

# Chapter 2

## Lecture # 3-3

- Recycle Structure of the Process
- Illustrative Examples

- 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).

# Basic Recycle Structures

- Separate and purify un-reacted feed from products and then recycle.
- Recycle feed and products together and use a purge stream.
- Recycle feed and products together but do not use a purge stream.

# 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 =  $79.8\text{ }^{\circ}\text{C}$

Normal boiling point of toluene =  $110\text{ }^{\circ}\text{C}$

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 feed and products together + use a purge stream

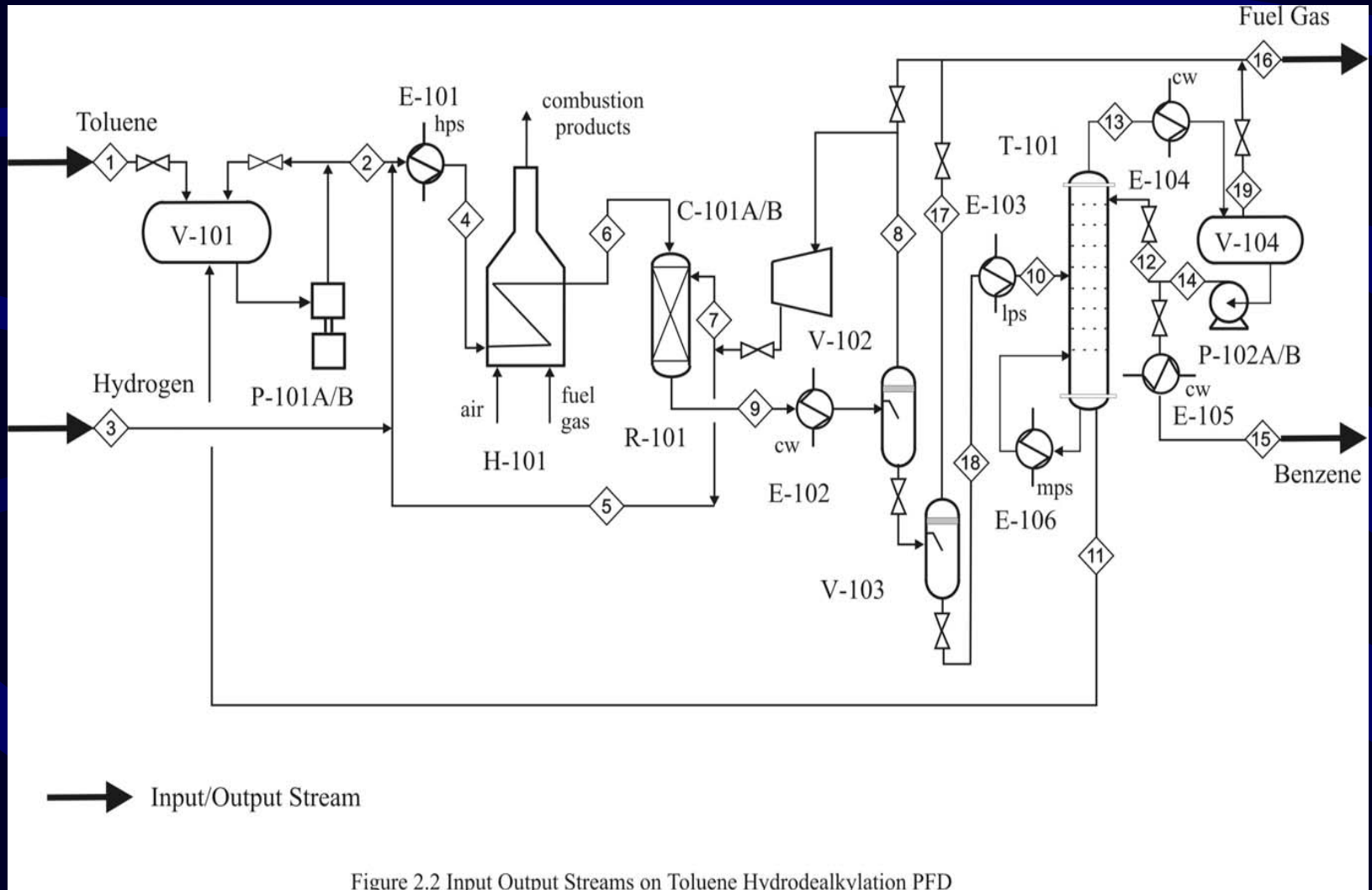


Figure 2.2 Input Output Streams on Toluene Hydrodealkylation PFD

# Recycle feed and products together without purge stream

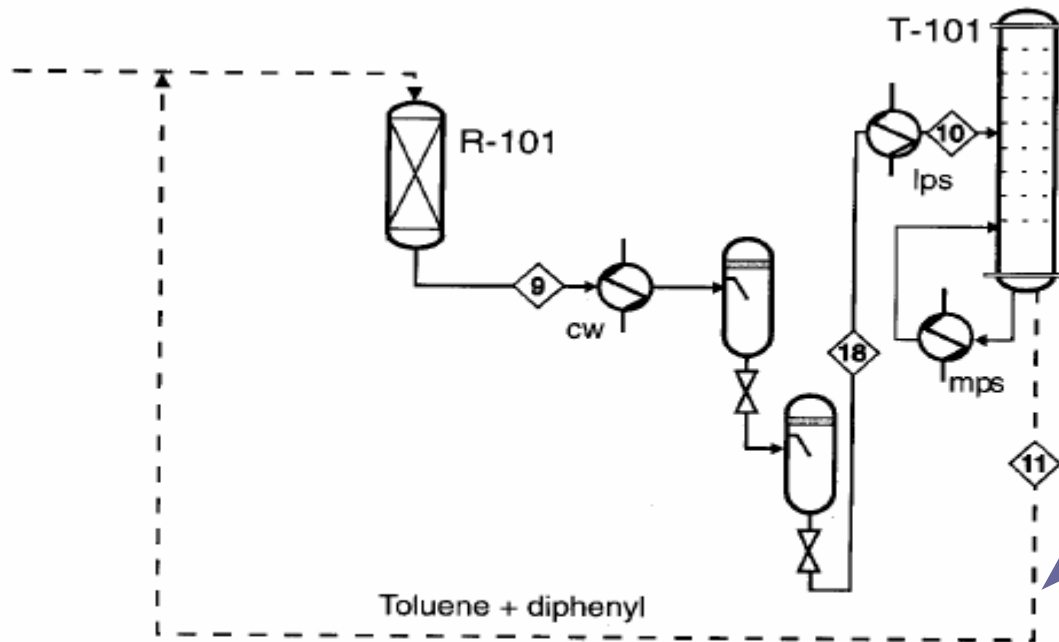


## Example 2.5

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

# Example 2.5

## Alternative A

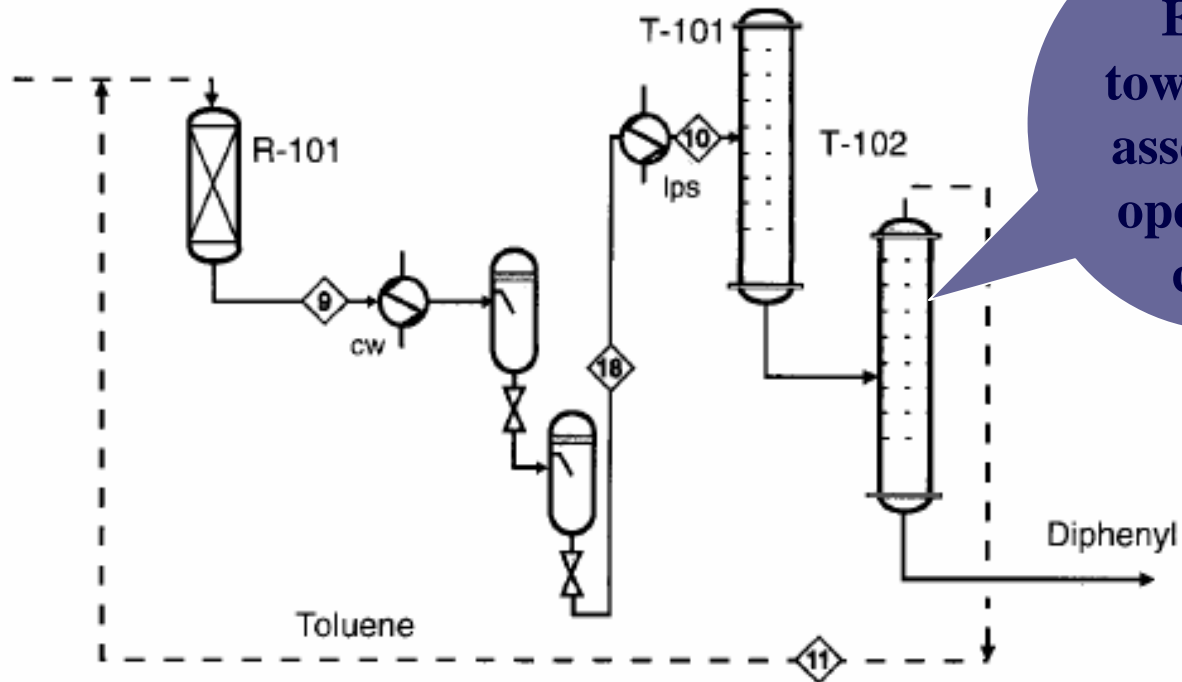


**Figure E2.5(a)** PFD for Alternative A in Example 2.5—Recycle of Diphenyl without Separation (E-101 and H-101 Not Shown)

As recycle increases,  
Equip and  
Op costs  
increases

# Example 2.5

## Alternative B



Extra  
tower with  
associated  
operating  
costs

**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

## Comments

- 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

## Calculations

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

Assume that reaction has reached equilibrium  
Using data from Table 1.5

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

# Example 2.5

## Calculations

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

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 Affecting the Recycle Structure That Lead to Process Alternative

- **Number of recycle streams**
  - Consider valuable reactant species.
  - If  $SPC < 90\%$ , then consider recycling.
- **How does excess reactant affect recycle structure?**
  - Size of Recycle Loop       $H_2 : \text{Toluene} = 5 : 1$

## Other Issues Affecting the Recycle Structure That Lead to Process Alternative

- **Reasons for multiple reactors:**
  - Approach to equilibrium
  - Temperature control
  - Concentration control
  - Optimization of conditions for multiple reactions.

## Other Issues Affecting the Recycle Structure That Lead to Process Alternative

- Do we need to purify prior to recycling ?
- Is recycling of an inert warranted ?
- Can recycling an unwanted inert material push equilibrium to produce less undesired products?
- Can recycling an unwanted inert control reaction ?
- Phase of Recycle Stream?

## Example 2.6

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

- **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

# 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**

## Example 2.6

- **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?**

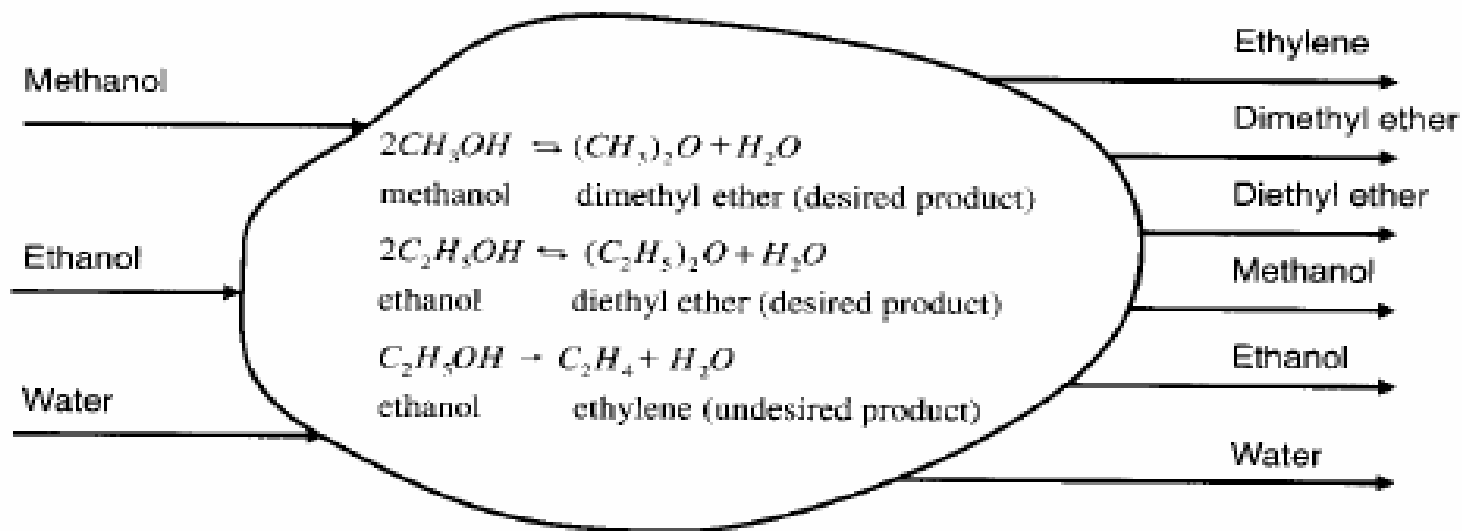
## Example 2.6

### 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

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

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

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

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

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

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

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

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

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

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

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

### 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

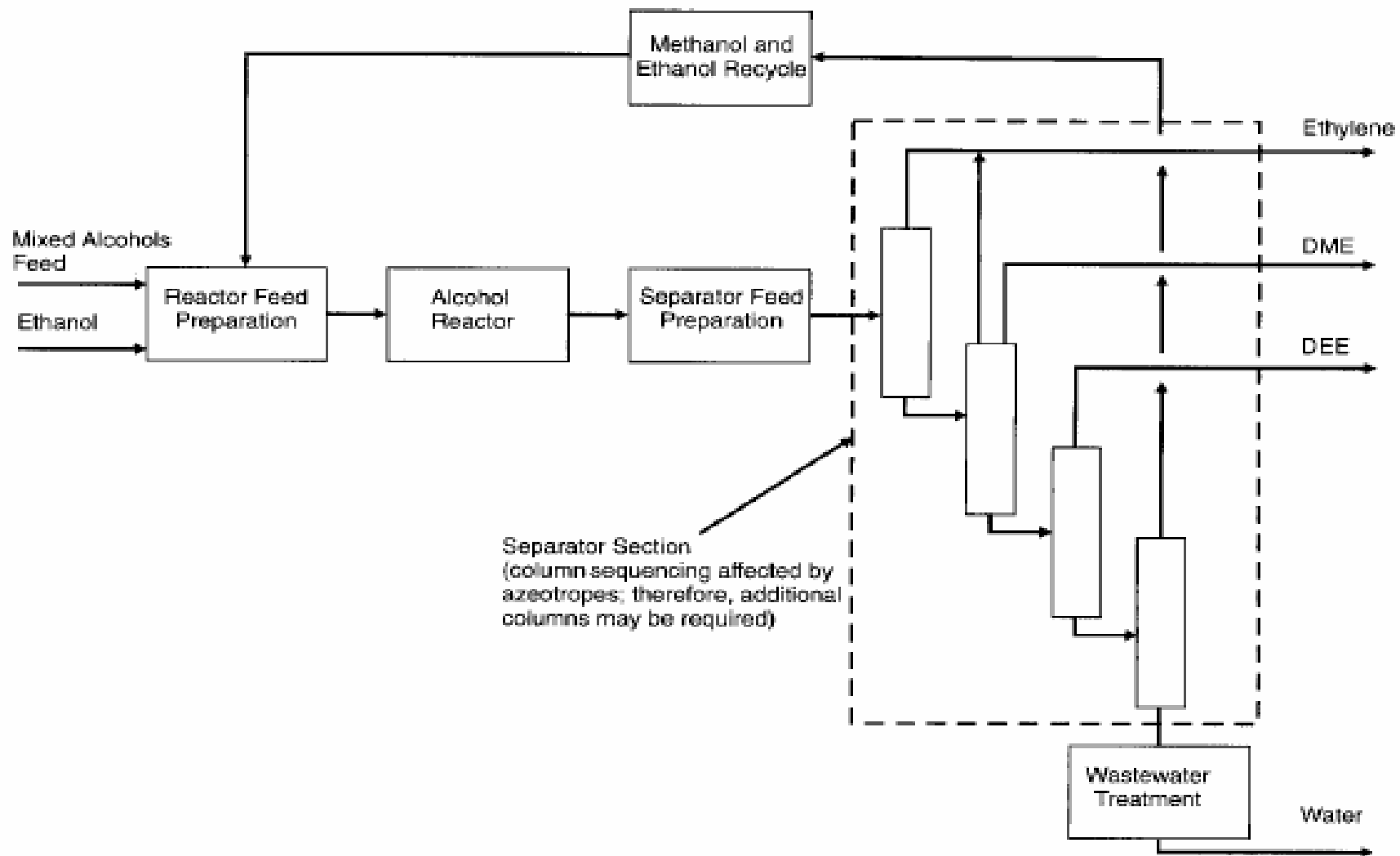


Figure E2.6 (b) Structure of Process for Alternative 1 in Example 2.6

# Example 2.6

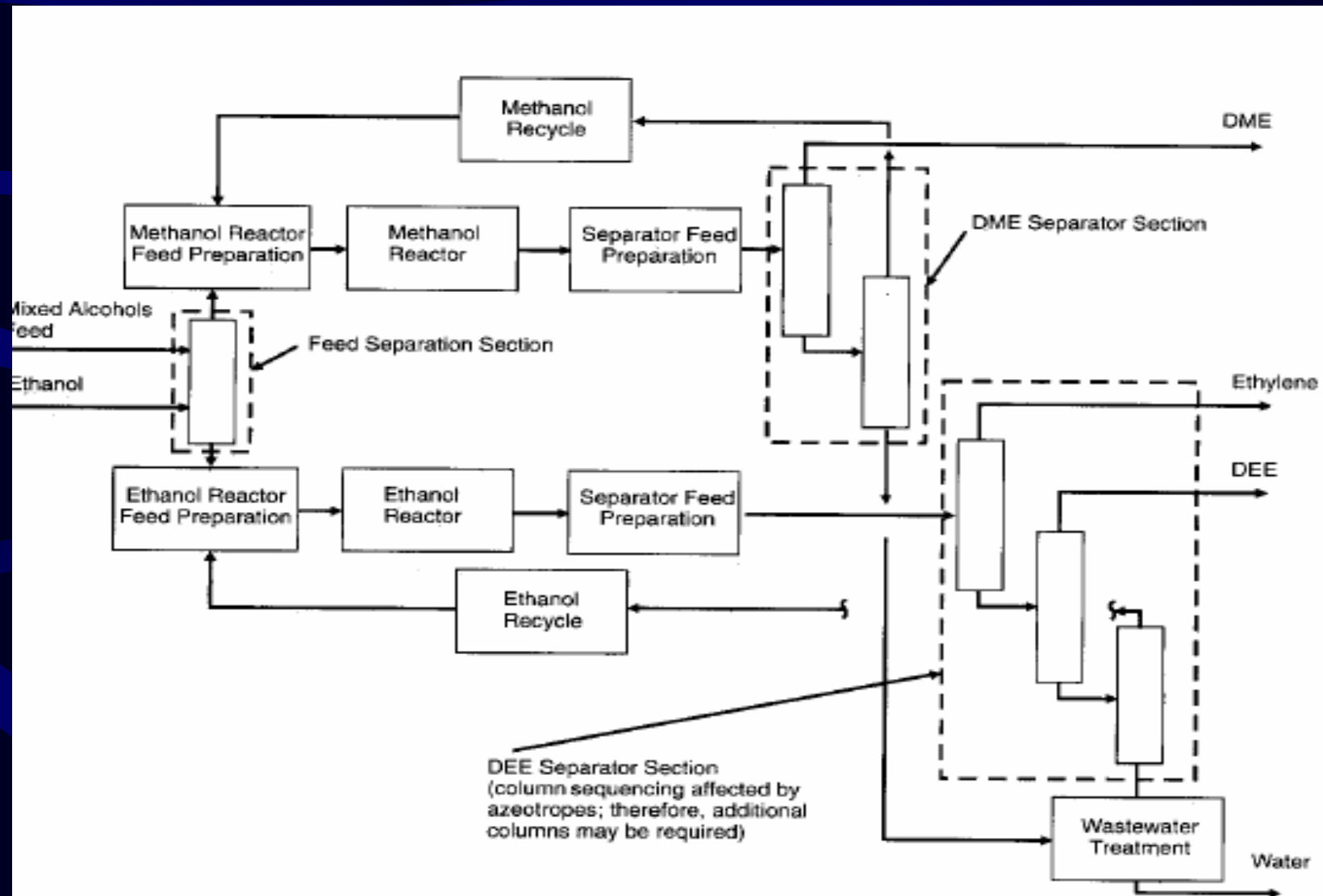
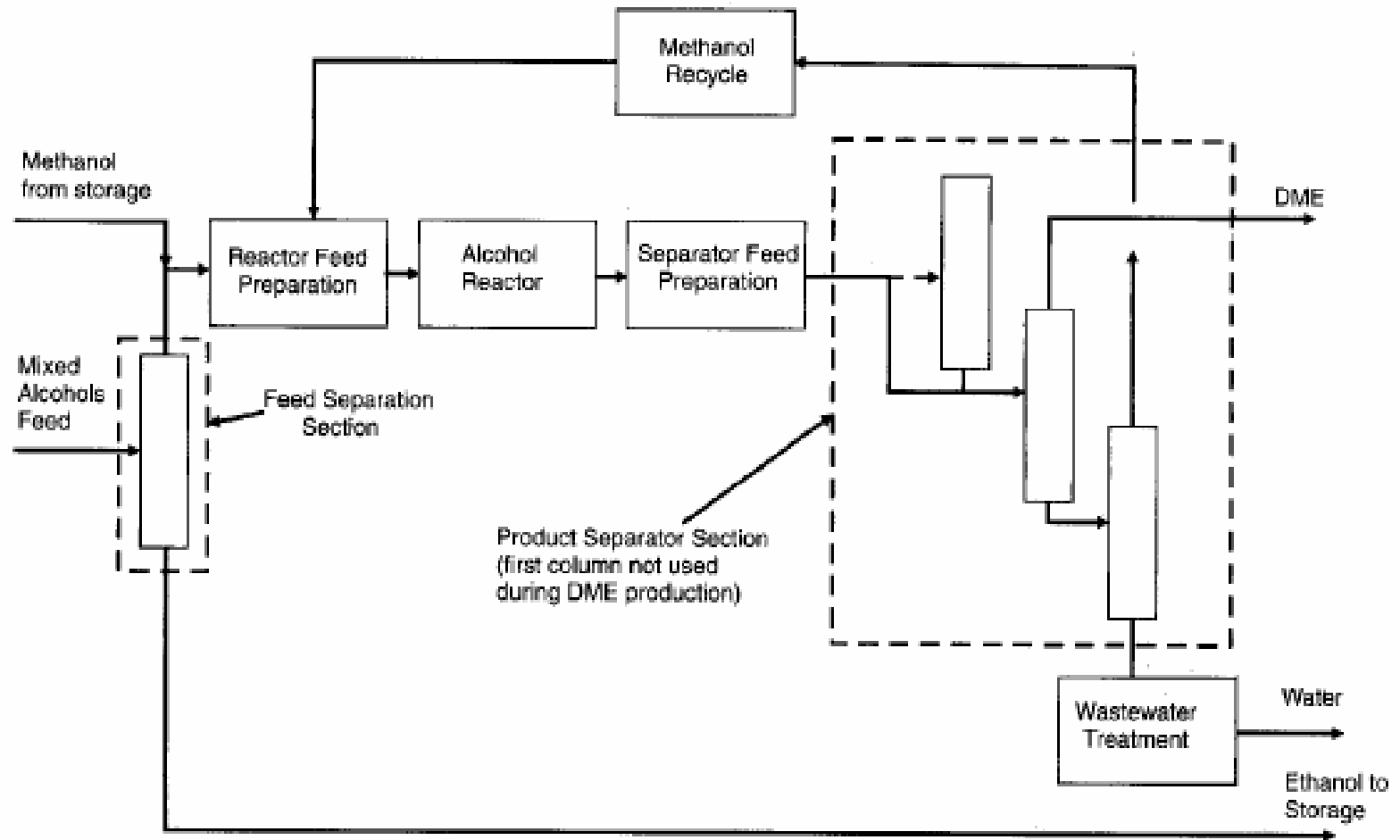


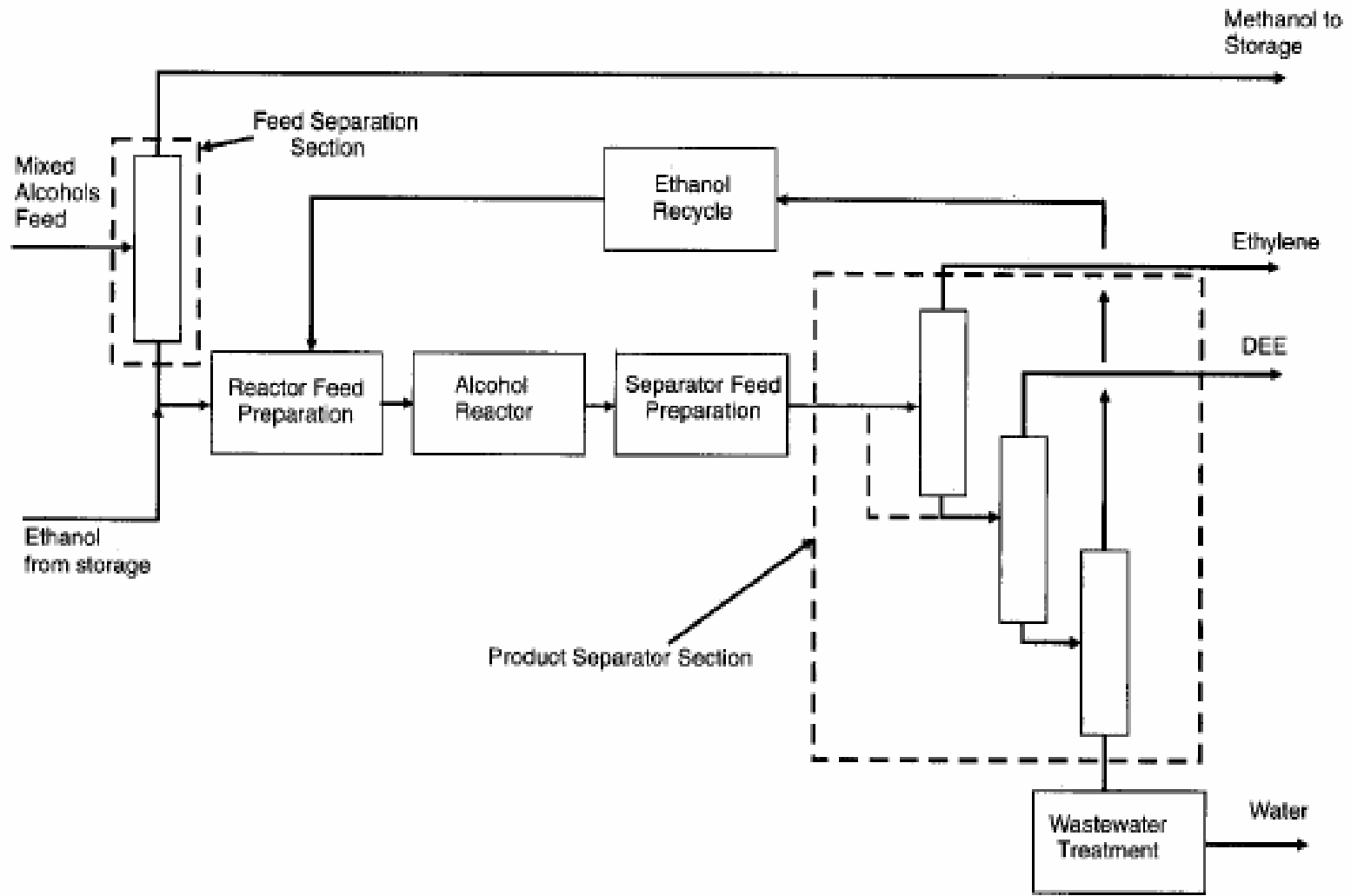
Figure E2.6(c) Structure of Process for Alternative 2 in Example 2.6

## Example 2.6



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

## Example 2.6



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