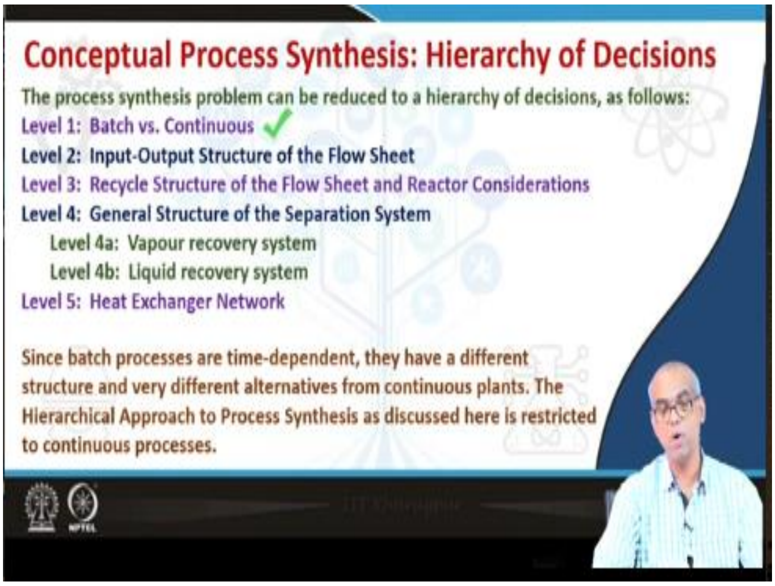
Plant Design and Economics
Prof. Debasis Sarkar
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture No -28
Hierarchical Approach to Process Synthesis -II

Welcome to lecture 28 of plant design and economics. We will continue our discussion on hierarchical approach to process synthesis. In the previous lecture, we have talked about various levels of decisions and discussed the level 1 decision which was about batch versus continuous operations. Today, we will talk about level 2 decisions. So, hierarchical approach to process synthesis design at level 2.

(Refer Slide Time: 00:50)



Conceptual Process Synthesis: Hierarchy of Decisions

The process synthesis problem can be reduced to a hierarchy of decisions, as follows:

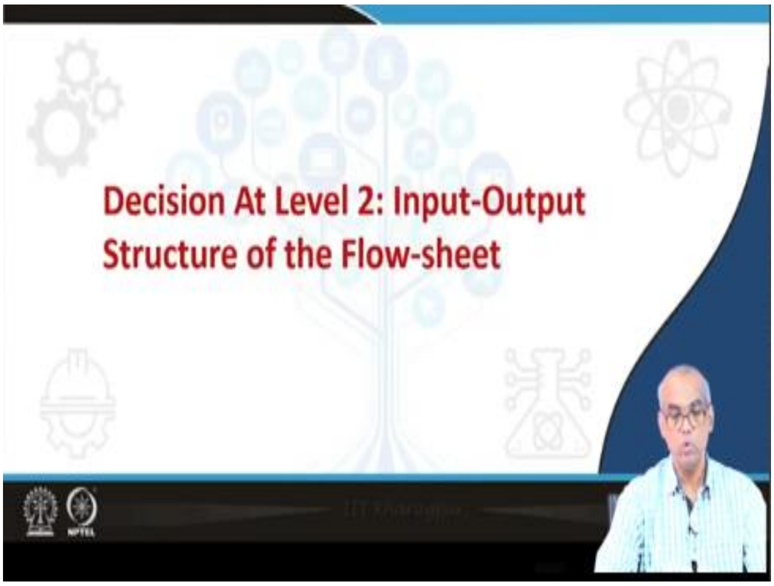
Level 1: Batch vs. Continuous ✓
Level 2: Input-Output Structure of the Flow Sheet
Level 3: Recycle Structure of the Flow Sheet and Reactor Considerations
Level 4: General Structure of the Separation System
    Level 4a: Vapour recovery system
    Level 4b: Liquid recovery system
Level 5: Heat Exchanger Network

Since batch processes are time-dependent, they have a different structure and very different alternatives from continuous plants. The Hierarchical Approach to Process Synthesis as discussed here is restricted to continuous processes.

So level 2 decisions. We have talked about that there are 5 different levels: batch versus continuous, input output structure of the flow sheet, recycle structure of the flow sheet and reactor considerations, general structure of the separation system and then under that vapour recovery system comes first and then comes liquid recovery system and that level 5 heat exchanger network.

Now, we have talked about batch versus continuous processes that is decisions at level 1. Since batch processes are time dependent, they have a different structure and very different alternatives from continuous plants. So the hierarchical approach to process synthesis as we discussed here is essentially restricted to continuous processes.

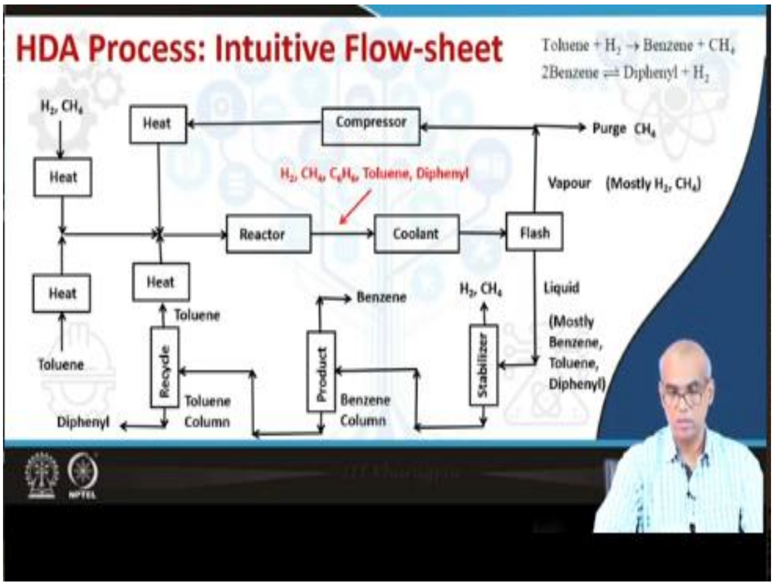
(Refer Slide Time: 01:59)



Decision At Level 2: Input-Output Structure of the Flow-sheet

So today we will look at level 2 decisions, which is about input output structure of the flow sheet.

(Refer Slide Time: 02:05)



HDA Process: Intuitive Flow-sheet

$\text{Toluene} + H_2 \rightarrow \text{Benzene} + CH_4$

$2\text{Benzene} \rightleftharpoons \text{Diphenyl} + H_2$

So before we go into the details of decisions at level 2, we quickly review the hydrodealkylation process of the toluene that we discussed in the previous class. So you know that toluene reacts with hydrogen to produce benzene and methane and then two molecules of benzene undergoes reversible reaction to produce one molecule of diphenyl and one molecular hydrogen.

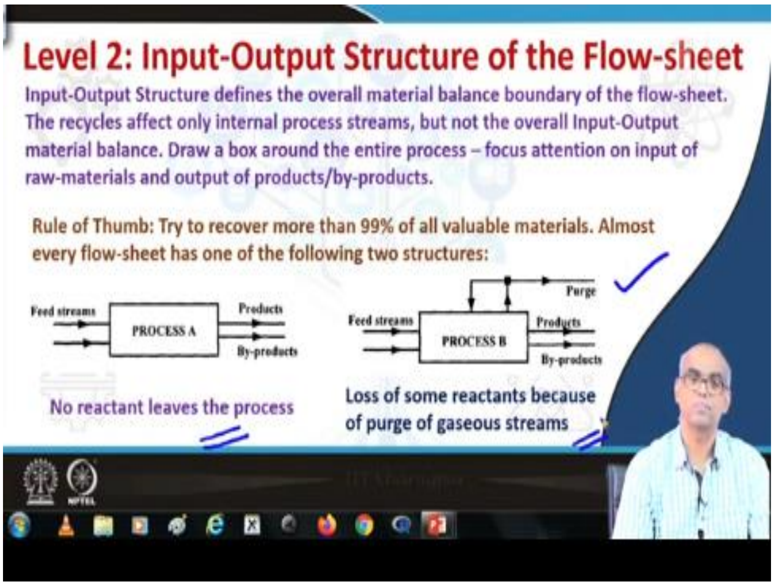
Now the flow sheet that we developed was hydrogen and methane are heated up, also toluene is heated up to vaporize and to raise temperature, they are mixed, fed to the reactor where this hydrodealkylation reaction takes place. So the effluence stream from the reactor will contain desired product benzene, undesired by-product diphenyl and also hydrogen, methane and unreacted toluene.

This reactor effluence stream will be cooled and then flashed. The vapour product will mostly contain hydrogen and methane would like to recycle the hydrogen but purge out the methane. So mostly the hydrogen stream is compressed, heated and fed back to the reactor again. The liquid stream that comes from the flash will mostly contain benzene, toluene and diphenyl, but will also have some amount of dissolved hydrogen and methane.

So when these stream goes to the stabilizer column, hydrogen and methane as separated out as top product. The bottom product which contains benzene plus toluene plus diphenyl goes as feed to the second column which is known as benzene column and benzene comes out as a top product there. The bottom product is mostly toluene and diphenyl which are separated as toluene and diphenyl in the third distillation column.

The toluene which comes as top product is heated and fed back to the reactor as recycle and the unwanted diphenyl comes as bottom product.

(Refer Slide Time: 04:33)



Level 2: Input-Output Structure of the Flow-sheet

Input-Output Structure defines the overall material balance boundary of the flow-sheet. The recycles affect only internal process streams, but not the overall Input-Output material balance. Draw a box around the entire process – focus attention on input of raw-materials and output of products/by-products.

Rule of Thumb: Try to recover more than 99% of all valuable materials. Almost every flow-sheet has one of the following two structures:

No reactant leaves the process

Loss of some reactants because of purge of gaseous streams

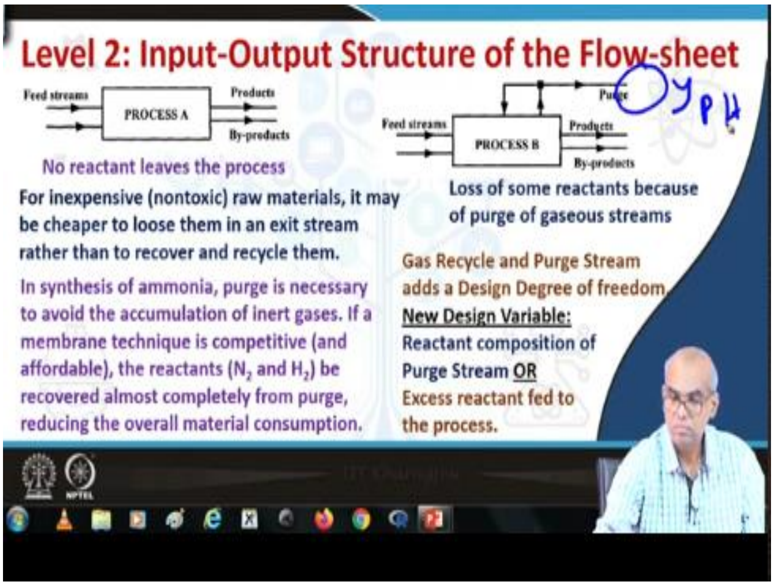
Now let us discuss the decision at level 2 in more detail and this decision is all about input output structure of the flowsheet. Input output structure defines the overall material balance boundary of the flow sheet. The recycles affect only internal process streams, but not the overall input output material values. So draw a box around the entire process and focus attention on input of raw materials and output of products as well as output of by-products.

The rule of thumb that one uses here is that we need to try to recover more than 99% of all valuable materials. Then almost every flow sheet has one of the following two structures that we just discussed now. The first flow sheet, the feed streams enter and the products and by product stream comes out. Look there is no recycle, there is no purge. So no reactant leaves the process.

The reactants are all converted to products and byproducts. Now, look at the second flow sheet. Here you see the existence of a purge stream and recycle loop. So this kind of flow sheet we will often see in gaseous reactions. If the gaseous feed stream contains an impurity or inert or an impurities produced during the reaction, this impurity or the inert must be purged out otherwise it will build in the recycle loop.

Note that the unconverted reactant you would like to send back to the reactor as recycler. But the inert or the impurity must be purged out from the process otherwise, it will build up in the recycle loop and stop the process. So in such a process flow sheet, you see that there is a purge stream, so there is loss of some reactants through this purge of gaseous streams. So in general almost all every flow sheet will have either this structure or this structure.

(Refer Slide Time: 07:53)



Level 2: Input-Output Structure of the Flow-sheet

No reactant leaves the process

For inexpensive (nontoxic) raw materials, it may be cheaper to loose them in an exit stream rather than to recover and recycle them.

In synthesis of ammonia, purge is necessary to avoid the accumulation of inert gases. If a membrane technique is competitive (and affordable), the reactants (N_2 and H_2) be recovered almost completely from purge, reducing the overall material consumption.

Loss of some reactants because of purge of gaseous streams

Gas Recycle and Purge Stream adds a Design Degree of freedom

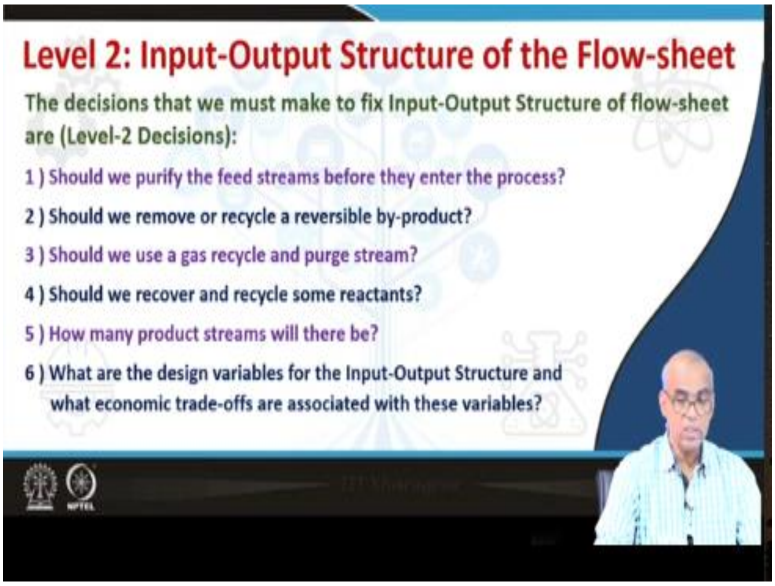
<u>New Design Variable:</u>
Reactant composition of Purge Stream <u>OR</u>
Excess reactant fed to the process.

For inexpensive and of course non-toxic raw materials, it may be cheaper to lose them in an exit stream rather than to recover and recycle them. If the raw material is toxic, then for environmental regulations, we will not be allowed to exit into the atmosphere. But if the raw material is nontoxic and not expensive, then it may be cheaper to lose them in an exit stream rather than to recover and recycle them because to recover and recycle this inexpensive raw materials, you have to invest money.

So for inexpensive raw materials, it may be cheaper to lose them in an exit stream. We have discussed about synthesis of ammonia long back. We have seen that purge was necessary to avoid the accumulation of inert gases. However, if you use a membrane-based separation process and if the membrane technique is competitive and affordable, the reactants nitrogen and hydrogen can be completely recovered or almost completely recovered from the purge and this will reduce the overall material consumption.

Note that when you use gas recycle and purge stream, it adds a design degree of freedom. So, the reactant composition of the purge stream or the excess reactant fed to the process will become a new design variable in the presence of gas recycle or purge stream. This we will discuss in more detail later. So the reactant composition, so in case of say the HDA process, the composition of hydrogen in this purge stream or the excess amount of hydrogen that is fed to the process will be considered as a new design variable. So the presence of gas recycle and purge stream adds a design degree of freedom.

(Refer Slide Time: 10:42)



Level 2: Input-Output Structure of the Flow-sheet

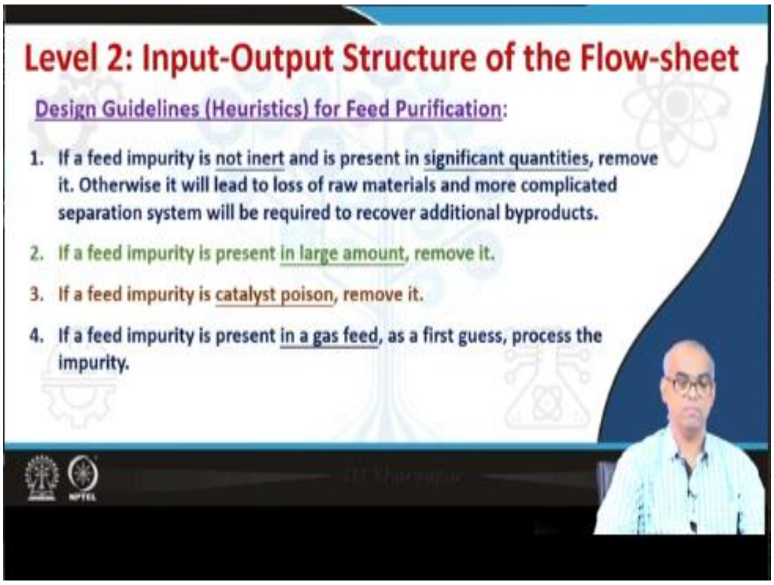
The decisions that we must make to fix Input-Output Structure of flow-sheet are (Level-2 Decisions):

1) Should we purify the feed streams before they enter the process?
2) Should we remove or recycle a reversible by-product?
3) Should we use a gas recycle and purge stream?
4) Should we recover and recycle some reactants?
5) How many product streams will there be?
6) What are the design variables for the Input-Output Structure and what economic trade-offs are associated with these variables?

Now, the decision that we must make to fix input output structure of process flow sheet are as follows: first should we purify the feed streams before they enter the process? So we are now going to raise several questions and these are the decisions that we must take to fix input output structure of the flow sheet. These are level 2 decisions. First should we purify the feed streams before they enter the process?

Should we remove or recycle a reversible by product? Should you use a gas recycle and purge stream? Should you recover and recycle some reactants? How many product streams will there be? What are the design variables for the input output structure and what economic tradeoffs are associated with these variables? So we need to take decisions about all these issues that we just discussed.

(Refer Slide Time: 12:01)



Level 2: Input-Output Structure of the Flow-sheet

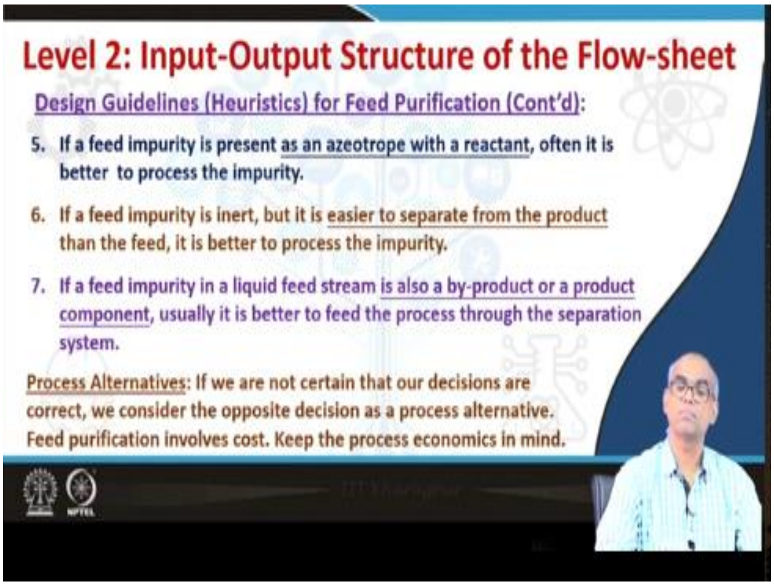
Design Guidelines (Heuristics) for Feed Purification:

1. If a feed impurity is not inert and is present in significant quantities, remove it. Otherwise it will lead to loss of raw materials and more complicated separation system will be required to recover additional byproducts.
2. If a feed impurity is present in large amount, remove it.
3. If a feed impurity is catalyst poison, remove it.
4. If a feed impurity is present in a gas feed, as a first guess, process the impurity.

Now, we will go one by one and see what are the heuristics or design guidelines available for these questions? First, what is the design guideline or heuristics available for feed purification? So this will answer to the question, should repurify the feed before it enters the process? If a feed impurity is not inert and is present in significant quantities, remove it. Otherwise it will lead to loss of raw materials and more complicated separation system will be required to recover additional by-products.

If a feed impurity is present in large amount, remove it. If a feed impurity is catalyst poison, obviously remove it otherwise it will hamper the reactor operation. If a feed impurity is present in a gas heat, as a first guess process the impurity.

(Refer Slide Time: 13:17)



Level 2: Input-Output Structure of the Flow-sheet

Design Guidelines (Heuristics) for Feed Purification (Cont'd):

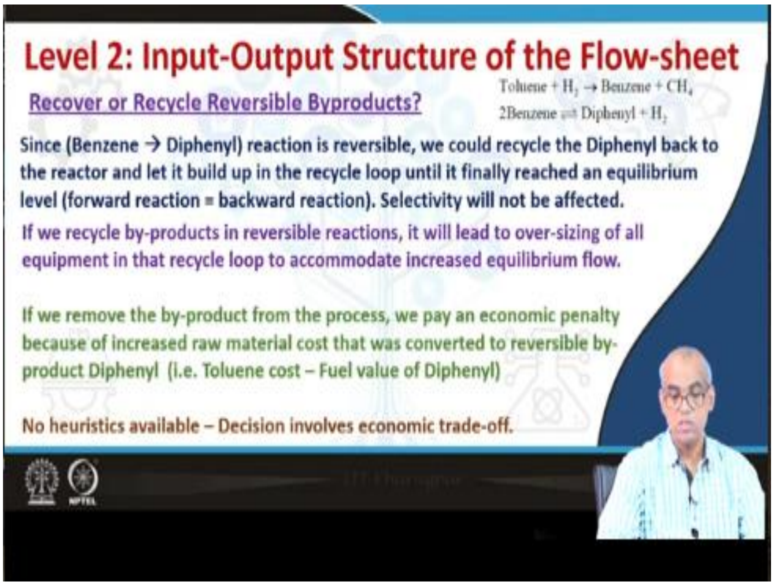
5. If a feed impurity is present as an azeotrope with a reactant, often it is better to process the impurity.
6. If a feed impurity is inert, but it is easier to separate from the product than the feed, it is better to process the impurity.
7. If a feed impurity in a liquid feed stream is also a by-product or a product component, usually it is better to feed the process through the separation system.

Process Alternatives: If we are not certain that our decisions are correct, we consider the opposite decision as a process alternative. Feed purification involves cost. Keep the process economics in mind.

If a feed impurity is present as an azeotrope with the reactant, often it is better to process the impurity. If a feed impurity is inert, but it is easier to separate from the product than the feed, it is better to process the impurity. If a feed impurity in a liquid feed stream is also a by-product or a product component, usually it is better to feed the process through the separation system.

So, these heuristics or design guidelines are available which will help us decide whether we should separate the impurity from the feed, that means remove it or we can actually process the impurity in the feed. Process alternatives: if you are not certain that our decisions are correct, we consider the opposite decision as process alternative. Feed purification involves cost. So always keep the process economics in mind.

(Refer Slide Time: 14:45)



Level 2: Input-Output Structure of the Flow-sheet

$\text{Toluene} + H_2 \rightarrow \text{Benzene} + CH_4$

$2\text{Benzene} \rightleftharpoons \text{Diphenyl} + H_2$

Recover or Recycle Reversible Byproducts?

Since (Benzene → Diphenyl) reaction is reversible, we could recycle the Diphenyl back to the reactor and let it build up in the recycle loop until it finally reached an equilibrium level (forward reaction = backward reaction). Selectivity will not be affected.

If we recycle by-products in reversible reactions, it will lead to over-sizing of all equipment in that recycle loop to accommodate increased equilibrium flow.

If we remove the by-product from the process, we pay an economic penalty because of increased raw material cost that was converted to reversible by-product Diphenyl (i.e. Toluene cost – Fuel value of Diphenyl)

No heuristics available – Decision involves economic trade-off.

Next, we will ask whether to recover or recycle reversible by-products? So what heuristics or design guidelines are available to decide whether to recover or recycle reversible by-products or not? Now benzene to diphenyl reaction is reversible. So you can recycle the diphenyl back to the reactor and let it build up in the reaction recycle loop until it finally reaches an equilibrium.

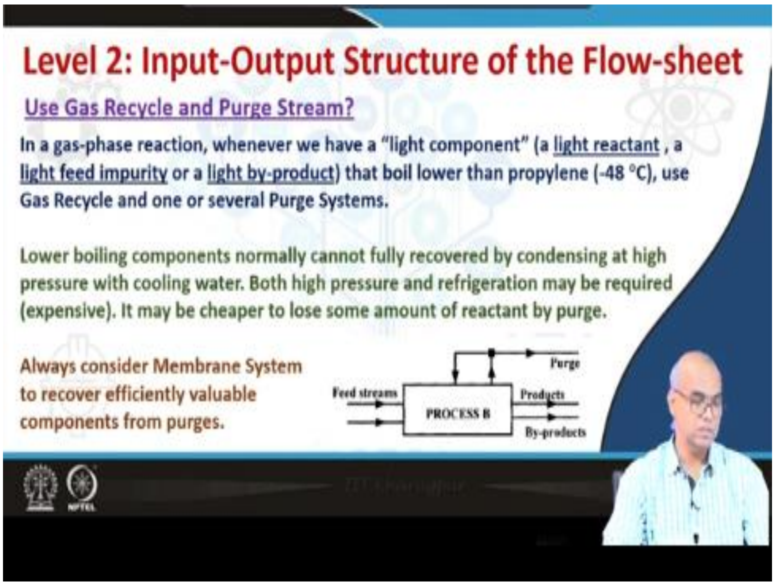
When it reaches at equilibrium, the forward reaction by which diphenyl is formed from the benzene will be equal to the backward reaction by which benzene is formed from diphenyl. Note that selectivity will not be affected here. Now if we recycle by-products in reversible reactions, it will lead to oversizing of all equipment in that recycle loop because you now have to accommodate the increase equilibrium flow.

But if we decide to remove the by-product from the process, then we pay an economic penalty because of increased raw material cost that was converted to reversible by-product diphenyl. So basically the cost of toluene and the cost of fuel value of diphenyl you look at. So, the toluene cost-the fuel value of diphenyl,this much of economic penalty will be there if we decide to remove the by-product from the process.

So since the benzene to diphenyl reaction is reversible, we can recycle the diphenyl to the reactor and let it build up to the recycle loop until it reaches an equilibrium. But if we do that, it leads to oversizing of the equipment in the recycle loop and if we decide to remove we pay an economic penalty. So, the decision involves economic trade off. So, there is actually no easy heuristics or design guides available for this decision.

Because decision involves economic trade off. So you have to do an economic analysis to come up to a proper conclusion.

(Refer Slide Time: 17:43)



Level 2: Input-Output Structure of the Flow-sheet

Use Gas Recycle and Purge Stream?

In a gas-phase reaction, whenever we have a "light component" (a light reactant , a light feed impurity or a light by-product) that boil lower than propylene (-48 °C), use Gas Recycle and one or several Purge Systems.

Lower boiling components normally cannot fully recovered by condensing at high pressure with cooling water. Both high pressure and refrigeration may be required (expensive). It may be cheaper to lose some amount of reactant by purge.

Always consider Membrane System to recover efficiently valuable components from purges.

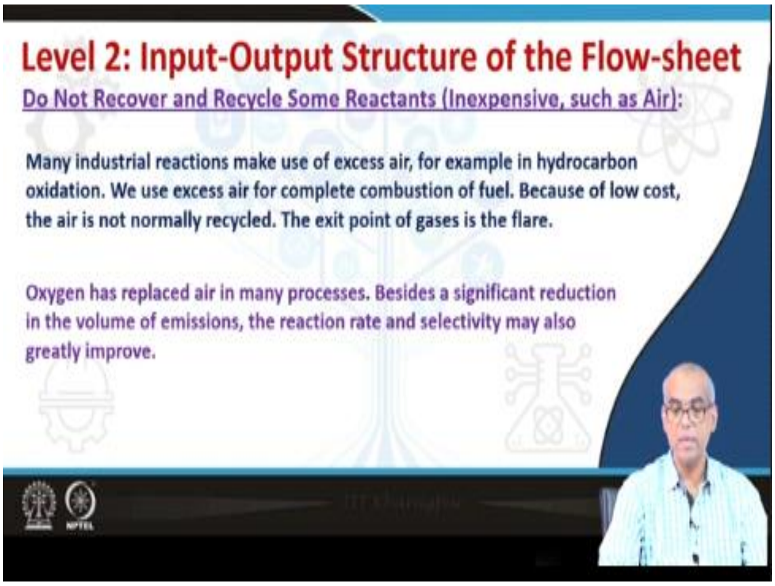
Next, whether to use gas recycle or purge stream? So what design guidelines or heuristics are available? Look at the flow sheet, you have the purge stream as well as the recycle stream. So that to use that gas recycle and purge stream in a gas phase reaction. So now let us talk about the heuristics or design guidelines that are available. In a gas phase reaction, whenever we have a light component.

What is light component? A light reactant, a light feed impurity or a light by-product that has a boiling temperature lower than the boiling temperature of propylene, which is -48 degree celsius. So in a gas phase reaction, whenever we have a light component that boil lower than propylene, use gas recycle and one or several purge streams. Lower boiling components normally cannot fully recover by condensing at high pressure with the available cooling water.

So lower boiling components normally cannot be fully recovered by condensing the stream at high pressure with the available cooling water. It means that you will require both high pressure as well as refrigeration and refrigeration is an expensive operation. So it may be cheaper to lose some amount of reactant by purge. So this is the justification behind this heuristics.

However, always consider membrane system to recover efficiently valuable components from purges. But note that membrane systems may be expensive. So you must perform economic analysis. So for inexpensive components, may not be economically viable to be recovered from the purge stream using membrane separation system, but you always consider that as an alternative to recover efficiently valuable components from purge stream.

(Refer Slide Time: 20:32)



Level 2: Input-Output Structure of the Flow-sheet

Do Not Recover and Recycle Some Reactants (Inexpensive, such as Air):

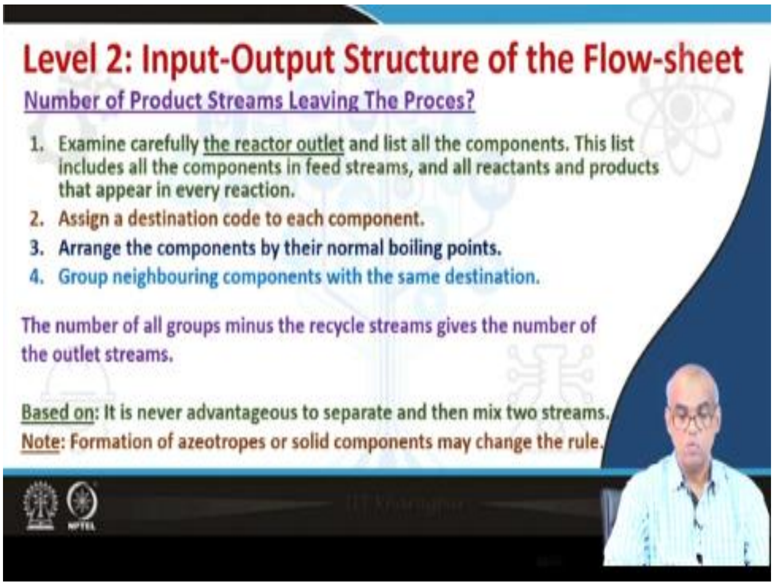
Many industrial reactions make use of excess air, for example in hydrocarbon oxidation. We use excess air for complete combustion of fuel. Because of low cost, the air is not normally recycled. The exit point of gases is the flare.

Oxygen has replaced air in many processes. Besides a significant reduction in the volume of emissions, the reaction rate and selectivity may also greatly improve.

Next, do not recover and recycle some reactants. What kind of reactants, which are inexpensive such as air. Air is used in several industrial operations. For example, in hydrocarbon oxidation. We use excess air for complete combustion of fuel. Now because of low cost the air is not normally recycled. The exit point of gases is the flare. Oxygen has replaced air in many processes.

There is an advantage in replacing air by oxygen. There will be significant reduction in the volume of emission. Also, the reaction rate will be improved as well as selectivity can also be greatly improved. So that is the reason that oxygen has now replaced here in many industrial operations so that you can significantly reduce the volume of emission as well as improve reaction rate and selectivity.

(Refer Slide Time: 21:54)



Level 2: Input-Output Structure of the Flow-sheet

Number of Product Streams Leaving The Proces?

1. Examine carefully the reactor outlet and list all the components. This list includes all the components in feed streams, and all reactants and products that appear in every reaction.
2. Assign a destination code to each component.
3. Arrange the components by their normal boiling points.
4. Group neighbouring components with the same destination.

The number of all groups minus the recycle streams gives the number of the outlet streams.

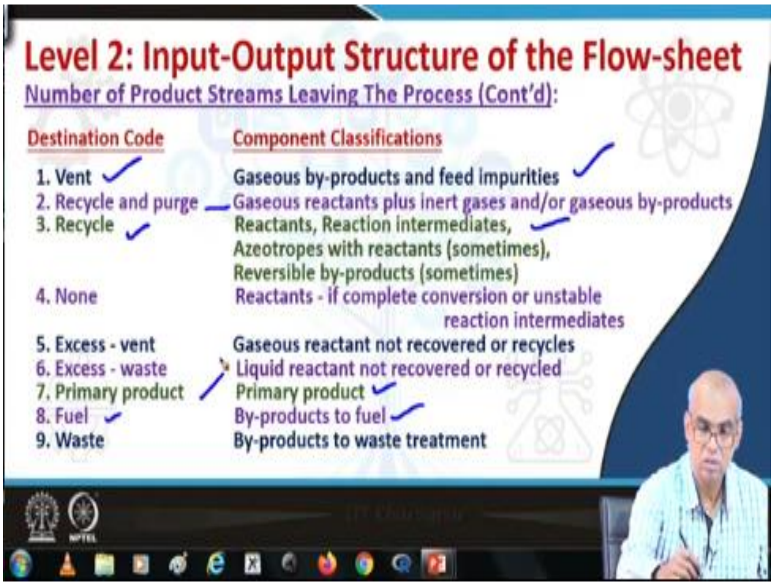
Based on: It is never advantageous to separate and then mix two streams.
Note: Formation of azeotropes or solid components may change the rule.

Now, how do you compute the number of product streams leaving the process? Let us follow the steps as we discussed now. First, examine carefully the reactor outlet and list all the components. So focus your attention on the reactor outlets, at least all the components. This list includes all the components in the feed streams and all the reactants and products that appear in every reaction.

Assign a destination code to each component. Arrange the components by their normal boiling points. And group neighbouring components with the same destination. We will see what are those destination codes the next slide. So these are the steps that we follow. First we examine carefully the reactor outlets and list all the components, assign a distinction code to each component, arrange the components by the normal boiling points and group neighbouring components with the same destination.

The number of all groups minus the recycle streams gives the number of outlet streams or number of product streams. So number of product streams or number of outlet streams is equal to the number of groups minus the number of recycled streams. So this is based on the idea that it is never advantageous to separate and then mix 2 streams. There is no point, you do not separate two streams and again mix them. However, formation of azeotropes or solid components may change this rule.

(Refer Slide Time: 23:59)



Level 2: Input-Output Structure of the Flow-sheet

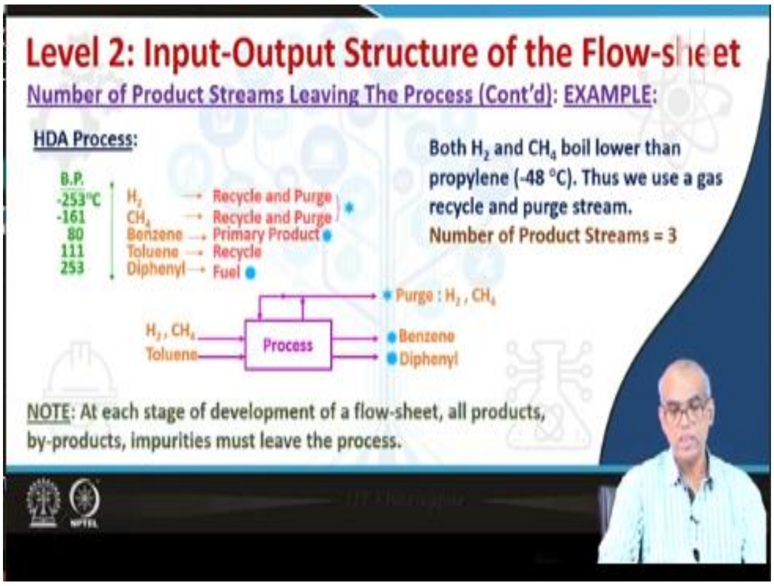
Number of Product Streams Leaving The Process (Cont'd):

Destination Code	Component Classifications
1. Vent ✓	Gaseous by-products and feed impurities ✓
2. Recycle and purge —	Gaseous reactants plus inert gases and/or gaseous by-products
3. Recycle ✓	Reactants, Reaction intermediates, ✓ Azeotropes with reactants (sometimes), Reversible by-products (sometimes)
4. None	Reactants - if complete conversion or unstable reaction intermediates
5. Excess - vent	Gaseous reactant not recovered or recycles
6. Excess - waste	Liquid reactant not recovered or recycled
7. Primary product	Primary product ✓
8. Fuel ✓	By-products to fuel ✓
9. Waste	By-products to waste treatment

Now, these are the destination codes and the associated component classifications. For example, if you have gases by products and feed impurities, this stream will be associated destination code vent. To reactance, reaction intermediates will assign destination code, recycle. Gaseous reactants plus inert gases and or gases by-products will assign recycle and purge as destination code.

By-products to fuel will assign fuel as destination code. Primary product will be assigned primary product as destination code. So we have a list of destination code and the associated component classification. You use this list to assign a destination code to each component.

(Refer Slide Time: 25:03)



Level 2: Input-Output Structure of the Flow-sheet

Number of Product Streams Leaving The Process (Cont'd): EXAMPLE:

HDA Process:

B.P.		
-253°C	H_2 →	Recycle and Purge *
-161	CH_4 →	Recycle and Purge *
80	Benzene →	Primary Product ●
111	Toluene →	Recycle
253	Diphenyl →	Fuel ●

Both H_2 and CH_4 boil lower than propylene (-48 °C). Thus we use a gas recycle and purge stream.

Number of Product Streams = 3

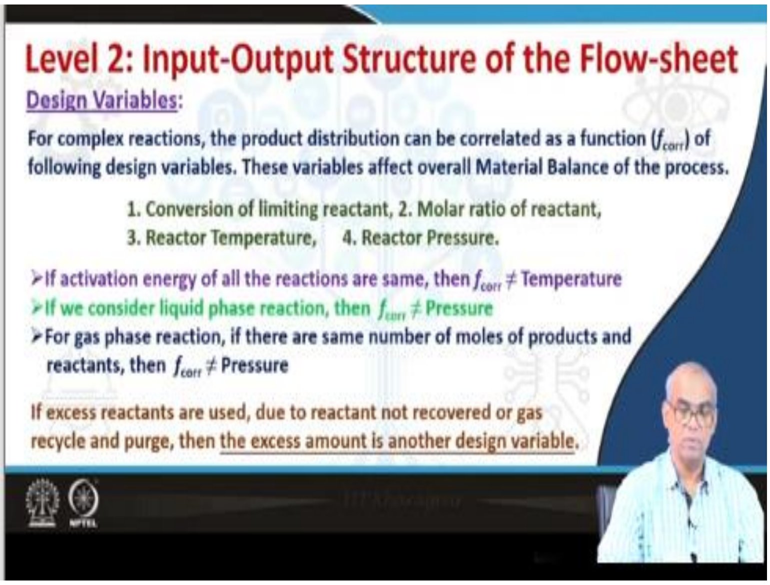
NOTE: At each stage of development of a flow-sheet, all products, by-products, impurities must leave the process.

Now, let us take this example from the hydrodealkylation process to understand how to compute number of product streams? So what are the components we have? Hydrogen, methane, benzene, toluene and diphenyl. So I arrange them according to normal boiling point. Note that both hydrogen and methane boil lower than the propylene. Propylene has boiling point -48 degree celsius, whereas hydrogen and methane has much lower boiling point.

So thus we will use a gas recycle and purge stream. So we have seen the heuristics that whenever in a gas phase reaction the light components boil below propylene, we will use gas recycle and purge stream, so use gas recycle and purge stream. Now, we have arrange the components according to the boiling point and assign a destination code. Hydrogen and methane has been assigned the recycle and purge, benzene has been assigned primary product, toluene has been assigned recycle and the diphenyl has been assigned fuel.

So how many product streams are there? We have 3 product streams; recycle and purge, primary product and the diphenyl of fuel product. At each stage of the development of a flow sheet, you must take care that all products, by-products, impurities must leave the process.

(Refer Slide Time: 27:05)



Level 2: Input-Output Structure of the Flow-sheet

Design Variables:

For complex reactions, the product distribution can be correlated as a function (f_{corr}) of following design variables. These variables affect overall Material Balance of the process.

1. Conversion of limiting reactant, 2. Molar ratio of reactant,
3. Reactor Temperature, 4. Reactor Pressure.

- If activation energy of all the reactions are same, then $f_{corr} \neq$ Temperature
- If we consider liquid phase reaction, then $f_{corr} \neq$ Pressure
- For gas phase reaction, if there are same number of moles of products and reactants, then $f_{corr} \neq$ Pressure

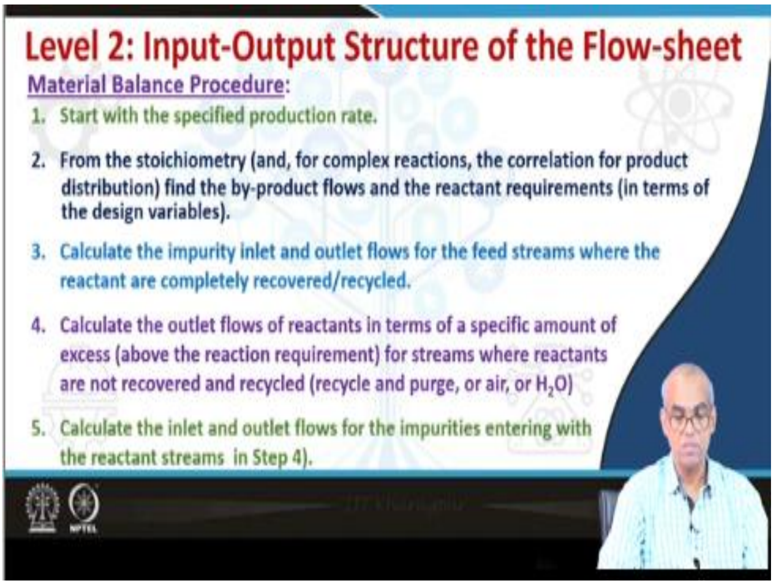
If excess reactants are used, due to reactant not recovered or gas recycle and purge, then the excess amount is another design variable.

Now the design variables. For complex reactions, the product distribution can be correlated as a function of certain design variables. These design variables affect overall material balance of the process. What are design variables? Conversion of limiting reactant, for example, in the HDA process the limiting reactant is toluene, so conversion of toluene will be a design variable, molar ratio of reactant, reactor temperature, reactor pressure, these are all design variables.

If the activation energy of all the reactions are same, then this correlation describing product distribution will not depend on temperature. Similarly, if we consider liquid phase reaction, then the product distribution correlation will not be a function of pressure. Also, for gas phase reaction if there are same number of moles of products and reactants, there also the correlation describing the product distribution will not be a function of pressure.

If excess reactants are used due to reactant not recovered or gas recycle and purge, then the excess amount is another design variable. So allowing conversion of limiting reactant, molar ratio of reactant, reactor temperature, reactor pressure, the excess amount of reactor, the excess amount is also another design variable.

(Refer Slide Time: 28:46)



Level 2: Input-Output Structure of the Flow-sheet

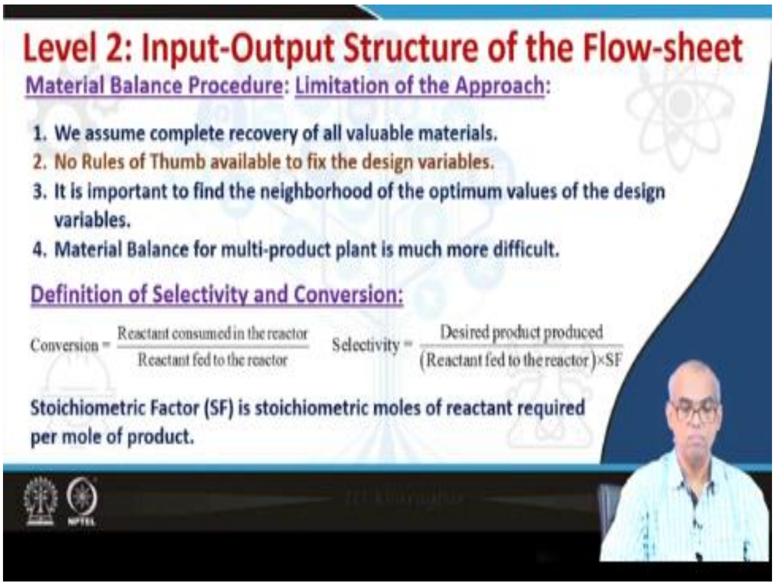
Material Balance Procedure:

1. Start with the specified production rate.
2. From the stoichiometry (and, for complex reactions, the correlation for product distribution) find the by-product flows and the reactant requirements (in terms of the design variables).
3. Calculate the impurity inlet and outlet flows for the feed streams where the reactant are completely recovered/recycled.
4. Calculate the outlet flows of reactants in terms of a specific amount of excess (above the reaction requirement) for streams where reactants are not recovered and recycled (recycle and purge, or air, or H_2O)
5. Calculate the inlet and outlet flows for the impurities entering with the reactant streams in Step 4).

Now we will see how to develop material balance for our process. So let us first discuss the procedure. We start with the specified production rate. From the stoichiometry, find the by-product flows and the reactant requirements. Calculate the impurity inlet and outlet flows for the feed streams where the reactants are completely recovered or recycled. Next, calculate the outlet flows of reactants in terms of a specific amount of excess for streams where reactants are not recovered and recycled.

Calculate the inlet and outlet flows for the impurities entering with the reactant streams in the previous step 4.So this is the procedure.

(Refer Slide Time: 29:48)



Level 2: Input-Output Structure of the Flow-sheet

Material Balance Procedure: Limitation of the Approach:

1. We assume complete recovery of all valuable materials.
2. No Rules of Thumb available to fix the design variables.
3. It is important to find the neighborhood of the optimum values of the design variables.
4. Material Balance for multi-product plant is much more difficult.

Definition of Selectivity and Conversion:

$$\text{Conversion} = \frac{\text{Reactant consumed in the reactor}}{\text{Reactant fed to the reactor}} \qquad \text{Selectivity} = \frac{\text{Desired product produced}}{(\text{Reactant fed to the reactor})\times \text{SF}}$$

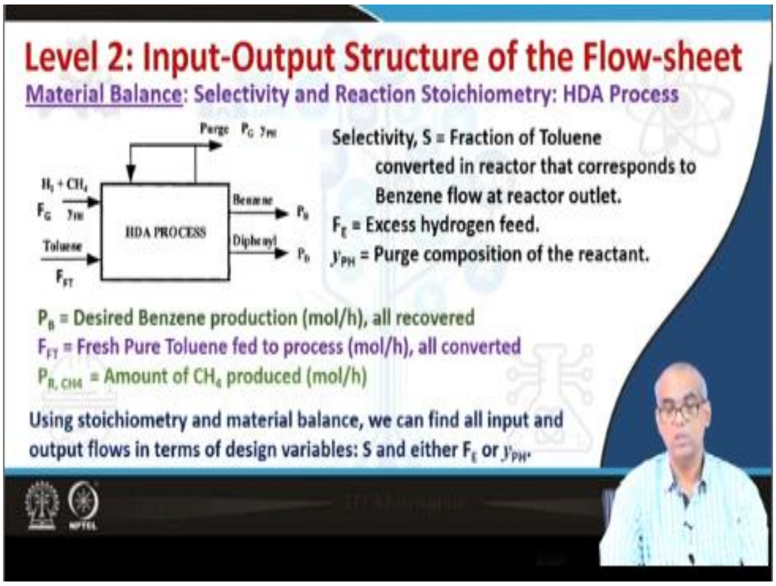
Stoichiometric Factor (SF) is stoichiometric moles of reactant required per mole of product.

Now, let us take the example of HDA process and develop the material balance. Before that let us discuss about the limitation of this approach. What we assume that we are able to completely recover all valuable materials. Heuristics we use that we should be able to recover 99% or more of the valuable materials. Here, we are assuming the 100% recovery, complete recovery which may not be possible always.

No rules of thumb available to fix the design variables. It is important to find the neighbourhood of the optimum values of the design variables. When your process has several products, the material balance for such multi product plant becomes much more difficult. Now before we discuss the material balance in details, let us define two terms; selectivity and conversion which will be using.

Conversion is reactant consumed in the reactor divided by reactant fed to the reactant. And selectivity is desired product produced divided by reactant fed to the reactor multiplied by stoichiometric factor. Stoichiometric factor is the moles of reactant required per mole of product.

(Refer Slide Time: 31:30)



Level 2: Input-Output Structure of the Flow-sheet

Material Balance: Selectivity and Reaction Stoichiometry: HDA Process

Selectivity, S = Fraction of Toluene converted in reactor that corresponds to Benzene flow at reactor outlet.

F_E = Excess hydrogen feed.

y_{PH} = Purge composition of the reactant.

P_B = Desired Benzene production (mol/h), all recovered

F_{FT} = Fresh Pure Toluene fed to process (mol/h), all converted

$P_{R,\,CH4}$ = Amount of CH_4 produced (mol/h)

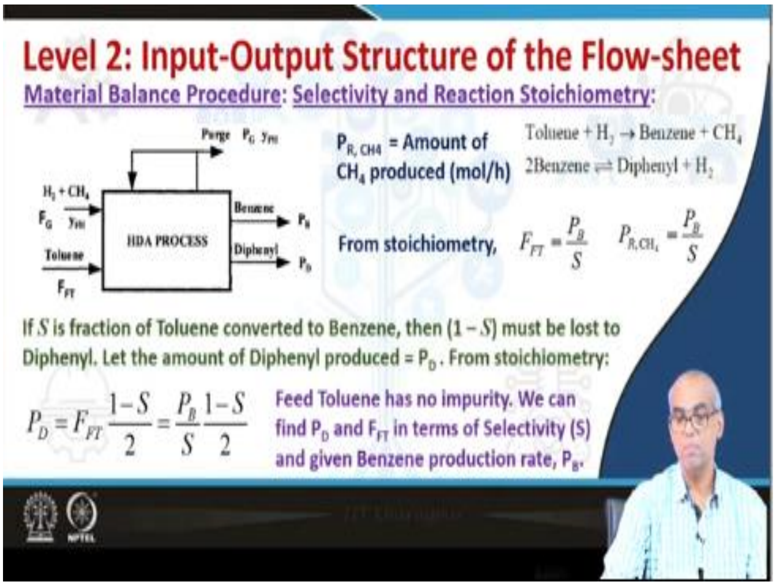
Using stoichiometry and material balance, we can find all input and output flows in terms of design variables: S and either F_E or y_{PH}.

So now, let us develop the material balance. First look at selectivity and reactions stoichiometry. We are taking the hydrodealkylation of toluene as example. So look at the flow sheet. The flows are indicated and these are all in terms of moles per hour. Selectivity is the fraction of toluene converted in the reactor that corresponds to the benzene flow at reactor outlet.

So, according to this selectivity definition, it will be the amount of benzene divided by 12. If FE is excess hydrogen fed and yPH is the purged composition of the reactant. PB is the desired benzene production moles per hour, we assume all benzene is being recovered. FFT is the fresh pure toluene fed to the process, again moles per hour, we assume that all the toluene is getting converted.

And PR, CH4 is the amount of methane produced in the process in moles per hour. Note that in the HDA process, methane is produced as well as enters the process as impurity. Using stoichiometry and material balance, we can find all input and output flows in terms of design variables, selectivity and either excess hydrogen FE or the hydrogen concentration or the mole fraction of hydrogen in the purge steam which is yPH.

(Refer Slide Time: 33:36)



Level 2: Input-Output Structure of the Flow-sheet

Material Balance Procedure: Selectivity and Reaction Stoichiometry:

$P_{R,CH4}$ = Amount of CH_4 produced (mol/h)

$$\text{Toluene} + H_2 \rightarrow \text{Benzene} + CH_4$$
$$2\text{Benzene} \rightleftharpoons \text{Diphenyl} + H_2$$

From stoichiometry, $F_{FT} = \frac{P_B}{S}$ $\quad P_{R,CH_4} = \frac{P_B}{S}$

If S is fraction of Toluene converted to Benzene, then $(1 - S)$ must be lost to Diphenyl. Let the amount of Diphenyl produced = P_D. From stoichiometry:

$$P_D = F_{FT}\frac{1-S}{2} = \frac{P_B}{S}\frac{1-S}{2}$$

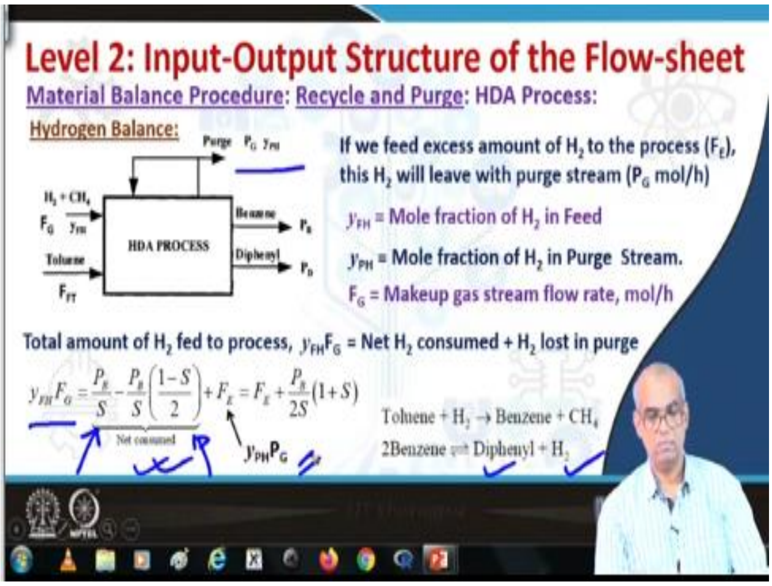
Feed Toluene has no impurity. We can find P_D and F_{FT} in terms of Selectivity (S) and given Benzene production rate, P_B.

So let us see how you do that? Now, look at the reaction. So one mole of toluene reacts with one mole of hydrogen to produce one mole of benzene and one mole of methane. So for stoichiometry we can say that FFT will be equal to PB by S. Note that the selectivity is equal to benzene by toluene. So the benzene is PB moles for hour, so FFT will be PB by S moles per hour.

Also, in the process the amount of methane produced is same as the amount of benzene, so 1 mole of benzene and 1 mole of methane is produced. So, the amount of methane produced is also PB by S moles per hour. If S is the fraction of toluene converted to benzene then 1-S must be lost to diphenyl. Let the amount of diphenyl produce is PD, so PD moles per hour. So from stoichiometry, we can say that pd will be equal to FFT into 1-s by 2.

Why 1-S by 2? Because 2 moles of benzene gives 1 mole of diphenyl. So PD equal to FFT into 1-S by 2 and we already seen that FFT equal to PB by S, so I get PB by S into 1-S by 2. So feed toluene has no impurity. We can find the diphenyl flow rate PD and the toluene flow that goes to the process FFT in terms of selectivity and given benzene production rate.

(Refer Slide Time: 36:05)



Level 2: Input-Output Structure of the Flow-sheet

Material Balance Procedure: Recycle and Purge: HDA Process:

Hydrogen Balance:

If we feed excess amount of H_2 to the process (F_E), this H_2 will leave with purge stream (P_G mol/h)

y_{FH} = Mole fraction of H_2 in Feed

y_{PH} = Mole fraction of H_2 in Purge Stream.

F_G = Makeup gas stream flow rate, mol/h

Total amount of H_2 fed to process, $y_{FH}F_G$ = Net H_2 consumed + H_2 lost in purge

$$y_{FH}F_G = \underbrace{\frac{P_B}{S} - \frac{P_B}{S}\left(\frac{1-S}{2}\right)}_{\text{Net consumed}} + F_E = F_E + \frac{P_B}{2S}(1+S)$$

$y_{PH}P_G$

$$\text{Toluene} + H_2 \rightarrow \text{Benzene} + CH_4$$

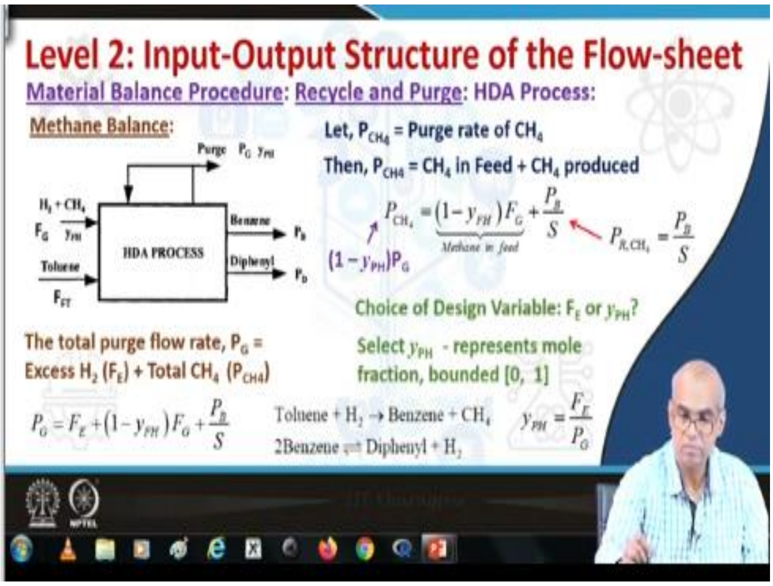
$$2\text{Benzene} \rightleftharpoons \text{Diphenyl} + H_2$$

Now let us look at the recycle and purge stream of the HDA process. We first do hydrogen balance. If we feed excess amount of hydrogen to the process, this hydrogen has to live with the purge stream. The flow rate of the purge steam is PG and the mole fraction of hydrogen in the feed is yFH and mole fraction of hydrogen in the per stem is yPH. FG is the makeup gas stream flow rate.

So this is. Now total amount of hydrogen fed to the process will be FG times yFH. So this has to be equal to the net hydrogen consume + hydrogen lost in the purge. Now the net hydrogen consume will have two parts - one is hydrogen is fed to the process is a reactant as well as hydrogen is produced during the process. So, we can write yFH into FG, which is the total amount of hydrogen fed to the process is equal to the net consumed PB by S.

This is required in the process minus this is produced the same amount of diphenyl. See the amount of diphenyl produce and amount of hydrogen produced is same and we have seen in the previous slide that amount of diphenyl produce is PB by S into 1-S by 2 and if FE is the excess hydrogen fed. So excess hydrogen fed has to live with the purge, so it has to be equal to yPH into PG. So this is the hydrogen balance.

(Refer Slide Time: 38:29)



Level 2: Input-Output Structure of the Flow-sheet

Material Balance Procedure: Recycle and Purge: HDA Process:

Methane Balance:

Let, P_{CH_4} = Purge rate of CH_4

Then, P_{CH4} = CH_4 in Feed + CH_4 produced

$$P_{CH_4} = \underbrace{(1-y_{FH})F_G}_{Methane\ in\ feed} + \frac{P_B}{S} \qquad P_{R,CH_4} = \frac{P_B}{S}$$

$(1 - y_{PH})P_G$

The total purge flow rate, P_G = Excess H_2 (F_E) + Total CH_4 (P_{CH4})

$$P_G = F_E + (1-y_{PH})F_G + \frac{P_B}{S}$$

Choice of Design Variable: F_E or y_{PH}?

Select y_{PH} - represents mole fraction, bounded [0, 1]

$$\text{Toluene} + H_2 \rightarrow \text{Benzene} + CH_4$$
$$2\text{Benzene} \rightleftharpoons \text{Diphenyl} + H_2$$

$$y_{PH} = \frac{F_E}{P_G}$$

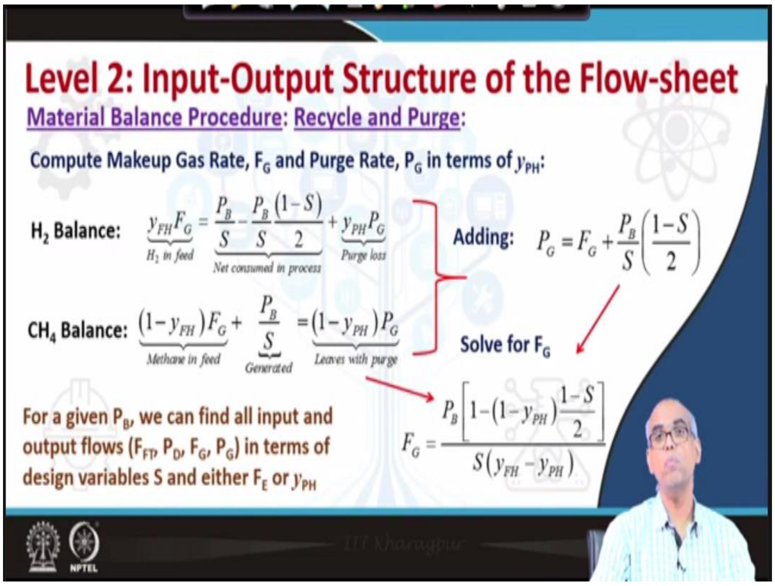
Similarly, you can also write the methane balance. Let PCH4 equal to purge rate of the methane. So this is the flow of methane living the process with the purge stream. So purge rate of methane which is CH, which is PCH4 will be equal to methane in the feed + methane produced. What is methane in the feed? The mole fraction of a hydrogen in the feed is yFH. So Y - FH must be the mole fraction of methane in the feed multiplied by the FG.

So will be methane in the feed and plus the methane produced in the process which is same as amount of benzene produced which is PB by S. Note that this methane flow in the purge will be the mole fraction of the methane in the purge stream multiplied by PG. If yPH is the mole fraction of hydrogen in the purge stream Y - PH will be the mole fraction of methane in the purge stream.

So the total purge flow rate PG will be equal to excess hydrogen FE + total methanePCH4. So now we have expression for both. So FE the excess hydrogen + the total methane in the purge stream. So this gives me the methane balance. Now what should be my choice of design variables? Excess hydrogen FE or hydrogen mole fraction in the purge yPH? We should select yPH because it represents a mole fraction.

So thereby it is bounded between 0 and 1, lower bound is 0, upper bound is 1. So FE the excess hydrogen will be equal to yPH into PG, so yPH equal to FE by PG.

(Refer Slide Time: 41:07)



Level 2: Input-Output Structure of the Flow-sheet

Material Balance Procedure: Recycle and Purge:

Compute Makeup Gas Rate, F_G and Purge Rate, P_G in terms of y_{PH}:

H_2 Balance: $$\underbrace{y_{FH}F_G}_{H_2 \text{ in feed}} = \underbrace{\frac{P_B}{S} - \frac{P_B}{S}\frac{(1-S)}{2}}_{\text{Net consumed in process}} + \underbrace{y_{PH}P_G}_{\text{Purge loss}}$$

CH_4 Balance: $$\underbrace{(1-y_{FH})F_G}_{\text{Methane in feed}} + \underbrace{\frac{P_B}{S}}_{\text{Generated}} = \underbrace{(1-y_{PH})P_G}_{\text{Leaves with purge}}$$

Adding: $$P_G = F_G + \frac{P_B}{S}\left(\frac{1-S}{2}\right)$$

Solve for F_G

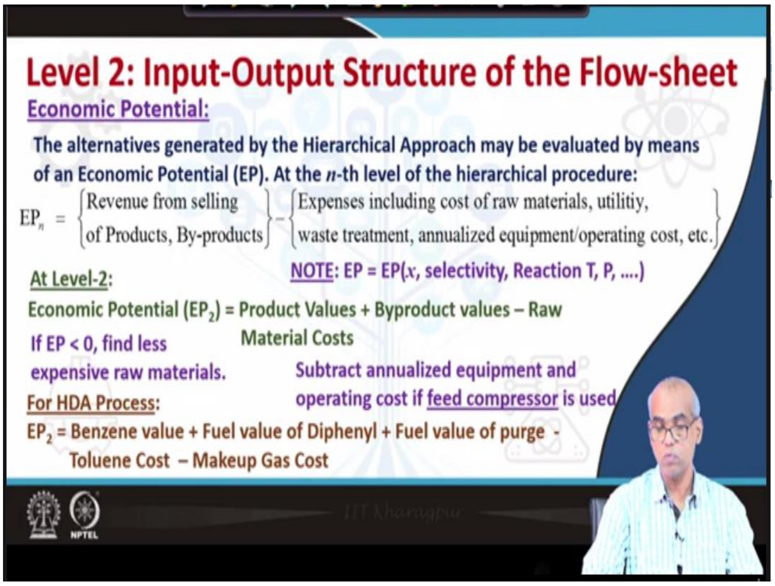
$$F_G = \frac{P_B\left[1-(1-y_{PH})\frac{1-S}{2}\right]}{S(y_{FH}-y_{PH})}$$

For a given P_B, we can find all input and output flows (F_{FT}, P_D, F_G, P_G) in terms of design variables S and either F_E or y_{PH}

Now, you can compute this makeup gas rate FG and the purge rate PG in terms of the mole fraction of hydrogen in the purge step, which is the design variable. To do that, you write the hydrogen balance that you have written in the previous slide. Also write the methane balance, just add up these 2. So we will get an expression for the purge rate PG. And now if you combine the methane balance and the expression for the purge rate, you can solve for FG which is the makeup gas rate in terms of selectivity S and hydrogen mole fraction in the purge step, which is, which are these 2 are design variables.

Note that PB is the benzene production rate, which is the desired rate, so that will be given. Also, yFH is the feed concentration of the hydrogen, mole fraction of hydrogen in the feed. So, we are able to express FG in terms of design variables S and mole fraction of hydrogen in the purge step. So, for a given design rate, for a given design flow rate for benzene, we can find all input and output flows; FFT, PD, FG, PG in terms of design variables selectivity and either hydrogen FE or mole fraction of hydrogen in the purge yPH.

(Refer Slide Time: 42:37)



Level 2: Input-Output Structure of the Flow-sheet

Economic Potential:

The alternatives generated by the Hierarchical Approach may be evaluated by means of an Economic Potential (EP). At the *n*-th level of the hierarchical procedure:

$$EP_n = \begin{Bmatrix} \text{Revenue from selling} \\ \text{of Products, By-products} \end{Bmatrix} - \begin{Bmatrix} \text{Expenses including cost of raw materials, utilitiy,} \\ \text{waste treatment, annualized equipment/operating cost, etc.} \end{Bmatrix}$$

NOTE: EP = EP(x, selectivity, Reaction T, P, ...)

At Level-2:

Economic Potential (EP_2) = Product Values + Byproduct values – Raw Material Costs

If EP < 0, find less expensive raw materials.

Subtract annualized equipment and operating cost if feed compressor is used

For HDA Process:

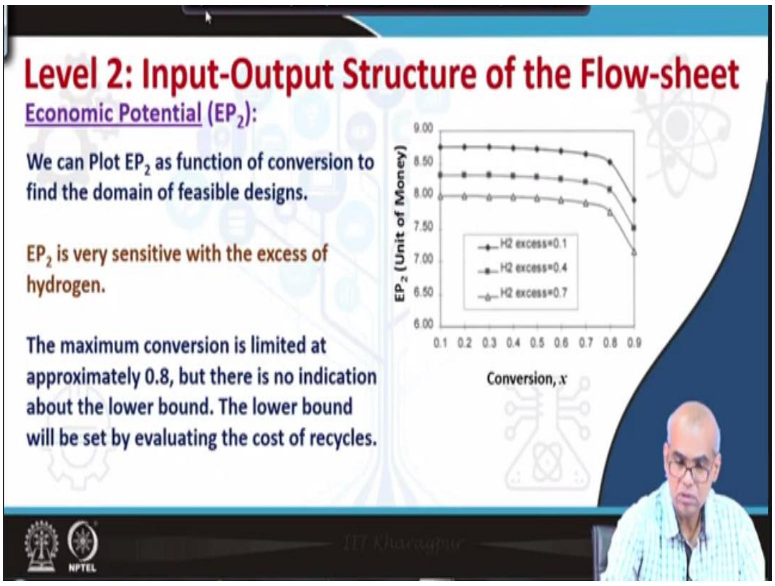
EP_2 = Benzene value + Fuel value of Diphenyl + Fuel value of purge - Toluene Cost – Makeup Gas Cost

Now economic potential, the alternatives generated by the hierarchical approach may be evaluated by means of an economic potential EP. At nth level of the hierarchical procedure: we can write EPn equal to revenue from selling of products, by products minus expenses including cost of raw materials, utility, waste treatment, annualized equipment, operating cost etcetera.

Note that this economic potential is a function of conversion, selectivity, reaction temperature, pressure etcetera, that means design variables. So basically economic potential is the revenue from selling products and by products minus all the expenses of raw materials utility, waste treatment, annualized equipment cost, annualized operating cost etcetera. At level 2, the economic potential EP2 will be product values + byproduct values- raw material cost.

So at this stage if economic potential is less than 0, it means that raw material is more expensive than the product. So we have to find less expensive raw materials. Also note that if you are using feed compressor, we have to subtract annualized equipment and the operating cost from the expression of EP2. For the hydro de-alkylation process EP2 will be benzene value + fuel value of diphenyl + fuel value of purge - toluene cost minus makeup gas cost.

(Refer Slide Time: 44:22)



Level 2: Input-Output Structure of the Flow-sheet

Economic Potential (EP_2):

We can Plot EP_2 as function of conversion to find the domain of feasible designs.

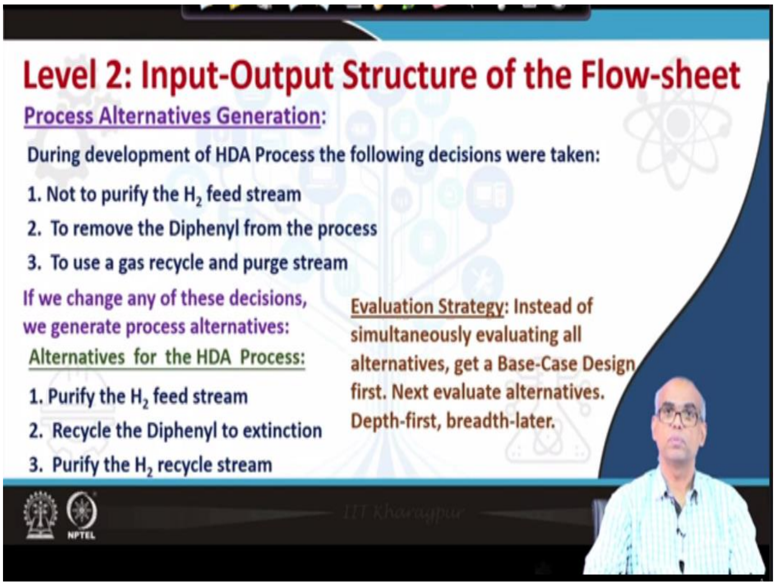
EP_2 is very sensitive with the excess of hydrogen.

The maximum conversion is limited at approximately 0.8, but there is no indication about the lower bound. The lower bound will be set by evaluating the cost of recycles.

We can plot the economic potential level 2 EP2 as a function of conversion to find the domain of feasible design. So you have plotted the EP2 versus conversion for various values of excess hydrogen 0.1, 0.4 and 0.7. What you see that EP2 is very sensitive with excess of hydrogen. The maximum conversion is limited at approximately 0.8. However, there is no indication about the lower bound.

You see that in this entire zone it is quite flat, it does not change much, the economic potential does not change much with conversion. So the lower bound of the conversion is not apparent. No indication of the lower bound here. The lower bound will be set when you evaluate the cost of recycles at level 3.

(Refer Slide Time: 45:26)



Level 2: Input-Output Structure of the Flow-sheet

Process Alternatives Generation:

During development of HDA Process the following decisions were taken:

1. Not to purify the H_2 feed stream
2. To remove the Diphenyl from the process
3. To use a gas recycle and purge stream

If we change any of these decisions, we generate process alternatives:

Alternatives for the HDA Process:

1. Purify the H_2 feed stream
2. Recycle the Diphenyl to extinction
3. Purify the H_2 recycle stream

Evaluation Strategy: Instead of simultaneously evaluating all alternatives, get a Base-Case Design first. Next evaluate alternatives. Depth-first, breadth-later.

We briefly discussed that process alternatives can be generated when you take an opposite decision. During development of HDA process the following decisions were taken not to purify the hydrogen feed stream, to remove the diphenyl from the process to use a gas recycle and purge stream. Now if we change any of this decisions, we will generate a process alternative.

For example purify the hydrogen feed stream, recycle the diphenyl to extinction, purify the hydrogen recycle stream. Now, we will follow the evaluation strategy which goes as follows. Instead of simultaneously evaluating all alternatives, we will first try to get a base case design and next we will evaluate alternatives. So we will first search depth and they will search at along the breadth.

So depth first, breadth later we will adopt. We will first try to guess, we will first try to get a base case design and then evaluate the alternatives. With this we stop our discussion on lecture 28.