Process Design Decisions and Project Economics
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Module - 2
Flowsheet Synthesis (Conceptual Design of a Chemical Process)
Lecture - 7
Input / Output Structure of Flowsheet (Part II)
And Recycle Structure of Flowsheet (Part I)

Welcome, we are now in the middle of module 2, we have seen in previous lectures the input output structure of the flow sheet and the factors, that govern the decision of badge versus continuous process. In previous lecture, we tried to develop overall material balance for a process from the input output structure of the flow sheet. That means, without going into the details of the process from outside the process, we tried to evaluate the flow of reactants, the flow of products and we tried to develop on material balance based on the selectivity of the process.

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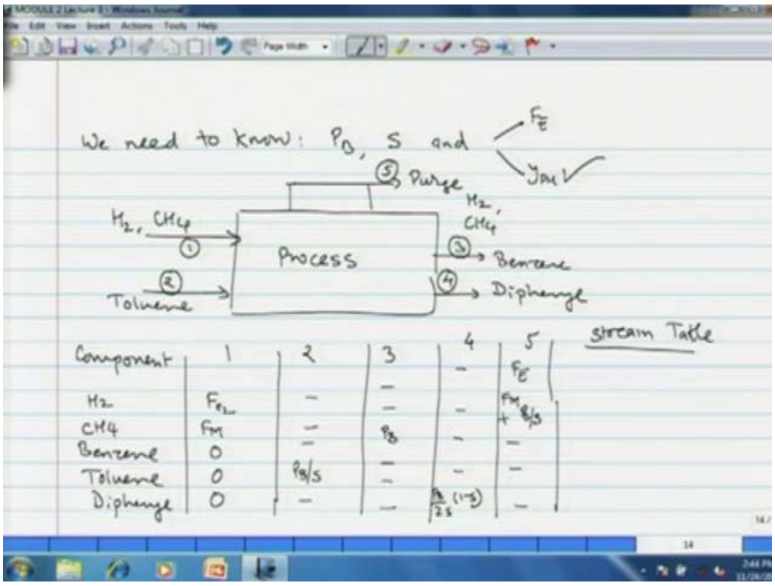

Component	1	2	3	4	5
H_2	F_{H_2}	–	–	–	F_E
CH_4	F_M	–	–	–	$F_M + P_B/S$
Benzene	0	–	P_B	–	–
Toluene	0	P_B/S	–	–	–
Diphenyl	0	–	–	$\frac{P_B}{2S}(1-S)$	–

And then we had developed stream table that now, I will show on, using HDA process as a case study, what you see on screen now is the input output structure of HDA process. The process with two feed streams hydrogen, methane and toluene and then the products are benzene, the main product and the side product diphenyl. The hydrogen is fed in excess therefore, it comes out as unreacted gas and then methane yields a impurity in the process, it enters also with the fresh hydrogen feed stream and it is generated in the process as a side product. And to keep the methane concentration under limit in the process, we have purge some of the unreacted gas so, we have a purge stream and a recycle stream.

So, this is the input output structure of a flow sheet then we tried to identify design variables, the design variables that we identified where, the rate of production of the benzene, the main product then the mole fraction of hydrogen in the purge gas and the selectivity. And based on that, we developed an overall material balance, in which tried to derive expression for the fresh feed rate of toluene.

Then, the fresh feed gas then the purge gas in terms of all the design variables, that the production rate of benzene P B, selectivity S and Y P H, which is the mole fraction of hydrogen in purge gas. Now, when we have only 2 reactions, as in case of HDA process, such kind of approach could be adopted. However, in many process, there are very large number of reactions, several main reactions several side reaction and therefore, we have to develop generalized material balance, in which we will use the conversion of each of the reaction as a variable.

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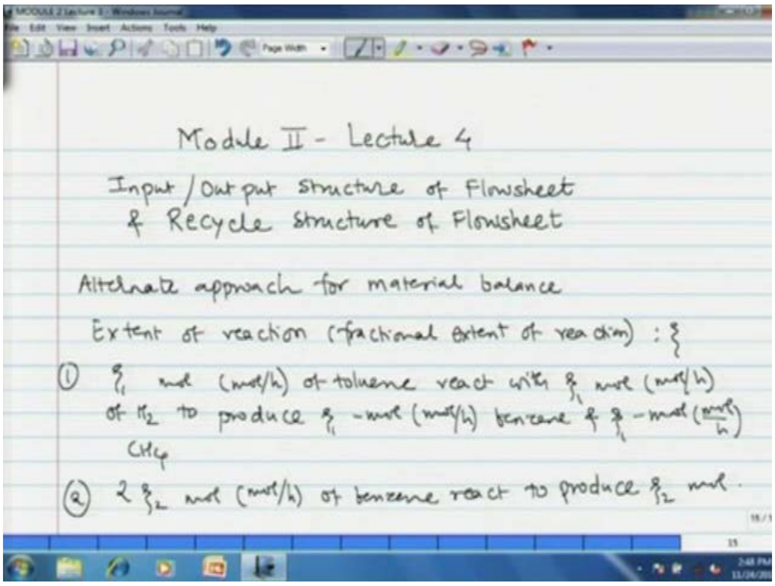

Module II - Lecture 4

Input / Output structure of Flowsheet
& Recycle structure of Flowsheet

Alternate approach for material balance

Extent of reaction (fractional extent of reaction) : ζ

① ζ_1 mol (mol/h) of toluene react with ζ_1 mol (mol/h) of H_2 to produce ζ_1 - mol (mol/h) benzene & ζ_1 - mol $\left(\frac{mol}{h}\right)$ CH_4

② $2\zeta_2$ mol (mol/h) of benzene react to produce ζ_2 mol.

Now, let us try to see that approach for the material balance, alternate approach for material balance. Now here, we will use the extent of a reaction as a parameter or fractional extent of a reaction and that, we will denote by letter zeta. Now, let us try to develop material balance for the HDA process with this approach. Let us say that, zeta 1 mole or mole per hour in case of continuous process of toluene, react with zeta 1 mole or mole per hour of hydrogen to produce zeta 1 mole of benzene or mole per hour again in place of continuous process. And thus, second product is ethane, this for the first reaction of the HDA process, in the second reaction, 2 zeta 2 mole or mole per hour of benzene react reversibly to produce zeta 2 mole of diphenyl and zeta 2 mole of hydrogen.

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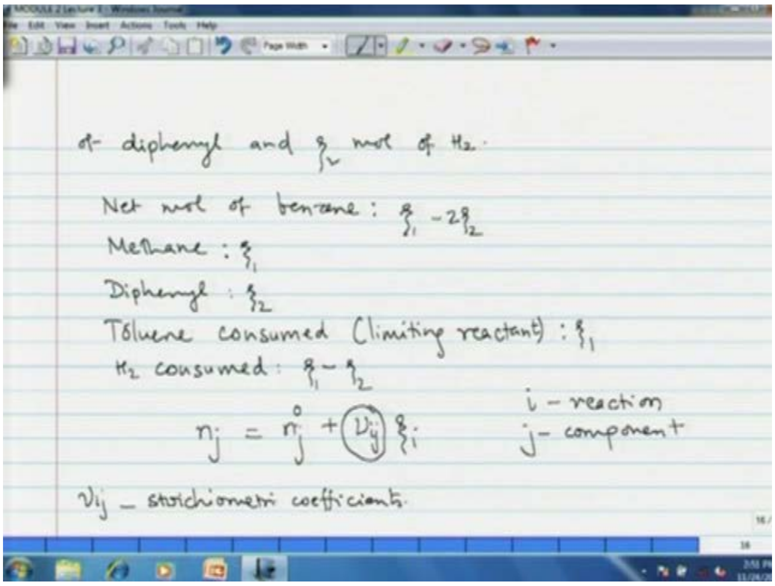

of diphenyl and ξ_2 mol of H_2.

Net mol of benzene : $\xi_1 - 2\xi_2$

Methane : ξ_1

Diphenyl : ξ_2

Toluene consumed (limiting reactant) : ξ_1

H_2 consumed : $\xi_1 - \xi_2$

$$n_j = n_j^0 + \boxed{\nu_{ij}}\,\xi_i$$

i – reaction

j – component

ν_{ij} – stoichiometri coefficients.

So, when we do material balance, the net moles of benzene become zeta 1 produced in the main reaction minus 2 zeta 2 consumed in the side reaction, methane is zeta 1 moles, diphenyl zeta 2, toluene consumed, which is the limiting reactant in the present situation is zeta 1. And hydrogen consumed is zeta 1 in the first reaction and zeta 2 moles, that are produced in the second reaction.

Now, in case of multiple reactions with multiple products, we can write a generalized expression as moles of a particular component j are equal to n j naught, which are the initial moles plus nu i j into zeta i. Now, i here indicates reaction and j as a component, which could be either reactant or product. Now, nu i j are what is known as reaction coefficients or stoichiometric coefficients.

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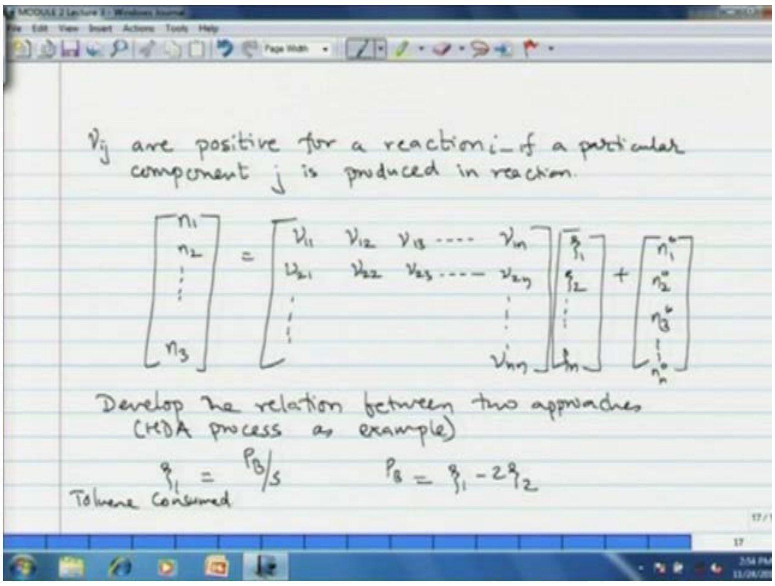

ν_{ij} are positive for a reaction i – if a particular component j is produced in reaction.

$$\begin{bmatrix} n_1 \\ n_2 \\ \vdots \\ n_3 \end{bmatrix} = \begin{bmatrix} \nu_{11} & \nu_{12} & \nu_{13} & \cdots & \nu_{1n} \\ \nu_{21} & \nu_{22} & \nu_{23} & \cdots & \nu_{2n} \\ \vdots & & & & \vdots \\ & & & & \nu_{nn} \end{bmatrix} \begin{bmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_n \end{bmatrix} + \begin{bmatrix} n_1^0 \\ n_2^0 \\ n_3^0 \\ \vdots \\ n_n^0 \end{bmatrix}$$

Develop the relation between two approaches
(HDA process as example)

$\xi_1 = P_B/S$ $\quad\quad$ $P_B = \xi_1 - 2\xi_2$

Toluene Consumed

Nu i j values are positive for a reaction, if a particular component is produced in the reaction like nu i j are positive for a reaction i, if a particular component j is produced in the reaction. And obviously, v i j will be negative for a reaction i, if a particular component j is consumed in the reaction or is the reactant in that reaction. Now, in such a approach, we can very easily create a matrix of calculation, in which we will write all the stoichiometric co-efficient in matrix form. And then multiplied by the matrix of extent of reactions, such a system can be very easily solved on a computer to get simul like material balance of all the components of the process.

Now, let us try to develop the relation between the two approaches, again using the HDA case study, as an example. Now, zeta 1, which was the moles of benzene produced in the earlier approach, we wrote as P B by S. Similarly, this zeta 1 is the toluene consumed, toluene consumed is P B by S as per the first approach and zeta 1 as per the second approach. Then the rate of production of benzene P B as per the second approach is zeta 1 minus 2 zeta 2.

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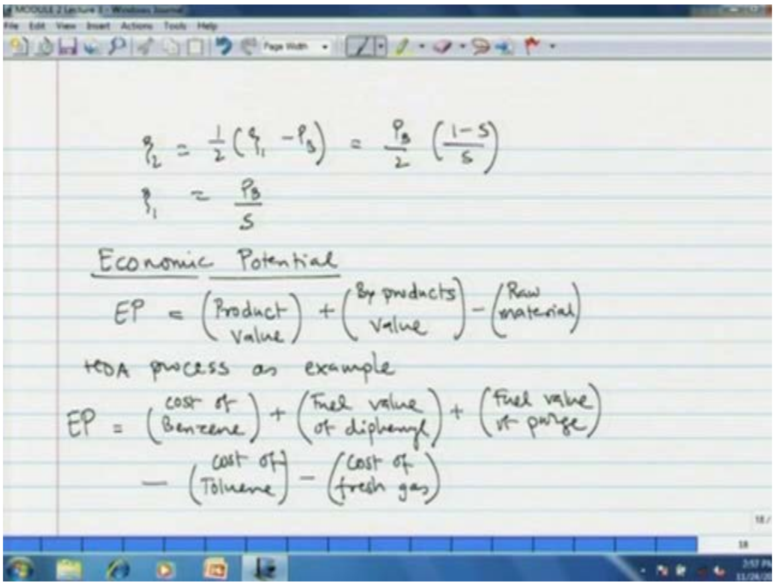

$$\zeta_2 = \frac{1}{2}(\zeta_1 - P_B) = \frac{P_B}{2}\left(\frac{1-S}{S}\right)$$

$$\zeta_1 = \frac{P_B}{S}$$

Economic Potential

$$EP = \begin{pmatrix}\text{Product}\\ \text{Value}\end{pmatrix} + \begin{pmatrix}\text{By products}\\ \text{Value}\end{pmatrix} - \begin{pmatrix}\text{Raw}\\ \text{material}\end{pmatrix}$$

HDA process as example

$$EP = \begin{pmatrix}\text{cost of}\\ \text{Benzene}\end{pmatrix} + \begin{pmatrix}\text{Fuel value}\\ \text{of diphenyl}\end{pmatrix} + \begin{pmatrix}\text{fuel value}\\ \text{of purge}\end{pmatrix} - \begin{pmatrix}\text{cost of}\\ \text{Toluene}\end{pmatrix} - \begin{pmatrix}\text{Cost of}\\ \text{fresh gas}\end{pmatrix}$$

And therefore, by combining these 2 expressions, we can write zeta 2 is equal to half zeta 1 minus P B, which is equal to P B by 2 into 1 minus S by S. So, essentially we have the 2 expressions, zeta 1 corresponds to P B by S and zeta 2 corresponds to P B by 2 into 1 minus S by S. Now, after evaluating all the molar fluids of streams, we have to evaluate the economic potential of the process. Based on the input output structure that we have developed, the economic potential E P would be, the cost of all the products plus cost of all the byproducts minus the cost of raw material because these 3 components we have determined. This would be the general definition of economic potential at the input output structure of the flow sheet that is, level 2 of the design.

Now, again for the HDA process, as example, we can apply this general definition, as economic potential is equal to product of the process is the benzene so, cost of benzene. Now, the side product of the process is diphenyl, which we utilize as a fuel in the process. So, the fuel value of diphenyl, the purge gas that comes out of the process comprises of hydrogen and methane, both are combustible gases. So, that purge gas can also be used as fuel in the process, captive consumption.

So, fuel value of purge minus now the raw materials, the first raw material is toluene and the second raw material is hydrogen, with impurity of methane. Now, this is a very crude definition of economic potential, what it means is that, we have a process that is existing and we do not pay anything for the utilities cost, which is of course, is not possible but this is what, this economic potential means.

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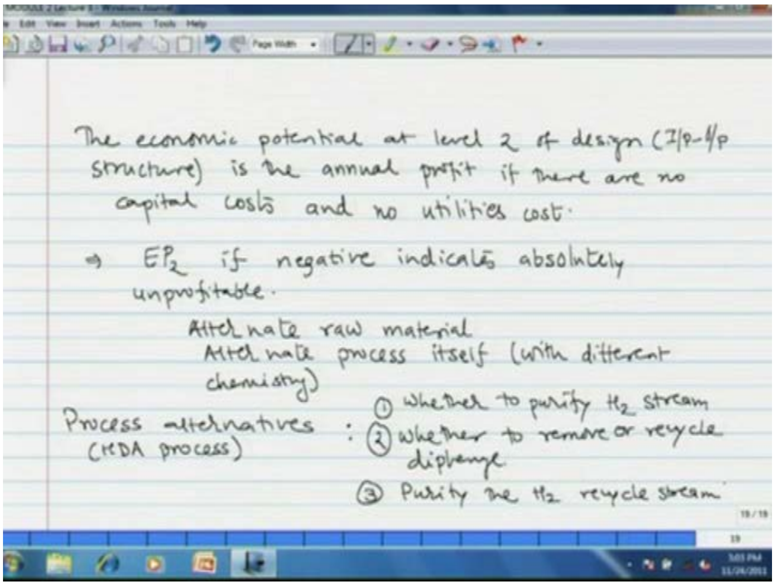

The economic potential at level 2 of design (I/P-O/P structure) is the annual profit if there are no capital costs and no utilities cost.

⇒ EP_2 if negative indicates absolutely unprofitable.

Alternate raw material
Alternate process itself (with different chemistry)

Process alternatives (HDA process) :
① Whether to purify H_2 stream
② Whether to remove or recycle diphenyl
③ Purify the H_2 recycle stream

So, that point we note, the economic potential at level 2 of the design input output structure of flowsheet is the annual profit, that we make, if there are no capital cost and no utilities cost. Now, if the economic potential at this stage comes out to be negative then the process is absolutely unprofitable. That means, there is no point in designing the process further now, in such case, we have to look for alternate raw material or alternate process itself that has different chemistry. So, to summarize this particular level of design, what we have done is that, we have identified the process variables, we have tried to derive an overall material balance. And with that analysis, we have developed the process alternatives, what are the process alternatives.

With again HDA process as example, first is whether to purify the hydrogen feed stream, second whether to remove recycle diphenyl and third is whether to purify the hydrogen recycle stream. Now obviously, with these process alternatives, we generate large number of flowsheets and it is interractical to design all the flowsheets to a great detail. Therefore, we are trying to develop a criteria for screening of these alternatives so that, we can shortlist only the best few, which we can design in detail, having said this, we now go to the next level of design.

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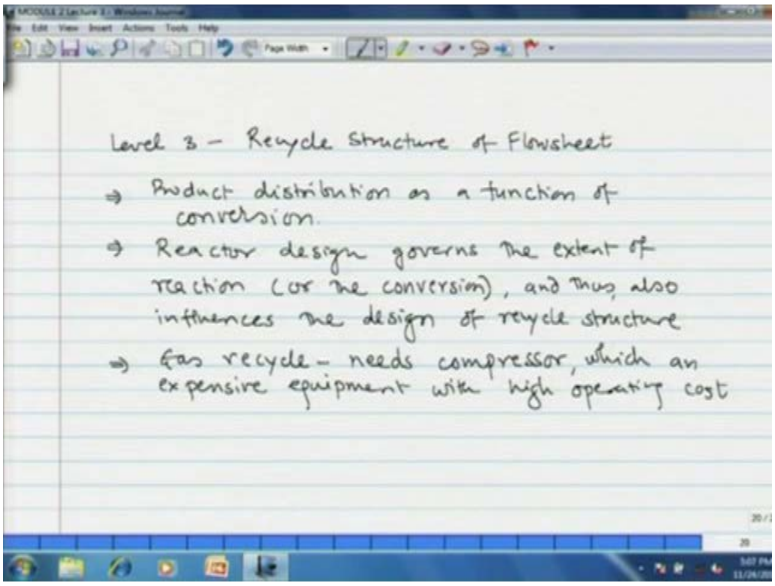

Level 3 – Recycle Structure of Flowsheet

⇒ Product distribution as a function of conversion.

⇒ Reactor design governs the extent of reaction (or the conversion), and thus, also influences the design of recycle structure

⇒ Gas recycle – needs compressor, which an expensive equipment with high operating cost

Level 3, which is the recycle structure of the flowsheet, we may know the product distribution as a function of conversion from the chemist. And if the desired products are formed at relatively low conversions then we have the problem of very large amount of unreacted reactant left out at the reactor exit, which we have to separate for a product and recycle back to the process.

Now, separation and recycling becomes an important aspect of process design especially for gaseous reactants, we need a compressor, which is an expensive piece of equipment in terms of both capital and operating cost. As far as liquid recycle is concerned, we may need only a pump, which is not at all an expensive component however, separation of the liquid reactants from the other products could be an energy intensive operation. Now, this usually takes place through distillation train so now, let us see, what decisions that we need to take, while deciding the recycle structure of the flowsheet. Of course, recycle structure of the flowsheet will also be dominated or will be influenced by the reactor design, because the conversion itself depends on the reactor design.

So, that point we note, that reactor design governs the extent of reaction or the conversion and thus, also influences the design of recycle structure. We also note the point of gas recycle needing compressor, which is an expensive piece of equipment with high operating cost. And thus, gas recycle is an important aspect of the overall recycle structure of the flow sheet.

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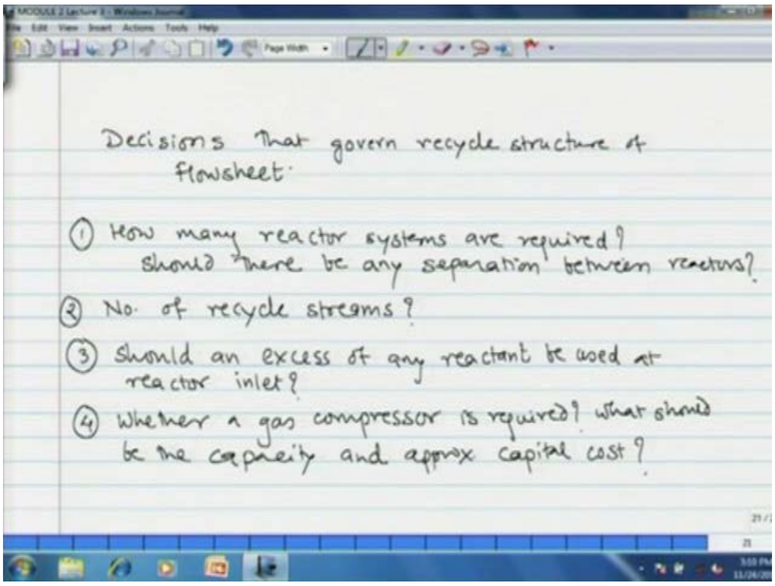

Decisions that govern recycle structure of flowsheet.

① How many reactor systems are required? Should there be any separation between reactors?

② No. of recycle streams?

③ Should an excess of any reactant be used at reactor inlet?

④ Whether a gas compressor is required? What should be the capacity and approx capital cost?

Now, let us list the decisions, that we need to make by deciding the recycle structure, the first decision that we need to make is, how many reactor systems are required and should there be any separation between these systems. The next decision is that, the number of recycle streams, how many recycle streams are required. We had dealt with such a decision before in case of input output structure where, we determined the number of product streams.

And then we said that, if the phase of the component and the destination of the component is same then these components could be sent through the same stream. And the thumb rule, that we used for such a decision was that, it is never beneficial to separate and remix 2 streams, we shall see a similar analysis in case of, number of recycle streams. Then third, should an excess of any reactant be used then the next decision is that, whether a gas compressor is required and then what should be it is capacity and the typical cost.

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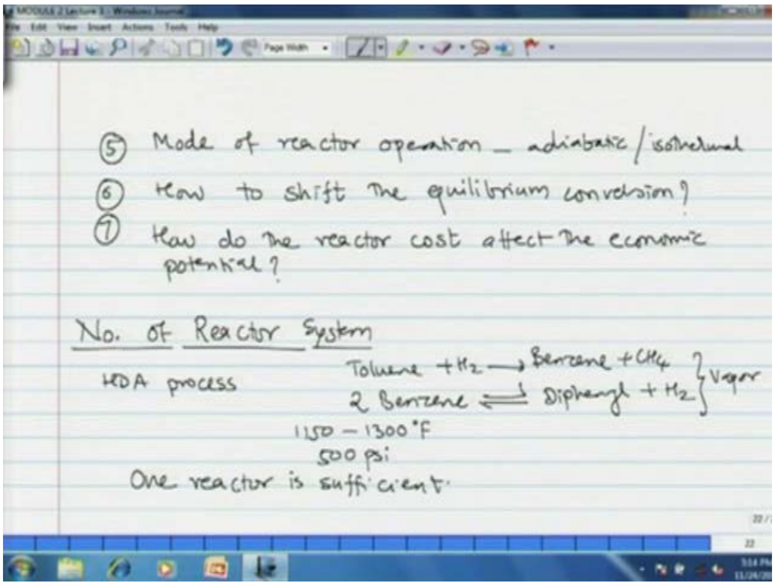

⑤ Mode of reactor operation – adiabatic / isothermal

⑥ How to shift the equilibrium conversion?

⑦ How do the reactor cost affect the economic potential?

No. of Reactor System

HDA process

$$\left.\begin{array}{l}\text{Toluene} + H_2 \rightarrow \text{Benzene} + CH_4 \\ 2\ \text{Benzene} \rightleftharpoons \text{Diphenyl} + H_2\end{array}\right\}\text{Vapor}$$

1150 – 1300 °F

500 psi

One reactor is sufficient.

Another decision that is indirectly associated with recycle structure of flow sheet is the mode of operation of the reactor, whether the reactor will be operated adiabatically or whether it should be operated isothermally. Now, this question will mainly occur for processes having highly high exothermic or highly endothermic heat of reaction. Then the next question that we have to answer is, how to shift the equilibrium conversion, if the reaction that is occurring in the process is reversible. And finally, we have to decide the economic potential that is, how do the reactor cost with recycle streams or with recycle structure affect the economic potential now, let us deal with these decisions one by one and with certain examples.

Now, the first decision that is number of reactor systems, we have been taking the hydrodealkylation process as the case study so far and we again go ahead with the same. Now, in case of HDA process, we have 2 reactions that is, toluene reacting with hydrogen to give benzene and methane, and 2 moles of benzene reacting reversibly to give 1 mole of diphenyl and hydrogen.

Now, both of these processes are vapor phase processes, their temperature and pressures are same. I had mentioned in previous lecture the range of temperature for this process that is, 1150 to 1300 degrees Fahrenheit and pressure of 500 psi. Now obviously, since both reaction are at the same temperature same pressure, only one reactor is sufficient. In addition we also note that, this is a non catalytic reaction then so for the HDA process, the number of reactors is 1 however, this may not be the case for other processes.

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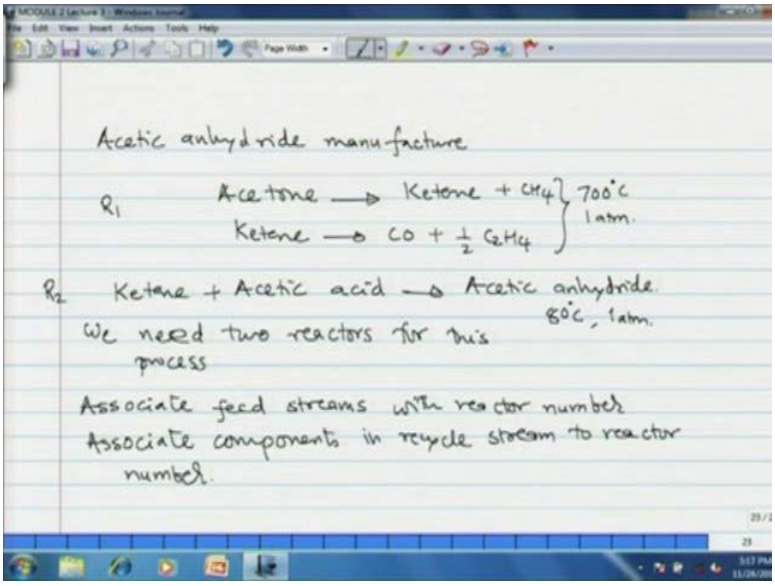

Acetic anhydride manufacture

$$\left.\begin{aligned} R_1 \quad & \text{Acetone} \longrightarrow \text{Ketene} + CH_4 \\ & \text{Ketene} \longrightarrow CO + \tfrac{1}{2} C_2H_4 \end{aligned}\right\} \begin{array}{l} 700^\circ C \\ 1\,\text{atm.} \end{array}$$

R_2 Ketane + Acetic acid $\longrightarrow$ Acetic anhydride. $80^\circ C$, 1 atm.

We need two reactors for this process

Associate feed streams with reactor number

Associate components in recycle stream to reactor number.

Now, we take example of acetic anhydride manufacture, the chemistry of the process is that, acetone is decomposed in a species called ketene with liberation of methane. Now, ketene is a unstable species, it forms only at high temperature and it can rapidly undergo conversion to more stable compounds like carbon monoxide and ethylene, this particular reaction occurs at 700 degree centigrade 1 atmosphere.

Acetone decomposing to ketene plus methane and ketene may undergo further dissociation to give carbon monoxide and ethylene. And then acetic acid is added to ketene yield acetic anhydride, this reaction occurs at 80 degree centigrade, although the pressure is same. Now, in this case we need more than 1 reactor, why because the temperatures of the two steps of the process are significantly different.

Therefore, we need 2 reactors for this process, the reactors are often numbered so, we say that, R 1 is the first reactor, in which acetone undergoes decomposition. And R 2 is the second reactor, in which the decomposition product ketene reacts with acetic acid to yield acetic anhydride. Now, while designing a particular flow sheet, it is a very useful to associate reaction steps with reactor number, that we just read and secondly, the feed streams with the reactor number. Now, acetone will be fed to the first reactor, acetic acid will be fed to the second reactor similarly, we can also associate the components in the recycle steam to the reactor number.

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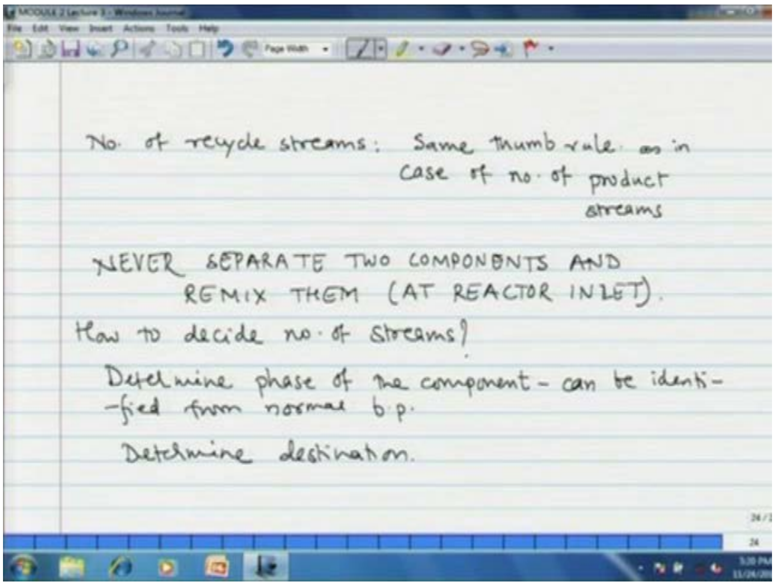

No. of recycle streams: Same thumb rule as in case of no. of product streams

NEVER SEPARATE TWO COMPONENTS AND REMIX THEM (AT REACTOR INLET).

How to decide no. of streams?

Determine phase of the component - can be identified from normal b.p.

Determine destination.

Now, we have to decide the number of recycle streams, we use the same thumb rule as we used for deciding number of product streams, for this, that it is never beneficial to separate 2 components and remix them. Now, having said this, how do we decide the number of recycle streams, again we see the phase of that particular stream and then the destination of that stream, that particular component. The phase of that particular component can be found from it is normal boiling point and then the destination. And if the destination of the particular component or different components is same and their phase is same, those components can be sent through the same stream now, let us try to apply this rule for the HDA process.

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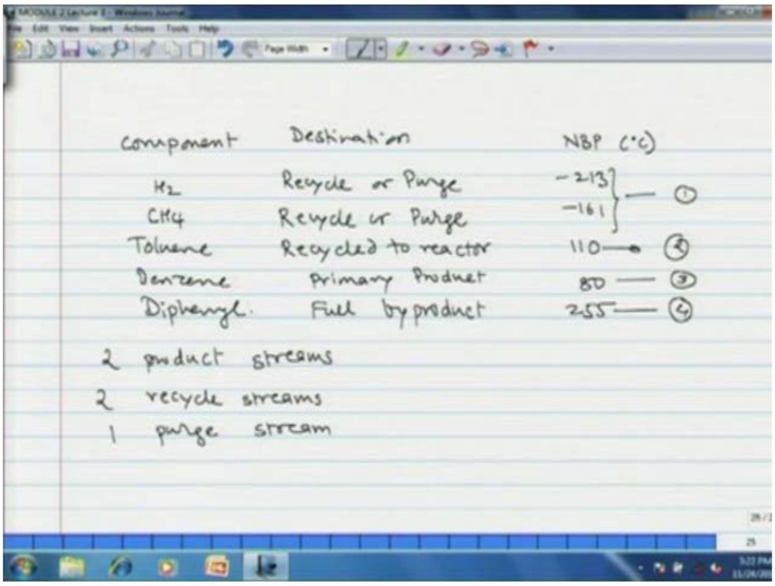

Component	Destination	NBP (°C)	
H_2	Recycle or Purge	−213	①
CH_4	Recycle or Purge	−161	
Toluene	Recycled to reactor	110	②
Benzene	Primary Product	80	③
Diphenyl.	Full by product	255	④

2 product streams
2 recycle streams
1 purge stream

What are the components of HDA process stream, that comes out of the reactor hydrogen, methane then unreacted toluene and 2 products benzene and diphenyl. The destinations of these components are hydrogen and methane, go to either recycle or purge, unreacted toluene is recycled to reactor but in liquid phase. Benzene is the primary product, which is recovered and goes for further processing and diphenyl is a side product, which is used as fuel in the process that is, captive consumption.

Now, the normal boiling points of these components are hydrogen minus 213, methane minus 161 degree centigrade, benzene 80, toluene 110 or 110.8 so, we can approximated 111 and diphenyl 255. Now obviously, hydrogen and methane can be sent together, toluene forms a separate stream because it is in liquid phase and it is recycled to the reactor, benzene is third stream and diphenyl is fourth stream. So, together we have 2 product streams, 2 recycle streams and a single purge stream where, methane and hydrogen are purged together. Now, let us try to apply the same for the acetic anhydride process that we saw.

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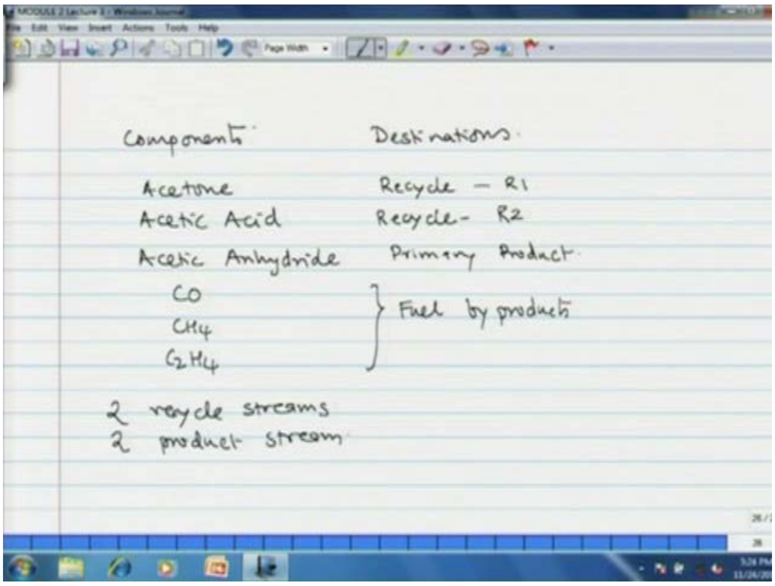

Components	Destinations
Acetone	Recycle – R1
Acetic Acid	Recycle – R2
Acetic Anhydride	Primary Product
CO	Fuel by products
CH_4	
C_2H_4	

2 recycle streams
2 product stream

Here we have many components, unreacted reactants acetone, acetic acid then the main product of the process, acetic anhydride then the 3 side products with decomposition of acetone, carbon monoxide, methane and ethylene. Their destinations are the gaseous products carbon monoxide, methane and ethylene are used as fuel, thereby products of the process and they undergo capital consumption as fuel.

Acetone is recovered and recycled however, to the first reactor and acetic acid is also recovered and recycled but to the second reactor and acetone anhydride being the primary product, is recovered and sent for further processing. Now in this case, there will be total 2 recycle streams, 1 product stream and 1 or you can even associate the fuel byproduct as a product stream so, essentially 2 recycle streams and 2 product streams. So, this is how we determine, the number of recycle streams of the process now, the question of excess reactant.

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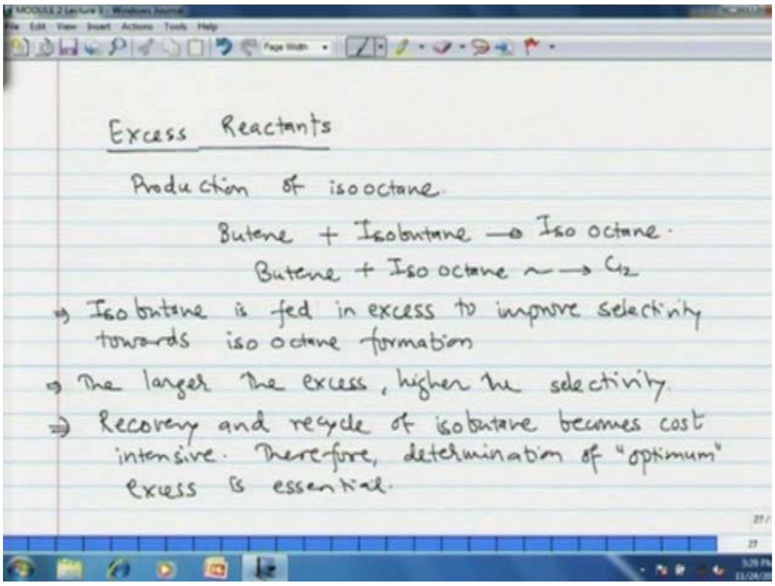

Excess Reactants

Production of isooctane.

Butene + Isobutane $\rightarrow$ Iso octane.

Butene + Iso octane $\sim\rightarrow C_{12}$

⇒ Isobutane is fed in excess to improve selectivity towards iso octane formation

⇒ The larger the excess, higher the selectivity.

⇒ Recovery and recycle of isobutane becomes cost intensive. Therefore, determination of "optimum" excess is essential.

Usually, excess reactants are fed to force the conversion of limiting reactant to completion. In some cases, the excess reactants are fed to suppress formation of side product in some cases, excess reactants are fed to prevent coke formation or they are also used as the heat diluents or heat carrier, which help in limiting the temperature rise of the process, in case of highly exothermic reactions.

So, now again, let us see some examples for determination of excess reactants now one example in this case, is the production of isooctane, in which butane reacts with isobutane to yield isooctane. And butane undergoes a side reaction with isooctane to yield higher hydro carbons like C 12. Now in this case, butene is an unsaturated molecules so, it has high reactivity and therefore, isobutane is fed in excess and this improves the selectivity towards isooctane formation.

The larger the excess, the higher the selectivity however, the stoichiometry is same, if we feed high excess of isobutene. We have high isobutane left unconverted at the reactor exit and recovery and recycle of isobutane becomes the cost expensive component. Therefore, while deciding excess of particular reactant, we have to determine the optimum excess now, take example of HDA, hydrodealkylation.

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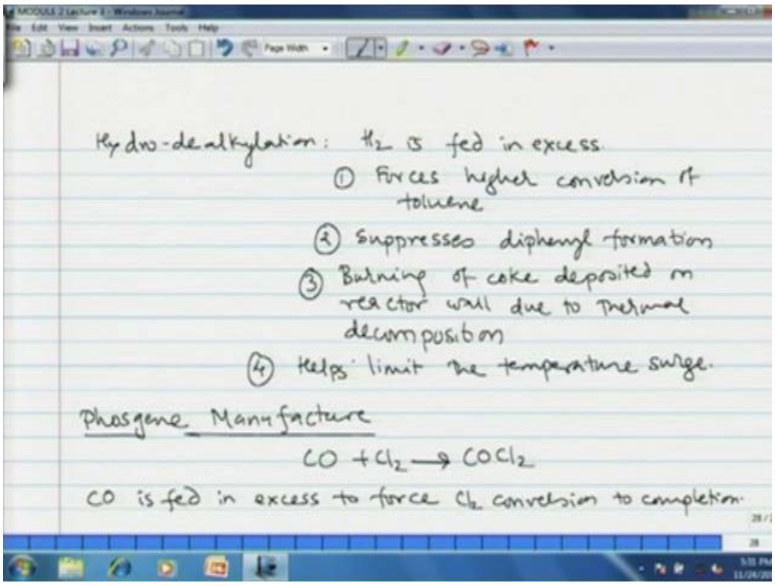

Hydro-dealkylation: H_2 is fed in excess.

① Forces higher conversion of toluene

② Suppresses diphenyl formation

③ Burning of coke deposited on reactor wall due to thermal decomposition

④ Helps limit the temperature surge.

Phosgene Manufacture

$CO + Cl_2 \rightarrow COCl_2$

CO is fed in excess to force Cl_2 conversion to completion.

In this case, hydrogen is fed in excess, now hydrogen has several roles like it forces higher conversion of toluene. Since hydrogen is also formed in the side reaction, reversible side reaction, excess of hydrogen shifts the equilibrium towards to the left towards the benzene side so, it suppresses diphenyl formation. Now in some cases, decomposition may occur like, if the temperature exceeds 1300 degrees Fahrenheit.

Then, toluene may undergo decomposition and coke that is formed, may deposit on the reactor wall, hydrogen helps in burning of that coke. So that third role excess hydrogen phase, is burning of coke deposited on the reactor wall due to thermal decomposition. And finally, excess hydrogen also helps in limiting the temperature of the process because it acts as a heat diluents, it absorbs heat. Another example could be that of a phosgene formation, phosgene is also known as war gas, in phosgene that carbon monoxide reacts with chlorine to give CoCl 2. Now in this case, carbon monoxide is fed in excess to force chlorine conversion to completion. In some cases, the products may be very difficult to separate from reactants due to chemical similarity.

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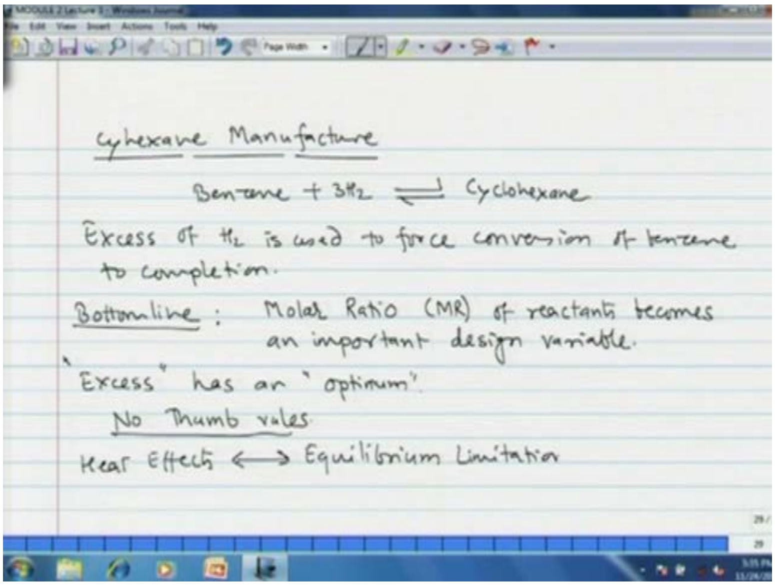

Cyhexane Manufacture

Benzene + $3H_2 \rightleftharpoons$ Cyclohexane

Excess of H_2 is used to force conversion of benzene to completion.

Bottomline : Molar Ratio (MR) of reactants becomes an important design variable.

"Excess" has an 'optimum'.

No Thumb rules.

Heat Effects ⟷ Equilibrium Limitation

A good example of this category is that of, cyclohexane manufacture now here, hydrogenation of benzene is carried out through a reversible reaction. Now, cyclohexane and benzene are chemically similar and the relative volatility is very close to 1 so, if any benzene remains unconverted in cyclohexane, removal of it is very difficult. Secondly, benzene is carcinogenic, it is one of the hazardous or toxic materials so, leaving impurity of benzene and cyclohexane is not desired.

Therefore, excess of hydrogen is used to force conversion of benzene to completion so, that point we note, excess of hydrogen is used to force conversion of benzene to completion. We shall see a detail analysis of this process later in this module, the bottom line is that, due to this excess, the molar ratio of reactants is an important design variables.

As we pointed out earlier in this lecture, the excess has an optimum, you have certain beneficial effects of using excess. However, there is always a undesired consequence of recovery and recycle of reactant and that needs to be considered, while finding out the optimum excess. Unfortunately, there are no thumb rules for this, we have to determine the optimum excess for particular process through iterations and that governs, these recycled structure of the flowsheets. Heat effects of the process are also related to the equilibrium conversion however, we shall deal with this topic in greater detail in the next lecture.