18.1. Introduction

In this chapter, a typical case study is taken to consider most of the CDU product streams into more process downstreams such as reformer, fluid catalytic cracking, delayed coker and alkylation. Hydroprocessing is mainly used to remove sulphur to meet the market product specifications.

The capacity of a crude distillation unit (CDU) is 100,000 barrels per stream day (BPSD). The unit produces raw products, which have to be processed in the downstream unit to produce products of a certain specification. This involves the removal of undesirable components like sulphur, nitrogen and metal compounds, and limiting the aromatic content. Typical products from the CDU are:

- Gases
- Light straight run naphtha (also called light gasoline, light naphtha)
- Heavy gasoline (also called military jet fuel)
- Kerosene (also called light distillate or jet fuel)
- Middle distillates called diesel or light gas oil (LGO)
- Heavy distillates called atmospheric gas oil (AGO) or heavy gas oil (HGO)
- Crude column bottoms called atmospheric residue or topped crude

18.2. The Case Study

In this case study 100,000 BPD crude oil, with an API of 26, is introduced to a distillation column. The produced naphtha cut (190–380 °F) is hydro-treated to remove sulphur and then fed to a reformer to produce a C$_5^+$ cut of 94 RON. The produced hydrogen in the reformer is used in the hydrotreater units.

The gas oil cut (580–650 °F) is hydrotreated to remove sulphur and then fed to the FCC unit of 75% conversion to produce gasoline, gases, gas oil and coke. Fluidized catalytic cracking (FCC) is the heart of the refinery and is where heavy, low value petroleum streams are upgraded into lighter products.
mainly gasoline and C3/C4 olefins, which can be used in the alkylation unit to produce ultra-clean gasoline (C7–C8 alkylates).

The residue cut (1050°F) produced from the CDU is fed to a delayed coker unit to produce gasoline, gases, gas oil and coke. Coking is the process of carbon rejection from the heavy residues producing lighter components lower in sulphur, since most of the sulphur is retained in the coke.

Gas streams are split to separate isobutane (iC4) and butene (C4) from other gases. iC4 and C4 are fed to an alkylation unit with an addition of make-up iC4 to produce alkylate. Alkylation is the process of producing gasoline range material (alkylates) from olefin butylenes (C4) and isobutane. Butylene is the most used olefin because of the high quality of the alkylate produced.

The typical flow chart of the full process is shown in Figure 18.1. The crude TBP-vol% analysis is shown in Table 18.1.

The crude TBP and API as a function of accumulated liquid volume % (LV%) are calculated as follows:

\[
TBP(°R) = \left\{ \left( 2.2 \ln \left( \frac{100}{100 - LV\%} \right) \right)^{2.7} + 1 \right\} 490 \quad (18.1)
\]

\[
API = -0.0004(LV\%)^3 + 0.05(LV\%)^2 - 2.4(LV\%) + 80 \quad (18.2)
\]

Material balance and property calculations are performed for each product streams using the methods outlined in Chapter 3 to 8 and 10. The details are as follows:

Considering the crude distillation unit:

**190–380°F cut**

Substituting in equation (18.1) to get LV% at IBP and EBP

\[
\text{Cut vol} \% = 33.05 - 25.92 = 7.134\%
\]

\[
\text{Cut mid volume} = 29.485
\]

Substituting the cut mid volume in equation (18.2) to get API = 42.45

\[
\text{Cut volume} = 0.07134(100,000) = 7134 \text{ BPD}
\]

\[
\text{Cut amount} = 7134(11.87) = 84,681 \text{ lb/h}
\]

Calculation of sulphur content:

\[
M = 42.965 \left[ \exp(2.097 \times 10^{-4} T_b - 7.78712 \text{ SG} + 2.08476 \times 10^{-3} T_b \text{ SG}) \right] T_b^{1.26007 \text{ SG}^{4.98308}}
\]

\[
T_b = ((190 + 380)/2 - 32)/1.8 + 273 = 413 \text{ K}
\]

\[
\text{SG} = 0.812
\]

\[
M = 109 \text{ lb/lb mol}
\]
Figure 18.1 Process flow chart
I = 2.266 × 10^{-2} \exp(3.905 \times 10^{-4} T_b + 2.468SG - 5.704 \times 10^{-4} T_bSG) T_b^{0.0572}SG^{-0.72} = 0.2632
\[ n = \left( \frac{1 + 2I}{1 - I} \right)^{1/2} = 1.439 \]
\[ R_i = n - \frac{d}{2} = 1.033 \]
\[ m = M(n - 1.475) = -3.924 \]
since \( M < 200 \)

sulphur wt\% = 177.448 - 170.946 R_i + 0.2258 m + 4.054 SG = 1.36 wt\%
sulphur amount = 0.0136(84,681) = 1152 lb/h

580–650°F cut
Substituting in equation (18.1) to get LV\% at IBP and EBP

Cut vol\% = 39.1 - 37.77 = 1.33%
Cut mid volume = 38.435

Substituting the cut mid volume in equation (18.2) to get API = 30.0

Cut volume = 0.0133(100,000) = 1330 BPD
Cut amount = 1330(12.77) = 16,984 lb/h

---

**Table 18.1 TBP-vol\% analysis**

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Cut temp. (°F)</th>
<th>vol%</th>
<th>SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>86</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>122</td>
<td>0.5</td>
<td>0.6700</td>
</tr>
<tr>
<td>2</td>
<td>167</td>
<td>1.2</td>
<td>0.6750</td>
</tr>
<tr>
<td>3</td>
<td>212</td>
<td>1.6</td>
<td>0.7220</td>
</tr>
<tr>
<td>4</td>
<td>257</td>
<td>2.7</td>
<td>0.7480</td>
</tr>
<tr>
<td>5</td>
<td>302</td>
<td>3.1</td>
<td>0.7650</td>
</tr>
<tr>
<td>6</td>
<td>347</td>
<td>3.9</td>
<td>0.7780</td>
</tr>
<tr>
<td>7</td>
<td>392</td>
<td>4.7</td>
<td>0.7890</td>
</tr>
<tr>
<td>8</td>
<td>437</td>
<td>5.7</td>
<td>0.8010</td>
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<tr>
<td>9</td>
<td>482</td>
<td>8.0</td>
<td>0.8140</td>
</tr>
<tr>
<td>10</td>
<td>527</td>
<td>10.7</td>
<td>0.8250</td>
</tr>
<tr>
<td>11</td>
<td>584</td>
<td>5.0</td>
<td>0.8450</td>
</tr>
<tr>
<td>12</td>
<td>636</td>
<td>10.0</td>
<td>0.8540</td>
</tr>
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<td>13</td>
<td>689</td>
<td>7.8</td>
<td>0.8630</td>
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<tr>
<td>14</td>
<td>742</td>
<td>7.0</td>
<td>0.8640</td>
</tr>
<tr>
<td>15</td>
<td>794</td>
<td>6.5</td>
<td>0.8890</td>
</tr>
<tr>
<td>Residuum</td>
<td>–</td>
<td>20.8</td>
<td>0.9310</td>
</tr>
</tbody>
</table>
Calculation of sulphur content:
\[ M = 42.965[\exp(2.097 \times 10^{-4} T_b - 7.78712 \text{ SG} + 2.08476 \times 10^{-3} T_b \text{ SG})] \]
\[ T_b^{1.26007}\text{ SG}^{4.98308} \]

\[ T_b = ((580 + 650)/2 - 32)/1.8 + 273 = 597 \text{ K} \]

\[ \text{ SG} = 0.83 \]

\[ M = 265\text{ lb/lb mol} \]

\[ I = 2.266 \times 10^{-2}\exp(3.905 \times 10^{-4} T_b + 2.468\text{ SG} - 5.704 \times 10^{-4} T_b \text{ SG}) \]
\[ T_b^{0.0572}\text{ SG}^{-0.72} = 0.2757 \]

\[ n = \left( \frac{1 + 2I}{1 - I} \right)^{1/2} = 1.4635 \]

\[ R_i = n - \frac{d}{2} = 1.0485 \]

\[ m = M(n - 1.475) = -3.0475 \]

since \( M > 200 \)

\[ \text{sulphur wt\%} = -58.02 + 38.463 R_i - 0.023 m + 22.4 \text{ SG} = 3.3 \text{ wt\%} \]

\[ \text{sulphur amount} = 0.033(16,984) = 560.5 \text{ lb/h} \]

Considering the naphtha hydrotreater unit:

\[ K = \left( \frac{T_b}{\text{ SG}} \right)^{1/3} = \left( \frac{190 + 380}{2} + 460 \right)^{1/3}/0.812 = 11.164 \]

\[ \text{SCFB H}_2 = 191 S_f - 30.7 = 191(1.36) - 30.7 = 229.06 \text{ SCFB} \]

Since the feed is 7134 BPD:

Required hydrogen is 359.3 lb/h

\[ \Delta \text{API}_p = 0.01(\text{SCFB H}_2) + 0.036(\text{API}_f) - 2.69 = 1.1288 \]

\[ \text{API}_p = 42.45 + 1.1288 = 43.58 \]

\[ \text{Paraffin vol\%} = 12.8K_f^2 - 229.5K_f + 1330 = 28.27 \]

\[ \text{Naphthenes vol\%} = -78.5K_f^2 + 1776.6K_f - 9993.7 = 56.42 \]

\[ \text{Aromatics vol\%} = 38.4K_f^2 - 894.3K_f + 5219.4 = 21.414 \]

Normalizing: \(P\ vol\% = 26.64, \ N\ vol\% = 53.8, \ A\ vol\% = 20.18\)
Considering the reformer unit:

Reformer feed = 7134 BPD

API = 43.58

Amount of feed to reformer = 7134(11.79) = 84,110 lb/h

\[ C_5^+ \text{vol}\% = 142.7914 - 0.77033 \times \text{RON}_R + 0.219122 \times (N + 2.4)_F \]

\[ = 142.7914 - 0.77033 \times 97 + 0.219122 \times (53.8 + 2(20.18)) \]

\[ = 90.876 \]

\[ H_2 \text{wt}\% = -12.1641 + 0.06134 \times C_5^+ \text{vol}\% + 0.099482 \times \text{RON}_R = 2.76 \]

\[ C_1 \text{wt}\% = 11.509 - 0.125 \times C_5^+ \text{vol}\% = 0.1495 \]

\[ C_2 \text{wt}\% = 16.496 - 0.1758 \times C_5^+ \text{vol}\% = 0.52 \]

\[ C_3 \text{wt}\% = 24.209 - 0.2565 \times C_5^+ \text{vol}\% = 0.9 \]

\[ C_4 \text{wt}\% = 27.024 - 0.2837 \times C_5^+ \text{vol}\% = 1.243 \]

\[ nC_4 \text{wt}\% = 0.585 \times \text{total C}_4 \text{wt}\% = 0.727 \]

\[ iC_4 \text{wt}\% = 0.415 \times \text{total C}_4 \text{wt}\% = 0.516 \]

Hydrogen produced = 0.0276 (84,110) = 2321 lb/h > 359.3 lb/h, this means that the hydrogen produced in the reformer is more than the required hydrogen in the hydrotreating reformer feed.

Considering the gas oil hydrotreater unit:

Middle distillate HT

\[ \text{SCFB H}_2 = 110.8 S_f + 10.2 (\text{HDS}\%) - 659 \]

Assume 100% severity of the hydrotreater

\[ \text{SCFB H}_2 = 110.8(3.3) + 10.2(100) - 659 = 726.64 \text{ SCFB} \]

Since the feed is 1330 BPD:

Amount of H\(_2\) required = 212.5 lb/h (This can be supplied from the reformer unit.)

\[ \Delta \text{API}_p = 0.00297(\text{SCFB H}_2) - 0.11205(\text{API}_f) + 5.5419 = 4.3385 \]

\[ \text{API}_p = 30 + 4.3385 = 34.3385 \]

Feed to FCC = 1330(12.45) = 16,559 lb/h

Considering the FCC unit:

Conversion = 75%
Coke wt% = 0.05356 \times \text{CONV} - 0.18598 \times \text{API} + 5.966975 = 3.5977
LCO LV = 0.0047 \times \text{CONV}^2 - 0.8564 \times \text{CONV} + 53.576 = 15.7835
Gases wt% = 0.0552 \times \text{CONV} + 0.597 = 4.737
Gasoline LV% = 0.7754 \times \text{CONV} - 0.7778 = 57.3772
iC_4 LV% = 0.0007 \times \text{CONV}^2 + 0.0047 \times \text{CONV} + 1.40524 = 5.7
nC_4 LV% = 0.0002 \times \text{CONV}^2 + 0.019 \times \text{CONV} + 0.0476 = 2.6
C_4= LV% = 0.0993 \times \text{CONV} - 0.1556 = 7.3
C_3 LV% = 0.0436 \times \text{CONV} - 0.8714 = 2.4
C_3= LV% = 0.0003 \times \text{CONV}^2 + 0.0633 \times \text{CONV} + 0.0143 = 6.45
Gasoline API = -0.19028 \times \text{CONV} + 0.02772 \times (\text{Gasoline LV%})
+64.08 = 51.4
LCO API = -0.34661 \times \text{CONV} + 1.725715 \times (\text{Feed API}) = 33.26

<table>
<thead>
<tr>
<th>Products</th>
<th>BPD</th>
<th>(lb/h)/BPD</th>
<th>lb/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases</td>
<td>784.4</td>
<td>784.4</td>
<td></td>
</tr>
<tr>
<td>iC_4</td>
<td>75.81</td>
<td>8.22</td>
<td>623.2</td>
</tr>
<tr>
<td>nC_4</td>
<td>34.58</td>
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<td>294.3</td>
</tr>
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<td>C_4=</td>
<td>97.1</td>
<td>8.76</td>
<td>850.5</td>
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<tr>
<td>C_3</td>
<td>31.9</td>
<td>7.42</td>
<td>237</td>
</tr>
<tr>
<td>C_3=</td>
<td>85.8</td>
<td>7.61</td>
<td>653</td>
</tr>
<tr>
<td>Gasoline</td>
<td>763</td>
<td>11.29</td>
<td>8614.3</td>
</tr>
<tr>
<td>LCO</td>
<td>210</td>
<td>12.53</td>
<td>2631.2</td>
</tr>
<tr>
<td>HCO</td>
<td>1275.3</td>
<td>1275.3</td>
<td></td>
</tr>
<tr>
<td>Coke</td>
<td>595.7</td>
<td>595.7</td>
<td></td>
</tr>
</tbody>
</table>

1050+ °F cut
Substituting in equation (18.1) to get LV% at IBP and EBP
Cut vol% = 100 - 44.9 = 55.1%
Cut mid volume = 72.45
Substituting the cut mid volume in equation (18.2) to get API = 16.45
Cut volume = 0.551(100,000) = 55,100 BPD
Cut amount = 55,100(13.96) = 769,196 lb/h

Considering the delayed coker unit:

\[ \text{Gas}(\text{C}_4^-) \text{wt\%} = 7.8 + 0.144 \times (\text{wt\% CCR}) = 9.528 \]
\[ \text{Naphtha wt\%} = 11.29 + 0.343 \times (\text{wt\% CCR}) = 15.406 \]
\[ \text{Coke wt\%} = 1.6 \times (\text{wt\% CCR}) = 19.2 \]
\[ \text{Gas oil wt\%} = 100 - \text{wt\% Gas} - \text{wt\% Naphtha} - \text{wt\% Coke} = 55.866 \]

Amount of gases produced = 0.09528(769,196) = 73,289 lb/h

Assume the average molecular weight for the gases is 22.12 lb/lbmol

\[ \text{Gases} = 73,289/22.12 = 3313 \text{ lbmol/h} \]
\[ \text{C}_4 = 0.024(3313)(56) = 4453 \text{ lb/h} \]
\[ \text{iC}_4 = 0.01(3313)(58) = 1922 \text{ lb/h} \]
\[ \text{nC}_4 = 0.026(3313)(58) = 4996 \text{ lb/h} \]

Considering the alkylation unit:

Amount of olefins = C_4^- \text{ coker} + C_4^- \text{ FCC}
\[ = 4453 + 850.5 = 53035 \text{ lb/h} \]

Amount of iC_4 = iC_4 \text{ coker} + iC_4 \text{ FCC} + iC_4 \text{ Reformer}
\[ = 1922 + 623.2 + 611.5 = 3156.71 \text{ b/h} \]
\[ \frac{\text{lb iC}_4}{\text{lb olefin}} = 1.1256 \]

Required iC_4 = 1.1256(5303.5) = 5969.6 lb/h

Make-up iC_4 = 5969.6 - 3156.7 = 2813 lb/h

BPD olefin = 5303.5/8.76 = 605.42 BPD

\[ \text{BPD} \text{ iC}_4 = \frac{5969.6}{8.22} = 726.23 \text{ BPD} \]

Total feed to alkylation = 605.42 + 726.23 = 1331.65 BPD

Volume of product = 1331.65/1.2 = 1109.71 BPD

Alkylate amount produced = 0.8236(1109.71) = 914 BPD

Summary of the case:

Total gasoline produced = Coker gasoline + FCC gasoline + reformer gasoline
\[ = 0.15406(769,196) + 8614.3 + 0.90876(7134)(11.37) \]
\[ = 118,502 + 8614.3 + 73,712.7 \]
\[ = 200,829 \text{ lb/h} \]