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Module - 2 Flowsheet Synthesis (Conceptual Design of a Chemical Process) Lecture - 6 Recycle Structure of Flowsheet – (Part III)

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Equilibrium Reaction	ns: Case Shu Phoduction	dy of cyclohexame
C6H6 + 3H2 2	Cettiz ccycl	o hexane).
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Benzene		
Reactors	separator	_ Gyclohexane
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Welcome, we are now approaching end of module 2 that is flowsheet synthesis. in the previous lecture we dealt with the recycle structure of the flowsheet, and then we had two topics, first is the recycle material balance and second the reactor heat effects. We saw many thumb rules to determine the size of the reactor, the exact heat transfer effects that can occur in a particular reactor and how we can deal with the reactor sizing on the basis of the heat effects.

In this lecture we shall deal with the two additional topics of recycle structure of the flowsheet, first is the equilibrium limitation or equilibrium reactions and second is the reactor design. As whether we have to use the pluck flow reactor or continuous straight reactor and how we go for addition of different reactants, so as to increase the selectivity and yield of the desired product.

Let us start with the first thing equilibrium limitation, equilibrium limitations are quite important. In the previous lectures we had the hydrodenyl collection process as our case study, and in that process the diphenyl was the side product and it was formed through equilibrium or reversible reaction. We had seen the process alternative of recycling the diphenyl or eliminating the reversible byproduct, and we saw the pros and cons of that particular decision. However, in many cases the equilibrium conversions are important because we have to see that the side products are not accumulated in the process and they are below the desired limit.

Now, how do we calculate the equilibrium conversion? We use exactly the same procedure of calculating process flows has a function of design variables conversion molar ratio of reactants etc. And then we substitute these flows into the equilibrium relationship for the particular product, and see whether the conversion that is obtained is above or below the equilibrium value. Obviously if it is higher than equilibrium value then our calculations are wrong because the conversion cannot exceed equilibrium value, and we have to go for iteration.

In some cases it is necessary to determine the exact failure of equilibrium conversion, as a function of design variable because this value appears in the kinetic module used to determine the reactor sites. We shall see all those all these things with an example of cylohexane production, so that point we note, equilibrium reactions case study of cyclohexane production. Cyclohexane is produced by hydrogenation of benzene, so the basic reaction is benzene plus 3 moles of hydrogen giving C6H12 that is cylcohexane.

A typical flowsheet for this particular process is that there is a reactor to which benzene and hydrogen are fed hydrogen often contains impurities, such as nitrogen or methane. This is a vapor face process so benzene is heated till it vaporizes and then the two reactants are mixed the react the reactant mixture is passed over the catalyst, in a catalytic reactor. And then the reactor affluent is then cooled and the product is distilled off. So, the reactor is followed by the separator and then cyclohexane comes as the main product, then there is a recycle stream of hydrogen, hydrogen is fed in excess in this situation, so as to force benzene conversion to near completion.

Benzene and cyclohexane have very similar properties, therefore any benzene left in the cylcohexane is difficult to separate, because relative volatilities are very close to 1. In

addition benzene is carcinogenic they its toxic, so we would like to have as little benzene unconverted as possible. But still we can show here recycle stream for benzene. So, this is a basic flowsheet at level 3, that is the recycle structure of the flowsheet. Now, let us do the material balance the material balance will obviously start with certain production rate of cyclohexane, we have to make certain assumptions that may be there are no losses recovery is recoverant recycle is hundred percent so that point we note.

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DE PION CONTRA . Z. 1. J. S. P. P. Assumption: Complete recovery and recycle with no besses. Production note Cette : 100 mole (Pe) benzene in fresh feed = 100 mot = Excess Hz fed to the process (fresh) Total H2 feed = 3% + FE = 0.375 F assumed to contain 2.5% Reackon Purge gas: All fresh Excess + Important = FE + 0.025 F

Assumption complete recovery and recycle with no losses, now the desired production rate of cyclohexane, we take as hundred mol power. We say that this is a continuous process so the typical working hours are eight thousand hours per year. And the production rate of cyclohexane that we denote by letters P c is hundred mol per hour. Here there is no side reaction so selectivity is one, therefore the benzene in fresh feed is also hundred mol per hour. We have already shown a recycle in per stream. So let us say that Fe denotes excess hydrogen fed to the process.

Remember this excess hydrogen is in the fresh gas stream, having said this we can immediately write the total hydrogen in the feed. The total hydrogen in the feed, would be the hydrogen that is required for the reaction, which will be 3 into P c because stoichiometry 3, 3 moles of hydrogen are required per mol of benzene. So, the hydrogen for the reaction will be 3 P c plus the excess hydrogen. Now, we assume here that the

hydrogen feed is about 97.5 percent pure, which 2.5 percent of impurities or inert such as nitrogen and methane.

So, this comes out to be 0.975 F g and here we note that fresh gas assumed to contain 2.5 percent of inert or impurities. The purge gas, purge gas should comprise of all fresh excess hydrogen plus the impurities with fresh gas. So, this becomes F e all fresh excess hydrogen plus 0.025 into F g so this is the purge gas. And now we make a balance for the fresh gas, which is also known as make up gas, some books give this terminology make up gas, we make balance only on hydrogen.

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Now, let y p h denote the composition of hydrogen in purge gas, so y p h will be F e divided by F e plus 0.25 F g the hydrogen in the purge gas divided by the total purge gas. Now, the fresh gas or make up gas contains 0.975 times 97.5 hydrogen, this hydrogen is utilized for the reaction and rest is purged. If we substitute for F e 0.975 into F g minus 3 p c, the total hydrogen fed to the process minus the hydrogen consumed in the reaction, then we can write 0.975 into F g is equal to 3 p c plus y p h into 0.975 into F g minus 3 p c plus 0.025 into F g. And then by rearranging we get F g is equal to 3 p c into 1 minus y p h divided by 0.975 minus y p h.

We are going almost the same way as we did calculation for the hydrogen alkaline process. We want to bring all the material balance in terms of few design variables, so that by playing with the design variable we can find out optimum values of the process flows. So, this is as far as the reactant flows into the process are concerned. Now, let us try to do the recycle balance.

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Like H D A process here also we introduce design variable, which is molar ratio the molar ratio of hydrogen to benzene, excess reactant to limiting reactant. And then the total benzene fed to the process is F B, which is which has to be equal to P c by x where x is the per pass conversion of benzene. You will recall that we had developed a very similar expression, for the total feed of toluene HDA process, where the total toluene ft was equal to f f t by x. Now, f f t is the fresh toluene fed to the process which is always converted, which is equal to the production rate of benzene in case of HDA process. So, that point we note here F p is the total benzene fed to the process.

Now, what will be the recycle gas let us say that the recycle gas is denoted by R G, the hydrogen in the recycle gas will be obviously R G into y p h, the mol fraction of hydrogen in purge as well as the recycle gas is same because recycle and purge are streams obtained by splitting the gas flow from the separator. So, the mol fraction of the hydrogen is same in both of these.

Now, P c by x is the amount of benzene and M R is the molar ratio of hydrogen, so the total hydrogen at the reactor inlet is P c by x into M R and out of this 0.975 into F g is the hydrogen contributed by the makeup gas or the fresh gas. Therefore, obviously the remaining hydrogen is from the recycle gas, so this is the recycle hydrogen, this is total

hydrogen at reactor inlet. And this is the hydrogen contributed by makeup gas stream, so by rearranging this, we can get expression for R G in terms of the design variables y p h and M R. So, that completes the recycle balance. Now let us look at the flow rates at reactor outlet or reactor effluent.

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PICOD Chum . TO 1. J. D. P. Reactor Effluent Flow Rate: cycloherane, Berrane, Hz Cyclohexane; Pe mayh Benzene: $\binom{P_{c}}{x}(1-x) = \frac{P_{c}}{x}\binom{1-x}{n}$ (MR -3) Pc with That: 0.025 F_{g} + (1- ypu) $R_{g} = \left(\frac{1-ypu}{y_{pu}}\right) \left(\frac{MR}{R} - 3\right) E$ Total Flow at Reactor: le [1 + (MR-3) John Equili mum

The reactor effluent will contain cyclohexane, it will contain unconverted benzene and it will contain hydrogen, x hydrogen which remains unreacted in addition to the impurities. So, let us identify the molar flow rates cyclohexane will be P c mol per hour because that is what we started with, benzene will be total benzene fed to the process is P c by x, out of which unconverted is one minus x, because x is conversion. So, that is P c into 1 minus x by x. And then hydrogen, hydrogen is total hydrogen fed is M R into x into P c and 3 P c is the hydrogen that is consumed in the process. So, the total hydrogen that exits the reactor is M R into P c by x minus 3 P c. So, we take P c common and M R by x minus 3 into P c is the total hydrogen flow rate at the reactor out let, then there are the inerts.

Now, these inerts will be the inerts entering through the fresh gas as well as the recycle gas. As far as fresh gas is concerned, the innerts are point 0.25 into F g 2.5 percent of the fresh gas plus the non hydrogen component of the recycle gas. That is one minus y p h y p h is the mol fraction of the hydrogen and recycle gas. So, the non hydrogen component of the recycle gas is inerts and then we substitute for R G and then we can if you

substitute for R G and F g you can get this expression, which is can be very easily obtained it is simple mathematical jugglery.

Now, if you add all these flows the total flow at reactor outlet would be P c into 1 by x plus M R by x minus 3 into 1 divided by y p h. Now, these algebraic simplifications am leaving as exercise for you, these are rather straight forward no complications. And then the equilibrium relation, the equilibrium constant will be K e which is equal to the fugacity of cyclohexane divided by the fugacity of benzene at reactor outlet, and the fugacity of hydrogen to the power 3 because of the stoichiometry.

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We try to write the same equilibrium constant in terms of fugacity co-efficient and mol fraction y c is the mol fraction of cyclohexane in the reactor exit flow, y h is the mol fraction of hydrogen in the reactor exit flow, y b is the mol fraction of benzene in the hydrogen in the reactor exit flow. Now you can very easily calculate y c, y h and y b by dividing the molar flow rate of either cyclohexane, or hydrogen, or benzene by the total flow rate. Now, fugacity co-efficient for hydrogen can be assumed to be one and the ratio of fugacity co-efficient for cyclohexane to benzene can be assumed to be about 1.13 and then if you substitute for all these quantities you can get the expression 1.13 into P tot cube.

P tot is the total pressure of the reactor into k e is equal to x e divided by 1 minus x e into y p h minus 3xe plus m r molar ratio divided by M R minus 3 x e into y p h whole

bracket cube. I leave the derivation of this particular simplified expression as homework. As I said the derivation is rather straight forward, we have already calculated all molar flows we have calculated the total molar flow rate at the reactor outlet, what you have to do is only to substitute for y c y h and y b. And the numbers for the fugacity co-efficient for hydrogen it is one ratio of fugacity co-efficients for cyclohexane and benzene as 1.13 and you can very easily obtain this particular expression. Now, as I said benzene and cyclohexane are very close boilers therefore, we would like to have almost no unconverted benzene left in the reactor effluent as possible. So, we have to force the equilibrium conversion to one that point we note.

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Benzene and cyclohexane being very close boilers are difficult to separate and hence the benzene conversion benzene equilibrium conversion is forced close to one. Now, we have obtained an expression for x e the equilibrium conversion, however it is not explicit. But by making some algebraic modifications for example, if we assume that for very low values of x, we can as take 1 divided by 1 plus x as 1 minus x some simplification. You can convert the same expression that we derived earlier in to this approximate equation. Remember I am not writing equal, but an approximate sign x e is equal to 1 plus 1 divided by 1.13 into k e into P tot cube into y p h plus M R minus 2 divided by M R minus 3 into y p h cube. And this whole thing rest to minus 1.

If we try to identify from this the design variables that affect equilibrium conversion, we can see these are the equilibrium conversion is a function of a reactor pressure, and molar ratio and of course, the temperature. Now hydrogenation reactions are exothermic reactions, so if you decrease temperature obviously the conversion goes up, but temperature we have not introduced in our analysis. So, we will mainly focus on the first two parameters or first two design variables that is reactor pressure and molar ratio.

Obviously, if reactor pressure increases or molar ratio increases, x e increases and that is what is indicated by this expression, the expression that we have derived as P tot increases as molar ratio increases x e increases. But what is the optimum limits for these variables can we increase the reactor pressure indeterminately no there is a limit.

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O Molal hatio: Large recycle flows, larger in cost.
3) Temp: Equilibrium conversion of with time
at cost of slower kinetics. Reactor of large size is required.

Let us try to identify the pros and cons of these design variables. If you use high pressure reactor, the reactor cost goes up and of course, you have to compress the feed to higher pressure. That means large feed compressor is required, which increases both operating and capital cost. If you use higher molar ratio of hydrogen, larger and larger amount of hydrogen is going to remain unconverted, in the first place the total hydrogen that is fed to the reactor increases. So, the compression cost increases, secondly larger and larger amount of hydrogen remains unconverted. So, the recycle cost goes up, so those points you note, large recycle flows larger compressor cost. So, these are the disadvantages or the side of the coin for the molar ratio.

Now, the temperature of course, we have not considered the temperature in our analysis, but we can identify the effects of temperature by simple principles of physical chemistry. If the temperature reduces obviously the equilibrium conversion will go up because reaction is exothermic. However the reaction kinetics goes down, so that point we note, equilibrium conversion increases with temperature reduction, but at cost of slower kinetics, which means that to achieve same conversion of benzene I would require reactor of a larger size, and that would add to both capital and operating cost.

So, this is this example basically demonstrates the treatment of equilibrium limited reactions. We have to first identify the variables that affect the equilibrium conversion, and then we have to identify the pros and cons of that particular design variable. Now, let us see some more examples, how to increase the equilibrium or how to get rid of the equilibrium limitations of a particular process.

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DECPICE CONTRACTOR separator. Reactor : withdrawl st me of me product to shift equilibrium to desired Example: Isoporpanol ___ Acetone + #2 At 300 F. The equilibrium conversion Xe = 0.32 Catalyst for process is suspended in high boiling solvent; isopropand is fed continuously and temp of system maintained above by of acetone. => A series of 3 (STRs with pump around lisp is wed to supply heat to reaction

One effective means or effective solution is separator reactor. The separate reactor essentially is based on withdrawal of one of the product as the reaction proceeds, withdrawal of one of the product to shift equilibrium to desired side, that is to have as much conversion as possible. And an example in this category is that of isopropanol dehydration sorry isopropanol dehydrogenation to produce acetone. At 300 degrees Fahrenheit, the equilibrium conversion of this process is quite small that is about 30-32 percent.

Now, what is done is that the catalyst for the process is suspended in a high boiling solvent by means of mechanical stirring, isopropanol is fed continuously to this solvent or it is mixed with the solvent. And the temperature of this particular system is maintained above the boiling point of acetone. Now, due to this as soon as acetone is formed it is evaporated from the reactor and it can be recovered along with hydrogen at the reactor outlet, or it can be removed from the reactor. And thus it helps shift equilibrium to the right side or to the product side. Sometimes series of 3 reactors all of them casters with a pump around loop is also used. Another example that can be given is that of sulfuric acid manufacture.

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PAD OF Chunn . TO 1. J. D. . Sutputic acid manufacture, SO2 + 1 02 = so3 DCDA. Note mode The stream of soz + 02 is contacted the times with catalyst bed with intel nediate coolic p => faster kinetics => smaller reaction valume Large recycle cot. P

In this process, the sulfur dioxide is oxidized to sulfuric trioxide over the catalyst vanadium pent oxide, and the process is highly isothermic. So, D C D A mode is used for reaction which means that the mixture of sulfur dioxide and oxygen is heated, and it is passed over the ((Refer Time: 35:08)) bed of temperature of the stream rises very fast. Then after certain conversion the stream containing SO 3, SO 2 and oxygen is taken out, it is cooled and then readmitted into a second catalyst bed, where further conversion takes place. So, that point we note process the stream of SO 2 and O 2 is contacted 2 times with catalyst bed, with intermediate cooling. And later on this SO 3 is absorbed in dilute H 2 SO 4 to generate H 2 oleum H2O7S2, which is diluted further to get sulfuric acid.

Now, high temperature would mean faster kinetics which would mean smaller reactor volume, but the equilibrium conversion is small and therefore, large recycle cost. So, the D C D A process basically tries to increase the conversion at a cost of 2 reactor beds, in many cases to force conversion to completion.

DECPADO COM . TO 1- 2- 9- ** Dilleent Addition: Example styrene manufacture Vetrystenzone = styrone + 12] EB ____ Bencene + Ethylene. (nos F ES -> Tolmene + Memane Add of steam/ methane at reactor inter to EB. Lowes me partial pressure of Styrene & He. It helps shift the convolution of 53 to styrene.

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Example in this category is that of styrene manufacture, the chemistry is like this ethyl benzene is dehydrogenated to generate styrene and hydrogen. And there are 2 side reactions that take place ethyl benzene can also go decomposition to produce benzene and ethylene. And ethyl benzene can also get disproportionated to produce toluene and methane in all of these reactions occur at more or less same temperature and pressure, 20 psi absolute pressure which is close to atmospheric and 1100 degrees Fahrenheit temperature.

Now in this case steam is added, either steam or methane at the reactor inlet to ethyl benzene. Now, what it does is that it lowers the partial pressure of styrene and hydrogen and therefore, it helps shift the equilibrium of the first reaction the ethyl benzene going to styrene and hydrogen to the right side. Now, steam remains as an impurity in the product styrene because it is used as a diluent and then it condenses after the reaction.

However, the water and hydrogen carbon mixture are usually in immiscible, so you can easily get rid of water by having a face split instead. In some cases where the organic material dissolves in water you can have the steam stripping off this particular organic solvent. So, recovery of the dissolved product from water is not so difficult and most of the times, there is no need to recycle the water.

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DECPACIO Comme . T. 2. 9.90 . Gas Recycle > Compressor Theoretical hp = $\left(\frac{3.03 \times 10^5}{Y}\right)^2 P_{\rm in} Q_{\rm in} \left[\left(\frac{P_{\rm neg}Y}{P_{\rm in}}\right)^2 - 1 \right]$ $P_{\rm in} = \frac{106}{f\epsilon^2} \quad Q_{\rm in} = \frac{f\epsilon^3}{{\rm win}} \quad Y = \frac{\left(\frac{Cq}{Cq} - 1\right)}{\left(\frac{Cq}{Cq}\right)}$ Tour = (fort) Efficiency of compressor: Efficiency ~ 30 %

Then we have a gas recycle and purge stream a major equipment adds to the process and that is the compressor. Then we have a gas recycle and purge stream a major equipment adds to the process and that is the compressor. The compressors are expensive piece of equipment both in terms of capital cost as well as operating cost. There are several types of compressors centrifugal compressor, reciprocating compressor, but the most popular compressors on industrial scale are the centrifugal gas compressor.

The theoretical horse power for the compressor is given as 3.03 into 10 to the power minus 5 divided by gamma into P in into Q in into P out by P in rest to gamma minus 1. Then this is a correlation, remember it is not a formula and now the P in is the inlet pressure, which is given in pound force per feet square, Q in is the inlet flow rate which is given in feet cube per minute, gamma is a constant given as C p by C v minus 1 divided by C p by C v. And since it is an adiabatic compression, the temperature that is reached after compression is T out by T in is P out by P in rest to gamma it is like a simple process polytrophic process.

Now, this is the theoretical horse power, we have to determine in the efficiency of the process of the compressor, you can easily assume an efficiency of 90 percent for initial design calculations. So, the driver efficiency or motor efficiency you can take it as 90

percent and then due to the fluid friction loss suction and discharge loses, frictional loss at the port or moving metal part or fluid turbulence, another 90 percent efficiency can be assumed that loss of efficiency to fluid friction then suction and discharge so and so forth, moving metal parts. The compressors are expensive piece of equipment I just mentioned even the repair is quite difficult.

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So, we always have to have spares of the compressors, the spares have to be kept in stock to take care of unforeseen failure, or unforeseen operational problems. Compressors are always installed in pair, where one is on stream or one is operational and another is stand-by. Moreover it is a convention that compressor once is installed, how to operate about 60 percent of the total load.

Now, in many cases you have to compress to very high pressure level, therefore a single compressor may not serve the job. So, you have to go for multi-stage compressor, multi-stage compressors always have inter stage cooling because compression is an adiabatic process. So, the temperature of the gas stream increases there therefore, we have to have inter stage cooling.

Now, due to the cooling if the gas contains some condensable components those can be easily separated and the inter stage coolers are always provided knock-out drums, which collects the condensate. Typically for a 3 stage compressor with inter stage cooling, the work that is required is given as the molecular weight M of the gas R, the gas constant into the inlet temperature into the summation of the 3 compression ratios from stage one to 2, rest gamma from stage 2 to 3 rest gamma plus stage 3 to exit rest gamma minus 1.

So, this is the work that is required for the compressor, now what should be the intermediate compression ratios? That is a design variable you can very easily show and I am leaving this as an exercise for you that the minimum work is obtained, when the intermediate compression ratios are equal, which essentially means.

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That p 2 by p 1 should be equal to p 3 by p 2 should be equal to p 4 by p 3, you can very easily show this particular result. I am giving the hint, you have to take the partial derivative of the work with respect to the intermediate pressures and then equal to 0 to get this result. The cost annualized installed cost of the of the particular compressor.

Now, usually the cost is correlated to break horse power, which is the theoretical horse power divided by 0.9 because we assumed 90 percent efficiency. Once the break horse power is known BHP is known you can use any cost correlation such as Gutherie's correlation to determine the installed cost. Now, Gutherie correlation for compressor is as follows, the inflation index now I am using Markel and swift index M and S divided by 280.

Now, 280 was a M and S index in 1969, when Gutherie's correlations were proposed into 517.5 into BHP rest 0.82 into 2.11 plus F c where F c is the correction factor for the

design. If you multiply this by approximately 1 by 3 that is capital charge factor you will get the annualized installed cost. So, this completes our discussion on the equilibrium limited process in the next lecture, we shall see the reactor design.