Chapter 2 - Structure and Synthesis of PFDs.

Steps for Conceptual Process Design

1) Batch or Continuous Process
2) Input-Output Structure
3) Recycle Structure
4) Separation Train
5) Heat Exchange Network

Step 1: Batch vs. Continuous

⇒ See Table 2.1 (p. 60-62, Turton et al.)
(Advantages & Disadvantages)

Factors:

2) Size

Pilot Scale → Batch
SMALL SCALE -> BATCH
LARGER SCALE -> CONTINUOUS

WHY? ECONOMY OF SCALE

b) BATCH ACCOUNTABILITY/PRODUCT QUALITY

FOOD AND PHARMA -> BATCH

WHEN PRODUCT (OFF-SPEC) CAN BE
BLEND ED -> CONTINUOUS

c) Operational Flexibility

VARIABLE OPERATION -> BATCH
(MIXING, REACTION, SEPARATION)

USUALLY VERY EXPENSIVE AND INEFFICIENT
TO DO THIS ON CONTINUOUS

d) STANDARD EQUIPMENT - MULTIPLE PRODUCTS

BROAD -> BATCH
NARROW -> CONTINUOUS
3) Process Efficiency

Higher throughput → Greater efficiency

→ Continuous

(insulation, heat-exchange networks, simpler recycle)

Problems with scheduling, control, changing products, not optimized

→ Batch is less efficient

f) Maintenance and operating labor

Higher → Batch

Lower → Continuous

g) Feedstock availability

Limited → Batch

Year-round → Continuous
h) PRODUCT DEMAND

SEASONAL → BATCH
YEAR-ROUND → CONTINUOUS

i) RATE OF REACTION

VERY SLOW → BATCH
MODERATE → CONTINUOUS
FAST → CONTINUOUS (BUT CONTROL ISSUES)

j) EQUIPMENT FOULING

SIGNIFICANT → BATCH
MINIMAL → CONTINUOUS

k) SAFETY

MORE EXPOSURE → BATCH
STANDARD PROCEDURES / CONTINUOUS
GOOD RECORD

l) CONTROL

MORE DIFFICULT → BATCH
SIMPLER → CONTINUOUS
STEP 2  INPUT-OUTPUT STRUCTURE

(ORGANIZATION)

CONCEPT DIAGRAM

INPUTS

REACTIONS

OUTPUTS

\[
\begin{align*}
C_7H_8 + H_2 & \rightarrow C_6H_6 + CH_4
\end{align*}
\]

If side reactions, include those as well.

Next, back to PFD...
PFD (Complex, but contains same inputs/outputs)

Feed enters on left.

Utilities shown on PFD.

Also,

- Perform material balance
- Generation in reactor
- Inerts
- Purge Streams

Product leaves on right.

Now, back to block flow diagram...
Blocks in Block Flow Diagram

1) Reactor Feed Prep
2) Reactor
3) Separator Feed Prep
4) Separator
5) Recycle
6) Environmental Control

Other considerations:

1) Feed purity
   a) Concentration
   b) Hard to separate
   c) Poison of catalyst → separate
   d) Impurity forms hazardous products
   e) Large quantity of impurities → separate

2) Addition of feeds to stabilize products

3) Inert feed to control exothermic reactions
Example: Steam

- Avoid explosion (flammability limit)
- Thermal ballast (heat of reaction)
- Need to separate from products

4) Addition of inert feed to control equilibrium

Example: Styrene production

\[ \text{H} \quad \text{O} \quad \text{O} \quad \text{H}_2 \]

- High temperature
- Low pressure
- Steam adds energy and reduces partial pressure of ethyl benzene.

Next, Recycle.
STEP 3: RECYCLE STRUCTURE

WHY? RAW MATERIALS ARE SIGNIFICANT FRACTION OF OPERATING COSTS

⇒ RECOVER & RECYCLE UNUSED REACTANTS

HOW TO JUDGE NECESSITY FOR RECYCLE:

EFFICIENCY,

1) SINGLE PASS CONVERSION (SPC)

SPC = \frac{\text{reactant consumed in reactor}}{\text{reactant fed to reactor}}

LOWER ⇒ MORE RECYCLE
(BUT MAY BE NECESSARY TO MINIMIZE SIDE REACTIONS)

2) OVERALL CONVERSION (OC)

OC = \frac{\text{reactant consumed in process}}{\text{reactant fed to the process}}
Higher is Better (not losing reactants)

3) Yield (Y)

\[ Y = \frac{\text{moles of reactant to produce desired product}}{\text{moles of limiting reactant reacted}} \]

How efficient is hydrodealkylation process?

(See Fig. 1.3 and Table 1.5)

Figure 1.3  Skeleton Process Flow Diagram (PFD) for the Production of Benzene via the Hydrodealkylation of Toluene
<table>
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<tr>
<th>Stream Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>59</td>
<td>25</td>
<td>225</td>
<td>41</td>
<td>600</td>
<td>41</td>
<td>38</td>
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<td>Pressure (bar)</td>
<td>1.90</td>
<td>25.8</td>
<td>25.5</td>
<td>25.2</td>
<td>25.5</td>
<td>25.0</td>
<td>25.5</td>
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<td>Vapor Fraction</td>
<td>0.0</td>
<td>0.0</td>
<td>1.00</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Mass Flow (tonne/h)</td>
<td>10.0</td>
<td>13.3</td>
<td>0.82</td>
<td>20.5</td>
<td>6.41</td>
<td>20.5</td>
<td>0.36</td>
<td>9.2</td>
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<tr>
<td>Mole Flow (kmol/h)</td>
<td>108.7</td>
<td>144.2</td>
<td>301.0</td>
<td>1204.4</td>
<td>758.8</td>
<td>1204.4</td>
<td>42.6</td>
<td>1100.8</td>
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<td>Component Mole Flow (kmol/h)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>Hydrogen</td>
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<td>0.0</td>
<td>286.0</td>
<td>735.4</td>
<td>449.4</td>
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<td>0.7</td>
<td>144.0</td>
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<td>22.7</td>
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<td>290.7</td>
<td>290.7</td>
<td>105.6</td>
<td>304.2</td>
<td>4.06</td>
<td>142.2</td>
<td>0.90</td>
</tr>
</tbody>
</table>

SINGLE PASS CONVERSION:

| 652.6 | 0.02 | 0.0 | 0.0 | 0.02 | 0.0 | 0.0 | 178.0 | 0.67 | 0.02 | 0.02 |
| 442.3 | 0.88 | 0.0 | 0.0 | 0.88 | 0.0 | 0.0 | 123.05 | 3.10 | 0.88 | 0.88 |
| 116.0 | 106.3 | 1.1 | 184.3 | 289.46 | 289.46 | 105.2 | 2.85 | 0.26 | 106.3 | 0.0 |
| 36.0 | 35.0 | 34.6 | 0.88 | 1.22 | 1.22 | 0.4 | 0.31 | 0.03 | 35.0 | 0.0 |

OVERALL CONVERSION:
YIELD:

How and When to Recycle

1) Separate and Purify Unreacted Feed Before Recycle

→ Temperature + Pressure

→ Exploit Differences in Properties
   (Selecting Separation Process)

See Examples 2.3 + 2.4 (p. 76-78) How to separate?

2.3 \( \text{H}_2 / \text{CH}_4 \)

2.4 Benzene / Toluene
2) Recycle feed and product w/ purge
   → Hard to separate
   → Purge prevents build-up of methane

3) Recycle feed and product w/o purge
   → Product must react further so it does not build up in system.

---

Other recycle issues:

1) Potential recycle streams (nearly all)
2) Which excess reactant? (and why?)
   → H₂ excess shifts equilibrium and prevents coking
3) # of reactors
   a) avoid equilibrium at reactor inlet
      NH₃ synthesis (high T&P)
b) Direct injection of reactant for temperature control (adiabatic reactor)
c) Concentration control (side reactions)
d) Multiple reactions (at different conditions)

4) Recycle individual reactants or mixed stream?

5) Recycle of inert?
   ⇒ Pollution prevention (water)

6) Recycle to shift equilibrium or control reactor

7) What phase is the recycle stream?

   GAS
   ⇒ compression ($$)
   ⇒ cooling ($$)
   ⇒ separation not common

   LIQUID
   ⇒ azeotropes (separation)
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:

\[
2\text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{O} + \text{H}_2\text{O} \hspace{1cm} \Delta H_{\text{react}} = -11,770 \text{ kJ/kmol}
\]

methanol dimethyl ether (desired product)

\[
2\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O} \hspace{1cm} \Delta H_{\text{react}} = -11,670 \text{ kJ/kmol}
\]

ethanol diethyl ether (valuable by-product)

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \hspace{1cm} \Delta H_{\text{react}} = -1,570 \text{ kJ/kmol}
\]

ethanol ethylene (less valuable by-product)

The reactions take place in the gas phase, over an alumina catalyst [14, 15], and are mildly exothermic but do not require additional diluents to control reaction temperature. The stream leaving the reactor (reactor effluent) contains the following components, listed in order of decreasing volatility (increasing boiling point):

1. Ethylene (C\(_2\)H\(_4\))
2. Dimethyl ether (DME)
3. Diethyl ether (DEE)
4. Methanol (MeOH)
5. Ethanol (EtOH)
6. Water (H\(_2\)O)

Moreover, because all of these are polar compounds, with varying degrees of hydrogen bonding, it is not surprising that these compounds are highly non-ideal and form a variety of azeotropes with each other. These azeotropes are as follows:

- DME – H\(_2\)O (but not with significant alcohol present)
- DME – EtOH
- DEE – EtOH
- DEE – H\(_2\)O
- EtOH – H\(_2\)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?