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Lecture No -29 Hierarchical Approach to Process Synthesis - III

Welcome to lecture 29 of plant design and economics. In this module, we are talking about conceptual process synthesis and in particular we are talking about hierarchical approach to process synthesis. So we will continue our discussion on hierarchical approach to process synthesis we have already discussed about decisions at level 1 and 2.

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Now we will discuss about decisions at level 3, which is about recycled structure of the flow sheet and reactor consideration.

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After deciding on the input-output structure of the flow sheet, that is what we have done at level 2. So after completing level 2 decisions, that means after you have taken a decision on the input-output structure of the flow sheet, we can now add the next layer of detail. So we can go to the next level of complexity and add next layer of details to the process, product distribution dominates design; therefore we now add the details of reactor system.

Note that, we consider the separation system as a black box here so we are not considered the details of the separation system. When you talk about reactors, details of separation systems will add in the next level that is level 4. So as far as level 3 is concerned, we will focus our attention on reactor details and recycle structure and consider the separation system as black box.

The behavior of the reactor determines the recycle structure of the flow sheet, the following decisions will fix the recycle structure; how many reactor systems are required? Is there any separation between the reactor systems? How many recycled streams are required? Do you want to use an excess of one reactant at the reactor inlet?

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Is a gas compressor required? What are the costs? For putting a gas compression in application. Should the reactor be operated adiabatically with direct heating or cooling? Or is the diluent or heat carrier required. Do you want to shift the equilibrium conversion? How do you do that? How do the reactor costs affect the economic potential? So at every level will consider the economic potential.

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If sets of reactions take place at differen catalysts, then we use different reactor s	t T and P, or if they require different systems for these reaction sets.	
$\frac{\text{HDA Process:}}{\text{Toluene} + \text{H}_2} \longrightarrow \text{Benzene} + \text{CH}_4$	Both the reactions take place at same T, P, without any catalyst.	
2Benzene \longrightarrow Diphenyl + H ₂ <u>Acetic Anhydride Process:</u> Acetone \rightarrow Ketene + CH ₄ Ketene \rightarrow CO + 0.5C, H ₄ 700°C, 1atm	Temperature range: from 620 °C to 700 °C Pressure: about 35 bar <u>Use one reactor system</u> .	
Ketene + Acetic Acid → Acetic Anhydride	80 °C, 1atm	

Now, so these are the decision that we must take to fix the reactor and recycle structure at level 3. So we start with the first question, how many reactor systems will there be, if a sets of reaction take place at different temperature, different pressure or if the required different catalyst, then we use different systems for these reaction sets. If they use same temperature and pressure, same catalyst or no catalyst we can use the single reactor system.

For example in hydrodealkylation process of toluene to benzene, we have seen that there are two reactions. In the first reaction toluene reacts with hydrogen to produce benzene and then benzene undergoes reversible conversion to diphenyl and hydrogen. Now this both this reaction takes place at same temperature and pressure, 620 to 700 degrees celsius 35 bar and there is no catalyst involved. So we can use one reactor system.

Now, take an example of another reaction set in particular acetic anhydride process. Now in these cases the acetone to ketene and methane reaction and ketene to carbon monoxide and C2H4 ethylene reaction takes place at 700 degrees celsius, 1 atmospheric pressure. Whereas the second set of reaction which is ketene plus acetic acid gives acetic anhydride takes place at 80 degree celsius and 1 atmospheric pressure.

So there is a huge difference between the temperature requirements for these two reactions so we will use to reactor systems.





So this is schematically shown here, the HDA process uses one reactor. Whereas the acetic anhydride process two reactors, reactor 1 where acetone goes as feed reactor 2 whereas acetic acid goes as feed. Note that, they also have separate recycle. So you will come to recycle later.

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Now the next decision that we have to take is about number of recycle systems. How many recycle systems will there; now recall how you computed number of outlet streams or number of product streams in your process. So you follow a similar approach, so to determine number of recycled systems we first list all the components that are leaving the reactor and arrange these components by the normal boiling point.

Assign a reactor number as destination code to each recycle stream. Note that there may be one reactor; there may be two reactors or more. So we will assign a reactor number as destination code to each recycle stream, group recycle components having neighboring boiling points if they have the same reactor destination. Then the number of recycle streams is the number of such groups.

So this is based on the heuristics that we should not separate two components and then remix them again at a reactor inlet.

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Now, let us take example from HDA process hydro dealkylation of toluene to benzene, to understand how to determine the number of recycle streams. So we list all the components, they are hydrogen, methane, benzene, toluene, diphenyl and they arranged according to their normal boiling point so each component has been given destination. Note that, there is only one reactor.

So all the recycle streams will go to the same reactor Hydrogen and Methane both gas recycle recycle plus purge, benzene is primary product and toluene is liquid recycle stream diphenyl is by product. So the product streams are purge, one single purge for hydrogen and methane gas, benzene and diphenyl. Whereas recycle streams are hydrogen and methane one that is gas recycle and toluene another one which is liquid recycle.

So there are two recycle streams note that, gas recycle will require compression, whereas liquid recycle will require pump using compressor is always more expensive than using pump.

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So this is schematically shown here for the HDA process, you have three product streams purge, benzene and diphenyl and two recycle streams one gas recycle stream another is liquid recycle stream.

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Component CO CH ₄ C ₂ H ₄ Ketene Acetone Acetic Acid Acetic Anhye	NBP, "F -312.6 -258.6 -154.8 -42.1 133.2 244.3 dride 281.9	Destination Ketene -> CO + 0.5C2Ha In Reactor Fuel by-product Ketene + Acetic Acid -> Acetic Anhyo Fuel by-product In Reactor Unstable reactant - Completely converted Reactant - Recycle to R1 - Liquid Reactant - Recycle to R2 - Liquid Primary product
oduct Stream (2): CO-	+CH4+C2H4, A	Acetic Anhydride

Now, let us take another example from acetic anhydride process. Now we have seen that the in case of acetic process you will require two reactor, because these two sets of reactions takes place at two different temperatures. So some recycle stream will go to reactor R1, other recycle streams will go to reactor R2. Now all the components are arranged according to the normal boiling point and the destination code attached Carbon monoxide, methane, ethylene all are fuel by product.

Ketene is an unstable reactant it is completely converted in the reactor, so there is no

question of recycling. Acetone is the reactant and liquid recycle stream, which will go to reactor R1, Acetic acid another liquid recycle stream, which will go to reactant R2 and acetic anhydride is primary product. So the product streams is 2 one is the fuel by product; carbon monoxide, methane, ethylene, they all go as one product streams and acetic anhydride is the primary product.

So two product streams similarly two recycle stream, acetone goes to reactor R1 and acetic acid goes to reactor R2.

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This is schematically shown here you see, the acetone recycle stream goes to reactor R1 whereas acetic anhydride goes to reactor R2 after being separated in the separator and this is the fuel byproduct stream, single stream which contains mixture of carbon monoxide, methane and ethylene and acetic anhydride is the primary product stream.

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Now the next decision that you have to take about whether we should use excess reactance or not? Now if we use excess reactants, excess reactants may shift product distribution it may improve selectivity. Larger the excess, greater the selectivity but higher is the cost to recover and recycle the excess reactant. So we have to find the optimum amount of excess by performing economic evaluations.

If you use access reactant it may force one component to be close to complete conversion. For example, consider the reaction carbon monoxide plus chlorine is phosgene is intermediate for production of di-isocyanate. Now this di-isocynate product must be free of chlorine, so you must have very high conversion of chlorine. So excess of carbon monoxide makes the conversion of chlorine very high.

So excess reactant may force one component to be close to complete conversion excess reactant may also shift equilibrium conversion. For example consider the reaction of benzene plus hydrogen which gives cyclohexane. So all the double bonds will be saturated and you will get the cyclic product cyclohexane, excess hydrogen shifts equilibrium to the right hand side.

Now there is an advantage here, now the benzene and the cyclohexane have similar boiling point. So they are close boiling mixtures, so if conversion is not very high you have to separate maybe through distillation the close boiling mixture of benzene and cyclohexane which becomes a difficult separation through distillation close boiling mixtures are difficult to be separated through distillation. So molar ratio reactants entering reactor is often a design variable.

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Now, we will learn how to perform material balances, recycle material balances. We will first start with the material balance of the limiting reactant in the process. In case of hydro dealkylation of toluene to benzene, the limiting reactant is toluene. Now look at the diagram so these envelope represents that around this envelope we took material balance, we perform material balance around this envelope at level 2, that was input output structure.

Where recycle stream did not come into picture, because recycle stream does not affect the overall material balance. So overall material balance is affected only by number of input streams and the output streams recycle is internal flow structure. So now we will see the material balance at level 3, which is shown by this color.

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Now we make an assumption, and the assumption is that 100% recovery and the cycle of the limiting reactant toluene. So you are able to recover and the recycle 100% of the limiting reactant toluene. Let the flow entering the reactor the FT. Note that, this is the flow of the toluene to the reactor; whereas this is the flow of toluene to the process place free all the storage in terms of moles per hour.

Now if we consider the conversion to be x, then if FT moles per hour enters the reactor then the toluene leaving the reactor will be FT times 1- x, because x is conversion. Now this FT into 1- x moles per hour of toluene is being separated and the same amount is being recycled back to the reactor. So, now we are able to make a balance on the limiting reactant toluene, focus your attention here.

Note that, around this envelope the toluene entering is FFT + FT into 1- X. So that must be equal to toluene that is entering reactor which is FT. So if you simplify we get toluene enter into the reactor FT is equal to the fresh free toluene FFT divided by x the conversion. This relation will always hold the limiting reactant when it is completely recovered and recycled.

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Now once we are able to estimate the flow of limiting reactant we can use molar ratio at the reactor inlet to compute recycle flows of other components. Again, let us take the example of hydrodealkylation of tolerant to benzene. Like MR represent molar ratio of hydrogen to toluene at reactor inlet. So MR represents hydrogen divided by toluene at the reactor inlet. Let RG represent the recycle gas flow moles per hour, yPH represents mole fraction of hydrogen in the purge stream so this is the purge stream.

Note that the hydrogen composition will be same here as well, so the hydrogen composition yPH is same in the purge stream as well as in the recycle gas stream. Composition of hydrogen will be same the flow rate will not be same and yFH is the mole fraction of hydrogen in the feed and FG is the mega gas flow rate. So with this nomenclature in mind with this definition of the variable, we will be now able to write the hydrogen balance.

So how much of hydrogen enters around this envelope FG into yFH + RG into yPH that enters the recycle stream so that must be equal to MR into FT that goes to the reactor we have already found out FT= FFT by X in the previous slide, so we have substituted here for FT by x. Note that this comes from the definition of MR, which is MR= hydrogen by toluene. So hydrogen=MR into FT.

Now if we specify the design variables, conversion, hydrogen composition in the part stream yPH and the molar ratio we can solve for the recycle gas flow RG. So, this is how we can compute the recycle gas flow rate.

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Now what are the heuristics available for design variables there is no design heuristics for selecting conversion x for complex reaction, there is no design heuristics for selecting purge composition yPH or molar ratio for single reaction. We can choose the conversion equal to 0.96 or 98% of equilibrium conversion as first guess, reversible byproducts should we recycle?

If we recycle a byproduct formed by reversible reaction and let the byproduct accumulate in the recycle loop to its equilibrium level then you can find the recycle flow using equilibrium relation at reactor exit. Look at the equilibrium relationship, so you can make use of the equilibrium relationship to find out the recycle flow.

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Reactor heat effects, we have to decide can the reactor be operated adiabatically with direct heating or cooling is a diluent or heat carrier required. Note that, when you add such extraneous components such as diluent or it carrier it may change our recycle and overall material balance. We have to decide this before considering specification of separation system.

So whether we will add heat carrier or diluent this must be decided before we consider specification of separation systems because this extraneous components you add may have a effect on separation process. So first find reactor heat load and flow rate through reactor heat load is nothing but heat of reaction multiplied by fresh feed rate. So in case of hydrodealkylation reaction heat load QR is delta heat of reaction multiplied by phase speed of toluene FFT. Now, we are able now to find out the adiabatic temperature change.

You now find out adiabatic temperature change, which is the difference between inlet temperature and outlet temperature of the reactor, so QR can be equated to the flow through reactor F specific heat multiplied by TRinlet -TRoutlet. So you can now find out the adiabatic temperature change.

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If adiabatic operation is not feasible, then use direct heating or cooling. Use heat flow to get an idea of heat transfer area required, so this is the heuristics. If adiabatic operation is not feasible then use direct heating or cooling, use heat load to get an idea of heat transfer area required. The heat load of a reactor is often fixed by the fresh feed rate of the limiting reactant, for example in HDR process it will be the flow of toluene. The adiabatic temperature change primarily depends on the flow through the reactor. Thus we can moderate the temperature change through the reactor by increasing the flow rate to monitor temperature change through reactor increase recycling or reactant or recycling of product or recycling of byproduct. If this is not possible then only use extraneous components such as heat carriers, note that use of such heat carriers, we will have effect on separation systems.

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Equilibrium limitations, first reversible exothermic reactions; such as sulfuric acid process, ammonia synthesis etcetera, high temperature increases reaction rate but decreases equilibrium conversion, it is necessary to optimize the temperature profile here. The reaction should start at a higher temperature and end at a lower one. Such reactions are often carried out in a series of adiabatic beds with intermediate heat exchangers to cool the gases.

In case of reversible endothermic reactions the reaction temperature should be set as high as the technological or environmental or safety constraints will allow us. Use of heat carriers such as steam, hot gas, or solid inert may be considered, if the number of moles increases by reaction, the dilution with inert shifts the equilibrium conversion to higher values. However, more energy is needed for inert recycling.

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Equilibrium limitation: equilibrium reaction with separation such as distillation, extraction etcetera. Removal of a by-product by means of separation operation such as distillation, stripping, extraction, membrane can bring the conversion to completion. An important application is reactive distillation, where the reaction separation can be simultaneously carried out in the same unit.

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Equilibrium conversion: calculate the process flows as a function of design variables conversion, molar ratio of reactants etcetera, substitute these values in the expression of equilibrium relationship and check if the conversion selected is above or below the equilibrium value. If the computed value is above equilibrium value, obviously the result has no meaning.

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Finally, let us see the economic potential at level 3.We have obtained economic potential at level 2. Now economic potential at level 3 will be economic potential at level 2 minus the cost of compressor or pump minus the cost of reactor. Economic potential exhibits a maximum because of the trade-off between material cost and reactor system and recycle cost, note that lower conversion gives larger recycle flows resulting in higher cost.

But higher conversion decreases the recycle flows and their cost, so because of the presence of trade-off between material cost and the reactor system and recycle cost EP3 will show a maximum and that is what you see in the diagram for EP3 versus conversion for different values of hydrogen composition in the part strip. So focus your attention on the range of conversion for which the EP 3 is above 0.

So there only you get positive economic potential. With this we stop our discussion on lecture number 29.