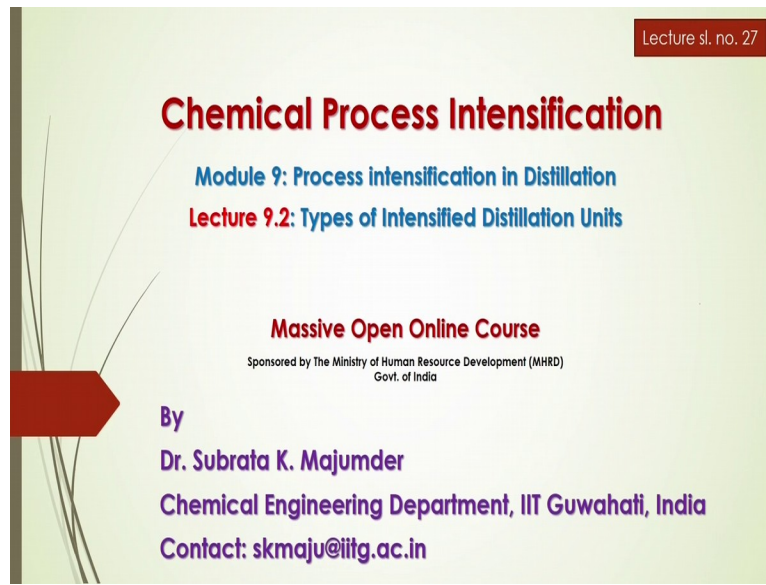


Chemical Process Intensification
Professor Subrata K. Majumder
Department of Chemical Engineering
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Module 9
Lecture No 9.2
Types of Intensified Distillation Units

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Lecture sl. no. 27

Chemical Process Intensification

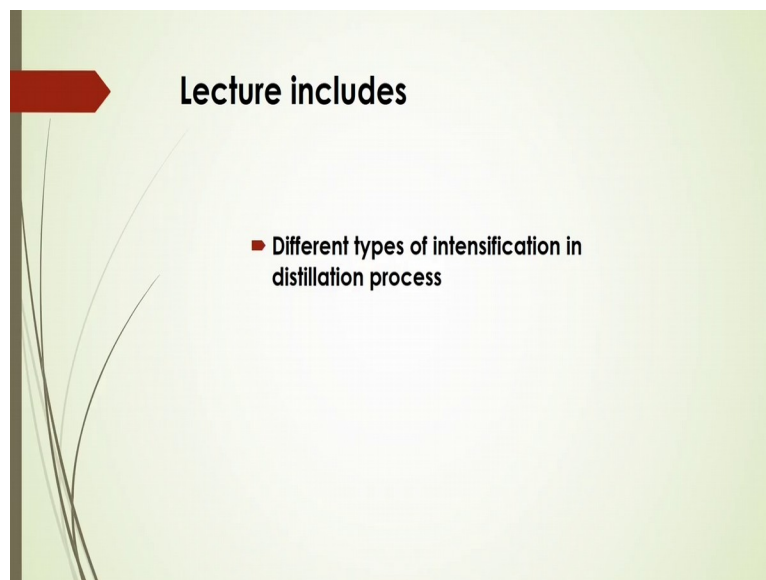
Module 9: Process intensification in Distillation
Lecture 9.2: Types of Intensified Distillation Units

Massive Open Online Course
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Govt. of India

By
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Welcome to massive open online course on chemical process intensification, so in the module 9 we are discussing something about process intensification in distillation system, so in this lecture we will discuss something more about the distillation system.

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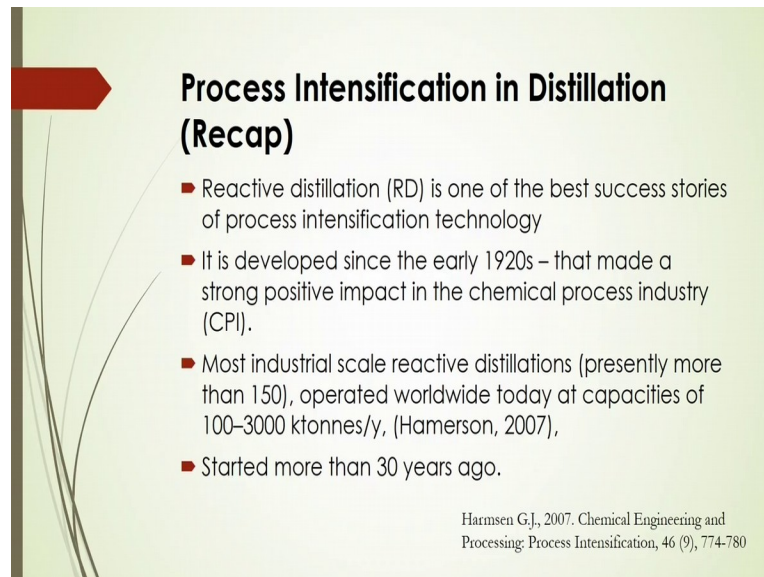


Lecture includes

- Different types of intensification in distillation process

Here we will discuss the types of different distillation units based on their intensification principal and we will discuss various types of you know, that intensification in distillation column, even application at a different aspect. We will of course trying to have some more information on this distillation process.

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Process Intensification in Distillation (Recap)

- Reactive distillation (RD) is one of the best success stories of process intensification technology
- It is developed since the early 1920s – that made a strong positive impact in the chemical process industry (CPI).
- Most industrial scale reactive distillations (presently more than 150), operated worldwide today at capacities of 100–3000 ktonnes/y, (Hamerson, 2007),
- Started more than 30 years ago.

Harmsen G.J., 2007. Chemical Engineering and Processing: Process Intensification, 46 (9), 774-780

Now as we already discussed that that reactive distillation is one of the best success stories of process intensification technology and it is developed since the early 1920s, that made a strong positive impact in the chemical process industry and most of the chemical, you know industrial scale reactive distillations that will be more actually than 150 and is being operated worldwide today, at capacities of 100 to 3000 kilotonnes per year and it is reported by Hamerson in 2007, so this is based on that period I think, to be more whatever he has reported. **So**, I can say that it would be more intensified unit based on this reactive process in the distillation column. This actually started more than 30 years ago, he has actually reported in his paper that the intensification unit so those are developed to be more than 150, so it maybe you know that, even more also nowadays.

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Different types of RD process intensification

Next level of process intensification would require more advanced RD configurations, which allow an additional range of operating conditions (not available in classic RD setups) such as:

- Reactive dividing-wall columns
- Reactive cyclic distillation (R-CyDist)
- Reactive (internally) heat integrated distillation column (R-HiDiC)
- Reactive HiGee distillation (R-HiGee)
- Membrane-assisted RD
- Microwave-assisted RD
- Ultrasound-assisted RD

So, what are the different types of the distillation process where reaction as well as distillation both are happening simultaneously? So, since the normal distillation column is intensified in different way, in that case we told that the reactive distillation is one of the most important distillation process where, the reactive distillation even it is intensified in the next level. So next level of the process intensification, in that case I would require more advanced reactive distillation configurations and that allow an additional range of operating conditions there.

So, this additional range of operating conditions actually will be incorporated in this type of you know, reactive distillation process where intensification has been implemented. So, in the conventional system that is called classic reactive distillation setup, in that case you know that additional range of operating conditions are not available, so for incorporating those additional range of operating conditions even with different you know, mechanism which are being incorporated with this classical reactive distillation process based on which that you know, that the reactive distillation processes are you know, intensified.

Now, these are some slides which is shown that these are some you know, important you know reactive distillation configurations where it is being developed based on that some process intensification. So like, you know reactive dividing wall columns, reactive cyclic distillation column, it is you know short form just call that R-CyDist that is R-CyDist and reactive internal heat integrated system are actually coming in to picture and these are also interesting in, you know, different scientific and you know the research community and in that case you know, it is called as HiDiC distillation column and then you know another

important you know, intensification of this reactive distillation it is called HiGee distillation, that is high gravity system, how this intensification of distillation systems are being actually incorporated.

So that is called reactive HiGee distillation and other you know, mechanism also sometimes incorporated to get that you know hybrid system of this reactive distillation system like membrane is actually integrated with that reactive distillation column, so in that case it is called hybrid distillation column. So, this hybrid distillation column is actually intensified based on that incorporation or adding the other mechanism for improvement of process performance in the reactive distillation column and also reducing the cost and other you know reaction you know, for kinetics.

Another important it is called you know, microwave assisted reactive distillation system, in that case how microwave is actually being incorporated for the intensification of the process of this reactive distillation and then ultrasound assisted reactive distillation system also are important, they are how the ultrasound also can actually, you know, that control the limits of the reactions there, in the reactive distillation system that are being actually developed based on this ultrasound mechanism and also, it will give you that intensification of the reactive distillation process by hybridisation. So, these are the different, you know types of reactive distillation process intensification so we will discuss something more about that individual you know, type of you know, reactive distillation process where intensification is incorporated.

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Reactive dividing-wall columns (RDWC)

- Dividing wall column (DWC) technology is expanding its use to azeotropic separations and reactive distillation (Kiss, 2013).
- Hence RD in a DWC is developed in academia and applied industrially.
- The advantages demonstrated by this highly integrated process are:
- high conversion, increased selectivity and product purity, significant energy and cost savings

Ref: Kiss A.A., 2013, Advanced distillation technologies - Design, control and applications, Wiley-Blackwell, Chichester, UK.

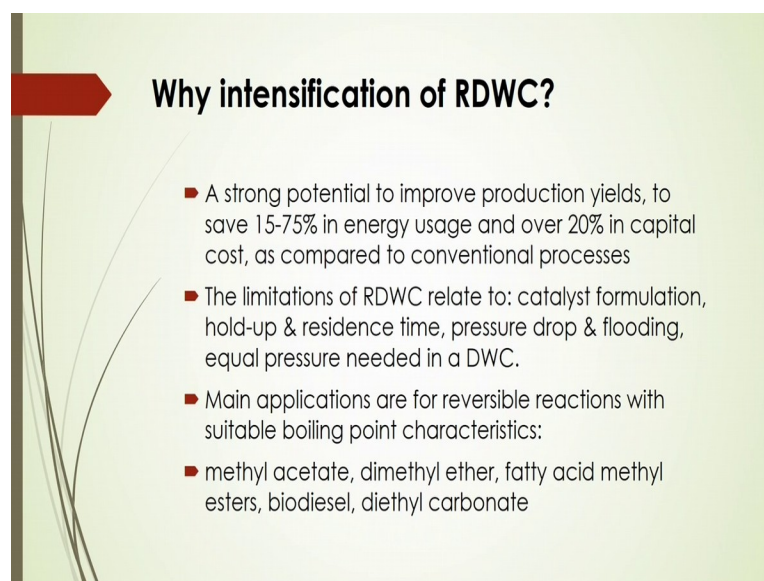
Typical configuration of an R-DWC as well as an application to the dimethyl ether process

The diagram illustrates the typical configuration of an R-DWC and its application to the dimethyl ether process. The top part shows a vertical column with a central 'Dividing-wall' and two side sections labeled 'Prefractionator' and 'Main column'. The bottom part shows a similar column with 'Methanol' and 'Methanol (recycle)' inputs, and 'DME' and 'Water' outputs.

Now if we talk about that reactive dividing wall columns for the intensification of the reactive distillation system. It can be actually given a short form of RDWC, that is dividing wall column, so technology is actually expanding its use of azeotropic separations and reactive distillation. So it is reported by Kiss in 2013 in you know, his book Advanced Distillation technologies - Design, control and application and according to his you know, opinion that, this reactive distillation in this reactive dividing wall column system is developed in, you know academia and applied industry and it will give you some you know, advantages of that integration process of this reactive distillation column, for high conversion in case to the selectivity and product purity, significant energy and cost savings.

So, with this reactive dividing wall columns see, how it is here like this distillation column it is being divided and this half portion of this you know, reactive distillation column is actually configured for this **pre-fractionator** here and then, you know that in this main column there will be, you know that reaction as well as you know that and other part will be that as a separation. So, in this case these are the example so generally two typical **configurations** of this you know, reactive dividing wall columns are you know, applied to, you know for the chemical engineering process intensification. This type of actually system can be used for you know that application to the dimethyl ether processes, so in that case you can get that high conversion, increased selectivity and product purity and in that case, you can save that significant amount of energy and also cost. So, this is the advantages of this reactive dividing wall columns.

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Why intensification of RDWC?

- A strong potential to improve production yields, to save 15-75% in energy usage and over 20% in capital cost, as compared to conventional processes
- The limitations of RDWC relate to: catalyst formulation, hold-up & residence time, pressure drop & flooding, equal pressure needed in a DWC.
- Main applications are for reversible reactions with suitable boiling point characteristics:
- methyl acetate, dimethyl ether, fatty acid methyl esters, biodiesel, diethyl carbonate

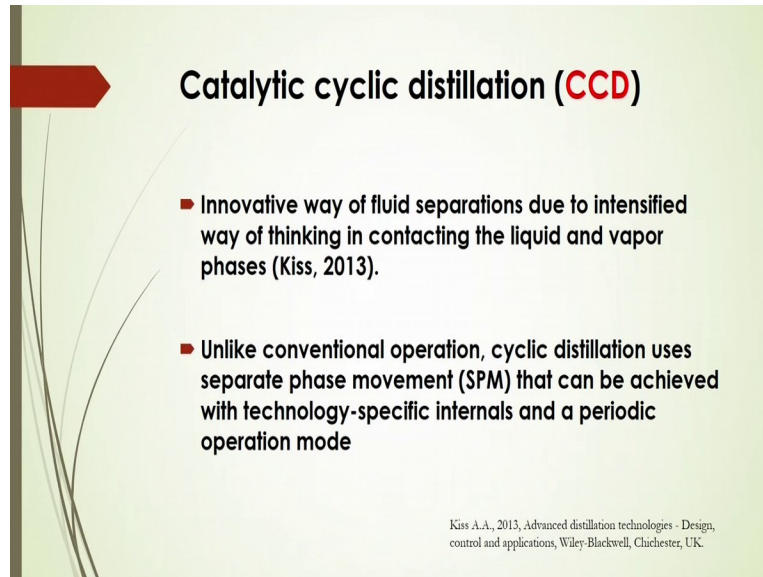
Now, in this case a strong potential to improve that production yields to save 15 to 75 percent in energy usage and also you can get over 20 percent in capital cost reduction as compared to the conventional processes and in this case some limitations of course will be there and the limitations is related to the catalyst formulation, hold up and residence time distribution and also pressure drop, flooding, equal pressure needed in a DWC.

So for this to actually work on those limitations in the case of you know, catalyst formulation hold-up and other hydrodynamic characteristics you have to do more research on this... Or some research also is going on, on that to get remediation of this you know, limitations based on their hydrodynamic aspects and in this **case, you** will see **main applications** are for the reversible reactions with suitable boiling point characteristics there, mainly applied for methyl acetate, dimethyl ether and fatty acid methyl esters, biodiesel production even you know, diethyl carbonate system also it is very important in this case.

So, that is why this dividing wall column systems are important for those you know reversible reaction, where the suitable boiling point characteristics to be you know incorporated. So, in this case you can get that improvement of the production yield and you can save some energy, you can save the capital cost also compared to that conventional processes and in this case of course, some you know, you can say that some limitations will come based on that it is hydrodynamics because, because of this dividing wall system you may get that higher pressure drop even residence time maybe you know that sometimes it will be lower for this reversible reactions and also hold-up should be you know, segregated in such a way that hold-up cannot be controlled sometimes you know that for the system.

So, hold-up distribution and flooding also is important there if you divide it into **two parts** or **three** parts, in that case may be flooding would be more disadvantages for that. So, you have to control **those flooding formations** and also catalyst formulation is one of the important things, their distribution of that you know catalyst and set the reactor that should be one important factor to you know get that you know, lower performance of the processes. So, to get that you know, improvement of that performance of the reaction that this type of hydrodynamic characteristics to be actually you know, studied more and so that you can you know, control those hydrodynamic characteristics for having more performance of the reactions.

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Catalytic cyclic distillation (CCD)

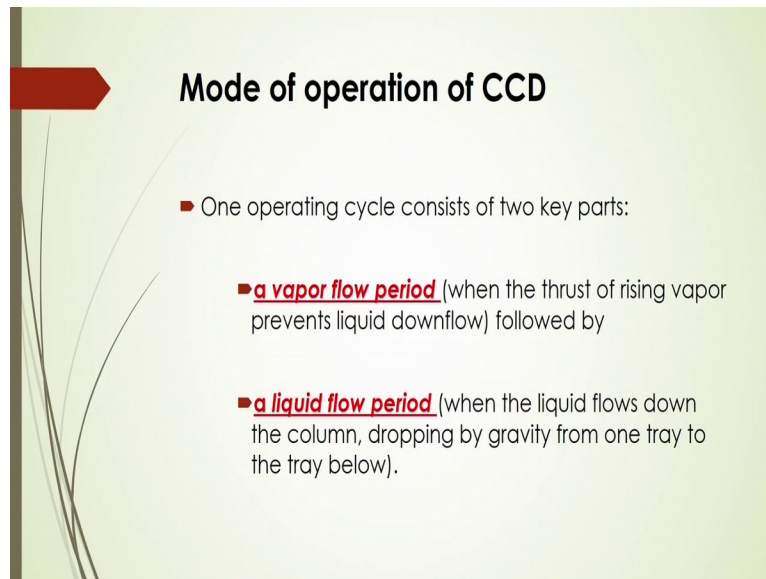
- Innovative way of fluid separations due to intensified way of thinking in contacting the liquid and vapor phases (Kiss, 2013).
- Unlike conventional operation, cyclic distillation uses separate phase movement (SPM) that can be achieved with technology-specific internals and a periodic operation mode

Kiss A.A., 2013, Advanced distillation technologies - Design, control and applications, Wiley-Blackwell, Chichester, UK.

Another important it is called catalytic cycling distillation process, in that case you know that in this process the intensification can be done based on the you know, innovative way of fluid separations due to intensified way of thinking in contacting the liquid and vapour phases. So, in that case, you know that unlike conventional operations this type of distillation uses separate phases movement and that can be achieved with you know technology specific internals and periodic operational mode.

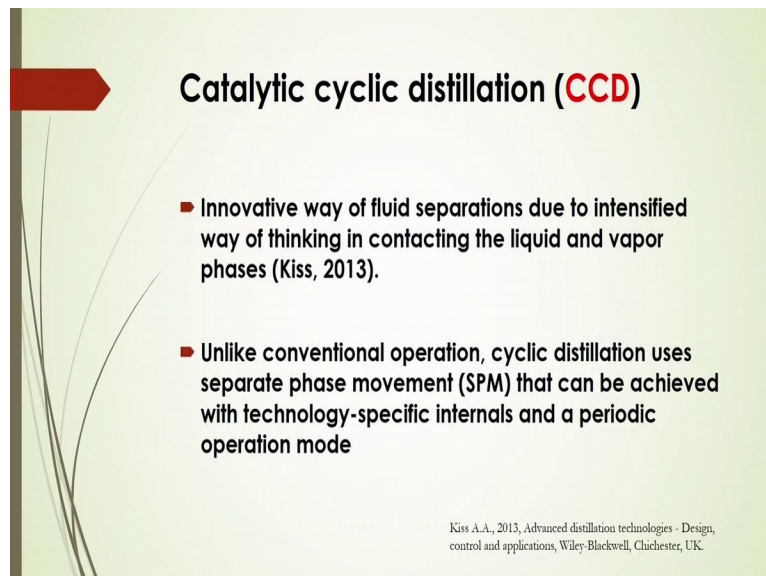
So this is important for the cycling distillation process where catalyst you know, cyclitisation is an important phenomena there, where you know that the liquid and vapour phases contact will be more important driving forces for the intensification of the processors and in that case how that liquid and vapour phases will be distributed, based on that you know their movement or momentum exchange of that liquid and vapour inside the column based on that specific internal in the columns. **So**, you can get that intensification based on **these** internal systems.

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Mode of operation of CCD

- One operating cycle consists of two key parts:
 - **a vapor flow period** (when the thrust of rising vapor prevents liquid downflow) followed by
 - **a liquid flow period** (when the liquid flows down the column, dropping by gravity from one tray to the tray below).



Catalytic cyclic distillation (CCD)

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- Unlike conventional operation, cyclic distillation uses separate phase movement (SPM) that can be achieved with technology-specific internals and a periodic operation mode

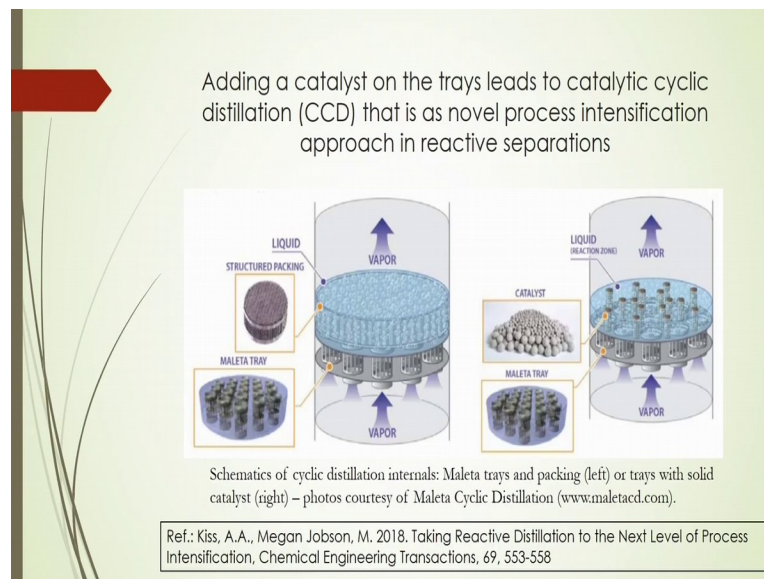
Kiss A.A., 2013, Advanced distillation technologies - Design, control and applications, Wiley-Blackwell, Chichester, UK.

And **of course**, you have to operate those you know that CCD that is cyclic distillation, catalytic cycling distillation named as CCD. One operating cyclic consist of 2 key parts there. In that case a vapour flow period when the thrust of rising vapour that may you know, prevents the liquid down flow that is followed by a liquid flow period, when the liquid flows down the column that dropped by gravity from one tray to **another** tray below. So, this is one of the important you know that mode of operation by these 2 key parts, in that case very important that there should be you know that, 2 period of that parts a vapour flow period and the liquid flow period.

So in the vapour flow period you will see that the thrust of the rising vapour prevents the liquid downflow, so in the parallel you will see that the liquid will be coming downwards, so

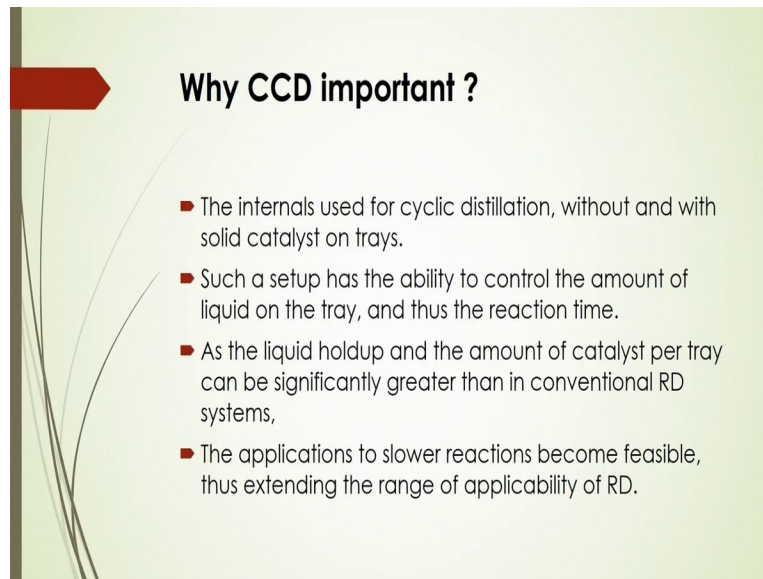
it will be better to get it upward, so it can be prevented by you know, that rising vapour you know sometimes it will be prevented by the liquid down flow and then you know that when the liquid flows downward in that case dropping by gravity from one tray to the tray below that may you know that, hinder the rising of the vapour there inside the column. In that case you can get the more residence time of the vapour elements there in the column.

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And adding a catalyst on the trays in that case leads to catalytic cyclic distillation that is, as a novel process intensification approach in this reactive distillation processes and in this **case**, you will see how this reactive distillation processes being happened as reported by this Kiss and Jobson in 2018 there. So this is for schematic of cyclic distillation internals there and in that case Maleta trays and packings in the left side or trays with solid catalyst you will see on the right side, you will see that how this are actually taking part in this you know, that distribution of the vapour and also liquid inside the column and also catalyst particles, how it is coming in contact with the vapour and liquid and that depends on the distribution of the liquid throughout the column. So, this is based on that contact performance this you know, catalytic cyclic distillation systems are being intensified for the reactive separation process.

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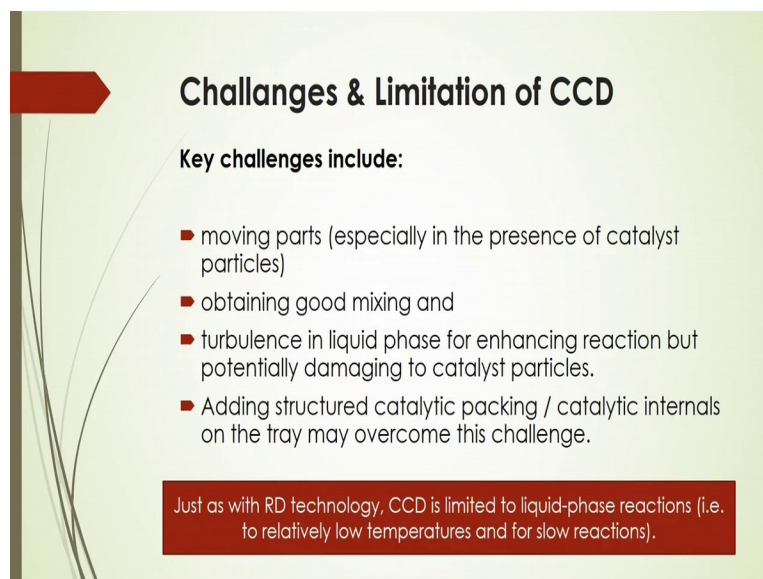


Why CCD important ?

- The internals used for cyclic distillation, without and with solid catalyst on trays.
- Such a setup has the ability to control the amount of liquid on the tray, and thus the reaction time.
- As the liquid holdup and the amount of catalyst per tray can be significantly greater than in conventional RD systems,
- The applications to slower reactions become feasible, thus extending the range of applicability of RD.

Now, why this CCD is more important in this case because the internals whatever it is being used for cyclic distillation process with or without solid catalyst on the trays this is important there and in that case a setup has the ability to you know, control the amount of liquid on the tray and also thus the reaction time there. As the liquid hold-up and the amount of catalyst per tray can be significantly greater than the conventional RD systems and applications to you know slower the reactions that will become feasible thus extending the range of applicability of the RD system. So, this is one important aspects of this cyclic distillation system.

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Challenges & Limitation of CCD

Key challenges include:

- moving parts (especially in the presence of catalyst particles)
- obtaining good mixing and
- turbulence in liquid phase for enhancing reaction but potentially damaging to catalyst particles.
- Adding structured catalytic packing / catalytic internals on the tray may overcome this challenge.

Just as with RD technology, CCD is limited to liquid-phase reactions (i.e. to relatively low temperatures and for slow reactions).

But in this case there are some other challenges and limitation of course will be there, in that case you know that, in this case you will see that moving parts especially in the presence of

catalyst are there and may be you know that some obtaining good mixing is required there in that case more research is, of course to be carried out and turbulence in the liquid phase for enhancing the reaction but potentially damaging to the catalyst particles is one of the important you know, shortcomings of this you know processes because you know that high turbulence may you know, damage that catalyst particles.

It may sometimes you know that, whatever arrangement of the catalyst particles would be made for the better contact that may you know change because of this high turbulence and also adding **structured catalytic packing or catalytic internals** on the tray may overcome this challenge. So, you have to you know structure that catalyst particles as a packing in such a way that high turbulence sometimes you know that, damaging of the catalyst particles **maybe** you know that overcome by this you know, structured catalytic packing arrangement. So that you have to think about that how that catalytic packing can be well structured, so that even high turbulence that may not that damage that catalyst particles.

So, this is one of the important **challenges** of getting more improvement of the catalytic cyclic distillation process for the reactions and just as with the reactive distillation technology you can say that, this catalytic cyclic distillation process is limited to you know liquid phase reactions that is to relatively low temperatures and for you know, slow reactions there. So in this case these are the challenges that you have to you know that overcome by you know doing and carrying out more research on this subject.

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Advantage of CCD

- This cyclic mode of operation leads to key advantages, compared to conventional trayed columns:
 - high throughput and equipment productivity,
 - high separation efficiencies (140-200% Murphree efficiency)
 - reduced energy requirements (20-35% savings), and
 - Increased quality of the products.

Ref.: Kiss, A.A., Megan Jobson, M. 2018. Taking Reactive Distillation to the Next Level of Process Intensification. Chemical Engineering Transactions, 69, 553-558

And advantage of that CCD of course, why this CCD is coming in picture and also how this process is being actually having more interest in the research community even in industrial sector that is very important because in this case you apply the high through put and equipment productivity for getting that more intensification process. Even high separation efficiency also can be obtained by this process, even 140 to 200 percent Murphree efficiency as per report by you know, that Kiss in 2018 and also you will see that, you can reduce the energy requirements 35 percent and you can also increase the quality of the products based on this you know, process intensification of the reactive distillation process in this cyclic catalytic cyclic distillation system.

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Reactive heat integrated distillation column (HIDiC)

- Heat pump assisted distillation which uses internal heat integration
- The whole rectifying section of a column is the heat source, while the stripping part acts as a heat sink

Heat is transferred from the rectifying section (operated at high pressure) to the stripping section.

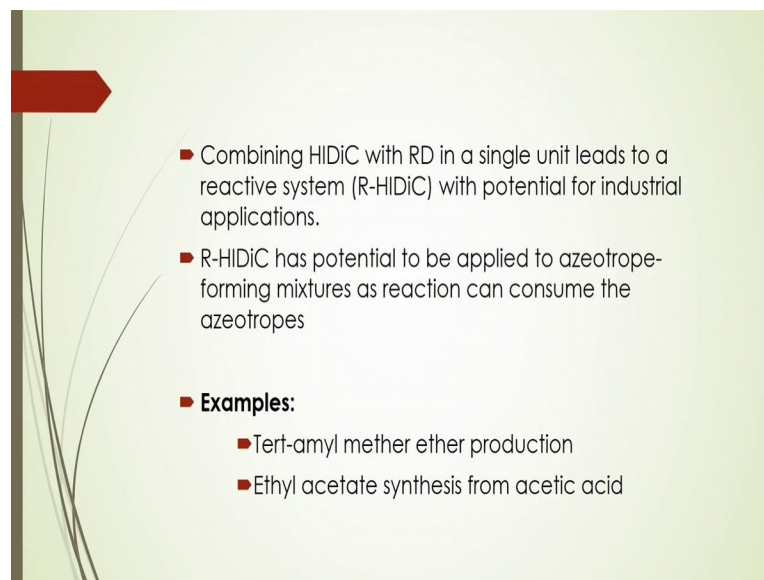
Heat integrated distillation column Reactive HIDiC configuration

Kiss, A.A., Megan Jobson, M. 2018. Taking Reactive Distillation to the Next Level of Process Intensification. Chemical Engineering Transactions, 69, 553-558

Another one of the important, even widely used you know, reactive distillation process where you are you know, operating this system with heat input and that heat integrated distillation column thus actually configured and developed for this reactive distillation system. In that case heat pump assisted distillation which uses internal heat integration **and, in this case,** the whole rectifying section, as shown in figure here in the slides you will see that, is the heat source and while the stripping part acts as a heat sink here, so there are one heating sections and one another is you call the stripping sections.

So, in the rectifying section of the column is the heat source there while the stripping heat acts as a heat sink there. In this case heat is transferred from the rectifying section that is operated at you know high pressure to the you know, stripping section, so here in this figure it is shown that this is your rectifying section and this is heat section here I will see that and also you will see that, the stripper section also in this figure. So, heat is going from this rectifying section to the heat section and then it is applied to the you know that, stripping section for the better separation there. So, this type of you know rectification column or you can say that distillation column in this case you can utilise that heat energy to get that you know, more intensification of the you know that processes by integration of this heat what is actually coming out from that you know rectification system at its higher pressure.

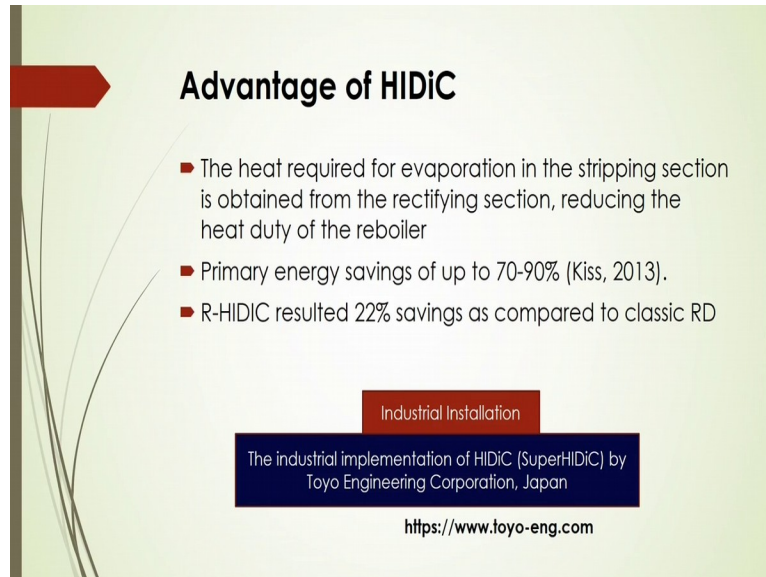
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Combining this HIDiC with reactive distillation in a single unit that may you know lead to a reactive system and with potential for the industrial applications and this you know, reactive system of this R-HIDiC has potential to be applied to azeotrope-forming mixtures as reaction that can be used for consume the azeotrope there and in that case some examples like Tert-

amyl methers you know ether production and ethyl acetate synthesis from acetic acid, so these other examples where you can integrate the heat to utilize it for the better performance of the reaction as for this azeotropic type of mixture as the reaction can consume the azeotropes there.

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Advantage of HIDiC

- The heat required for evaporation in the stripping section is obtained from the rectifying section, reducing the heat duty of the reboiler
- Primary energy savings of up to 70-90% (Kiss, 2013).
- R-HIDiC resulted 22% savings as compared to classic RD

Industrial Installation

The industrial implementation of HIDiC (SuperHIDiC) by Toyo Engineering Corporation, Japan

<https://www.toyo-eng.com>

And in this case the heat whatever it is required for the evaporation in the stripping section is obtained from the rectifying section and that reduces the heat duty of the reboiler and primary energy savings of up to 70 to 90 percent as per report of Kiss in 2013 and also you can save up to you know, 22 percent of that is, cost as compared to the classic reactive distillation system. In this case you remember that industrial implementation of HIDiC it is done by you know, that super HIDiC system by Toyo engineering Corporation, Japan and you can go to this website to get more details about this you know, that this heat integrated system of you know that, reactive distillation system.

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Disadvantage of HiDiC

The range of applicability (beneficial to equilibrium-limited reactions) is likely to be narrower than that for conventional RD, i.e. close-boiling mixtures (to avoid high pressure ratio in rectifying and stripping sections).

And of course, every system has some disadvantages in this case also you may have some disadvantages of this using integrated system of heat, heat integrated system of this reactive system, in that case the range of applicability it may be beneficial to the equilibrium limited reactions and which is likely to be narrower than that for the conventional reactive distillation system. That is close boiling mixtures to avoid high-pressure ratio in a rectifying and stripping sections there, so the range of applicability is limited here it is beneficial to equilibrium limited reactions only. So, you can do more research on this to get that you know, wide applicability of the reaction systems where you can you know, control that equilibrium of the reaction system.

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Reactive High Gravity (HiGee) distillation

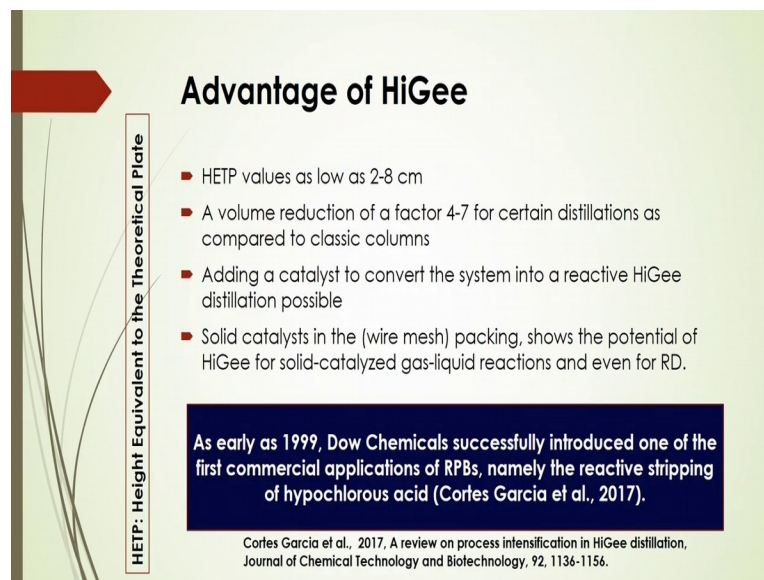
- High gravity (HiGee) technology replaces the usual gravitational field by a centrifugal field achieved in a specially shaped rotating device
- The high gravity field (100-1000 g) shifts the flooding limit and allows the use of dense packing materials with a high interfacial area.

Rotating packed-bed for (reactive) HiGee distillation (Kiss and Jobson, 2018)

Kiss, A.A., Megan Jobson, M. 2018. Taking Reactive Distillation to the Next Level of Process Intensification, Chemical Engineering Transactions, 69, 553-558

Next another important intensification of this reactive distillation it is called high gravity distillation system, so it is HiGee distillation system and in this case we will see that this technology actually replaces the usual gravitational field by a centrifugal field that is achieved by this high gravity field in a you know, specifically shaped rotating device and in this case high gravity field whatever it is meant in generally 100 to 1000 gravity that may shifts the flooding limit and allows the use of dense packing materials with a high interfacial area. So, these are the advantages of using high gravity you know, reactive distillation system. So, this is also one of the **intensifications** of the process based on which you can get more for performance of the reaction system in the reactive distillation column as a hybrid system.

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Advantage of HiGee

- HETP values as low as 2-8 cm
- A volume reduction of a factor 4-7 for certain distillations as compared to classic columns
- Adding a catalyst to convert the system into a reactive HiGee distillation possible
- Solid catalysts in the (wire mesh) packing, shows the potential of HiGee for solid-catalyzed gas-liquid reactions and even for RD.

HETP: Height Equivalent to the Theoretical Plate

As early as 1999, Dow Chemicals successfully introduced one of the first commercial applications of RPBs, namely the reactive stripping of hypochlorous acid (Cortes Garcia et al., 2017).

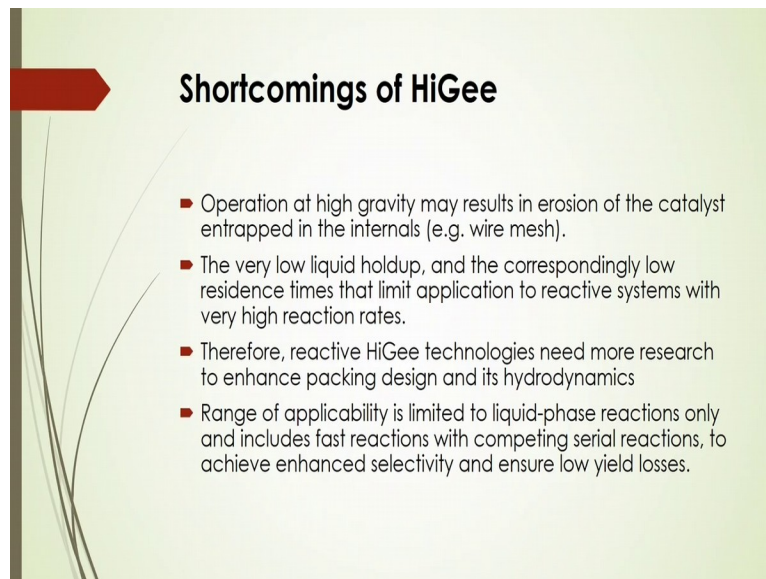
Cortes Garcia et al., 2017, A review on process intensification in HiGee distillation, Journal of Chemical Technology and Biotechnology, 92, 1136-1156.

And in this **case**, you will see that height equivalent to the theoretical plate may be within the value of 2 to 8 centimetre in this case a volume reduction of the factor 4 to 7 for certain distillations as compared to the classic columns. Adding a catalyst to convert the system into a reactive HiGee distillation in this case, it is very advantageous you can you know, easily you know, incorporate this catalyst to the converter of the system into a reactive distillation and in this case a solid catalyst in the you know, sometimes different geometric shape like wire shape, wire mesh packing shows the potential of the HiGee for you know, solid catalysed gas liquid reactions and even for the reactive distillation also.

In this case you know, in 1999 Dow **Chemicals, successfully** introduced one of the first commercial application of this you know RPBs namely the reactive stripping of hypochlorous acid as per report by Cortes Garcia et al 2017. So, this is you know that reactive distillation

process where the Dow Chemicals they have successfully installed this technology for the process intensification at their commercial stage by, you know, the developing is called rotating packed bed system, that is RPBs namely for this reactive stripping or you know, hypochlorous acid there. So, this is one of the important you know process intensification for getting that you know incorporating the packing system to get more interfacial area for the mass transfer even for you know that, the better efficiency of the process.

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Shortcomings of HiGee

- Operation at high gravity may results in erosion of the catalyst entrapped in the internals (e.g. wire mesh).
- The very low liquid holdup, and the correspondingly low residence times that limit application to reactive systems with very high reaction rates.
- Therefore, reactive HiGee technologies need more research to enhance packing design and its hydrodynamics
- Range of applicability is limited to liquid-phase reactions only and includes fast reactions with competing serial reactions, to achieve enhanced selectivity and ensure low yield losses.

But it has some shortcomings like you know that, it may operate at you know, high gravity that may result in erosion of the catalyst which is entrapped in the internals and also in this case you can get the low liquid hold-up and also the low residence time that mainly may limit to the application to the reactive systems with high reaction rates; and also you will see that reactive HiGee technologies in this case because of this liquid hold-up distribution, even residence time distribution of you know that reaction limits, so in that case you may need to do the more research on this technology to enhance packing design and its hydrodynamics and range of applicability is limited to liquid phase reactions only and in that case it includes fast reactions with competing serial reactions and also it may be you know that, applied to achieve enhanced selectivity and ensure the low yield losses. So these are some shortcomings of this HiGee technology for the process intensification.

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	RD	R-DWC	CCD	R-HIDiC	R-HiGee
Process design & simulation (availability of methods & tools)	+++	+++	++	++	+
Process dynamics and control (availability of methods & tools)	+++	++	++	+	+
Practical challenges (ease of implementation)	+++	++	++	+	+
Range of applicability (variety of chemical reactions)	+++	++	++	+	+
Technology-readiness (pilot & industrial experience)	+++	++	+	n/a	n/a
Energy savings range (compared to classic processes)	15-80%	15-75%	20-35%	50-90%	n/a
Capital savings (compared to classic processes)	+++	+++	+++	n/a	+++

Ref.: Kissa, A.A., Megan Jobsona, M. 2018. Taking Reactive Distillation to the Next Level of Process Intensification, Chemical Engineering Transactions, 69, 553-558

Now let us have a look of comparison of these reactive distillation processes that combined with other process intensification technologies, like in terms of if you think about the process design and simulation that is, availability of methods and tools in that case, classic reactive distillation of course it is advantageous compared to the you know, HiGee technologies, even R-DWC is more advantageous than CCD and even RD is more advantageous than CCD, even R-HIDiC also is more advantageous. And you will see that process dynamics and control also these are some you know that, advantages and disadvantages of their you know, level based on the availability of methods and tools but some, you know technologist has more advantageous than other, that is based on that different aspects like practical challenges, range of applicability, technology, readiness, even energy saving range, capital savings all these things, but you see that capital saving in that case compared to classic processes you will see that RD you know that, will be more advantageous even R-DWC also is giving advantages even CCD also it is advantageous and HiGee technology is more advantageous.

So capital cost savings are more in this processes whereas, energy-saving ranges will be you know, it will be more in case of R-HIDiC systems where it is 50 to 90 percent, whereas for RD systems that is reactive distillation system, which is giving only 15 to 80 percent whereas CCD is giving 20 to 35 percent, but in this case you know, R-DWC that is, dividing wall column is giving also higher energy saving range, it is 15 to 75 percent but in case of readiness of the technology you will see that reactive distillation is of course is at its commercialisation stage but for intensification of this reactive distillation stage this is RDW, CCD are not even you know, in commercialisation stage for as readily used technology in the

scientific community and also in industry. And range of applicability you will see that in this case reactive distillation is more that is compared to the other you know, geometric base intensification like R-DWC, CCD and also R-HIDIC even for as compared to that R-HiGee technology.

So, in all those processes of course that practical challenges are there but you have to do scientific community even research community they are doing you know, more research on this you know, process intensified unit of this reactive distillation system to get more you know, advanced stage for the improvement of the process performance there.

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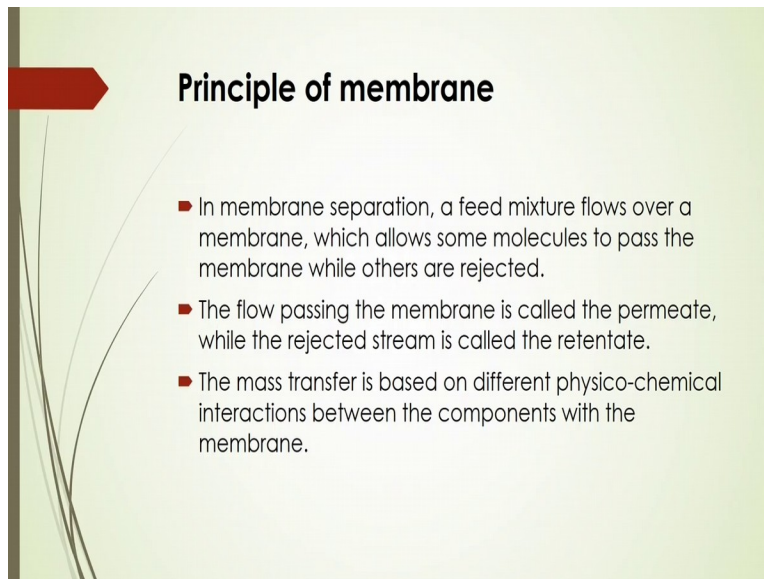
Membrane-assisted RD (MARD)

- Hybrid separation processes combine two or more unit operations, which contribute to a given separation task by means of different physical phenomena.
- They are integrated such that synergetic effects allow to overcome the limitations of the individual unit operations
- Membrane-assisted distillation processes constitute one possible type of a hybrid separation process.

Lutze and Gorak (2013), Chemical Engineering Research and Design, 91 (10) 1978-1997

Also you will see another that I told that, if you integrate this reactive distillation by several mechanism for intensification the process by you know that, hybridisation of this process by integrating of this other mechanism then you can get better performance of this you know, distillation column, so in this case hybrid separation processes that combines **two** or more unit operations which contribute to a given separation task by means of different physical phenomena, like they are integrated you know, such that synergetic effects that may allow to overcome the limitations of the individual unit operations and membrane-assisted distillation process that may constitute one possible type of a hybrid separation process.

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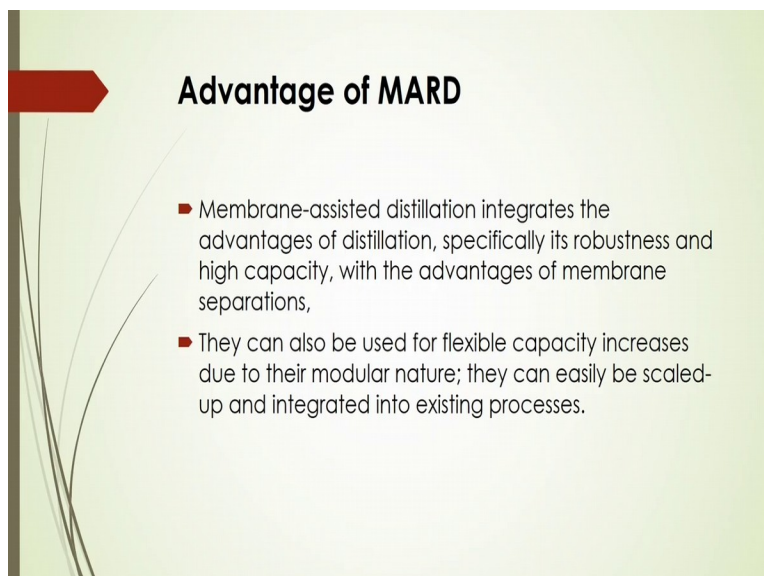


Principle of membrane

- In membrane separation, a feed mixture flows over a membrane, which allows some molecules to pass the membrane while others are rejected.
- The flow passing the membrane is called the permeate, while the rejected stream is called the retentate.
- The mass transfer is based on different physico-chemical interactions between the components with the membrane.

And in this case the membrane separation, a feed mixture flows over a membrane which allows you know, some molecules to pass the membrane while others are rejected and in the case of you know that, membrane process you will see that the flow passing the membrane, it is called the permeate while the rejected this cream is called the retentate. So,, the mass transfer is generally based on the different physico-chemical interactions between the components with the membrane, so this is the basic principles of the membrane.

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Advantage of MARD

- Membrane-assisted distillation integrates the advantages of distillation, specifically its robustness and high capacity, with the advantages of membrane separations,
- They can also be used for flexible capacity increases due to their modular nature; they can easily be scaled-up and integrated into existing processes.

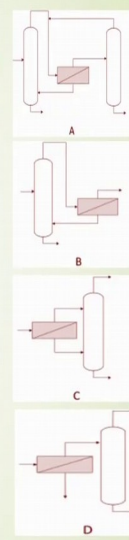
And if we apply this membrane by integrating this unit with the distillation column you may you know have that advantages like you know, it may give that you know, higher capacity for your you know, operation and it may be used for the flexible capacity increases due to the

modular nature of that membrane and they can easily be you know, scaled up and integrated into the existing processes. So, these are the advantages you know, you can get from this membrane assisted reactive distillation column.

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Different configurations of (MARD)

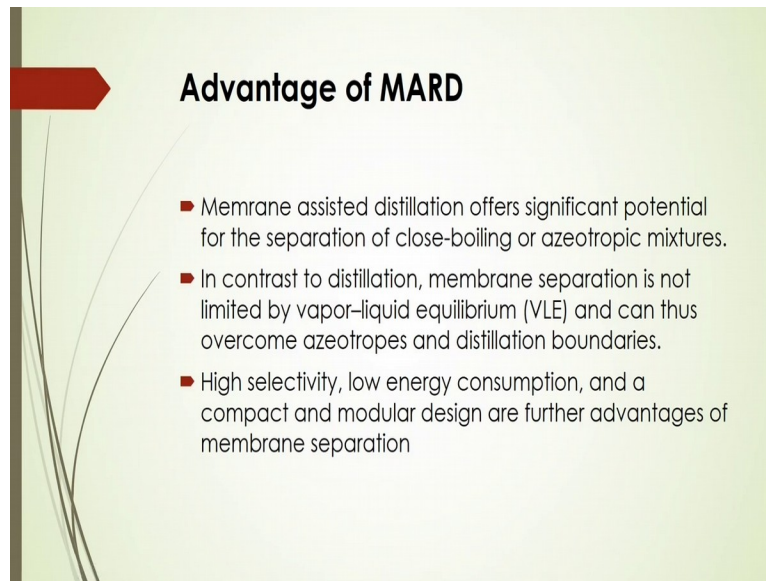
- **In configuration A**: the feed mixture is separated until occurrence of a separation boundary, e.g., a low boiling azeotrope, which exits as a distillate.
- **Configuration B**: may consist of a membrane at the bottom if a homogenous catalyst containing some reactant needs to be recycled into a reactive distillation via a retentate recycle
- **Configuration C**: represents the high selectivity of the membrane used to pre-fractionate the mixture, which relieves the distillation column. This process may lead to smaller distillation columns and lower reflux ratios.
- **In configuration D**, the membrane is used to separate a three-component mixture.



There are several you know that, configuration of this membrane assisted distillation columns like you know that configuration A, configuration B, configuration C and configuration D as shown in figure, in the slides. In this case you know that, in the configuration A the feed mixture is separated until occurrence of you know, separation boundary like you know, that all low boiling azeotrope which exist as a distillate there and see that figure in this distillation column and how this membrane is being incorporated or integrated with this distillation column and in this configuration A, in this configuration B, C and D.

In configuration B that, you will see that configuration may consist of a membrane at the bottom if a homogenous catalyst containing some reactant needs to be recycled into the reactive distillation via a retentate recycle. Whereas in configuration C we will see that it will give the high selectivity of the membrane, that is used to pre-fractionate the mixture which relieves the distillation column and this process may lead to smaller distillation columns and lower reflux ratios and the configuration D you will see that case the membrane is used to separate the **three-component** mixture. So, these are the 4 different types of configurations that are being used in the reactive distillation process.

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Advantage of MARD

- Membrane assisted distillation offers significant potential for the separation of close-boiling or azeotropic mixtures.
- In contrast to distillation, membrane separation is not limited by vapor-liquid equilibrium (VLE) and can thus overcome azeotropes and distillation boundaries.
- High selectivity, low energy consumption, and a compact and modular design are further advantages of membrane separation

And then in this case you will see that, whenever you are using this membrane assisted distillation columns it may offer you know, significant potential for the separation that is close boiling or you know, azeotropic mixture type feed and in contrast to distillation membrane separation is not limited by vapour liquid equilibrium and in that case this can be you know, overcome by you know that overcome that azeotropic and also distillation boundaries and in that case high selectivity, low energy consumption and a compact and modular design are you know, further advantages of this membrane based separation.

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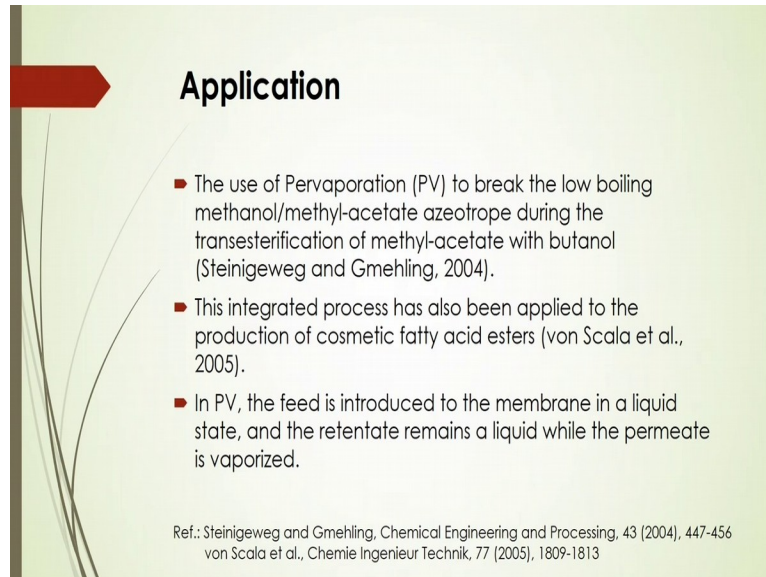


- Membrane processes are usually not economically viable if a large permeate flow rate or high purities of both permeate and retentate streams are required.
- Membrane-assisted distillation combines the advantages of both separation principles, operates without an additional separation agent, and can result in reduced energy demand, emissions, and investment cost.

And this membrane processes are usually not economically viable if a large permeate flow rate or high **purity of** both the permeate and retentate systems are required, so these are the

one disadvantage of this and also membrane assisted distillation combines the advantages of both separation principals, operates without an additional separation agent and can result in reduced energy demand, emissions and investment cost. So, this is the important aspects of or advantages of membrane assisted distillation column.

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Application

- The use of Pervaporation (PV) to break the low boiling methanol/methyl-acetate azeotrope during the transesterification of methyl-acetate with butanol (Steinigeweg and Gmehling, 2004).
- This integrated process has also been applied to the production of cosmetic fatty acid esters (von Scala et al., 2005).
- In PV, the feed is introduced to the membrane in a liquid state, and the retentate remains a liquid while the permeate is vaporized.

Ref.: Steinigeweg and Gmehling, Chemical Engineering and Processing, 43 (2004), 447-456
von Scala et al., Chemie Ingenieur Technik, 77 (2005), 1809-1813

You can use this you know, membrane assisted distillation column like you know, some application in this case you can say, the use of pervaporation to break the low boiling methanol or methyl acetate azeotrope during the transesterification of methyl acetate with butanol, as per you know that report of you know Steinigeweg and Gmehling you know, the 2004 and this integrated process has also been applied to the production of cosmetic fatty acid esters and also this pervaporation, the feed is introduced to the membrane in a liquid state and the retentate remains a liquid while the permeate is vaporised there.

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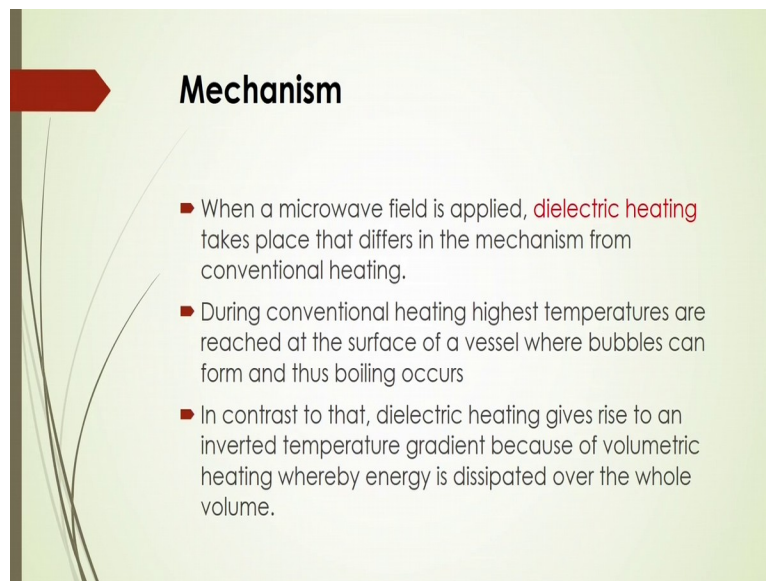
Microwave-assisted RD (MWARD)

- Microwave-assisted reactive distillation can be a useful alternative to the use of alternative energy forms in industrial esterification
- Advantages of microwave heating:
 - Selective energy absorption,
 - non-pollution,
 - high energy efficiency and
 - high product quality

Synthesis of Di-2-ethylhexyl phthalate (DOP), consisting 10 kW microwave generator,

So, another important you know, micro wave assisted reactive distillation column is you know, gaining importance to the research community, academic and scientific community where this micro wave system can be used for intensification of the distillation process. It can be used as an you know, alternative you know, source of you know, energy supplied for the distillation process for that you know, esterification process as an example you can say and also it may use that you know, selective energy absorption, non-pollution, high energy efficiency and high production quality you can get these type of advantages by this microwave assisted distillation system. And this case you will see that how microwave can be you know that, utilised here and this is your reactive distillation column and from this source of this microwave generator and you can apply this energy for you know that, intensification of the process like you know synthesis of Di-2-ethylhexyl you know, that phthalate that is called DOP that consisting you know, 10 kilowatt microwave generator here that is used for that you know, intensification of the process for this synthesis of this DOP. So, in that case you can get that you know that, energy absorption efficiency, you can get that products that will be non-polluted even you can get that high energy efficiency, high product quality based on this microwave assisted column.

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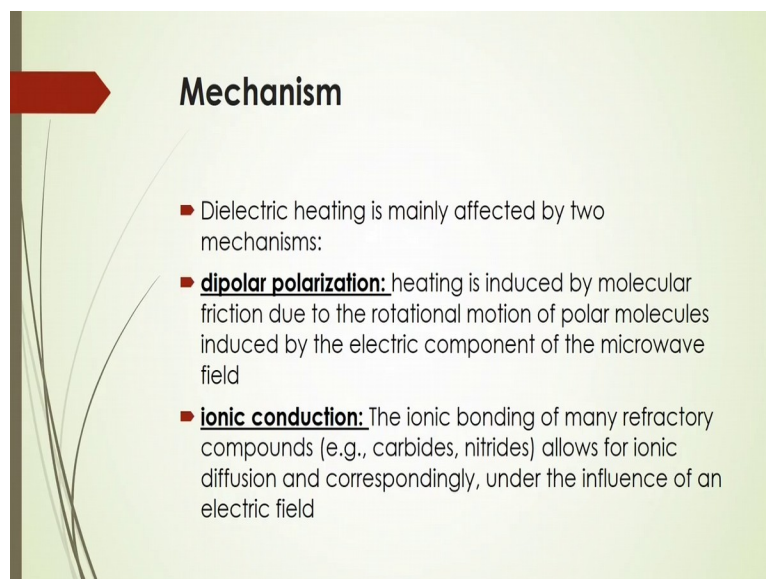


Mechanism

- When a microwave field is applied, **dielectric heating** takes place that differs in the mechanism from conventional heating.
- During conventional heating highest temperatures are reached at the surface of a vessel where bubbles can form and thus boiling occurs
- In contrast to that, dielectric heating gives rise to an inverted temperature gradient because of volumetric heating whereby energy is dissipated over the whole volume.

In this case when a microwave field is applied you will see that dielectric heating takes place that differs in the mechanism from conventional heating and during that conventional heating highest temperatures are, you know, reached at the surface of a vessel where bubbles can form and thus boiling occurs. This is the conventional heating system whereas, in contrast to this conventional heating system you can apply this dielectric heating that may give you better way to get you know, in what temperature radiant because of volumetric heating where energy is dissipated over the whole volume by this you know, dielectric heating system.

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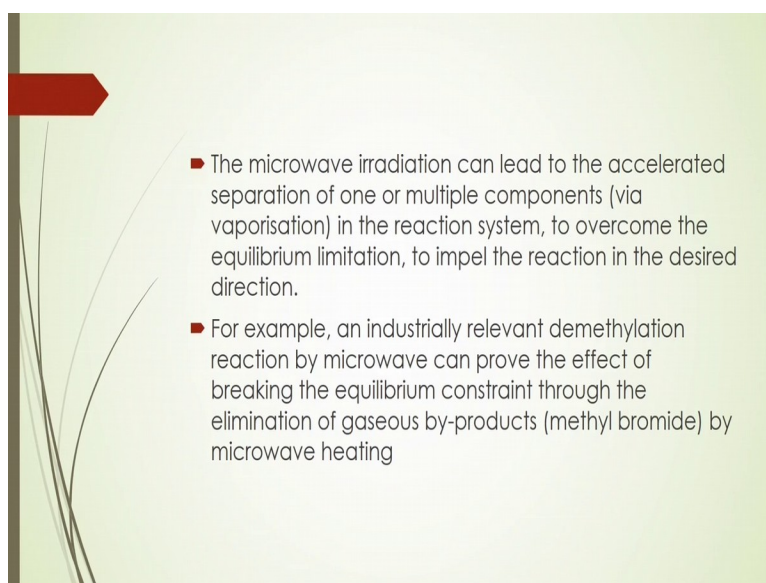
Mechanism

- Dielectric heating is mainly affected by two mechanisms:
- **dipolar polarization:** heating is induced by molecular friction due to the rotational motion of polar molecules induced by the electric component of the microwave field
- **ionic conduction:** The ionic bonding of many refractory compounds (e.g., carbides, nitrides) allows for ionic diffusion and correspondingly, under the influence of an electric field

And dielectric heating is mainly affected by **two** mechanisms what is called dipolar polarism and also ionic conduction and in this **case, heating** is, in the case of dipolar polarisation the

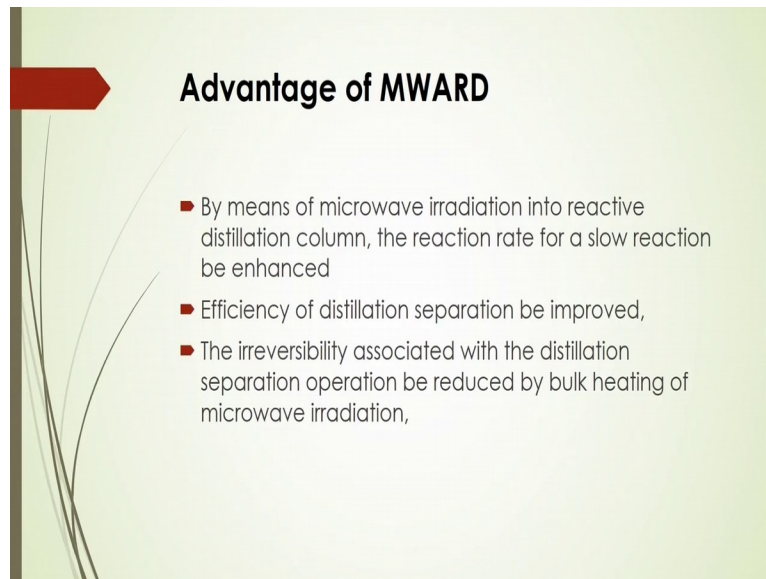
heating is induced by the molecular friction due to the rotational motion of the polar molecules that is induced by the electric component of the microwave field. Whereas ionic conduction in that case ionic bonding of the many refractory compounds like carbides, nitrides always you know, those are allows for ionic diffusion and correspondingly you can say that under the influence of an electric field that enhanced that diffusion, ionic diffusion and hence that you know, in case of the enhancement of the reactions, kinetics and also you can say that more better way or you can say that intensification way of production of by-products by saving your energy as well as your cost.

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In this case the microwave radiation can lead to the accelerated separation of one or multiple components via vaporisation in the reaction system and also, it can overcome the equilibrium limitation to impel the reaction in the desired direction. And industrially relevant reactions like demethylation reaction by microwave can prove the effect of you know, breaking the equilibrium constraint through the elimination of gaseous by-products by microwave heating.

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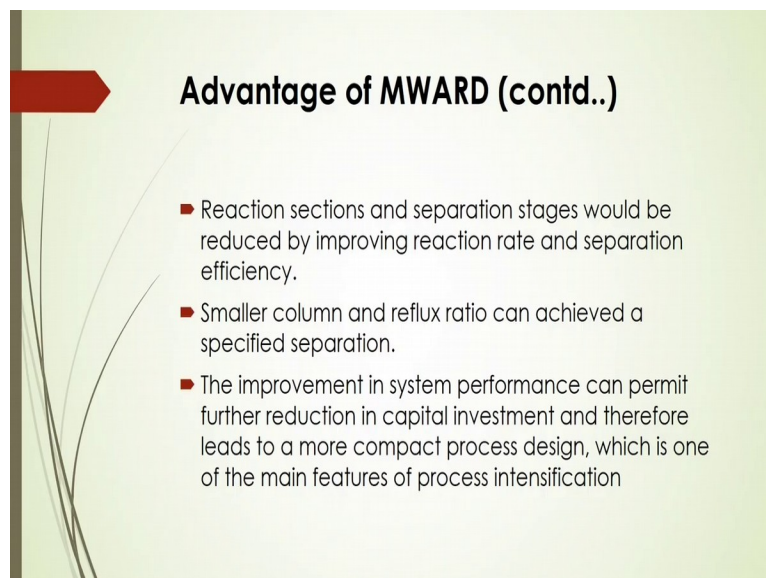


Advantage of MWARD

- By means of microwave irradiation into reactive distillation column, the reaction rate for a slow reaction be enhanced
- Efficiency of distillation separation be improved,
- The irreversibility associated with the distillation separation operation be reduced by bulk heating of microwave irradiation,

And in this **case**, you can get some advantage like, you know that, by means of this microwave irradiation into the reactive distillation column, the reaction rate for a slow reaction be enhanced and also efficiency of distillation separation can be improved and the irreversibility associate with the distillation separation operation may be reduced by bulk heating of microwave irradiation.

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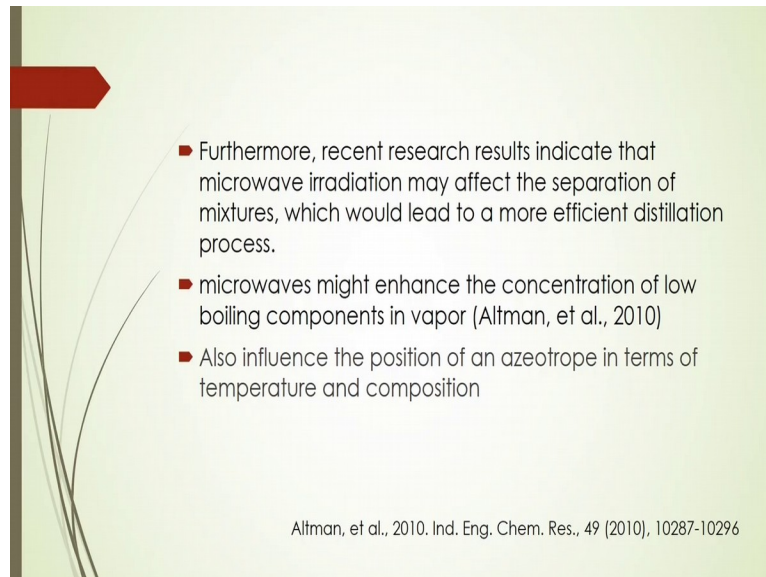
Advantage of MWARD (contd..)

- Reaction sections and separation stages would be reduced by improving reaction rate and separation efficiency.
- Smaller column and reflux ratio can achieved a specified separation.
- The improvement in system performance can permit further reduction in capital investment and therefore leads to a more compact process design, which is one of the main features of process intensification

Also, you can you know, achieve smaller columns and also reflux ratio by specific separation process and also, you can improve the system performance and that performance can permit further reduction in the capital investment and therefore leads to a more compact you know, process design which is one of the main features of the process intensification and also the

reaction section and separation stage would be reduced by improving you can say, that reaction rate and separation efficiency.

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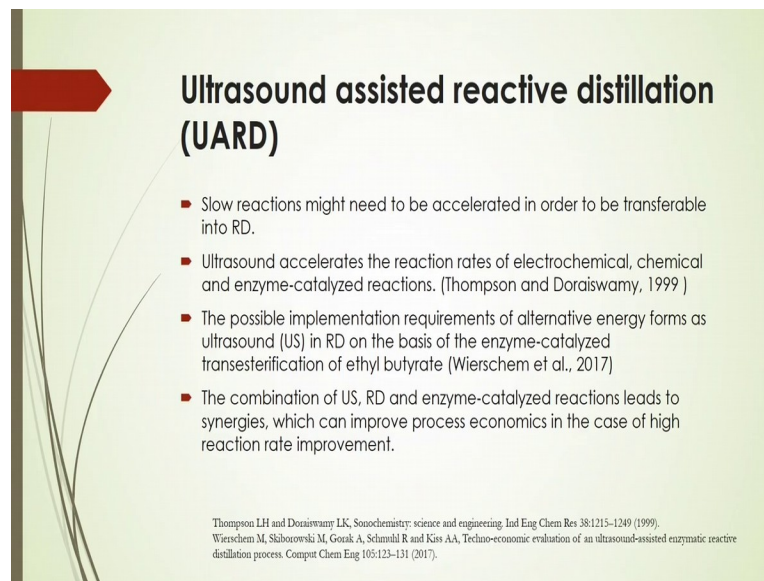


- Furthermore, recent research results indicate that microwave irradiation may affect the separation of mixtures, which would lead to a more efficient distillation process.
- microwaves might enhance the concentration of low boiling components in vapor (Altman, et al., 2010)
- Also influence the position of an azeotrope in terms of temperature and composition

Altman, et al., 2010. Ind. Eng. Chem. Res., 49 (2010), 10287-10296

Also, you can say that this research of course, is required to get more intensification of this you know, microwave-based reactive distillation process and recent research results indicate that microwave irradiation may **affect** the separation of the mixtures which would lead to a more efficient distillation process that is reported by Altman in 2010 and according to the report they concluded that this microwaves might enhanced the concentration of the low boiling components in the vapour and also, you know that influence the position of an azeotrope in terms of temperature and composition. So, this is the, you know that mechanism based which you can get that intensification of the process of reactive distillation just by applying this microwave irradiation.

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Ultrasound assisted reactive distillation (UARD)

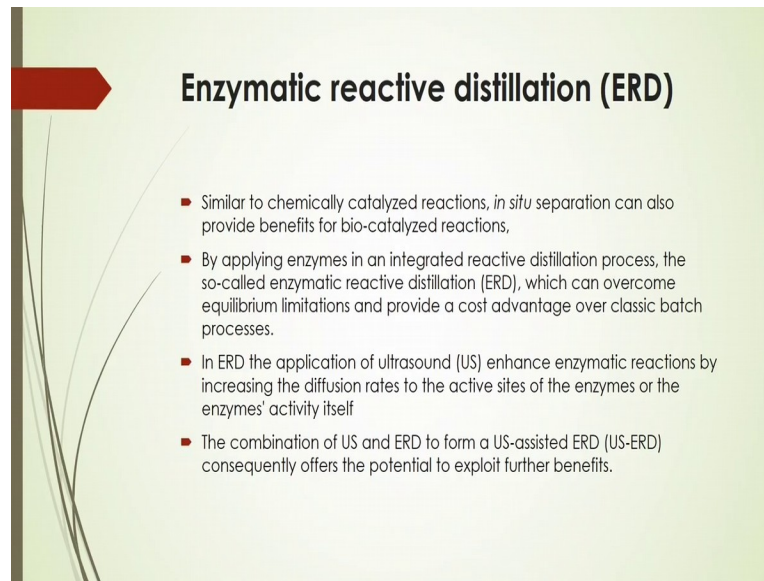
- Slow reactions might need to be accelerated in order to be transferable into RD.
- Ultrasound accelerates the reaction rates of electrochemical, chemical and enzyme-catalyzed reactions. (Thompson and Doraiswamy, 1999)
- The possible implementation requirements of alternative energy forms as ultrasound (US) in RD on the basis of the enzyme-catalyzed transesterification of ethyl butyrate (Wierschem et al., 2017)
- The combination of US, RD and enzyme-catalyzed reactions leads to synergies, which can improve process economics in the case of high reaction rate improvement.

Thompson LH and Doraiswamy LK, Sonochemistry: science and engineering. Ind Eng Chem Res 38:1215-1249 (1999).
Wierschem M, Sziborowski M, Gozik A, Schmittl R and Kiss AA, Techno-economic evaluation of an ultrasound-assisted enzymatic reactive distillation process. Comput Chem Eng 105:123-131 (2017).

Another you know, most important you know, reactive distillation which is you know very in nascent stage to get that intensification of the, you know distillation process that is called ultrasound assisted reactive distillation. In that case you know some limitations of course will be there because this type of you know, reactive distillation system slow reaction of course to be required for the acceleration of the reaction in order to transferable into the reactive distillation system.

So, slow reactions might need to be accelerated in order to you know, be transferable into reactive distillation. Ultrasound accelerates the reaction rates here of electrochemical, chemical and enzyme catalysed reactions and also, the combination of you know that ultrasound and reactive distillations and also you know, using of enzyme catalysts reaction that leads to synergies, you know, which can improve process economics in the case of high reaction rate improvement and the possible implementation requirements of you know, alternative energy forms as ultrasound in the reactive distillation on the basis of enzyme catalysts, transesterification of ethyl butyrate is one of the important you know, aspects of this ultrasound assisted reactive distillation.

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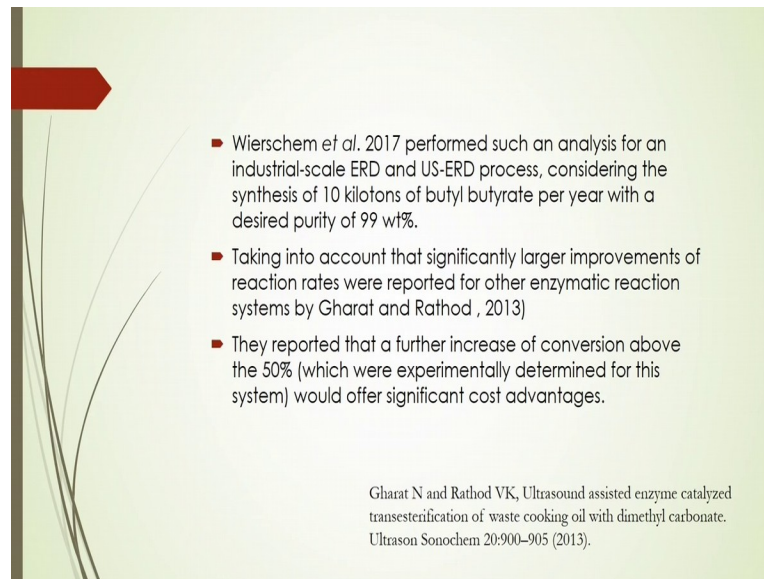
Enzymatic reactive distillation (ERD)

- Similar to chemically catalyzed reactions, *in situ* separation can also provide benefits for bio-catalyzed reactions.
- By applying enzymes in an integrated reactive distillation process, the so-called enzymatic reactive distillation (ERD), which can overcome equilibrium limitations and provide a cost advantage over classic batch processes.
- In ERD the application of ultrasound (US) enhance enzymatic reactions by increasing the diffusion rates to the active sites of the enzymes or the enzymes' activity itself
- The combination of US and ERD to form a US-assisted ERD (US-ERD) consequently offers the potential to exploit further benefits.

And similar to **these chemically catalysed reactions** *in situ* separation can also provide the benefits for the you know, bio-catalysed reactions and in that case by applying these enzymes in an integrated reactive distillation process, the so-called enzymic reactive distillation which can overcome equilibrium limitations and this may provide a cost advantage over the classic batch processes.

And in the enzymatic reactive distillation processes you will see that the application of this ultrasound enhance that enzymatic reactions by you know, increasing the diffusion rates to the active sites of the enzymes or the enzymes activity itself; and the combination of this US that is called ultrasound and ERD that is, enzymatic reactive distillation if you combine these 2 mechanism of form a US assisted you know, ERD that may you know consequently offers the potential to the exploitation of further benefits of this you know process intensification of reactive distillation process.

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- Wierschem et al. 2017 performed such an analysis for an industrial-scale ERD and US-ERD process, considering the synthesis of 10 kilotons of butyl butyrate per year with a desired purity of 99 wt%.
- Taking into account that significantly larger improvements of reaction rates were reported for other enzymatic reaction systems by Gharat and Rathod, (2013)
- They reported that a further increase of conversion above the 50% (which were experimentally determined for this system) would offer significant cost advantages.

Gharat N and Rathod VK, Ultrasound assisted enzyme catalyzed transesterification of waste cooking oil with dimethyl carbonate. Ultrason Sonochem 20:900–905 (2013).

And in this case you will see you have to remember that whenever you are going to analyse this process you know, industrial scale ERD and US ERD processes you have to consider the synthesis of some you know, specific reactions where you can get that more process intensification like we have given one example like, if you consider the synthesis of 10 kilotonnes of you know butyl butyrate per year with a desired purity of 99 weight percent then you can get you know that, this ultrasound assisted process intensification as an example; and also taking into account that significantly larger improvement of the reaction rates were reported for you know, other enzymatic reaction system by you know, Gharat and Rathod in 2013.

They reported that a **further increase** of you know, conversions above the 50 percent which were experimentally determined for this system by them would offer a significant **cost advantage**. So that is why it is very interesting to develop this ultrasound assisted, even conjugation of this ultrasound and enzymatic you know, reactive distillation system you can get more you know process intensification of this reactive distillation process. So we have discussed several you know, aspects of this intensification of this reactive distillation process and what are the different improvement of the stages of you know that intensification for this reactive distillation system.

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Further reading.....

- David Reay, Colin Ramshaw, and Adam Harvey, Process Intensification: Engineering for efficiency, sustainability and flexibility, IChemE, 2nd edition, 2013, Elsevier.
- Kamelia Boodhoo and Adam Harvey. Process Intensification for Green Chemistry Engineering Solutions for Sustainable Chemical Processing, Edited by Kamelia Boodhoo and Adam Harvey, School of Chemical Engineering & Advanced Materials Newcastle University, UK. Wiley, 2013
- Juan Gabriel Segovia-Hernández, Adrián Bonilla-Petriciolet Editors, Process Intensification in Chemical Engineering Design Optimization and Control, Springer, 2016.



Thank You

You can have more also information about those things by further reading of **these** references, so I would suggest you to go further for your better understanding even more you know information about this reactive distillation system. So, thank you for your attention for this lecture today, so next lecture onward we will try to discuss something more about that process intensification with some other mechanism and also other process intensification unit. Thank you.