**Hydrotreating**

Hydrotreating achieves the following objectives:

- Removing impurities, such as sulphur, nitrogen and oxygen for the control of a final product specification or for the preparation of feed for further processing (naphtha reformer feed and FCC feed);
- Removal of metals, usually in a separate guard catalytic reactor when the organo-metallic compounds are hydrogenated and decomposed, resulting in metal deposition on the catalyst pores (e.g. atmospheric residue desulphurization (ARDS) guard reactor); and,
- Saturation of olefins and their unstable compounds.

**Role of Hydrotreating**

Hydrotreating units are needed in the refinery to clean streams from material such as sulphur, nitrogen or metals harmful to the catalysts. That is why they are located before the reformer, hydrocracker and FCC as shown in Figure below.
They are also needed to adjust the final product specification for various streams, such as light naphtha, kerosene and low sulphur fuel oils (LSFOs). Hence, the main role of hydrotreating can be summarized as follows:

1. Meeting finished product specification.
   - Kerosene, gas oil and lube oil desulphurization.
   - Olefin saturation for stability improvement.
   - Nitrogen removal.
   - De-aromatization for kerosene to improve cetane number, which is the percentage of pure cetane in a blend of cetane and alpha-methyl-naphthalene. The latter matches the ignition quality of kerosene sample.

2. Feed preparation for downstream units:
   - Naphtha is hydrotreated for removal of metal and sulphur.
   - Sulphur, metal, polyaromatics and Conradson carbon removal from vacuum gas oil (VGO) to be used as FCC feed.
   - Pretreatment of hydrocracking feed to reduce sulphur, nitrogen and aromatics.

**Hydrotreating reactions**

1. Desulphurization
   a. Mercaptanes:

   \[
   \text{RSH} + H_2 \rightarrow \text{RH} + H_2S
   \]

   b. Sulphides:

   \[
   \text{R}_2\text{S} + 2H_2 \rightarrow 2\text{RH} + H_2S
   \]

   c. Disulphides:

   \[
   (\text{RS})_2 + 3H_2 \rightarrow 2\text{RH} + 2H_2S
   \]

d. Thiophenes:

   \[
   \begin{align*}
   \text{HC} & \quad \text{CH} \\
   & \quad \text{HC} \quad \text{CH} \\
   S & \quad \text{CH}
   \end{align*} + 4H_2 \rightleftharpoons \text{C}_4\text{H}_{10} + H_2S
   \]

2. Denitrogenation
   a. Pyrrole:

   \[
   \text{C}_4\text{H}_4\text{NH} + 4H_2 \rightarrow \text{C}_4\text{H}_{10} + \text{NH}_3
   \]

   b. Pyridine:

   \[
   \text{C}_3\text{H}_5\text{N} + 5H_2 \rightarrow \text{C}_3\text{H}_{12} + \text{NH}_3
   \]
3. Deoxidation
   a. Phenol:
\[ C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O \]
   b. Peroxides:
\[ C_7H_{13}OOH + 3H_2 \rightarrow C_7H_{16} + 2H_2O \]
4. Hydrogenation of chlorides
\[ RCl + H_2 \rightarrow RH + HCl \]
5. Hydrogenation of olefins
\[ C_5H_{10} + H_2 \rightarrow C_5H_{12} \]
6. Hydrogenation of aromatics
\[ C_6H_6 + 3H_2 \rightarrow \text{Cyclohexane} \]
\[ \text{Naphthalene} + H_2 \rightarrow \text{Tetraline} \]

7. Hydrogenation of organo-metallic compounds and deposition of metals

8. Coke formation by the chemical condensation of polynuclear radicals

Hydrotreating Catalysts
The hydrotreating catalyst is a porous alumina matrix impregnated with combinations of cobalt (Co), nickel (Ni), molybdenum (Mo) and tungsten (W). The reactivities of each catalyst are given in Table below:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Hydro-de sulphurization</th>
<th>Hydro-denitrogenation</th>
<th>Aromatics hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–Mo/Alumina</td>
<td>Excellent</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>Ni–Mo/Alumina</td>
<td>Very good</td>
<td>Very good</td>
<td>Good</td>
</tr>
<tr>
<td>Ni–W/Alumina</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
Hydrotreating Processes

Hydrotreating processes are similar in common elements and in general can be represented as shown in Figure below. The liquid feed is mixed with hydrogen and fed into a heater and the mixture is brought to the reaction temperature in a furnace and then fed into a fixed bed catalytic reactor. The effluent is cooled and hydrogen-rich gas is separated using a high pressure separator. Before the hydrogen is recycled, hydrogen sulphide can be removed using an amine scrubber. Some of the recycle gas is also purged to prevent the accumulation of light hydrocarbons (C1 – C4) and to control hydrogen partial pressure. The liquid effluent for the reactor is introduced to a fractionator for product separation.

![Diagram of hydrotreating process](image_url)

The main elements of a hydrotreating process

Make-up Hydrogen

A certain hydrogen partial pressure should be maintained in the reactors by recycling un-reacted hydrogen and adding a make-up hydrogen to compensate for the amount consumed. The make-up hydrogen can be calculated by the following expression:

\[
\text{Make-up hydrogen} = \text{hydrogen in feed} - \text{hydrogen consumed for chemical requirement} - \text{hydrogen purged} - \text{amount of hydrogen dissolved in product}
\]

Hydrogen purge is the amount of hydrogen lost with the purging of light hydrocarbons (C1-C4) and hydrogen sulphide (if not removed by amine treatment). This hydrogen can be predicted using flash calculation, or using the purge gas ratio. The purge ratio is defined as:

\[
\text{Purge ratio} = \frac{\text{volume of hydrogen in the purged gas}}{\text{volume of hydrogen in the make-up gas}}
\]

Operating Conditions

The operating conditions of the hydrotreating processes include pressure, temperature, catalyst loading, feed flow rate and hydrogen partial pressure. The hydrogen partial pressure must be greater than the hydrocarbon partial pressure. Increasing hydrogen partial pressure improves the removal of sulphur and nitrogen compounds and reduces coke formation. Higher temperatures will increase the reaction rate constant and improve the kinetics.
However, excessive temperatures will lead to thermal cracking and coke formation. The space velocity is the reverse of reactor residence time. High space velocity results in low conversion, low hydrogen consumption and low coke formation. The range of operating conditions for hydrotreating of different feed fractions is given in Table below.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Naphtha</th>
<th>Kerosene</th>
<th>Gas oil</th>
<th>Vacuum gas oil</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen pressure, bar</td>
<td>5–10</td>
<td>15–30</td>
<td>15–40</td>
<td>40–70</td>
<td>120–160</td>
</tr>
<tr>
<td>Hydrogen consumption, wt%</td>
<td>0.05–.1</td>
<td>0.1–0.2</td>
<td>0.3–0.5</td>
<td>0.4–0.7</td>
<td>1.5–2.0</td>
</tr>
</tbody>
</table>

*NLSV = Liquid volumetric flow rate at 15°C [ft³/h]/Volume of catalyst [ft³]

**Naphtha and Gas Oil Hydrotreating Correlations**

The standard cubic foot of hydrogen per barrel of feed (SCFB) required for complete sulphur removal is calculated as:

\[
\text{SCFB } H_2 = 191 S_f - 30.7
\]

Where \( S_f \) is the sulphur wt% in feed.

The increase in the API gravity of a product is calculated as:

\[
\Delta(\text{API})_p = 0.01 \times (\text{SCFB } H_2) + 0.036 \times (\text{API})_f - 2.69
\]

Where \( p \) and \( f \) refer to product and feed, respectively. In some cases, if it is required to saturate aromatics and naphthenes to the corresponding paraffin, a set of correlations for PNA analysis is required to predict the naphtha composition. These are:

\[
\text{Vol} \% \text{ Paraffins} = 12.8K_f^2 - 259.5K_f + 1330.0
\]

\[
\text{Vol} \% \text{ Naphthene} = -78.5K_f^2 + 1776.6K_f - 9993.7
\]

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

Where \( K_f \) is the feed Watson characterization factor.

**Example:**

It is required to hydrotreat naphtha which has 1 wt% S and API = 50. Find: a) How much hydrogen is required to remove all the sulphur in the feed by empirical correlations? b) How much of this \( H_2 \) is used for chemical requirements. c) If the mean average boiling point of this naphtha is 135 F and assuming that the naphthenic and aromatic present in the naphtha are cyclohexane and benzene, respectively. Find the volume of hydrogen (SCFB) to convert all cyclohexane and benzene into hexane.
Solution:
Assume a basis of one bbl naphtha feed

a. Hydrogen required for desulphurization:

$$\text{SCFB } H_2 = 191(1) - 30.7 = 160.3$$

Hydrogenated naphtha API:

$$\Delta (\text{API})_P = 0.01(160.3) + 0.036(50) - 2.69 = 0.7$$
$$\text{(API)}_P = 50 + 0.7 = 50.7$$

b. To find the chemical hydrogen required:

For the given feed of API = 50, $\rho = 273$ lb/bbl

Amount of $S = 273 \times 0.01 = 2.73$ lb/bbl

Mole $S = 2.73/32 = 0.0853$ mol/bbl

For reaction $S + H_2 \rightarrow H_2S$

$H_2$ required $= 0.0853$ mol $\times 379 \text{ ft}^3$/mol $= 32.3$ ft$^3$/bbl

(Note: At standard gas condition, 1 lb mol occupies 379 ft$^3$.)

difference in $H_2$ requirement $= 160.3 - 32.3 = 128$ ft$^3$

This difference includes purge and dissolution hydrogen.

c. From API = 50 then $SG = 0.78$

$$K_f = \frac{(135 + 460)^{1/3}}{0.78} = 10.9$$

$\text{Vol}\%$ Paffins(hexane) $= 22.07$ vol$\%$

$\text{Vol}\%$ Naphthenes(cyclohexane) $= 44.33$ vol$\%$

$\text{Vol}\%$ Aromatics(benzene) $= 33.60$ vol$\%$

Hexane does not need $H_2$.

One mole of cyclohexane needs one mole $H_2$:

$$C_6H_{12} + H_2 \rightarrow C_6H_{14}$$

One mole of benzene needs 4 moles $H_2$:

$$C_6H_6 + 4H_2 \rightarrow C_6H_{14}$$

Thus the following Table can be constructed for the calculation of the volume of $H_2$ required to convert cyclohexane and benzene to hexane.

The final amount of $H_2$ required can be summed up as:

$$H_2 \text{ required } = 6.80 \text{ mol } \times 379 \text{ ft}^3/\text{mol} = 2577 \text{ ft}^3/\text{bbl}$$

It can be seen that the amount of hydrogen for naphthenes and aromatics saturation is much higher than that needed for other requirements such as sulphur removal.
Middle Distillate Hydrotreating Correlations

The amount of hydrogen required can be calculated as:

$$ \text{SCF} \ \text{H}_2/\text{bbl} = 110.8 \times (S_f) + 10.2 \times (\text{HDS\%}) - 659.0 $$

Where $S_f$ is the wt% sulphur in the feed and HDS% is the percent of hydrodesulphurization required (degree of severity). The increase in product API is calculated as:

$$ \Delta(\text{API})_p = 0.00297 \times (\text{SCF} \ \text{H}_2/\text{bbl}) - 0.11205 \times (\text{API})_f + 5.54190 $$

This equation is used for feed sulphur content of 0.5–6.0 wt%.

Example:

Gas oil has an API of 30, and a sulphur content of 1.5 wt% is fed into a hydrotreater. It is required to carry out HDS at a severity of 90%. Calculate the hydrogen required and the product API.

Solution:

Assume 1 bbl of GO, API = 30 (306 lb/bbl)
Amount of S in feed = 306 \times 0.015 = 4.6 lb/bbl feed
Total hydrogen required (SCFB H$_2$)

$$ = 110.8(1.5) + 10.2(90) - 659 = 425 \ \text{ft}^3/\text{bbl} $$

$$ \Delta(\text{API})_p = 0.00297(425) - 0.11205(30) + 5.54190 = 3.4 $$

Product API = 30 + 3.4 = 33.4