Chemical Process Intensification
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Lecture 11.2 (lec34)
Process Intensification by Micro-reactors

Welcome to massive open online course on Chemical Process Intensification. So we are discussing under module 12 the topic is Micro process technology for process intensification and under this module, today we will discuss something more about that process intensification. And the list will include the process intensification of micro-reactors and some barriers and its challenges.

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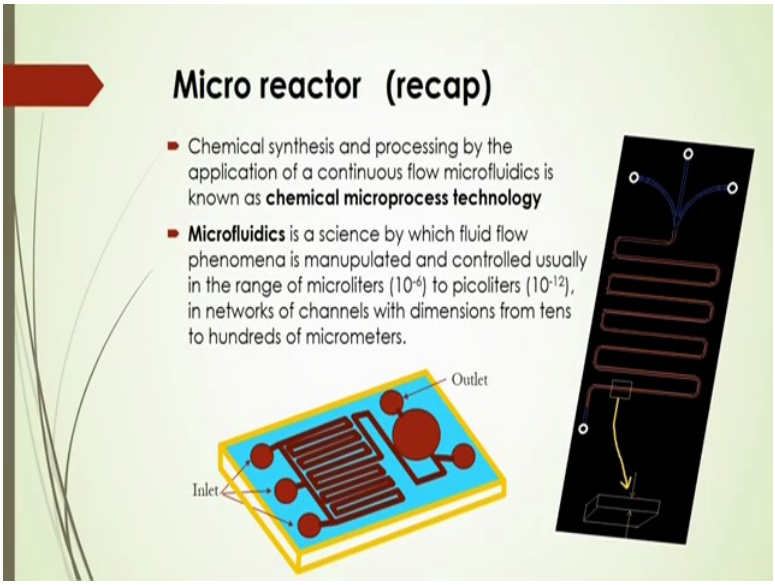

Now, we have already discussed that what is that Micro Reactor? So we will just look, around that previous some introductory portions of that micro-reactor. We know that chemical synthesis and processing by application of a continuous flow microfluidics is known as chemical microprocessor technology. And microfluidic is a science by which that fluid flow phenomena is manipulated and controlled usually in the range of microliters to Pico liters in networks of channels with dimensions from tens to hundreds of micrometers.

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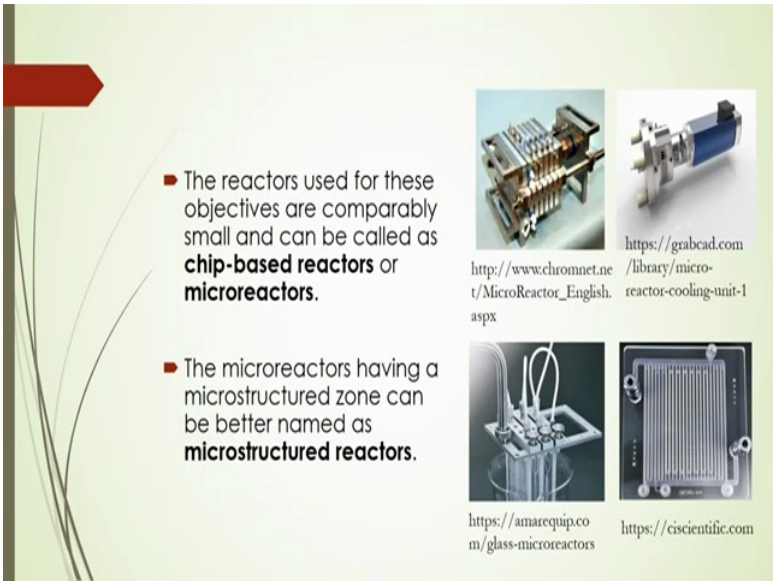

And also, we discussed about that reactor used for these objectives are comparatively small and can be called as chip based reactors or simply called as micro-reactors. And these micro-reactors having a micro-structured zone that can be also referred to as micro-structured reactors.

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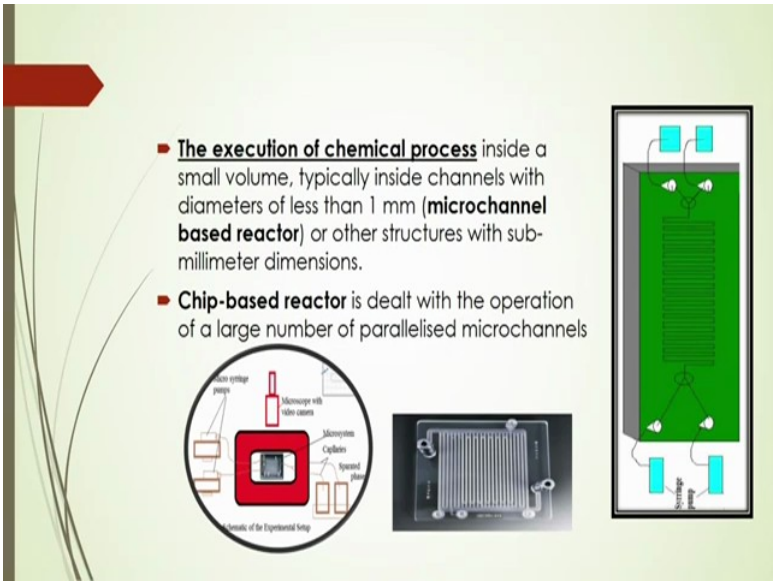

And the execution of chemical process inside a small volume like micro-reactors, typically inside channels with a diameter of less than 1 mm this is generally called as micro channel base reactor or other structures with sub-millimeter dimensions. Also, we have discussed that chip based reactor is dealt with the operation of large number of parallelized micro channels.

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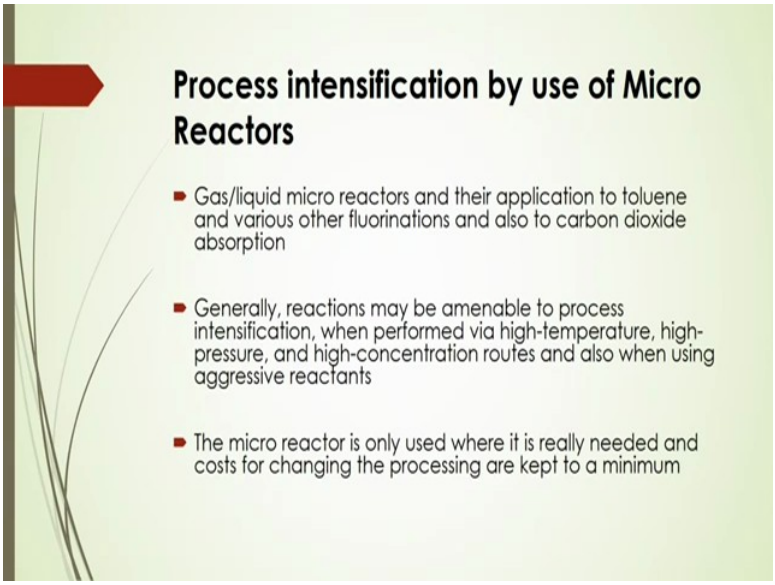

And in that case, how those micro-reactors are being used or for chemical processes as a process intensification, so process intensification by use of micro-reactors. You can have different application of this micro-reactors where, maybe gas liquid system even some other multiphase systems or liquid-liquid systems. Even some reactive system, so in that case several application of this micro-reactors based on the process intensification are actually being carried out and also that is commercialize based on that performance of the reaction and separation process based on this micro-reactor and also micro-process technology.

Now in that case if you consider that gas liquid micro-reactors and can be applied like that as an example toluene and various other fluorinations reaction and also to carbon dioxide absorption. And this type of reaction generally, happend in a channel, where that you can enhance the mass transfer and heat reaction there and reactions maybe that amenable to process intensification when performed via high-temperature, high pressure and high concentration routes.

And also when using aggressive reactants. Micro-reactor is only used when it is really needed and of course you have to consider the cost factor for changing the processing and also, you have to keep it as minimum as possible.

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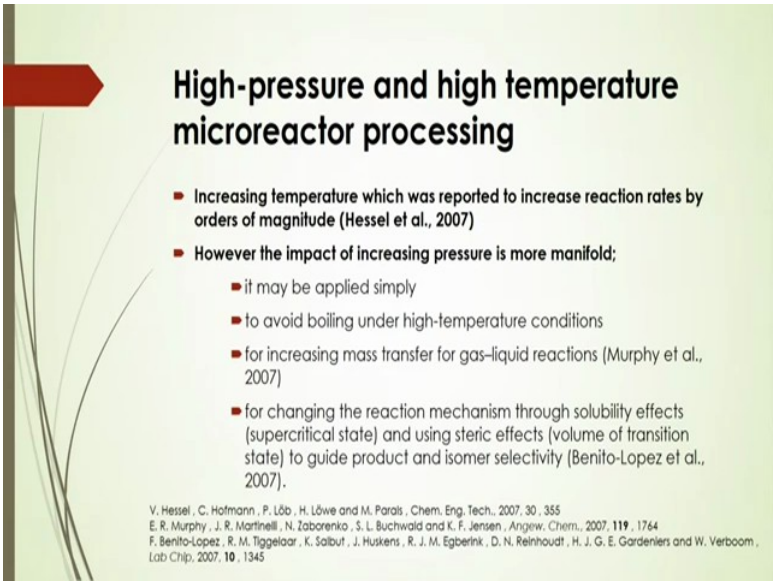

Now, if we consider that high-pressure and high-temperature micro-reactor processing that we have discussed in our previous lecture that several aspects of implementation process intensification by this micro-reactor processing. There Of course, pressure and temperature are two important factors by which you can have that process intensification in the micro-reactor systems. In this case that if you increase the temperature, maybe it will increase the reaction rates by orders of magnitude as per reported by Hessel 2007.

However, the impact of increasing pressure is more manifold. Maybe based on that several aspect, maybe applied simply to avoid boiling under high-temperature conditions and also for increasing mass transfer for gas liquid reactions and also it may be impacted for that changing the reaction mechanism through solubility effects or you can say that through supercritical states.

And also using, that steric effects like that volume of transition state and also it may guide product and isomer selectivity based on this high-pressure and high-temperature micro-reactor processing. So these are some impact of increasing pressure on this, reacting system in a micro-reactor.

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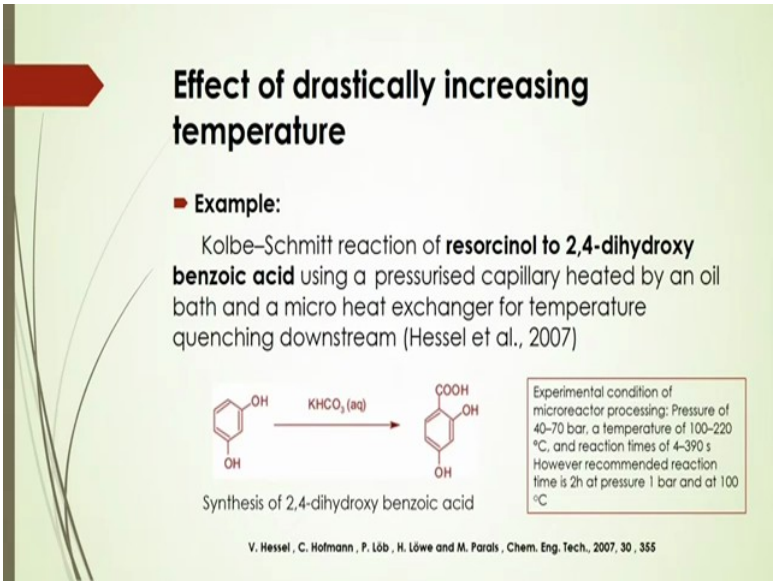

As an example, if we consider that for drastically increasing temperature like Kolbe-Schmitt reaction of resorcinol to 2, 4-dihydroxy benzoic acid. In that case, if you use that pressurized capillary heated system by an oil bath and a micro heat exchanger for the temperature quenching in that case you can get that increase of yield for this reaction and if you do it for certain conditions of this pressure and temperature, you may get that intensification of this process.

Now experimental condition of in this case micro-reactor processing for this type of reaction in that case, pressure, maybe of 40 to 70 bar a temperature of 100 to 220 degree centigrade and reaction times of 4-390seconds. However, recommended reaction time is 2 hour at pressure of one bar and at 100 degree centigrade.

So anyway directions is going to that process intensification based on the micro- reactor processing. Severally when research also to be carried out too. How to get that reduce reaction based on low pressure as well as optimum temperature there. So this is one example where you can increase temperature and get that reaction performance in the micro channel based reactor.

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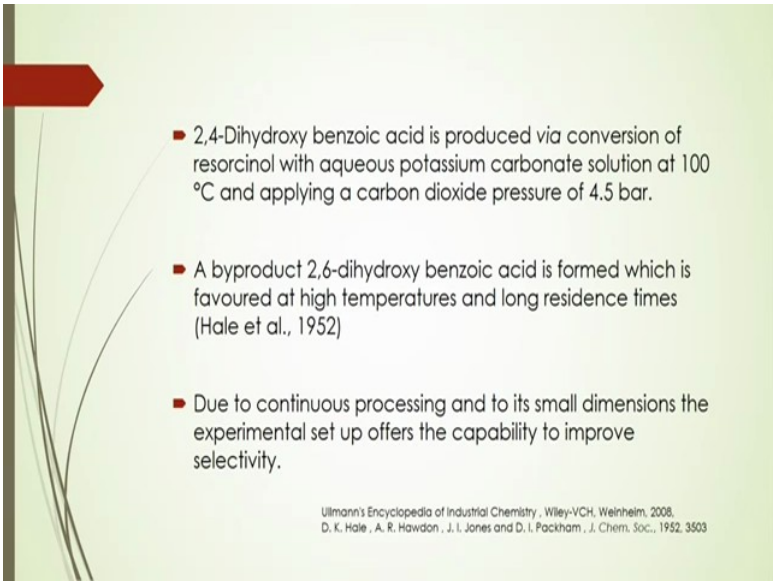

And in this case 2,4, dihydroxy benzoic acid is produced via conversion of resorcinol with aqueous potassium carbonate solution at 100 degree centigrade and applying a carbon dioxide pressure of 4.5 bar and also is formed the byproduct which is formed is favored at high-temperature and long residence time. So in that case due to the continuous processing and it is a small dimensions the experimental setup offers the capability to improve selectivity.

So that is why here that process intensification at this high pressure and temperature which you can get the improvement of the selectivity by this micro-process technology.

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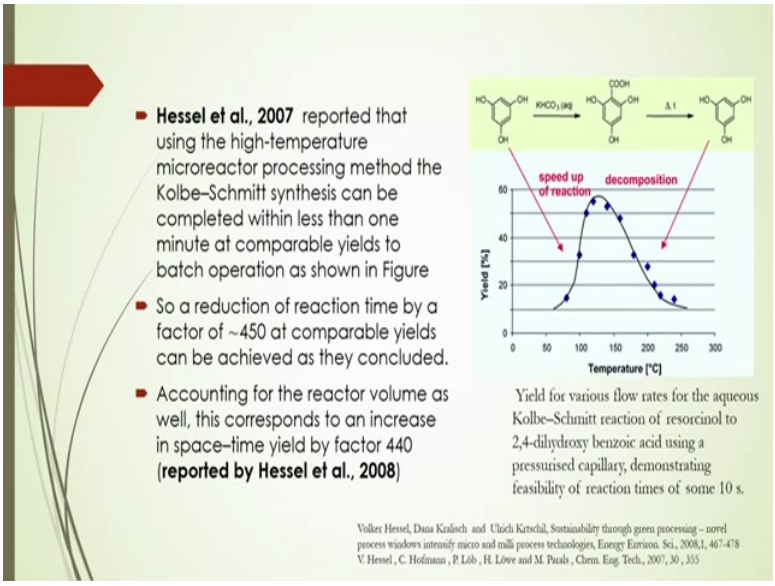

So in this case Hessel et al. 2007 reported that using the high-temperature micro-reactor

processing method the Kolbe-Schmitt synthesis can be completed within less than one minute at comparable yields to batch operation as shown in figure here. And in that case a reduction of reaction time hence by a factor of 450 around at comparable yields can be achieved as they concluded.

And also this main account for the reactor volume as well this corresponds to an increase in space-time that yield by factor 440 that is reported by Hessel again in 2008. Now this picture is generally giving that yield with respect to temperature for various flow rate for the aqueous Kolbe-Schmitt reaction of resorcinol to 2, 4-dihydroxy benzoic acid using pressurized capillary demonstrating feasibility of reaction times of some 10 seconds.

So this is the intensification where we can get micro channel base reactor for the better that selectivity of this reaction in the micro channel.

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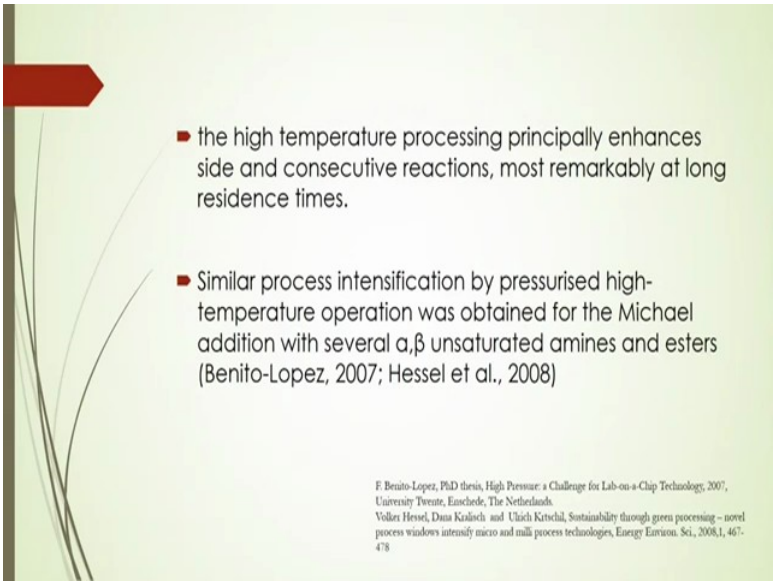

And the high-temperature processing principally enhances side and consecutive reactions most remarkably at long residence times. And similar process intensification by pressurized high-temperature operation was obtained for the Michael addition with several alpha, beta unsaturated amines and esters by that Benito-Lopez in 2007 even by Hessel et al 2008 there. So they have reported that this process intensification by the pressurized high-temperature operation can be obtained for the Michael addition with several alpha, beta unsaturated amines.

So this is the direction of that process intensification for that reaction at high pressure and

high-temperature.

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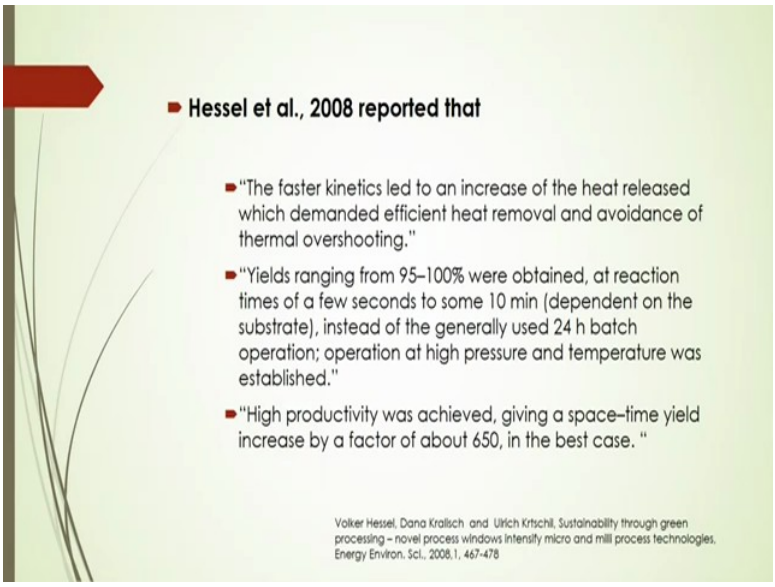

Also Hessel 2008 reported that faster kinetics led to an increase of the heat released which demanded efficient heat removal and also avoidance of thermal overshooting. In that case the yields that may be ranging from 95-100 percent and at reaction times of few seconds to some 10 minutes that may be dependent on the substrate. And also you can say that the operation of high-pressure and high-temperature can be established based on this micro channel base reactor.

And also high productivity that can be achieved, giving a space-time yield increased by a factor of about 650 the best case as per in Hessel et al 2008.

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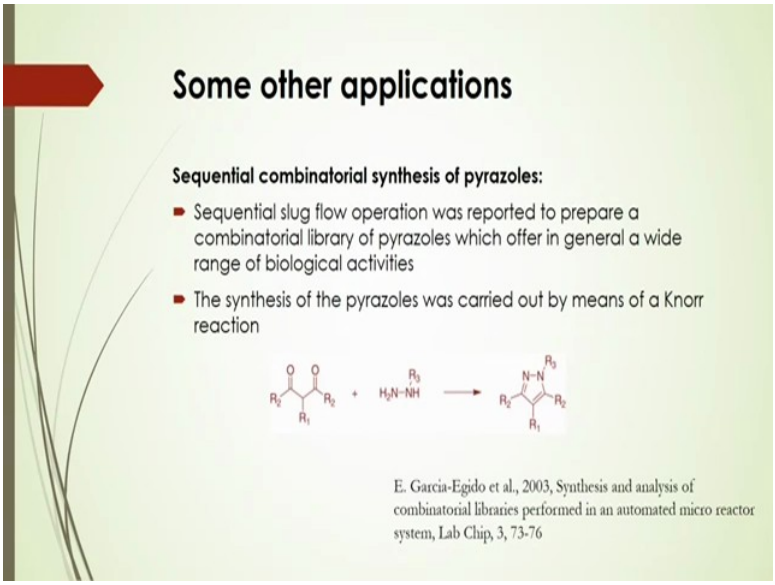

Some other applications like sequential combinatorial synthesis of pyrazoles. In that case sequential slug flow operation was reported to prepare a combinatorial library of pyrazoles which offer in general a wide range of biological activities. So this is also one important because whenever fluid will be flowing through the micro channel maximum mostly the flow pattern is slug flow.

So they have done here I think E Garcia-Egido et al. 2003, they have reported that slug flow pattern also give that process intensification for this synthesis of pyrazoloes that is carried out by the means of a Knorr reaction as given in the slides here. So this is also possible based on that flow pattern of the fluid during that reaction and also how that kinetics of the reaction are changing based on that flow pattern through the channel.

So it is the one of the important example of this synthesis of pyrazoles based on that flow pattern and how that intensification is possible for this reaction system.

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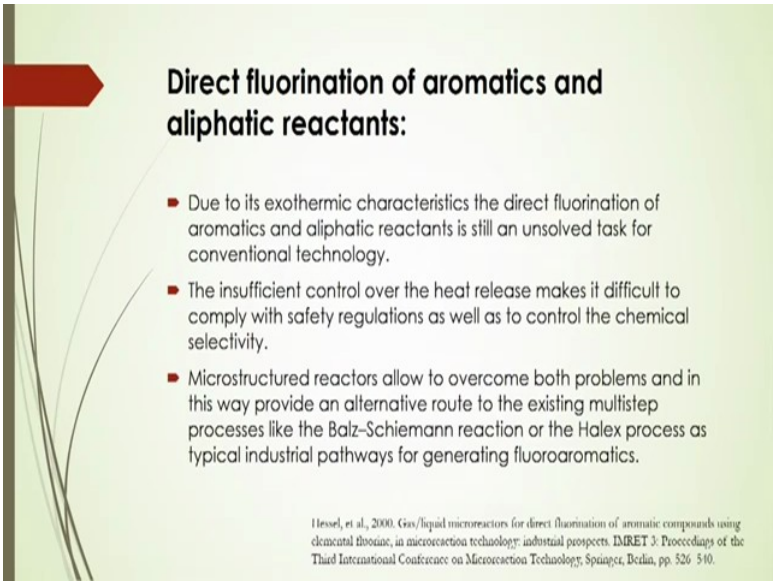

Another example it is called that direct fluorination of aromatics and aliphatic reactants. In that case these are also very important reactions that are actually being carried out in the micro channel base reactor. And in this case this direct fluorination of aromatics and aliphatic reactants are several still disadvantages carrying out this reactions in micro channel based reactor even in conventional system also.

But still since research is going on there are several aspects going to consider how to actually intensify the process and how it can be carried out in the micro channel and by the microprocessor technology. In that case the insufficient control over the heat release makes it difficult to comply with safety regulations as well as to control the chemical selectivity. So research is going to overcome those disadvantages of this reactions to be carried out in micro channel or conventional system.

But micro-structured reactors that may allow to overcome both problems and in this way provide an alternative route to the existing multistep processes like the Balz-Schiemann reaction and also Halex process as typical industrial pathways for generating fluoroaromatics there. So micro-structured is giving some extent of the solution for this problem over this conventional technology but still research is to be carried out for better and better understanding as well as that improvement of the process performance by this micro-structured reactors.

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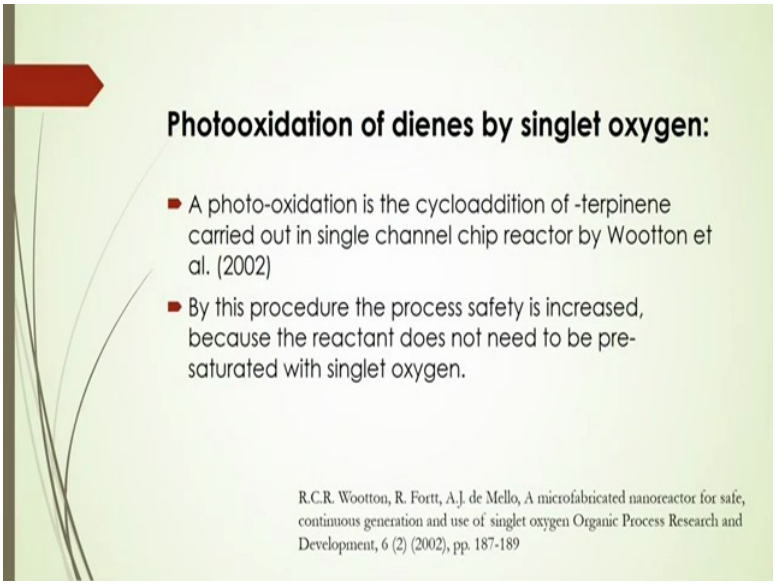

Photo oxidation of dienes by singlet oxygen also are being carried out in a micro-reactor system. In this case photo oxidation is the cycloaddition of terpinene that is carried out in a single channel chip reactor by that is investigated by Wootton et al. 2002. And they have reported that by this procedure the process safety can be increased because the reactants does not need to be pre saturated with the singlet oxygen.

So this is also another one of the important applications of channel based micro reactor like chip reactor there.

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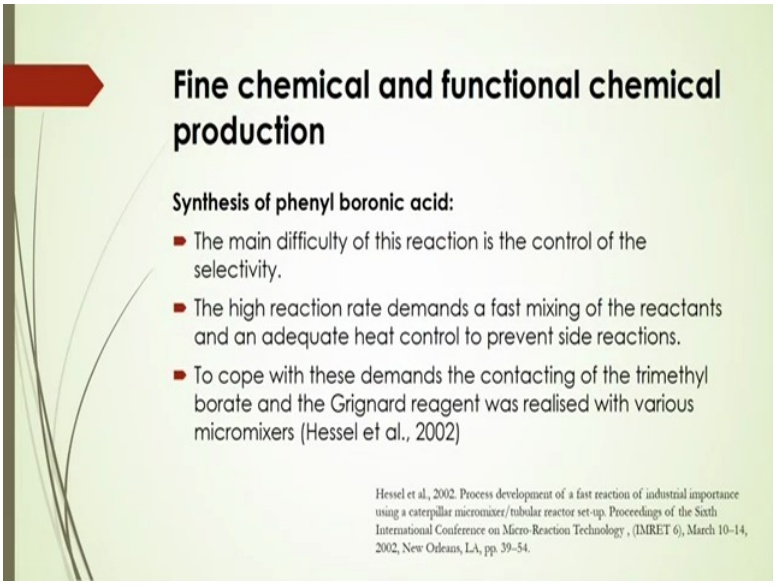

Also this micro-reactive systems are also important for the application of fine chemical and

functional chemical production. In this case if we consider synthesis of phenyl boronic acid the main difficulty of this reaction is the control of selectivity. And the high reaction rate sometimes demands fast mixing of the reactants and the adequate heat control to prevent side reactions.

So to actually take the advantage of the micro-reactor technology to overcome this fast mixing of reactants and adequate heat controlled to prevent side reactions are actually demanding and also suggesting to actually research commenting they are suggesting to do this reaction for this fine chemical and functional chemical production in the channel base reactor. And also since the mixing is one the important issues there, so that should be used in a micro-base reactor there. So to cope this demands the contacting of the tri-methyl borate and the Grignard reagent generally was realized with various micro-mixers as per report of Hessel et al 2002.

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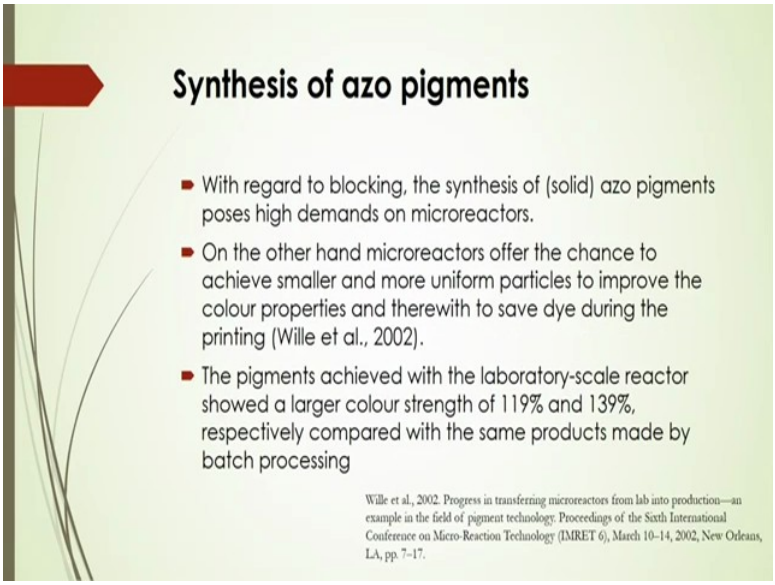

Now there are other synthesis like as azo pigments synthesis with regard to blocking the synthesis of azo pigments possess high demands on micro-reactors and micro-reactor offer the chance to achieve smaller and more uniform particles to improve the color properties and also here with to save dye during printing there, so azo pigments are very useful chemicals for that printing purpose.

So to synthesize this azo pigments the micro-reactors are also one of the important aspect of the process intensification there and this pigment achieved with laboratory-scale reactor showed a sometimes larger color strength of 119 percent and 139 percent respectively

compared with the same products that is made by batch processing. So see that how micro-reactor systems are giving better performance as for process intensification.

And as per report by this Wille et al. 2002 that they observe that this pigments in the laboratory scale reactor showed a larger color strength of 119 percent and 139 percent respectively compared with the same products that is made by batch processing there.

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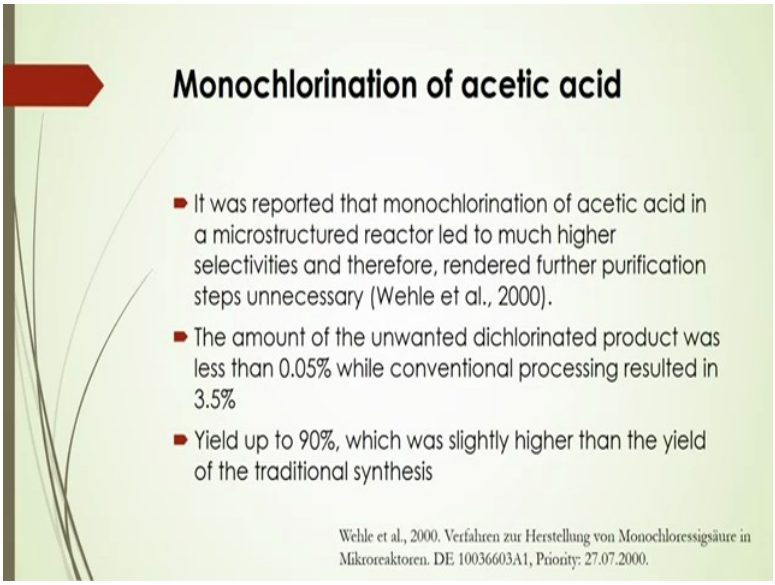

And also a Monochlorination of acetic acid is one of the important reaction that is carried out in micro-reactor there. For getting that the yield even more and more compared to that traditional synthesis. In this case yield up to 90 percent which was slightly higher than the yield of traditional synthesis that is reported by Wehle et al 2000 and it was also reported that this Monochlorination of acetic acid in micro-structured reactor led to much higher selectivities and therefore rendered further purification steps are necessary there.

And in this case the amount of the unwanted dichlorinated products that is coming out was less than 0.05 percent while in the conventional processing that may result that more than 3 percent there.

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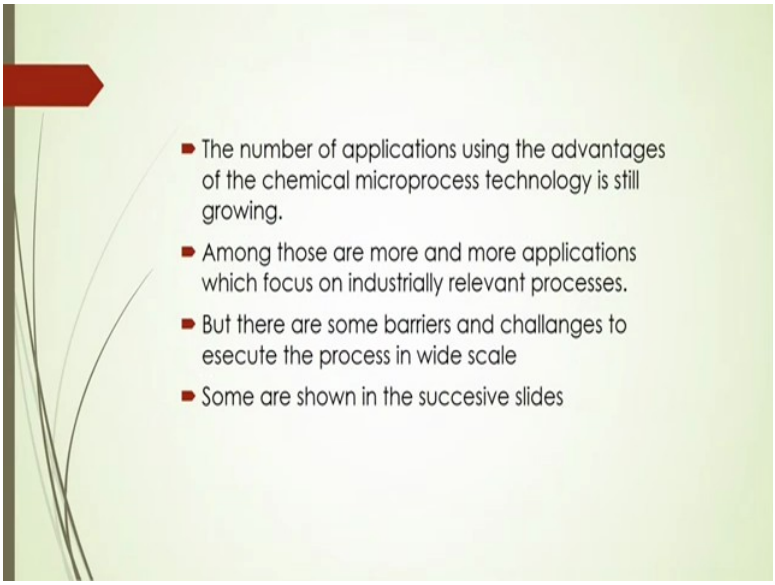

And the number of applications that is using the advantages of the chemical micro-process technology we can say it is still growing because there are several issues which is to be overcome for getting more better way of that product even green product also you can say that more intensified way, so among those are more and more applications which focus on industrially relevant processes to be considered there.

But there are some barriers and of course challenges to be executed for this several reactions when you are considering that to be intensified in the economic way and even greenery way. So the Green synthesis that are green sustainable way of development that is required for this process intensification just like considering all those shortcomings what is coming during process intensification in the micro-reactor.

So that should be considered for the further research and also those are very important aspects that actually even some barriers and challenges here like that we will discuss some barriers of that in later.

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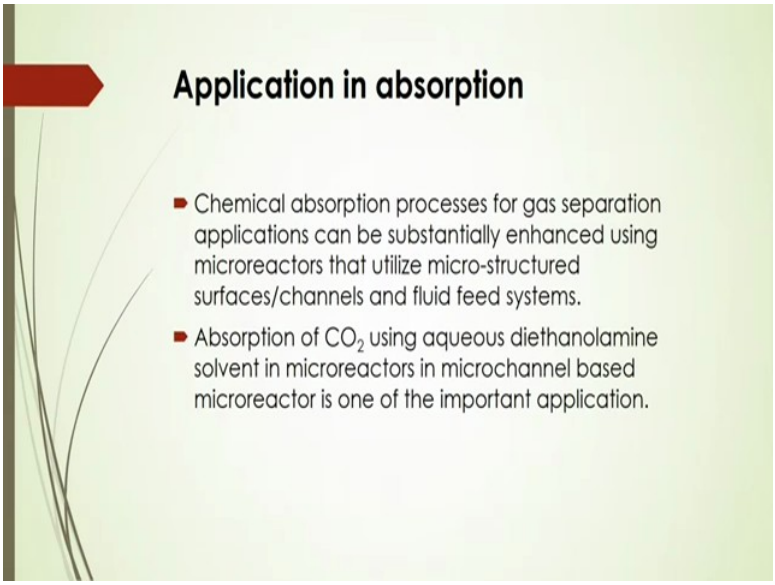

Let us see other applications of the micro-reactor like absorption reaction, chemical absorption processes for gas separation applications that can be substantially enhanced using the micro-reactors that utilize micro-structured, surfaces, channels and fluid feed systems. And if you considered that absorption of carbon dioxide that uses aqueous diethanolamine and even other solvent you can use in micro-reactors in micro channel base micro-reactor and that is also one of the important aspect of the process intensification for the separation of the gaseous.

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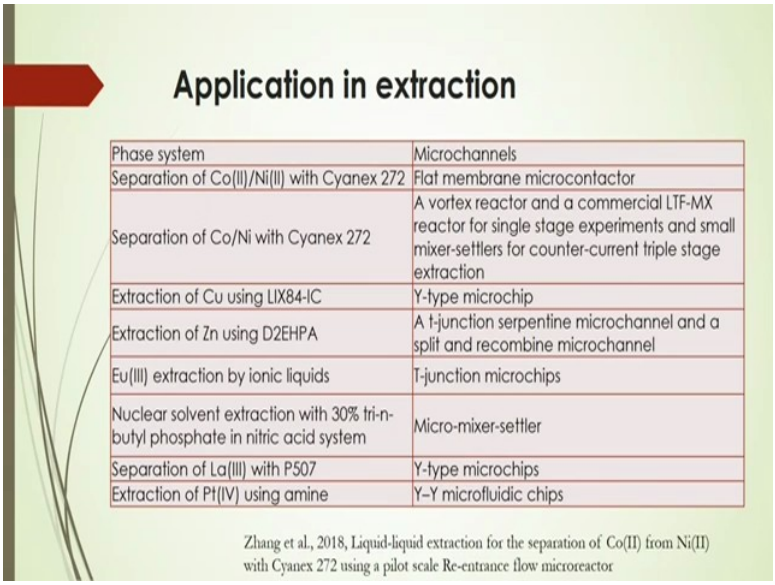

Like other application here extraction process also can be done in liquid-liquid extraction in

the micro channel base micro-reactor. There will see that some application of that separation process based on that intensification in extraction is given in the slides. I think there are several aspects their extraction of copper using some Solvent extraction of zinc using solvent.

Even uranium extraction by ionic liquids, even separation of Platinum using amine, so those are different aspects of application where you can do it in a micro channel even chip reactor micro-reactor. Sometimes membrane micro-reactor sometimes it may be chip type reactor. Sometimes it may be that T-junction base microchips reactors, micro-mixer-settler, even that Y-type microchips base micro-reactors, microfluidic chips.

So all those different types of micro-reactors that can be used for the extraction processes. Even here given some examples of those extraction processes. So please go through this application of this extraction which can be done in a micro channel for the process intensification.

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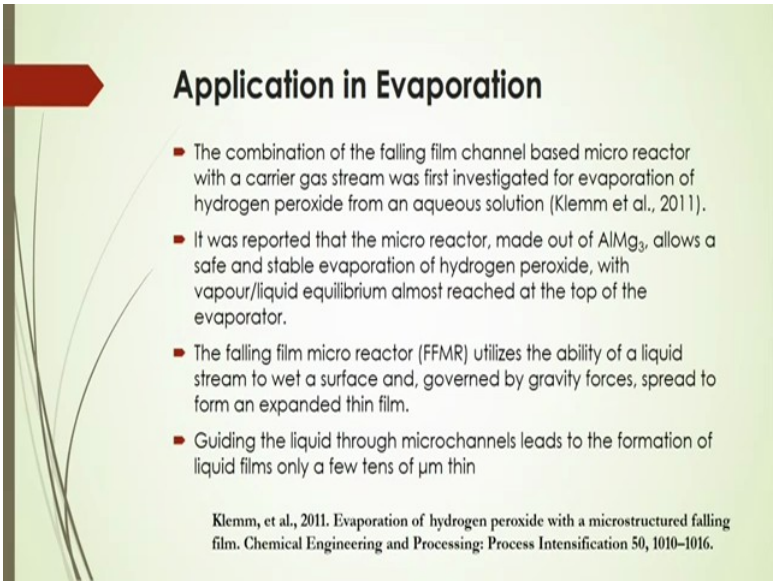

Even you can apply this micro-reactors in evaporation process. In that case the combination of the falling film channel-based micro-reactor to be developed with a carrier gases system. And it is generally made out of aluminum, magnesium alloys for getting that safe and stable evaporation of hydrogen peroxide with vapor or liquid equilibrium that almost reached at the top of the evaporator. And also the following film micro-reactor that utilizes the ability of liquid stream to wet a surface and also governed by gravity forces spread to form an expanded thin-film that is reported by Klemm et al. 2011.

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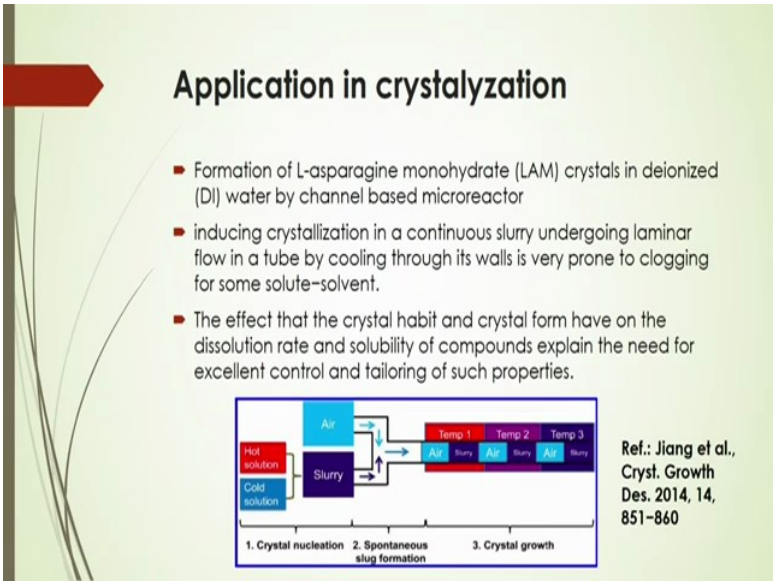

You can apply crystallization also in that micro channel base micro-reactor as per Jiang et al. you will see that in 2014 they have reported that the formation of L-asparagine monohydrate crystals in deionized water by channel based micro-reactor it can be done and in that case including crystallization in a continuous slurry undergoing laminar flow in a tube by cooling through its walls that will be very prone to clogging for some solute solvent.

So that should be taken care sometimes whenever crystals will be formed in the channel that may be clog other flow, so that is why nowadays that thinking about crystallization process where that Nano crystals can be found in that micro channel in a process intensification way.

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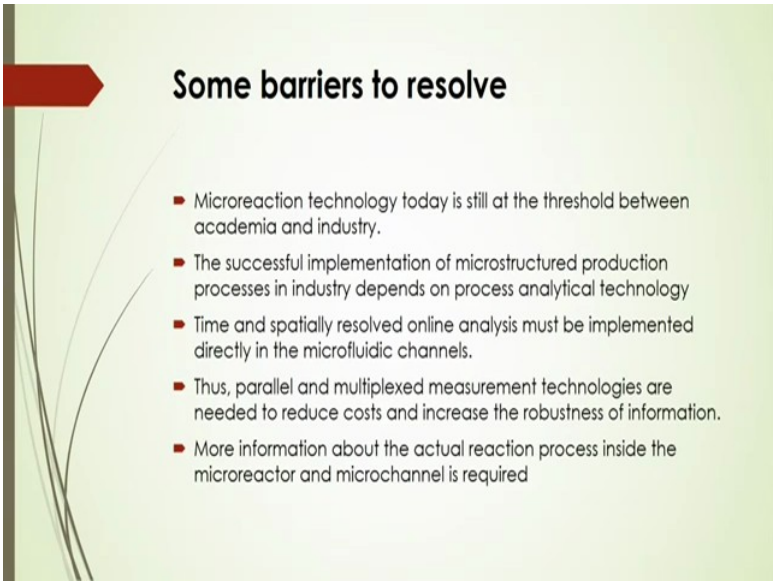

Now what we discuss that there will be of course in the different application like absorption, crystallization, extraction and even some other different reaction systems that whenever we are applying this micro-reactor for this application to be carried out there will be some barriers and also some challenges which is to be solved also. So there are several researches going on how to recover, how to overcome those problems or barriers there.

Some barriers like here micro-reaction technology today implementation problem. So the successful implementation of microstructure production process in industries that depends on the process analytical technology because you have two analyses anyway whatever product is coming out. Maybe online analysis of that micro channel base reactor it is very difficult.

So whenever you are going to carry out that reactions in a micro channel how that kinetics of that reaction and also how that concentration of that reactant systems are changing and conventional changing that should be analyzed by analytical sophisticated analytical system and which is still under down because of that several pros and cons in development, so still research is going on there so anyway the successful implementation of the micro-structured production process in industries of course to be depending on that process analytical technology.

And also time and spatially resolved online analyses must be implemented directly in the microfluidic channels. And the parallel and multiplexed measurement technologies are also needed to reduce cost and increase the robustness of information for this micro-technology. Now more information about the actual reaction process that is inside the micro-reactor and micro channel is also required by that sophisticated micro-analyses.

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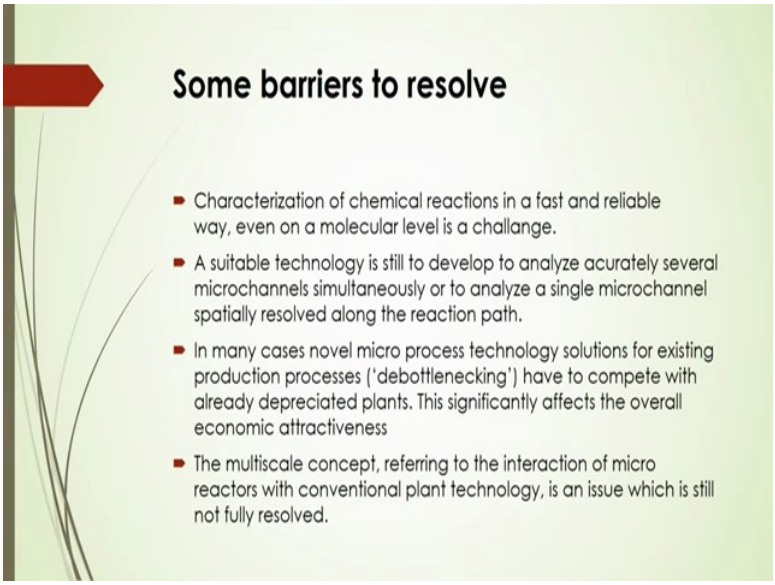

And characterization of chemical reactions in a fast and reliable way even on a molecular level is also a challenge. Also in many cases you will see that novel micro-process technology solutions for existing production processes have to compete with already depreciated plants this significantly affects the overall economic scenario. Also a suitable technology still to develop to analyses accurately several micro-channels simultaneously or to analyze a single micro channel specialty that is resolved along the reaction path.

The multi-scale concept, referring to the interaction of micro-reactors with conventional plant technology, is an issue which is still not actually fully resolved as per statement of the Hessel et al. 2004.

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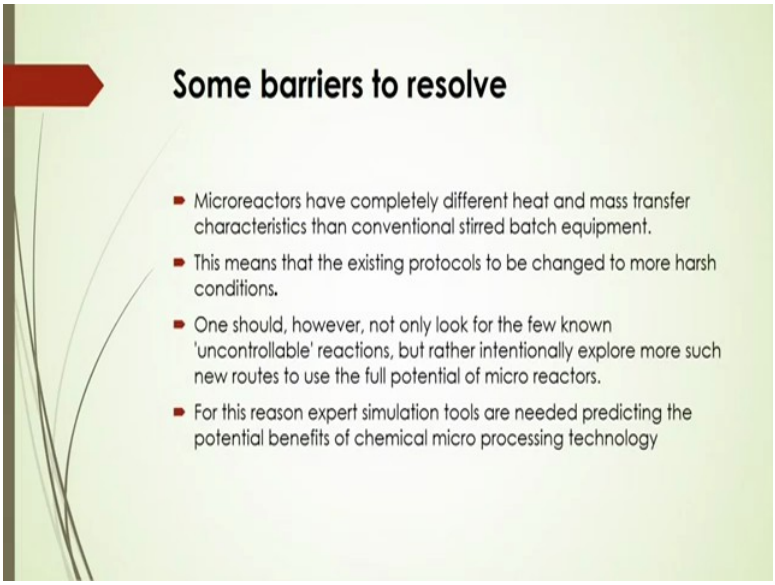

And micro-reactors have completely different heat and mass transfer characteristics than conventional stirred batch equipment. So in that case you have to follow some existing protocols to be change to more harsh conditions there. And for this reason, expert simulation tools sometimes to be needed to predict that potential benefits of chemical micro-processing technology for that heat and mass transfer characteristics analyses in the micro-reactor.

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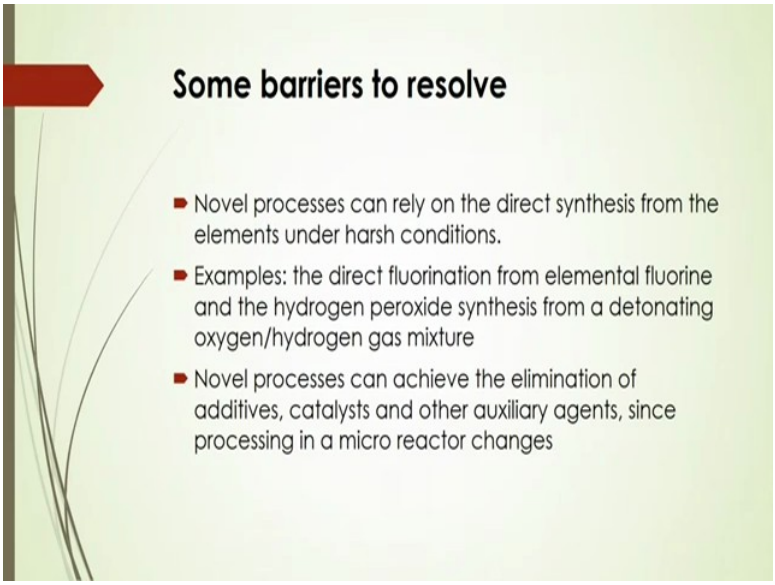

And also novel processes can rely on the direct synthesis from the elements under harsh conditions. And a direct fluorination from elemental fluorine and the hydrogen peroxide synthesis from a detonating oxygen hydrogen gas mixture is one of the important examples,

where you can get that barriers to get this intensified way of that yield of the reaction. Novel processes can achieve the elimination of additives, catalyst and other auxiliary agents, since processing in a micro-reactor that is change.

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Also you can say some challenges involving reactor design, engineered catalysts specifically designed for micro channel reactors. Methods of fabrication results in technological insides and also innovations that spurred future development. And also initial catalyst investigation in 1996 that revealed that direct wash coating of micro channel walls presented significant hurdles to rapid development.

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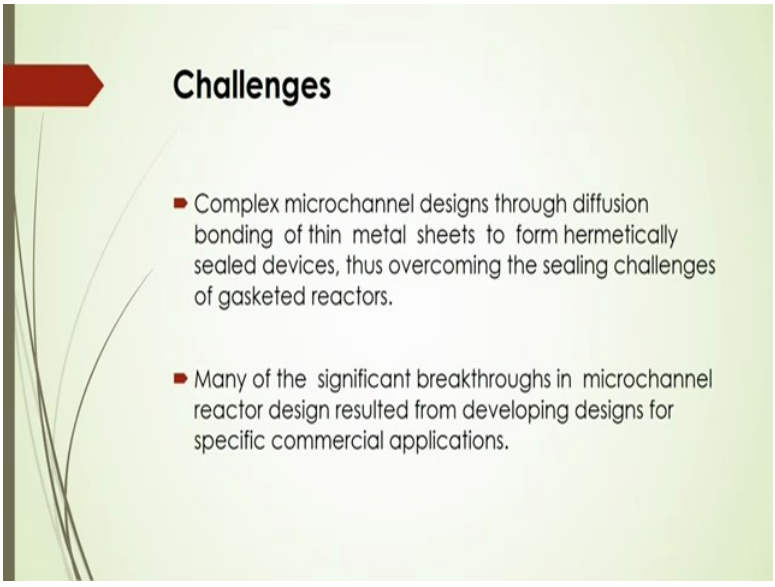

Many of the significant breakthrough in micro channel reactor design resulted from the developing designs for specific commercial applications. So challenges there that you have to design that micro channel base reactor in such a way that there will be that some complex micro channel system to be easily design based on different thin metals, based on different on other economic aspects and even how to overcome that corrosion even other aspects of that reactor systems where that chemicals whatever it will be used that will be used that may be reacting with that surface of the reactors in micro channel.

So that should be also considered during that design. So that is why the design aspect of the micro channel which is to be rigorously taken care of those breakthrough points where it can be considered for the design for that micro channel base reactor to get more intensified way.

So there are several other issues also in micro channel based reactor design there and also concepts whatever is there may be in terms of mass transfer characteristics and heat transfer characteristics.

Even some other reaction kinetics systems also to be considered and also residence time of the reactants and also for the physical process, how that micro-reactor can be used for separating that or creating that interfacial area to get more yield of that reactive separations or you can say that absorption system adsorption system separation, physical separation all those things. So micro channel based micro-reactors are nowadays that important aspects for process intensification in chemical engineering.

So I think we have discussed lot about that application of micro channel based reactor and there are some barriers and challenges. I think it is useful for better understanding of that micro channel based reactor here. Also whatever reactions or separation processes are there in micro channel, all those separations reactions kinetics that depends on that hydrodynamics of that micro channel base micro-reactor.

So it is also to be known what are the different hydrodynamics characteristics of these micro channel base reactor that this to be also known? And how those hydrodynamics may effects on that mass transfer and heat transfer for the reaction system in the micro channel base, so we will discuss more about this micro channel based reactor for their how that hydrodynamics and other characteristics even mixing characteristic is one of the important aspects that also to be discussed in the coming lecture.

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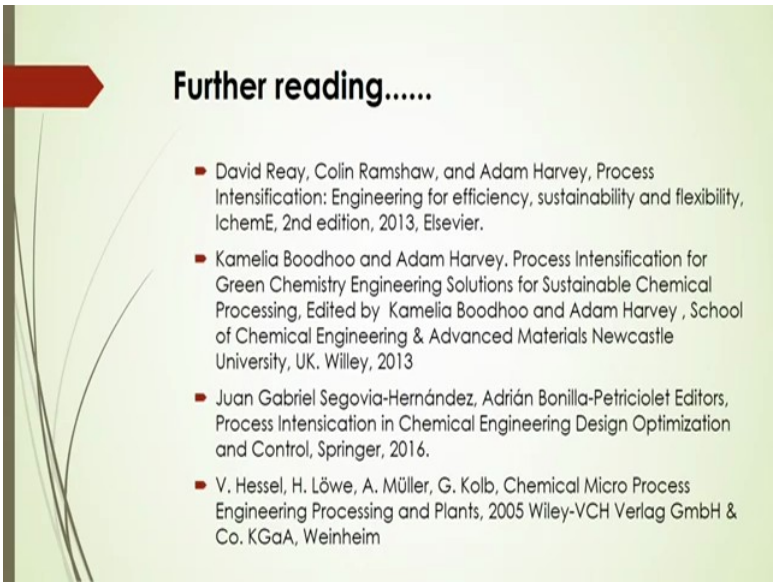

So I will suggest you to go further for the application of this chemical micro-process engineering and processing also how they are using this reactor system in industrial system. I will suggest you to go through this references for more information about this. So thank you.