



# **CHE 425**

# **Engineering Economics and Design Principles**



# **CHAPTER 2**

## **The Structure and Synthesis of Process Flow Diagrams**



## PURPOSE OF CHAPTER 2

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- ❑ To show that the evolution of every process follows a similar path.
  
- ❑ To provide a framework to generate alternative PFDs for a given process.

### Factors determining choice of alternative route

- Cost of raw materials
- Value of by-products
- Complexity of the synthesis
- Environmental impact of waste materials



# Hierarchical Approach to Conceptual Design

- Five step process to tackle a conceptual process design
  - ① Batch vs. continuous
  - ② Identify the Input-output structure
  - ③ Identify and define recycle structure of process
  - ④ Identify and design general structure of separation system
  - ⑤ Identify and design heat-exchanger network or process energy recovery system

**Designing New Process:** [1-2-3-4-5]

**Analyzing Existing Process:** [5-4-3-2-1]



## Batch vs. Continuous

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A batch process is one in which a finite quantity (batch) of product is made during a period of a few hours or days.

Continuous process is one in which feed is sent continuously to a series of equipment, with each piece usually performing a single unit operation.



## Batch vs. Continuous (cont)

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### Variables to Consider:

#### □ Size

- Batch < 500 tonne/yr ~ 1.5 tonne/day  
(< 2 m<sup>3</sup> of liquid or solid per day)
- Continuous > 5000 tonne/yr

#### □ Flexibility

- Batch can handle many different feeds and products – more flexible
- Continuous is better for smaller product slate and fewer feeds



## Batch vs. Continuous (cont)

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- ❑ Continuous will allow you to benefit from the “Economy of Scale” but you will pay the price for less flexibility
  
- ❑ Other Issues
  - Accountability and quality control – Government should require batch accountability
  - Safety – batch is more accident prone
  - Scheduling of equipment – may be most important issue
  - Seasonal demands – ex. Antifreeze, food products

## Input – Output Structure (Process Concept Diagram)

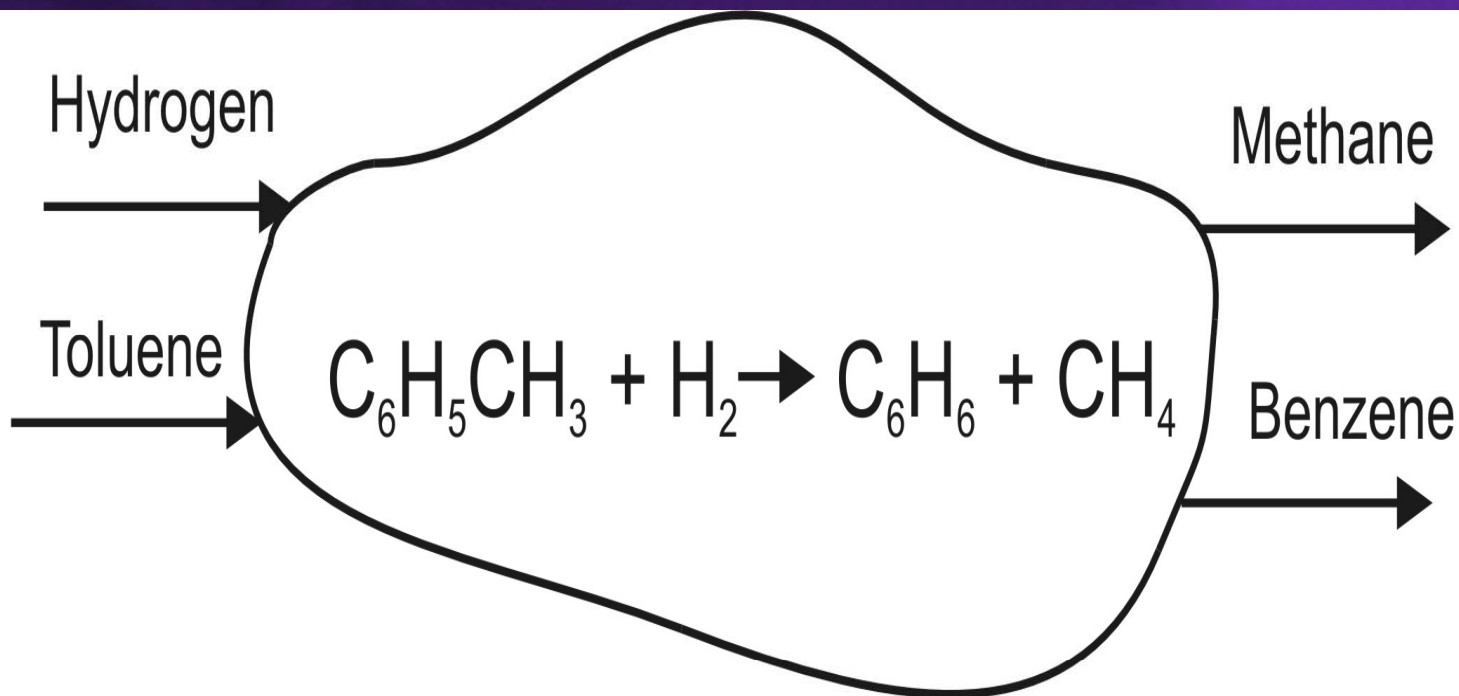


Figure 2.1: Input-Output Structure of Process Concept Diagram for the Toluene Hydrodealkylation Process



# Input – Output Structure of The PFD

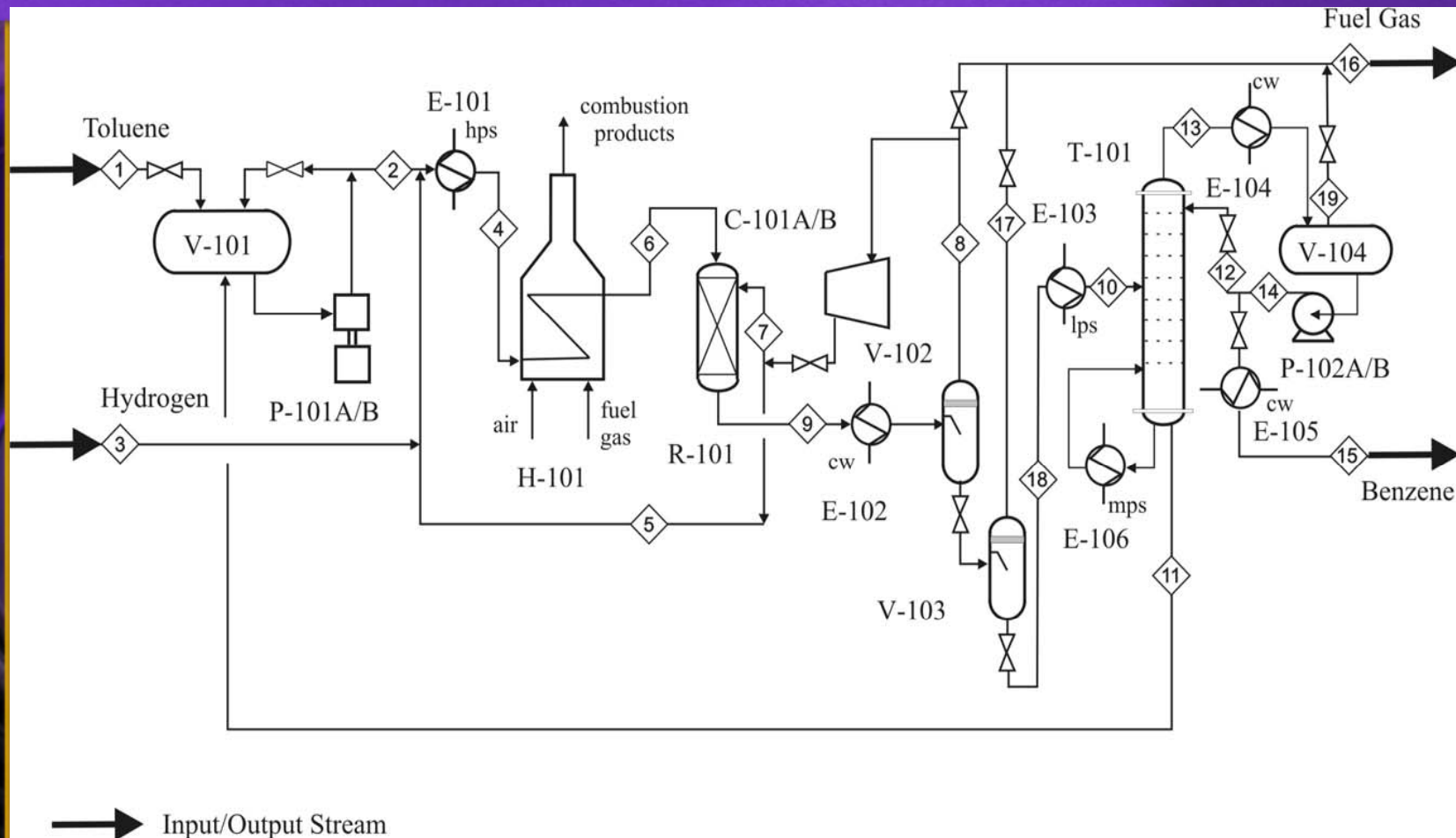


Figure 2.2 Input Output Streams on Toluene Hydrodealkylation PFD



## Input – Output Structure of The PFD (cont)

Important factors to consider in analyzing the overall input output structure of a PFD

- ❑ Chemicals not consumed are either required to operate a piece of equipment or are inert material.
- ❑ Any chemical leaving a process must have either entered in one of the feed streams or have been produced by a chemical reaction within the process.
- ❑ Utility streams are treated differently from process streams. Utility streams rarely directly contact the process streams. They usually provide or remove thermal energy or work.

# Input – Output (Utility Streams)

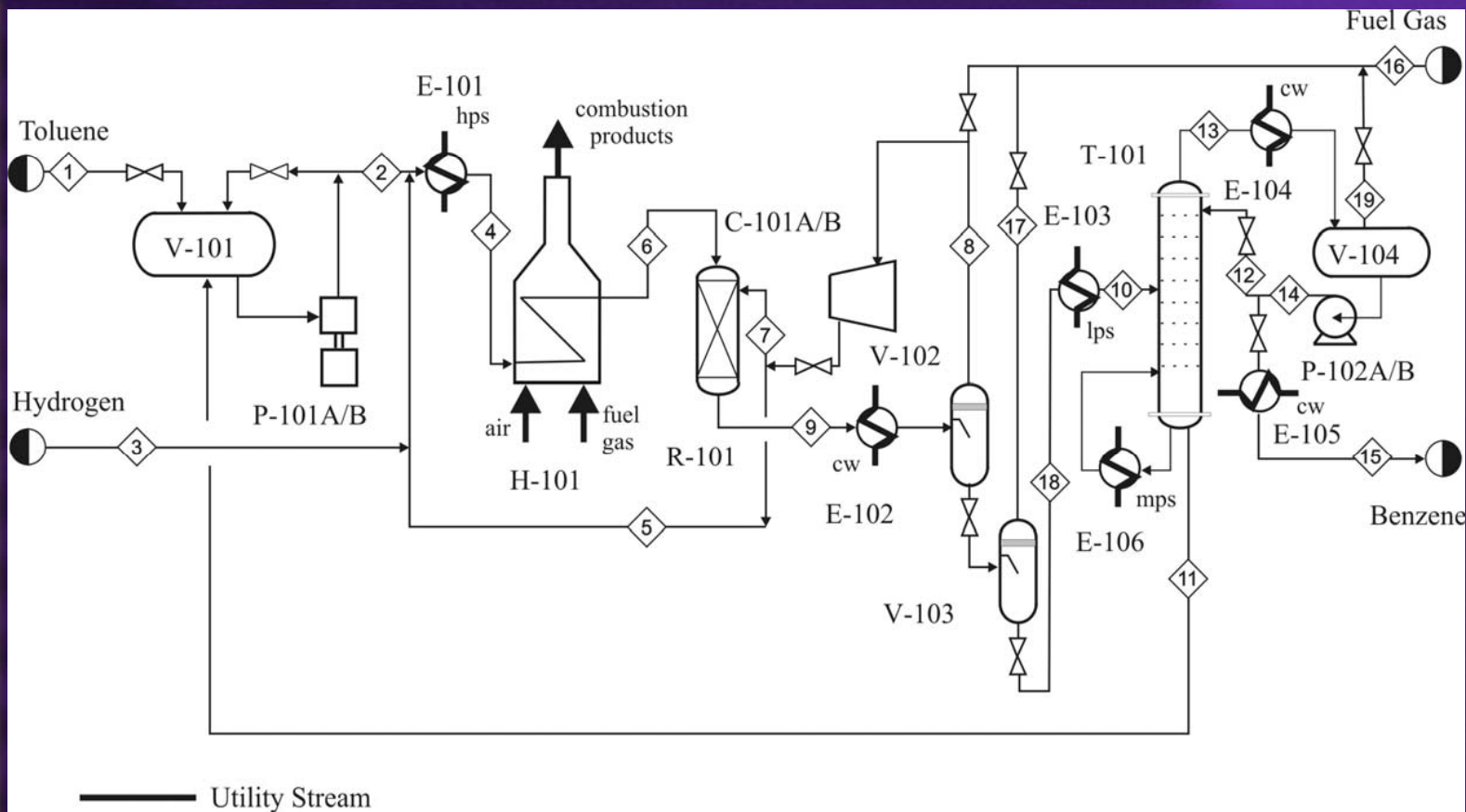
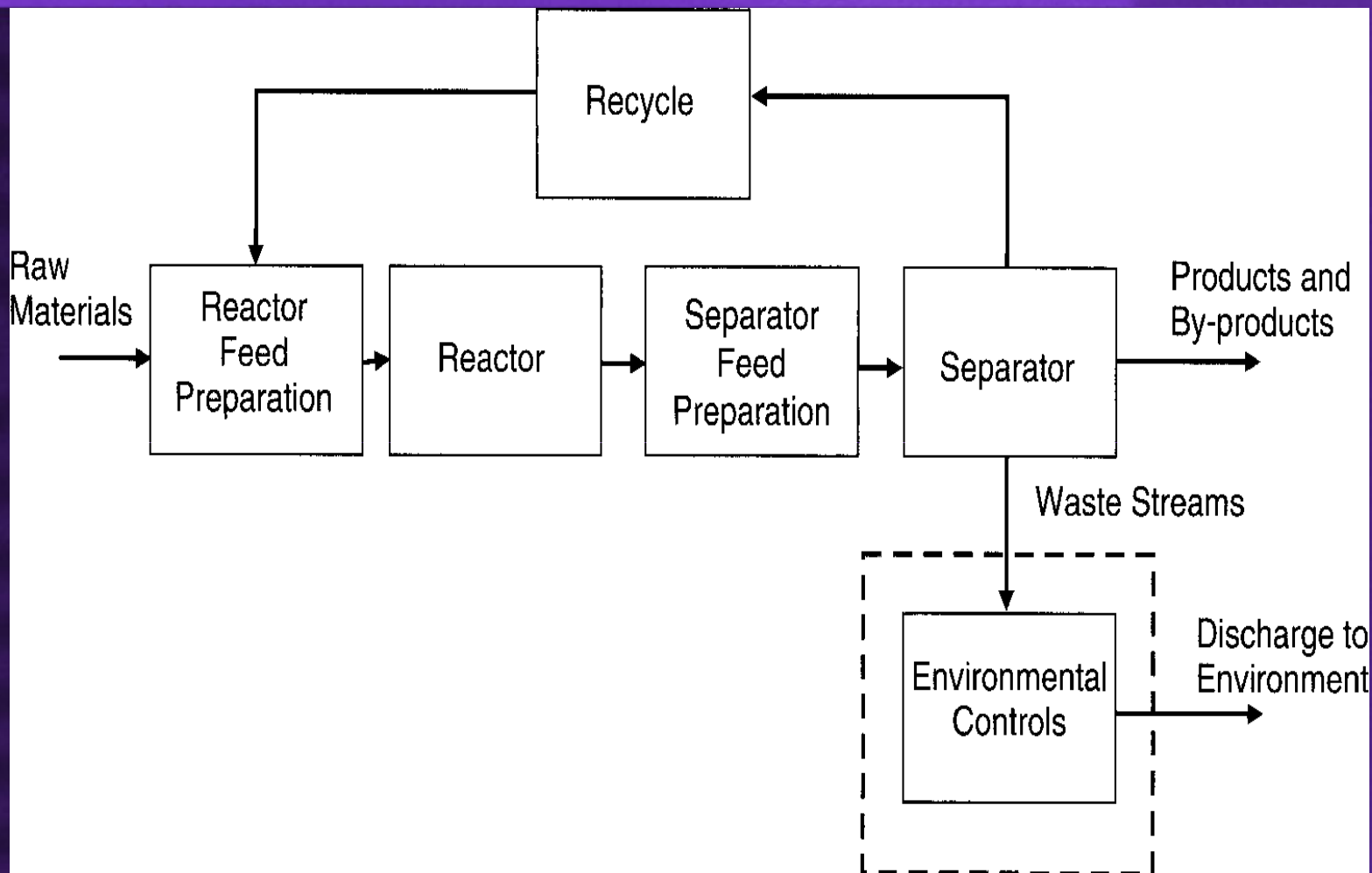


Figure 2.3: Identification of Utility Streams on the Toluene HDA PFD

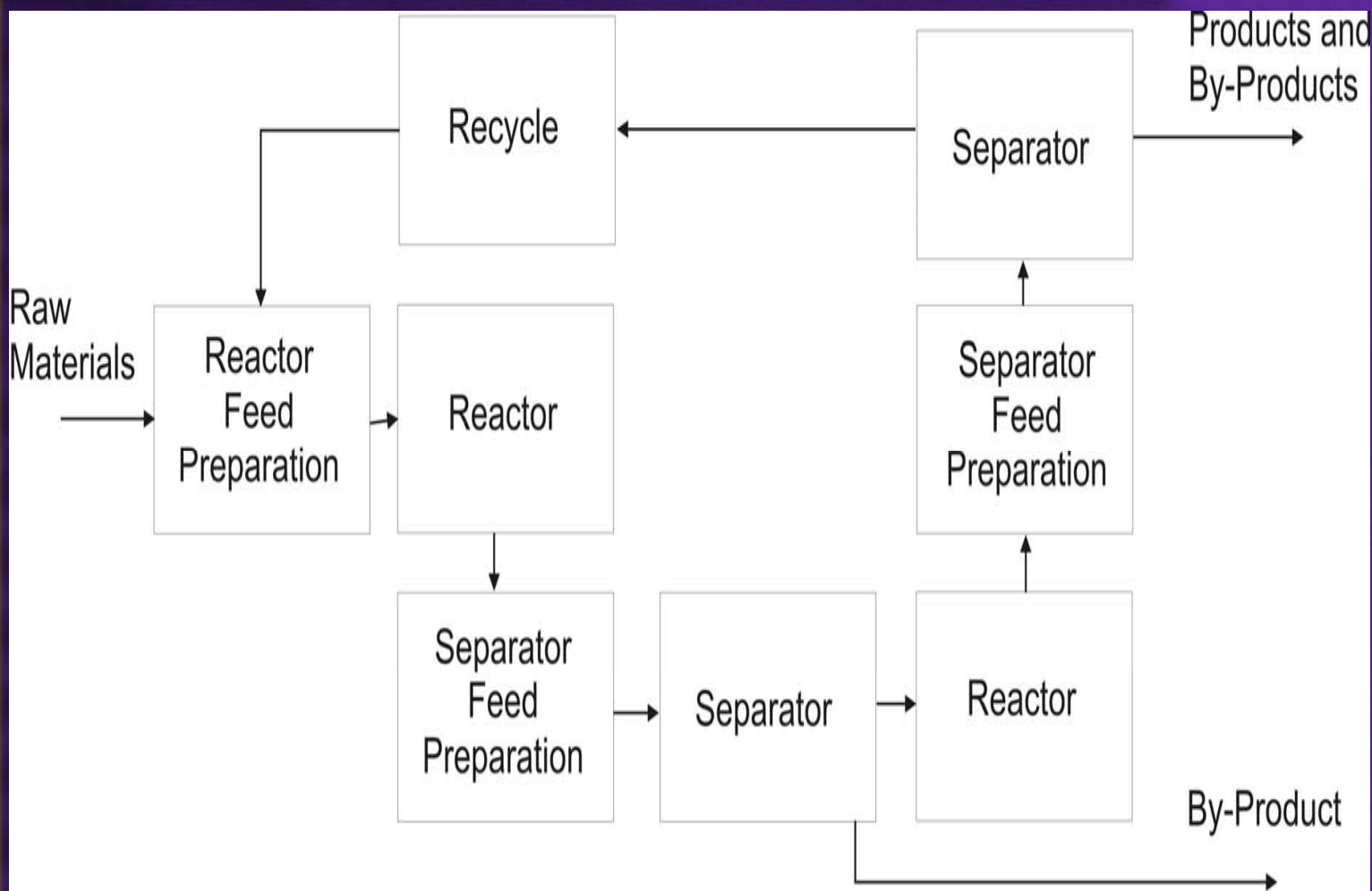


## Generic Structure of PFD





## Generic Structure of PFD (cont)





## Other Considerations for Input – Output Structure

### □ Feed Purity and Trace Components

- Small Quantities and “Inerts” – Do Not Separate

E.g.  $H_2$  in feed to THDA process contains  $CH_4$

$CH_4$  does not react

so, do not remove



## Other Considerations for Input – Output Structure

- If Separation of Impurities is Difficult – Do Not Separate
  - Azeotrope – (water and ethanol)
  - Gases – (requires high P and low T)
  
- If impurities foul or poison catalyst then separate
  - Sulfur – Group VIII Metals such as iron, nickel, and platinum
  - A guard bed of activated carbon (or Zinc Oxide) is placed upstream of the reactor for protection



## Other Considerations for Input – Output Structure (cont)

- If impurity reacts to form difficult-to-separate material or hazardous product then separate

- Phosgene Example



- Impurity in large quantities then purify – why?

- A notable exception is air





## ADD MATERIAL TO FEED

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- ❑ Stabilize Products
- ❑ Enable Separation/Minimize Side Reactions
  - Anti-Oxidants and Scavengers
  - Solvents and Catalysts



## INERT FEED

### □ Control Exothermic Reactions

- Steam for oxidation reactions

### □ Control Equilibrium

- Adding inerts shifts equilibrium to the right

Example: styrene reaction





## Information Obtained From Input-Output Diagram

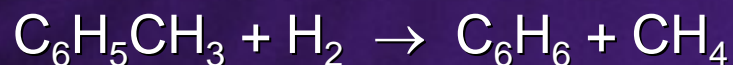
- ❑ Basic economic analysis on profit margin.
- ❑ What chemical components must enter with the feed and leave as products.
- ❑ All the reactions, both desired and undesired, that take place.

## Profit Margin (PM)

$$\text{PM} = \text{Value of products} - \text{Cost of raw materials}$$

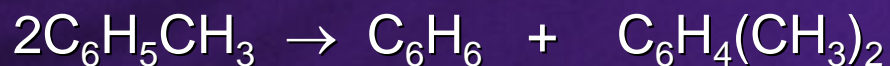
- If  $\text{PM} < 0$ , then don't bother to pursue this process but start looking for an alternate route

### Toluene HDA vs. Toluene Disproportionation



Toluene

benzene



Toluene

benzene

xylene

Toluene used  
more  
efficiently



## Profit Margin (PM)

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- ❑ Some processes are more sensitive to product and feed prices than others.
- ❑ Average cost data over a period of several years should be used in evaluating PM.
- ❑ Cost of raw materials play a role in deciding which chemical path to choose to produce a given product.



## Example 2.1

Evaluate the profit margin for the HDA process.

From Tables 6.3 and 6.4 (Year 2001)

Benzene = \$ 0.349/kg

Toluene = \$ 0.322/kg

Natural gas (methane and ethane, MW =18) = \$ 6.00/GJ = \$  
6.7/1000 std. ft' = \$ 0.293/kg

Hydrogen = \$ 0.721 /kg

Using 1 kmol of toluene feed as a basis



## Example 2.1 (cont.)

### Cost of Raw Materials

92 kg of Toluene = (92 kg)(\$ 0.322/kg) = \$ 29.62

2 kg of Hydrogen = (2 kg)(\$ 0.721/kg) = \$ 1.44

### Value of Products

78 kg of Benzene = (78 kg)(\$ 0.349/kg) = \$ 27.22

16 kg of Methane = (16 kg)(\$ 0.293/kg) = \$ 4.69

### Profit Margin

Profit Margin = (27.22 + 4.69) - (29.62 + 1.44) = \$ 0.85  
or \$ 0.0092/kg toluene

### Conclusion

Further investigation of this process is probably marginally warranted



## Example 2.1 (cont.)

Consider 1993 prices

### Cost of Raw Materials

92 kg of Toluene = (92 kg)(\$ 0.24/kg) = \$ 22.08

2 kg of Hydrogen = (2 kg)(\$ 0.312/kg) = \$ 0.624

### Value of Products

78 kg of Benzene = (78 kg)(\$ 0.27 /kg) = \$ 21.06

16 kg of Methane = (16 kg)(\$ 0.126/kg) = \$ 2.016

### Profit Margin

Profit Margin = (21.06 + 2.016) - (22.08 + 0.644) = \$ 0.372 or  
\$ 0.0040/kg of toluene

### Conclusion

This is significantly lower than the 2001 margin. Production of benzene via the HDA of toluene would probably not be economical





## Example 2.2

Evaluate the profit margin for the toluene disproportionation process.

From Tables 6.4 (Year 2001)

Mixed Xylenes = 0.323 \$/kg

Using 2 kmols of toluene feed as a basis

### Cost of Raw Materials

184 kg of Toluene = (184 kg)(\$0.322/kg) = \$ 59.25

### Value of Products

78 kg of Benzene = (78 kg)(\$0.349/kg) = \$ 27.22

106 kg of xylene = (106 kg)(\$0.323/kg) = \$ 34.24



## Example 2.2

### Margin

$$\text{Profit Margin} = 34.24 + 27.22 - 59.25 = \$ 2.21$$

or \$ 0.012/kg toluene feed

Currently this process is significantly better than the hydrodealkylation process.

### Year 1993

$$\text{Mixed Xylenes} = 0.323 \text{ \$/kg}$$

$$\text{Margin} = (78)(0.27) + (106)(0.25) - (184)(0.24) = \$ 3.4$$

or \$ 0.0185/kg of toluene

We conclude that the margin for the disproportionation process is significantly less sensitive to product and feed prices than is the hydrodealkylation process.



## Recycle Structure of the Process

- ❑ Raw materials are very valuable.
- ❑ They make up 25 to 75% of total operating costs.
- ❑ Separation and recycling of unused reactants is very important.
- ❑ Exception is when raw materials are very cheap
- ❑ Extent of recycling of unused reactants depends on ease of separation.



## Efficiency of Raw Material Usage

$$\text{Single-pass Conversion} = \frac{\text{reactant consumed in reaction}}{\text{reactant fed to the reactor}}$$

$$\text{Overall Conversion} = \frac{\text{reactant consumed in process}}{\text{reactant fed to the process}}$$

$$\text{Yield} = \frac{\text{moles of reactant to produce desired product}}{\text{moles of limiting reactant reacted}}$$



## Efficiency of Raw Material Usage

- ❑ **Single-pass Conversion (SPC)**
  - SPC tells us how much of the reactant that enters the reactor is reacted.
  - The lower the SPC the greater the amount of recycle.
  - SPC affects equipment size and utility flows.
  - Raw material costs are not changed significantly by SPC.
  - SPC of hydrogen in HDA process is kept low to reduce coking of the catalyst.



## Efficiency of Raw Material Usage

- ❑ Overall Conversion (OC)
  - OC tells us tells us what fraction of the reactant in the feed to the process is converted to product.
  - High OC (e.g 99.3 %) is typical for chemical processes.
  - High OC shows that unreacted raw materials are not being lost from the process.
  - Low OC of hydrogen in the HDA process indicates poor raw material usage.



## Efficiency of Raw Material Usage

### □ Yield

- Yield tells us what fraction of the limiting reactant ends up in our desired product.
- Competing or side reactions may reduce the yield.
- Yields for hydrodealkylation process are generally high (e.g 98-99 % for DETOL, Lummus).



## 3 Basic Recycle Structures

- ❑ Separate and purify un-reacted feed from products and then recycle, e.g., Toluene
- ❑ Recycle feed and products together and use a purge stream, e.g., hydrogen with purge as fuel gas
- ❑ Recycle feed and products together but do not use a purge stream - must come to Equilibrium







## Separate and purify

Ease of separation depends on:

- ❑ What conditions (T and P) are necessary to operate the process?
- ❑ Are the differences in physical and chemical properties for the species to be separated large or small?



## Example 2.4

What process should be used in the separation of toluene and benzene?

### Distillation

Normal boiling point of benzene = 79.8 °C

Normal boiling point of toluene = 110 °C

Separation should be easy using distillation, and neither excessive temperatures nor pressures will be needed. This is a viable operation for this separation of benzene and toluene in the HDA process.

## Recycle Structure in PFD

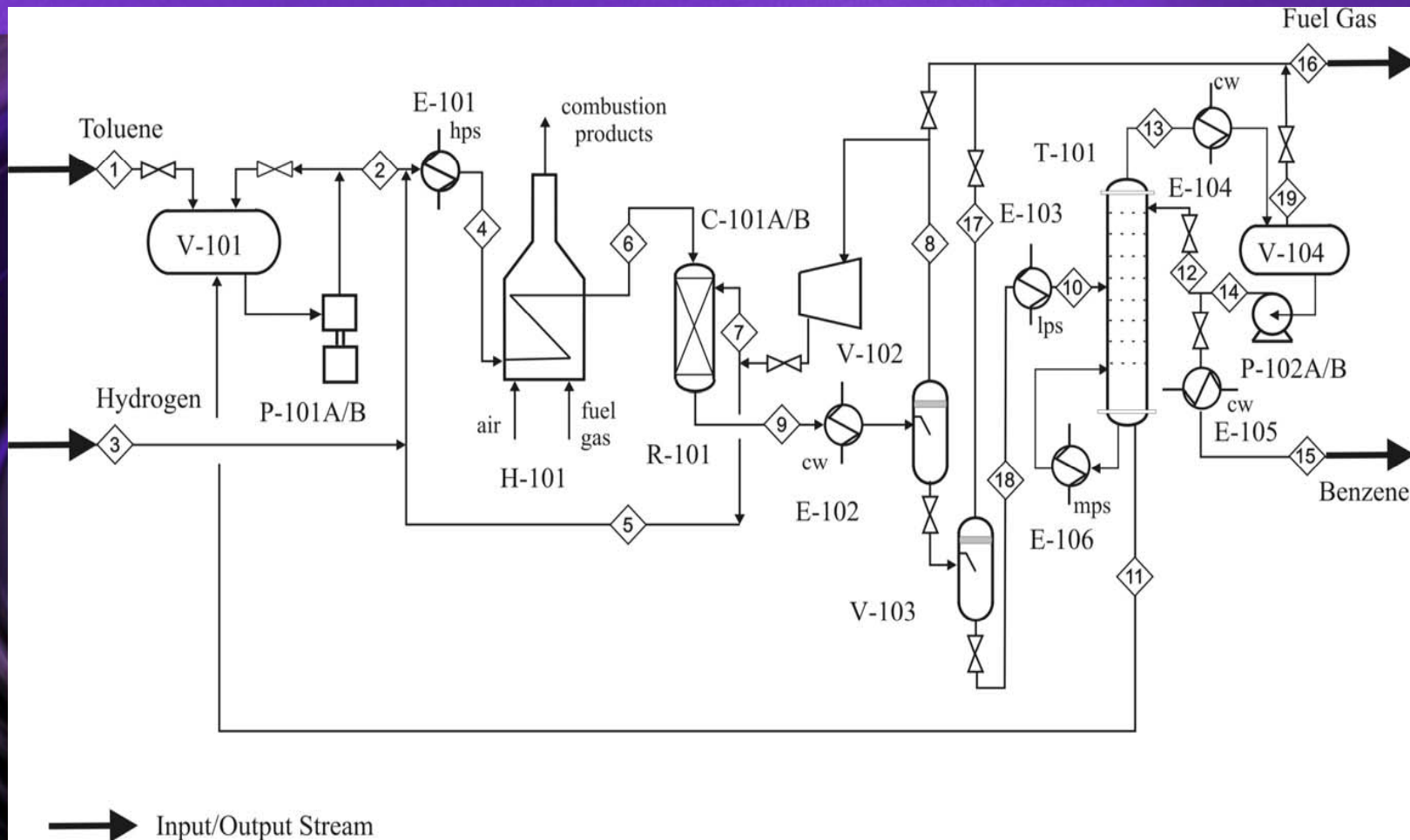
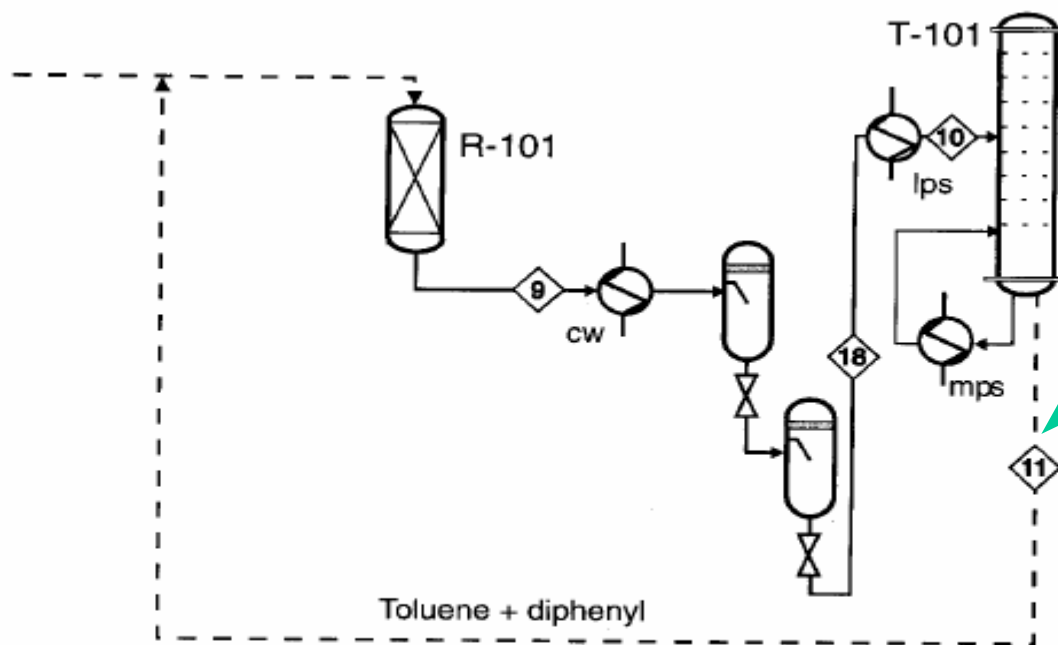


Figure 2.2 Input Output Streams on Toluene Hydrodealkylation PFD

## Example 2.5

Consider the following two process alternatives for the toluene HDA process when the side reaction of benzene to form diphenyl occurs.

### Alternative A



**Figure E2.5(a)** PFD for Alternative A in Example 2.5—Recycle of Diphenyl without Separation (E-101 and H-101 Not Shown)

## Example 2.5 (cont.)

### Alternative B

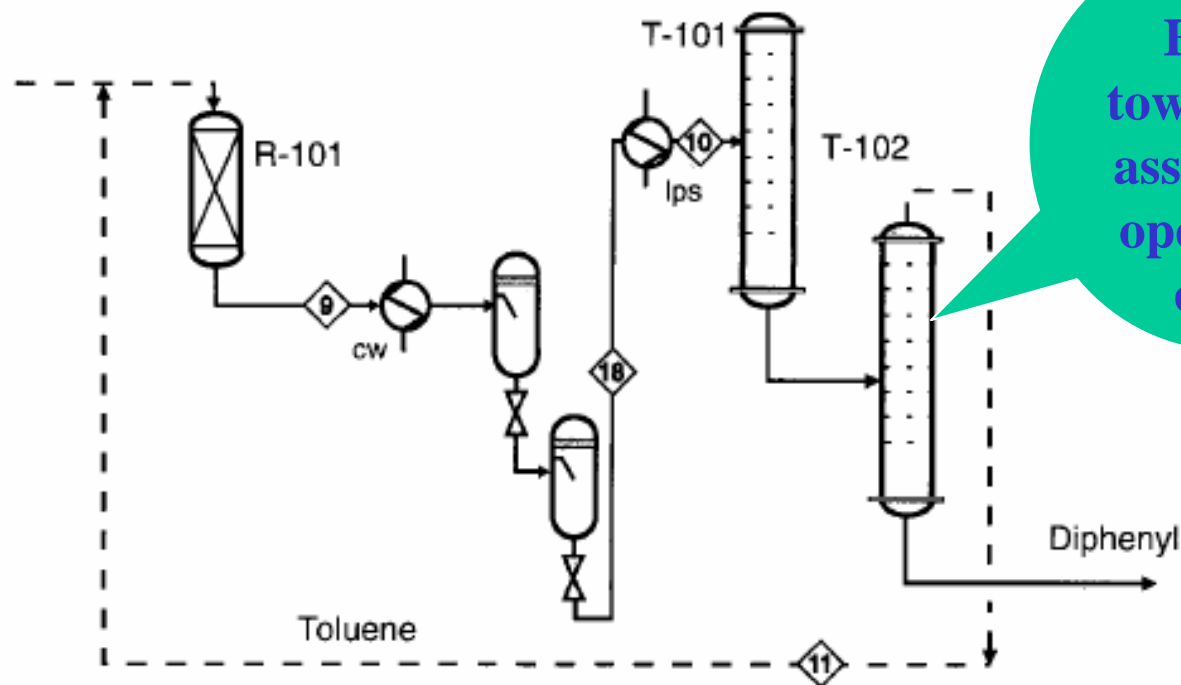


Figure E2.5(b) PFD for Alternative B in Example 2.5—Recycle of Diphenyl with Separation (E-101 and H-101 Not Shown)



## Example 2.5 (cont.)

Clearly for Alternative B, we require an additional separator, shown here as a second distillation column T-102, along with the associated equipment (not shown) and extra utilities to carry out the separation. For Alternative A, we avoid the cost of additional equipment, but the recycle stream (Stream 11) will be larger (because it now contains toluene and Diphenyl), and the utilities and equipment through which this stream pass (H-101, E-101, R-101, E-102, V-102, V-103, T-101, E-106) will all be greater. Which is the better (economically preferable) alternative?

The answer depends on the value of  $K_{eq}$

## Example 2.5 (cont.)

$$\ln K_{eq} = 1.788 - \frac{4135.2}{T(K)}$$

Assume that reaction has reached equilibrium  
Using data from Table 1.5

$$K_{eq} = \frac{[C_{10}H_{12}][H_2]}{[C_6H_6]^2} \Rightarrow \exp \left[ 1.788 - \frac{4135.2}{(654 + 273)} \right] = \frac{(x)(652.6 - x)}{(116 - 2x)^2}$$

$$x = 1.36 \text{ kmol/h.}$$

Thus, the toluene recycle, Stream 11, will be increased from 35.7 to 37.06 kmol/h, an increase of 4%, while the increases in Streams 4 and 6 will be approximately 0.1%.

Based on this result, Alternative A will probably be better (less expensive) than Alternative B.



## Other Issues on Recycle

- ❑ Number of recycle streams
  - Consider valuable reactant species.
  - If SPC < 99 %, then consider recycling.
  
- ❑ How does excess reactant effect recycle structure?
  - Size of Recycle Loop  
 $H_2 : \text{Toluene} = 5 : 1$
  
- ❑ Reasons for multiple reactors:
  - Approach to equilibrium
  - Temperature control
  - Concentration control
  - Optimization of conditions for multiple reactions.





## Other Issues on Recycle (cont.)

- ❑ Do we need to purify prior to recycling ?
- ❑ Is recycling of inerts warranted ?
- ❑ Can recycling an unwanted inert material push equilibrium to the right?
  - Gasification of coal – CO<sub>2</sub> recycle .



## Other Issues on Recycle (cont.)

- ❑ Can recycling an unwanted inert control reaction ?
  - CO<sub>2</sub> in Gasifier
  
- ❑ Phase of Recycle Stream?



## Example 2.6

*Illustrative Example Showing the Input/Output and Recycle Structure Decisions Leading to the Generation of Flowsheet Alternatives for a Process.*

Consider the conversion of a mixed feed stream of methanol (88 mol%), ethanol (11 mol%), and water (1 mol%) via the following dehydration reactions:





## Example 2.6 (cont.)

Components in reactor effluent listed in order of decreasing volatility

- Ethylene (C<sub>2</sub>H<sub>4</sub>)
- Dimethyl ether (DME)
- Diethyl ether (DEE)
- Methanol (MeOH)
- Ethanol (EtOH)
- Water (H<sub>2</sub>O)



## Example 2.6 (cont.)

### Azeotropes

- DME - H<sub>2</sub>O (but not with significant alcohol present)
- DME – EtOH
- DEE - EtOH
- DEE - H<sub>2</sub>O
- EtOH - H<sub>2</sub>O

The mixed alcohol stream is available at a relatively low price from a local source (\$0.25/kg). However, pure methanol (\$0.22/kg) and/or ethanol (\$0.60/kg) streams may be purchased if necessary. The selling price for DME, DEE, and ethylene are \$0.95/kg, \$1.27/kg, and \$0.57/kg, respectively. Preliminary market surveys indicate that we can sell up to 15,000 tonne/y of DEE and up to 10,000 tonne/y of ethylene.

For a proposed process to produce 50,000 tonnes/y of DME, determine what are the viable process alternatives?

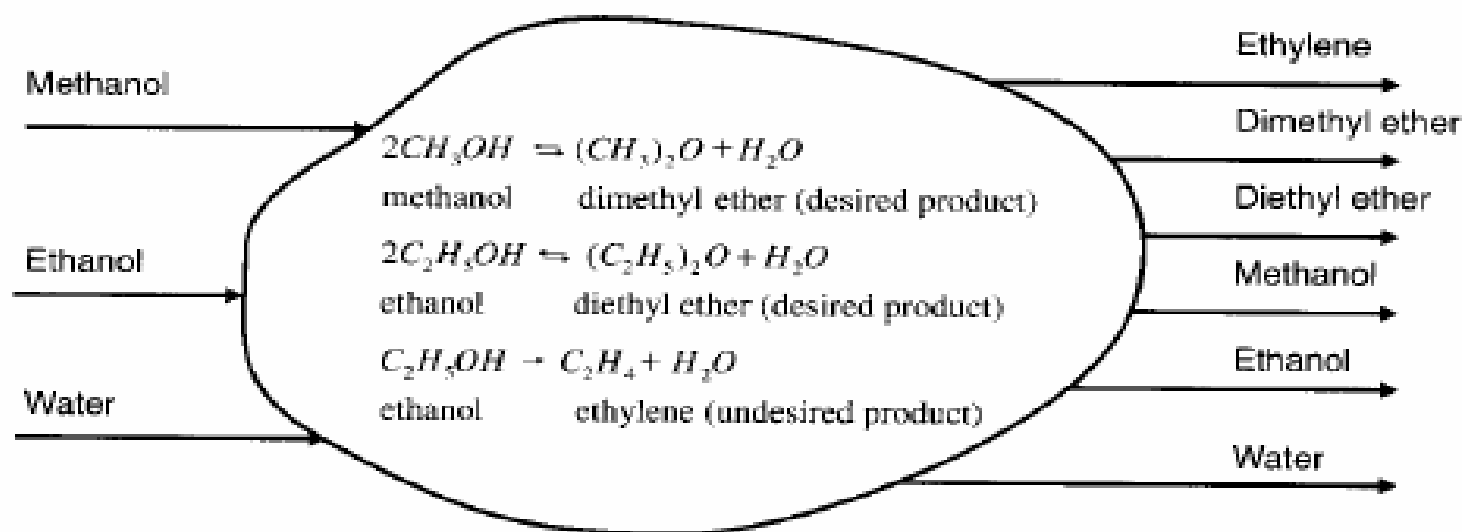
## Example 2.6 (cont.)

### Step 1: Batch vs Continuous

For a plant of this magnitude, a continuous process would probably be chosen. However, we will return to this issue after considering some process alternatives and see that a hybrid batch/continuous process should also be considered.

### Step 2: Define the Input-Output Structure of the Process

The basic input-output diagram of the process is shown in the process concept diagram of Figure E2.6(a).



**Figure E2.6(a)** Process Concept Diagram for the Mixed Ethers Process of Example 2.6

## Example 2.6 (cont.)

First, consider a material balance for the process and estimate the profit margin:

$$\text{Desired DME production} = 50,000,000 \text{ kg/y} = \frac{50 \times 10^6}{46} = 1.087 \times 10^6 \text{ kmol/y}$$

$$\text{Required MeOH feed} = (2)(1.087 \times 10^6) = 2.174 \times 10^6 \text{ kmol/y}$$

$$\text{EtOH feed entering with methanol} = \frac{2.174 \times 10^6}{88} (11) = 0.2718 \times 10^6 \text{ kmol/y}$$

$$\text{Maximum DEE production} = \frac{0.2718 \times 10^6}{2} = 0.1309 \times 10^6 \text{ kmol/y or } 9.69 \times 10^3 \text{ tonne/y}$$

$$\text{Maximum ethylene production} = 0.2718 \times 10^6 \text{ kmol/y or } 7.61 \times 10^3 \text{ tonne/y}$$

$$\begin{aligned} \text{Cost of Feed} &= \left( (2.174 \times 10^6)(30) + (0.2718 \times 10^6)(46) + \frac{(2.174 \times 10^6)}{88}(18) \right) \\ &(0.25) = \$19.54 \times 10^6 \end{aligned}$$

$$\text{Value of DME} = (50 \times 10^6)(0.95) = \$47.5 \times 10^6/\text{y}$$

$$\text{Value of DEE (maximum production)} = (0.1309 \times 10^6)(74)(1.27) = \$12.30 \times 10^6/\text{y}$$

$$\text{Value of ethylene (maximum production)} = (0.2718 \times 10^6)(28)(0.57) = \$4.34 \times 10^6/\text{y}$$

Margin will vary between  $(47.5 + 12.3 - 19.54) = \$40.26$  million and  $(47.5 + 4.34 - 19.54) = \$32.30$  million per year.



## Example 2.6 (cont.)

### Important Points

Because making ethylene is far less profitable. In addition, the maximum amount of DEE that the market can support is not currently being produced. Therefore, supplementing the feed with ethanol should be considered.

Since the main feed stream contains both reactants and an impurity (water), separation or purification of the feed prior to processing should be considered.

In order to minimize the production of by-products (ethylene), the selectivity of the DEE reaction should be optimized.



## Example 2.6 (cont.)

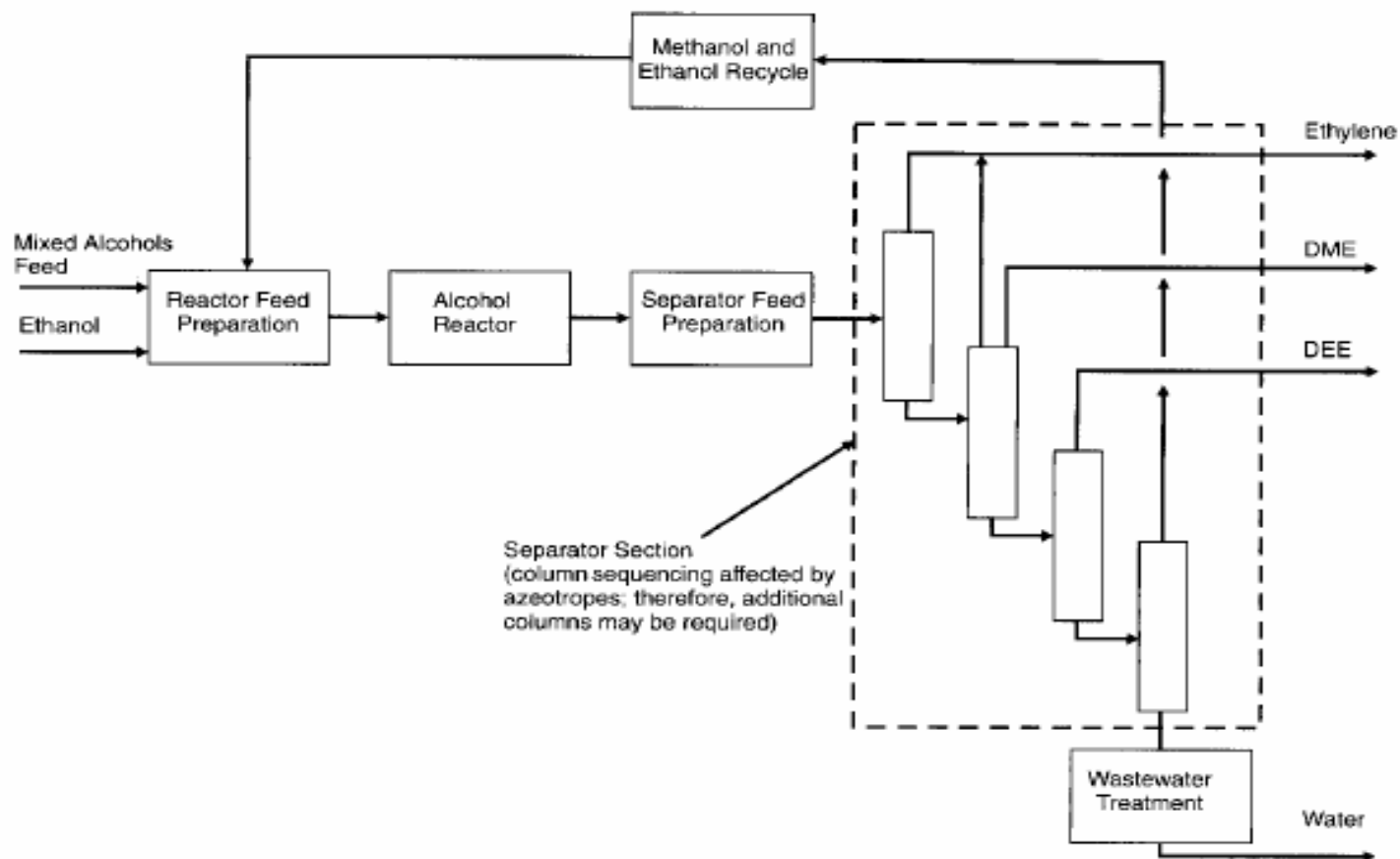


Figure E2.6(b) Structure of Process for Alternative 1 in Example 2.6

## Example 2.6 (cont.)

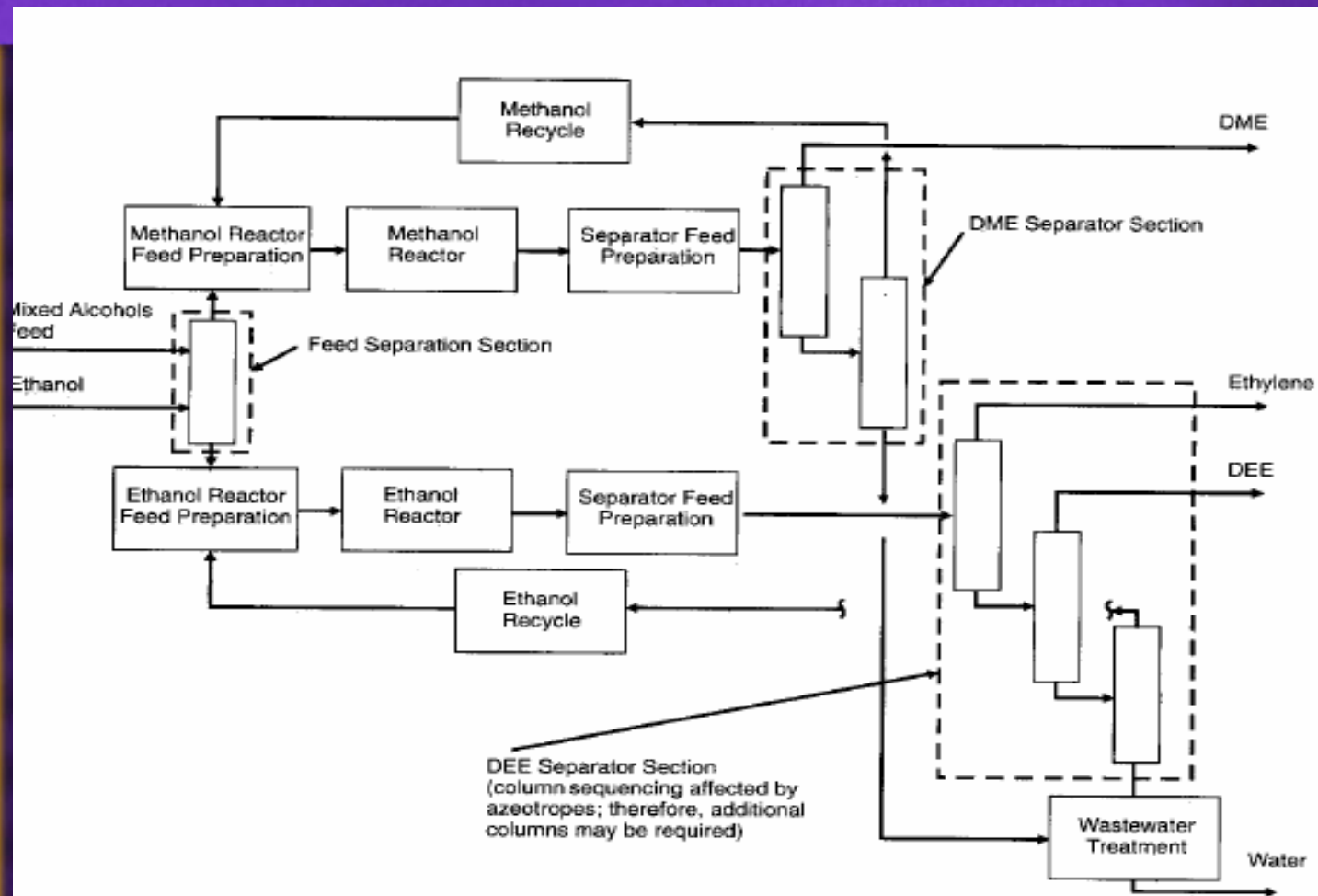
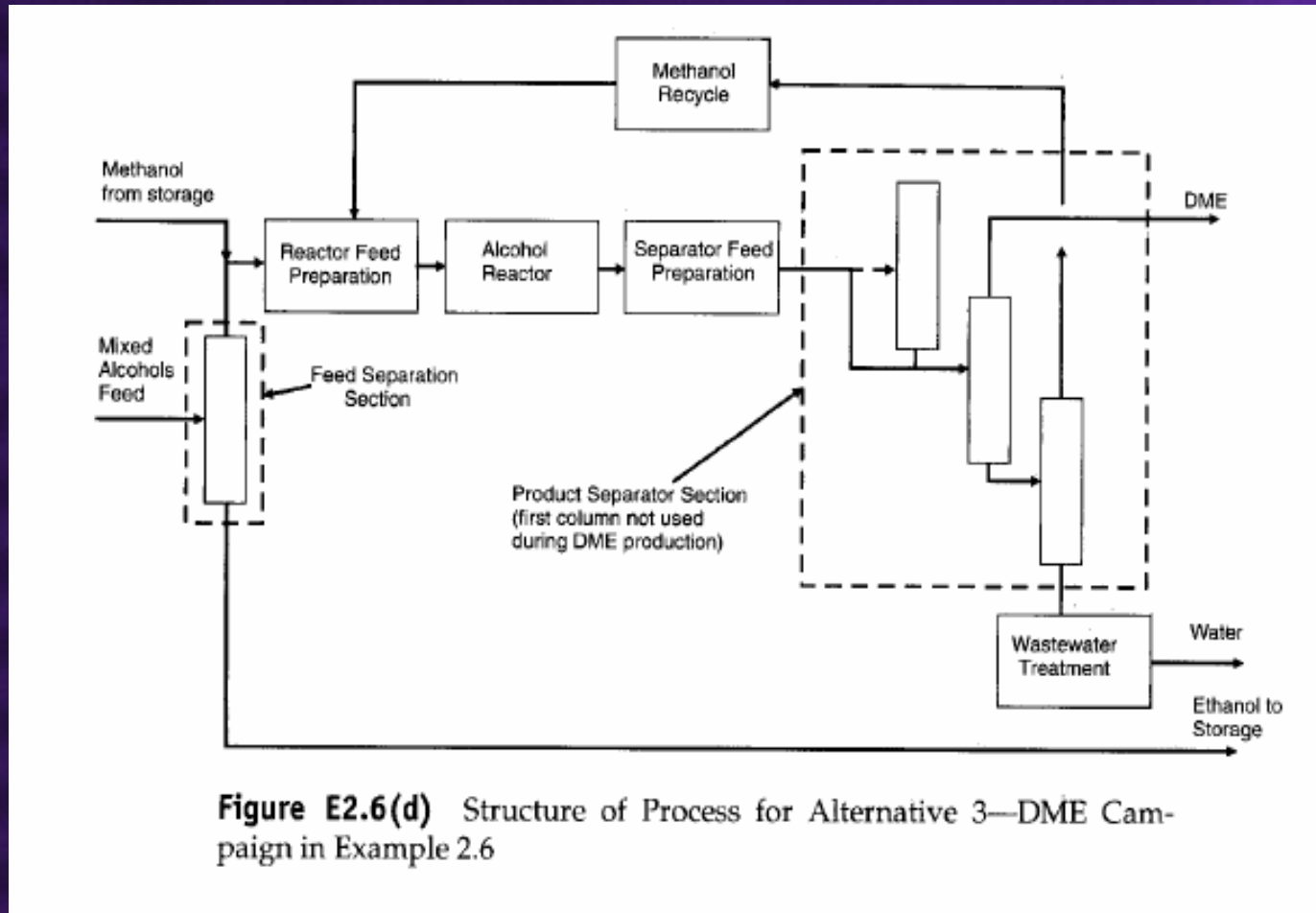
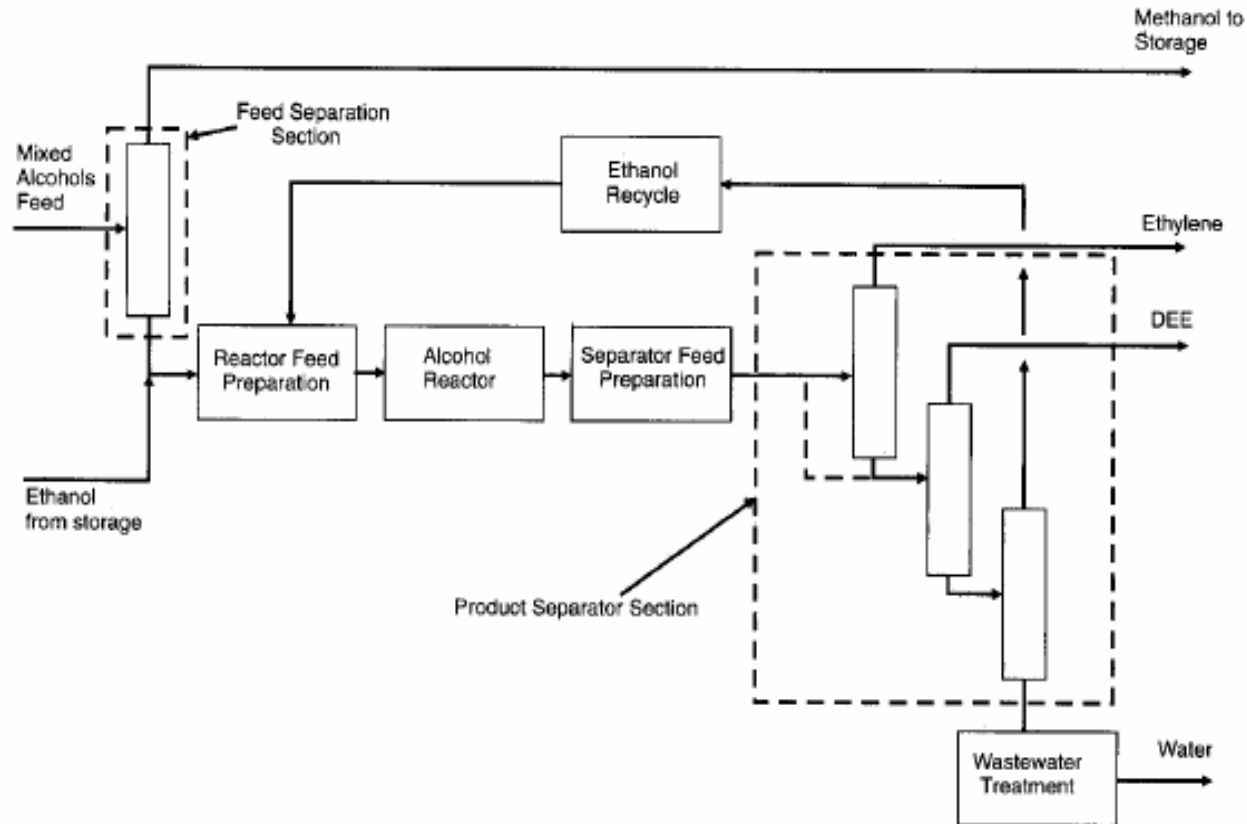


Figure E2.6(c) Structure of Process for Alternative 2 in Example 2.6

## Example 2.6 (cont.)



## Example 2.6 (cont.)



**Figure E2.6(e)** Structure of Process for Alternative 3—DEE Campaign in Example 2.6



## Course Outcomes

- Upon successful completion of this course, the student will be able to:
  - ① Understand the process flow diagrams of a chemical process.
  - ② Understand and justify the process conditions
  - ③ Be able to use heuristics in process design and analysis



## **Course Outcomes (cont.)**

- ④ Estimate capital investment.
- ⑤ Estimate manufacturing cost.
- ⑥ Understand engineering economics and perform profitability analysis.
- ⑦ Be familiar with using simulation for equipment design.