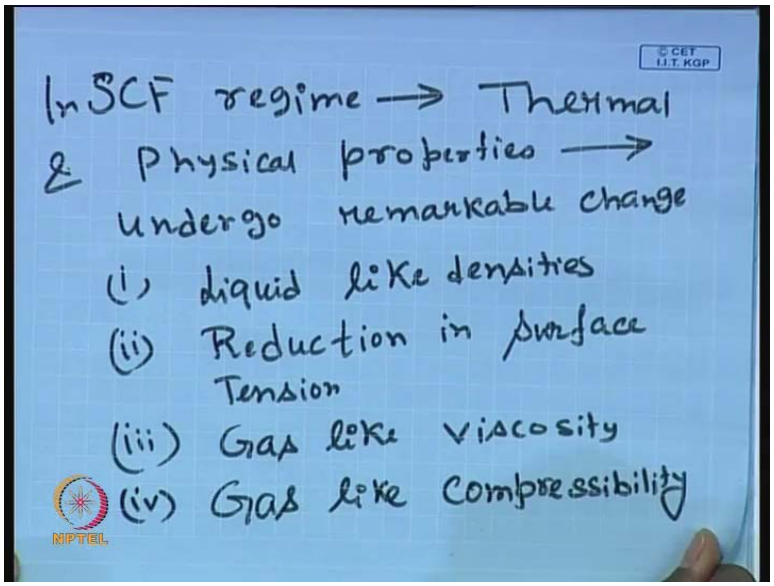

So, I write S C F in super critical fluid regime. The Thermal and Physical properties. they undergo a remarkable change. What are the changes, Number one they process the liquid like densities. The process the liquid like densities, there is a tremendous reduction in surface tension, Surface tension you can have a gas like viscosity. The viscosity will be extremely small, extremely low gas like viscosity. So, will be having a liquid a density the density will be high layer. But will be at the same time will be having a gas like viscosity. Gas like viscosity of the gas is typically two order of magnitude less than the viscosity of the liquid. The surface tension is reduced tremendously you can have the compressibility like gas and diffusivities are becoming quite large and they becomes higher than the liquids.

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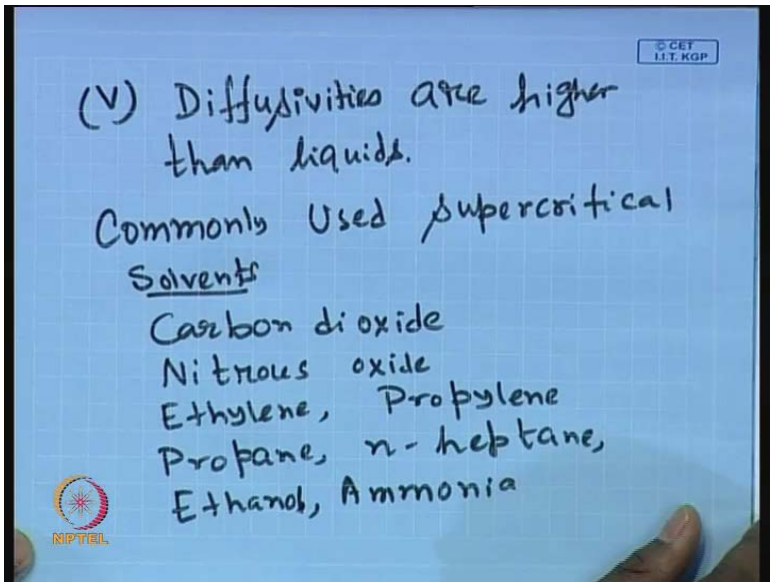

So, these properties become very important and they play a crucial load (( )) in the extraction of the solute in a super critical fluid. Now let us look into some of the commonly used super critical solvents. The commonly used super critical solvents first one is Carbon dioxide, Nitrous oxide, Ethylene, Propylene, Propane, n-heptanes, Ethanol, Ammonia, these are some of the commonly used super critical solvents among them the most quietly used on the popular is carbon dioxide.

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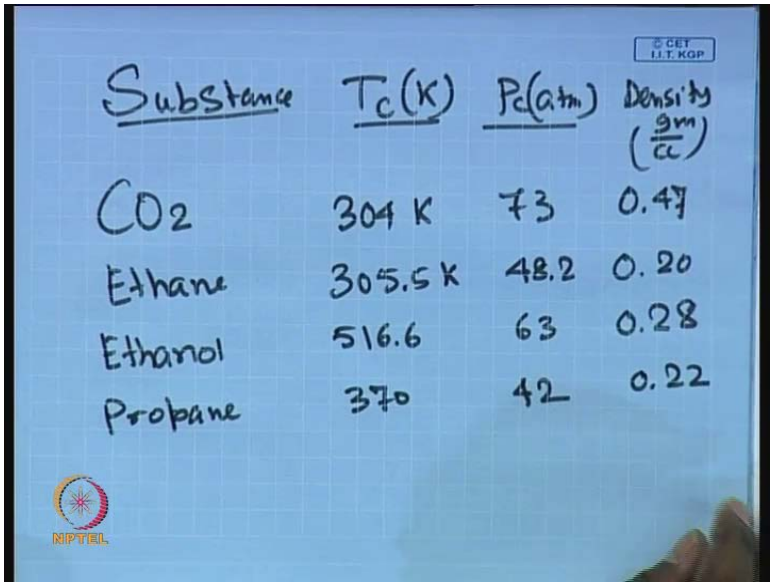

Now, let us look into the sum of the critical conditions of this fluids the substances; that means, the compound we are talking about critical temperature in degree Kelvin, critical pressure in atmosphere, let say density in gram per cc. Carbon dioxide is critical temperature is thirty one around 31 degree centigrade 304 Kelvin, the critical pressure is tremendous it is 73 atmosphere and its density is 0.47. Ethane has a critical temperature in the same range around 35.5 e degrees Kelvin, but it has a lower critical pressure 48.2 atmosphere and it density further lower. you have Ethanol, the critical temperature is 516.6 is 63 atmosphere and the value of density around 0.28 and Propane has a critical temperature 370 Kelvin its critical pressure is quite low 42 and it is density is 0.22 now. So, this are the various substances use for the super critical fluid.

Now, will be looking into some of the properties for the super critical fluid that made them. So, superior compare to the other species.

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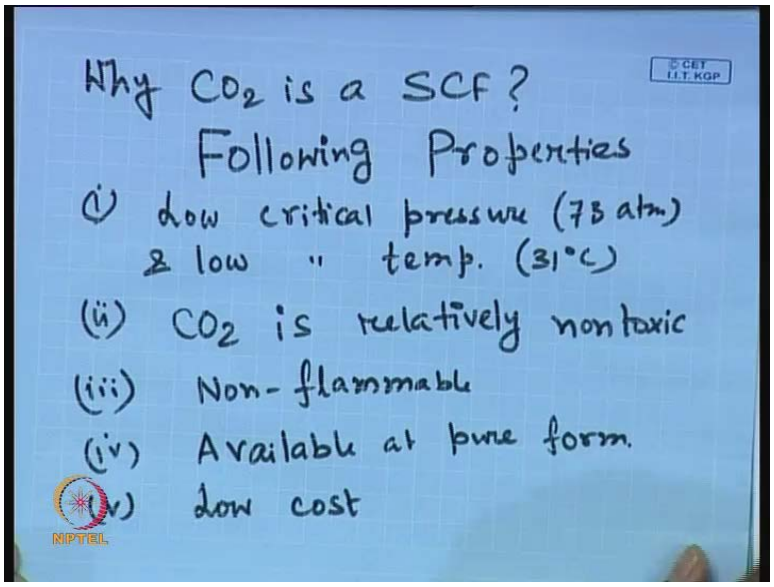

So, the first question is going to we are going to answer is why Carbon dioxide is a Super Critical Fluid? Now are just listing some of the properties that qualify Carbon dioxide as a good candidate for super critical fluid because of following properties. What is this property is listed some of the properties, low critical pressure it is only 74 atmosphere low critical pressure and temperature. Secondly, Carbon dioxide is relatively nontoxic, this is very important properties it is in inflammable and it is non-flammable. Fourth one

is the available at high priority generally the Carbon dioxide is available more or less relatively high priority available at pure form.

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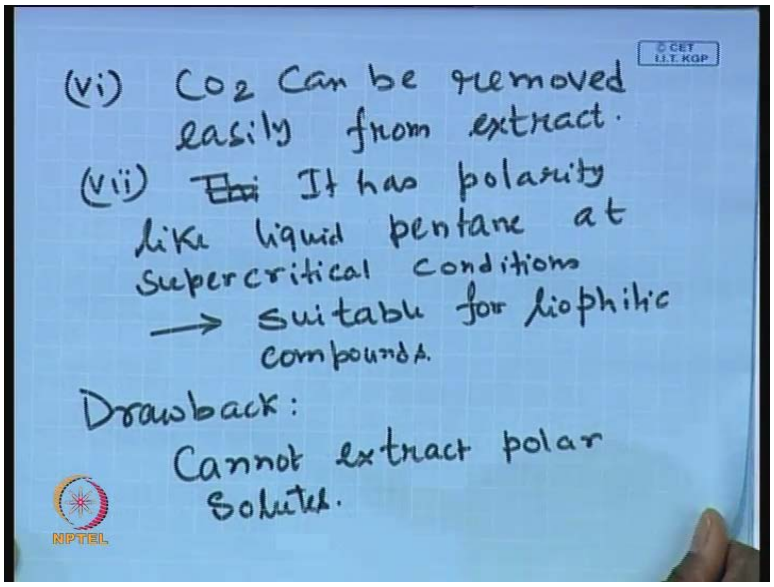

The cost is low, this can easily the removed from the extract that is an important property. Because if the solvent is there, in the extract that becomes a contaminant. So, how easily or how quickly we can remove the solvent from the product that becomes you know an in important property. So, the carbon dioxide can be removed quit easily from extract. It has polarities like liquid pentane at super as (( )). It contains it has polarity like liquid pentane at super critical condition. Therefore, is best suited for the lymphatic compounds. So, and these are the various advantages of Carbon advantages properties to the Carbon dioxide dialysis will be a super critical fluid. That the main drawback is this advantage of carbon dioxide is it cannot extract the polar solutes.

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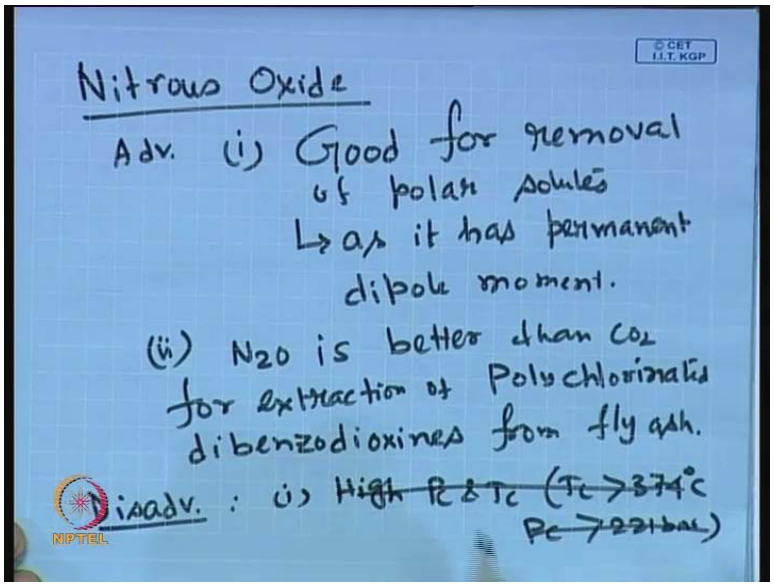

Then, we see some couple of more super critical fluid next super critical fluid is Nitrous oxide, Nitrous oxide the main advantage is it is good for removal of polar solute. Why it is good in this particular aspect, because it has permanent dipole moment, as it has permanent dipole moment dipole moment a typical example of Nitrous Oxide is you know the Nitrous oxide is better than CO2 for extraction of polychlorinated dibenzodioxines from fly ash. So, this is called P c d. These are very (( )) (( )), but main disadvantage of using Nitrous oxide is that it has relatively high critical conditions high pressure high critical pressure high P c and T c is greater than 374 degree centigrade and P c is greater than 221 bar.

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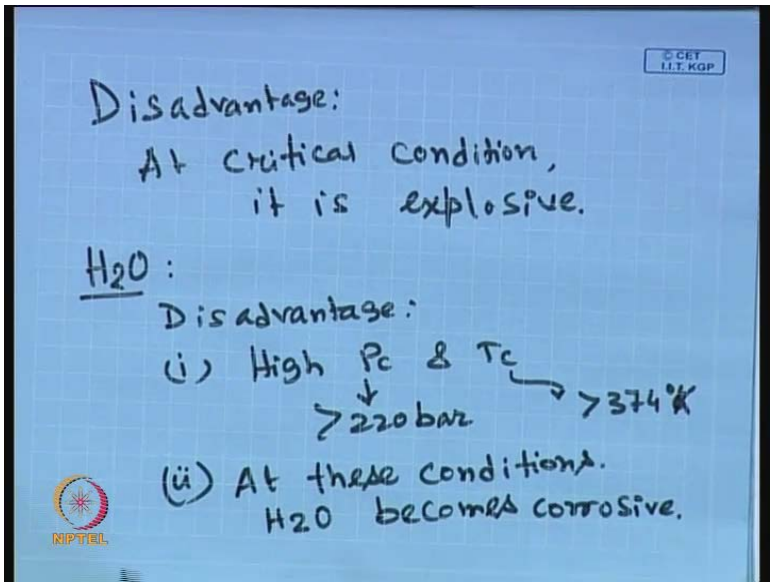

So, it has high you know critical pressure and critical temperature and no it give this basically it Nitrous oxide becomes very explosive sorry at critical condition it becomes explosive, that is the main disadvantage. At critical condition it is explosive. The next material that will be looking for is discussing about H 2 O the water. The main disadvantage of water for using of water as super critical fluid as it has a very high critical condition high critical pressure and temperature. Critical pressure is more than 220 bar; that means, 220 atmosphere and T c is greater than 374 degree Kelvin. Now at this conditions the point is at this conditions the water becomes corrosive.

Now, let us look in to the; So, this are the some commonly used super critical fluid and we just countdown (( )) just some of the advantage and disadvantage of this properties, you know various solvents and depending on the system, we have to use to select a particular solvent to extract for the extract purposes the most commonly extractant that is used it Carbon dioxide.

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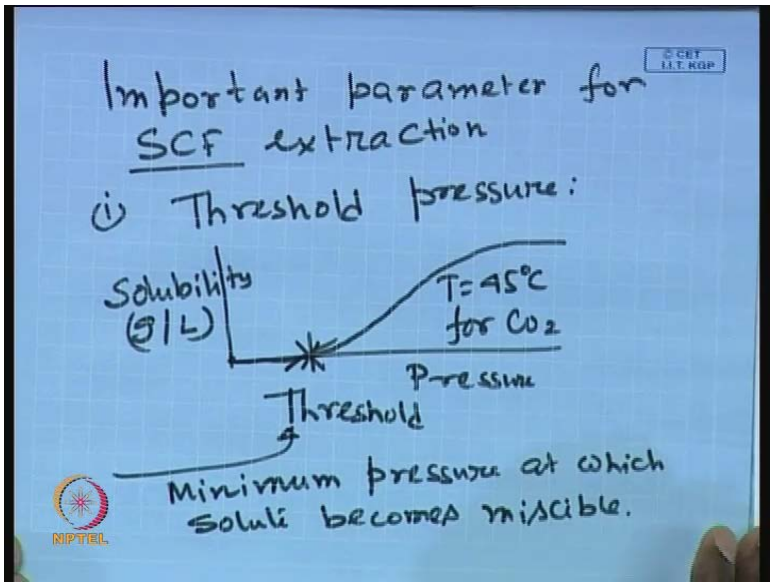

Now let us look into the some of the important properties, important you know parameter for super critical fluid extraction process. Number one is threshold pressure, what is the threshold pressure? This is the pressure at the normal pressure and temperature condition, there will be the miscibility of the solute and the solvent gas will be 0. Almost there is no miscibility. If you go on increasing the pressure at a beyond the particular pressure, beyond the critical pressure onwards the solutes becomes soluble. It becomes miscible. That means, solubility increases in the solvent the particular pressure where the solubility just becomes some value apart from the 0 that particular pressure is known as the threshold pressure.

So, if you plot the solubility curve let say gram per litre and verses pressure then beyond the particular pressure the solubility starts this is the you know so, the solubility curve for at 45 degree centigrade for Carbon dioxide. This particular pressure is called the threshold pressure. This threshold value basically indicates the minimum pressure at which solute becomes miscible.

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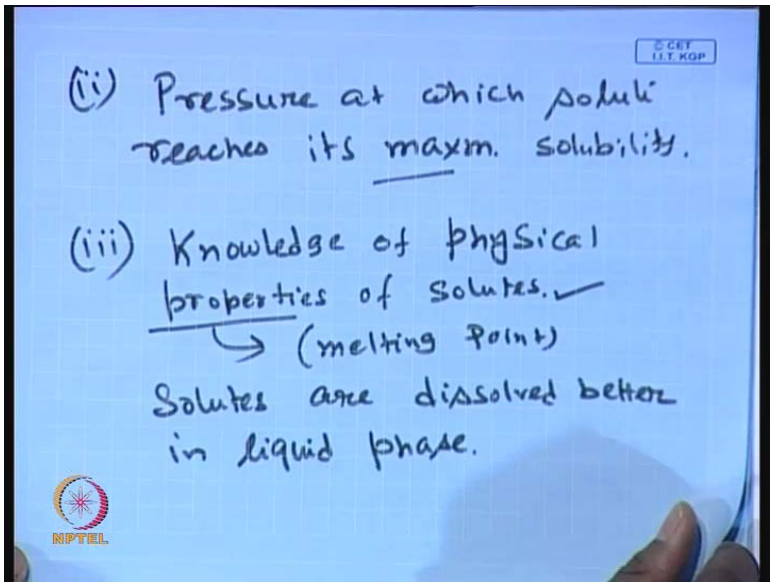

Second one is the pressure attains the maximum solubility you will be getting that is a very important parameter. Pressure at which solute reaches its maximum solubility, this is very important parameter; that means, if you can identify the pressure by the solute is the solute is solubility is maximum, you need not to go for you know higher pressures. So, that gives a limit on the operating condition that we are operating the system.

The third important parameter that we are going to see is the knowledge of physical properties of solutes. The solutes are dissolved better if they are in the liquid state compare to the solute state. So, this knowledge of the physical state of the solutes. For example, the physical property the important physical property in the talking about is the melting point. Solute are solubilised solute are dissolved better in liquid phase compare to the solute state.

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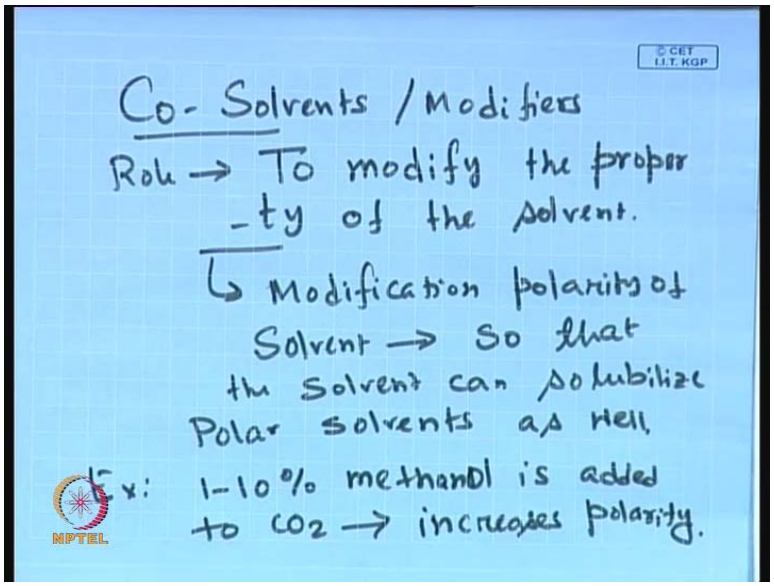

So, this knowledge of the physical properties are solutes are very important sometimes one uses the co solvent or modifiers .What are the co-solvents, this are known as the co-solvents or modifiers. What is the role the purpose the purpose is to modify the property of the solvent. The co-solvent are added to a small extend in order to modify the property of the solvent.

For example, what is the modification of the property the modification of the property may be you know modify modification of polarity of solvent so, that the soluble capability of the solvent will be more. So, it can it can solubilise polar solvent as well. So, that the solvent can solubilise polar solvents as well. We can give an example 1 to 10 percent methanol is added to C O 2 in order to increasing its polarity. The polarity of the carbon dioxide will be increased if you use some co-solvent or modifier present in the system so, that you know it is solubilisation capability will be increasing.

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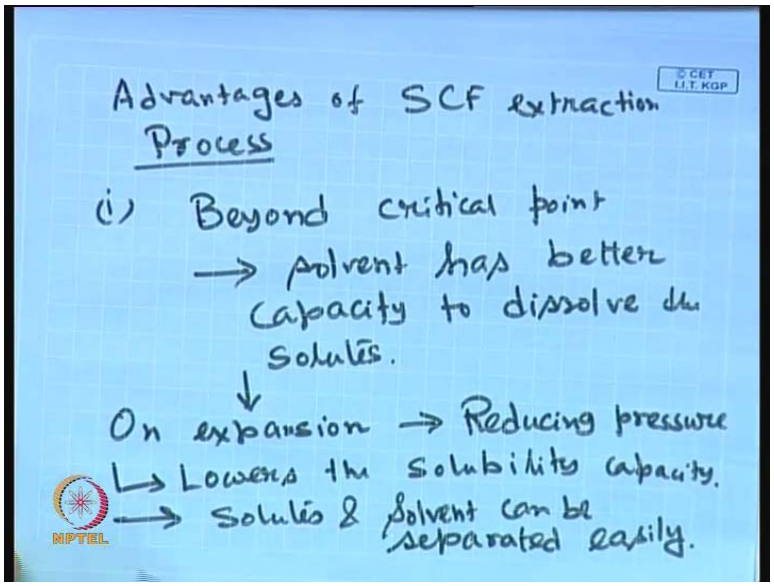

Now, let us jot down some of the advantages of super critical fluid extraction process. The first advantage it is in the is that the simple expansion of super critical fluid leads to lowering in solubilisation capability. That means, beyond critical point beyond critical point my solvent has greater affinity to solve to dissolve. The solute solvent has better or higher capability capacity to dissolve. The solutes on the other hand if you expand it expansion means in a reducing the pressure on expansion; that means, one expand expansion means on reduction of pressure reducing pressure the solubilisation the solubility of the solutes becomes less this lowers the soluble solubility capability capacity. Because of this property the solute can easily be separated from the super critical fluid solutes and solvent can be separated easily.

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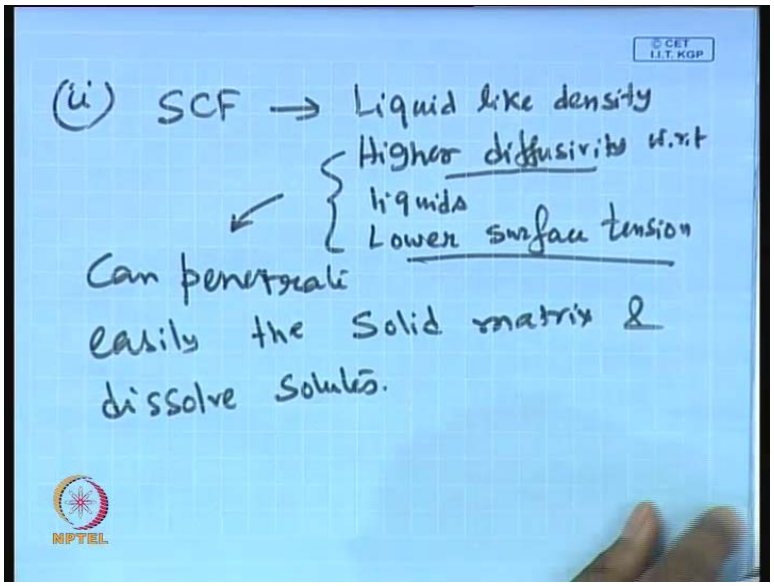

The second advantage that will be getting in is that they have this super critical fluid they have the liquid like a density, but higher diffusivity compare to liquid with respect to liquids. They have at the lower surface tension because of this two properties their mass transfer resistance becomes mass transfer behaviour is much much superior when you are talking about the penetration of the solvent in to the solid matrix to salute to dissolve more solvent those the present inside solute matrix.

So, since that surface tension is very small and the diffusivity of the solvent will be pretty high. So, they will be they can penetrate easily, the solid matrix and dissolve solute that means, if you are a material for the solutes are present on the surface as well as inside the material. Because the property for the super critical fluid lower surface tension of higher diffusivity they can they can penetrate from the surface inside the material can attack the solution can dissolved them and can take them out. So, these are the two important advantages of any super critical fluid extraction.

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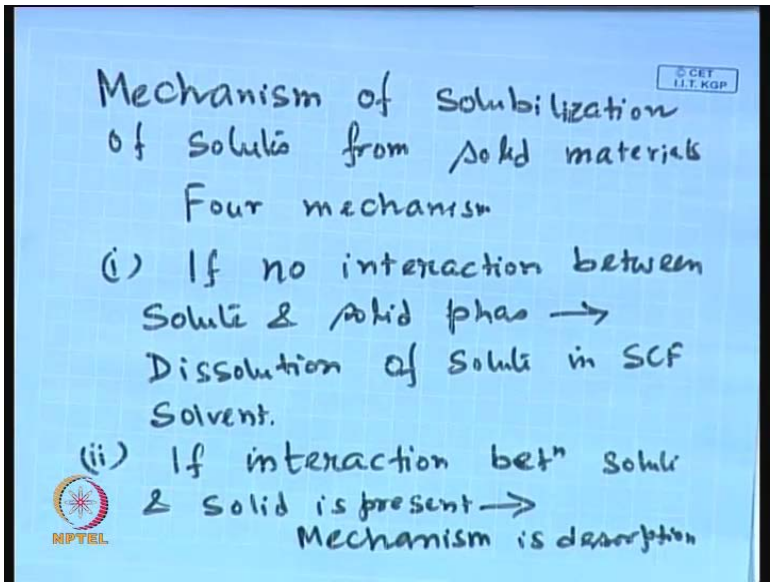

Now let us look into the mechanism of solubilisation of the solute from the solid materials.

There exist four mechanisms, what are these? number one if there is no interaction between the solute and the solute phase if there is no interaction between the solute and the solute phase the process is known as the dissolution of solute it is the mechanism is dissolution of solute in super critical fluid solvent. Now, if there is an interaction between the solute and solid is present then the mechanism is desorption. It is just the reverse of absorption. So, in an absorption column what is done the basically, in the solid phase the solute gets attached to the solute phase and the attachment is by (( )) force is physical absorption chemical absorption so on and so forth. On the other hand if you have to remove the remove those solids present in the solid phase the absorbent phase you have to run liquid and by that absorption, this solute will be coming out from the solid phase of the absorption phase and this desorption will be detailed by the desorption equilibrium.

Similarly, in the case why there is an interaction between the solute from solute (( )) matrix is present; that means, interaction means the solutes are attached to the solute matrix at by (( )) forces or chemical forces. Now, if you add the super critical fluid now this solute will be coming out of the solid matrix of the mechanism is exactly like

desorption and desorption will be basically dictated by the equilibrium isotherm. It will be dictated by desorption equilibrium isotherm.

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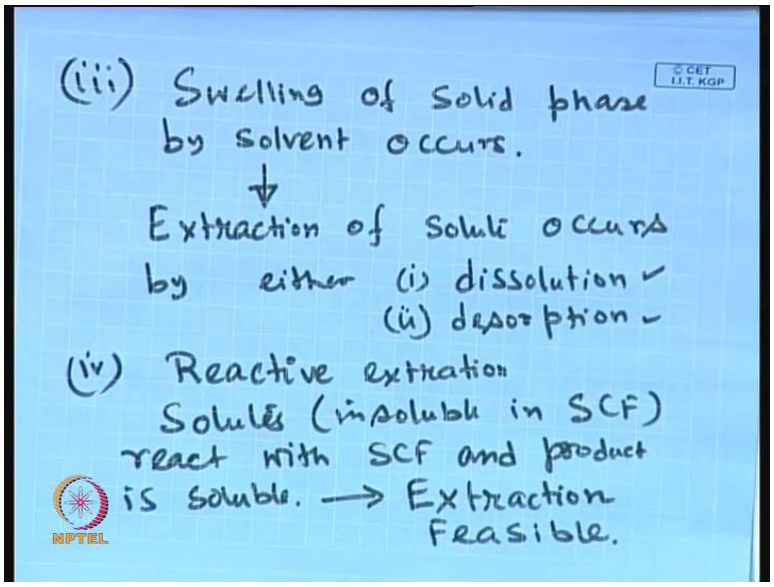

Then third mechanism one can have swelling of solid phase by solvent occurs. The solid phase takes up some amount of solvent and it swells and then extraction of (( )) to the first mechanism. Once the solid phase gets soiled then extraction of solute occurs by either dissolution or desorption. If there is no interaction of solute and solute matrix then the mechanism is dissolution in other case there is an interaction it will be the desorption. The fourth one is reactive extraction, in this case the in soluble solutes react with the solvent and product are soluble and hence the extractable. So, solutes which is basically insoluble, insoluble in super critical fluid they react with super critical fluid and becomes and this product becomes soluble. So, therefore, the product comes to the super critical fluid not the reactant.

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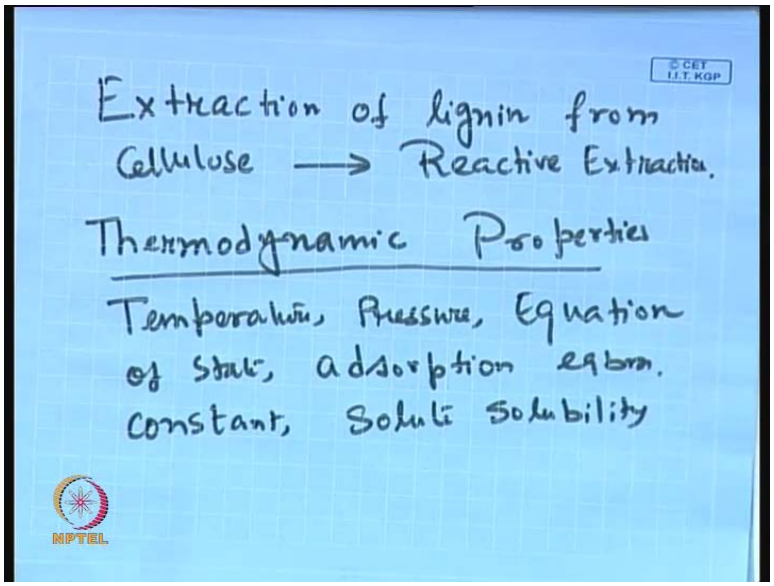

So, once it comes to super critical fluid it can be extracted. This leads to a feasible extraction process. The example of the lignin extraction from cellulose is one example of reactive extraction. Then, you can look into the thermodynamic properties, since we are talking about the critical conditions absorption desorption so, it must be very clear now that some of the thermodynamic properties are various become very important in case of super critical fluid extraction. So, temperature, pressure, equation of state, adsorption equilibrium constant, solute solubility. This is very important a thermodynamic property is the quite relevant super critical fluid extraction.

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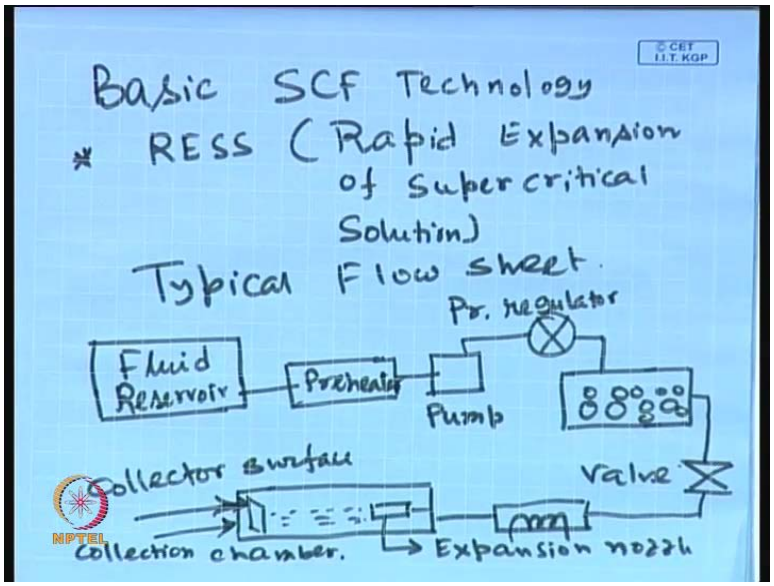

Now, let us look into some of the basic and simplest form of super critical fluid extraction technology. Basic SCF technology, this is known as RESS this is rapid expansion of super critical solution. So, in this case the super critical solvent takes up super critical the beyond the critical condition the feed becomes solvent, becomes super critical, super critical fluid becomes more powerful in order to solubilise the solutes. Once it will solubilise solute it will be expanded rapidly. So, what is what the essence because of that its solubility decreases significantly. So, the solute that has been solubilise it will be will be separated and will be just recovered the solvent and the extraction will take place.

So, a basic typical flow sheet we can draw of this process is something like this. You have a fluid reservoir, then it goes through pre heater, here we have to heat it up to raise its temperature. Then there must be a pump, pressure regulator, goes to the material, the solute and solute matrix, where the solute has to be removed of once. So, the super critical fluids dissolves the solute present here, then it is expanded through this valve. There may be heating region, and it will be after heating it may be expanded and this is the expansion of nozzle and there may be a collector here and this is the collector surface. After expansion it becomes, the solute becomes less soluble and they will be collected and this is basically nothing but a collection chamber, this is the collection surface and this is the collection chamber.

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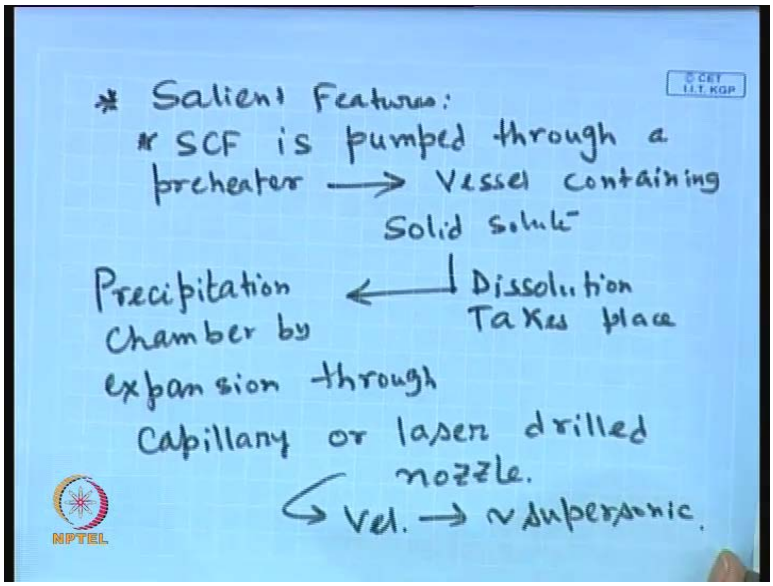

So, this is the typical flow sheet of a R E S S process and let us look into the some of the salient feature of this process. We have the super critical fluid to be pumped through the pre heater. Why it has to be pumped? It has to be pumped into a vessel containing solute, solid solute and the solution is then sent to the precipitating chamber by expansion through it, applied (( )) nozzle. Then the dissolution takes place dissolution of solute in the super critical fluid takes place, there it moves to a precipitation chamber by expansion to capillary or laser drilled nozzle. And what happens in the precipitation chamber at through this laser drilled nozzle it is expanded. That means, it the pressure is released since the pressure released is velocity is very high the velocity of the solvent may be supersonic, velocity may be supersonic. So, we have we have just releasing pressure from the high pressure is your just releasing at the atmosphere or at the low pressure.

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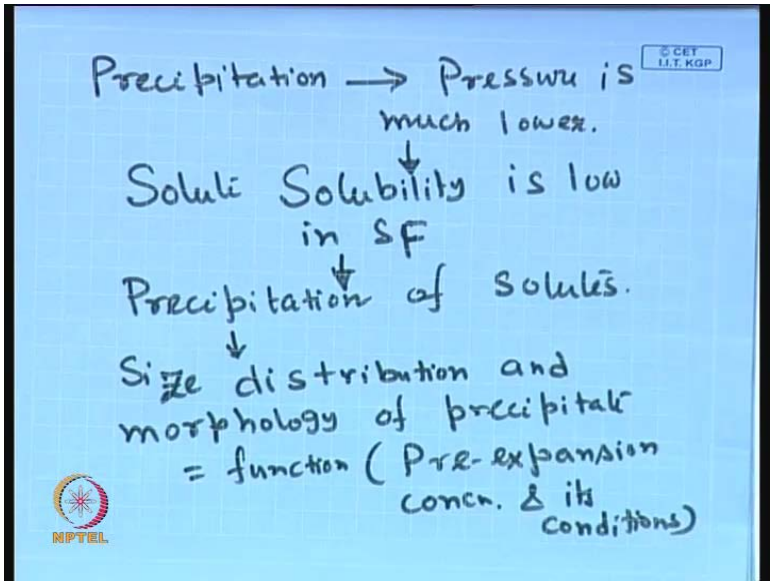

So, it will be coming out at a great velocity and let us say what happens in the precipitation chamber. In the precipitation chamber pressure is much lower and at that lower pressure the solubility of the solute becomes quite low. Solute solubility is low in super critical fluid. So, therefore, the solute comes out of the solution; that means, it precipitates so, this leads to precipitation of solutes. Now, so, there so basically it will be separated out and size distribution and morphology of the precipitated material is basically a function of its concentration in various condition. Morphology is a function of pre expansion concentration and it is conditions.

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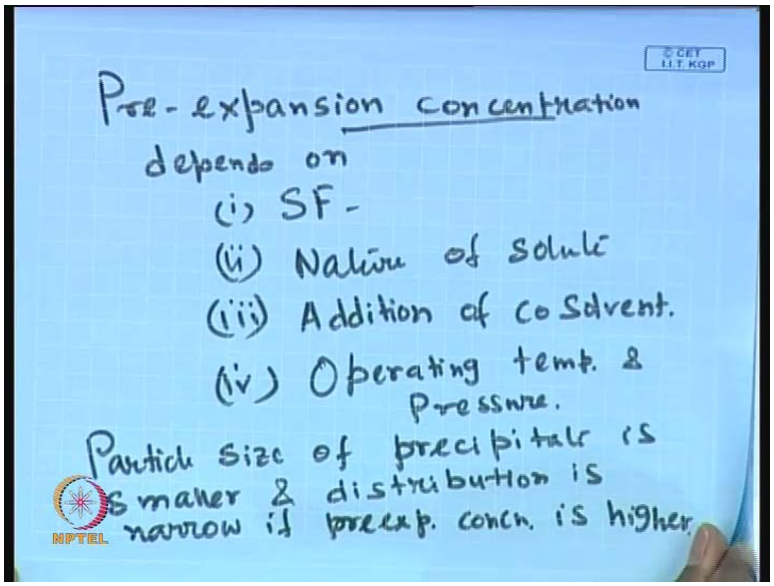

And pre expansion concentration is depends on several factors. Depends on number one the super critical fluid. Suppose a particular solute is more soluble in a particular super critical fluid may be in Carbon dioxide. If you use Nitrous oxide then the concentration of solute will be low because the solubility is less. So, it depends on the concentration it nature of the super critical fluid that we are going to use.

Secondly, of course the nature of the solute if you are using Carbon dioxide as super critical fluid and you are using a polar solute to dissolve the dissolution of the solubilisation will be less. So, nature of the solute is also a factor then addition of the co solvent or modifier. Now, if you are using carbon dioxide and if you are using a if you like to extract, the polar solute then if you add a cosolvent then that will increase its polarity and is solubilisation capability of the polar solutes. So, the addition of cosolvent is also very important factor and of course, the operating temperature and pressure. Now, generally it is found that particle size of precipitated is smaller and distribution is narrower if pre expansion concentration is higher.

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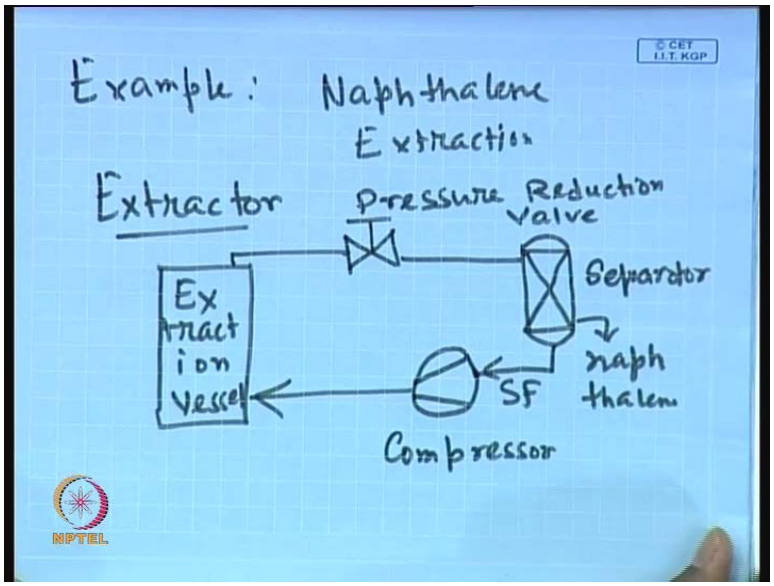

Now, we will just take a particular example that we will be talking about is that example of Naphthalene extraction. The process typical naphthalene extractor looks something like this. We will be having the extraction vessel. In this extraction vessel the super critical fluid is mixed of the naphthalene and naphthalene is dissolved in the super critical fluid. Then, it is going through a pressure reduce pressure reduction of the valve so, expansion. So, once you goes through a pressure reduction valve what happens the solubility of the naphthalene which was very high in the super critical fluid at the operating conditions it becomes suddenly low.

So, it goes to a separator here, you separate out. The naphthalene is separated out and the super critical fluid what is it? It should not be wasted, it will be compressed it will be is pressure will be increased and it will be the sent back to the extraction chamber. So, super critical fluid comes here via a compressor and it is sent back to the extraction vessel so that thing the whole a system become a continuous process.

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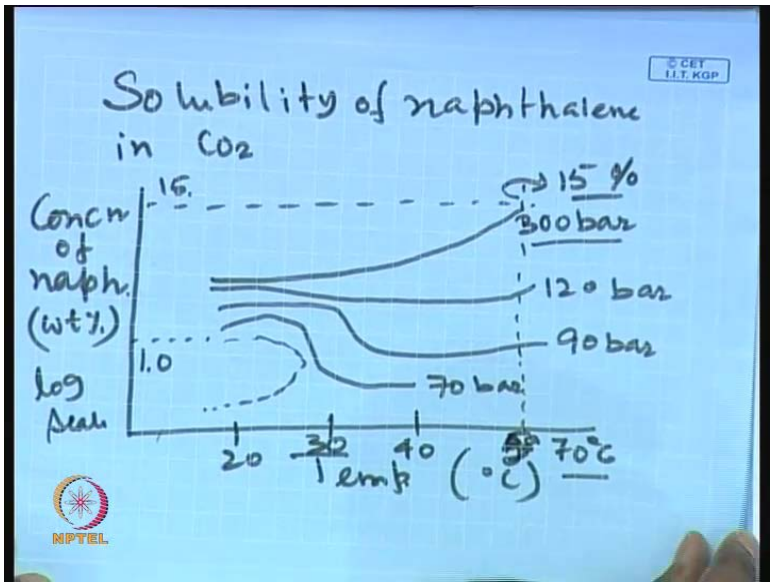

Now, in draw a solubility diagram of typical naphthalene under super critical condition in CO 2. This is the concentration of naphthalene that is with percent in a log scale and this side is temperature degree centigrade. Typically, the plots look something like this, the solubility cost becomes very high at 300 bar at this temperature, this 120 bar, this is 90 bar, this is 70 bar and this temperature is 20 here, 30 there, it is around 40 here. So, it is around 65 there and this value is around 15 and this will be here after 1 the solubility is 1 percent here.

The solubility should the 15 percent here, the solubility 15 percent when you are operating at 65 degree centigrade and it is around 55 degree centigrade and 300 bar. So, now this is around 70 degree centigrade. So, when you are going for high pressure like 300 bar and high temperature 70 degree centigrade the concentration (( )) becomes very high. So, it dissolved in to a large extend in a carbon oxide.

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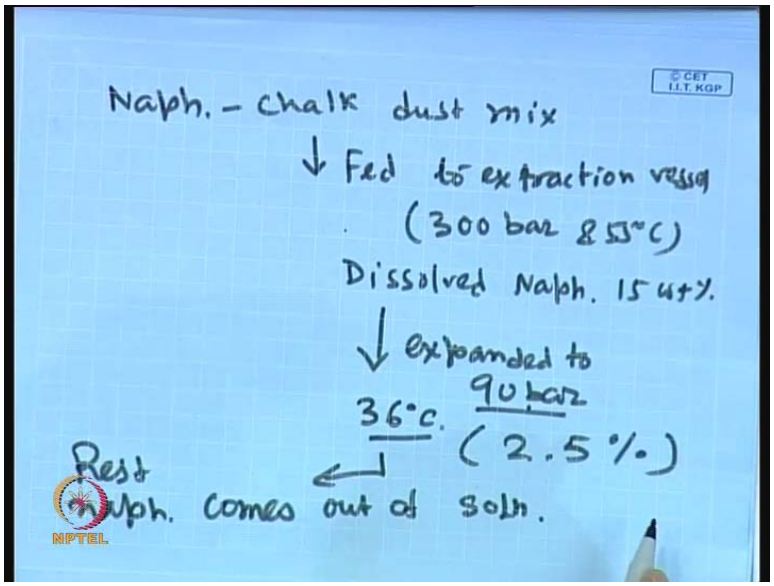

Now the naphthalene chalk dust mixer is fed to the extraction vessel and the condition is let us say 300 bar and 55 degree centigrade. Now, at this condition the carbon dioxide contains dissolved naphthalene, that is around 15 (( )) percent. Then it expanded to 90 bar through a pressure reduction valve and after that the temperature becomes 36 degree centigrade. Now, at this condition, at this pressure, at this temperature, the solubility of naphthalene is only 2.5 percent. So, reste of the naphthalene falls out of the solution. So, rest naphthalene comes out of the solution. The precipitate naphthalene then collected and the super critical carbon dioxide is then compressed to 300 degree bar and at 55 degree centigrade its temperature is rising to 55 degree centigrade and it will be sent back and recycled to the extracted. So, that is the total process, typical process here.

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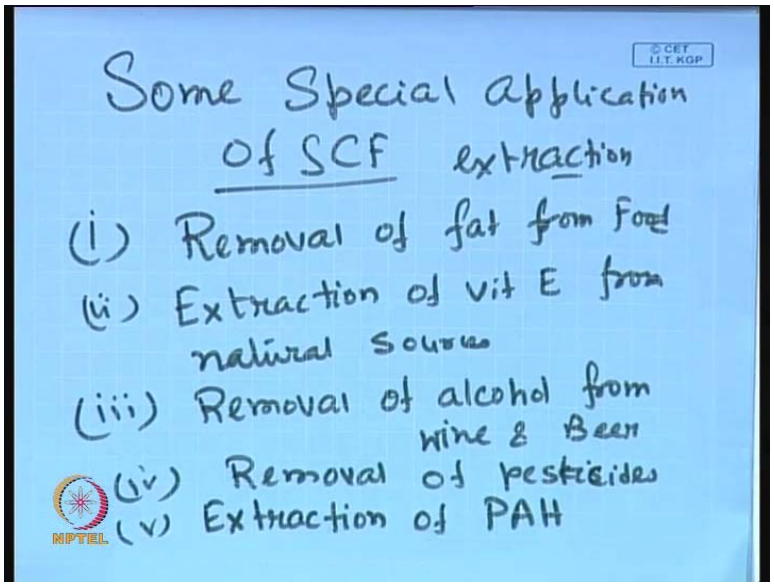

Now, I just mentioned some of the special application of super critical fluid extraction. Number one, removal of fat from foods, extraction of vitamin E from natural resources, removal of alcohol from wine and beer, fourth one is removal of pesticides and finally, you we can extract poly aromatic hydrocarbons which are (( )) in nature and ensure they are called P A H Poly Aromatic Hydrocarbons and follicular penguin P C B and all these (( )) in a organic solute, they can be removed by super critical fluid extraction. So, in this separation process we have seen the quality of the super critical fluid and we have looked into the various you know solvents.

What are the advantages and disadvantages for the (( )) solvents and the basic principle of how they will be operating the thermal (( )) mixed the increased the solubility beyond the critical points of the solute becomes very important and when you reduce the pressure, when you reduce the pressure and the solubility of the solute in the super critical fluid falls drastically. Therefore, the desorption solute will be precipitated out and can take out the super critical fluid and further composite and send it back to that factor. In fact, one can look in to the Moliere charge and do some thermal level (( )) calculation and can find out what will be the amount, that will be extracted per unit mass per k g or per pound of the super critical fluid and what are the you know relevant energy associated with it. So, with this come to the can you know finish the super critical fluid extraction process and basically this is the last of that (( )) of course, and if you remember that we have it will looked, but the you can see that we are talked out about

various novel separation process ranging from membrane phase separation process is detailed, and the (( )) separation process, super critical fluid extraction, centrifuge processes, ion exchanges and electro phonetic separation process is so on and so forth. Thank you very much.