Chemical Process Intensification
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Lec_06
Intensification in reactive system

So welcome to massive open online course on chemical process intensification. So in this lecture we will discuss about intensification in reactive system. In the previous lecture we have discuss the various aspects of process intensification, based on the mixing characteristics, so along with that mixing characteristics how the process can be intensified in the reactive system, will discuss some the more about that.

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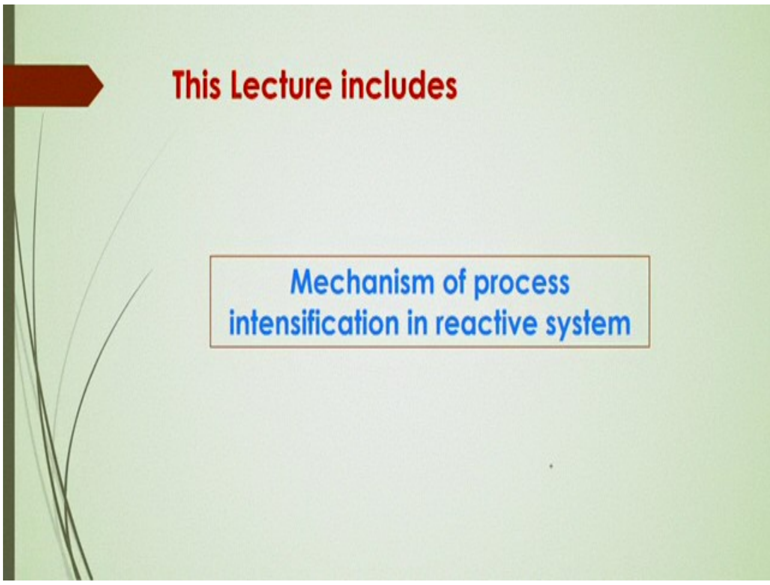

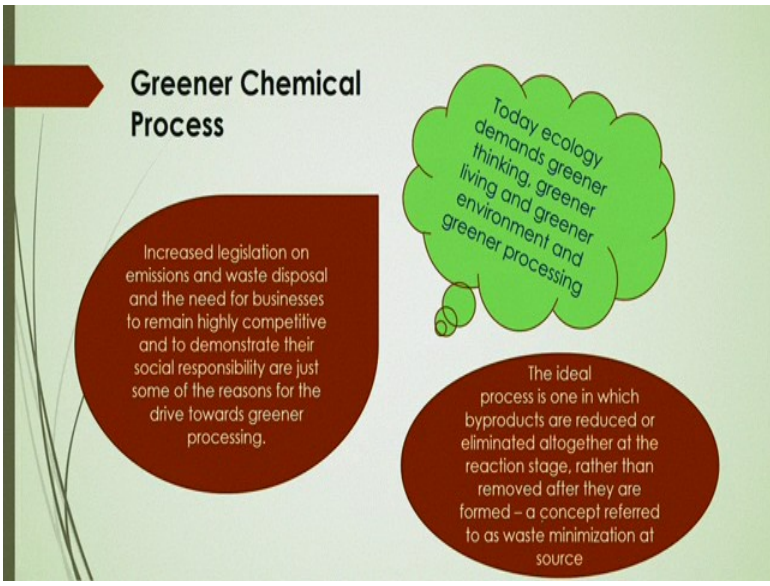

So, this lecture includes the mechanism of process intensification in reactive system, you know that, nowadays increased legislation on emission and the use of waste and also disposal of the waste and also the need for businesses to remain highly competitive environment and to demonstrate its product to the society, you know that some important reasons for the drive towards the greener processing.

So greener processing nowadays is coming because of that environmental impact of different by-products which are coming during the reactive system and for that you have to take some measurement as per legislation act, that you have to produce the by-products or products in such a way that some hazardous material which are coming out as a by-product should be minimized or should be removed.

So today ecology actually demands that thinking of that process intensification, how it can be done to reduce that hazardous materials which is coming out as a by-product in reaction system in a particular process. So nowadays, the peoples are thinking our greener way and how to actually people can live in greener way, that is greener living and also in a greener environment by developing some process in the chemical industry, which products being actually used in our daily life.

So, the ideal process in which by-products are reduced or eliminated altogether at the stage of reactions, so in that case, if you are developing some process where by-products are coming at its reaction states can be actually eliminated or reduced rather than removed after they are formed and that concept should be developed and that concept are called that why is minimization concept at source. So, this is the, you know that thinking nowadays to shift the conventional process to the greener process where you can get that more greener living, more greener thinking and greener environment and also greener, you know that sustain the development in the society

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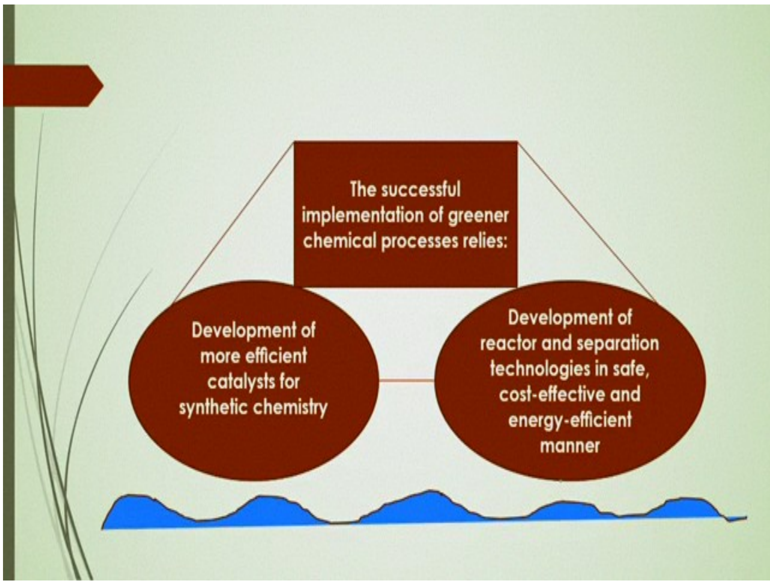

And the successful implementation of the greener chemical process actually relies on that development of more efficient catalysts for the synthetic chemistry, because whatever products will be produced by a certain process, you know that chemistry works behind, so as per you know synthesis by the chemistry the products that you have to, you know develop some more efficient catalysts for the synthetic chemistry, so that you can get less number of hazardous materials for that particular synthesis process.

And another aspect is to develop the reactor and separation technologies which will be more safer and cost-effective and also energy efficient, so you have to implement the greener chemical process based on this is two concepts, first is development of more efficient catalysts for the synthetic chemistry and development of reactor and separation techniques in safe, cost-effective and the energy efficient manner.

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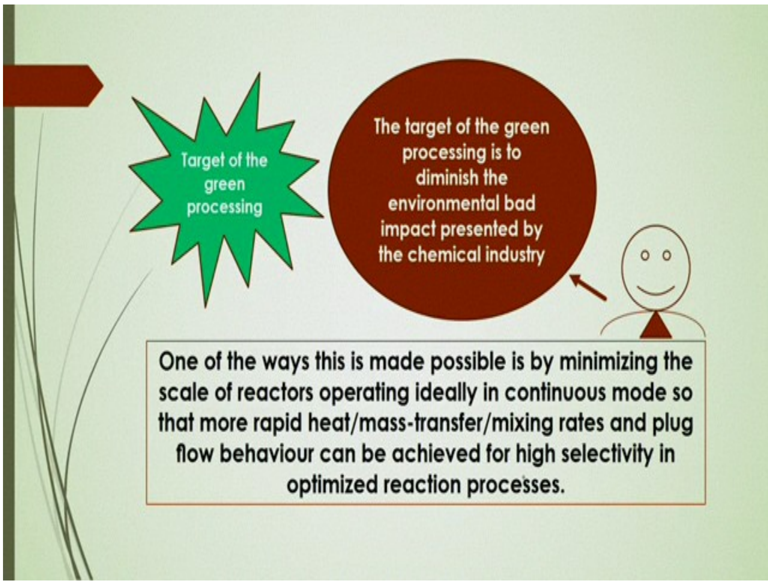

Now main target of that green processing is to diminish the environmental bad impact that is processed by the chemical industry and one of the ways which can be made possible is by minimizing the scale of reactors, operating that will be ideal in continuous mode, so that more rapid heat and mass transfer even in mixing effects and plug flow behaviour can be achieved and also for high selectivity in the optimised reaction processes can be achieved.

So, the target of the green processing that actually includes the way of thinking of that minimizing the or scale or you can say that, you know that minimizing the back mixing in the operating system or making the plug flow of system where you can get that products with high selectivity and at an optimized reaction process in a continuous mode.

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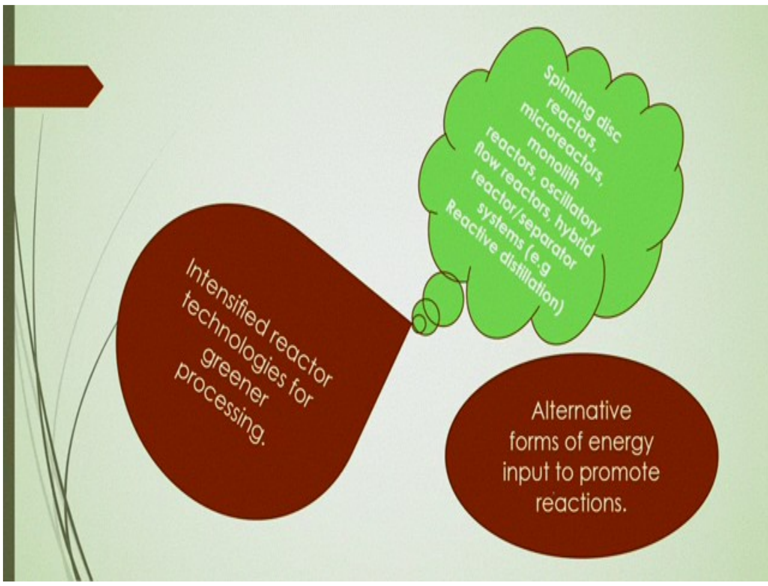

And you know that there are several reactors are being developed nowadays industries based on that, you know that optimization of this separation techniques and also you can say that reaction systems, so in that case, some intensified reactors technologies for the greener processing are being developed and, in that case, you have to you some alternative forms of energy to promote that reactions.

And like in that case, several reactors here spinning this reactors, micro reactors, monolith reactors, oscillatory flow reactors, hybrid you know that reactors or separator systems like you know the reactive distillation, a reactive extraction system, those are important phenomena, where that you know intensified reactor technology can be used for the greener processing by using that, you know that alternatives forms of energy to promote that reaction into the reactor system.

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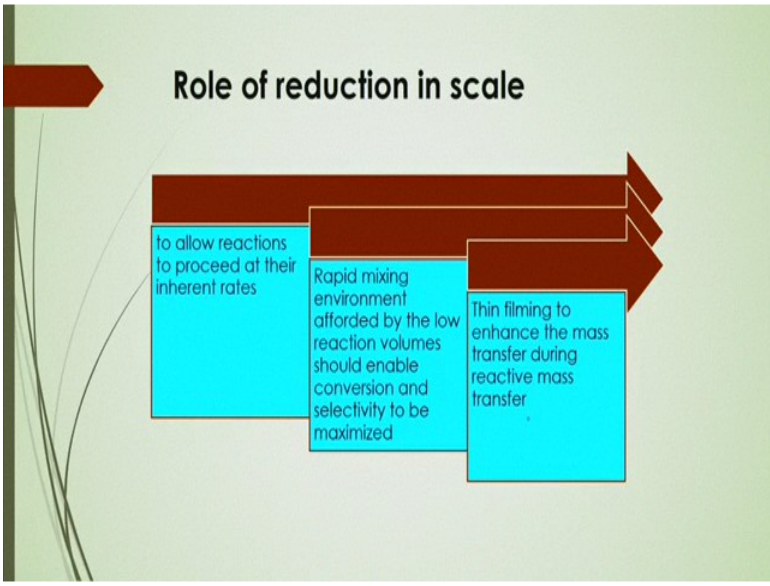

Now, what should be the role of reduction in scale? It generally allows the reactions to proceed at their inherent rates and also rapid mixing environment that afforded by the low reaction volumes that should enable conversion and selectivity to be maximized, also you know that if you reduce the scale of the reactor just by making, like that microchannel based reactor, in that case, thin film will be produced to enhance the mass transfer during the reactive mass transfer operation.

So, the reduction in scale has some role to proceed the reactions in there, you know that inherent rates and also the reducing the back mixing and also increase the, you know mixing phenomena afforded by low reaction volumes and also conversion and selectivity can be actually obtained at the, its maximized stage and also that you know, thin film produced to get enhance mass transfer during the reactive operation system.

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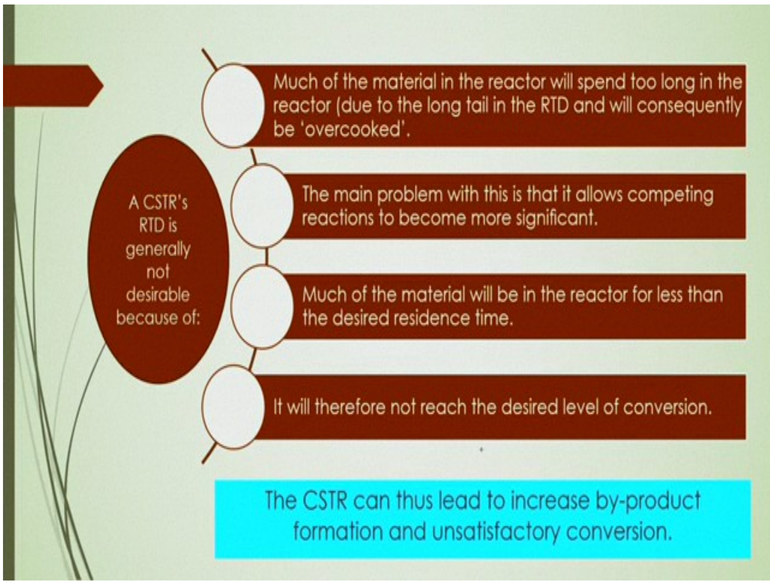

Now, as of now know that there are several, you know reactors are produced for the process intensification for this reactive system, earlier, you know that generally that CSTRs are being used for that reactive system, nowadays it is not desirable because of some reasons, because this CSTRs that is continuous starting reactors, whatever RTD is generally we are getting by that, you know CSTR that is not a desirable because mass of the material in the reactor will spend too long in the reactor due to the long tail in the RTD profile and will consequently be, you know that the overcooked sometimes the reactive system.

And the main problem with this is that it allows competeting reactions to become more, you know significant and also you can say that it will not give you that desired level of conversion and mass of the material will be in the reactor for less than, you know that desired residence time, because in a maximum cases for a high rapid mixing will give you that, you know that small-scale system, if you are having the larger scale, there may be you know that radial distribution of the liquid element and in that case, you know that back mixing is, you know, sometimes will hinder the selectivity of the or you can that yield of the reaction and in that case, that is desired to actually reduce that you, you know back mixing and getting the higher residence time and it can be possible only by reducing the scale.

So CSTRs are not actually nowadays that is important because as per process intensification concept, there are several, you know that different type of reactors that is reactions can be by, you know carried out just by reducing the size and also making the thin film of the fluid element through which that mass transfer can be achieved more, you know intensified way.

And CSTR can thus lead the increase by-product formation and unsatisfactory conversion in that case if you are getting that back mixing in that case, you can get more, some other by-products and also it may reduce the yield of the reactions, so that is why that unsatisfactory conversion may actually, you know that give you or you can get by this CSTR, so it cannot be actually suitable nowadays for the process intensification.

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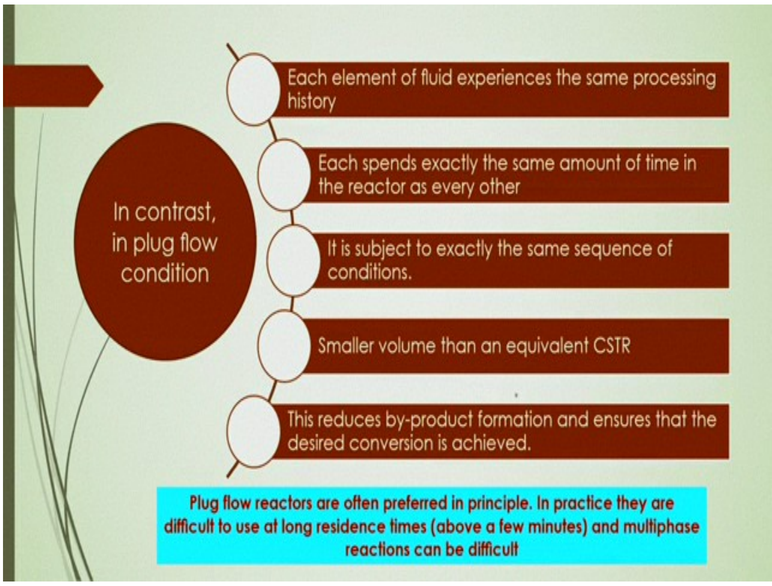

Now, in contrast of this plug flow condition, you will see that we can reduce that back mixing and, in that case, more residence time also can be obtained. Now each element of the fluid that will experience the same processing history and also each molecules will spend exactly the same amount of time in the reactor as every other and it is subject to exactly the same sequence of conditions and also by, you know that in plug flow condition, smaller volumes than an equivalent CSTR will give you the advantage of that, the yield of the reaction and also the plug flow systems, this will reduce the by-product formation and ensures that the desired conversion can be achieved.

So, plug flow reactors are often preferred in principles. In practice, they are difficult to use at long residence times above a few minutes, you can say and multiphase reactions can be difficult, so all reactors have some advantage and disadvantage, though it has the reduction in back mixing and it can give you the better yield, but sometimes you know that handling of this, you know micro scale reactors, it is very difficult and also multiphase processing also difficult in this type of reactors.

So only for single phased flow, it is sometimes okay, fine was, suppose in higher scale even you know that, large scale system also it is not possible. So, some suitable, you know the chemical engineering processes, where this plug flow phenomena can be actually utilised as a process intensification and in that case, you know it will be suitable for that particular long residence time and also you know that for smaller volume handling of that particular processes.

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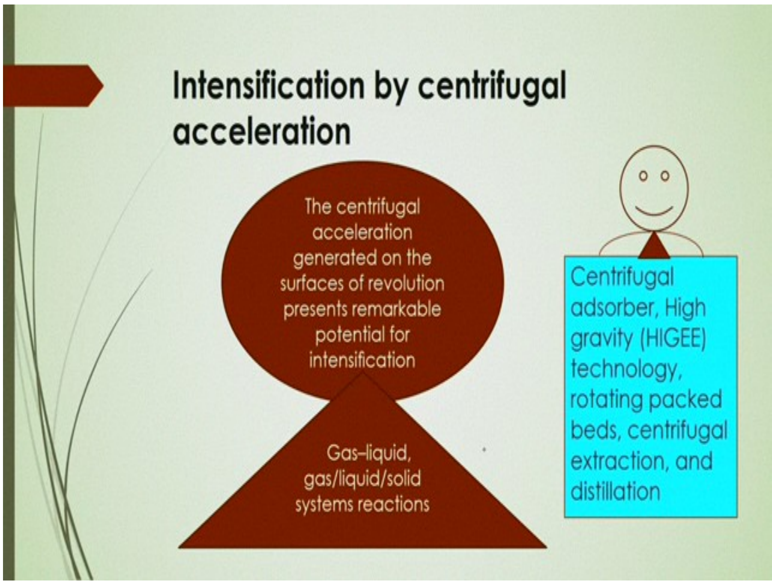

And some other processes in reactive systems, some other mechanism also possible to intensify the reactive system in chemical engineering processes, like you know that centrifugal acceleration is one of the important, you know mechanism by which you can intensify the process, like the centrifugal acceleration that generated on the surfaces of the revolution that represents remarkable potential for the intensification.

Like in that case by this centrifugal acceleration you can handle the multiphase, you know reactions also gas liquid, gas liquid, solid system reactions, so whereas the plug flow systems, you know one-dimensional system in that case, it is very difficult to handle that multiphase processes, wherein centrifugal acceleration system, it is possible in both 2 and 3 phase systems. Like centrifugal adsorber, high gravity technology, rotating packed beds, centrifugal extraction or you know that distillations are the some important, you know that technology and some, you know unit where you can process multiphase system at its reaction condition.

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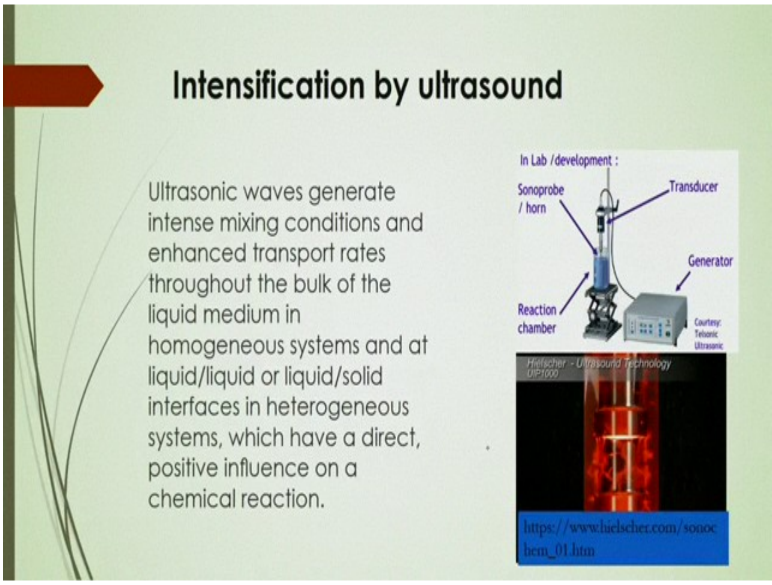

Now another important mechanism, it is called ultrasound system for the process intensification. In this case, you know ultrasonic waves that will generate the, you know intense mixing conditions and enhanced the transport rates throughout the bulk of the liquid medium in homogeneous systems and at, you know liquid, liquid or liquid, solid interfaces in heterogeneous systems, so which have a direct, you know that positive influence on a chemical reaction.

So main important thing is that, ultrasonic waves are being used to generate the interfaces between the, you know phases, like if you are handling that gas liquid process or liquid-liquid process, so this ultrasonic waves will generate that, you know drop or bubbles where that you can get that interfaces between the phases, so that phase through that, you know that interfaces, this mass transfer system happen.

Even sometimes it is advantageous for, you know that some systems where liquid liquid or liquid solid interfaces to be produce in heterogeneous system, it is sometimes, you know that advantageous. Even some you know only single bulk liquid medium where homogeneous systems are to be produced by these ultrasonic waves for gas liquid operation to distribute the gas throughout the liquid medium, in that case, this ultrasonic wave also advantageous.

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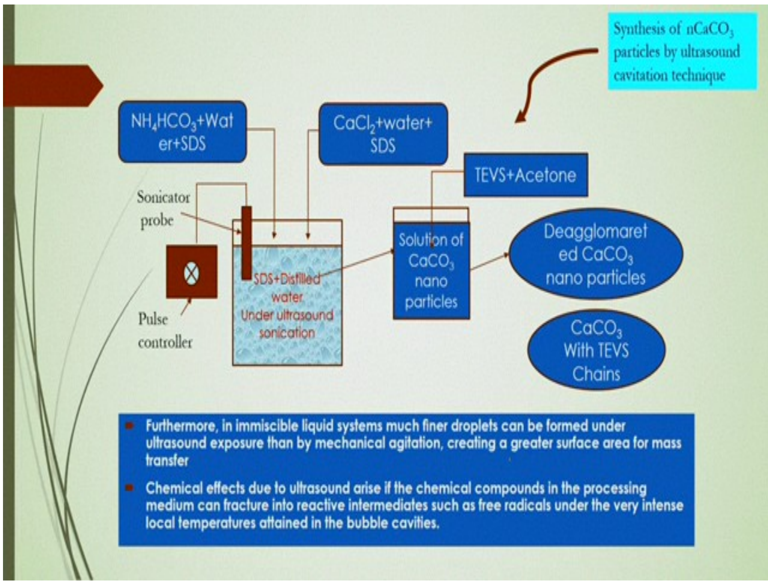

And like example in this case of, you know a nano particles of calcium carbonate particles by ultrasound cavitation techniques. In this case, you know that the immiscible liquid system produces fine droplets and this can be formed under ultrasonic exposure, then by mechanical agitation, you know that creating generating surface area for mass transfer. And in that case chemical effects that due to ultrasound, in that can arises if the, you know chemical compounds in the processing medium can fracture into, you know reactive intermediates, such as free radicals to be produced under the very intense local temperatures attained in the bubble cavities.

So, this is the way any one synthesis process given in the slides by which can produce that calcium carbonate and nano particles, here in this case, you know pulse controller to be used to generate that ultrasound waves by sonicator probe and in that case, some input and outputs are given in the slides, so please go through this process by which you can get this calcium carbonate particles.

Here two solutions are to be use, solution one known as ammonium bicarbonate and waters and with SDS and also solution two calcium chloride and water plus SDS to be used in a, you know that distilled water under ultrasound condition, in presence of, you know some surfactants, so that you can produce more interfacial area there in the reactor.

And after that if you get this solution after this sonication reaction, then solution of calcium carbonate nano particles can be produced and if you mix some TEVS and acetone in that solution, you can get the, you know that agglomeration and then you have to deagglomaret that calcium carbonate nano particles to get its, you know that calcium carbonate with TEVS, by you know chains. So, in this way, you know, you can do some reaction in this ultrasound environment.

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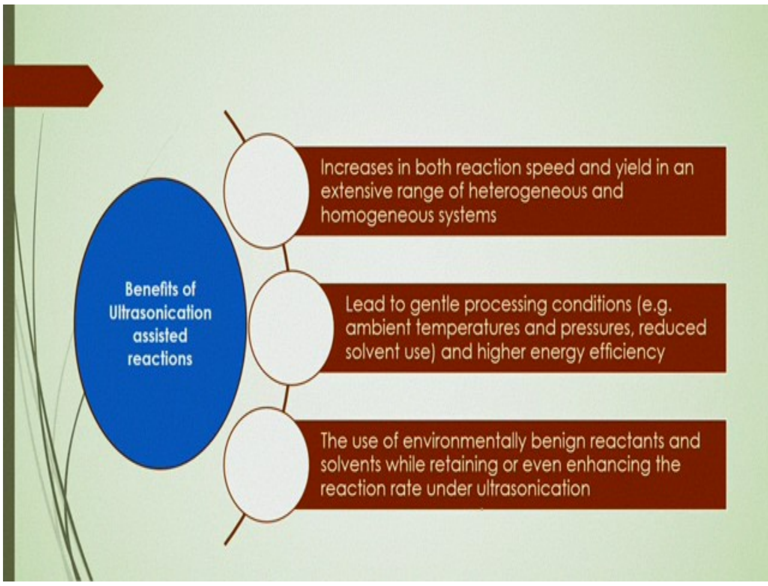

And benefits of this ultrasonication assisted reactions are the increase in both reaction speed and yield in an extensive range of, you know heterogeneous and homogeneous systems and it will lead to gentle processing conditions, that is, you know that ambient temperatures and pressures, reduced solvent use and also higher energy efficiency, it will also give the benefits of the use of environmentally, you know that benign reactants and you know solvents, while you know retaining or even enhancing the reaction rate under ultrasonication.

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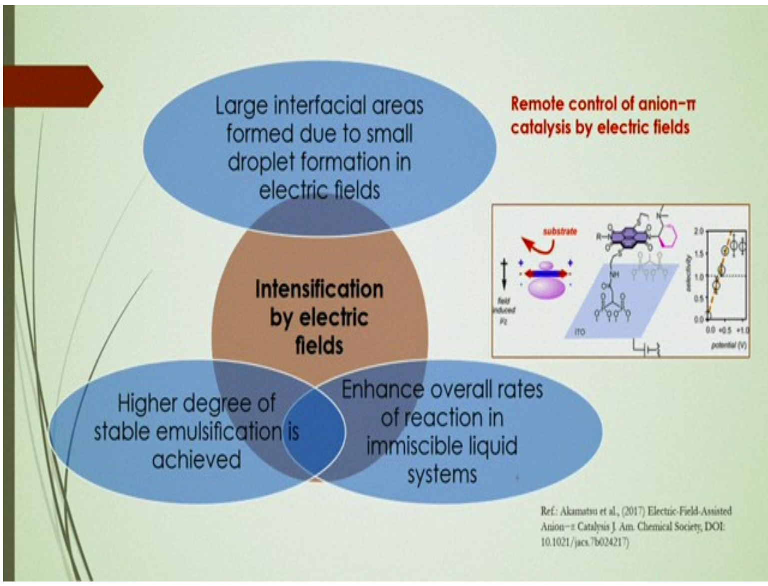

So, in that case you will see that many important aspects of that ultrasound is that to generate the interfacial area, through which the reaction and mass transfer will be happened parallelly. Now another important mechanism, it is call that electric fields, you can apply the electric fields to, you know intensify the reaction, in that case again that by this electric fields you can produce large interfacial areas and by producing, you know small droplet formation, in that case, you know higher degree of stable emulsions can be, you know achieved and also it can enhance the overall rates of reaction in immiscible liquid systems.

So, formations in, you know that the droplet formations, small droplet formations will give you the larger interfacial area in electric fields and based on which you can intensify the reactions by producing, you know that stable emulsions in the system, like here, you know example, remote control of anion pie catalysis by electric fields which is one example there.

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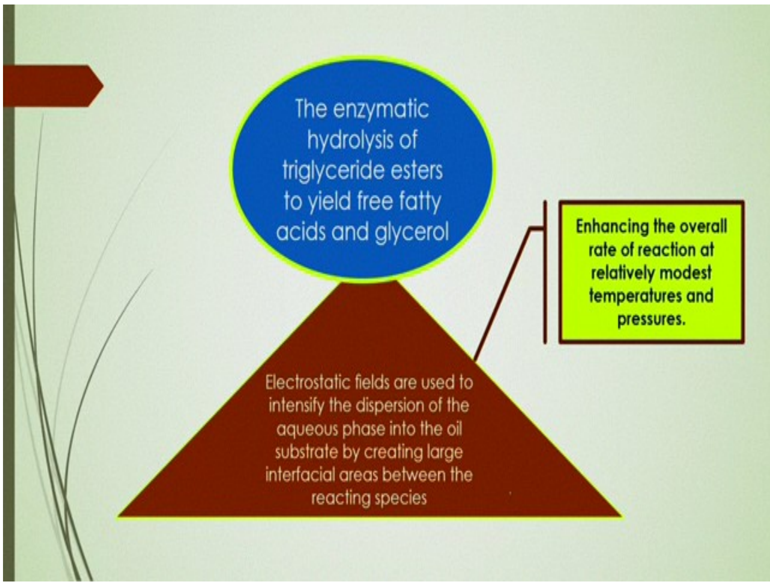

And another example of electrostatic fields which are being used to intensify the dispersion of the aqueous phase into the oil substrate by creating large interfacial areas between the reacting species, like enzymatic hydrolysis of triglyceride esters to yield free fatty acids and glycerol in that case, you can produce droplet of, you know that aqueous phase in the oil substrate and also produce a large interfacial area between this reactive species by this electric field. So, in that case, enhance the overall rate of reaction at relatively modest temperatures and pressures.

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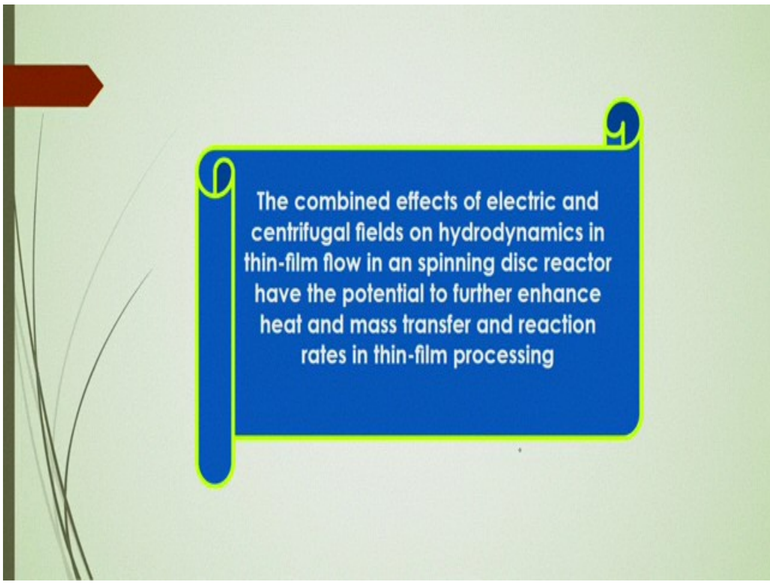

And also the combine effects of electric and centrifugal fields on hydrodynamics in thin film flow in and spinning disc reactor have a, you know that greater potential to further and hence heat and mass transfer and reaction rates in thin film processing, so you know that not only producing that interfacial area by making that, you know that why immiscible phase particles but you can increase the heat and mass transfer or reaction by producing the thin film without producing that droplets of bubbles there also, so in that case combination of electric and centrifugal fields that can be used for this hydrodynamic, to produce the thin film flow in a spinning disc reactors.

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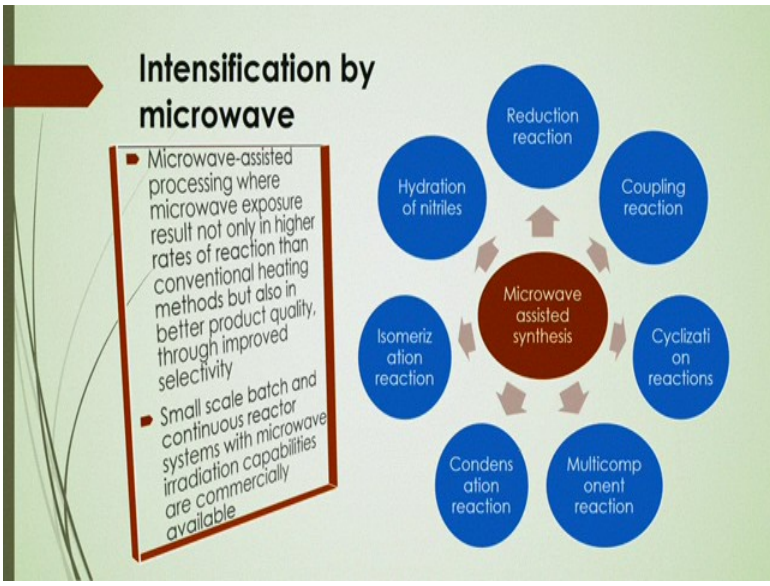

Another important mechanism, it is called that microwave using for the intensification of the process in chemical engineering process, like you know that microwave sometimes assist the process where microwave exposure results not only in higher rates of reaction than conventional heating methods, but also in better product quality through improved selectivity. Now in that case, you know that small scale batch and continues reactor systems with microwave irradiation capabilities are, you know commonly used in commercially sectors nowadays.

So, some you know that microwave assist synthesis has some advantages like, you know that some reactions are being happened by this, you know, microwave system, microwave assisted, synthesis process, like reduction reaction, like coupling reaction, cyclization reactions and also, you know that multicomponent reaction, condensation reaction, even isomerization reaction, even hydration of nitriles, all these reactions are based on this microwave assisted synthesis, where you can get the intensification compared to the conventional process.

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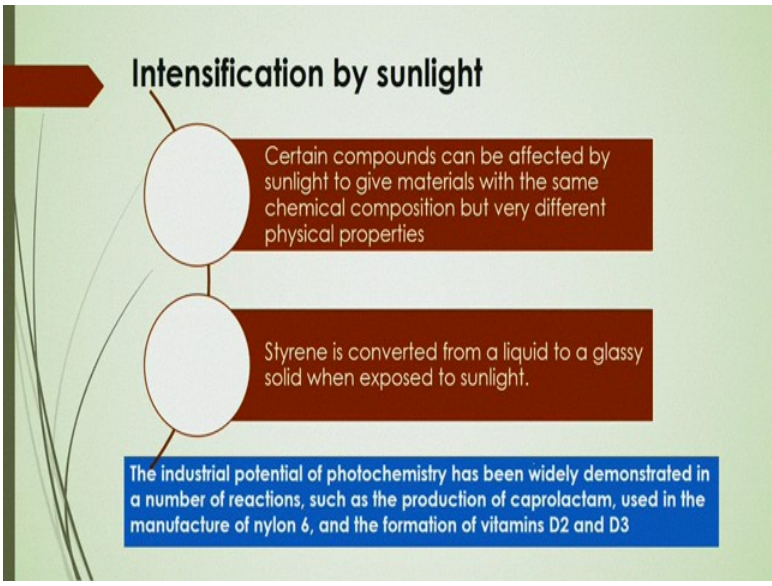

Now if you use the sunlight also, there may be you know that intensification of the reactions, like certain compounds that can be affected by sunlight to give materials with the same chemical composition, but very, you know different physical properties, like styrene is converted from a liquid to a, you know glassy solid when it will be exposed to the sunlight.

So in that case, you know that a photochemistry that is potential of a photochemistry has been widely demonstrated in industrial sectors, in a number of reactions like, such as production of, you know caprolactam that is used in the manufacture of nylons 6 and the formation of vitamins D2 and D3, so sunlight assisted, you know that reactions is also one of the important, you know figure in the intensification of the process in chemical industry.

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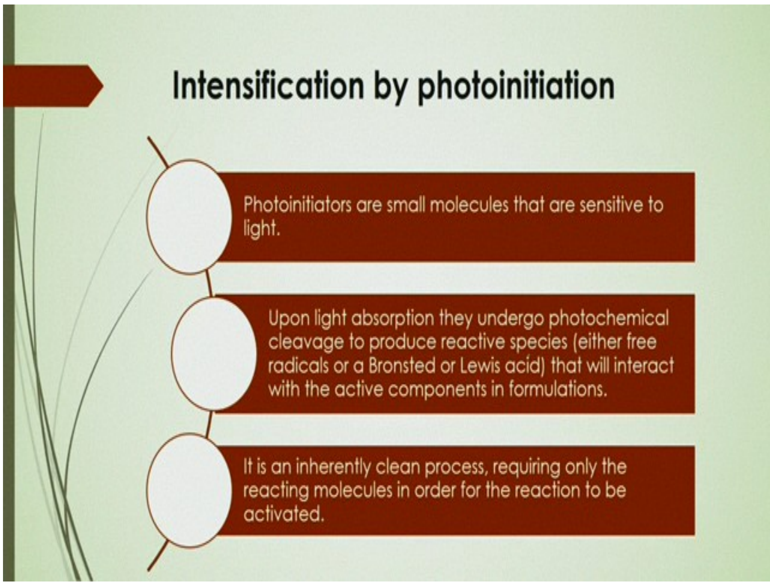

Another important mechanism, it is called photo, you know initiation, in that case, small molecules that are sensitive to the light, in that case, photoinitiators are being used to make the small molecules to sensitive to the light and upon light absorption on the molecules they undergo, you know photochemical cleavage to produce reactive species either free radicals or you can say that Bronsted or Lewis acid is called, that will interact with the, you know active components in formulations.

So it is an inherently, you can say that a clean process and requiring only the reacting molecules in order for the reaction to be activated, so photoinitiation is also one of the important, you know process intensification in chemical industry, where molecules are being actually undergo the photochemical cleavage to produce the reactive species by absorbing the, you know sunlight or some other light also, not only sunlight that you can say some, you know that light, light also you can use for that, so it is an inherently clean process, where you can produce the products without having a so much, you know that hazardous materials and in that case, requiring only the reacting molecules in order for the reaction to be activated there.

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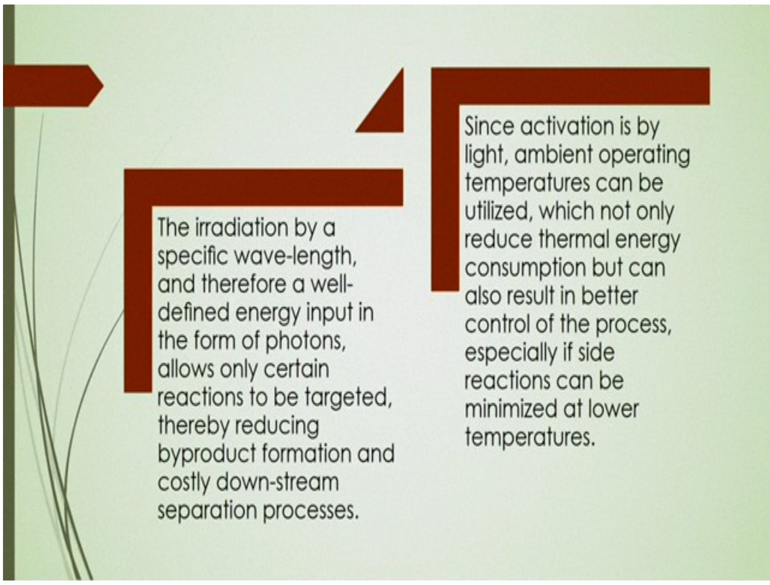

Now, the irradiation by a specific wavelength and therefore a well-defined energy input in the form of photons which is required and which will allow only certain reactions to be targeted, thereby reducing by-product formation and costly down-stream separation processes, since activation is by light, the ambient operating temperatures can be utilized, which not only reduce that thermal energy consumption, but can also result in better control of the process, especially if there any side reactions are there not and can be minimized at lower temperatures in this case.

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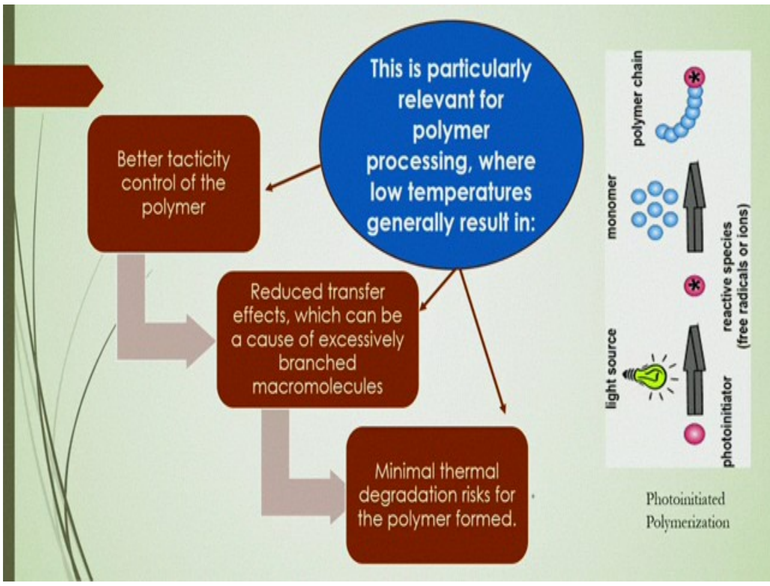

And this is particularly relevant for, you know that polymer processing, where low temperatures generally resulting, like better tacticity control of the polymer, you know reduced transfer effects and also which can be a cause of, you know excessively branched macromolecules and in this case, you know minimum thermal degradation risk for the polymer formed can be achieved, so that is why particularly it is relevant for this polymer processing for this photoinitiated that polymerization.

So, in this case you will see the schematic of this photoinitiated polymerisation given in the slide, your light sources are being used in a photoinitiator after that, reactive species will be formed based on this absorption of this photon and free radicals or ions will be formed, and then the monomer this polymer chain will be formed based on this reactive environment.

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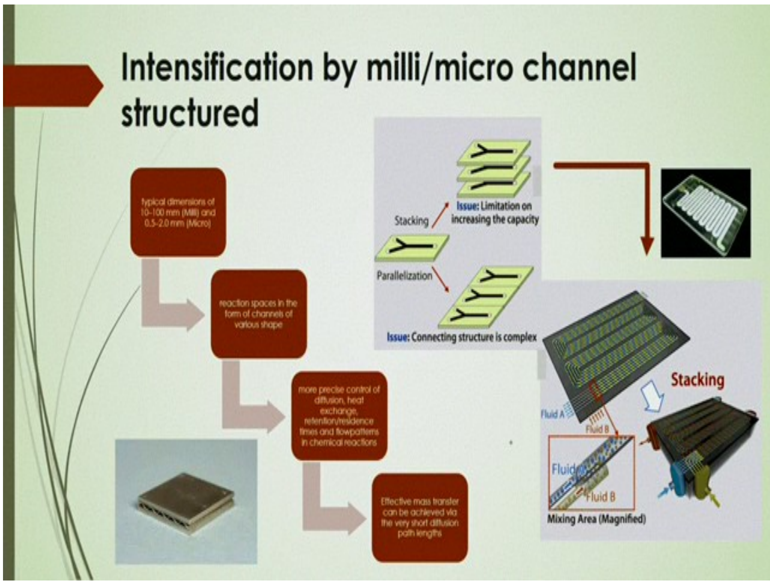

Now, intensification by milli or micro channels structured, you know, one of the important aspects of this process intensification, that already you have discussed that producing the plug flow phenomena and the residence time, intense of the residence time and also reducing the back mixing there and it is being important, so that milli and micro channel structured reactors are being used for the intensification of the process.

Like typical dimensions of this, you know milli or micro channel based reactors are 10 to 100 millimetre for milli channel and 0.5 to 2.0 millimetre for microchannel reactors and in that case reactions species in the form of channels of the various shapes can be actually, you know developed or can be used and also that more precise control of diffusion can be done, heat exchange can be, you know actively obtained and retention and residence time and flow patterns in chemical reactions can be, you know that achieved based on this milli or micro channel structure reactor. And here in the slide some diagrams are shown here, the some, you know that how this micro channel based or milli channel-based reactors are being developed.

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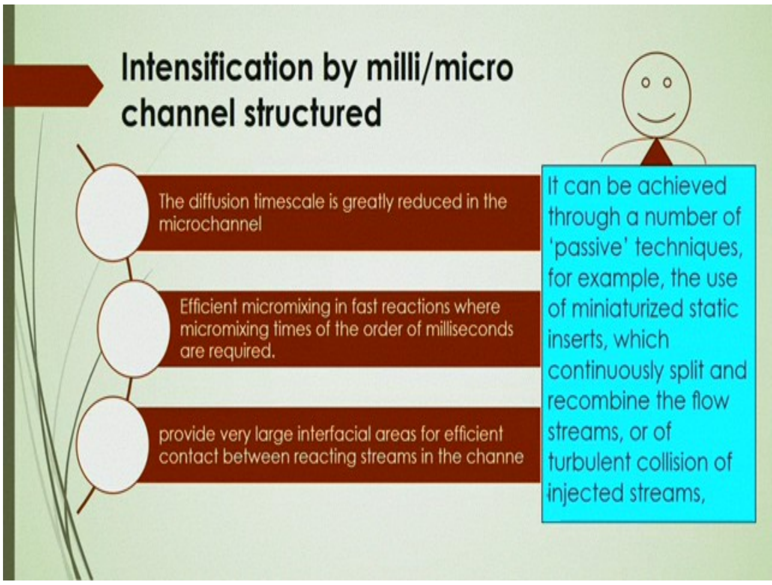

Now, intensification by this milli or macro channel have some advantages like the diffusion timescale is greatly reduced in this microchannel based reactor. Efficient micromixing in fast reactions where micromixing times of the order of milliseconds can be actually obtained and which are required for this particular reaction system and it will provide very large interfacial areas for efficient contact between reactive streams in the channel and it can be achieved through a number of passive techniques.

For example, the use of miniaturized static inserts, will continuously split and recombine the flow streams or you can say of turbulent collision of the, you know that injected streams which are being used for that reaction. So, you can say that these microchannel based structures will reduce the, you know that diffusion timescale and also you know plug flow phenomena, efficient micromixing and also you can say that large interfacial area which is being produced in the channel and it can be actually also achieved by collision of this, you know turbulent collision of this injected streams which are being used.

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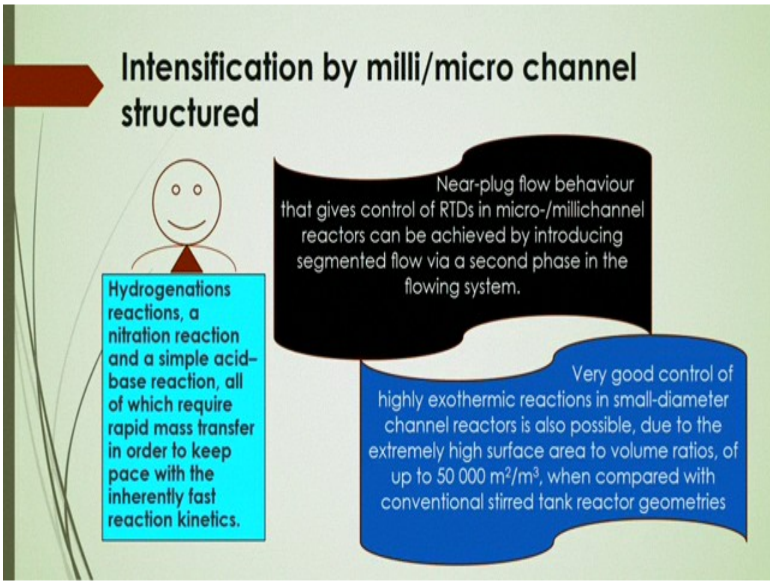

And like hydrogenation reactions, say nitration reaction and a simple acid-base reaction, all of which require maybe mass transfer in order to keep pace with the inherently fast reaction kinetics, so in that case, this type of reactions are suitable in, you know micro scale reactors like, you know millichannel for microchannel based reactors and in this case, since you can produce that plug flow phenomena, so this plug flow behaviour that gives control of RTDs in micro or millichannel reactors and that can be achieved by introducing that is segmented flow via a second phase in the flowing systems.

And very good control of highly exothermic reactions in small diameter channel reaction is also possible, due to the extremely high surface area that is produced during the flow in the channel and also you know that the surface area to the volume ratio is high and it is up to 50,000 meter inverse, when compared with conventional stirred tank reactor service are being used for reactions in earlier stage.

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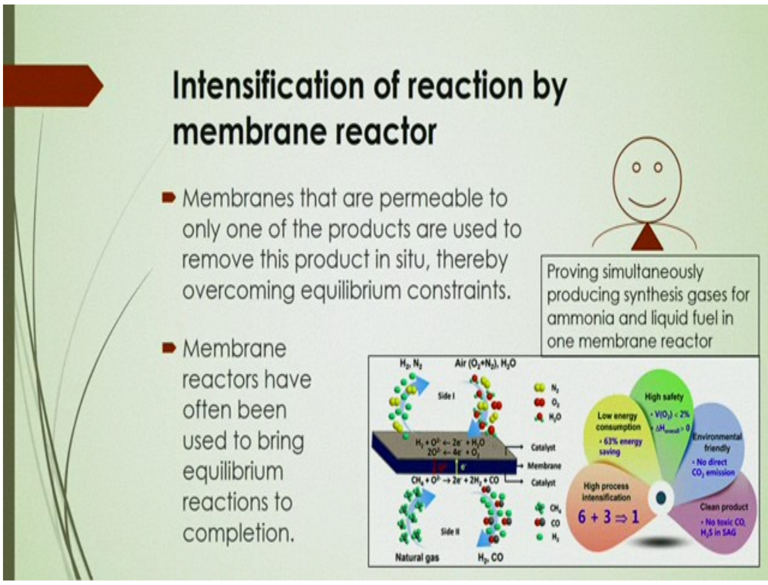

And you know another important mechanism, it is called membrane reactor development by which you can intensify the reactions system and membranes that are, you know, sometimes permeable to only one of those products are used to remove this product in situ, thereby you can overcoming the equilibrium constants, so equilibrium to, you know that receive that smooth equilibrium condition you can also do that intensification reaction or you can that membrane reactor, you can use for that particular reactive systems.

And it will provide you simultaneously producing synthesis gases for ammonia and liquid fuel in one membrane reactor as an example and about this membrane reactors have often been used to bring, you know that equilibrium reactions to completion. So for the complete reactions you can do this process in membrane reactors, in that case, you know that permeability should be one important factor by which you can, you know assess the degree of reactions by this membrane reactor.

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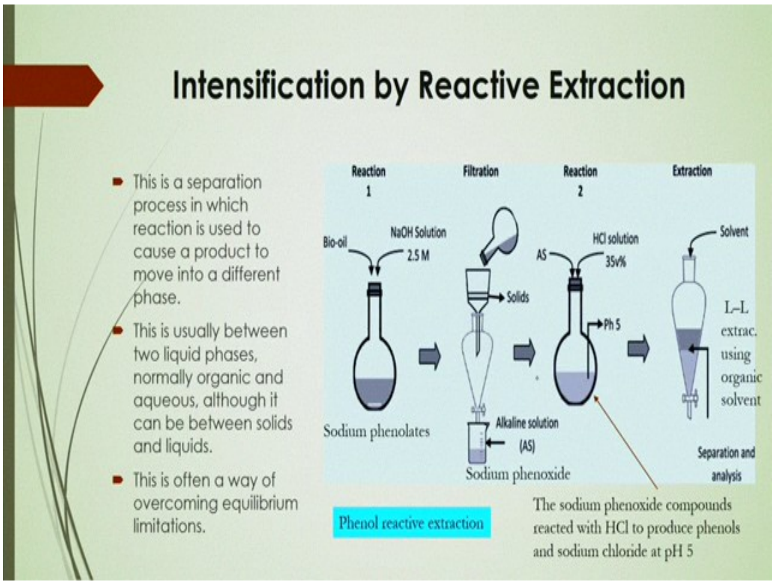

Intensification by reactive extraction is also one important, you know nowadays that reaction as well as extraction both will be simultaneously carried out that is called integrated system, so this is a separation process in which reaction is used to cause a product to move into a, you know different phases, where you can you separate those products and this is usually between two liquid phases, normally organic and you know that aqueous system and also you can say that it can be between solids and liquids, so there should be multiphase systems and this is often a way of overcoming equilibrium limitations.

So, if you integrate the system of reaction as well as extraction, you can use that reactive extraction system, where you can, you know get the intensification for the separation process as well as you can reduce the unit and simultaneous occurrence of the reaction and extraction and also energy efficient it will be process and you can overcome also the limitation of the equilibrium of the reaction.

So here, one example is given in the slide that phenolates extractive in a reactive environment and phenolate extraction, so in that case reaction one where sodium phenolates to be produced by, you know that sodium hydroxide from this bio-oil and after that you have to do the filtration, where the sodium phenoxide is being actually separated and after that there will be reaction with that sodium phenoxide and along with that, some alkaline solution and with hydrochloric acid solution with a certain percentage that certain pH value.

And after that whatever product this coming out that sodium phenoxide compounds which will be actually reacted with a hydrogen chloride that will give you the phenols and sodium chloride at pH5 and after that you have to extract that, you know that solvents liquid liquid extraction that will give you the separation of this products to its certain degree of, you know purity, so in that case reaction and extraction both will be carried out in a single unit

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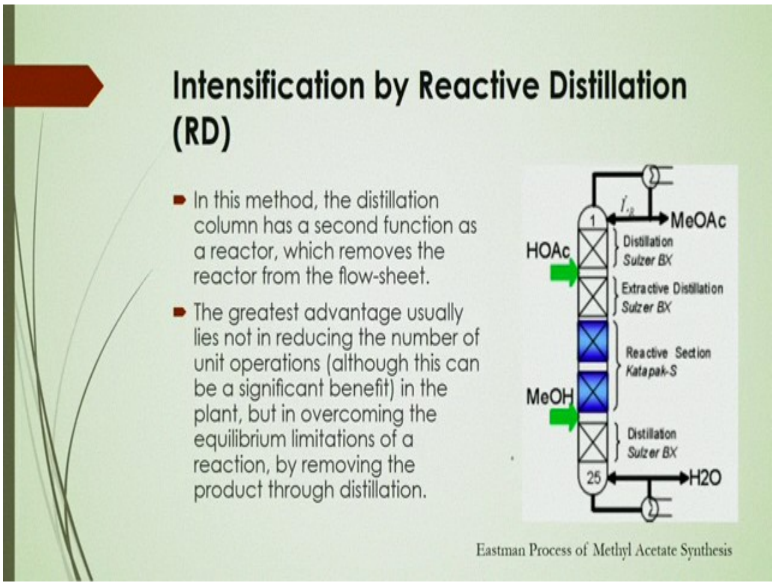

And also, that intensification by reactive distillation is also another aspect of that getting the process intensification. Simultaneously considering that reaction and distillation, in this method, distillation column has a second function as a reactor, which removes the reactor from the flow sheet and the greater advantage usually lies not in reducing the number of unit operations, although this can be a significant benefit in the plant, but in overcoming the equilibrium limitations of a reaction, by removing the product through distillation, like you know that Eastman processes of, you know, methyl acetate synthesis, where this reactive distillation systems are being used.

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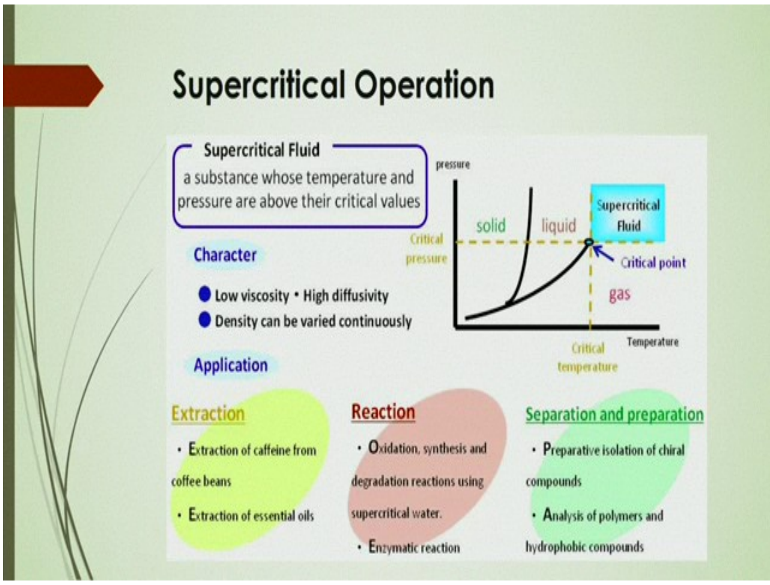

Supercritical operation also one of the important aspects of that, you know process intensification in chemical processes, like a substance whose temperature and pressure are about their critical values and using that, you know the properties of that supercritical fluids you can use that for the process intensification in reactive system also, like in that case, supercritical fluid has some characteristics, like low viscosity, high diffusivity and density can be varied continuously and in that case, extraction, reaction, separation and preparation all can be done by this you know, supercritical operating condition.

In that case, extraction of caffeine from coffee beans can be done by the supercritical extraction process, extraction of essential oils also are being done, nowadays by the supercritical process, supercritical, you know method and reaction like oxidation, synthesis and degradation, reactions using supercritical water and enzymatic reactions are being carried out by this supercritical fluid system, separation and preparation also can be done, in that case, you know preparative isolation of, you know chiral compounds and also the analysis of polymer and hydrophobic compounds are being done based on this supercritical condition.

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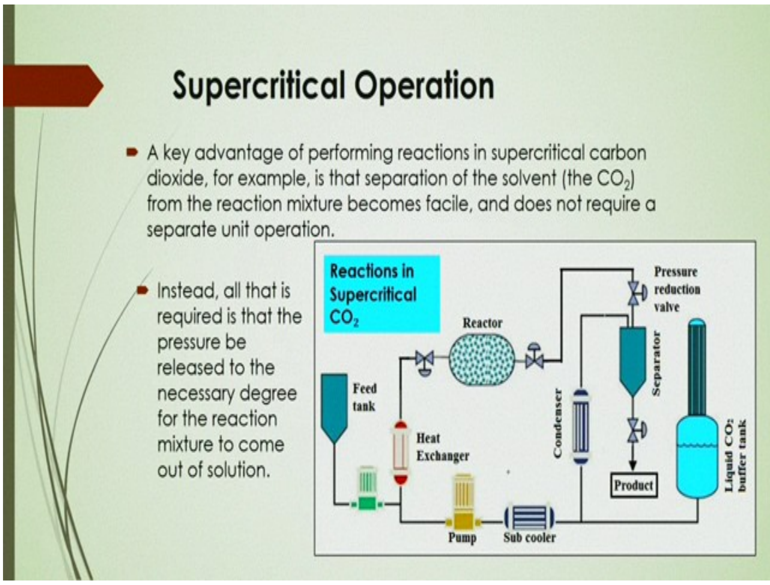

A key advantage of performing a reaction in the supercritical carbon dioxide, for example, is that separation of the solvent the carbon dioxide from the reaction mixture that becomes facile and it does not require a separate unit operation, so this is the advantage and instead you can say that, all that is required is that the pressure be released to the necessary degree for the reaction mixture to come out of solution. So, this is important for this supercritical operation based on which you can perform the reactions in supercritical carbon dioxide for the separation of solvent from the reaction mixture and without, you know using that separate unit operation.

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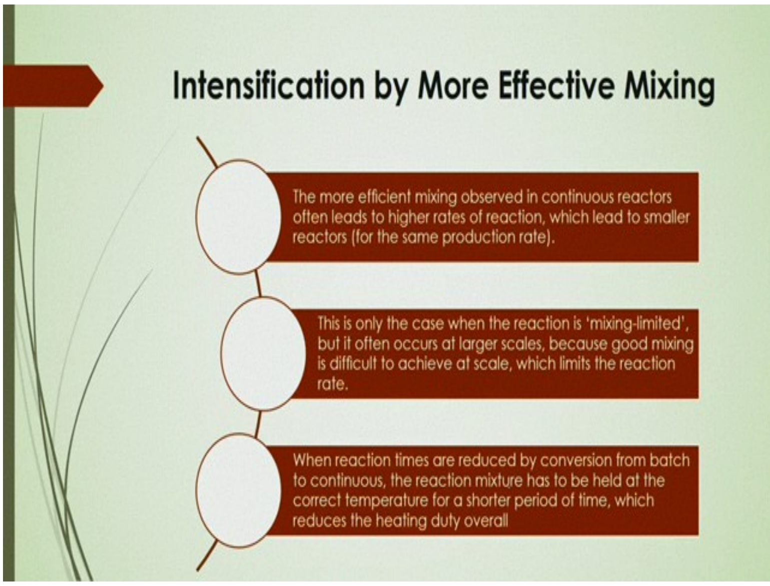

And you know that other important aspects of the process intensification, that you can have the intensified, you know process by more effective mixing, like more effective mixing observed in continuous reactors often lead to higher rates of reaction, which lead to smaller reactors for the same production rate and when the reaction is, you know, mixing limited, but it often occurs at larger scales, in that case, good mixing is difficult to achieve that scale, which limits the reaction rate and when reaction times are reduced by conversion from batch to continuous, the reaction mixture has to be held at the correct temperature for a shorter period of time, which reduces the heating duty in that particular reactive system overall.

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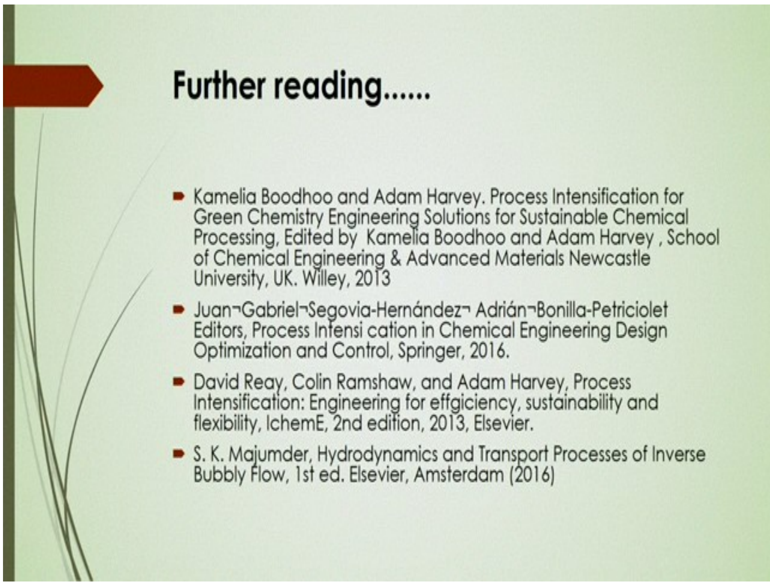

So, I think we have discussed, we have, you know that learned something about the process intensification mechanism based on this, you know that the reactive environment, how it can be done? How actually the reduction of back mixing will help that, you know that reactive system for the process intensification. You know reduce the limitations of the equilibrium and also how we can, you know that control the residence time of the phases and also, you know that mixing characteristics.

And also how to produce the interfacial area by different, you know that mechanism like electric field or you know that cavitation process or you can that, if you can use some, you know photon systems in, you know that photoinitiation method, where you can, you know produce that interfacial area and also activate the species for this, you know process intensification in reactive systems.

So, several you know that mechanisms are, you know discussed in this lecture, so you can have more information, I will suggest for further reading of this, you know textbooks that is given in the slides or in an also, you know that in the course handout there in the core system. So, thank you for this lecture today.