Organic Chemical Technology
Prof. Nanda Kishore
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 13
Fermentation Industry – Ethanol

Music Welcome to the MOOCs course organic chemical technology. The title of today's lecture is fermentation industry ethanol. Before going into the details of today's lecture of ethanol production by fermentation processes what we are going to do? We are going to have a recapitulation of what we have discussed in the previous lecture on fermentation. So, fermentation actually utilizes microbiology to produce chemical compounds. In this part of process utilizing microbiology different reactions may take place like conventional oxidation, reduction, hydrolysis, esterification, etc. Those kind of reactions may also take place.

In general, what happen in the production of simple elements chemical compounds like ethanol, butanol, etc. Then such kind of easy reactions may be there. But sometimes in what happens in production of complicated or complex molecules like you know antibiotics other medicines etc. Then what happens you know the reaction mechanism could be very complicated.

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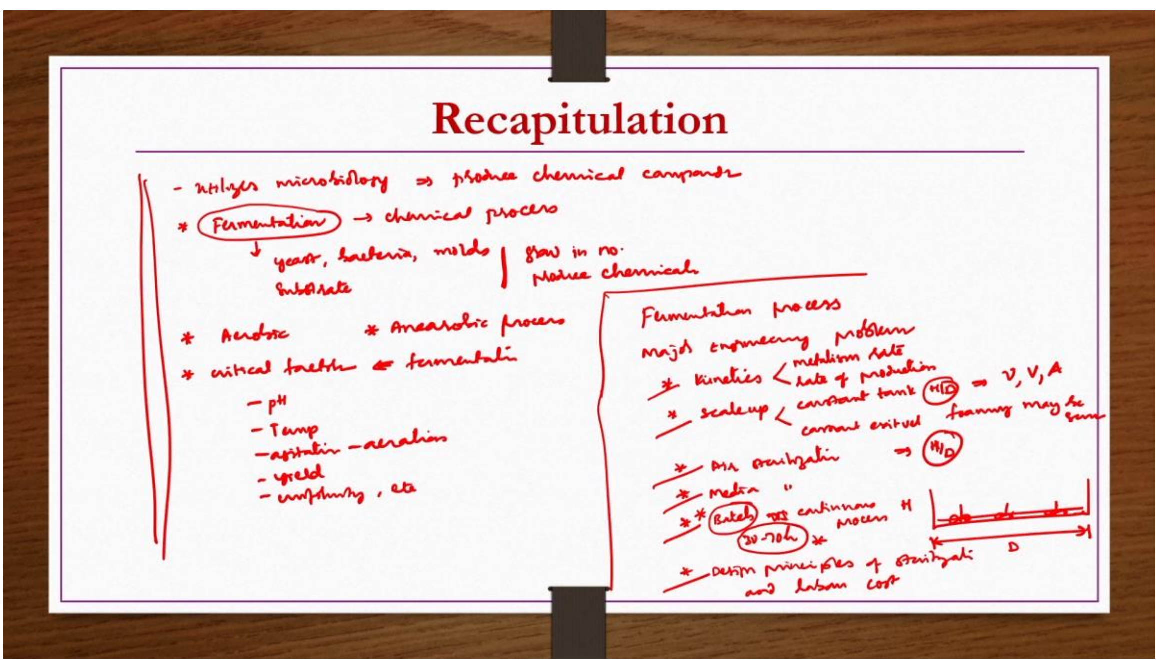

So, this fermentation process itself has been considered as a kind of a chemical process because reaction mechanism that involved in the entire fermentation process is very complex. So basically, in the fermentation what we have? We have a micro vegetative microorganism like yeast, bacteria, molds, etc. we are having. These will act on substrates. So, then what happen they will grow in number this yeast etc. and then produce some chemicals that is what it happens. So now in this fermentation process you know depending on the environment if it is done in the presence of oxygen then such processes we call aerobic process. If they are occurring in the absence of oxygen then such process we call anaerobic fermentation processes. Now in general what are the critical factors that affects the fermentation those things also we have seen. Here what we have seen something like pH, temperature, then agitation, aeration, yield and then uniformity of products etc. these kind of things are you know very essential parameters that is what we seen. Actually, all these details you know we have seen for a generalized kind of fermentation process. For any generalized fermentation process if you see major engineering problems then what you can realize that most of these parameters or most of the problems associated with fermentation processes are very common for most of the fermentation industries not only specific to one or two process but mostly common to most of the fermentation processes. That is the reason a kind of generalized engineering problems also we have discussed in the previous lecture. They include something like you know obviously whenever there is a reaction kinetics are important then scale up issues would also be there.

So which factor should be taken for the scale up etc. In the kinetics you know metabolism rates we have taken and then rate of production those things we have discussed. In the scale of issues you know what should we take as a scaling of issues we have taken like you know if you take a constant tank H by D ratio then what will happen. So, then we have taken the volumetric flow rate of air supplied per volume of the liquid and then we have taken the total volume of the tank then we have taken the escape velocity etc. And then when we consider all these parameters what we have seen that if you maintain constant H by D what will happen you know foaming may be severe and you may not able to control.

So that kind of problems may be there. So then other issue then other way if you take like let us say if you take the constant exit velocity and then try to fix this H by D then you can have then if you have you know then you know large diameter tanks with smaller H values or smaller height values tanks are preferable. But in such conditions mixing may not takes place properly. So that kind of issues may also be there. So scaling up is a kind of a compromise amongst the many parameters that are involved and then you have to make a compromise at certain point definitely. So then that compromise is based on the chemical that you are producing and then other factors associated with the plant design etc. Then other important engineering problems are sterilization in which air sterilization is very essential. Media sterilization is also very essential that is what we have seen not only air and media sterilization but also sterilization of different parts of the plant also very essential because you know this yeast etc. very sensitive to the impurities. So, if there are impurities so then you may not get the desired product and unnecessary products may take place or even the growth of the micro vegetative microorganism may also not take place properly.

Then we have also seen batch versus continuous process. Though the continuous processes are efficient in terms of providing the uniformity in the product yield etc. uniformity in the mixing etc. Batch processes are preferred because the fermentation time that is required is very high sometimes in a few days also. In general, at least 30 to 70 hours may be required. When the residence time or process time is so high then it is better to go for the batch process that is the reason though continuous process has several advantages it is better to go for the fermentation process. In fact, in the fermentation plants only this fermentation section is operated on batch mode and rest other things purification related things are operated on a continuous basis as we are going to discuss in one of the examples of ethanol production anyway. Then other engineering problem which is very common for most of the process industries fermentation industries is the design principles of a sterilization processes and labour cost also. So, these kind of engineering problems are very common to almost all fermentation industries and then when we are going to discuss about the production of ethanol and other chemicals subsequently there also we can see some of these engineering problems are going to reappear in specific to certain kind of chemicals that are being produced.

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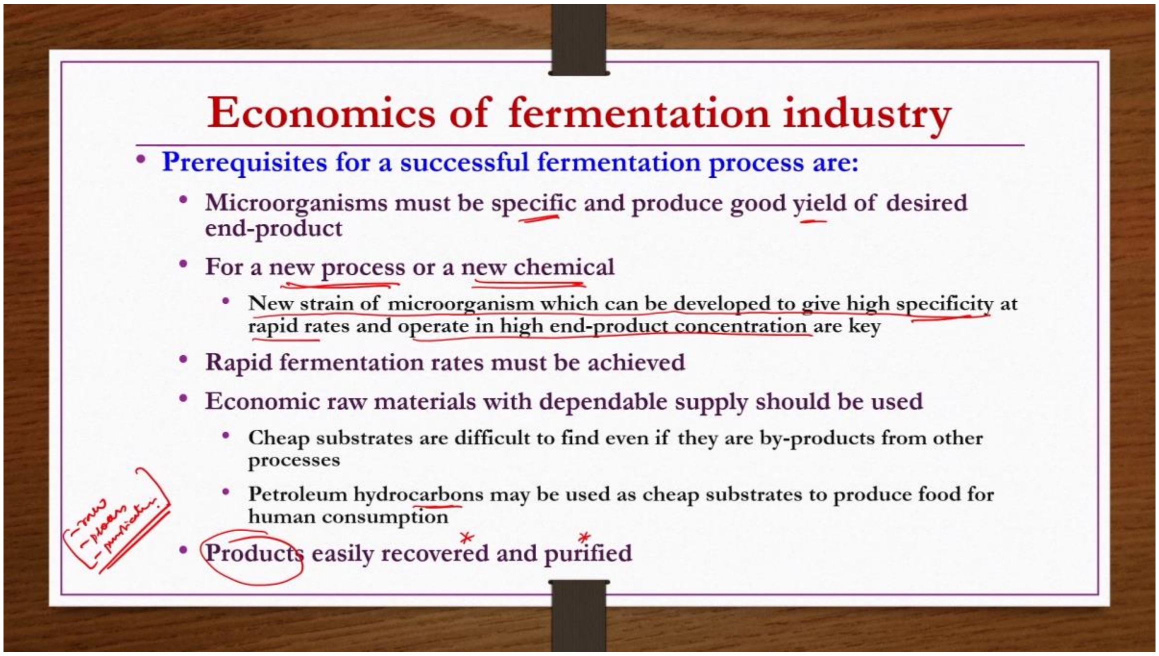

Then coming to the economics of fermentation industry rather economics what are the prerequisites of any fermentation industry so that to make the process or fermentation process economical you know one has to be careful. So some of the parameters which are very essential from the successful fermentation operation point of view are listed out here. Microorganisms must be specific to the product what product are you going to produce and then accordingly that microorganism micro vegetative microorganism must be developed and it has to be kept under very much sterile conditions. So they should produce good yield of desired end product if it is a known process then this is about known process but if you are developing some new process or new chemical you are trying to produce by fermentation process then you may also need to pay attention to some additional aspects also something like you know what new strain that you are developing that new strain of microorganism can be developed to give high specificity at rapid rates and operate in high end product concentration. These things are very essential if you are developing a new fermentation process or producing a new chemical using a fermentation process. Then fermentation processes are very slow as I mentioned sometimes they take days also if you are finishing fermentation process in few hours that is a very rapid fermentation process. If you are finishing a fermentation in 2 to 5 hours or 6 hours that means it is a very rapid fermentation process. So, you have to make sure the fermentation rates must be sufficiently rapid enough. In some processes at least 30 to 40 hours or 50 hours are required for the fermentation. Example that ethanol that production that we are going to discuss today that at least 30 to 70 hours required for the fermentation to complete so that to get the desired product. So, but process either process or the microorganism you have to specifically develop such a way that the rapid fermentation should take place. And then also raw materials economic raw materials are required. So, because the fermentation process itself is slow process and then if the yield is also low let us say unfortunately for a given process and then raw material is also expensive then that process cannot be economically feasible. So sometimes even getting this economic raw material also very difficult even if those raw materials are byproduct from other processes. Let us say molasses etc you get from the sugar industry while producing the sugar from the sugar industry you get the molasses. But sometimes what happens such kind of you know substrates or raw materials may not be available at economic cost.

So, one has to be clear about such kind of raw material also. But however nowadays petroleum hydrocarbons may be used as a economic substrate to produce food for human consumption and then most important thing is that the product whatever formed by the fermentation process that should be easily recoverable and then that should be purified easily. So, whatever the aspects of the raw materials and then process chemical process and then purification steps which are very essential for any of the chemical industry those are also true here in the fermentation industry. In fact, fermentation industry is also a natural product chemical industry.

Now we discuss about the production of specific chemicals. In India ethanol or ethyl alcohol and penicillin are more economic if they are produced by fermentation process. So, we start with ethyl alcohol in today's lecture. Let us start with the pertinent properties of ethanol. Molecular weight is 46.07, density is 0.791820 degrees centigrade, melting point is minus 112 degrees centigrade, boiling point is 78.3 degrees centigrade, flash point is 21 degrees centigrade whereas the ignition temperature is 372 degrees centigrade. It is also explosive lower limits of ethanol in explosives is 3.5 percent by volume whereas upper limit is 19 percent by volume.

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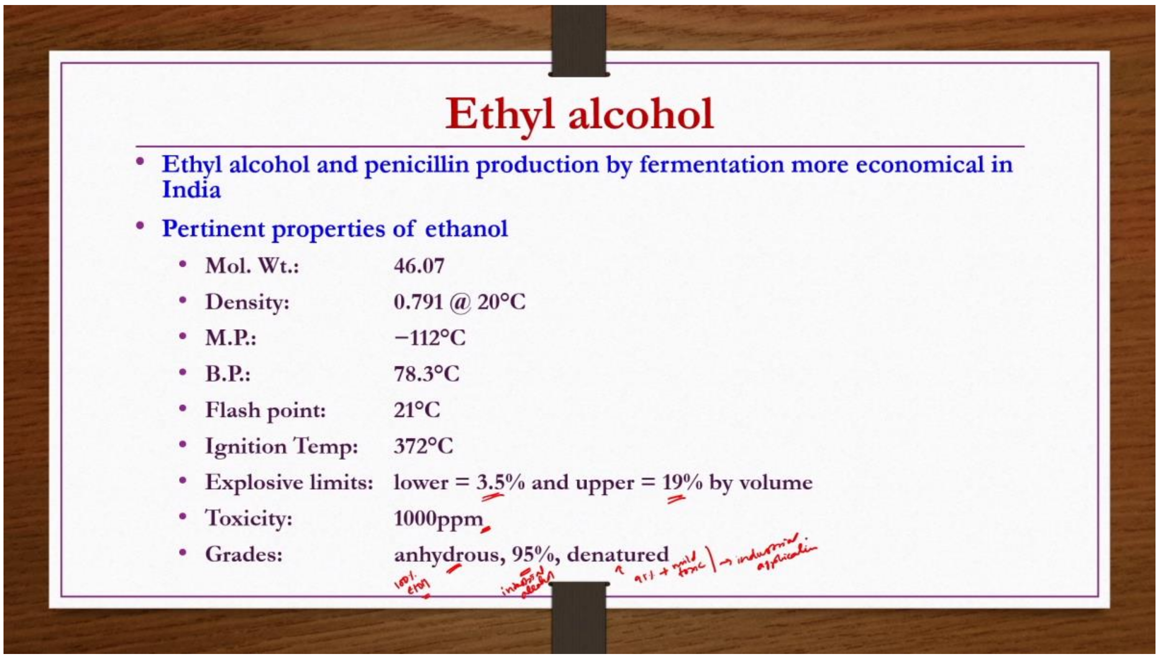

If it is present in more than 1000 ppm it should be regarded as toxic. It should not be more than 1000 ppm in the environment if at all nearby the ethanol plants also it should not be more than that in the environment. According to the grades, anhydrous or absolute alcohol where 100 percent ethanol is there that is one grade and then 95 percent alcohol which is also known as the industrial alcohol in general and then denatured alcohol where whatever this 95 percent ethanol is there in that one you can add some mild toxic components and then use for industrial applications. So denatured alcohol is in general used for the industrial applications.

Ethyl alcohol primarily when it was investigated it was found to be very much useful if it is blended with the petroleum products like gasoline etc. so that to use in transportation vehicles etc. That was primarily the major important role of ethanol compared to the other applications. But however, petroleum petrochemical refineries have taken a boost after 1940s or something like that then use of ethyl alcohol as blend in petroleum products is almost disappeared virtually disappeared. But however, ethyl alcohol is having n number of applications some of them are shown here. It is used as intermediate for a number of other chemical products such as synthetic rubber. It is also used as solvent for polyethylene production it is used. Portable spirits production it is used. For plastics production also, it is used.

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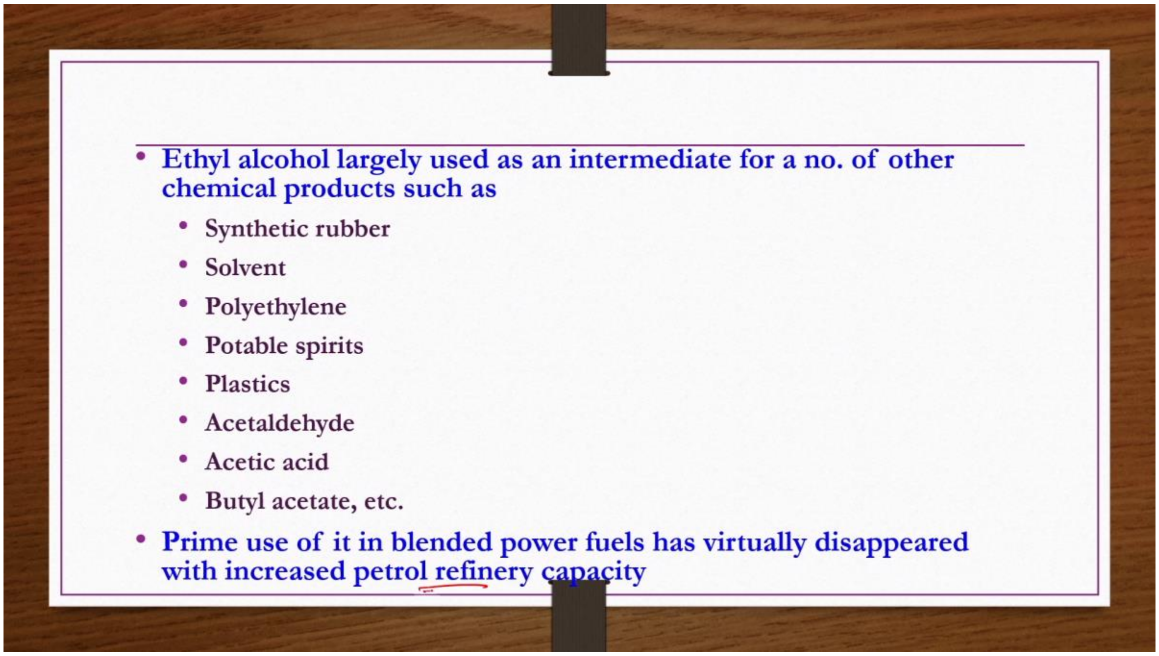

Acetaldehyde production also it is used. Acetic acid production, butyl acetate production etc. so many things are there. Some use of it in blended power fuels has virtually disappeared with increased petroleum refinery capacity.

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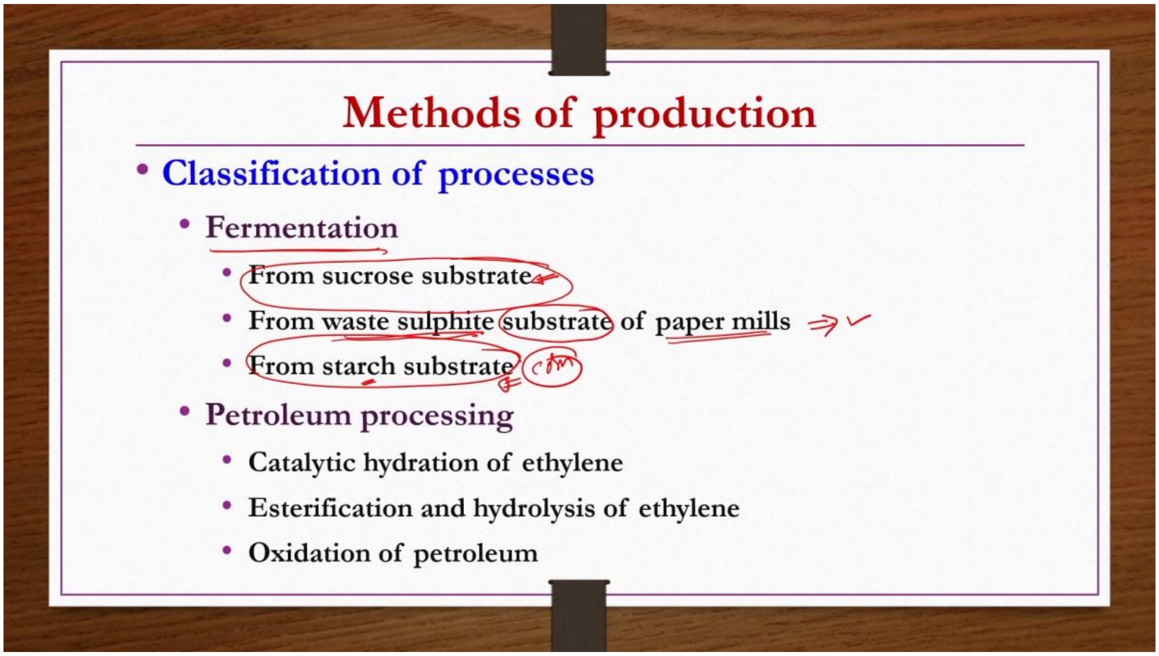

Coming to the methods of production this ethanol can be produced either by the fermentation process or by the synthetic process as well or by both processes. Depends on the economics one has to choose the process. Let us say under the fermentation processes we have ethanol production from sucrose substrate like molasses whatever you get from the sucrose sugar production plants that you can use as substrate and then do the fermentation to get the ethyl alcohol. In the subsequent chapter we are going to discuss about the pulp and paper industries. There also we have something like waste sulfite which is like containing lot of water along with the some waste sulfite cellulose etc. would also be there. So that can also be used as a substrate to produce ethanol and then in previous chapter we have discussed about the production of different types of alcohols and then oils etc. from the starch and then also sugars starch derivatives etc. we have seen. So, there we have seen that you know it is also possible to produce different type of alcohols there also ethanol can be produced using starch substrate. Now going to the petroleum processing catalytic hydration of ethylene is one process esterification and hydrolysis of ethylene is another process and oxidation of petroleum is another process. So, this chapter is primarily on fermentation. So what we are going to discuss we are going to discuss how to produce ethanol from the sucrose substrate like molasses etc. We are also going to discuss how to produce ethanol from the corn because corn is also used to produce starch that we have seen. Whereas production of ethanol from waste sulfite substrate of paper mills probably we will be discussing in the next chapter when we discuss about pulp and paper industries.

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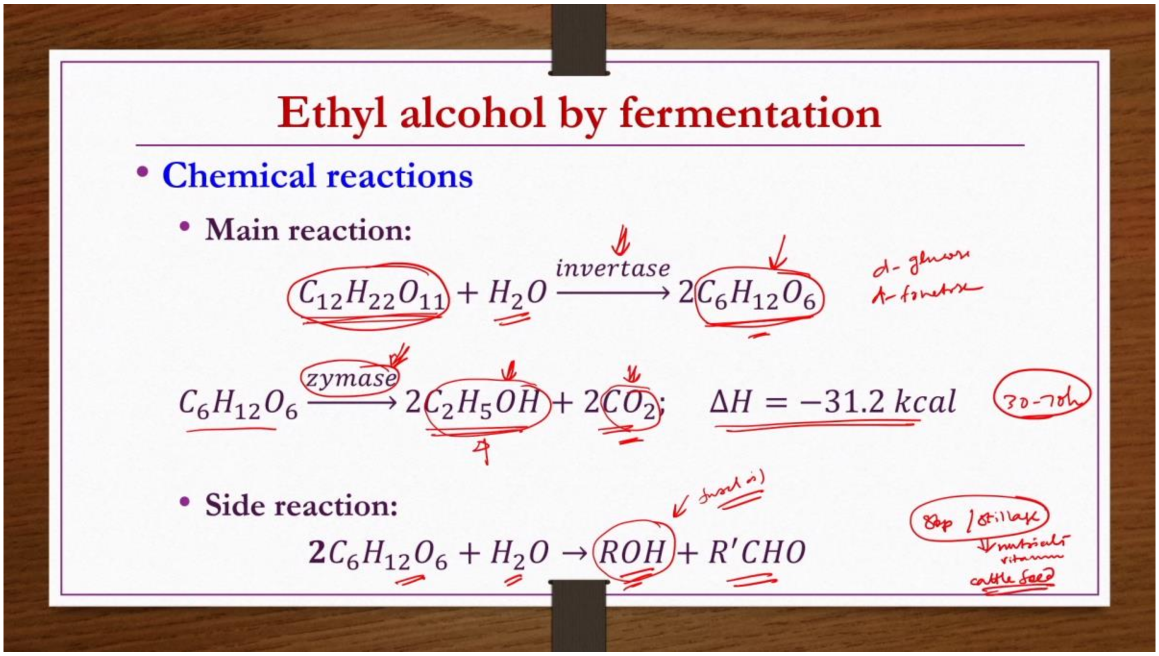

So, let us talk about ethyl alcohol production by fermentation. Chemical reactions now here what we are taking we are taking molasses as a you know a substrate. So that is actually containing sucrose. So that sucrose is nothing but C12H22O11. We have seen in the sugar and starch industries if this sucrose content that whatever present in the sugarcane if it is not properly processed it may be hydrated and then inversion reaction may take place to give d glucose and then d fructose. Both of them are having chemical formula C6H12O6. So, there we have written separately now we are writing 2 C6H12O6 that is the only difference. Because our primary you know we look at this one because this whatever the C6H12O6 is there that would be further reacting by using the zymase enzyme catalyst to produce ethanol and then carbon dioxide. So basically, process is what you are taking the substrate which is having this content and then we are adding water and then required enzymes or micro vegetative microorganisms we are adding and then we are allowing the reaction to take place. So that in that process this is taking place C6H12O6 and then further by this enzyme what is happening this is being converted into the ethanol and then carbon dioxide. So after the fermentation process of 30 to 70 hours what you have when you mix this one with the yeast you will get ethyl alcohol and then carbon dioxide. So now here what you can see this reaction is exothermic so that means during the process of fermentation temperature may increase. So, you might be requiring cooling facilities as well because fermentation does not occur if the temperatures goes beyond 35, 40 degrees centigrade in general for most of the cases. In this case there is a possibility of side reaction also where this C6H12O6 may be reacting with water to give high molecular weight alcohols and then aldehydes. So now it is unavoidable the side reaction is unavoidable in fermentation process. So, you are not only getting this ethanol but also you are getting carbon dioxide as one product so you can recover it and then also you are getting high molecular weight alcohols which you can collect as fusel oils. So, there is a byproduct also along with the main product here one is the CO2 another one is the high molecular weight alcohols and then slopes are stillage two terms are used that is another raw material which is rich in the nutrients and then some kind of vitamins etcetera proteins etcetera. So, this can be evaporated or purified to get a material which is suitable for cattle feed. So that can also be taken as a third product depending on the economics of the plant.

Quantitative requirements here 1 ton of 100 percent alcohol actually producing 95.6 percent or less than 95.6 percent alcohol you may not require much of the water and other chemicals in general but if you are producing 100 percent absolute alcohol or anhydrous alcohol then so many additional quantities of steam and then water process water etcetera may be required. So, let us do the calculation for 1 ton of 100 percent alcohol with a 90 percent yield from total sugar. So, then what are the requirements of the raw materials?

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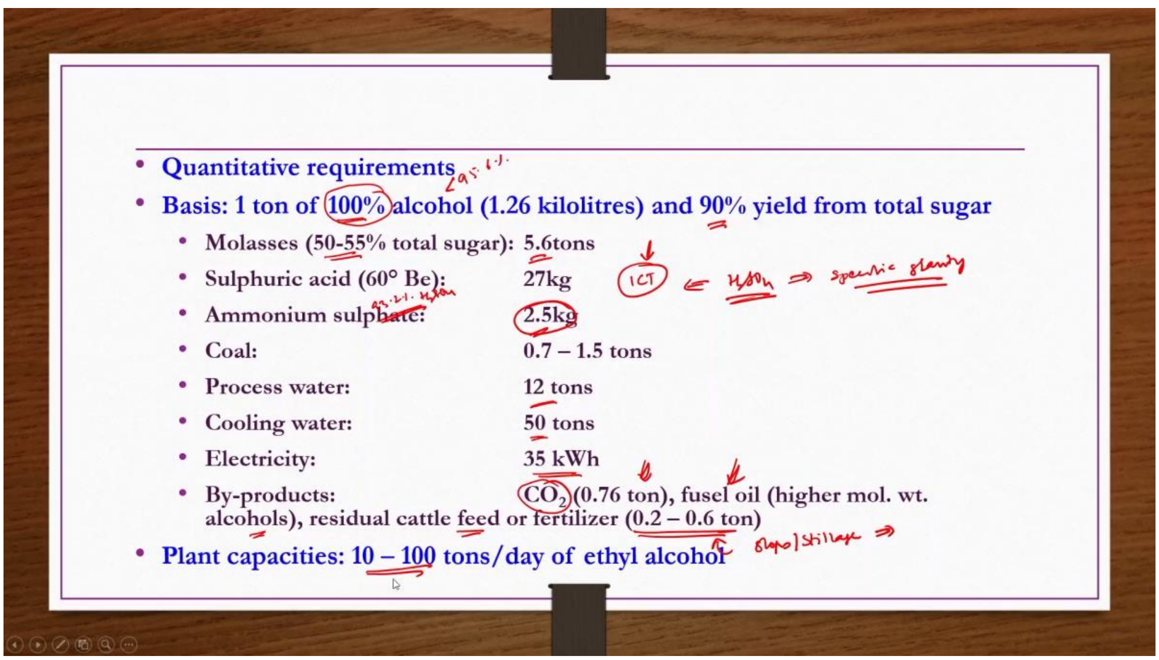

Molasses having 50 to 55 percent total sugar that is C12H22O11 whatever is there that should be 50 to 55 percent in molasses that you required 5.6 tons. Then sulfuric acid 60 Baume degrees 27 kgs this is nothing but approximately 93.2 percent of H2SO4. Actually, in the ICT course inorganic chemical technology course we have discussed about this H2SO4 production. It is acid it is very difficult to control parameters during the production. So then if you wanted to measure the concentration of the acid during the production whether it is sufficient you know whether it is having sufficient concentration or not. So, then what you do you measure the specific gravity that specific gravity measurement whatever is there that is measured into the Baume degrees and then that if it is 60 degrees that means it is known as 93.2 percent H2SO4 is there. That is what this mean by Baume degree if you are not gone through this course so then probably you can see such videos on sulfuric acid presented in the inorganic chemical technology course of NPTEL modules. Then ammonium sulfate 2.5 kgs this is required in case if you have to add some kind of nutrients to the substrate or the yeast or whatever the microorganisms that you have taken for that if it is required to provide sometimes energy food. So, then some nutrients may be required so under such condition these things may be required. Coal 0.7 to 1.5 tons, process water 12 tons, cooling water 50 tons, electricity 35 kilowatt hour, byproducts CO2 you can get up to 0.76 tons whereas the residual cattle feed or fertilizer 0.2 to 0.6 tons. This is coming from where this is coming from the slopes or stillage from the bottom of beer distillation column that we are going to see. So this if you purify then whatever things that you get that is nothing but in a fertilizer or that can be used as a cattle feed. Then fusel oil which is nothing but higher molecular weight alcohols mixture that can also be taken as a byproduct. Capacity is in general 10 to 100 tons per day of ethyl alcohol.

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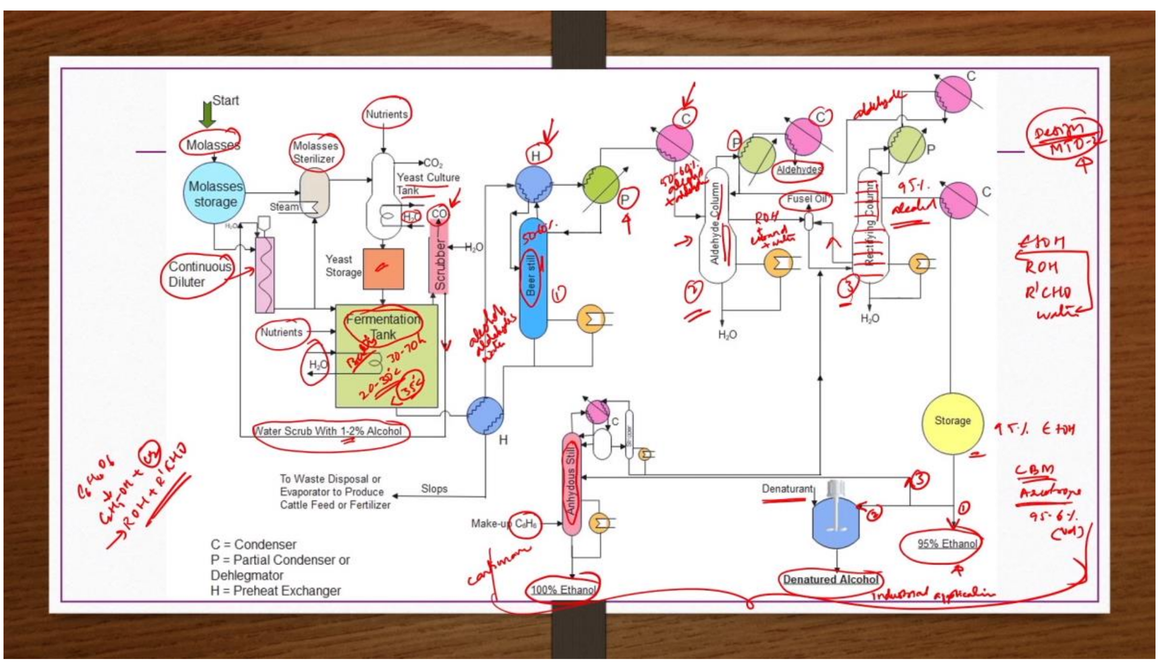

Now we see the flowchart for the ethyl alcohol production from the molasses. So here in this flowchart some symbols H, C and then P are there. H stands for the preheat exchangers, C stands for the total condense or condenser, P stands for the partial condenser which is also known as the dephlegmator. So now here what happens the molasses that you have taken that you take to the molasses storage then you dilute it in a continuous diluter. In a continuous diluter you dilute this molasses using the water or water scrub with 1 to 2 percent alcohol that is coming from this scrubber section. Why this dilution is required when you do the dilution of this molasses then when it interacts with the yeast in the fermentation tanks it will help the growth of a yeast that is the reason the dilution is required. Now this diluted molasses whatever is there that you take to the fermentation tank along with the nutrients etc. if required. Whereas separately what you have, you have the yeast culture tank in which you take the yeast and into this also you can add the nutrients if required. Sometimes what happens the whatever the molasses is there that would be sterilized by molasses sterilizer and then that sterilized molasses is also added to the yeast tank. The purpose is again is to maintain the sterilized conditions in the yeast culture as well as the allowing the molasses will improve the growth of the yeast etc. that is the for that is also one purpose but it should be this molasses should be sterilized one. So that yeast you take to the yeast storage tank. So, if you are adding because sterilization of the media as well as the air etc. required as a common engineering problem of fermentation industry that is what we have seen. So here if you are doing sterilization so then some kind of heat may be evolving so that heat has to be removed by the water. So that yeast you can take to the storage. Now this yeast and then whatever the diluted molasses along with the nutrients may be taken to the fermentation tank. So, some of the diluted molasses may also be taken to the molasses sterilizer. It can be directly molasses can be taken or diluted molasses can be taken to the molasses sterilizer for the sterilization purpose as per the requirement. It depends how much sterilization is required for the given process. So now here in the fermentation tank the reaction takes place for about 30 to 70 hours. So, the temperature should be maintained between 20 to 30 degrees centigrade for that cooling is required. At the end of the reaction may be around after 60 hours or 65 hours temperature may even go up to 35 degrees centigrade also but it should not be allowed to go beyond 35 degrees centigrade otherwise fermentation may not take place. So, when the fermentation is taking place in the reaction we have seen that $C_6H_{12}O_6$ is giving what C_2H_5OH ethanol and then CO_2. When side reaction is occurring so some kind of alcohols and then aldehydes also forming that is what we have seen by the side reaction. So other than gases all of them are in the liquid states. So, the gases are primarily CO_2 that CO_2 may also be containing some amount of ethyl alcohol which is volatile compared to the other components that are present in the liquid. So that CO_2 has to be scrubbed before leaving out and then collected as a product if it is required and then if it is useful from the economics point of view. So, when you pass this CO_2 through water scrubbers so the water whatever is there that will be absorbing the alcohol and then that water scrub whatever is there that would be having CO_2, CO_2 percent of ethanol that is used for a diluting the molasses. Whereas the liquid that is there in the fermentation tank after the completion of the fermentation that would be passed through a preheat exchanger and then after passing another preheat exchanger that will be taken to the beer still because it is primarily having alcohols, aldehydes and then water only now. So now here in this beer still the concentration of the beer would be increased to 50 to 60 percent and then that would be taken to the aldehyde section. Before going to the aldehyde section that would be passed through a partial condenser. Partial condenser purpose of this partial condenser is that it will condense the vapors only to the little bit only or only some amount of vapors would be condensed and then whatever the condensed vapors are there they will be fed back to the distillation column. We are writing still but they are all distillation columns, column or steel whatever written here all of them are distillation column. So, by refluxing or supplying back that partially condensed liquid to the steel or the distillation column the concentration of alcohol will increase, will grow that is the purpose of this partial condensation. So once the concentration reaches up to 50 to 60 percent then you do the total condensation. So then that product you take to the aldehyde column. Here what you have primarily you have 50 to 60 percent alcohol plus aldehydes would be there. So, this mixture would be taken to the aldehyde and then here again the same distillation process would be done. So, aldehydes would be the more volatile here. So, they will be evaporating more or they would be present more in the top product. That top product again passed through a partial condenser and then whatever partially condensed vapors are there they will be fed back to the column so that to improve the concentration of aldehyde and then once the aldehyde concentration reaches maximum in the aldehyde column they would be condensed in a total condenser and then collected as a aldehyde products.

Whereas from the side stream of the aldehyde column whatever the higher alcohols and then ethanol etc. are there they would be collected of course there would be some water also. So, they will be collected and then passed through a separator where higher alcohols would be separated and then ethanol water would be taken to the rectifying column section. So here in the rectifying column section if at all some traces of higher alcohols or higher molecular weight alcohols are there they will be collected from the bottom of the rectifying column and then sent to the separator where the fusel oils are separated and collected as a product. So, from the top what you get you primarily get you know 95 percent pure alcohol remaining 5 percent water would be there that you take to this storage. So in this process of getting this 95 percent alcohol if at all some aldehydes are also there they will be collected from the top whereas this alcohol you are collecting from the side stream. From the top whatever you are getting those would be partially condensed and then reflexed and then after the concentration becomes sufficiently higher then they will be sent to a total condenser and then that will be sent back to the aldehyde because these are primarily having aldehydes in pure aldehydes they are present in the mixture of you know alcohol higher molecular weight alcohols and water. Now what you can see here in all these 3 columns 1, 2, 3 columns all of these 3 columns all 3 things are there not only ethanol high molecular weight alcohols and then aldehydes and then water would also be there. But the percentages point of view most of the aldehyde is removed in the second one and then most of the higher molecular weights are removed in the separator and then rectified sections like that. After that only primarily ethanol and then water would be there they will be taken to the storage this will be having only 95 percent ethanol because beyond this one you know you cannot separate because of a constant boiling mixture or azeotrope formation takes place when the ethanol concentration is around 95.6 percent by volume and then remaining is water by volume. When the constant boiling mixture or azeotrope forms the separation is not possible conventionally separate routes are there that we are going to do. So that is the reason the distillation stops or the top product is collected at 95 percent alcohol. All these columns are distillation column different trays are there actually you know so the feeding to which tray the feed has to come to which tray the reflex has to come from which tray the side stream has to be collected all these engineering calculations or design calculations are part of you know other course like you know mass transfer operations too. Usually mass transfer operation course is divided in two parts in the second part you discuss on this distillation. So, we are not going into those parts. Now this 95 percent ethanol whatever is there you can use three ways directly you can use and then sell it as per the government norms and then other option is that you can add some mild toxic components as denaturants and then you get denatured alcohol for industrial applications.

Other option is that see now three options are there one option two option and then this is the third option one two three option. Third option is that you take it to the anhydrous still or azeotropic distillation that we are going to discuss separately where you are using makeup benzene and then try to get 100 percent ethanol separated out. So, this is also we are going to discuss separately in the subsequent part of the today's lecture anyway. So, this is what happens in general in ethyl alcohol production from the molasses by fermentation process.

Now in this process what are the things that you have to see only the fermentation is operating in the batch mode. After that whatever this separation purification steps are there all these steps are you know continuous operating in continuous mode. Whereas this fermentation is alone operating in a batch mode because residence time is 30 to 70 hours.

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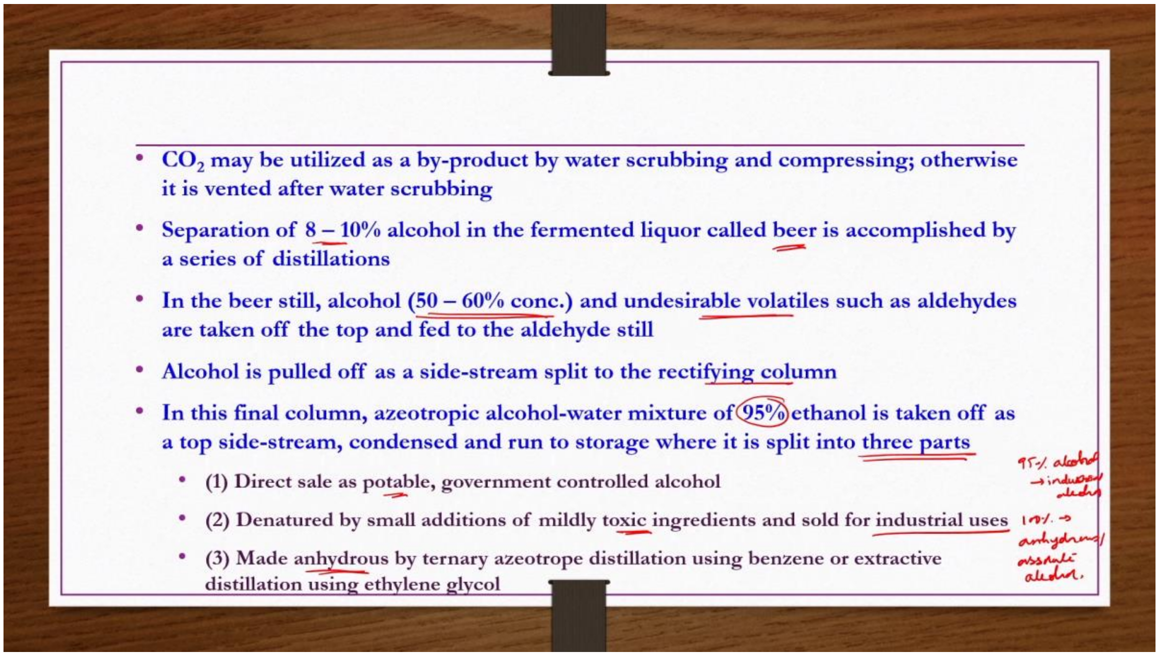

Now whatever we discussed in the flow chart all that information is provided as a text here from the learning point of view. Molasses is diluted to 10 to 15 percent sugar concentration and adjusted to pH of 4 to 5. So, this can be done by the addition of H2SO4 or by addition of slopes or stillage. This dilution support yeast growth which furnishes invertase, zymase, catalytic enzymatic reaction that we have seen. If molasses lacking nutrients then ammonium and magnesium, sulfate or phosphate are added as nutrients that depends on the requirements. This diluted mixture is called as mash and is run into large wood and steel fermentation tanks. Yeast solution is grown by inoculating sterile mash. This yeast solution is added and fermentation ensues with evaluation of heat which is removed by cooling coils. Temperature maintained at 20 to 30 degrees centigrade over 30 to 70 hours period rising to 35 degrees centigrade near the end of the reaction period. CO2 may be utilized as a byproduct by water scrubbing and compressing otherwise it is vented after water scrubbing. Separation of 8 to 10 percent alcohol in the fermented liquor called beer is accomplished by a series of distillations. In the beer distillation alcohol concentration 50 to 60 percent increased and undesirable volatiles such as aldehydes are taken off the top and fed to the aldehyde steel. Alcohol is pulled off as a side stream split to the rectifying column, third column. In this final column azeotropic alcohol water mixture of 95 percent ethanol is taken off as a top side stream condensed and run to storage where it is split into 3 parts as per the requirements. First part is direct sale as portable government-controlled alcohol. Second is denatured by small additions of mildly toxic ingredients and sold for the industrial applications. Third one is made anhydrous or absolute alcohol by ternary azeotrope distillation using benzene or extractive distillation using ethylene glycol. So here actually some terminologies are there, you know whatever the 95 to 95.6 percent alcohol is there that is known as the industrial alcohol in general. Whatever 100 percent alcohol is there that is known as the anhydrous or absolute alcohol. Some different terminologies are used based on the percentages that is it.

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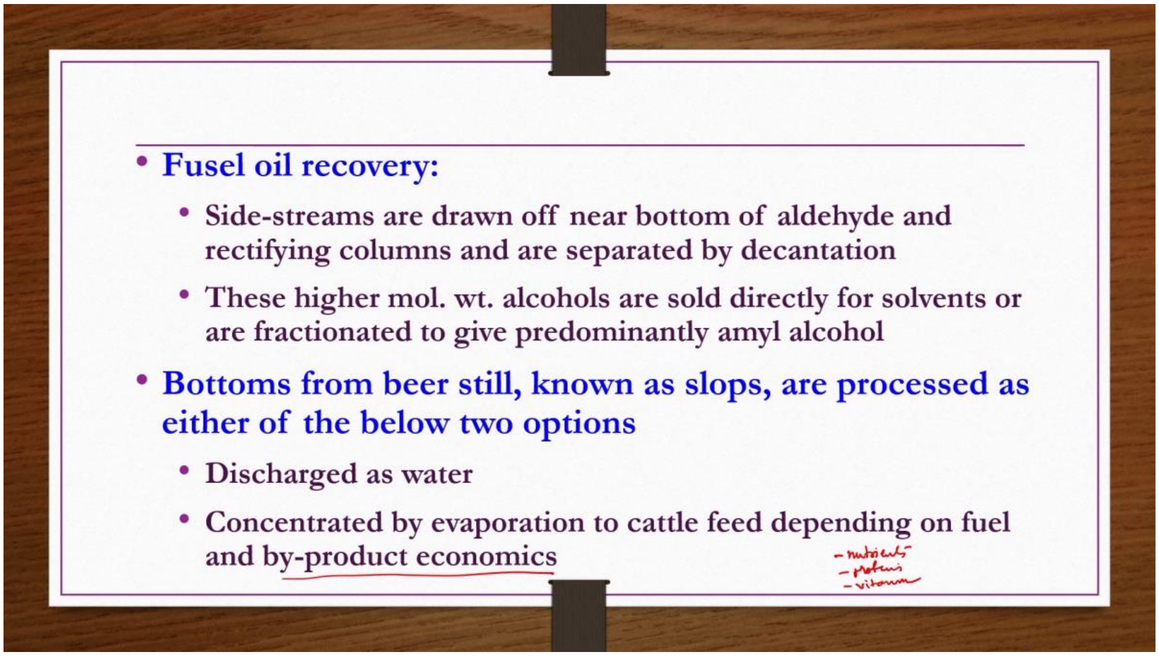

Fusel oil recovery, side streams are drawn off near bottom of aldehyde and rectifying columns and are separated by decantation. These higher molecular weight alcohols are sold directly for solvents or fractionated to give predominantly amyl alcohols. Bottoms from beer still known as slops are also known as the stillage are processed as either of the below 2 options, discharged as water or concentrated by evaporation to cattle feed depending on fuel and byproduct economics because it also contains nutrients, proteins, vitamins, etc.

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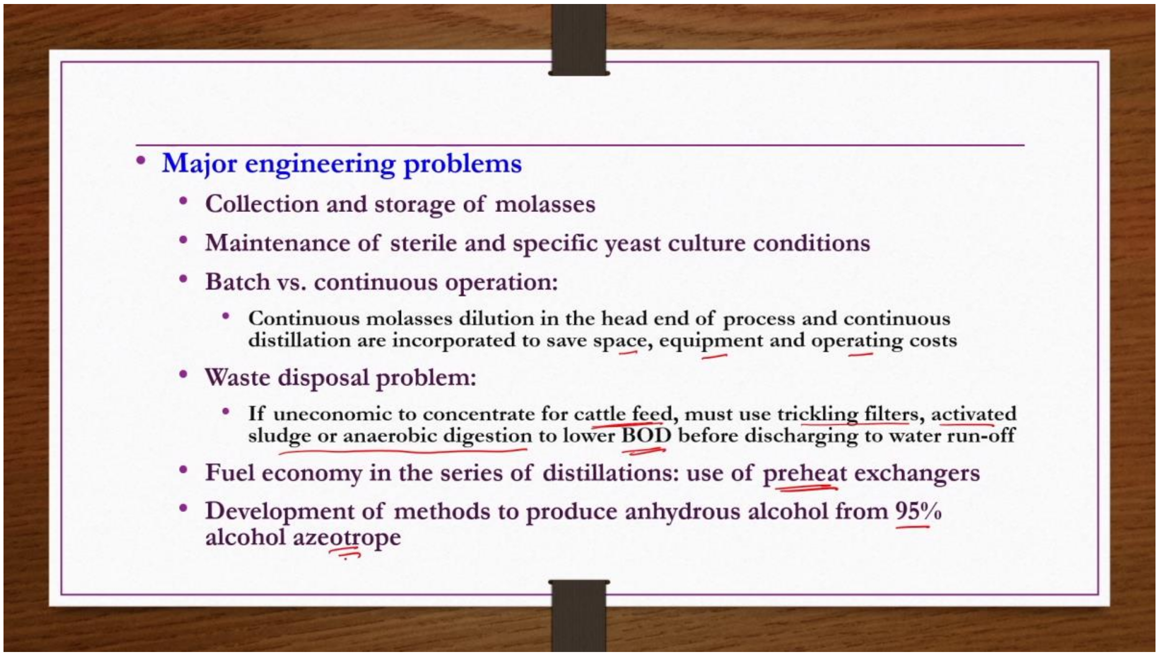

Major engineering problems, first is collection and storage of molasses. Molasses you know collection and storage because of that one you know its composition may be changing because on storage also it may be undergoing some natural fermentation kind of thing. Also, if it is stored for long time it smells very badly that it is it may causing you know problem to the surrounding. So collection and storage of molasses is a problem. So that should be properly taken care. It should be collected just before the start of the run. Just before the start of the run in the sense within a day or 2 you have to collect and then do not store for the weeks and months in the industry rather you do the fermentation within 1 or 2 days after collecting it. Maintenance of sterile and specific yeast culture conditions. Any of the fermentation process it is very essential to maintain sterile media, substrate and then parts of the plant etc. Batch versus continuous operations. In this process only, the fermentation process is batch process whereas the purification steps all that 3-distillation column all of them are operated under the continuous mode. It will save the space, equipment and operating cost as well. Waste disposal problem. If at all if you are not using the slops etc. as a animal feed or if it is not economic to produce animal feed from the slops then the disposal is a problem. So, for that what you have to do if you are not using as cattle food after concentrating then what you should do you should use trickling filters, activated sludge and anaerobic digestion processes to lower the BOD before discharging to water runoff. Fuel economy is very much essential wherever distillation is involved. So, in this case at least 3 distillation columns are there. So, use of preheat exchangers are found to be providing fuel economy required in any plant. Development methods to produce anhydrous alcohol from 95% alcohol azeotrope. So, this anyway we are going to see what are the methods are available now.

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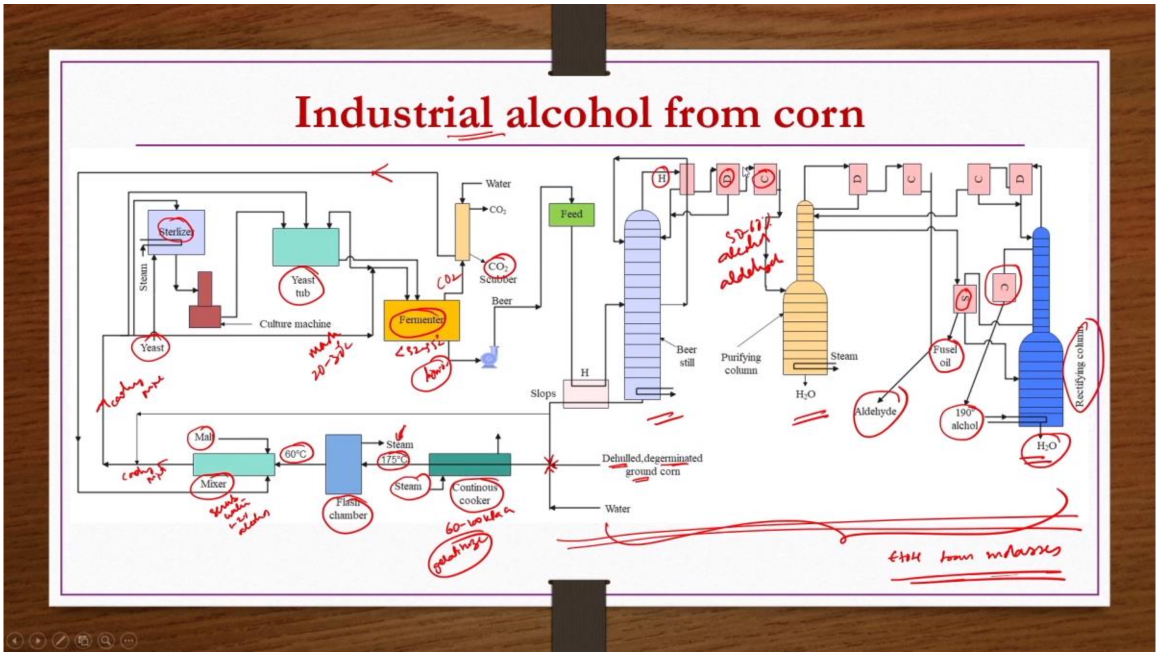

Now we try to produce the industrial alcohol from corn that is basically whatever the alcohol that production we have seen until now that is from the molasses or sugar substrate. So now we try to do the similar one from the corn because we have 3 options from the sugar substrate from the starch substrate etc. So, corn is a better source for the starch and then that process we can see as a second one. Third option was using the sulphite waste from the paper industry that probably we discuss in the next week when we discuss about pulp and paper industry. So that all 3 options of a fermentation processes to produce ethyl alcohol would be covered. One we covered by using sugar or sucrose substrate. The second one starch or corn substrate we are using and then how to produce the ethanol from that starch or corn that we are going to discuss now. Now again here again the terminology industrial alcohol is given that means it would be this process is up to producing the so called 95 or 95.6 volume percent of ethanol. Here what you do whatever the corn is there you do the dehulling, degermination and ground it then you add slops or stillage and then also you add water all of them you take to a continuous cooker to which you supply the steam and then maintain the pressure of 100 to 60 to 100 kilo Pascal gauge pressure. So then here in the continuous cooker cooking of this corn would take place. It is very essential to gelatinize the mixture. So once this it is done it is actually done for 1 or 2 minutes or less than 5 minutes only. Then whatever the mixture is coming that would be at 175 degree centigrade. This you pass through a flash chamber where steam is removed and then because of this steam removal the temperature would be suddenly dropped to 60 degree centigrade. Then what you do to this one you can add malts and then nutrients mixture and then scrub water which is having 1 to 2 percent of alcohol etc. those things you can add here. So, the temperature is still 60 degree centigrade. So, then this mixture is has to be passed through cooling pipes. It has to pass through cooling pipes because now this line is going to the fermenter. In the fermentation section temperature should not be more than 32 to 35 degree centigrade. But after this mixing whatever the mixture is there that is approximately 60 degree centigrade. So, when it passes through the cooling pipe not only the temperature decreases but also the starch, dextrins, etc. would be produced from the corn or gelatinized corn mixture whatever you are getting. So, this you take it to the fermenter. You can take directly to the fermenter or you can do some kind of sterilization if required sterilizing the substrate, media sterilization. Then separately in the yeast tub you are producing the yeast that should also be sterilized if required and then this yeast can be taken to the fermenter. So, this can be done either way it can be taken directly or it can be you know mixed with the culture and then or it could be mixed with the you know this mixture corn starch mixture and then that should be taken to a fermenter. So this yeast and then whatever the mash or the mixture after adding the malt etc. all that at around 20 to 30 degree centigrades or less than that temperature are added to the fermenter either individually or mixed before and then sent to the fermenter. In the fermenter reaction takes place about 30 to 70 hours temperature tried to maintain less than 32 degree centigrade. Now here again upto this process everything is same you get the CO_2 and then liquids. CO_2 you scrub with water to recover if at all some ethanol is being carried by the CO_2 gases. So that scrub water you recycle to the mixture this scrub water whereas CO_2 that you get you get as a kind of product use it as a product or release in the atmosphere after checking its concentration etc. This liquid then you send it to the beer still then aldehyde section then rectifying section etc. which is similar to the previous process where you know ethanol produced from molasses. So exactly the same thing first you take to the beer section where you try to increase the concentration to the 50 to 60 percent of alcohol remaining or aldehydes etc. This aldehyde should be separated out in the aldehyde section and then collected as product whereas the after removing the aldehydes primarily you are having the fusel oil and then alcohol only fusel oil that is nothing but high molecular weight alcohols and then ethanol water mixture are there that will be taken to the rectifying column where water you take it as a bottom product. From the top product you can take ethyl alcohol after condensation whereas from the side stream you can get back you know so called stream which is rich in the high molecular weight alcohols they would be again separated in a separator and then you get a fusel oil. So, all these process are similar the purification steps are similar like previous one. Here again this H stands for the preheat exchanger, D stands for the dephlegmator or partial condenser, C stands for the total condenser.

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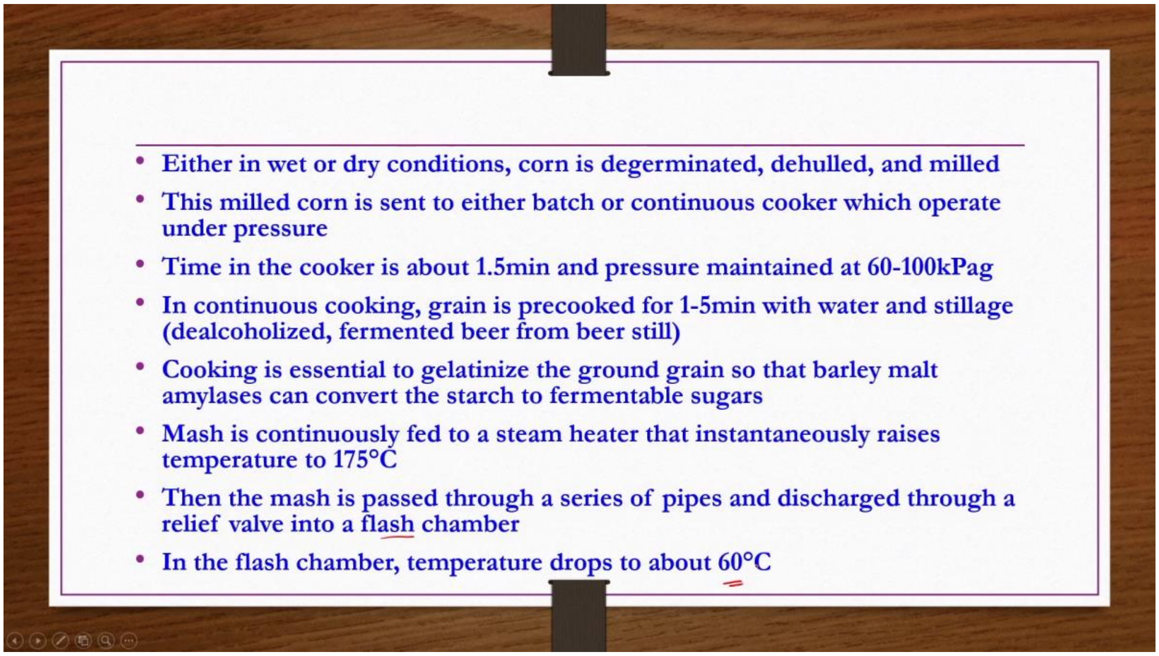

So whatever process that is shown in the flowchart the same is presented here from the learning point of view. Either in wet or dry conditions corn is de-germinated, de-hulled and milled. This milled corn is sent to either batch or continuous cooker which operate under pressure. Steam in the cooker is about 1.5 minutes and pressure maintained at 6200 kilopascal gas pressure. In continuous cooking grain is pre-cooked for 1 to 5 minutes with water and stillage or slops which is nothing but de-alcoholized fermented beer from the beer still. Cooking is essential to gelatinize the ground grain so that barley malt amylases can convert this task to fermentable sugars. Mash is continuously fed to a steam heater that instantaneously raises temperature to 175 degrees centigrade. Then the mash is passed through a series of pipes and discharged through a relief wall into a flash chamber. In flash chamber temperature drops to about 60 degrees centigrade.

Gelatinized cooked grain mash is mixed with malted barley and water. This mixture is pumped through a pipeline which is also a converter for 2 minutes at 60 degrees centigrade and then sent to fermenters through pipe coolers because before entering the fermenters the temperature has to be reduced from 60 to approximately 20-25 degrees centigrade. Starch is hydrolyzed to about 70 percent maltose and 30 percent dextrins in short time in the converter. Stillage with 20 to 25 percent of final mash volume from beer still is added to converted grain mash prior to fermentation.

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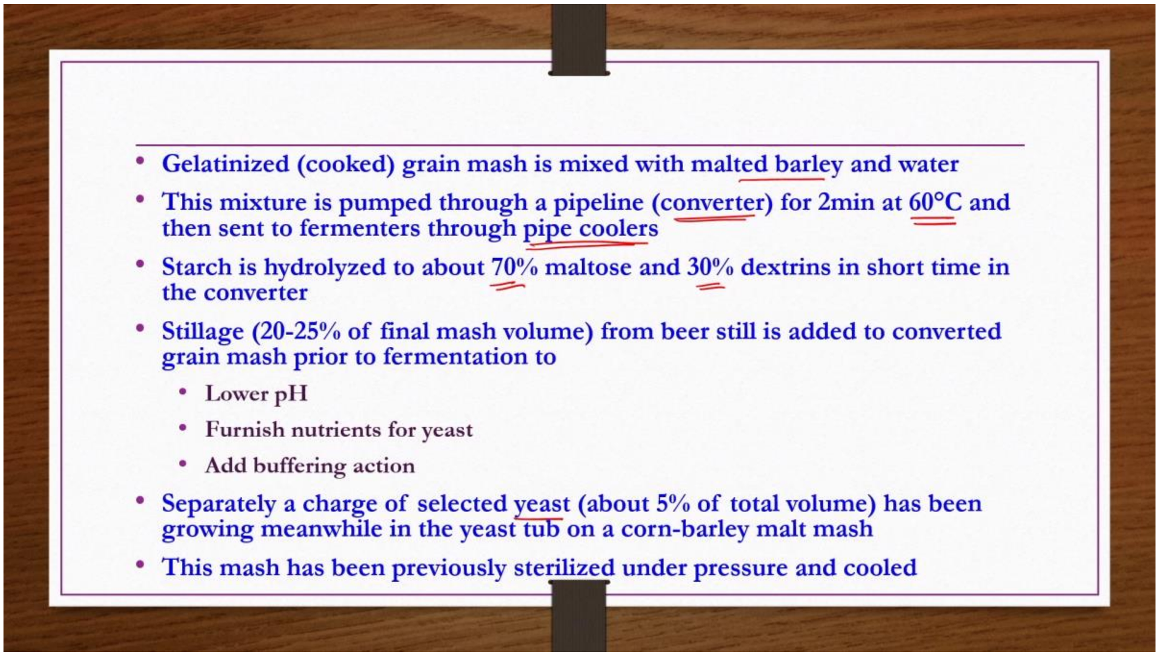

The purpose is to lower the pH and then furnish nutrients for yeast if required and then adding buffer action as well. Separately a charge of selected yeast about 5 percent of total volume has been growing meanwhile in the yeast tub on a corn barley malt mash which was previously sterilized under pressure and cooled.

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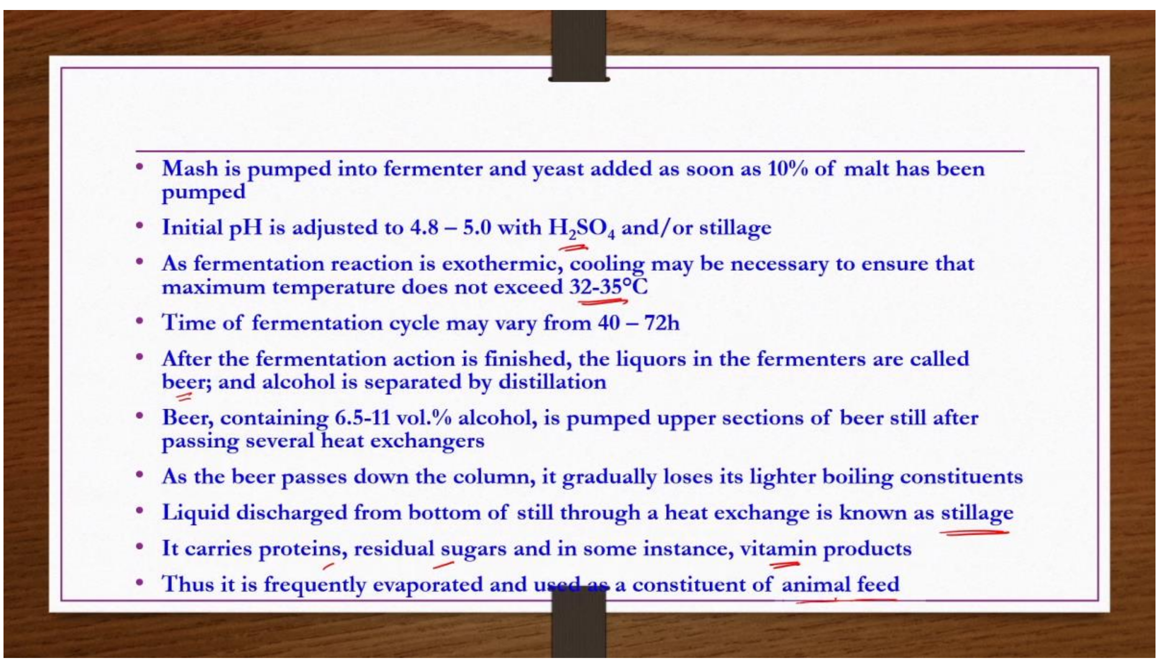

Mash is pumped into fermenter and yeast added as soon as 10 percent of malt has been pumped. Initial pH is adjusted to 4.85 with sulphuric acid and distillates. As fermentation reaction is exothermic cooling may be necessary to ensure that maximum temperature does not exceed 32 to 35 degrees centigrade otherwise fermentation will cease. Time of fermentation cycle may vary from 30 to 70 hours or roughly 72 hours. After the fermentation action is finished the liquors in the fermenters are called beer and alcohol is separated by distillation. Beer containing 6.5 to 11 percent alcohol is pumped upper sections of beer still after passing several heat exchangers. As the beer passes down the column it gradually loses its lighter boiling constituents. Liquid discharge from bottom of still through a heat exchange is known as stillage or slop. It carries proteins, residual sugars, nutrients and in some instances even vitamins also. So, it is frequently operated and used as a animal feed constituent.

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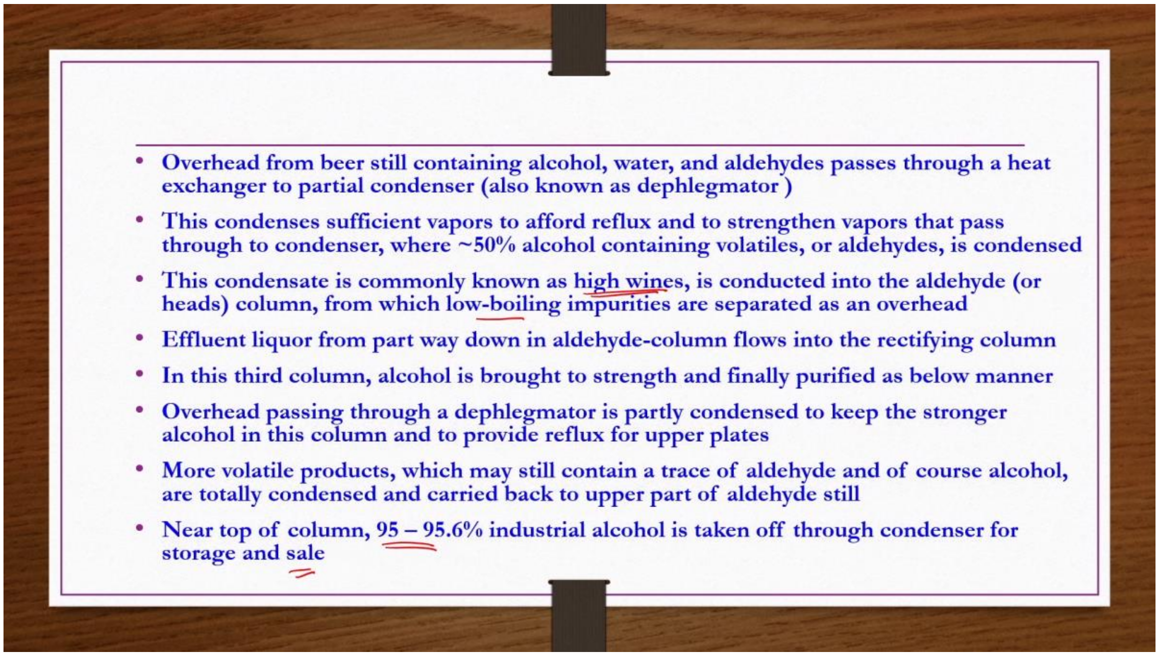

Overhead from a beer still containing alcohol, water and aldehydes passes through a heat exchanger to partial condenser. This condenses sufficient vapors to afford a reflux to strengthen vapors that pass through to condenser where 50 percent alcohol containing volatiles or aldehydes is condensed. This condensate is commonly known as high vines is conducted into the aldehyde column from which low boiling impurities are separated as overhead. Effluent liquor from part of way down in aldehyde column flows into the rectifying column. In this third column alcohol is brought to strength and finally purified as below manner. Overhead passing through a dephlegmator or partial condenser is partly condensed to keep the stronger alcohol in this column and to provide reflux for upper plates. More volatile products which may still contain a trace of aldehyde and of course alcohol are totally condensed and carried back to upper part of aldehyde steel. Near top of column 95 to 95.6 percent industrial alcohol is taken off through condenser for storage and sale. This is all we discussed already in the flow chart. So that is just it is provided in a text form for the benefit of the learners.

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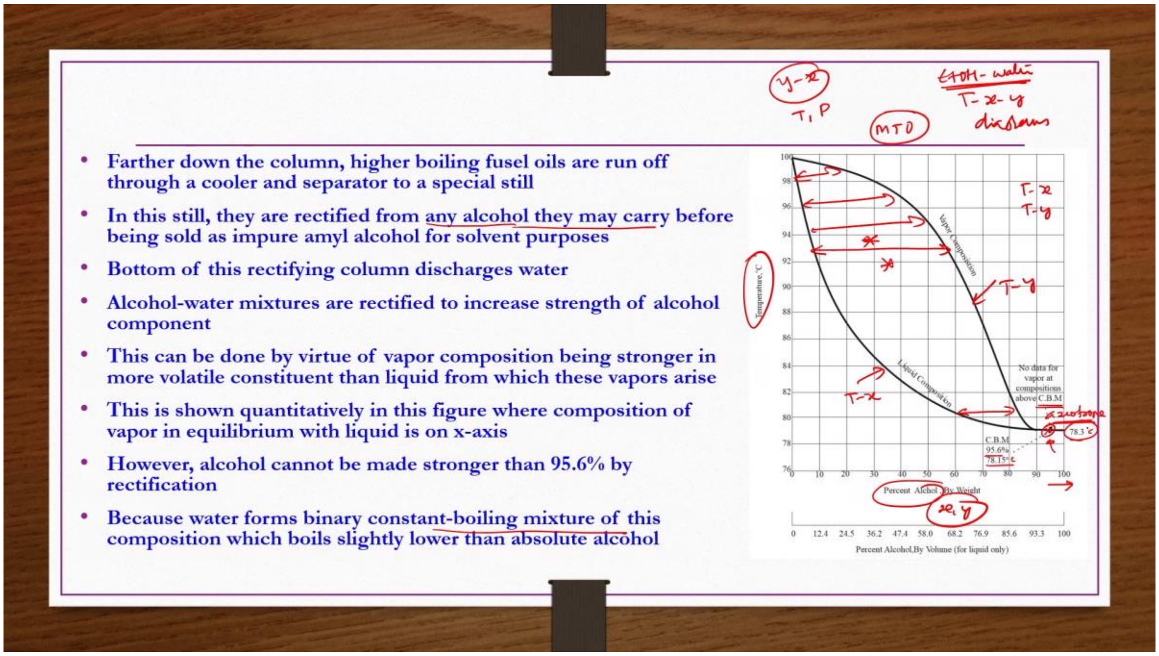

Now let us say if you wanted to improve that 95 or 95.6 percent of ethanol to 100 percent so then what should be done? So, there are some approaches that we are going to see and then we wind up today's lecture after that. Further down the column higher boiling fusil oils are run off through a cooler and separated to a special still. In this still they are rectified from any alcohols if at all present they may carry before being sold as impure amyl alcohol for solvent purposes. Bottom of this rectifying column discharges water. Alcohol water mixtures are rectified to increase strength of alcohol component. This can be done by virtue of vapour composition being strong in more volatile constituents and liquid from which these vapours arise that you can see here in this picture. Actually this is T-x-y diagram for ethanol water mixture. Equilibrium diagram that is what we can call it actually. x is nothing but you know volume fraction of ethanol in liquid phase, y is nothing but volume fraction of same ethanol in the vapour phase which are in equilibrium to each other. Let us say that equilibrium that whatever the y versus x information is there that changes with temperature and pressure. Let us say if you keep pressure constant and then keep changing the temperature then whatever the T-x diagram and then T-y diagram are there they are provided here. So, this is nothing but T-x temperature versus composition of that ethyl alcohol in liquid phase and then this is temperature versus composition of that ethanol in vapour phase. So you can see these 2 curves are forming hysteresis. The gap is more that indicates that the mixture can be easily separable or water ethanol mixture whatever is there that can be easily separated into pure ethanol pure water. If the hysteresis is very thin and then gap is very less then separation would be very difficult that is what this hysteresis loop indicates between this T-x and T-y diagram. So, such things you learn in the mass transfer course where you talk about distillation and then etc those kind of things. However, some information is provided here. So now let us say at this particular temperature if you draw a horizontal line that is known as the tie line and then that gives the concentration gradient that whether it is possible to do separation of ethanol or water or ethanol from the ethanol water mixture or not that is what it indicates. So every temperature gap is different. So here the gap is less and then as the temperature decreasing the gap is increasing. But further as the temperature going down very much around 80 degrees centigrade the gap is decreasing and there is a point where both of them are having the same composition. So that point is known as constant boiling mixture. So, where the concentration is 95.6 percent ethanol is there and remaining is water and then that is occurring at 78.15 degrees centigrade or 78.3 degrees centigrade. So here at this point what you understand that whatever ethanol concentration is there that is same in either vapor phase or liquid phase so then separation is not possible. So, for that purpose you know you have to do some other processes those we are going to discuss. So, this point CBM constant boiling mixture or azeotropic point we call it. So, all those details are part of the mass transfer course there you can learn in detail anyway. However, quickly we have seen some information. So, this T versus x, y that plot is this one T x, y diagram.

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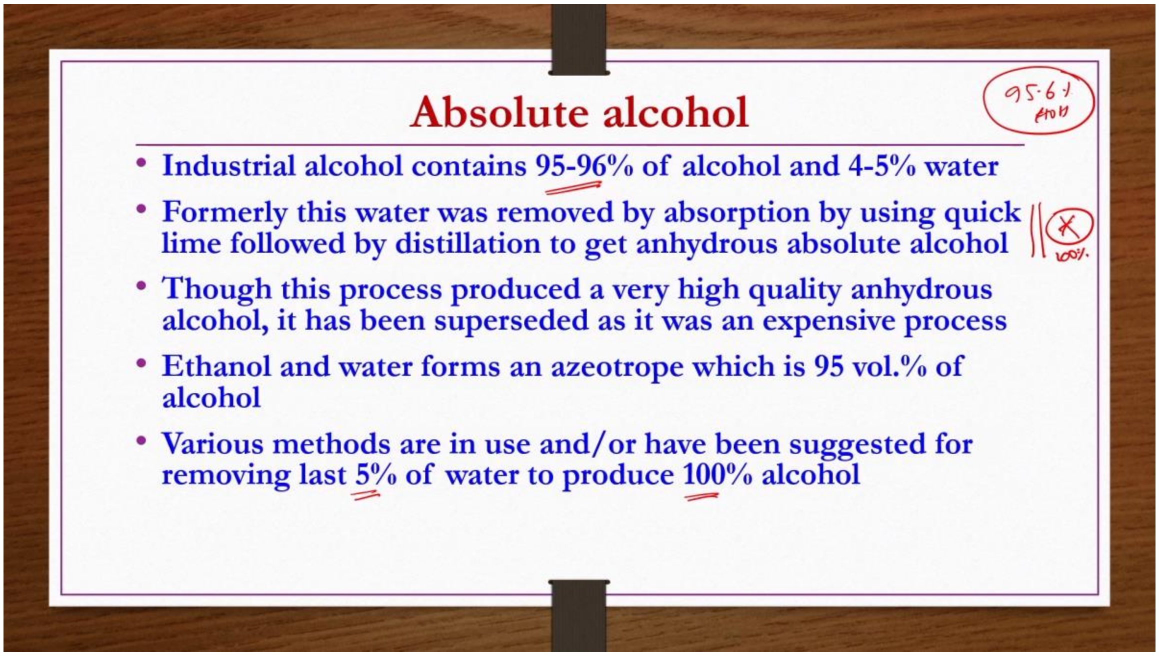

So, this diagram is to show that you know after certain point you know separation is not possible or this T x and T y curves are joining together that is what it mean by. However, alcohol cannot be made stronger than 95.6 percent by rectification because water forms binary constant boiling mixture of this composition which boils slightly lower than absolute alcohol. Now absolute alcohol how to get that is what we are going to see. Industrial alcohol contains 95 to 96 percent of alcohol and 4 to 5 percent water. Actually, whatever 95.6 percent ethanol and then remaining water is the azeotropic mixture that we are calling that is such precisely calculation is possible theoretically but experimentally 95 to 96 percent like that you can in general write. Because it is very difficult to control such precisely at industry level in the lab level we can control. Formally this water was removed by absorption by using quick lime followed by distillation to get anhydrous absolute alcohol and it was very good approach. 100 percent ethanol was able to produce high quality absolute alcohol was able to produce but this process was very expensive that is the reason it was superseded by the other methods that we are going to discuss. Ethanol and water forms an azeotrope which is 95 volume percent of alcohol. Various methods are in use and are have been suggested for removing last 5 percent of water to produce 100 percent of alcohol and then some of them are provided here in a tabular column.

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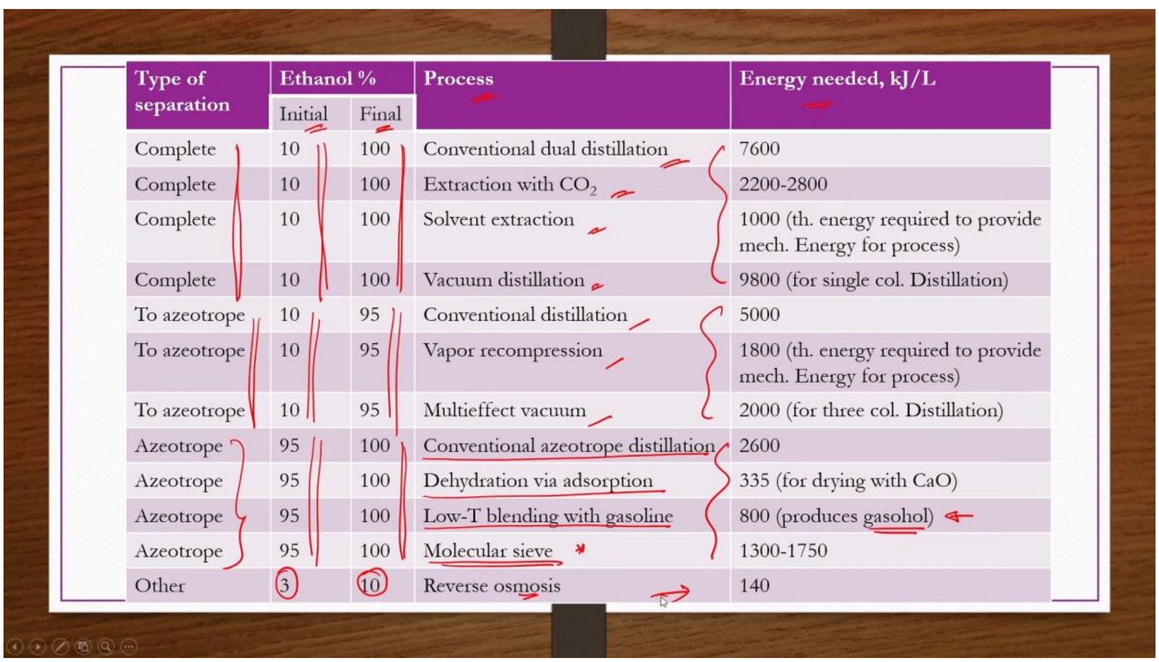

Type of separation	Ethanol %		Process	Energy needed, kJ/L
	Initial	Final		
Complete	10	100	Conventional dual distillation	7600
Complete	10	100	Extraction with CO_2	2200-2800
Complete	10	100	Solvent extraction	1000 (th. energy required to provide mech. Energy for process)
Complete	10	100	Vacuum distillation	9800 (for single col. Distillation)
To azeotrope	10	95	Conventional distillation	5000
To azeotrope	10	95	Vapor recompression	1800 (th. energy required to provide mech. Energy for process)
To azeotrope	10	95	Multieffect vacuum	2000 (for three col. Distillation)
Azeotrope	95	100	Conventional azeotrope distillation	2600
Azeotrope	95	100	Dehydration via adsorption	335 (for drying with CaO)
Azeotrope	95	100	Low-T blending with gasoline	800 (produces gasohol)
Azeotrope	95	100	Molecular sieve	1300-1750
Other	3	10	Reverse osmosis	140

See the type of separation initial ethanol concentration final ethanol concentration what type of process used and then how much energy is required that is given. Quickly if you see type of separation is complete separation when your initial concentration is 10 and then final concentration is 100 percent then so many process are there conventional dual distillation extraction with CO2 solvent extraction vacuum distillation are there and then their energy calculations are slightly different from each other. Likewise, azeotropic distillation or azeotropic separation process is there where you get from the initial 10 percent concentration to 95 percent concentration of ethanol for this conventional distillation vapor recompression multi effect vacuum distillations are possible here also the energies are different. But azeotrope separation where from 95 initial concentration to 100 percent final concentration of ethanol if you want to produce the process like conventional azeotropic distillation dehydration via adsorption using lime as drying medium and then low temperature blending with gasoline to get gas. This was conventionally followed long back when the primary application of ethanol was to blend with the petroleum products and then recent development of molecular sieves etc. also used. So, what we do now we discuss this conventional azeotrope distillation process. There are also some process like reverse osmosis where initial concentration may be 3 and then final concentration up to 10 percent you can get but this is not required anyway for us.

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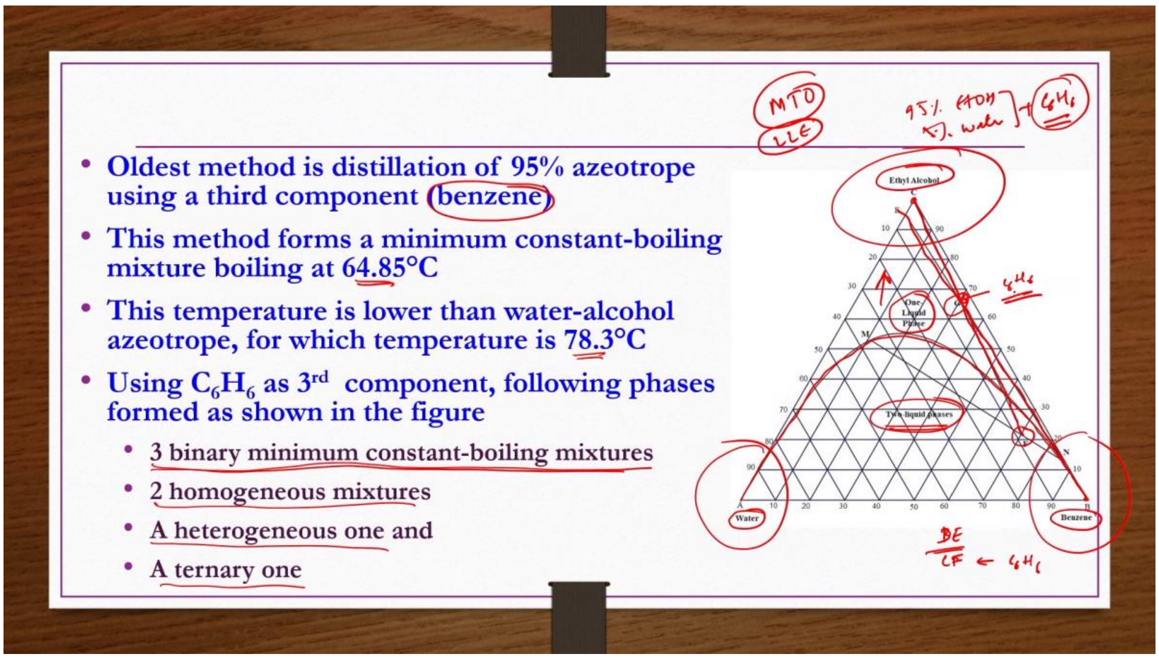

Now oldest method is distillation of 95 percent azeotrope using a third component benzene. This method forms a minimum constant boiling mixture boiling at 64.85 degrees centigrade. This temperature is lower than a water alcohol azeotrope for which temperature is 78.3 degrees centigrade. Now the thing is that benzene you are adding to disturb the azeotropic composition primarily that is the purpose of adding this third component. But how much should it be added that is again the question in order to understand that one what should be the composition of the benzene that should be initially added for that purpose how to do calculation that we are going to see. Let us say if you use benzene as third component following phases may form as shown in the figure like 3 binary minimum constant boiling mixtures, 2 homogeneous mixtures and then one heterogeneous phase and then one ternary phase. The equilibrium composition of this mixture of ethanol water and benzene because initially 95 percent ethanol is there, 5 percent water is there. To this one you are adding benzene to disturb the azeotrope formation so that you can easily separate 100 percent ethanol. May be water going with the benzene or water also be recovered purely so that is also good. But how much benzene should be added? Let us say these things also you study in mass transfer especially in the liquid-liquid equilibrium calculations. These are very important part but we are not going into the details of all those things. Primarily this diagram talks about the equilibrium concentrations of 3 components, 3 component mixtures. So, when you add benzene to the ethanol water azeotropic mixtures so then 2 liquid phases may be forming, 1 liquid phase may be forming and then there is a ternary phase also forming. So that ternary phase composition is f indicated by a figure. So actually when you draw this one what happens you get an envelope like this. This is the equilibrium curve. Like T-x, T-y diagram previously we have seen. Now here whatever the 3 component their equilibrium composition if you draw in this triangular diagram so then you get envelope like this. Below which you get the 2 liquid phases, above which you get single liquid phases. Towards this corner you get the water rich phase, towards this corner you get the benzene rich phase and then towards this one you get the ethanol rich phase. Those things are different and that is what is made by 3 binary minimum constant boiling mixtures etc. So now the problem is that you have to know how much C6H6 benzene should be added so that to disturb that one. So, for this there is a technique. Actually, you know this ternary component mixture F. From this point you join this line to C point where the pure ethanol is there here. Whereas from the benzene here this benzene point is there. From this benzene point to this equilibrium curve whatever to this envelope or equilibrium curve is there to that one you draw a tangent like this. That tangent if you draw like this you get this BE line and then that CF line 2 lines are there now actually. So actually, initial concentration whatever that or initial benzene whatever you supposed to add that composition should be falling on CF line. But this CF line is not one point so which one should be the more economical that you have to find out. For that purpose this EB line or BE line is formed by drawing a tangent to this equilibrium curve at B point that is forming B. Wherever they are intersecting that point gives you the that point gives you the point of a benzene composition. So that point whatever is there corresponding to that point whatever the benzene composition is there that much amount minimum has to be added to the ethanol water mixture to get or to disturb the ethanol water azeotropic composition.

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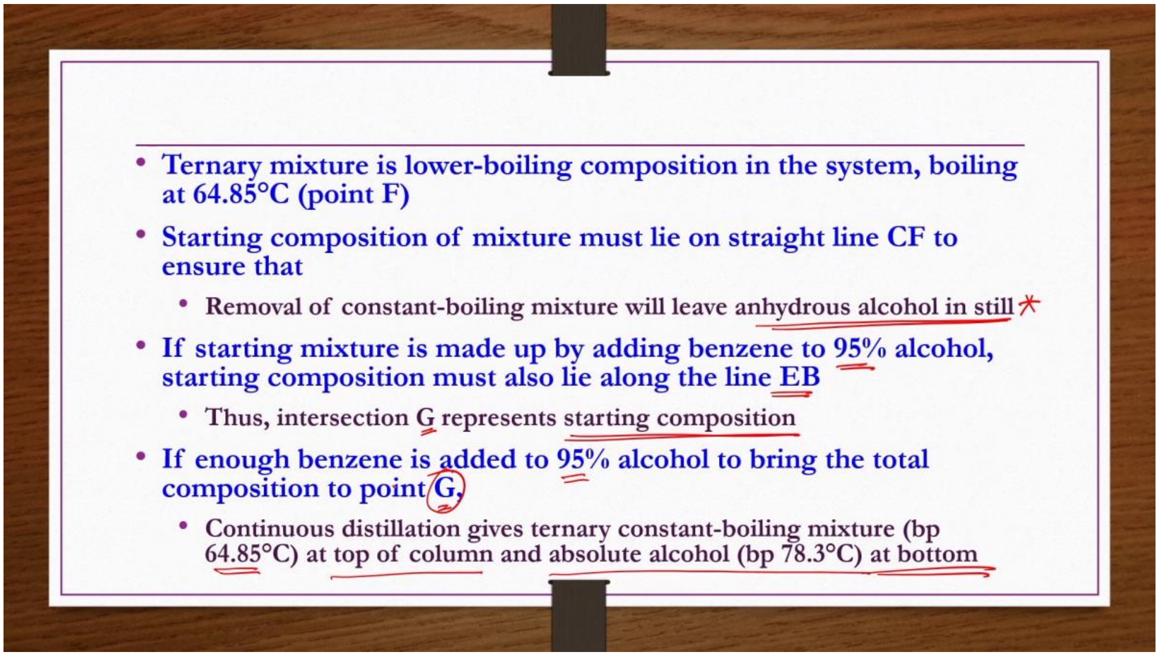

Ternary mixture is lower boiling composition in the system boiling at 64.85 degrees centigrade point F that is shown in the picture. Starting composition of mixture must lie on straight line CF to ensure that removal of constant boiling mixture will leave anhydrous alcohol in the still for this purpose only this calculation is required whatever I have discussed in the previous slide. If starting mixture is made up by adding benzene to 95 percent alcohol starting composition must also lie along the line BE or EB. Thus, intersection point G represents the starting composition. If enough benzene is added to 95 percent alcohol to bring the total composition to point G then continuous distillation gives ternary constant boiling mixture having boiling point 64.85 degrees centigrade at the top of the column and absolute alcohol having 78.3 degrees centigrade boiling point at bottom. So that is the purpose of finding this composition.

So that if you do here so finally now this is the distillation column to this distillation column you are adding so called you know whatever the mixture that C_2H_5OH water is there and to this one you are adding benzene makeup. The compositions are such a way that G point whatever shown in the triangular diagrams according to that one benzene is added. So then here distillation takes place from the bottom of the still you get the 100 percent C_2H_5 whereas from the top you get ternary mixture having all these three C_6H_6, H_2O, C_2H_5 all these things would be there and then they will be forming a constant boiling mixture azeotropic at 64.85 degrees centigrade. That is taken to a separator which is operating at 20 degrees centigrade where that would be separated or decanted it is actually separated into two layers top layer and bottom layer. Top layer is almost like pure in benzene and then that is taken as a feedback to the column way as along with the makeup benzene.

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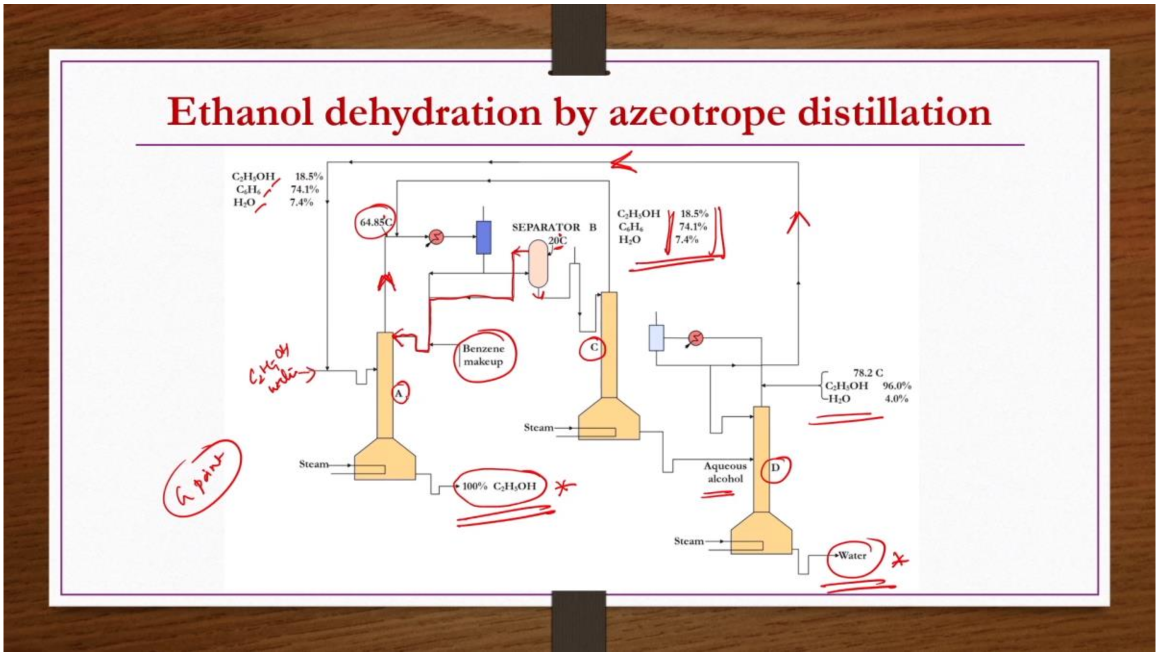

Whereas the bottom layer whatever is there that bottom layer is you know having benzene free aqueous alcohol that is taken to the section C. Here aqueous alcohol is collected from the bottom and then that aqueous alcohol is by conventional distillation separated into the pure water and then whatever the 95 or 96 percent of ethanol as the top product that top product is again fed back to the this you know section A as a recycle. So here bottom pure ethanol you are getting here pure water you are getting. Whereas from the top of the section C what you get? You get a composition which is having ethanol, benzene and then water as per this composition this is also azeotropic mixture. So, this should also be fed back to the separator along with the top product of the first column A. So, this is how you get the anhydrous dehydrated ethanol without water.

Quickly if you see the points in this process dehydration of 96 percent ethanol to absolute alcohol by azeotrope distillation with benzene occurs at 101 kilopascals. In the flow chart column A has 95 percent alcohol fed into it and benzene is introduced. Ternary azeotrope is taken overhead in this column and absolute alcohol is obtained as a bottoms in the column A. Overhead vapors are condensed and passed to a decontour or separator B which is operating at 20 degrees centigrade in which two liquid layers forms. Upper layer rich in benzene is returned to column A as reflex. Whereas the lower layer is fed to column C which produces a ternary azeotrope as overhead product and benzene free aqueous alcohol as bottom product.

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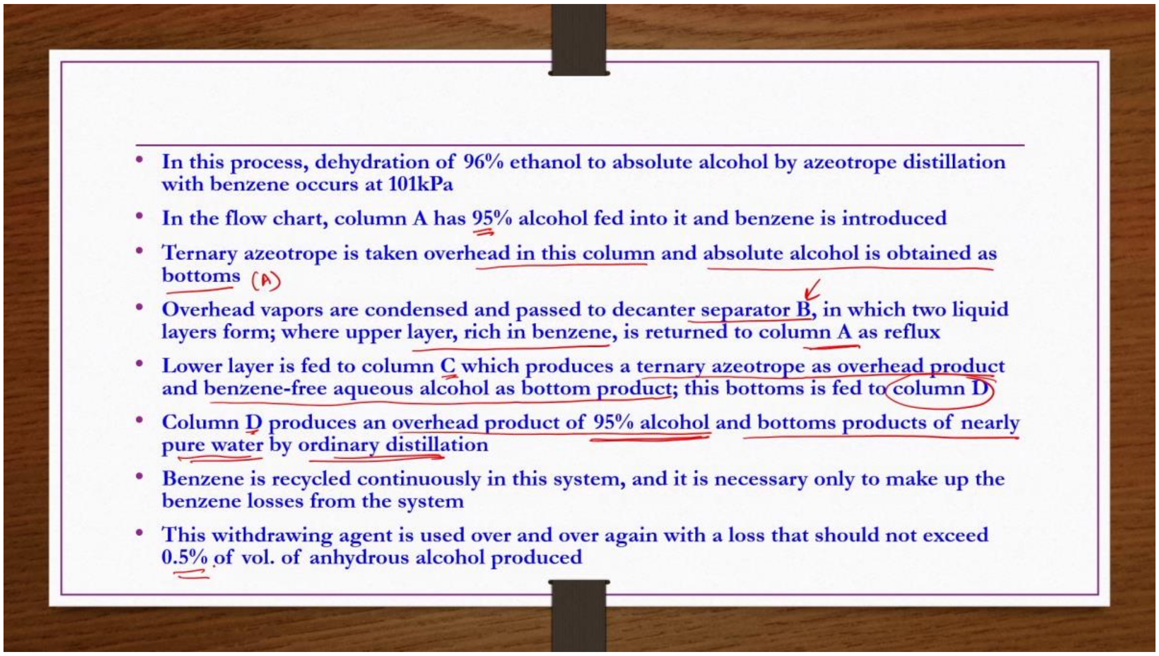

This bottom product is fed to column D. In this column D it produces an overhead product of 95 percent alcohol which is again azeotropic mixture and then that is sent back to column A as a recycle.

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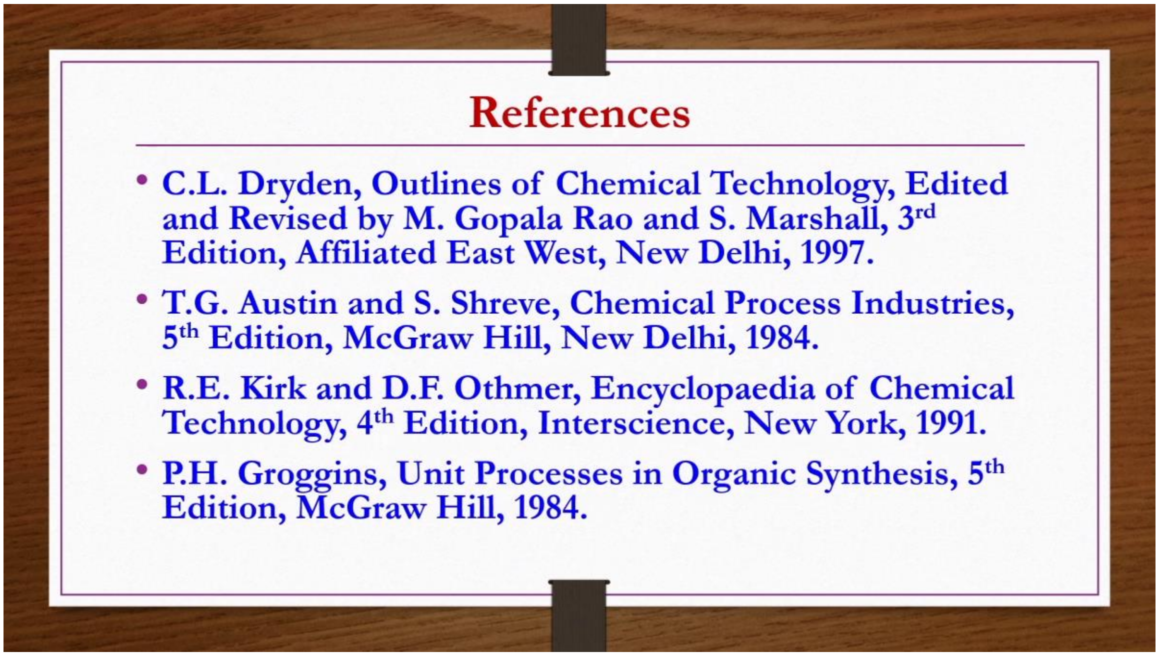

Bottoms products of column D are nearly pure water and this in the column D ordinary distillation is taking place. Benzene is recycled continuously in the system and it is necessary only to make up the benzene losses from the system. This withdrawing agent is used over and over again with a loss that should not exceed 0.5 percent of volume of anhydrous alcohol produced. So, this is all about alcohol and then anhydrous alcohol production process. Alcohol is produced by the fermentation process and then whatever the azeotropic mixture that you get between water and alcohol that has been further processed by extractive distillation to get anhydrous or absolute alcohol having 100 percent ethanol only. References for this lecture are provided here. Thank you.