Chemical Process Intensification
Professor Subrata K. Majumder
Department of Chemical Engineering
Indian Institute of Technology Guwahati
Module 9: Process Intensification in Distillation
Lecture 9.1: Introduction and Principles

Welcome to massive open online course on Chemical Process Intensification, so we will start here module 9 as process intensification in distillation. We have discussed something about process intensification just by improving the interfacial area, that has already been discussed in the previous module. So in this module we will discuss more about that process intensification in distillation system and under this module, the lecture 1 under this module it will be something about that how the process intensification can be done in distillation system and their principles.

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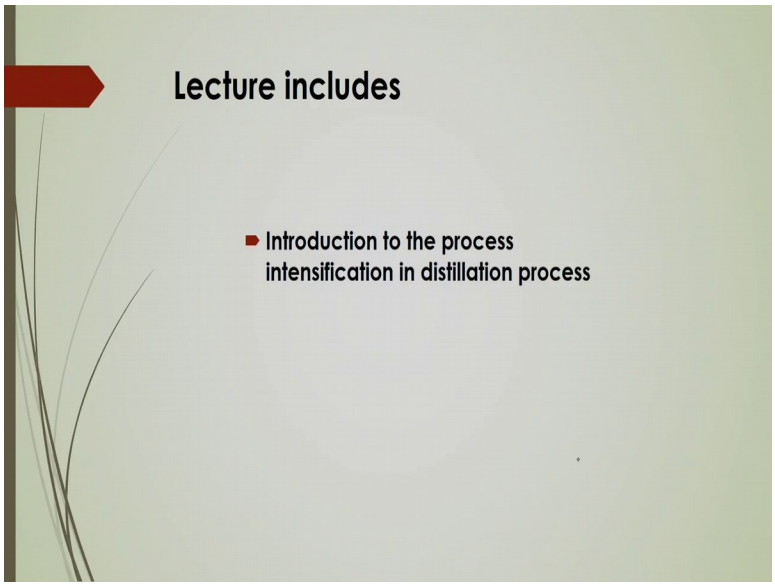

So, we will discuss the Introduction to the process intensification in the distillation process and so for that we have that conventional distillation system which are being used in refinery industry for just having different products based on their density difference, even volatility, all those things like that refinery distillation there. So that conventional distillation system of course, those are being used for long time from 1920s and even before also. But how to improve that distillation system that is actually being under investigation and that is in the direction of process intensification.

So, in that case reactive distillation is one of the best success stories of the process intensification in distillation system. In that case it is generally developed since 1920s onward and in that case, it is made a strong positive impact actually in the chemical process industry and most of the industrial scale reactive distillation process in that case operated worldwide today based on that process intensification and based on this process intensification this distillation system actually being operated and presently more than 150 installed that distillation system for this reactive integration. So, the reactive distillation is simply that distillation as well as that reaction and then separation will be happened simultaneously.

So, the most industrial scale reactive distillation system actually, the capacities that capacities of 100 to 3000 kilo tonnes per year, that is reported by Hammerson in 2007 and it has started more than 30 years ago that is as per their report actually.

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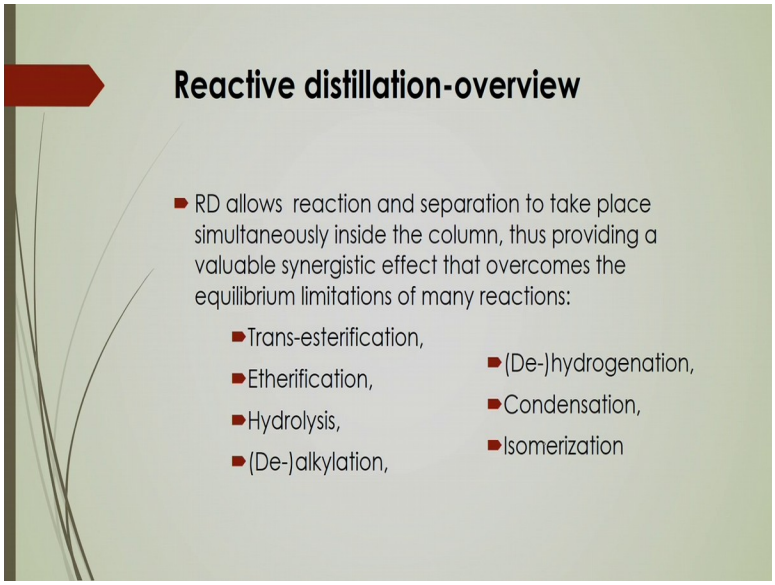

And in that case, there are several applications of this reactive distillation to get that economic benefit and social benefit based on this reactive distillation system, so we will keep that overview of that reactive distillation here, so this reactive distillation allows reaction and separation to take place simultaneously inside the column, thus it will provide a valuable synergistic effect that overcomes the equilibrium limitations of the many reactions. Like you know transesterification, etherification, hydrolysis even you know de-alkylation, even condensation process, isomerisation process, even the de-hydrogenation process, all those processes are being actually carried out based on this process intensification in the reactive distillation system.

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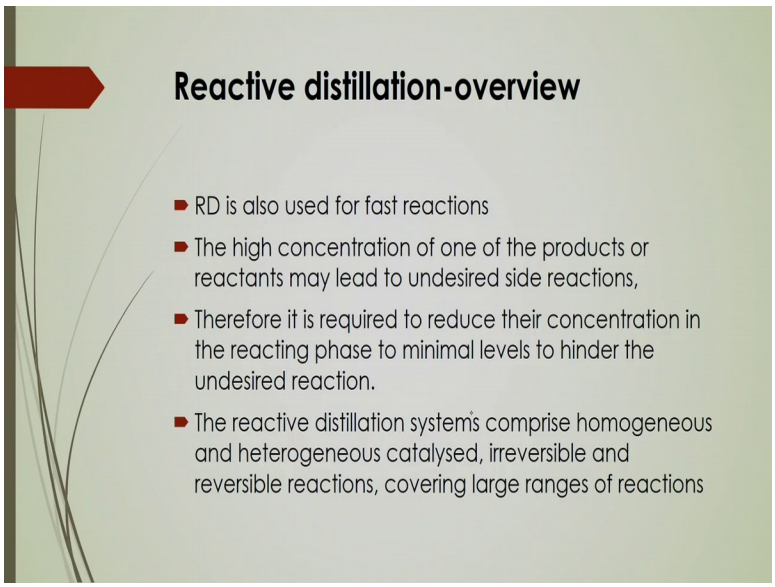

In that case you will see that this reactive distillation has high actually you know demand for the industry because there are several advantages over there and also this reactive distillation used for fast reactions and the high concentration of one of the products or you can say the reactants that may lead to undesired side reactions, so in that case this reactive distillation is used for fast reaction system.

Therefore, it is required to reduce there you know concentration in the reacting phase to minimal levels to hinder the undesired reaction. So, you have to reduce their concentration in the reacting phase so that you can get minimum amount of undesired products and the reactive distillation systems of course it will consist of homogeneous and heterogeneous catalyst and in that case it may be irreversible reactions and reversible reactions which will convert large ranges of reactions based on this reactive distillation principles.

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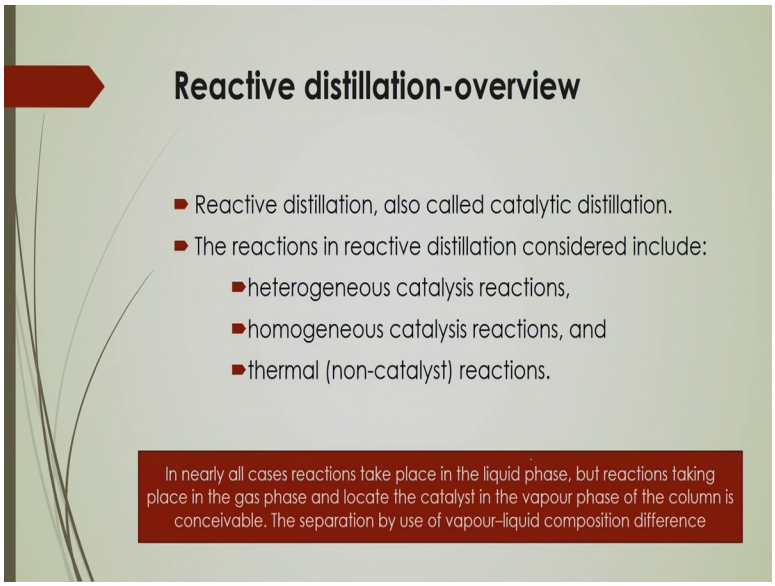

And this reactive distillation also it is called that catalytic distillation that is the reactions in reactive distillation that considered like heterogeneous catalysis reactions, homogeneous catalysis reactions and you can say that thermal non-catalytic reactions also. And you will see that in nearly all cases reactions take place in the liquid phases but reactions is taking place in the gas phase and locate the catalyst in the vapour phase of that columns is you know sometimes conceivable and in that case the separation by use of the vapour liquid composition will be there based on their that composition difference.

So you can say that there are several types of reactions will be or can be carried out in the reactive distillation system. In that case sometimes that well distributed catalyst system, even

you say that heterogeneous catalysis system, even mix catalysis system, even you can say some thermal degradation and thermal reactions also will be there, there may be catalyst will not be required but that things also can be done in the reactive distillation.

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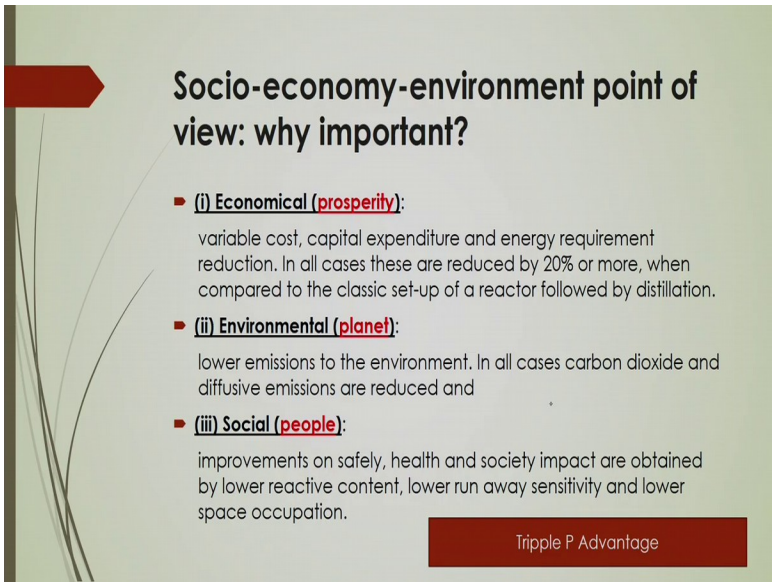

Now why that reactive distillation is important or why that process intensification is going in the direction of that reactive distillation system? Now you will see there are several benefits like you know that economical, environmental even social, so that is why these 3 types of benefits are there, so that is why it is called triplet P advantage. So however economical like you know that prosperity in that case you can reduce that variable cost, capital expenditure and energy requirement and also in all cases you will see that these are reduced by 20 percent or more when compared to the classic set of reactors, that is followed by the distillation system. Whereas in environmental system you will see that lower emissions to the environment will be there if you are doing this you know that reactive distillation instead of separating of that reaction as well as separation there. And in all cases carbon dioxide and diffusive emissions are reduced there and also you can get the social benefit, it is called people.

In that case you can improve the safety, health and society impact and that is obtained by the lower reactive content, lower runaway sensitivity and also lower space occupation. So in this 3 directions you can get that benefit of this you know that use of this reactive distillation systems for getting reduction of cost, even reduction of carbon dioxide gas emission, even you can improve the health condition which will be very impact on the social environment. So, these are the 3 benefits you can get from this reactive distillation system.

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Now you will see it, for hydrogenation the following specific advantage you can get if you are considering that there is a certain specific reaction where that benefit we can get. Now if you…you will see that do the hydrogenation reactions you can get this type of advantages like you know that lower capital expenditure due to no recycle compressor there and also lower capital expenditure due to integrated heat removal there. So main important is that whatever heat is released by that reactions or the process that heat can be utilised for the other processes.

So the integration of these heat systems is very important aspects of this reactive distillation system. Even lower capital expenditure due to the lower hydrogen pressure 5 to 15 bar i.s.o or 25 to 40 bar there, so in that case in this hydrogenation reaction in that case pressure in the system is very important. You can reduce that or you can get the lower hydrogen pressure in this case, so that is why it will be beneficial. Even sometimes you will see that some feedstock cost is sometimes very important to analyse that reaction performance even the overall processes. So lower feedstock cost due to the higher selectivity by product by lower compressor across the reaction zone you can have based on this hydrogenation reaction in reactive distillation.

Even in this case you will see that you can get advantage of having the longer catalyst life due to washing with the clean reflux. Even you can reduce the oligomer formation, you can have that retention time of the catalyst for its activity for the longer time and in that case reduce that oligomer formation in this particular hydrogenation process because dimer goes to the bottom non-reacting zone there. So, this is one important advantage for these

hydrogenation reactions. Actually, it is demonstrated by CDTECH Company for the selective hydrogenation of MAPD via catalytic distillation and it is actually reported in ERTC Petrochemical Conference in 2002.

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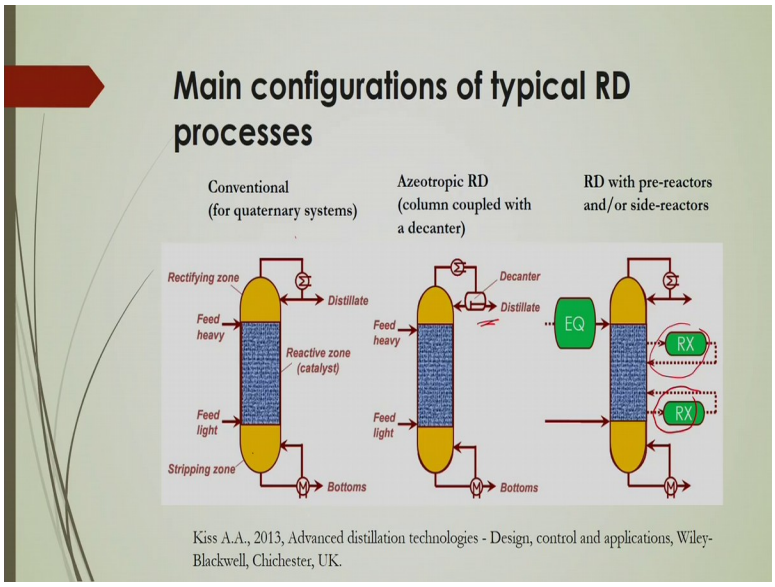

Now there are several configurations that you to know where that this reactive distillation can be done. In that case generally you will see that 3 types of configurations of this reactive distillation process can be obtained. Here it is given in the slides that conventional for quaternary systems here it is given like this. In this case this reactive system, reactive distillation system you will see there will be a common zone of that reactive zone which will be intact with the catalyst and in that case the heavy feed will be supplied to this catalyst medium.

Also parallelly at the bottom that feed light also should be allowed to pass to these and then after distillation along with that reactive system you know that bottom products there will be whatever it will be becoming that will be stripped, that is separated by that absorption process, absorption process there and also and the top product they will be distillate that is called rectifying zone, so this total you know column will be divided into 3 parts. One is that bottom zone it is called the stripping zone that is some gaseous products which may be separated out by that some solvent or some other absorbent and then the top one that is rectifying section there you will see that also that volatile components which are coming that will be separated in that portion.

So, this is one conventional method whereas you will see that azeotropic type if there is a mixture then in that case you can do that azeotropic reactive distillation column that coupled with a decanter there, so in that case you can use this decanter to separate that azeotropic mixture which is coming out as a volatile component. Whereas reactive distillation with pre-reactors and or side reactions also there will be there, so you have to use that side reactors there to complete that reactive reactions in that case before that going to separation in the columns. So, there will be that recycle of this whatever unwanted or incomplete reactions will be there, you can use that you know that side reactors also there.

And also, whatever by-products will be coming, maybe that by-products would be converted to other usable products by that side reactors also. So generally, these three types of configurations you can get or you can design for that typical or particular specific you can say that reactive distillation process.

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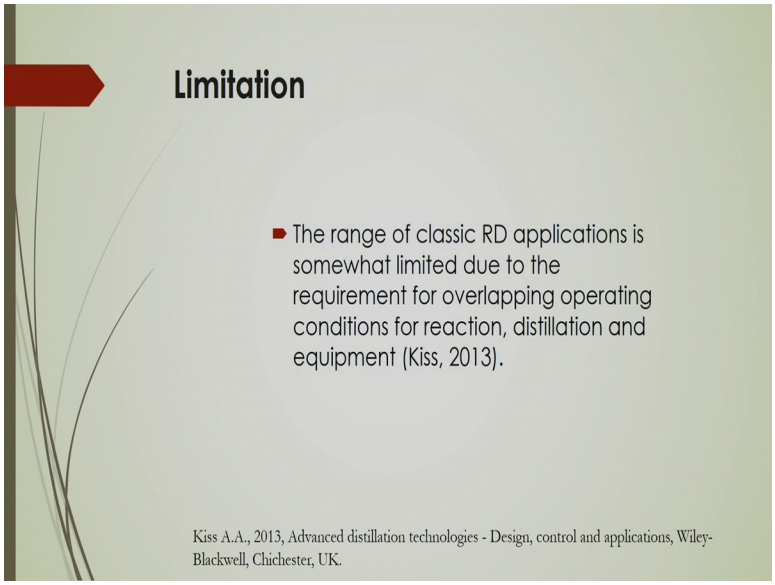

Now there are some limitations also this reactive distillation system for the process intensification. In this case the range of classic reactive distillation applications is somewhat limited due to the requirement for overlapping operating conditions for the reactions, so sometimes you know that operating conditions to be maintained or controlled in such a way that they should not be overlapping of that operating conditions. So, distillation and equipment you have to wisely design for that in which cases at what conditions that you have to maintain for that particular sections that you can easily separate all those products which is coming after reactions.

So, it is sometimes very difficult to control all those things because there are several other conditions simultaneously would be happened which is very difficult to then optimise based on that process or that different variables would be interacting to each other. You cannot say that only these variables will give these products but there are whenever one variable should be imposing on that particular reactions maybe other variables will interact with that. So that is why overlapping of that operating conditions for the reactions is one important limitations of this type of reactive distillation.

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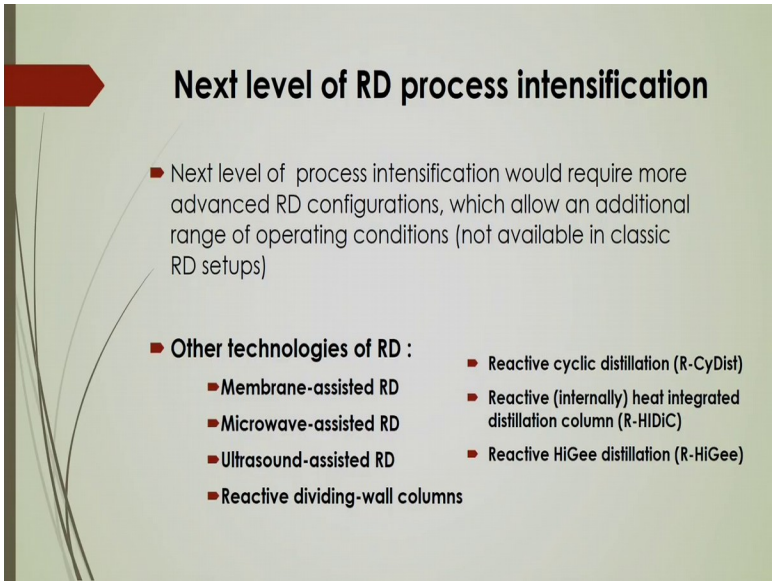

Now this is the normal reactive distillation whatever we are getting that you know that different configurations but based on that normal you know that reactive distillation principles, later on you will see that there are several windows were open to intensify those reactive distillation process also. There may be sometimes that this reactive distillation process will be integrated with some other mechanism so that you can get more intensification of the process, more output, more that economic, more that eco-friendly and also safer.

So, in that case there are several aspects is coming, different mechanisms are considered in the research and development sections that how actually integrate those mechanism in that normal reactive distillation systems, so that is why based on those researches the next level of the process intensification of the distillation systems are coming. So next level of process intensification would require more advantage and also more advanced reactive distillation configurations and this allow an additional range of you know that operating conditions and, in that case, not available in the classic reactive distillation systems.

So,we can say that several other you know that options are open for that intensification of this reactive distillation process like you know that if you integrate those distillation process by membranes, so it will be called as membrane assisted reactive distillation. Sometimes you know microwave mechanisms are integrated to intensify the process, so it is called microwave assisted reactive distillation. Also, you will see that ultrasound assisted reactive distillations are coming.

Sometimes you will see that columns, whatever columns that may be that internals will be that changed or designed in such a way that you can get more intensified way of that reactive distillation, like reactive dividing wall columns is one of the important reactive distillation columns and also reactive cyclic distillation there. Reactive, you know internally heat integrated systems are there. Reactive HiGee distillation high gravity distillation systems are there. So, these are different level of intensification of this reactive distillation systems and all those processes have certain pros and cons and based on which you can apply those you know that intensified mechanism, intensified process for that specific reactions.

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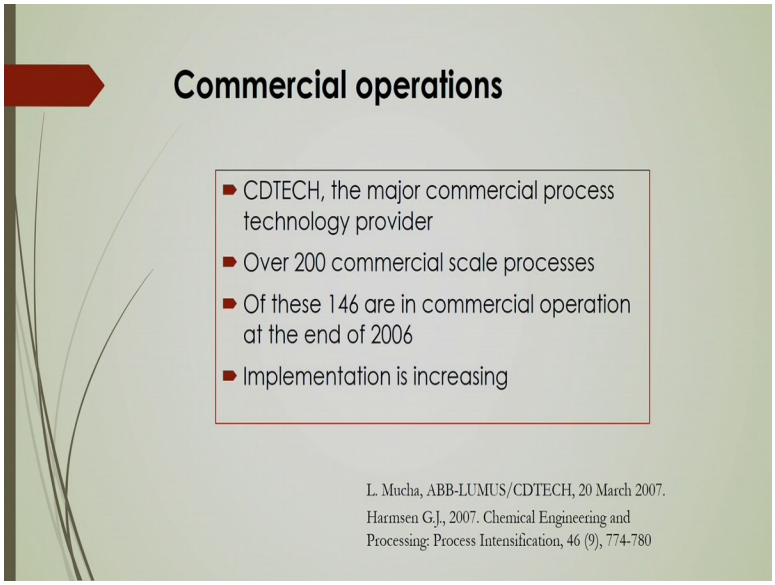

Now let us see that what are the different mechanism of those different next level of this reactive distillation, so in that case several industries they have actually tried to install those intensified reactive distillation systems in their company and they are actually trying to get that intensified way of output by this distillation column. In that case CDTECH is one of the that major commercial sector where you can have that technology from those companies, they are giving that this reactive distillation technology based on this next level intensification of the process of this reactive distillation.

Even they have you know that installed that over 200 commercial scale processes there, of these 146 seats are in commercial operation at the end of 2006 they have given, of course it is reputed by Mucha in 2007 and they have published in chemical engineering and process intensification in 2007. So, implementation of these you know that next level of reactive distillation are very interesting and it is increasing day by day because they are having several advantages compared to that general reactive distillation system.

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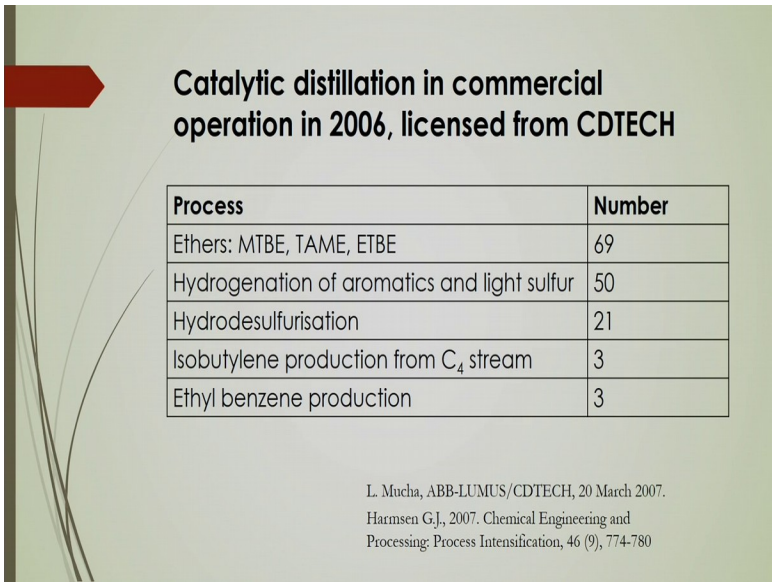

Now catalytic distillation in commercial operation is done in 2006 that is the license got by that CDTECH technology, in that case they have installed several that reactive system for their business and like you know that Ethers, MTB, TAME, ETBE they have installed 69 numbers of these processes in different locations and hydrogenation of aromatics and light sulfur also they have installed 50 units there for this hydrogenation of aromatics and light sulfur and for hydrodesulfurisation they have installed 21 units worldwide.

Even isobutylene production from C4 stream they have installed 3 units based on this process intensification of this reactive distillation system. Even ethyl benzene production, they have installed these three numbers there, so according to this Mucha 2007 we are getting this information of course that is from…You know it is reported in 2007 but till now maybe more process units are developed and they have installed based on this reactive distillation system.

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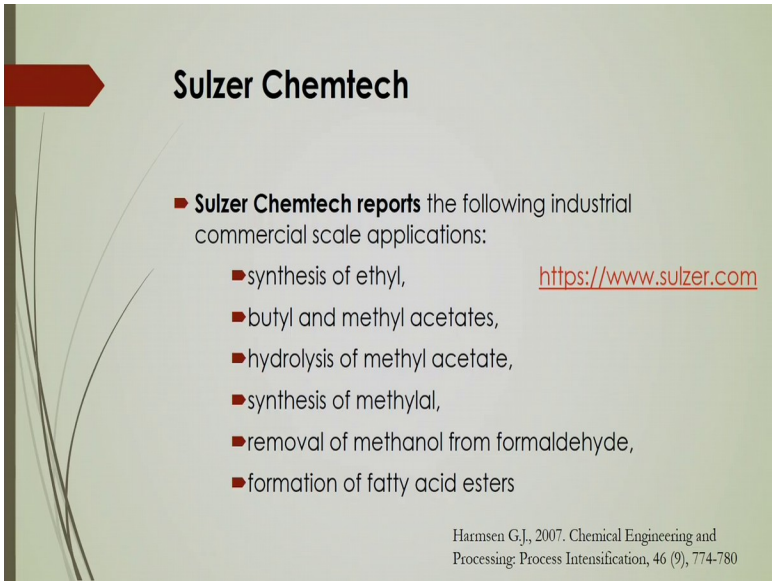

Even Sulzer Chemtech they have reported the polling industrial commercial scale applications like synthesis of ethyl, butyl and methyl acetates, hydrolysis of methyl acetate, synthesis of methylal and that removal of methanol from formaldehyde, even formation of fatty acid esters, so these are the process that is being carried out in reactive distillation and this reactive distillation system installed by this Sulzer Chemtech and it is also reported in 2007.

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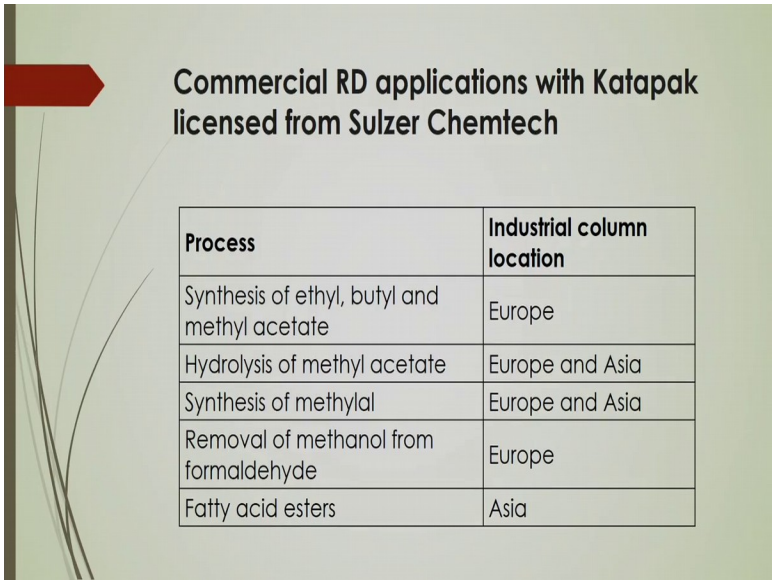

Commercial reactive distillation applications with Katapak licensed from Sulzer Chemtech, they have installed several also industrial units in different country like in Europe they have you know they have installed this unit for the synthesis of ethyl, butyl and methyl acetate.

Even for hydrolysis of methyl acetate, they also installed this unit in Europe and Asia and synthesis of methyl you know that they have also installed it in Europe and Asia and removal of methanol from the formaldehyde also fatty acid esters, they have commercialised this process based on this reactive distillation system in different country.

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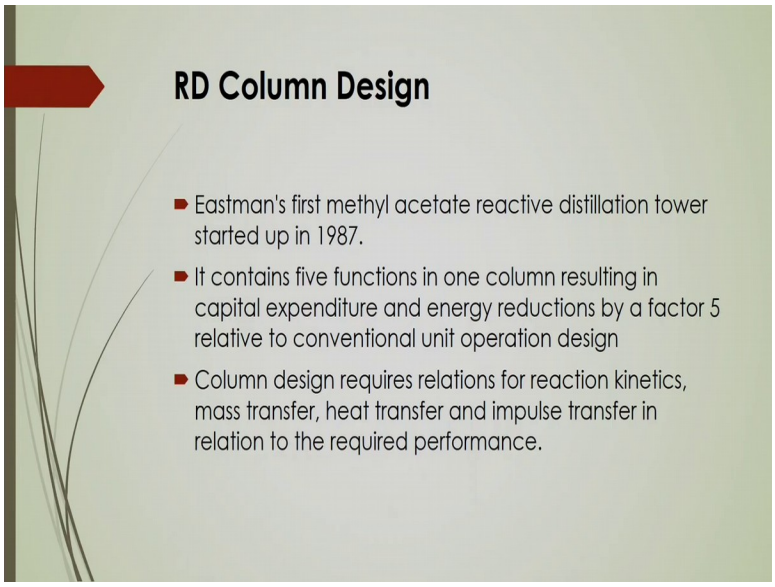

Now how to design that reactive distillation column? In this case something you have to remember that I am not giving that more details of the design aspect but some points you have to remember during that design aspect of this reactive distillation. So in that case Eastman's first methyl acetate reactive distillation they have started up in 1987 and in that case they reported that it will contain 5 functions in one column that will result in capital expenditure and energy reductions by a factor of 5 relative to conventional unit operation design, so they have designed in such a way they can get that more advantages that is 5 times of that overall that is relative to the conventional unit operation. And in that case column design requires relations for the reaction kinetics, mass transfer, heat transfer and impulse transfer in relation to the required performance.

So, whenever you are going to design any reactive distillation column you have to have the study of the reaction kinetics, what type of reactions you are going to perform in that reactive distillation column, that kinetic should be known. Even mass transfer during that reaction system you know that how reactive mass transfer is happened parallelly, mass transfer coefficient and based on which it will be designed and heat transfer of course will be that how heat will be distributed properly and based on the heat transfer study you can then assess this and also the design parameter in that case heat transfer coefficient is very important.

So that is why before going to design you have to study all those parameters and also interrelation of those transport processes like mass transfer, heat transfer, reaction kinetics, all those things but before going to that you have to study also the small scale you know that hydrodynamics of this flow characteristics in that particular reactive distillation system because anyway this hydrodynamic characteristics will actually effect on this reaction kinetics, mass transfer phenomena, heat transfer phenomena, so based on which you can design of this reactive distillation column.

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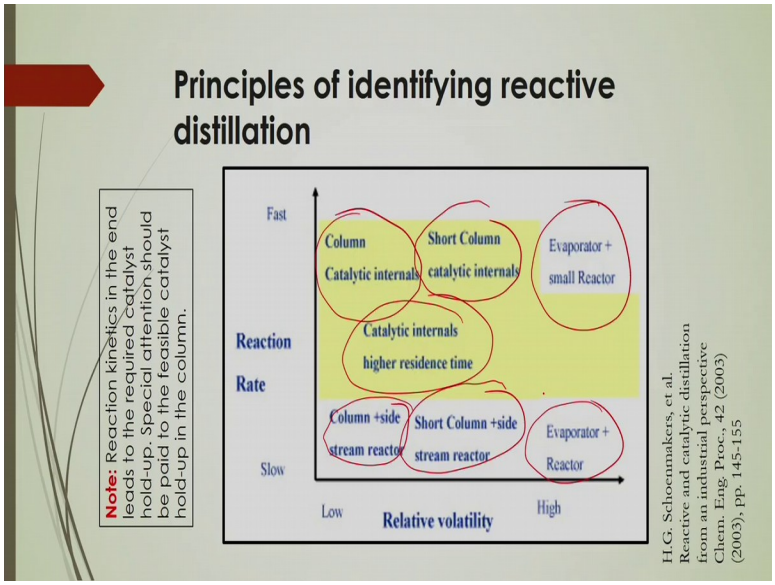

Now before going to that design aspect you have to know something that what type of you know that what type of reaction rate should be maintained or what is the reaction and what the rate of the reaction should be maintained based on the relative volatility of the components or reactants there. So, in that case sometimes you will see that some reactions will be fast, some reactions will be slow. So even sometimes relative volatility, sometimes it will be high and sometimes it will be low, so based on which you can that get some, infer based on this that table here or figure.

So here it is shown that reaction rate versus relative volatility, and the reaction rate may be slow to the fast and relative volatility should be low to higher and if you have that lower volatility components then if you want to do that first reaction, so you have to design this type of column where catalytic internals to be there. Whereas if you are having middle that is you know that the relative that is intermediate relative volatility, you can say that short column of catalytic internals can be done and, in that case, if you have that higher volatility of the first reactions then you have to design this evaporator plus small reactors.

And if you are having that intermediate rate of this reaction then you can design this type of catalytic internals higher resistance time where you can get those type of columns you can design based on this you know that intermediate range of relative volatility. For the slow reactions if you increase the relative volatility from low to high, then you have to design this type of columns like column with side stream reactors even short columns with side stream reactors, even for the high relative volatility you have to design that evaporator plus reactor there. So, in this case what you have to remember that reaction kinetics in the end that will leads the required catalyst holdup, special attention should be paid to the feasible catalyst holdup in the column and also you have to know that what should the relative volatility of the reactants that are being actually used for your reaction system.

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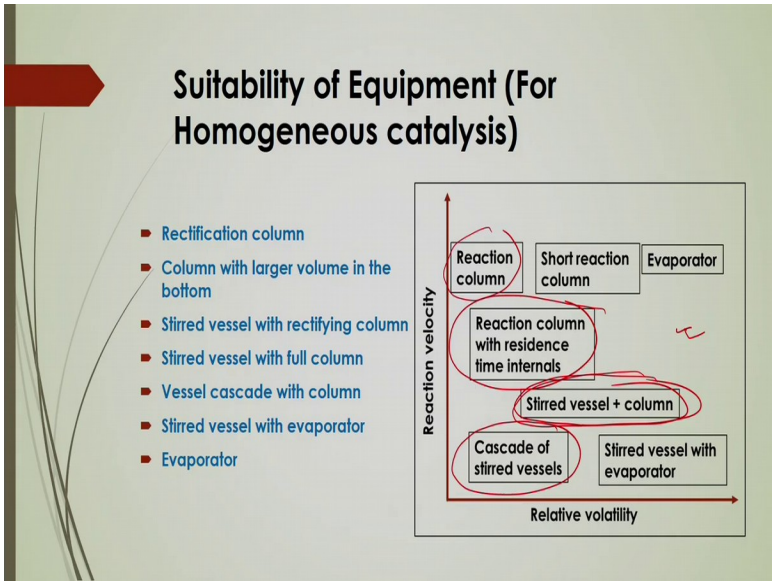

And also, suitability of the equipment for the homogeneous catalysts that is very important, you have to know that again that can be select based on that reaction velocity based on the relative volatility of the reactants there. In that case you will see that for high or fast reactions that reaction column should be designed like this for the low relative volatility and in this figure respective you know that at low to high volatility and reaction velocity according to that how you have to design this reaction column with the residence time internals. Even start vessel with the column should be designed, in that case you know that the immediate range of reaction velocity and if you are having that intermediate range of relative volatility then you have to use the stirred vessel with the column.

Whereas cascade type of stirred vessel you have to design when that relative volatility will be little bit low whereas reaction velocity will be slow, so in that case you have to use this

homogeneous catalyst, so this catalytic reaction will be you know that there. So, rectification column should be there, column with larger volume in the bottom, stirred vessel with the rectifying column, stirred vessel with the full column, even vessel cascade with column, stirred vessel with evaporator and evaporator all those units should you know that conjugated they are based on their reaction velocity and relative volatility.

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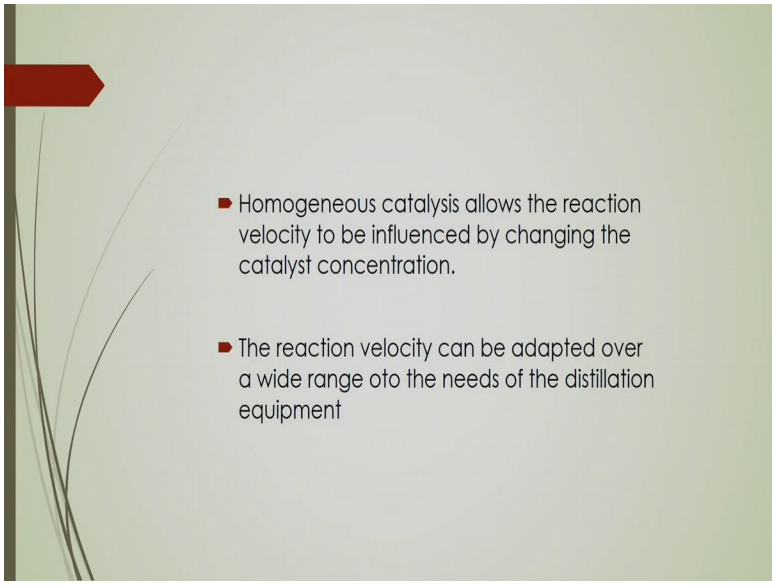

And the homogeneous catalysis allows the reaction velocity to be influenced by the changing of the catalyst concentration and the reaction velocity can be adapted over a wide range to the needs of the distillation equipment.

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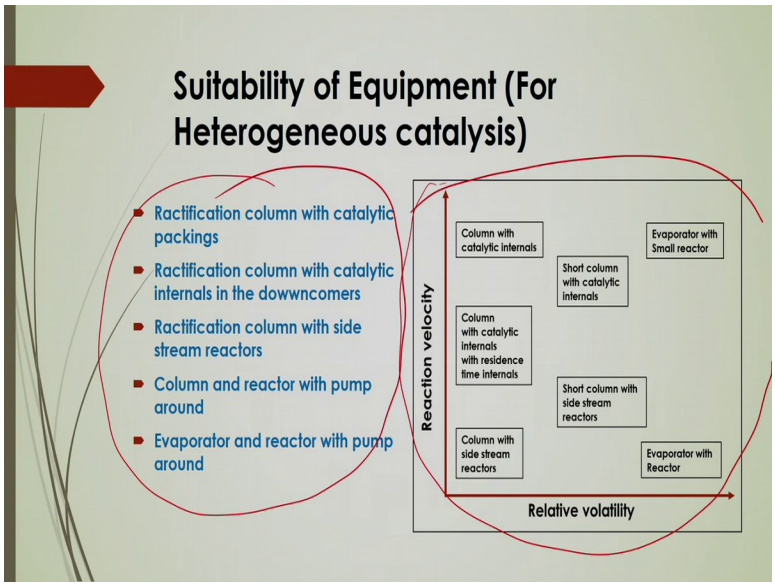

Whereas in case of heterogeneous catalysis, there you can design that rectification column with catalytic packings, rectification column that is distillation column with the catalytic internals in the dowwncomers and reaction, side reaction that rectification column will be designed, even column and reactor with pump around also can be designed and evaporator and reactor with the pump around also you can design for that reaction, that will be based on that relative volatility.

So, all those options you have to design based on that reaction velocity and relative volatility for this heterogeneous catalysis there, so this figure will give you that when actually you have to design the short column with the catalytic internals, in that case you have to consider that our intermediate range of relative volatility and of first reaction. Similarly, others also you can get or you can assist before going to design of any reactive distillation column.

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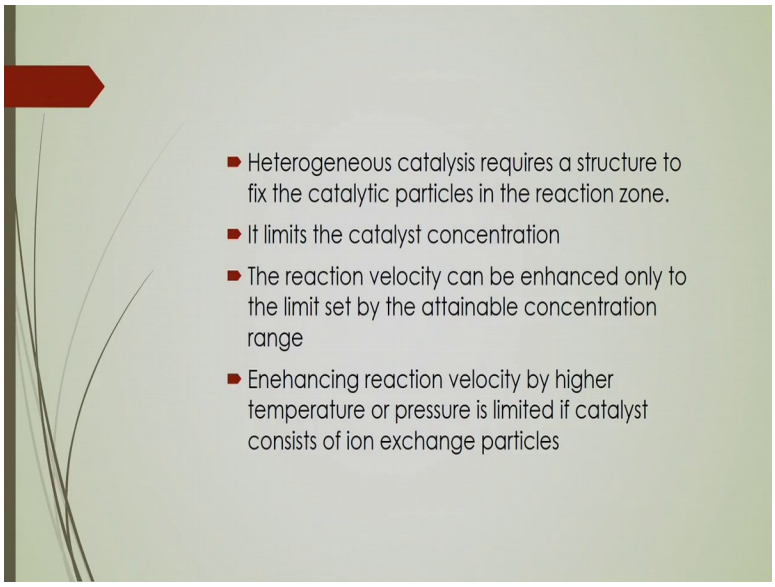

In this case this heterogeneous catalysis that will require a structure to fix the catalytic particles in the reaction zone and it may limit the catalytic reactions based on their catalyst concentration and the reaction velocity can be enhanced only to the limit if you set by the attainable concentration range and enhancing the reaction velocity by higher temperature or pressure that will be limited if the catalyst consist of ion exchange particles are there.

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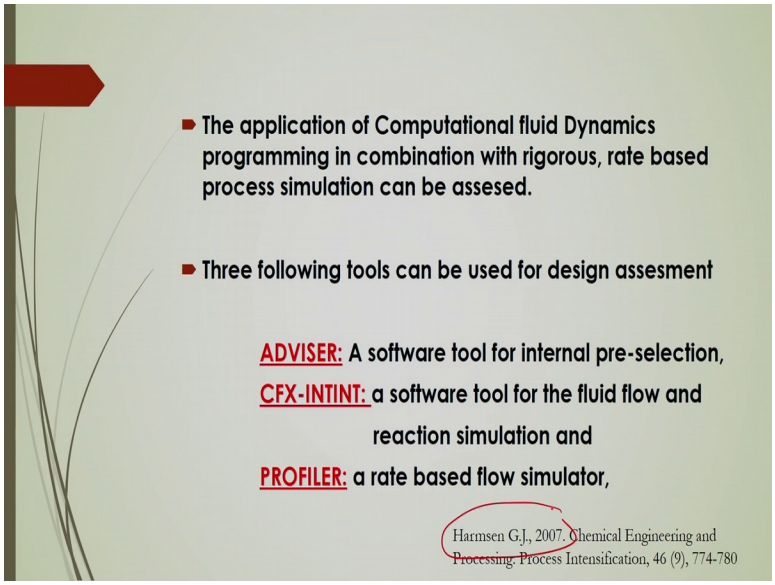

And the application of computational fluid dynamics programming is one of the important components of design of reactive distillation column. By this computational tool you can assess what should be the internal structure of that reactive distillation column based on the fluid flow operation there, so before assessing for the design of the reactive distillation column you have to do that analysis by the computational fluid dynamics programming in the combination with rigorous rate-based process simulation there.

So, three following tools can be used for the design assessment there, it is called advisor that is a software tool for internal pre-selection, CFX-Intint there is software tool for the fluid flow and the reaction simulation and also Profiler is also one of the important simulators that is rate based flow simulator. So, you can get more information on this software based design assessment that is given in this volume of this chemical engineering and process intensification of here in this Journal that is reported by this Harmsen in 2007.

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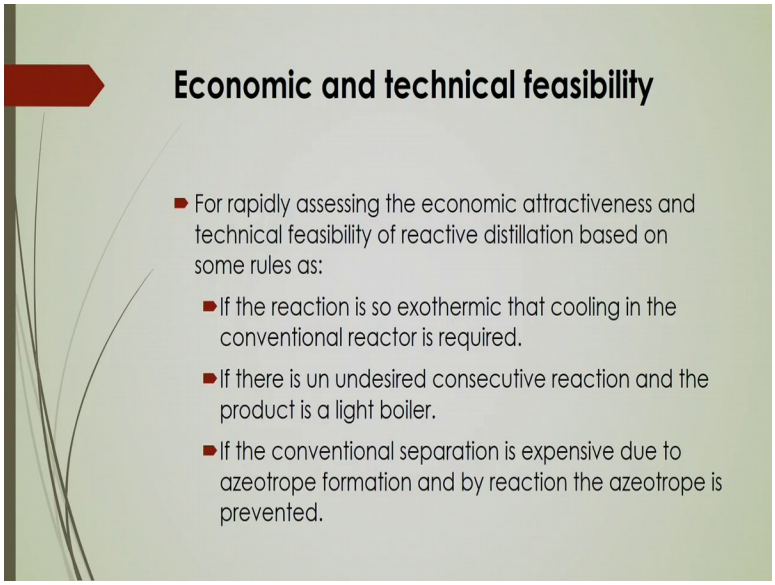

Even you will see that whenever you are going to design a reactive distillation column you have to think about how this design will be economic or how this technically it will be feasible. So, for rapidly assessing the economic attractiveness and technical feasibility of the reactive distillation column based on the some you know that rules will be there, so in that case if the reaction is so exothermic that cooling in the conventional reactor is required, so you have to design in that direction.

If there is undesired consecutive reaction and the product is a light boiler, so in that case you can design you can think in that case that how to minimise that you know undesired product by getting that suitable reaction mechanism and if the conventional separation is expensive due to the azeotrope formation and by reaction in the azeotrope then you to sometimes prevent that azeotropic reaction there for the conventional separation. So, the conventional separation it will be expensive because of that azeotrope formation, so you have to prevent before going to that design for that economic way of having those designs.

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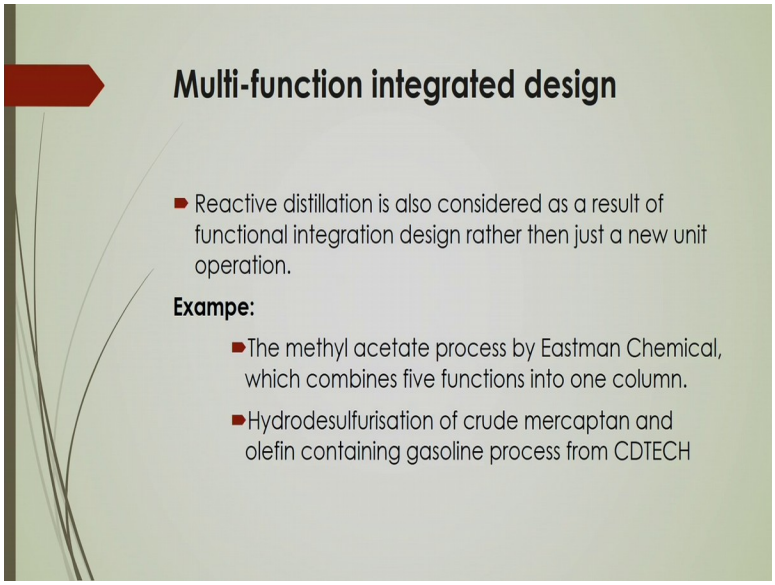

And then multifunctional integrated design is also another component for the design of this reactive distillation column, so in that case reactive distillation is considered as a result of functional integration design rather than just a new unit operation there, so in that like example as this that the methyl acetate process by Eastman Chemical which combines five functions into one column and for hydrodesulfurisation of the crude mercaptan and olefin containing gasoline process from the CDTECH that you can have this idea for this multi-functional integrated design.

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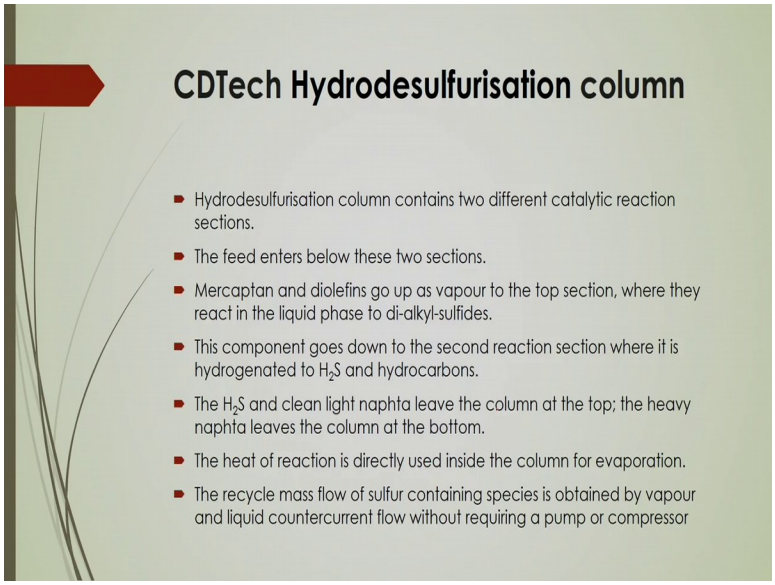

CDTech hydrodesulfurisation column, in that case they are designs as per their design this hydrodesulfurisation column contains 2 different catalytic reaction sections. The feed enters

below these 2 sections. Mercaptan and diolefins go up as vapor to the top section where they react in the liquid phase to di-alkyl-sulfides and this competent goes down to the second reaction sections where it is hydrogenated to hydrogen sulphide and several hydrocarbons. And the hydrogen sulphide and clean light naphtha that leave column at the top and the heavy naphtha leaves the column at the bottom and in that case the heat of reaction is directly to be used inside the column for the evaporation system and the recycle mass of sulphur containing species is obtained by vapour and liquid countercurrent flow without requiring any pump or compressor there.

So as per their CDTech you know hydrodesulfurisation column it is actually to be noted that how actually they are considering that design of that reactive distillation system. So, I actually discussed here just simple what is that reactive distillation column and how in different way or based on the different mechanism even integration way that this reactive distillation column can be intensified for the different chemical engineering processes, for reactions as well as separations in the distillation column.

In the next lecture we will discuss something more about that what are the different types of that distillation column based on this level of process intensification and what are their advantage, disadvantage and also in which mechanism they are working and how we can get the benefit from those different types of intensified unit of this reactive distillation system.

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I would suggest you to read further from this reference work to get more information about this reactive distillation column with even ample of examples of reactions system for this reactive distillation mechanism. So, thank you for this lecture today.