Downstream Processing
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Lecture - 18
Liquid-Liquid Extraction (Continued)

For extraction will the efficiency go up or go down that is the question that is asked, so same amount of solvent, but it is now divided into 4 parts, and you are doing 4 extractions it is like a 4 stage cross flow system.

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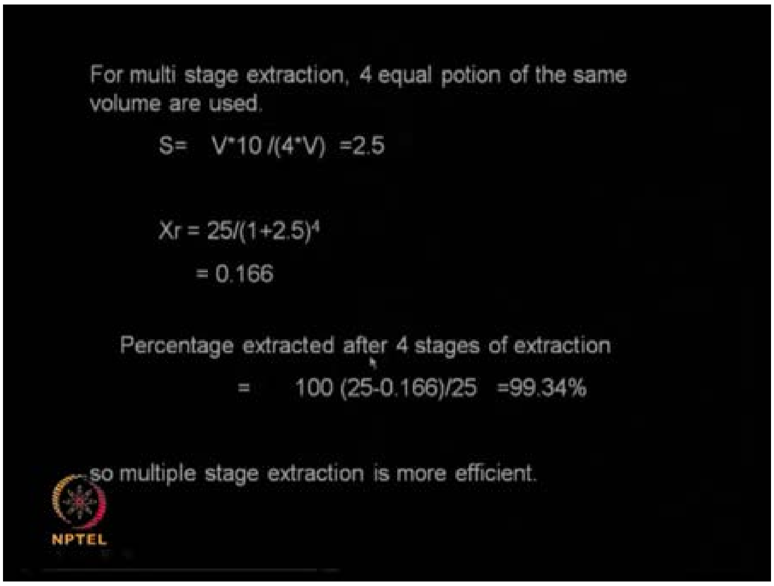

So, what happens the equation gets slightly modified the equation will become X r is equal to X f divided by 1 plus E raise to the power n, where n is equal to 4. Now, again we can calculate you are a extraction efficiency E, E is given by 2.5 because, you have a now the quantity of the solvent is divided by 4. So, the it is become instead of E being 10 in the previous case E is 10 in the previous case, now E is become 2.5, so the equation is X r is equal to X f is 25 divided by 1 plus 2.5 raise to the power 4, so you get X r as 0.166.

So, you are starting from 25 and after 4 stages of extraction with 1 4'th the amount of solvent, you are able to extract 99.34 percent of the protein. You see in the previous case, when you put all the solvent into 1 stage, you are able to extract 91 percent, but when you divide it into 4 equal parts, and do the extraction in 4 disctint stages you are able to recover 99.3 percent of the protein. That means, a multiple stage extraction is always efficient, even if you are using less solvent, multiple stage extraction is always efficient.

So, that is the main take away from these two problems, so instead of using a large amount of solvent and putting it in 1 stage, you divide that solvent into many stages, many portions, and then perform an extraction; that means, a mixing equilibration separation. Then mixing equilibration separation, like that if you do it in multiple stages it is much more efficient, that is why in labs we do not add all the solvent in one go and try to extract, we always put little solvent extracted remove the solvent. Again add little solvent to the feed or the broth again extract it and by doing that we are actually achieving a much higher separation efficiency, rather than putting all the solvent in one lot.

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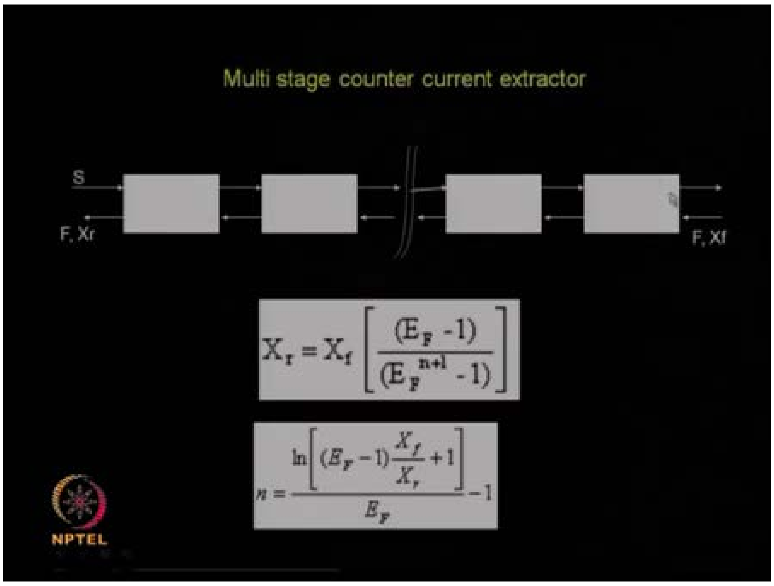

Now, let us look at another problem, this is a multistage counter current extraction; that means, the solvent is flowing in one direction, your feed or the heavies is flowing in another direction, that is why it is called a counter current. The solvent when it is entering it is devoid of any solute, so the concentration of solute in the solvent layer is 0. Now, feed is entering at solute concentration of X f and the raffinate that is leaving on the other end has a concentration of X r.

If you remember this the equation which I showed few classes back, where X r and X f are related by this a particular relationship. Where you get E, E is the efficiency of a extraction, we will assume that efficiency is constant in each stage, and the quantity of solvent or feed does not change, when it moves from one stage to another stage. That means, the miscibility of the solvent and the heavy is 0, so the E remains constant in each stage and n here in the denominator is the number of stages. So, this is the equation for a multi stage counter current process, so if you remember the previous equation for a system, where you have a cross flow and if you look at this counter current both are very different type of equation.

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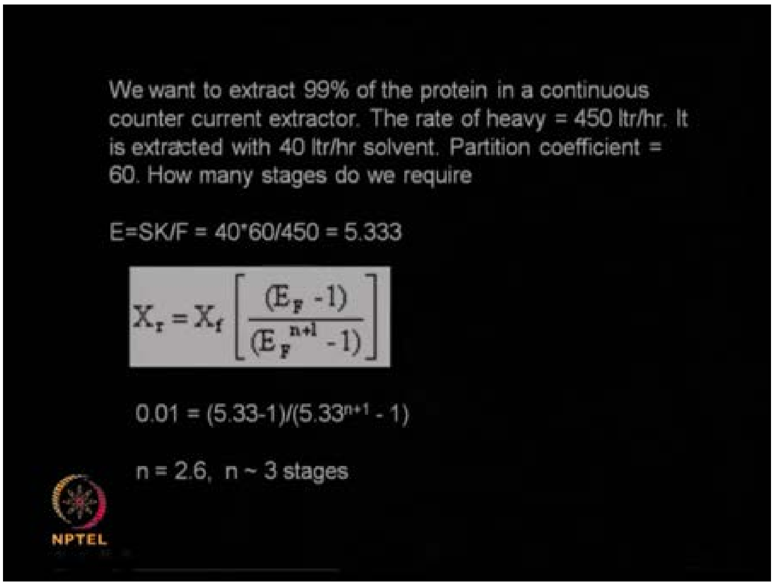

Now, we want to extract 99 percent of a protein in a continuous counter current extractor, the rate of heavy is 450 liters per hour that is feed, and it is extracted with 40 liters per hour of solvent that is S partition coefficient is given 60. So, how many stages do you require, again E is given by this formula S into K by F, S is the solvent rate K is the partition coefficient, F is the feed rate. So, if I substitute all these I get E as 5.33, now you take this equation, I want to extract 99 percent.

So, X r by X f will be 0.01; that means, only 1 percent of the solute is left behind in the raffinate, then I substitute all these terms here. Once I substitute all these terms I get n is equal to 2.6; that means, I need 3 stages I need 3 counter current stages to perform this extraction. That means, if I want to extract 99 percent of my solute using a solvent of 40 liters per hour flow rate, and the heavy flow rate of 450 liters per hour I need at least 3 stages.

So, the most important condition or the assumption here is the streams that are leaving each stage are in equilibrium that is very, very important a assumption in all these a type of a design calculation actually. So, with 3 stages I will be able to extract 99 percent, and the main advantage of a the continuous flow system is the extraction can be performed in a continuous fashion. We looked at a different types of a problems now let us look at a something different another type of extraction concept, this is called super critical fluid extraction.

It is becoming very popular especially in the area of foods, nutrition, nutraceuticals, natural product chemistry, and natural product based drug design and, so on actually. For example, your instant coffee if you want to remove the toxins, if you want to remove the caffeine present in the coffee. Now, people are resorting to super critical fluid extraction, the main advantage of a super critical is you do not have to use high temperature; that means, chemicals or nutritious material or nutraceuticals or vitamins that are present will not get denatured or deactivated that is the main advantage of super critical actually.

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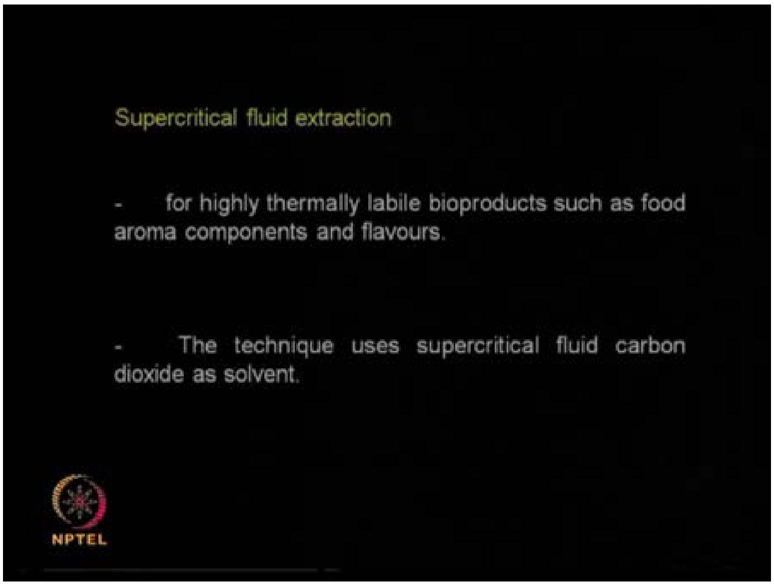

So, you can retain the aroma, aroma will not a get a affected because, of changes in p H or changes in temperature. Flavors will not get affected, so super critical is becoming a very big area in the food and flavor industry, generally carbon dioxide is used as the solvent because, it is available in plenty, it is got a very good critical pressure and temperature. So, with the reasonably good values of pressure you will be able to get a super critical carbon dioxide. So, it acts as a solvent super critical fluid is neither a gas or a liquid, so it is in between, so it is got a very interesting properties, which is made is of in the super critical fluid extraction.

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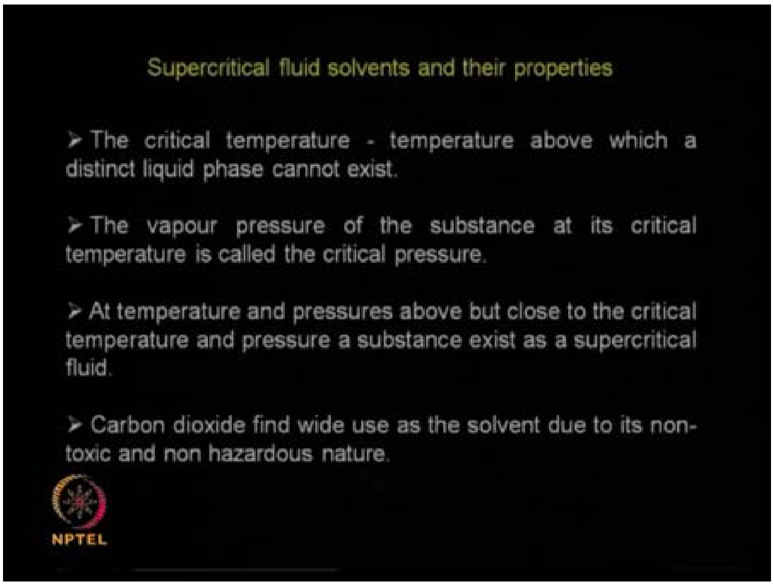

So, there are certain definitions which you need to know and the most important definition is critical temperature and critical pressure. So, what is a critical temperature, the temperature above which liquid cannot exist that is called a critical temperature, so the vapor pressure of the substance that is critical temperature is called critical pressure. So, at these temperature and pressures; that means, at critical temperature and pressure, you will have a substance and that exist as super critical fluid.

Why carbon dioxide is used, as I said it is got a good reasonably, good super critical temperature and pressure number 1 and 2, and it is nontoxic and it is not flammable it is also nonhazardous. So, that is why carbon dioxide is become extremely popular, and another advantage is as soon as you reduce the pressure, the super critical carbon dioxide will immediately go into gas, leaving behind your metabolite or aroma or whatever solute you are trying to extract. So, that is the main advantage then again you can pressurize the carbon dioxide and convert it into a super critical fluid.

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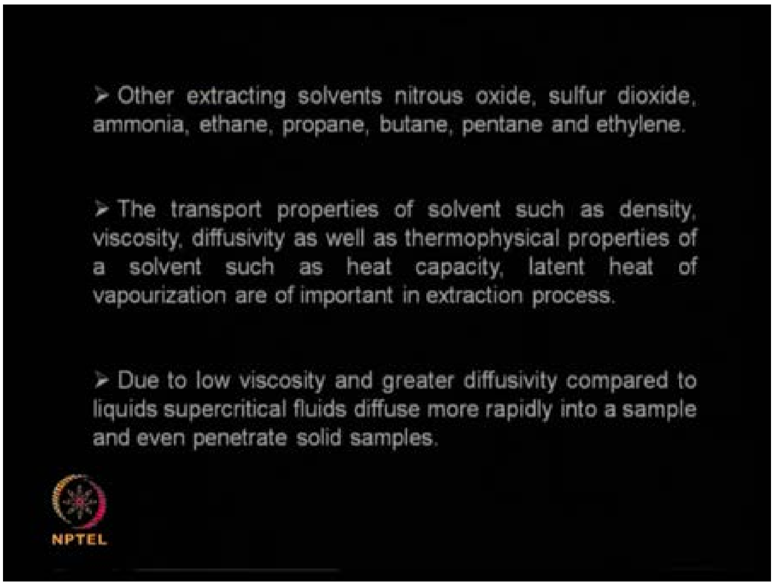

Sometimes other solvents are also used for super critical process, like nitrous oxide, sulfur dioxide, ammonia, ethane, propane, butane, pentane and ethylene and, so on. So, the transport properties of solvent such as density, viscosity, diffusivity, thermo physical properties heat like heat capacity, latent heat of vaporization all these are very, very important in an extraction process. And the super critical fluid will have a less viscosity, if you compare it with respect to a normal liquid, super critical fluid will have less viscosity.

And it will also have very good diffusivity; that means, this super critical fluid can diffuse in to materials, very small pores and extract. So, if I have a solid, a natural product and I want to extract the flavor of fragrance from that, then it can penetrate through small pores. And then extract the flavor of fragrance, and also because, it is got low viscosity, the flow properties are also extremely good when compared to a normal liquid.

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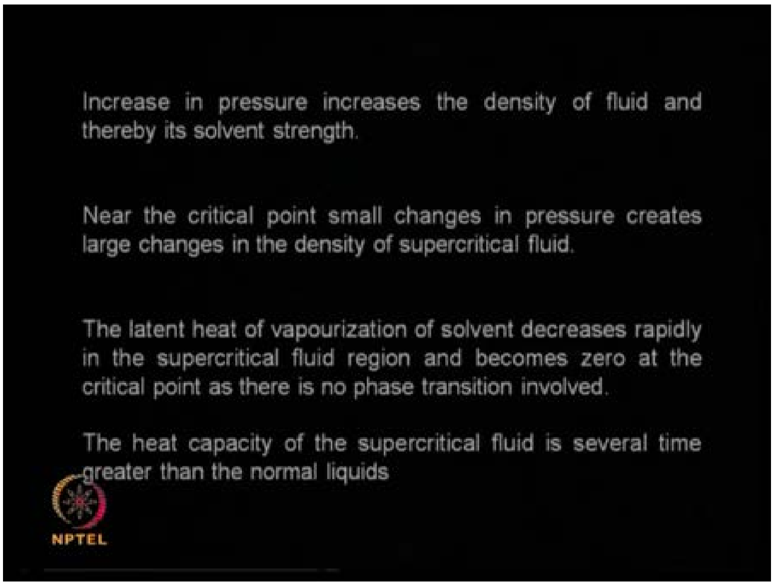

So, increase in pressure increases density of fluid and thereby the solvent strength also, so especially near the super critical point. That means, it is called the critical point even when you change the pressure little bit, you see large changes in the density of the super critical fluid. And also the latent heat of vaporization of solvent, decreases for a super critical fluid, and almost becomes 0 at the critical point. Because, there is no phase transition; that means, it is not going to become move from one phase to another that is why the latent heat of vaporization becomes 0. And also the heat capacity of the super critical fluid will be several times greater than the normal liquids.

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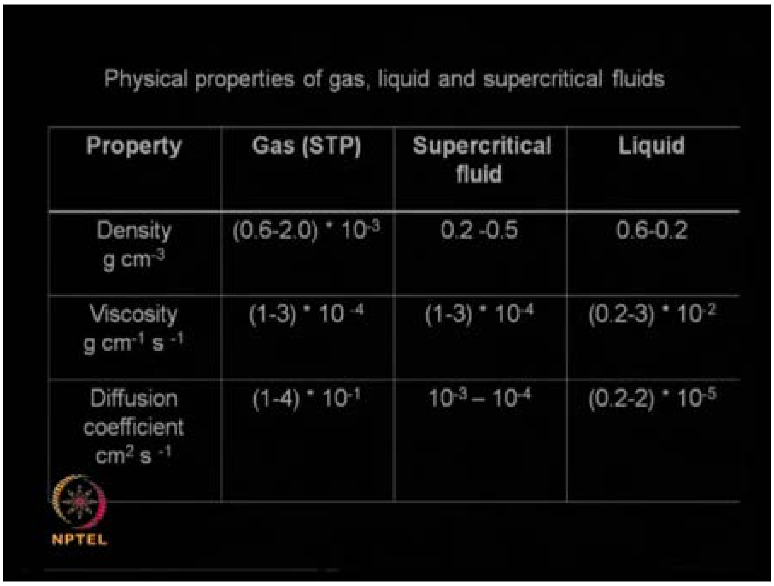

Physical properties of gas, liquid and supercritical fluids

Property	Gas (STP)	Supercritical fluid	Liquid
Density g cm^{-3}	(0.6-2.0) * 10^{-3}	0.2 -0.5	0.6-0.2
Viscosity g cm^{-1} s^{-1}	(1-3) * 10^{-4}	(1-3) * 10^{-4}	(0.2-3) * 10^{-2}
Diffusion coefficient cm^2 s^{-1}	(1-4) * 10^{-1}	10^{-3} – 10^{-4}	(0.2-2) * 10^{-5}

If you look at a physical properties of gas liquid and super critical fluids, so as I said super critical fluids fall between gas and the liquid and, so it gets the advantages of gas, it gets the advantages of liquid. At the same time it discards the disadvantages of both these, if you look at density for example, in grams per CC, gas densities are extremely small 10 per minus 3. If you look at liquid it may come up to almost 1, but super critical will be in between that, if you look at viscosity liquid viscosities are extremely high.

So, super critical fluid viscosity is almost close to the gas, look at the diffusion coefficient. Gas a diffusion coefficient are very, very large, liquid diffusion coefficients are very, very small, super critical diffusion coefficient are in between 10 per minus 3 whereas, liquid diffusion coefficients are 10 per minus 5. So, you get almost 100 times enhancement in the diffusion coefficient of a super critical fluid. So, it is got very good viscosity comparable to gas and the diffusion coefficient is much higher than of the liquid, and the density also much higher when compared to the gas. So, you see that is it is got the good points from liquid, and good points from the gas that is why super critical fluid has become a very important technology for food industry and flavor industry.

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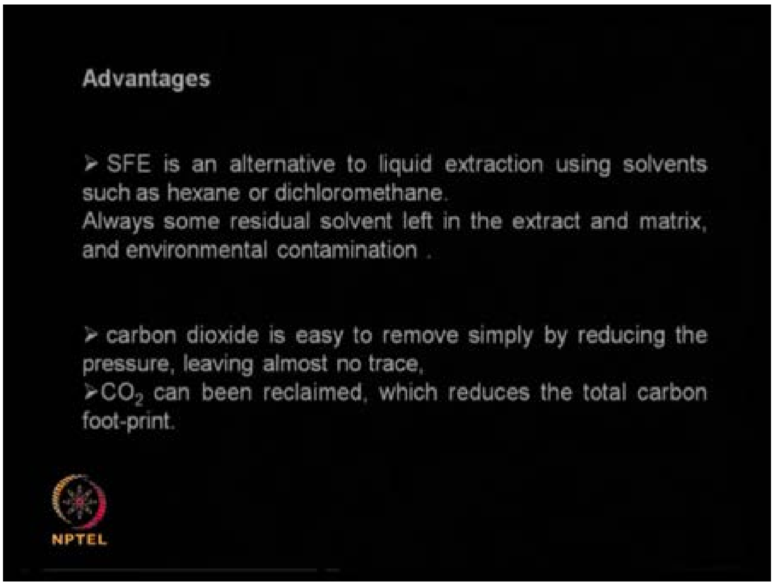

Many advantages are there, so there are other alternate liquid extraction using solvents such as hexane or dichloromethane. Because, when you use hexane that has been a traditional chemical used in food and flavors, even in natural product chemistry, but what happens is some residual solvent will be left behind, which may be very toxic. And if it is a food product, then you do not want a toxicity present in your food.

And then you are going to have environmental hazard, environmental contamination of these toxic hexanes or dichloromethane. And also you may have flash point, and explosion hazards if you are using such low boiling solvents, so that way the super critical fluid like a CO 2 is extremely good, there are it is not going to be left behind in the food or flavor, it is not going to be an environmentally contaminating chemical.

Because, CO 2 is present in plenty in our environment, and it does not have any explosion or flammable hazards. And the super critical fluid containing CO 2 is a produced from the CO 2 found in my atmosphere, so it is not also going to leave any carbon foot print that way it is not going to add to the carbon dioxide, already present in our atmosphere, so it is not going to create an extra greenhouse gas.

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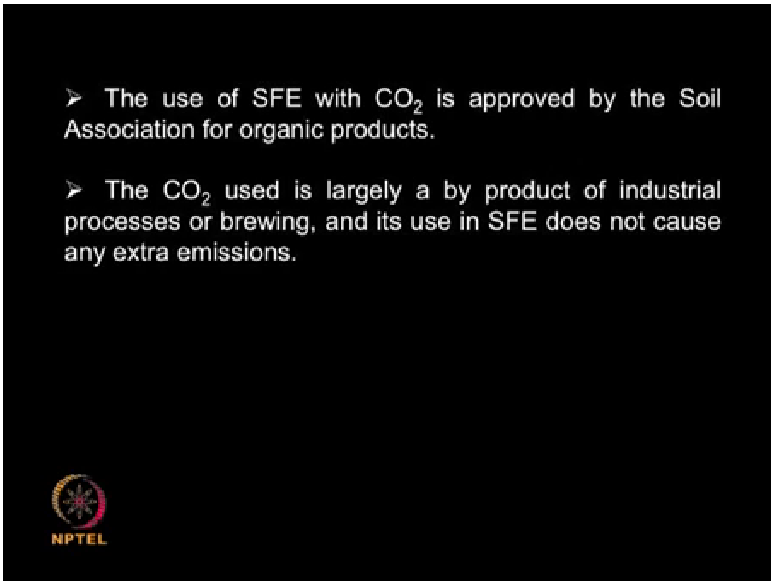

So, it is also approved by the soil association, if you want to remove organic containment’s present in soil. And also CO 2 is found in plenty, when you go to a brewing industry, fermentation industry because, when you are fermenting sugars your CO 2 is one of the bi product. So, it is not creating any extra emission, so industries where CO 2 is one of the products can be located, next to your industry which makes use of this CO 2 for producing the super critical fluid, which can be then used in the food and flavoring industry.

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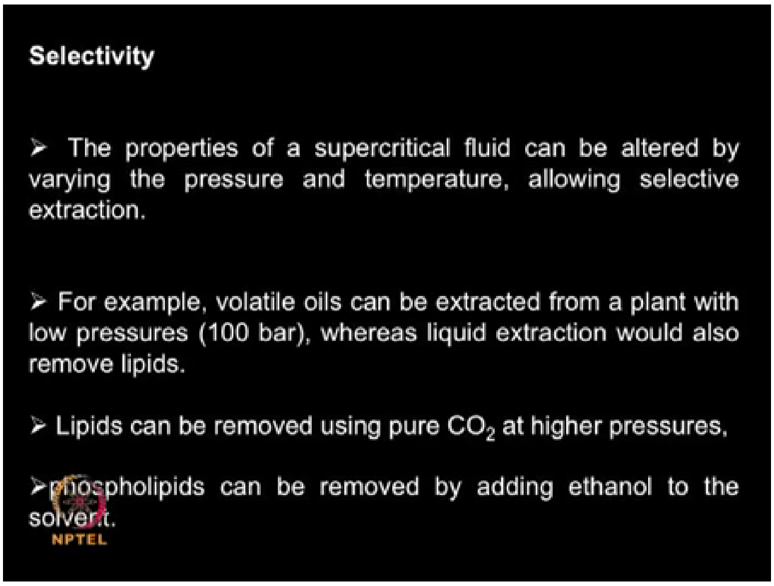

So, we can change the selectivity by changing the pressure and temperature for example, volatile oils can be extracted from a plant, at a pressure of a 100 bar whereas, if you are using a liquid like hexane, it may also remove a lipids. So, super critical fluid that way can be very selective I can use CO 2 at very high pressure to remove lipids alone, and I can remove phospholipids by just adding ethanol to the solvent. That means, you are adding entrainer to this super critical CO 2.

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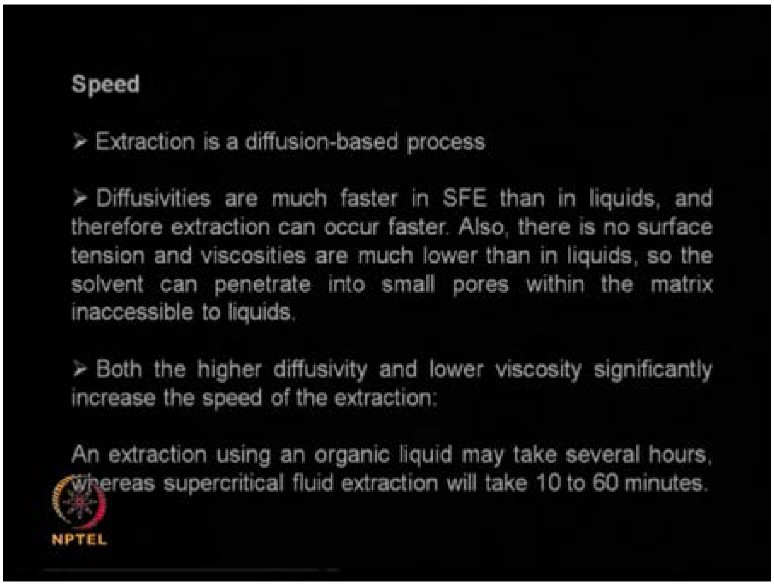

Speed, speed is very fast because, it is based on diffusion and as I showed in a few slides back, the diffusion coefficients are very high as against a diffusion coefficient of a liquid solvent. There is no surface tension and viscosities because, they are much lower than in liquids, the viscosity is much lower almost close to a gas, so it can enter very small pores, it can enter matrix and matrixes which are in accessible by liquids.

So, the speed of extraction is also very fast, if a organic liquid takes several hours to complete the extraction, if I use a super critical fluid I can do it in 10 to 60 minutes. So, we are talking in terms of an improvement in speed by a factor of 3 or 4, but there are limitations also. So, if you are going to use very high pressure; that means, your equipment also has to be very high pressure that is one of the disadvantages your capital cost of a super critical unit is high. So, you need to re cooperate the capital cost, and CO 2 is a non polar and it is got a very limited dissolving power. So, cannot be used for polar solute, polar solutes means solutes which are hydrophilic in nature.

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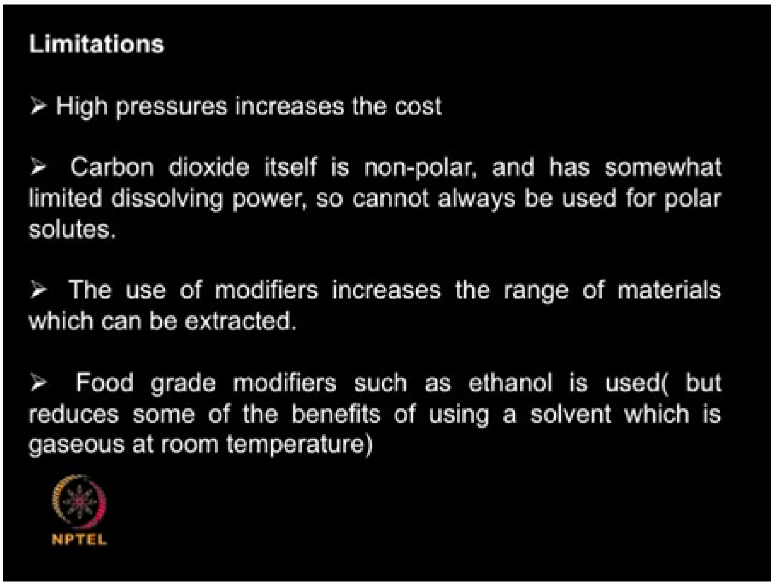

So; that means, you need to add some modifiers ethanol for example, is used as a modifier. Generally if you are using for food grade, then ethanol is the only solvent that is allowed actually, but then if you are going to use ethanol at room temperature ethanol will be in the liquid form not like a vapor. So, if I bring the after the extraction, if I bring the gases to room temperature and pressure CO 2 will become vapor, but ethanol will be left behind. So, that is a disadvantage of a using entrainer, but then if you want extract polar liquids or polar solutes or polar metabolites, then we need to add entrainers. Because, CO 2 is a nonpolar material, this is a typical schematic diagram of a super critical extractor system.

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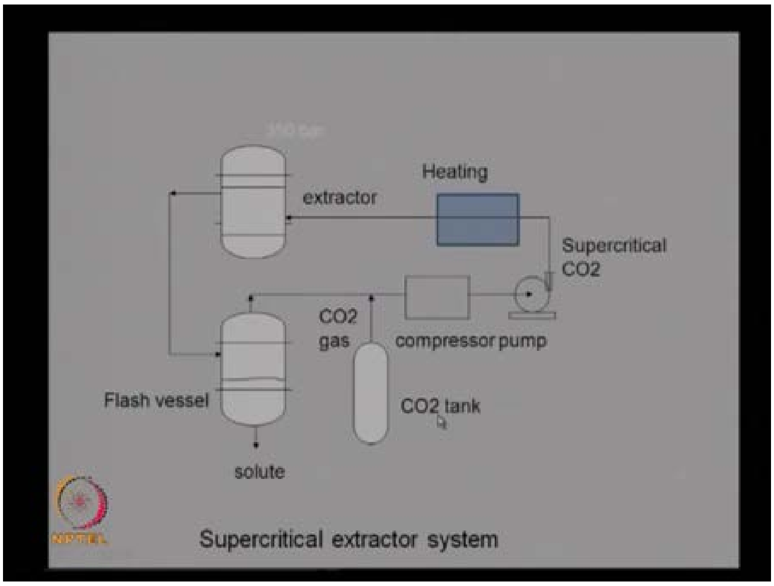

So, we may have a CO 2 tank series of large a cylinders containing CO 2, then you have a compressor, I compress the CO 2 then you pump. So, initially you have a CO 2 it becomes a super critical fluid after compression, then it is pumped you may need to heat depending upon the type of a extraction operation that is being carried out, you may heat or you might not heat. Then this is where you have you are a solids, matrix, natural product or any food material, extraction takes place, and then this is called a flash vessel.

So, the pressure is brought down to ambient condition, the CO 2 goes as gas and again it is collected back and recycled. So, the main advantage here is I can keep on recycling my CO 2 except for very minimal losses, so the solute here if it is in the form of liquid at ambient condition, will settle down as liquid which can be drained. So, it could be a flavoring or it could be a unwanted toxic chemical, which you would like to remove from your food for example, like removing caffeine or from coffer or theanine from tea those sort of toxic chemical.

So, you are talking about 350 bar, so some of the design should be able to take care of this 360 bar that is why, the capital cost of a this system becomes bit expensive. But, you do have laboratory scale equipment’s for super critical, you may have 500 ml extractor, 1 liter extractor going up to 5, 10, 100 liter extractor. So, when you talk about 100 liter extractor; that means, about 70, 80 percent of the volume could be used to fill your solid end.

So, this is a typical schematic a diagram of a super critical unit and of course, because of the high pressure, you may require extra alarms, and extra pressure relief systems and, so on, in this particular system. Optimization is a very, very important a study we need to do what should be the pressure at which I get the maximum extraction efficiency.

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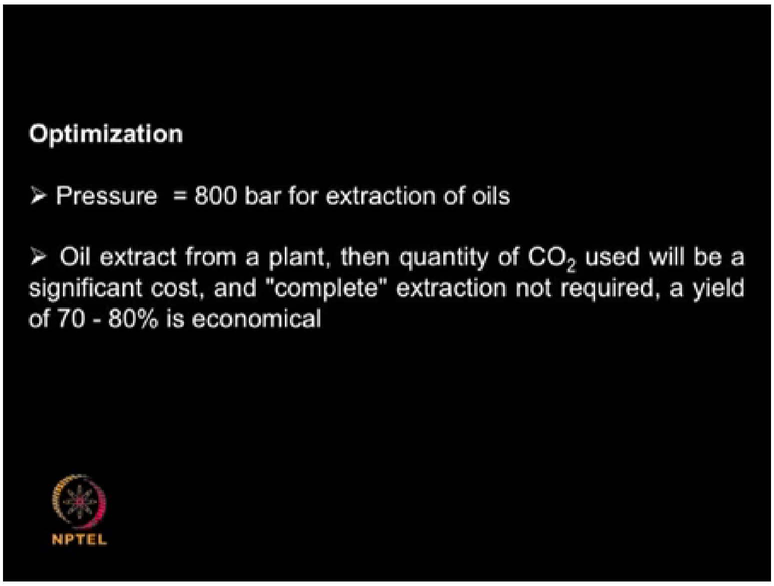

So, if you are talking about extracting oils I may go up in pressure because, if you take an oil extraction plant, then the quantity of CO 2 used will be a significant cost and complete extraction might not be required even a yield of 70 to 80 percent is economical, and the most of the cost is because, of the quantity of CO 2 that is used actually.

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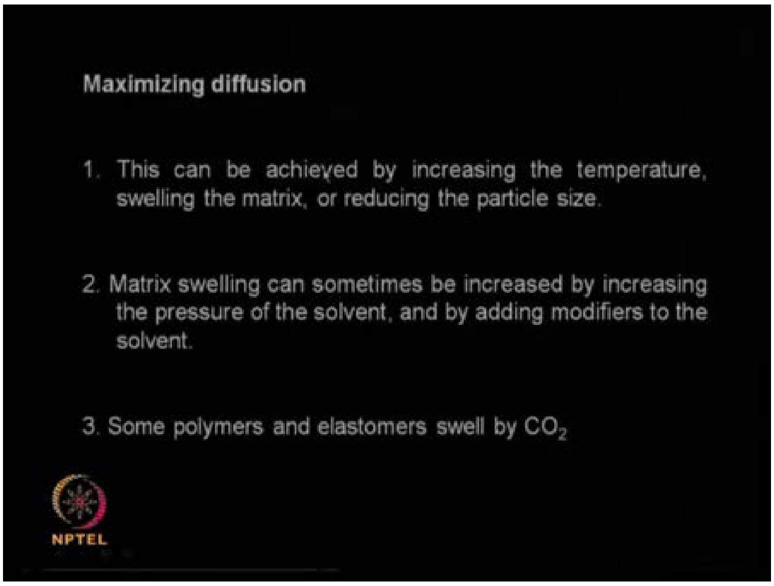

If you are talking about optimization we need to also consider the improving the diffusion. So, this can be achieved by increasing the temperature, assuming that the chemicals that are getting extracted, do not get degraded at higher temperature swelling the matrix. So, if you have a solid plant material or if you have a solid food product, by swelling it you can allow the fluid super critical fluid to enter through the interstices, small pores and, so on.

So, you like to swell the matrix reducing the particle size, smaller the particle better will be the extraction. Because, it is you are talking about a fluid solid interaction and any fluid solid interaction will be governed by the area of contact, so using smaller sized solids will always be good for extraction. So, how do you swell the matrix, so we can increase the pressure of the solvent, we can add modifiers and, so on, so that the solid matrix gets swollen. Even some polymers and elastomers can be swollen by carbon dioxide actually, so if you have polymeric material, the super critical CO 2 will swell that matrix.

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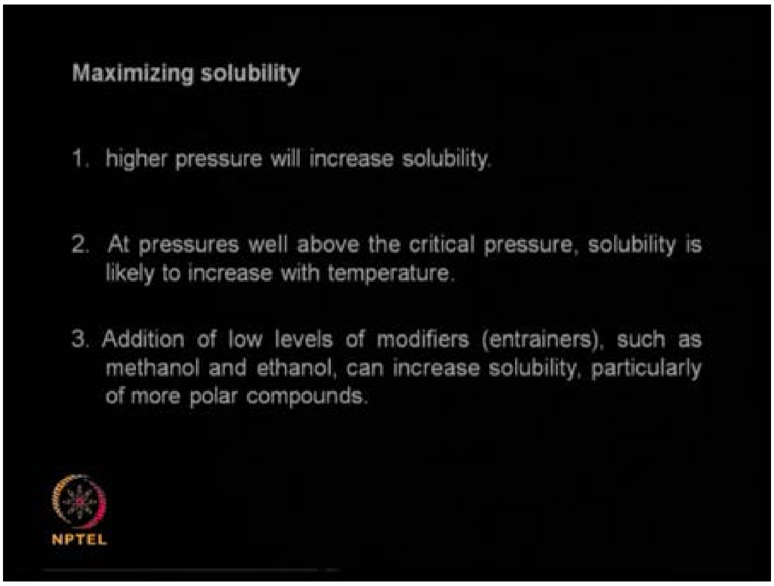

How do you maximize solubility, so we can use higher pressure when you use higher pressure solubility increases. At pressures well above critical pressures solubility is likely to increase temperature also, so if you are using very, very high pressure, than the super critical CO 2 temperature also may be very high. So, you may have to cool; that means, you need to put in an cooling system, to cool the super critical fluid.

Sometimes addition of methanol or ethanol modifiers can increase a solubility, especially for more polar compounds because, as I said CO 2 is a non polar. So, when I add little bit of methanol and ethanol, then a it is very good for polar compounds, when we talk about polar systems now a day's super critical water is also becoming very, very fancy. But, the main problem in super critical water is the pressures are extremely high when compared to CO 2; that means, the hardware design is a big challenge number 1, number 2 super critical water is also very corrosive.

So, the material of construction of the material of the equipment also becomes very critical. So, that is why super critical water although is extremely good for removing polar solutes, unlike super critical CO 2, but the pressures required are very high, the corrosion issues are also very serious. So, we need to consider those aspects when we are a designing super critical water systems actually.

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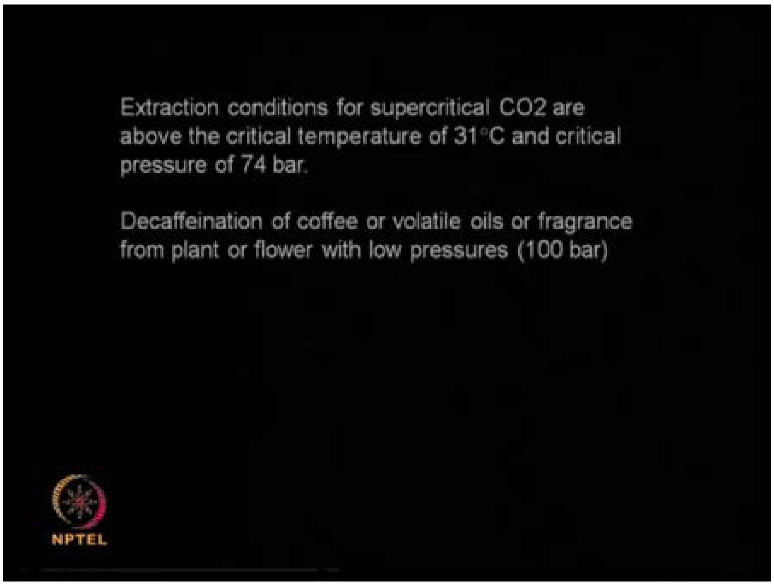

So, what are the extraction conditions for super critical CO 2 for example, I can the critical temperature is 31 degree centigrade, and critical pressure is 74. That means, if I am above this temperature, and above this pressure CO 2 will be in the form of a super critical fluid. And I can process any system, and by modifying the pressure I can improve the solubility’s, and I can modify the temperature to improve the diffusion coefficients.

As long as the solids, which you are trying to treat can agree or can allow this type of temperature and pressure. For example, if I want to decaffeinate coffee or if I want to extract volatile oils or fragrance from plant or flower 100 bar is enough 100 bar is consider as a low pressure. So, at 100 bar and ambient temperature I can remove the volatile oils and fragrance from flowers, and plant material. Because, here you do not want to increase the temperature, otherwise the fragrance will lose it is the fragrant molecules will lose their activity. Similarly I can decaffeinate coffee at such low pressures.

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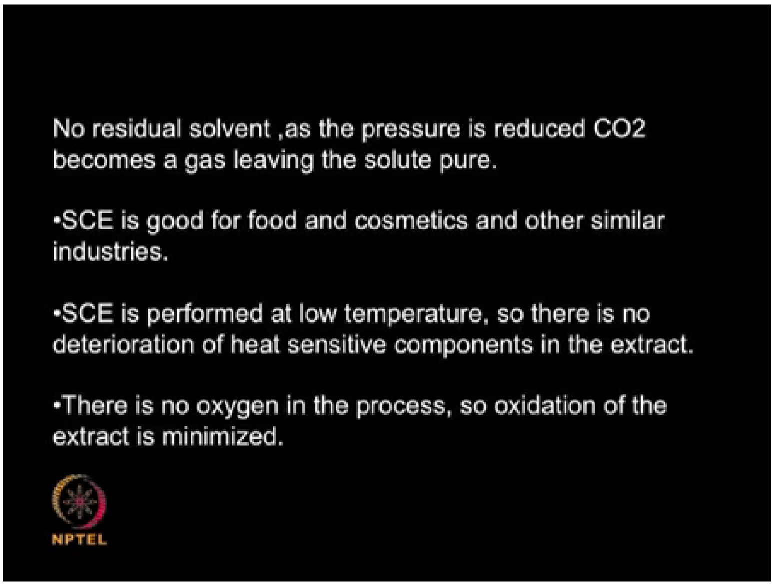

Main advantage here is I can reduce the pressure, and convert the super critical carbon dioxide into the gas. So, there is no residual solvent left behind with the solute, so the solute will be 100 percent pure, so it is good for food and cosmetic and other similar industries, cosmetic industry also love super critical. Because, in a normal cosmetic industry they use to use ethanol, pentane, ethyl acetate that sort of solvent, so you need to select solvent which are not toxic to human.

So, using super critical advantages there are no solvents left behind, so the solute will be pure. So, you are also carrying out the extraction at low temperature; that means, you are carrying it out at ambient conditions, so there is no detrition of heat sensitive components in the extract that is another main advantage. In a CO 2 system there is no oxygen coming into; that means, you are not going to have oxidation of the extract, so practically there is not going to be any oxidation happening, rancidity happens because, of oxidation formation of peroxides and, so on.

So, such things which normally are found in food products will be very absent, when I resort to super critical CO 2 type of extraction. So, there is no residual solvent left behind, you are doing it at low temperature, so thermally labile materials do not deteriorate, and there is no oxygen during the process, so there is no oxidation that is taking place, so these are the three main advantages of using a super critical CO 2. So, what are the applications, the applications of a super critical CO 2 is plenty in food and pharmaceutical industries as well, fragrance industry and cosmetic industry and, so on actually.

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So, we can use it for a decaffeinating coffee and tea; that means, toxins in coffee and tea can be removed, we can a use it for extracting fish oils, cause a fish oils is finding lot of applications in a some of the a nutraceutical type of area. So, we can use it for extracting it, we can use it for extracting vegetables oils from, we can use it for extracting flavors, natural resources from a plants, fruits from flowers and, so on. So, which can go into a nutraceutical industry, so it is very, very advantageous there.

Extraction of ingredients from spices and red pepper, so if one is interested in a packaged food, we need to add lot of spices and condominium. So, those type of material could be extracted using a super critical type of approach, extraction of fat from food products even a with the health consciousness, the entire population of the world would like to have food, which have low fat content. So, there super critical fluid extraction technology can be applied.

So, that the amount of fat present in the food is also much less, we can use it for fractioning polymeric materials, we can a separate out a polymers based on it is molecular weights. So, if one is interested in separating out polymeric materials more natural polymers, as well as a synthetic polymers based on molecular weight, low molecular weight content and higher molecular weight content polymeric material. Then super critical fluid extraction is a very good approach for that.

Extraction from natural products, this is one area where it is finding application especially if you are talking about drugs from natural products, drugs from phytochemicals. So, as you know most of the phytochemicals will contain in several different metabolites, may be 20 to 50 different metabolites, and separating them and a recovering the active ingredient or the most important component is a big challenge. If you use chemical methods, it may be impossible to separate out all these 20, 30 fraction and you may lose the activity because, of the higher temperature.

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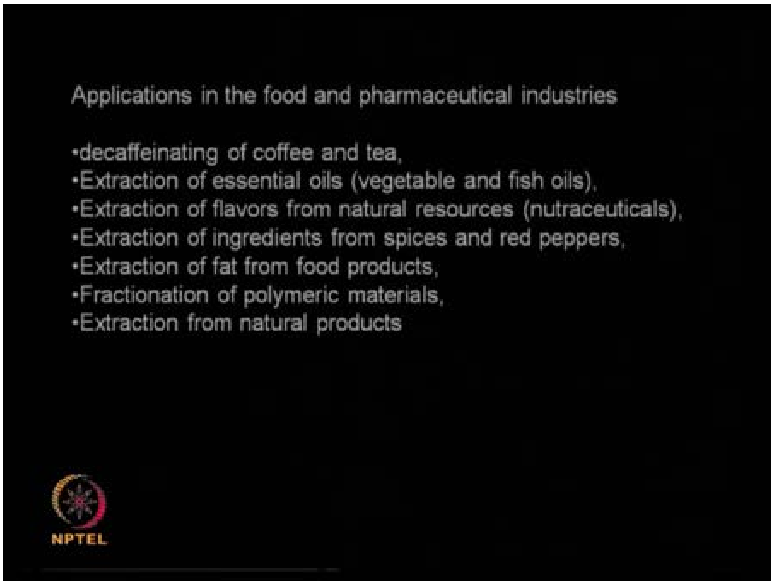

Again super critical fluid extraction technique can be used for separating out a phytochemicals, towards a drug design. Super critical fluid is also used in analytical technique, just like a normal high pressure liquid chromatograph, where you are using a mobile solvent for separating out various phases. We can use a super critical carbon dioxide to separate the metabolites present in a mixture of components. The main disadvantage or the most only point we need to consider is it is a non polar liquid.

So, it is like separation using a non polar continuous phase, so you can separate out large number of compounds using the super critical. And then by reducing the pressure we may be able to extract the complete pure component, without any solvent present in a that actually. So, that these are many advantages of a super critical fluid system, both in the food pharmaceutical, and when you talk about food, we are talking about the flavoring industry, nutraceutical industry and health care products and a health care industries.