Hydroprocessing Units

November 2004
Why Hydroprocessing?

BEFORE

CO, NOx, HC, Particulates

NOW
Why Hydroprocessing?

Desulphurisation units become more and more important in refineries.
Why Hydroprocessing?

Market of solid catalysts in refining, (IFP data, 1994)

<table>
<thead>
<tr>
<th>Process</th>
<th>Tons / Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic cracking</td>
<td>440,000</td>
</tr>
<tr>
<td>Hydroprocessing</td>
<td>80,000</td>
</tr>
<tr>
<td>Claus</td>
<td>20,000</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td>8,000</td>
</tr>
<tr>
<td>Reforming</td>
<td>5,000</td>
</tr>
<tr>
<td>Isomerization</td>
<td>1,000</td>
</tr>
<tr>
<td>Other</td>
<td>12,000</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>566,000</strong></td>
</tr>
</tbody>
</table>

More than 80% of refined molecules see at least one catalyst in their liver!
Hydroprocessing Units Layout in a Refinery Scheme
Hydroprocessing Units Layout in a Refinery Scheme

- Atmospheric Distillation
- Crude
- HDT
- Hydrodesulphurisation (HDS)
- Vacuum Distillation
- Visbreaking
- Catalytic Cracker (FCC)
- Amine wash
- Reforming
- Hydrogen (H2)
- Propane butane
- Naphtha
- Gasoline
- Kerosene
- Diesel
- Heavy fuel
### Typical operating conditions of Hydrodesulphurisation Units

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Flowrate/catalyst volume (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naptha</td>
<td>7-30</td>
<td>280-320</td>
<td>3-10</td>
</tr>
<tr>
<td>Kerosene</td>
<td>15-50</td>
<td>300-330</td>
<td>2-6</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>15-90</td>
<td>320-390</td>
<td>1-4</td>
</tr>
<tr>
<td>VGO</td>
<td>30-100</td>
<td>340-410</td>
<td>1-2</td>
</tr>
<tr>
<td>ARDS</td>
<td>80-200</td>
<td>370-410</td>
<td>0.2-0.5</td>
</tr>
<tr>
<td>VGO, residue hydrocracker</td>
<td>100-200</td>
<td>370-410</td>
<td>0.5-1.5</td>
</tr>
</tbody>
</table>

- The most important parameters followed in these units (apart from product qualities!) are the temperature and unit pressure drop.

- The difference on activity and stability of different catalysts is measured by °C.
### Chemical Reactions in Hydroprocessing

#### Hydrogen consumption

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction</th>
<th>$\Delta H$ (kcal . mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercaptans</td>
<td>$R-SH + H_2 \rightarrow RH + H_2S$</td>
<td>$-17$</td>
</tr>
<tr>
<td>Sulfides</td>
<td>$R-S-R' + 2H_2 \rightarrow R-H + R'-H + H_2S$</td>
<td>$-28$</td>
</tr>
<tr>
<td>Thiophane</td>
<td>$\begin{array}{c}S \ \hline \end{array} + 2H_2 \rightarrow C_4H_{10} + H_2S$</td>
<td>$-29$</td>
</tr>
<tr>
<td>Thiophene</td>
<td>$\begin{array}{c}S \ \hline \end{array} + 4H_2 \rightarrow C_4H_{10} + H_2S$</td>
<td>$-67$</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>$\text{[image]} + 5H_2 \rightarrow \text{[image]} + H_2S$</td>
<td></td>
</tr>
</tbody>
</table>

**Refractory compound**

Not limited by thermodynamics
Chemical Reactions in Hydroprocessing
Chemical Reactions in Hydroprocessing

Soufre total = 6 ppm
# Chemical Reactions in Hydroprocessing

<table>
<thead>
<tr>
<th>Amines</th>
<th>R−NH₂</th>
<th>H₂ → RH + NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyrrole</strong></td>
<td><img src="image" alt="Pyrrole" /></td>
<td><img src="image" alt="Pyrrole" /></td>
</tr>
<tr>
<td></td>
<td>2H₂ →</td>
<td>2H₂ →</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Pyrrole" /></td>
<td>C₄H₉NH₂</td>
</tr>
<tr>
<td></td>
<td>H₂ →</td>
<td>H₂ →</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Pyrrole" /></td>
<td>C₄H₁₀ + NH₃</td>
</tr>
<tr>
<td><strong>Pyridine</strong></td>
<td><img src="image" alt="Pyridine" /></td>
<td><img src="image" alt="Pyridine" /></td>
</tr>
<tr>
<td></td>
<td>3H₂ →</td>
<td>H₂ →</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Pyridine" /></td>
<td>C₅H₁₁NH₂</td>
</tr>
<tr>
<td></td>
<td>H₂ →</td>
<td>H₂ →</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Pyridine" /></td>
<td>C₅H₁₂ + NH₃</td>
</tr>
<tr>
<td><strong>Carbazole</strong></td>
<td><img src="image" alt="Carbazole" /></td>
<td><img src="image" alt="Carbazole" /></td>
</tr>
<tr>
<td></td>
<td>H₂ →</td>
<td>H₂ →</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Carbazole" /></td>
<td><img src="image" alt="Carbazole" /></td>
</tr>
<tr>
<td></td>
<td>H₂ →</td>
<td><img src="image" alt="Carbazole" /></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Carbazole" /></td>
<td><img src="image" alt="Carbazole" /></td>
</tr>
<tr>
<td><strong>Quinoline</strong></td>
<td><img src="image" alt="Quinoline" /></td>
<td><img src="image" alt="Quinoline" /></td>
</tr>
<tr>
<td></td>
<td>2H₂ →</td>
<td>2H₂ →</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Quinoline" /></td>
<td><img src="image" alt="Quinoline" /></td>
</tr>
<tr>
<td></td>
<td>H₂ →</td>
<td><img src="image" alt="Quinoline" /></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Quinoline" /></td>
<td><img src="image" alt="Quinoline" /></td>
</tr>
</tbody>
</table>
Chemical Reactions in Hydroprocessing

* Partially hydrogenated intermediates

HDAr

HDS

C_{29}H_{59} - S - CH_{2} \xrightarrow{H_{2}} C_{29}H_{60} + H_{3}C - CH_{2} + H_{2}S

HDN

C_{3}H_{7} \xrightarrow{H_{2}} C_{3}H_{7} + NH_{3}
Chemical Reactions in Hydroprocessing
Chemical Reactions in Hydroprocessing

- Hydroprocessing reactions are exothermic
- Temperature and pressure are needed for hydroprocessing reactions
- Reactor delta temperature:
  8-9°C rise per 1 wt% sulphur removal
  1-2°C rise per 1 vol% of polyaromatics removal
  1°C rise per bromine number removal
Simplified Scheme of an Hydrodesulphurisation Unit

- Raw feed
- Make-up compressor
- Heat Exchangers
- Furnace
- Partial by-pass
- Recycle compressor
- H.P. Flash drum
- Stripper
- Air coolers
- Quench
- Make-up hydrogen to fuel gas
Hydroprocessing reactor and internals

- Inlet diffuser
- Catalyst bed
  - Varies between 3 to 15 m
- Catalyst support grid
- Mixing chamber
- Quench distributor
- Vapor/liquid distribution tray
- Reactor diameter varies between 1.5 to 4.5 m
- Unloading nozzle
- Outlet collector
Hydroprocessing Reactor and Internals

Catalyst bed

reactor outlet collector
Hydroprocessing Reactor and Internals
Hydroprocessing Reactor and Internals

What techniques can be used to check the gas-liquid distribution inside the reactor?

Radial temperature dispersion
Radioactive tracers
Unit start-up
Unit response to flow variations
Hydroprocessing Catalysts

- Generally HDS catalysts are constituted by metal oxides from columns VIA (Mo,W) and VIIIA ((Co),Ni) periodic table
- The active phase of HDS catalysts consists in the sulphided form of these oxides – MoS$_2$ slabs
- Co or Ni are activity promoters and ‘decorate’ the edge of MoS$_2$ slabs
- CoMo catalysts are generally used for low pressure units and were the main objective are HDS reactions
- NiMo catalysts are generally used for higher pressure units and were the main objective is density and cetane gain (hydrogenation reactions)
Hydroprocessing Catalysts

Fresh CoMo catalyst 1.2-2.5 mm
Oxide state

Used catalyst
Sulphide + coke

Regeneration of used catalyst is possible by carefully burning sulphur and coke. The resulting catalyst will be in its oxide form.
Hydroprocessing Catalyst’s Life

Were should I go on holidays?
Why not a reactor of a diesel hydrotreater?

Let’s do it again

Nice staying here, it’s always hot!
however, it’s also always raining and it smells!!

Unloading under inert atmosphere as I’m quite keen to react with air

Spent Catalyst
Hot Air

Rotary Kiln
Oven

Catalyst loading
Catalyst Loading

Main advantages of dense loading:
- Faster and safer loading
- Homogeneous loading (no channeling)
- More active material in a given volume

Gain in catalyst loading density of:
- Beads: up to 10%
- Extrudates: up to 20%

SOR pressure drop increases but remain more stable during the cycle.
Catalyst loading
Catalyst loading

Catalyst bed grading must be adapted in order to avoid pressure drop build-up
Different particles are available to be loaded above the main catalyst and minimize pressure drop build-up.
Catalyst Activation

Oxide catalyst MoO₃ reactor

- Reduction to MoO₂ Unactive phase
  - Under H₂ T > 230-250°C

Active catalyst MoS₂ reactor

- In situ Sulphidation
- H₂ Activation
- Final step

‘preSulphided’ MoOxSy ex situ

‘preSulphiding’ Sulficat, Acticat, EasyActive

Oxide catalyst MoO₃ ex situ

Active catalyst MoS₂ ex situ

ex situ sulphiding Totsucat, XpresS

H₂S

DMDS
1. Catalyst wetting at lower temperature allows better gas-liquid distribution
2. The drying step should always be below 150°C to avoid molybdenum oxide reduction
3. DMDS injection 1 hour before reaching presulphiding step
4. Maximum reactor exotherm should be below 15°C to avoid high catalyst temperatures in without H₂S
5. Catalyst sulphiding step temperature depends on catalyst type and unit operation
Kinetic Models

\[
\frac{d[S]}{dt} = -k \times [S]
\]

\[
\int_{S_{in}}^{S_{out}} \frac{d[S]}{[S]} = -\int_{0}^{t_c} k \, dt \iff \int_{S_{in}}^{S_{out}} \frac{d[S]}{[S]} = \int_{0}^{t_c} k \, dt
\]

\[
\ln\left(\frac{S_{in}}{S_{out}}\right) = k \times t_c = \frac{k_0 \times e^{\frac{E_{act}}{R \times T}}}{LHSV}
\]

\[
T = -\frac{E_{act}}{R \times \ln\left(\frac{\ln(S_{in} / S_{out}) \times LHSV}{k_0}\right)}
\]
Kinetic Models

Typically, for HDS reactions on diesel and VGO
Eact = 25000 - 29000 cal/mole
Example - Catalyst volume = 200 m³

Catalyst A
Flowrate = 300 m³/h
Bed 1 Tin = 345°C, Tout = 365°C, Bed 2 Tin = 360°C, T = 370°C
WABT = 362,5°C
Sin = 7000 wtppm
Sout = 40 wtppm
k₀ = 1,5E10 h⁻¹

Catalyst B
Flowrate = 280 m³/h
Bed 1 Tin = 342°C, Tout = 362°C, Bed 2 Tin = 352°C, T = 362°C
Sin = 7000 wtppm
Sout = 33 wtppm
WABT = 359,9°C
k₀ = 1,4E10 h⁻¹

Catalyst A is 2°C more active than catalyst B
(this value is higher with more precise models!)
Kinetic Models - Cycle Length

Other parameters that must be taken into account in the kinetic models are:
- hydrogen partial pressure
- feed severity (nitrogen, density, aromatics, T95, other)
- hydrogen/oil ratio, hydrogen sulphide and ammoniac partial pressure
Kinetic Models - Cycle Length

Poor catalyst performance

High pressure drop

Feed rate

Max temp

Temperature

Cycle length

Time

Feed rate

Max temp

Temperature

Cycle length

Time
- Average Reactor Temperature = \( \frac{1}{3} \) inlet \( T \) + \( \frac{2}{3} \) outlet \( T \)
- Temperature increase with time due to coke formation and poisons adsorption
- 3.5°C/month deactivation
- Normalized temperature allows to correct for unit conditions and feed variations
- Assessment of the real performances of the unit and the catalyst are much more precise
Advantages: higher H2% in recycle gas, simpler, light feeds can be processed

Disadvantages: lower energy efficiency, larger high pressure separator
Hydroprocessing Unit
Hot Scheme

Advantages: better energy efficiency, no need for stripper feed heating (most cases)

Disadvantages: need for recycle gas amine wash, loss of hydrogen
Hydroprocessing Unit
Stripping section

The objective of the stripping section is to removed light ends from the diesel (H2S, CH’s) and/or to remove products lighter than the unit main product.
**Hydroprocessing Units**

**Gasoline hydrotreaters**

In general, the objective of the gasoline hydrotreaters is to remove sulphur and nitrogen from reformer or isomerization feeds. Indeed, sulphur and nitrogen will poison and degrade the performances of reforming and isomerization catalysts.

Gasoline hydrotreaters operate on 100% gaz phase, there is no need for distribution trays.

**Kerosene and Diesel hydrotreaters**

The objective of the diesel hydrotreaters is to remove sulphur, reduce density and improve cetane index. In the case of kerosene hydrotreaters, the objective is also to respect aromatics specification (naphthalenes and smoke point).

Diesel hydrotreaters operate in gas/liquid phase – reactor needs good distribution trays.

**Vacuum Gasoil hydrotreaters**

The objective of the VGO hydrotreaters is to remove sulphur and nitrogen to prepare the FCC feed. The objective is to be able to produce 10 wtppm S gasoline and to improve FCC yields.

VGO hydrotreaters operate in gas/liquid phase – reactor needs good distribution trays.
## Hydroprocessing Units

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Effluent</th>
<th>Process conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gasoline</td>
<td>Kerosene</td>
<td>diesel</td>
</tr>
<tr>
<td></td>
<td>LCO</td>
<td>VGO</td>
<td></td>
</tr>
<tr>
<td>Sulfur (wt%)</td>
<td>0.002-0.08</td>
<td>0.1-0.2</td>
<td>0.1-1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5-2.2</td>
</tr>
<tr>
<td></td>
<td>1.2-3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen (wtppm)</td>
<td>1.40</td>
<td>1.20</td>
<td>50-400</td>
</tr>
<tr>
<td></td>
<td>400-1000</td>
<td>800-2000</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>0.70-0.75</td>
<td>0.75-0.80</td>
<td>0.82-0.87</td>
</tr>
<tr>
<td></td>
<td>0.90-0.95</td>
<td>0.91-0.96</td>
<td></td>
</tr>
<tr>
<td>Initial Boiling Point (°C)</td>
<td>20-70</td>
<td>170-190</td>
<td>180-230</td>
</tr>
<tr>
<td></td>
<td>320-350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final Boiling Point (°C)</td>
<td>170-210</td>
<td>240-270</td>
<td>340-370</td>
</tr>
<tr>
<td></td>
<td>570-590</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur (wtppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt; 0.5</td>
<td>-</td>
<td>2.50</td>
</tr>
<tr>
<td>Nitrogen (wtppm)</td>
<td></td>
<td></td>
<td>1000-2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400-1200</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>290-320</td>
<td>290-330</td>
<td>330-390</td>
</tr>
<tr>
<td>Reactor exotherm (°C)</td>
<td>0-30</td>
<td>5</td>
<td>15-30</td>
</tr>
<tr>
<td>Pressure (bara)</td>
<td>7.30</td>
<td>15-50</td>
<td>15-90</td>
</tr>
<tr>
<td></td>
<td>30-70</td>
<td>30-90</td>
<td>30-100</td>
</tr>
<tr>
<td>Pressure drop (bara)</td>
<td>2.4</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>LHSV (hr⁻¹)</td>
<td>3.10</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>H₂/oil ratio (Nm³/m³)</td>
<td>50-90</td>
<td>70-120</td>
<td>70-250</td>
</tr>
<tr>
<td></td>
<td>250-450</td>
<td>75-120</td>
<td></td>
</tr>
<tr>
<td>H₂ cons. (Nm³/m³)</td>
<td>0-20</td>
<td>10-20</td>
<td>20-60</td>
</tr>
<tr>
<td></td>
<td>100-150</td>
<td>200-500</td>
<td></td>
</tr>
<tr>
<td>Cracking (wt%)</td>
<td></td>
<td>3.5</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15-35</td>
<td></td>
</tr>
<tr>
<td>Vaporized feed in reactor (wt%)</td>
<td>100</td>
<td>70</td>
<td>10-50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-50</td>
<td>5</td>
</tr>
</tbody>
</table>
Kinetic Models

\[
\frac{d[S]}{dt} = -k \times [S]^n, \quad n > 1
\]

\[
\int_{S_{in}}^{S_{out}} \frac{d[S]}{[S]^n} = -\int_0^{tc} k \, dt \iff \int_{S_{out}}^{S_{in}} \frac{d[S]}{[S]^n} = \int_0^{tc} k \, dt
\]

\[
\frac{1}{n-1} \times \left[ \frac{1}{S_{out}^{n-1}} - \frac{1}{S_{in}^{n-1}} \right] = k \times tc = \frac{k_0 \times e^{\frac{E_{act}}{R \times T}}}{\text{LHSV}}
\]

\[
T = -\frac{E_{act}}{R \times \ln \left( \frac{1}{n-1} \times \left[ \frac{1}{S_{out}^{n-1}} - \frac{1}{S_{in}^{n-1}} \right] \times \text{LHSV} / k_0 \right)}
\]