Solution 4.1

Basis 100 kmol benzene at reactor inlet

Reactor:

\[
\begin{align*}
\text{Cl}_2 \text{ at reactor inlet} & \quad = (100)(0.9) \quad = 90 \text{ kmol} \\
\text{C}_6\text{H}_6 \text{ converted} & \quad = (100)(0.553) \quad = 55.3 \text{ kmol} \\
\text{C}_6\text{H}_5\text{Cl produced} & \quad = (55.3)(0.736) \quad = 40.70 \text{ kmol} \\
\text{C}_6\text{H}_4\text{Cl}_2 \text{ produced} & \quad = (55.3)(0.273) \quad = 15.10 \text{ kmol} \\
\text{Cl}_2 \text{ reacted} & \quad = 40.70 + 2(15.10) \quad = 70.90 \text{ kmol} \\
\text{HCl produced} & \quad = 70.90 \text{ kmol} \\
\text{Cl}_2 \text{ unreacted} & \quad = 90 - 70.90 \quad = 19.10 \text{ kmol}
\end{align*}
\]

Separator:

Gas phase: \[
\begin{align*}
\text{Cl}_2 & \quad 19.10 \text{ kmol} \\
\text{HCl} & \quad 70.90
\end{align*}
\]

Liquid phase: \[
\begin{align*}
\text{C}_6\text{H}_6 & \quad = 100 - 55.3 \quad 44.70 \text{ kmol} \\
\text{C}_6\text{H}_5\text{Cl} & \quad 40.70 \\
\text{C}_6\text{H}_4\text{Cl}_2 & \quad 15.10
\end{align*}
\]

Absorber:

\[
\begin{align*}
\text{HCl In} & \quad = (70.90)(36.5) \quad = 2588 \text{ kg} \\
\text{Water for 30\% w/w acid} & \quad = \frac{2588}{0.30} \quad = 8626 \text{ kg} \\
\text{Therefore, Solution Out} & \quad = 11,214 \text{ kg}
\end{align*}
\]

Neglect water vapour carried over with chlorine

Assume all HCl absorbed together, with 2 percent of the chlorine

\[
\begin{align*}
\text{Cl}_2 \text{ recycled} & \quad = (19.10)(0.98) \quad = 18.72 \text{ kmol}
\end{align*}
\]
Distillation:

Feed:  
\[ C_6H_6 \quad 44.70 \text{ kmol} \]
\[ C_6H_5Cl \quad 40.70 \]
\[ C_6H_4Cl_2 \quad 15.10 \]

Overheads:
With 0.95% recovery, \( C_6H_6 = (44.70)(0.95) = 42.47 \text{ kmol} \)

Bottoms:  
\[ C_6H_6 = 44.70 - 42.47 = 2.33 \text{ kmol} \]
\[ C_6H_5Cl \quad 40.70 \]
\[ C_6H_4Cl_2 \quad 15.10 \]

Reactors with recycle feeds –

Fresh feeds:  
\[ C_6H_6 = 100 - 42.47 = 57.53 \text{ kmol} \]
\[ HCl = 90 - 18.72 = 71.18 \text{ kmol} \]

Scaling factor –

Product required = \( 100 \text{ t d}^{-1} = \frac{1000}{24} = 41.67 \text{ kg h}^{-1} = \frac{41.67}{112.5} = 0.37 \text{ kmol h}^{-1} \)

So, 57.53 kmol fresh feed of benzene to the reactor produces 40.70 kmol of product.

Therefore, scaling factor for flow sheet  
\[ \frac{0.37}{40.70} = 0.0091 \]

I would use a slightly higher factor to give a factor of safety for losses, say 0.0095.
A second, and possibly a third, column would be needed to separate the monochlorobenzene from the dichlorobenzene and unreacted benzene – see Chapter 11, Section 11.6.2.

Solution 4.2
1. Reactor
2. MTBE column
3. Absorber
4. MeOH distillation
5. Recycle splitter (tee)

\[ g_{10k} = \text{feed stock + MeOH} \]
\[ g_{20k} = \text{pseudo feed MTBE} \]
\[ g_{30k} = \text{water make-up} \]

Components (k’s):
1. C4’s, other than isobutane
2. methanol (MeOH)
3. isobutane
4. MTBE
5. water

Number of split fraction coefficients = \((N - 1) + R = (5 - 1) + 2 = 6\)
Equations (matrix) 5 units

\[
\begin{array}{ccccc}
1 & 2 & 3 & 4 & 5 \\
1 & 1 & \alpha_{21k} & 0 & 0 & 0 & g_{10k} \\
2 & 0 & 1 & \alpha_{32k} & 0 & 0 & g_{20k} \\
3 & 0 & 0 & 1 & \alpha_{43k} & 0 & g_{30k} \\
4 & \alpha_{14k} & 0 & 0 & 1 & \alpha_{54k} \\
5 & 0 & 0 & \alpha_{35k} & 0 & 1 \\
\end{array}
\]

Estimation of \( \alpha \)'s and \( g \)'s –

Basis 100 kmol h\(^{-1} \) feed-stock

Spilt fraction coefficients, \( \alpha \) 's, subscripts give without punctuation.

\( k = 1 \): C4’s, other than isobutane.

Assume they pass through unchanged, no reaction and no absorption.

\[
\begin{align*}
211 &= 1.0 \\
431 &= 0.0 \text{ (sent to storage, other uses)} \\
321 &= 0.0 \\
541 &= 0.0 \\
351 &= 0.0 \\
141 &= 0.0 \\
\end{align*}
\]

Fresh Feeds, \( g_{101} = \Sigma \text{C4’s} = 2 + 31 + 18 = 51 \text{ kmol} \)

\( k = 2 \): MeOH

With 10% excess and 97% conversion,

\[
\begin{align*}
\text{Feed of iC4} &= 49 \text{ kmol} \\
\text{So, Inlet MeOH} &= (1.1)(49) = 53.9 \text{ kmol} \\
\text{MeOH reacted} &= (0.97)(49) = 47.5 \text{ kmol} \\
\text{MeOH Out} &= 53.9 - 47.5 = 6.4 \text{ kmol}. \\
\end{align*}
\]
212 = \frac{6.4}{53.9} = 0.12

322 = 1.0 \text{ MTBE (pure so, negligible loss of MeOH)}

432 = 0.99 (99\% recovery)

542 = 0.01 (99\% recovery)

142 = 0.99 (99\% recovery)

352 = 0.9 (10\% purge)

Fresh feed, g102 = 49 (put equal to isobutane in feed and adjust after first run to allow for losses)

\text{k = 3: isobutene}

213 = 1 - 0.97 = 0.03 (97\% conversion)

323 = 1 - 0.99 = 0.01 (99\% recovery)

433 = 1.0

543 = 1.0 (no MTBE)

143 = 1.0

153 = 1.0

Fresh feed, g103 = 49 kmol

\text{k = 4: MTBE}

214 = 1.0

324 = 0.005 (99.5\% recovery in column)

434 = 0.0 (assumed not absorbed)

544 = 1.0

354 = 1.0

144 = 1.0

Fresh feed, 104 = 47.5 kmol, (produced in reactor)
\( k = 5: \) water

\[
\begin{align*}
215 & = 1.0 \\
325 & = 1.0 \\
435 & = 0.965 \quad \text{(allow for carry over with C4’s, see note 1.)} \\
545 & = 0.99 \quad \text{(99\% recovery)} \\
355 & = 0.9 \quad \text{(10\% purge)} \\
145 & = 0.01 \quad \text{(recycle?)}
\end{align*}
\]

Fresh feed, \( 302 = 8 \text{ kmol} \) \quad \text{(see note 2)}

Notes:

Carry over of water with C4’s from column.

Vapour pressure of water at \( 30^\circ \text{C} \) = 0.0424 bar \quad \text{(approximately 4.2\%)}

C4’s flow = 51 kmol

\[
\text{Loss of water} = \frac{51}{1 - 0.042} = 52.24 \text{ kmol}
\]

Water flow rate, recycle, = 64 kmol \quad \text{(notes)}

\[
\text{Split fraction} = \frac{2.24}{64} = 0.035
\]

Water Fresh Feed:

Concentration of MeOH at absorber base = 10\%

\[
\begin{align*}
\text{MeOH} & = (0.13)(49) = 6.37 \text{ kmol} \\
\text{Total flow} & = \frac{6.37}{0.1} = 63.7 \text{ kmol} \\
10 \% \text{ purge} & = (63.7)(0.1) = 6.4 \text{ kmol} \\
\text{Water} & = (0.9)(6.4) = 5.8 \text{ kmol}
\end{align*}
\]

If we add the loss with C4’s leaving column, \( \text{Total} = 5.8 + 2.2 = 8 \text{ kmol} \).

Solution

Use spread sheet or the program MASBAL to solve. My solution, using the split fractions and fresh feeds given above, is set out below. The table shows in flows at the inlet of
each unit, rounded to one place, (in kmol h\(^{-1}\)).

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit 1</th>
<th>Unit 2</th>
<th>Unit 3</th>
<th>Unit 4</th>
<th>Unit 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. C’4s</td>
<td>51</td>
<td>51</td>
<td>51</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MeOH</td>
<td>55.9</td>
<td>6.7</td>
<td>6.8</td>
<td>6.7</td>
<td>0.1</td>
</tr>
<tr>
<td>iC4</td>
<td>49.0</td>
<td>1.5</td>
<td>trace</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>MTBE</td>
<td>0</td>
<td>47.5</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H2O</td>
<td>0.6</td>
<td>0.6</td>
<td>57.6</td>
<td>55.6</td>
<td>54.6</td>
</tr>
</tbody>
</table>

Total: 156.5 107.2 115.6 62.3 54.6

The other stream flows can be obtained form mass balances round the units or by including dummy unit in the information diagram.

Iterate on split fraction and fresh feeds, as necessary to match the constraints.
For example, the water purge seems low.

**Solution 4.3**

What follows is a partial solution and notes.

Careful choice of the starting point will avoid the need for iteration.
Start at the inlet to the decanter, where the composition is fixed at the ternary azeotrope.
Take the basis as 100 kmol h\(^{-1}\) feed to the decanter. Let F1 be the flowrate of decanter stream returned to the first column and F2 the stream going to the second column. A component material balance will determine these stream flows.

\[
\begin{align*}
\text{Benzene} & \quad 54 = (F1)(0.74) + (F2)(0.04) \\
\text{Water} & \quad 22 = (F1)(0.04) + (F2)(0.61)
\end{align*}
\]

Solving gives: \(F1 = 71.3 \text{ kmol h}^{-1}\) and \(F2 = 28.7 \text{ kmol h}^{-1}\)
All the benzene going to Column 1 from the decanter leaves in the column overhead and so the overhead rate, \( F_3 = 71.3 \left( \frac{0.74}{0.54} \right) = 97.7 \text{ kmol h}^{-1} \)

The balance to make up the 100 kmol h\(^{-1}\) to the decanter is the overheads from Column 2. \( F_8 = 100 - 97.7 = 2.3 \text{ kmol h}^{-1} \)

No water leaves the base of Column 1 and so the water entering the column in the feed, \( F_5 \), and the stream from the decanter, go overhead.

A water balance gives \( F_5 \):

\[
0.11 F_5 + (71.3)(0.04) = (97.7)(0.22)
\]

\( F_5 = 68.5 \text{ kmol h}^{-1} \)

A balance on ethanol gives the bottoms flow, \( F_6 \):

\[
(68.5)(0.89) + (71.3)(0.22) = F_6 + (97.7)(0.24)
\]

\( F_6 = 53.2 \text{ kmol h}^{-1} \)

The only source of this product ethanol is the fresh feed to the column, \( F_7 \) and so:

\[
F_7 = \frac{53.2}{0.89} = 59.8 \text{ kmol h}^{-1}
\]

So the recycled overhead product from the third column, \( F_4 \) is:

\( F_4 = 68.5 - 59.8 = 8.7 \text{ kmol h}^{-1} \)

All the water leaves the system in the bottoms for Column 3 and so the bottoms from this column, \( F_8 \), will be:

\( F_8 = (59.8)(0.11) = 6.6 \text{ kmol h}^{-1} \)

The flow sheet is to be drawn for a production rate of 100 kmol/h of absolute alcohol, so the scaling factor required is \( \frac{100}{53.2} = 1.88 \). (Say 1.9)

The make up benzene can be added in the stream from the decanter to Column 1.

**Solution 4.4**

Notes/Hints:

There are three main pieces of equipment involved in the flow sheet calculations: the reactor, absorber, and stripper, and two minor pieces: the vent scrubber and dryer.

The reactor flows can be calculated from the stoichiometry of the reaction.
It is not necessary to make repetitive calculations to determine the flow of recycled acid to the absorber. The recycle flow is fixed by the change in the specified acid concentration from inlet to outlet.

In the dryer, the purge stream rate is determined by the amount of water removed and the acid concentration. The acid recycle rate will be a design variable in the design of the drying column.

**Solution 4.5**
Refer to the solution to Problem 4.2

**Solution 4.6**
Refer to the solution to Problem 4.2