3

PROCESSES RELATED TO ENVIRONMENTAL ISSUES
3.1.1 Introduction

The term hydrotreating designates a vast number of catalytic hydrogenation processes widely used in the refining industry, for purposes ranging from the saturation of both olefinic and aromatic hydrocarbons to the removal of undesired elements (sulphur, nitrogen, oxygen and metals) from various petroleum fractions.

Whereas in saturation reactions the hydrogen/carbon ratio of the molecule involved is simply increased, in the reactions eliminating the undesired element the species in question is transformed into a hydrocarbon, undergoing more or less minor modifications in its molecular structure, and losing the heteroatom in the form of simple inorganic species:

\[
\begin{align*}
R \ce{==CH-CH2+H2} & \rightarrow R \ce{==CH2-CH3} \\
R \ce{==SH+H2} & \rightarrow RH+H2S \\
R \ce{==NH2+H2} & \rightarrow RH+NH3 \\
R \ce{==OH+H2} & \rightarrow RH+H2O
\end{align*}
\]

where \( R \) indicates a hydrocarbon portion of the molecules.

Hydrotreating is the most widespread class of catalytic processes in the refining industry; it differs from hydrocracking, which instead affects the structure of the molecule through cracking and isomerization reactions. Hydrotreating processes serve both to improve the characteristics of the finished product (so as to respect commercial and environmental specifications), and to prepare the feed for other processes where catalysts and operating conditions require the minimum possible presence of sulphur, nitrogen, metals or unsaturated molecules.

The various processes take different names according to the main function they carry out: saturation or hydrogenation (HYD), hydrodesulphurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM), Conradson carbon reduction (CCR). Table 1 shows the main types of hydrotreating processes, together with the main refinery streams that can be subjected to these treatments, while the flow-sheet in Fig. 1 shows how hydrotreating processes (in this case, above all hydrodesulphurization) can be incorporated in a traditional refinery scheme. Hydrotreating of first distillation gasolines serves to prepare the feedstock of the isomerization and reforming processes, practically eliminating sulphur and nitrogen, which act as poisons for catalysts. The purpose of treating kerosene and gas oils with hydrogen is to standardize (by means of desulphurization) the product intended for marketing. The scheme in Fig. 1 does not consider the specific processes for the saturation of aromatics.

Apart from particular cases, sulphur, nitrogen, oxygen and metals are eliminated simultaneously in a single process. As sulphur is the undesired element contained in the largest quantity and most subjected to environmental and commercial constraints, desulphurization reactions are particularly important. As a matter of fact, they often identify in the refinery the relevant hydorefining processes, which in fact take the name of hydrodesulphurization processes in ordinary terminology, even though they also carry out other functions than desulphurization.

3.1.2 Evolution and diffusion of hydrotreating processes

The evolution of environmental sensitivity and of regulations has undergone a progressive acceleration ever since the last two decades of the Twentieth century, with a further intensification in the early years of this century. Gradually more
severe specifications have been introduced for motor vehicle and other fuels, also on the basis of directives that have set precise limits for emissions of motor vehicle exhaust gases (Fig. 2). The Auto-Oil programmes in the United States and in Europe have provided the political decision-makers with an objective assessment of the complex of measures (including fuel quality) necessary to reduce emissions of vehicular traffic.

All this has led to an evolution and to greater diffusion and importance of hydrotreating processes, in particular for the reformulating of motor fuels and fuels in general. The need to reduce the sulphur content to levels progressively closer to zero has entailed modifications in the processes and the catalysts for hydrodesulphurization, as will be pointed out below. The reduction in the content of aromatics in middle distillates, apart from improving the cetane number and hence the quality of diesel fuels, reduces fumes and particulate emission, as well as the emission of polycyclic hydrocarbons and of nitrogen oxides; hence the need, especially from the turn of the century, to introduce specific processes for hydrogenating aromatics and reducing polycyclic hydrocarbons.

The simultaneous spread of conversion processes for the reduction of heavy oils and of residues in general has further increased the volume of products to be subjected to hydrotreating. Also the direct use of heavier feedstock, including synthesis fuels obtained

| Table 1. Refinery flows subjected to hydrotreating and reason for treatment |
|-------------------------------|-----------------|---------------------------------|
| **MAIN REACTION** | **FLOW** | **MAIN PURPOSE OF TREATMENT** |
| HYD* (Hydrogenation) | Kerosene and jet fuel, Diesel | Hydrogenation of aromatics to improve the smoke point
|                       | Cracking feed | Hydrogenation of aromatics to improve the cetane index and to upgrade to the specifications
|                       | Products of catalytic cracking | Partial saturation of polyaromatics to improve conversion and selectivity and to decrease coking on the catalyst
|                       | Gasolines from pyrolysis | Hydrogenation of olefins: increased stability, reduction of rubbers
|                       | Gas from steam cracking (petrochemistry) | Hydrogenation of olefins: increased stability, reduction of rubbers
|                       | Lubricating oils | Selective hydrogenation: elimination of acetylenic compounds
|                       | * also reduction of sulphur content, if present | Treatment of virgin and spent oils to improve their stability and quality |
| HDS (Hydrodesulphurization) | Feed to catalytic reforming, Diesel, Various fuels, Miscellaneous products of distillation, Feed to hydrotreatment of residues, Feed to steam cracking, Coking feed, Residues | Elimination of poisons for the catalyst
| | | Upgrading to specifications
| | | Upgrading to specifications
| | | Elimination of odours (solvents) and stabilization
| | | Reduction of poisons for the catalyst
| | | Elimination of poisons for the catalyst
| | | Reducing sulphur in the coke produced
| | | Upgrading to specifications or pretreatment of feeds to upgrading processes
| HDN (Hydrodenitrogenation) | Lubricating oils, Feed to catalytic cracking and hydrocracking of residues | ‘Polishing’ to improve stability
| | | Elimination of poisons \(\text{NH}_3\) for acid sites
| HDM (Hydrodemetallization) | Feed to catalytic cracking unit and to hydrocracking of residues, Residues | Removal of metal deposition, non-selective cracking, coke depositing, destruction of zeolites
| | | Reduction in deposition of metals
| CCR (Conradson carbon reduction) | Residues and feed to cracking | Reduction in coke deposition on catalysts
from coal and from tar sands or shales, has broadened the sphere of action of hydrotreating processes, while also increasing the importance of hydrometallization and hydrodenitrogenation.

3.1.3 Chemistry and thermodynamics of the process

General
Hydrotreating reactions may be subdivided into two main classes:
- Saturation of unsaturated hydrocarbons.
- Elimination of heteroatoms (sulphur, nitrogen, oxygen, vanadium, nickel) from the molecules containing them.

As already stated, the second group of reactions are often carried out (more or less completely) in a single process (HDS). Fig. 3 shows the main types of aromatic and heteroatomic compounds present in oil;

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**Fig. 1.** Hydrotreating (HDS) processes included in a typical refining cycle.

**Fig. 2.** Evolution of European specification limits for sulphur content in fuels.
olefinic, diolefinic and acetylenic, not originally present, may form following particular processes, such as cracking (thermal and catalytic).

**Fig. 4** shows some typical hydrotreating reactions. Both hydrogenation reactions and those of breaking the bonds C—S, C—N and C—O are exothermic. The exothermicity differs for the various reactions; in any case it is generally in the 50-70 kJ/mol H$_2$ interval for the C—S and C—N bond-breaking reactions, while it is higher for the hydrogenation of olefinic bonds (70-130 kJ/mol H$_2$) (Tøpøe et al., 1996; Giavarini, 1999; Heinrich and Kasztelan, 2001).

Both classes of reactions are generally favoured by the increased hydrogen pressure and, compatibly with the kinetics, by a decrease of temperature. The hydrogenation of aromatics requires more drastic conditions than that of olefins.

The stoichiometry of the reactions depends on the nature of the heteroatom and of the unsaturation. Even with an equal heteroatom, the various compounds present in petroleum have different reactivities and kinetics; the presence of aromatic rings further complicates the sequence of possible reactions.

1) $\text{C}_2\text{H}_5\text{SH} + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{S}$
2) $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5 + 2\text{H}_2 \rightarrow 2\text{C}_2\text{H}_6 + \text{H}_2\text{S}$
3) $\text{RSSR'} + 3\text{H}_2 \rightarrow \text{R R'H} + 2\text{H}_2\text{S}$
4) $\text{S} + 2\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{H}_2\text{S}$
5) $\text{S} + 4\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{H}_2\text{S}$
6) $\text{S} + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{H}_2\text{S}$
7) $\text{RNH}_2 + \text{H}_2 \rightarrow \text{RH} + \text{NH}_3$
8) $\text{C}_3\text{H}_7 + 4\text{H}_2 \rightarrow \text{C}_3\text{H}_7 + \text{NH}_3$
9) $\text{ROH} + \text{H}_2 \rightarrow \text{RH} + \text{H}_2\text{O}$
10) $\text{O} + 4\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{H}_2\text{O}$
11) $\text{OH} + \text{H}_2 \rightarrow \text{OH} + \text{H}_2\text{O}$
12) $\text{OH} + 3\text{H}_2 \rightarrow \text{OH}$
13) $\text{C}_3\text{H}_{11}\text{CH} = \text{CH}_2 + \text{H}_2 \rightarrow \text{C}_3\text{H}_{11}\text{CH}_2 - \text{CH}_3$

**Fig. 3.** Heteroatomic and aromatic compounds present in oil fractions (Tøpøe et al., 1996).

**Fig. 4.** Typical hydrotreating reactions.
Hydrogenation (HYD)

Hydrogenation reactions concern olefins and diolefins, which tend to polymerize in the products, as well as aromatics and polyaromatics; polyaromatics and diolefins are precursors of coke. A number of streams of the petrochemical industry could require the selective hydrogenation of given classes of unsaturated hydrocarbons: one typical example is hydrogenation of acetylene and/or of butadiene to olefins in the steam cracking products.

Catalytic hydrogenation of olefins is relatively easy, even at low hydrogen pressure values (0.2-0.3 MPa), and it is characterized by high exothermicity. Reactivity decreases with the increase in length of the chain and of the substituting groups adjacent to the double bond. If there is an appreciable quantity of olefinic compounds (e.g. in fractions from thermal processes), hydrogenating pretreatment may be necessary to saturate them, before the hydrodesulphurization process.

As opposed to olefins, the hydrogenation of the aromatic ring requires high hydrogen pressures; this is therefore relatively difficult under the conditions of normal hydrodesulphurization processes, as will be seen below. Fig. 5 shows the equilibrium conversion percentage of the benzene-cyclohexane system at various pressures and temperatures. The hydrogenation kinetics of the various aromatic compounds greatly depend on the nature of the catalyst. With the traditional hydrodesulphurization catalysts based on cobalt and molybdenum (Co/Mo), such kinetics generally increase with the number of rings present in the molecule. An exception to this is phenanthrene which, while having the same number of rings as anthracene, shows a different reactivity with hydrogen, because of the different distribution of the electron density. Thus, the kinetic constants for benzene, phenanthrene, naphthalene and anthracene are in the ratio of 1:4:20:40.

Also the presence of substituent groups on the benzene ring affects the hydrogenation kinetics: hence, it is easier to hydrogenate ethylbenzene than toluene and the xylenes, in their turn more reactive than benzene. In structures with condensed rings, such as are found in the heaviest oil fractions, the hydrogenation of the external ring or rings is easier; the inner rings in fact offer greater resistance to saturation.

Contrary to the Co/Mo catalytic systems, metal catalysts in the eighth group of the periodic table (Ni, Pt) instead preferably hydrogenate benzene and unsubstituted rings. Their use in hydrocracking is however restricted to processes in which the feedstock does not contain any noxious elements for the catalysts, as for example sulphur-free hydrocarbon fractions.

Hydrodesulphurization (HDS)

Among the hydrotreating reactions, those of desulphurization are traditionally the most important ones, and those most studied, as sulphur is the most common undesired element and the first to be

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Distillation interval (°C)</th>
<th>Sulphur content (weight %)</th>
<th>Mercaptans</th>
<th>Sulphides</th>
<th>Thiophenes</th>
<th>Benzothiophenes and heavy sulphides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasolines</td>
<td>70-180</td>
<td>0.02</td>
<td>50</td>
<td>50</td>
<td>traces</td>
<td>-</td>
</tr>
<tr>
<td>Kerosene</td>
<td>160-240</td>
<td>0.2</td>
<td>25</td>
<td>25</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Gas oil</td>
<td>230-350</td>
<td>0.9</td>
<td>15</td>
<td>15</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Vacuum gas oil</td>
<td>350-550</td>
<td>1.8</td>
<td>5</td>
<td>5</td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td>Vacuum residue</td>
<td>&gt;550</td>
<td>2.9</td>
<td>traces</td>
<td>traces</td>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>
subjected to environmental and commercial restrictions. Sulphur compounds tend to concentrate in the heavier fractions of oil, as shown in Table 2.

The reactivity of sulphur compounds depends on their structure and on their sizes. Thus, mercaptans are more reactive than the cyclic compounds; thiophene and benzothiophene, in their turn, are more reactive than dibenzothiophene. The desulphurization of the lighter fractions (gasolines), which are richer in mercaptans and in compounds with a relatively simple structure, is far easier than desulphurizing the fractions with higher boiling points (e.g. gas oils). The substituent groups adjacent to sulphur atoms give rise to steric hindrance, which slows down the desulphurization reaction, while the alkyl groups far from the sulphur make it easier, as they increase the electron density on the sulphur atom.

Hydrodesulphurization reactions are characterized by the presence of various stages, and are often kinetically controlled by diffusion within the catalyst. As an example, for thiophene two different reaction schemes can be envisaged, one working through the formation of tetrahydrothiophene, and the other through butadiene:

\[
\text{S} \quad \xrightarrow{H_2} \quad \text{CH}_3 \text{CH}_3 \text{S} \quad \xrightarrow{H_2} \quad \text{C}_4\text{H}_6 \quad \xrightarrow{H_2} \quad \text{C}_4\text{H}_{10} + \text{H}_2\text{S}
\]

With traditional molybdenum and cobalt-based catalysts, the hydrodesulphurization reactions in thiophenic compounds take place primarily through direct hydrogenolysis (the lower mechanism shown); the reaction via hydrogenation followed by hydrogenolysis is much slower.

Bisphenyl (BP) is therefore, for example, the main intermediate product of the hydrodesulphurization of dibenzothiophene (DBT), a compound present in heavy distillates:

\[
\text{DBT} \quad \xrightarrow{H_2} \quad \text{BP} \quad \xrightarrow{H_2} \quad \text{C}_4\text{H}_6 \quad \xrightarrow{H_2} \quad \text{C}_4\text{H}_{10} + \text{H}_2\text{S}
\]

The upper hydrogenolysis reaction is much quicker that the hydrogenation reaction of the benzene ring. In this case the increase in hydrogen pressure has little effect on the reaction.

Eliminating sulphur from molecules with steric hindrances is far more difficult, as in the case of 4,6-dimethyl(dibenzothiophene (DMDBT, boiling point 360°C), where the methyl substituents in position β (with respect to sulphur) considerably restrict the angle of contact between the sulphur orbitals and the catalyst:

In the process with Co/Mo catalysts, desulphurization of DMDBT is approximately 20 times slower than that of DBT, so that in practice it does not occur (Gosselink, 1998).

With the very low sulphur levels required by current standards, it is necessary to desulphurize even the ‘difficult’ molecules, such as DMDBT. This problem concerns the desulphurization of gas oils and the heavy fractions (or residues) rather than that of gasolines. In this case the preliminary hydrogenation of the benzene ring has to be reconsidered, so as to give the molecule flexibility and increase the angle of access by the sulphur to an active site of the catalyst. The process to be activated thus takes place as represented in the lower part of the following scheme (Duée et al., 2002):

The hydrogen pressure, together with the use of a suitable catalyst, in this case becomes decisive.

In the most general case, apart from the structure of the molecule, its size must also be considered, as it has to be smaller than the pores of the catalyst.

Being exothermic, desulphurization reactions are favoured thermodynamically by low temperatures, which limit secondary reactions and the formation of coke. An indication as to choice of the most suitable temperature is seen in Fig. 6 which sets out, for some of the reactions listed in Fig. 4, the logarithms of the equilibrium constants \(K\) as a function of the reciprocal of the temperature. Up to around 400°C the values are generally clearly positive: this means that below this temperature the equilibria are shifted all the way over to the right, provided hydrogen is present in an at least stoichiometric quantity. In practice, industrial processes are carried out in the presence of heavy excesses of hydrogen, both to help the reaction, and to limit coke formation. The temperatures cannot go below given values (around 280-300°C) for kinetic reasons and must not in general exceed 400-420°C, due to the

Table 2.

![Fig. 4](image_url)
above-mentioned thermodynamic reasons and to avoid secondary reactions (formation of coke).

**Hydrodenitrogenation (HDN)**

The elimination of nitrogen regards mainly the fractions with the highest boiling points (starting from gas oils) and the residues. The importance of this process is increased by the tendency to treat heavy feedstocks and residues.

Of the nitrogen compounds, the aliphatic amines are those with the most favourable decomposition kinetics. However, they are seldom present in crude oils, which tend to contain heterocyclic compounds, far more refractory to hydrotreating; the process of denitrogenating cyclic molecules is in fact thermodynamically less favoured than hydrodesulphurization.

Contrary to what happens in hydrotreating processes, hydrogenation is the decisive stage, as it is necessary to ‘free’ the carbon atom in position α with respect to the nitrogen, as illustrated in Fig. 7 for pyridine and quinoline. The denitrogenation of quinoline, a typical gas oil molecule, can take place following two alternative pathways, including several hydrogenation steps, after which the breakage of C—N bonds occurs.

Also in the case of nitrogen compounds, the steric hindrances due to alkyl substituents of the ring/s reduce reactivity and the facility of denitrogenation. The polycyclic compounds are the most refractory of the heterocyclic compounds.

As a consequence of the different reaction mechanism, denitrogenation requires higher temperatures and, above all, higher pressures than desulphurization. In this way, greater hydrogenation of the product is also achieved: under conditions favourable to hydrodenitrogenation, saturation of the aromatic ring is in fact facilitated.

The increase in the hydrogen partial pressure is favourable not only from the thermodynamic, but also from the kinetic standpoint. With the increase in the mean molecular weight of the oil fraction, the content of polycyclic nitrogen compounds increases and, consequently, the severity of the hydrodenitrogenation process and the consumption of hydrogen should also increase.

The denitrogenation of the oil fractions is more difficult, and therefore slower, than desulphurization, which is always complete when working under conditions favourable to denitrogenation, as evidenced in Fig. 8.

**Hydrodeoxygenation (HDO)**

Organic compounds containing oxygen (phenols, ethers, furans) are present above all in fractions coming from cracking processes and in synthesis fuels obtained from coals and shales; to a far lesser extent they occur in crudes, in the form of napthenic acids and fats.
Reactivity with hydrogen is very variable: ethers are easily convertible, as are alcohols and ketones, while cyclic compounds, especially those of furanic type, are not very reactive.

Hydrodemetallization (HDM)
Metals, especially vanadium and nickel, are present in crude oils within porphyrinic and other structures (containing also nitrogen). They therefore occur mostly in the heavy fractions of crude. Hydrodemetallization takes place with a preliminary hydrogenation step of the metalloporphyrins, followed by a breakdown into metallic sulphides and hydrocarbons. In general, the velocity of hydrometallization reactions increases with the temperature and the hydrogen pressure and is greater for the porphyrins of vanadium than for those of nickel. Metals ‘extracted’ from porphyrins in the form of sulphides, tend to be deposited on the catalysts, decreasing their activity in the course of time (Topsøe et al., 1996).

Secondary reactions
Apart from the reactions mentioned above, hydrocracking reactions which cause an increase in hydrogen consumption and lead to the formation of lighter products, are often inevitable, especially under extremely severe conditions and when heavy feedstocks are treated. Inevitable, too, above all at very high temperatures, are the secondary reactions responsible for the formation of carbon-rich products, generically indicated as coke; these form mainly through the condensation of diolefinic and polynuclear compounds. The formation of coke, which affects all the processes in which hydrocarbons are heated at medium-high temperatures, causes catalysts to become coated and deactivated. In the case of hydrodesulphurization processes applied to medium and heavy products, secondary reactions become appreciable beyond 400°C.

3.1.4 Catalysts
The thermodynamic need to conduct hydrotreating processes at temperatures that are as low as possible makes it necessary to use catalysts to increase the velocity of reaction. Choice of catalyst depends on the specific application (hydrogenation, desulphurization, etc.), the type of feedstock and the specific requests for the product. For given applications, the optimal solution can be that of using various types of catalysts in the same reactor.

Traditionally the most common combinations of active elements in hydrotreating are cobalt-molybdenum (Co/Mo), nickel-molybdenum (Ni/Mo) and nickel-tungsten (Ni/W), generally on a γ-alumina support (Chianelli and Daage, 1989; Topsøe et al., 1996; Gosselink, 1998; Marcilly, 2003). To reach the active state, the metals have to be transformed into sulphides. The metal content (weight %) is relatively high if compared with those of other catalytic systems: 8-16 % Mo; 1-4 % Co; 12-25 % W; 1-4 % Ni.

Co/Mo-based catalysts are excellent for hydrodesulphurization processes, but are less active for hydrodenitrogenation reactions and for hydrogenating aromatics, with the consequent lower consumption of hydrogen. The Ni/Mo combination is instead more specific for hydrodenitrogenation and for hydrogenation, and is therefore preferred for treating the unsaturated fractions; the consumption of hydrogen is thus greater. Ni/W catalysts cost more and they are very active in the hydrogenation of aromatics, although this must take place in the presence of low H₂S pressures.

To sum up, for conventional hydrotreating processes, the catalysts may be classified as follows, in decreasing order of activity:

- Hydrogenation: Ni/W > Ni/Mo > Co/Mo.
- Hydrodesulphurization: Co/Mo > Ni/Mo > Ni/W.
- Hydrodenitrogenation: Ni/Mo = Ni/W > Co/Mo.

However, the necessity of obtaining products practically sulphur-free has introduced certain new elements of judgement in the classification set out above. It has in fact been seen that the Co/Mo combination is effective in removing ‘easy’ sulphur.
with direct hydrogenolysis reactions; but deep desulphurization implies also the necessity of eliminating the more ‘difficult’ sulphur, such as that which is sterically hindered, contained in ring structures of the DMBDT type (see above). In this case, instead of direct hydrogenolysis, the prehydrogenation stage should be preferred to reduce the rigidity of the aromatic ring, thereby enabling the catalyst to approach the active site. The most effective catalyst proves to be the one with a Ni/Mo base, in the presence of higher hydrogen pressures (Mayo et al., 2001).

The use of high hydrogen pressures can bring about the hydrogenation of the aromatics, causing an increase in hydrogen consumption and a worsening of the octane quality.

The assumption of using both systems (Co/Mo and Ni/Mo) in the right order might be oversimplifying the case. The catalytic system must in any case show a high activity and must be optimized to adapt it to the chemical species present and to the reaction conditions. Also the presence of appreciable quantities of nitrogen (e.g. coming from LCO, a light recycled oil produced by cracking) can make it preferable to use the Ni/Mo system. ‘Mixed’ catalysts have in any case been developed, with a Ni/Co/Mo base, capable of reducing the consumption of hydrogen compared with Ni/Mo catalysts.

For the preliminary activation of the catalyst, consisting in the formation of metal sulphides (presulphiding), a stream of hydrogen containing molar 2-5% of H₂S can be used, or else a desulphurized distillate containing controlled quantities of dialkylsulphides (dimethylsulphide, DMS, or dimethyldisulphide, DMDS), CS₂, or other sulphide compounds, can be used. Expressed in a simplified form, the following are the sulphiding reactions:

- \( \text{MoO}_3 + 3.5 \text{O}_2 \rightarrow \text{MoO}_3 + 2 \text{SO}_2 \)
- \( \text{Co}_9 \text{S}_8 + 12.5 \text{O}_2 \rightarrow 9 \text{CoO} + 8 \text{SO}_2 \)
- \( \text{C(coke)} + \text{O}_2 \rightarrow \text{CO}_2 \)
- \( \text{H}_2(\text{cork}) + 0.5 \text{O}_2 \rightarrow \text{H}_2\text{O} \)

The duration of each working cycle of the catalyst before regeneration varies from a few years to a few months, according to the type of feedstock; it is considerably shorter for heavy feedstocks rich in sulphur, nitrogen and metals.

**Structure of Co/Mo catalysts**

To explain how catalysts based on bimetal sulphides work, and to justify the promoting effect of cobalt and nickel, various models have been proposed (Gates et al., 1979; Chianelli and Daage, 1989; Topsøe et al., 1996;...
The great dispersion of the active species and the simultaneous presence of a number of crystalline and amorphous phases, together with the difficulty of studying these systems in situ during operation, have for long been obstacles to interpreting the phenomena. Pure sulphides thermodynamically stable under reaction conditions (approximately 320-380°C and 0.3-0.6 MPa) are Co₉S₈ and MoS₂. A ternary Co-Mo-S region has however been identified in the catalyst, consisting of structures similar to that of molybdenum disulphide, MoS₂, with the atoms of the promoter arranged along the edges (Fig. 9). This region, which contains the active sites, can possess a vast range of structures, with a broad spectrum of cobalt concentrations, having a variety of properties and functions (Lauritsen et al., 2001).

Scanning Tunnelling Microscopy (STM) techniques have enabled images of nanoclusters exposed to hydrogen to be resolved at atomic level. Fig. 10 shows the formation of two sulphur vacancies at the edges of a nanocluster of MoS₂ type (white circle), which represent the active sites for hydrodesulphurization (Derouane, 2000). The STM images also show that the promoter modifies the morphology of nanoclusters: these, which appear in the form of triangular particles in the absence of promoters, take the form of truncated hexagons in the presence of cobalt (Lauritsen et al., 2001).

Catalytic activity varies considerably with the addition of the promoters Co or Ni, increasing up to a maximum corresponding to a Co/Mo or Ni/Mo ratio of 0.3-0.5. The promoting effect probably takes place in various ways, according to the phases present and to the type of hydrotreating process: from a structural indirect promotion effect, which limits the sintering of the catalyst, to an electron promotion effect, and to an influence on the sulphur vacancies (Gates et al., 1979; Chianelli and Daage, 1989; Topsøe et al., 1996; Lauritsen et al., 2001).

Industrial catalysts

Industrial catalysts are constituted by metal sulphides of Co/Mo, Ni/Mo or Ni/W supported on a refractory oxide, generally γ-alumina (but also silica-alumina, zeolites, kieselguhr), having a large surface area, up to 300 m²/g and more. Alumina makes it possible to control the acid properties of the catalyst and keep them low, favouring cracking reactions. Apart from the form γ, also other modifications of alumina can be used (Topsøe et al., 1996; Heinrich and Kasztelan, 2001). For treatment of residues, catalysts having greater porosity are used, capable of accumulating the metals produced by hydrometallization reactions without being rapidly deactivated by the deposition of coke.

There are various geometrical forms (generally obtained by extrusion), as shown in Fig. 11; the diameters are of 1.5-2 mm with a length of 3-5 mm. The most usual forms are tri- or pentalobe ones or hollow-cylinder shaped, capable of providing a large external area.

Catalysts are normally prepared by impregnation of the support with solutions of salts (e.g. ammonium salts and nitrates) of the necessary metals (Co, Mo, Ni, W) followed by calcination; thereby transforming the salts into oxides. Another preparation process is based on thermal treatment of mixtures of alumina hydrate and of Co, Mo, Ni, W metal salts. As already mentioned the catalyst, loaded into the reactor in the form of oxides, becomes effective after a presulphiding treatment to transform the oxides into sulphides.

Fig. 10. Scanning microscope image (tunnelling effect) of an MoS₂ nanocluster exposed to atomic hydrogen at 673 K (Derouane, 2000).

Fig. 11. Geometrical forms of industrial hydrotreating catalysts (diameter 1.5-2 mm, length 3-5 mm).
3.1.5 Kinetics and reaction mechanisms

The most studied reactions from the kinetic standpoint are those of hydrodesulphurization on catalysts based on metal sulphides, the first ones to be used in these processes.

It has already been seen that the removal of heteroatoms by means of hydrogenolysis is relatively easy for sulphur and more difficult for nitrogen. The reaction mechanisms are often complex and pass through various stages, including also hydrogenation reactions. In the case of cyclic structures, the hydrogenation of the ring containing the heteroatom often takes place before the breaking of the carbon-heteroatom bond. An exception is the bond between sulphur and carbon in thiophenic compounds, relatively weak and able to directly undergo hydrogenolysis.

The main differences between the most usual catalytic systems (Mo on Al2O3, Co/Mo on Al2O3, Ni/Mo on Al2O3, Ni/W on Al2O3) regard their selectivity and their relative reactivity, rather than the reaction mechanism. The kinetic equations most commonly used are of the Langmuir-Hinshelwood type (Le Page, 1987; Topsøe et al., 1996), on the assumption that the slowest stage (the one that controls the overall velocity of the reaction) is the reaction between the organic species and hydrogen, both adsorbed on the surface of the catalyst.

For light fractions and in the presence of compounds which inhibit the process (H2S, nitrogen and metals), the reaction is often of the first order with respect to hydrocarbons (HC) and hydrogen, and may thus be expressed in the following way:

\[ r = k_p \frac{p_{HC}}{p_{H2}} \]

where \( r \) is the rate of conversion, \( k_p \) the apparent kinetic constant, and \( p_{HC} \) and \( p_{H2} \) the partial pressures of the hydrocarbons and of hydrogen, respectively (Heinrich and Kasztelan, 2001).

Other kinetic equations have also been proposed, based on single species taken as the model. But as the oil fractions to be subjected to hydrotreating are extremely complex and diverse in composition, more or less empirical formulae must usually be applied, generally elaborated by the suppliers of the catalyst and/or of the process; they depend on the type of reagents, the working conditions, and other parameters. As the only possible reference is the initial and final content in the element concerned (e.g. sulphur), the expressions used normally make reference to this parameter (S). An example of these expressions relating to the HDS process is (Heinrich and Kasztelan, 2001):

\[ r = k_o e^{-\frac{E_o}{RT}} S^n \]

where \( E_o \) is the apparent activation energy, \( k_o \) the frequency factor, \( R \) the gas constant, and \( n \) the apparent order of reaction. Conversion is defined as a function of the concentration of sulphur in the feedstock (\( S_o \)) and in the product (\( S_f \)):

\[ \text{HDS conversion} = \frac{S_o - S_f}{S_o} \]

In practice the first order \((n = 1)\) is valid for the lighter fractions. The heavier fractions (gas oils and residues) include complex components that can react in very different ways, so that \( n \) increases progressively with the complexity of the fraction, up to values equal or close to 2 for heavy gas oils and vacuum residues.

Other expressions (Trambouze and Euzen, 2002) make reference to two families of sulphur compounds, one ‘easy’ and the other one ‘difficult’ to be desulphurized, with apparent kinetics including two reactions of the first order.

3.1.6 Processes

The typical scheme of hydrotreating processes is similar in conception to that of other processes operating in the hydrogen cycle (Fig. 12 A). The reactor, catalyst and working conditions are however adapted to the type of feedstock to be treated (vaporized or partly liquid) and to the final results to be achieved.

The hydrogen necessary for the process comes from catalytic reforming; should this not be sufficient for the requirements of the refinery, it can also come from a hydrogen production (steam reforming) plant.

Working with an excess of hydrogen, a large part of the gas has to be recycled to the reactor, after making up the reacted or consumed hydrogen. The recycle gas may be subjected to one or more treatments to separate the H2S (in HDS processes) and light hydrocarbons, thereby increasing the partial pressure of the hydrogen and improving the efficiency of the process.

In hydrodesulphurization processes, the separation of H2S and H2 can be carried out, after cooling of the reaction products, in two stages (Fig. 12 B): the first one at high pressure, for the separation of the hydrogen, which is directly recycled to the reactor after making up what has been consumed in the reaction, and the second one at lower pressure, for the separation of H2S, which is conveyed to the plant for recovery of the sulphur (Claus process).

Both flash-separated hydrogen and H2S contain more or less large quantities of light hydrocarbons (formed by cracking or originally present); the hydrogen, moreover, can carry away part of the H2S.
To reduce the hydrocarbon content, the hydrogen can be ‘washed’ in backflow with a portion of the desulphurized product or purified with other systems. In deep desulphurization processes an alkaline absorption stage (using amine) for the recycle gas must be installed: desulphurization reactions are equilibrium processes and are therefore hampered by the presence of \( \text{H}_2\text{S} \), which furthermore, being by preference chemically absorbed, inhibits the action of the catalyst. It is necessary to have the maximum hydrogen concentration also in the make-up flow, inserting, for example, purification by means of PSA (Pressure Swing Adsorption).

In other configurations, above all in the treatment of heavy feeds, the insertion of a cooling step after the heat exchange with the feedstock can be carried out downstream rather than upstream of the first separator (Heinrich and Kasztelan, 2001); in this case there is a first separation (called ‘high temperature separation’) followed by a second one at low temperature. With this scheme the \( \text{H}_2 \) stream comes from the second separator and is rich in \( \text{H}_2\text{S} \); it has to be sent to an absorption unit with amine, before recycling to the reactor.

Considering that in the world there are several hundred refineries and that in general each refinery has at least one desulphurization plant (normally more than one), it can be stated that hydrodesulphurization is the most widespread catalytic refining process. For this reason reference will be made to this type of hydrotreating in describing a typical plant. Further on there is mention of other configurations and other uses of hydrotreating.

From the conceptual point of view, there are no substantial differences between the HDS processes of virgin naphtha, kerosene and gas oils. However the plants present various degrees of complexity and different operational conditions (Parkash, 2003). The purpose of hydrodesulphurizing virgin naphtha is to prepare the feedstock for the isomerization and reforming units, whose catalysts require a sulphur and nitrogen content in the feedstock of less than 0.5 ppm. The reactions take place in the vapour phase, with a reduced hydrogen consumption (0.05%-0.1% with respect to the feedstock). Considering the type and size of the molecules involved, the desulphurization targets are reached in not too severe conditions of temperature (320-350°C) and pressure (20-40 bar), with space velocities of more than 3-4 h\(^{-1}\).

Desulphurization of gas oils is more difficult for the reasons mentioned above, and requires more drastic conditions: 350-390°C and pressures of more than 40 bar. For high-level desulphurization (up to less than 10 ppm in the product) special units and even more drastic conditions are necessary, as will be emphasized below (Lawler and Robinson, 2001); hydrogen consumption is in any case far higher than...
in hydrotreating gasolines. The lifetime of the
catalyst, too, between one regeneration and another,
is different: 2-4 years for gasolines, and one year or
less, on average, for gas oils.

**HDS plant flow sheet**

As an example of an HDS plant, a typical
process scheme is shown for the desulphurization of
gas oils, with two separators, at high and low
pressure, respectively (**Fig. 13**). This process in fact
has a greater degree of complexity than the process
dedicated to virgin naphtha, and enables a series of
additional considerations to be made in relation to
the plant and its working conditions.

The plant is provided with two columns for
absorption with amine of the H\(_2\)S contained in the gas
flows from both separators. The hydrogen-rich high-
pressure separator gas is recycled to the reactor; the
H\(_2\)S-rich flow from the low-pressure separator is
conveyed to the Claus unit for the production of
sulphur; a single column outside of the plant carries
out the regeneration of the amine.

**Fig. 13.** Diagram of a typical HDS unit with two separators, at high and low pressure.

**Fig. 14.** Fixed-bed tubular reactor for hydrodesulphurization.
Prior to the cooling stage the gaseous products are washed with water to eliminate the salts present (ammonium chloride and sulphide) which could give rise to deposits and cause corrosion problems. Lines are also foreseen for the injection of reagents (e.g. dimethyldisulphide) used for sulphiding the catalyst.

For hydrotreating processes in general, and the hydrodesulphurization process in particular, fixed-bed and vertical-flow reactors are normally used, with one or more catalyst beds (Fig. 14), with dimensions that vary from a few tens to a few hundreds of cubic metres. The solution with two or more beds is required when the feedstock contains unsaturated compounds, and for high-level desulphurization of relatively heavy fractions. It is in fact possible to have better control of the temperature by means of intermediate quench with cold hydrogen (it is recalled that reactions are globally exothermic), at the same time lowering the partial pressure of the H₂S produced by the reaction; this configuration also makes it possible to operate, if necessary, with different catalysts in the single beds. The quench operation can also be performed with the reactor’s liquid effluent, so as to save the hydrogen compression energy.

With low boiling-point fractions (gasoline and kerosene) the hydrocarbon feed reaches the reactor completely vaporized; with heavier feeds vaporization is partial and in the reactor there is a three-phase solid-liquid-gas (trickling flow) system. In this case a perfect distribution of the liquid and gaseous phases has to be ensured, as well as complete soaking of the catalyst granules; great importance, therefore, attaches
to the relative rate of gaseous and liquid flows (Ng and Chu, 1987).

The classical scheme with two separators at high and low pressure can undergo some modifications. Thus, to keep the content of light hydrocarbons in the recycling gas low, the pressure can be kept high in both separators, maintaining a lower temperature in the second separation stage (flow-sheet in Fig. 15, with hot and cold separators). In this case a single gaseous flow is separated, which, after absorption of H₂S, is recycled to the reactor (provided, in the layout, with intermediate quenches with gas oil, instead of hydrogen).

The product leaving the separators is conveyed to the stripping-stabilizing section to get rid of any traces of H₂S that remain in the liquid and of the lighter hydrocarbons formed by the secondary cracking reactions.

For heavier feeds and for high-level desulphurization, the stripping can be combined with vacuum drying (see again Fig. 15) to eliminate the remaining traces of water and of light compounds (including sulphur compounds), so as to make the desulphurized product conform to specifications.

Materials

The presence of organic sulphur compounds, H₂S and hydrogen at relatively high pressures and temperatures, makes it essential to consider with attention the metallic materials to be used in hydrosulphurization units. In particular, hydrogen sulphide in the presence of hydrogen becomes extremely corrosive above 260-300°C.

Ample use is made of low-alloy steels (5-9%) with a chromium and molybdenum base, to withstand creep and hydrogen attack. Molybdenum keeps the modulus of elasticity high even when hot, while chromium (7-9%) confers mechanical and chemical resistance up to 500-600°C.

The base material can be protected, especially in reactors, by a sheet of stainless austenitic steel, particularly if naphthenic acids are also present; in which case series 316 and 317 steels can be used or steels of type 18-8 (18% chromium and 8% nickel). It is advisable to use stainless steel in making pipes, exchangers and valves that are exposed, at high temperatures and pressures, to H₂-H₂S environments. During shut-down, areas that are even weakly corroded may be subjected to the formation of polythionic acids: the iron sulphide formed by the corrosion combines with oxygen and with the humidity in the air, causing intergranular corrosion and fragility. The addition of stabilizers, such as titanium and niobium, to austenitic steels minimizes this phenomenon.

3.1.7 Operating variables

With reference especially to hydrodesulphurization, the main operating variables in a hydrotreating process are the following:

- Quality of the feed.
- Reaction temperature.
- H₂ partial pressure.
- Space velocity.

Important secondary variables are:

- Hydrogen/hydrocarbon ratio.
- H₂S partial pressure.
- Reactor pressure (correlated to the H₂ partial pressure).

Operating conditions are varied in time as a function of the activity of the catalyst; as deactivation of the catalyst proceeds, the temperature increases and the space velocity is reduced. The reactor pressure and the H₂/feed ratio are instead normally kept constant.

Quality of the feed

The quality of the feed, with special reference to the sulphur content, to the carbonaceous residue and to the content of unsaturated elements and metals, has a decisive effect on the result obtainable and on the life of the catalyst. High contents of metals (V, Ni, As, Na) lead to deposits on the catalyst, reducing its effective life. Carbonaceous particles and products of corrosion coming from the upstream units cause fouling of the catalytic bed and losses of feed.

Variations in the sulphur and olefin content influence the consumption of hydrogen and the reaction heat. Exposing the feed to air, especially in the presence of olefins, leads to the formation of polymers which produce deposits in the exchangers and on the catalyst.

The feedstock distillation curve, and in particular its final point, have an influence on the results attainable and on the working conditions; high final points can in fact be correlated with higher carbonaceous residues and sulphur contents. A parameter (Weight Average feedstock Temperature, WAT) that combines the 5%, 50% and 95% points of the distillation curves ASTM D-86 is sometimes used.

Reaction temperature

The temperature in the reactor is determined by that of the feed, by controlling the heater outlet temperature, and by the quench hydrogen, if the reactor has more than one catalytic bed. The reactor outlet temperature depends on the type and quality of the feed and is generally higher than the inlet temperature, because of the exothermicity of the reactions; it is generally varied by acting on the inlet temperature. To represent the average reaction
temperature of the catalytic bed, reference is made to an average temperature (Weight Average Bed Temperature, WABT):

\[
WABT = \frac{T_1 V_1 + T_2 V_2 + \ldots + T_n V_n}{V}
\]

where \( V \) is the total volume of the catalyst, \( V_1, V_2 \ldots V_n \) are the volumes of single portions, and \( T_1, T_2 \ldots T_n \) are the respective temperatures. Simplified expressions may also be used, of the following type:

\[
WABT = T_{in} + \frac{2}{3} (T_{out} - T_{in})
\]

where \( T_{in} \) and \( T_{out} \) are the inlet and outlet temperature, respectively, of the reactor (or of the catalytic bed).

An increase in temperature accelerates the desulphurization reactions, but also the secondary reactions and coke formation, shortening the time between two regenerations of the catalyst; an excessive increase can turn the gas oil dark.

During the operation, the temperature necessary to obtain a product having the required characteristics increases as the deactivation of the catalyst proceeds; the temperature increase in the reactor must be kept under constant control to ensure that it does not exceed the design temperature. This is particularly important when feed rich in unsaturated elements is used, as saturation reactions are strongly exothermic. The average temperature of the reactor at the start of the run (SoR) varies with the type of feed and is generally between 330 and 370°C; at the end of the run (EoR) it can reach as high as 380-400°C, beyond which cracking and coke formation become excessive. After each run (between one regeneration and the next) the SoR temperature must be increased, causing also an increase in the EoR temperature; when the latter reaches the maximum level fixed by the supplier of the catalyst (and/or of the process), the catalyst has to be replaced.

For the same inlet temperature of the reactor, the application of intermediate quenching reduces the WABT, with advantages both in terms of thermodynamic yields and for the lifetime of the catalyst. In practice, this makes it possible to operate under conditions closer to isothermicity.

**Hydrogen partial pressure and reactor pressure**

It has already been stressed that the hydrogen partial pressure is of fundamental importance for the success of hydrotreating reactions. The hydrogen shifts the reactions in the desired sense and limits the secondary reactions that lead to the formation of coke on the catalyst.

Light feeds require a lower hydrogen pressure for desulphurization than heavy feeds. According to the desulphurization required, for a gasoline pressures from about 2 to 4 MPa are sufficient, while for a gas oil pressures from 3 to 7 MPa are needed (the higher values in these intervals are necessary for deep desulphurization).

To reduce the aromatics and to increase the cetane number, \( \text{H}_2 \) pressures generally higher than 6 MPa are required (Table 3). The working pressure \( P \) of the reactor depends on the \( \text{H}_2 \) partial pressure:

\[
P = \frac{\text{H}_2 \text{ partial pressure}}{\text{H}_2 \text{ molar fraction}}
\]

\( P \) is controlled in the high-pressure separator or, in any case, in the hydrogen-rich flow separator.

The pressure in the separator must be kept constant for the following reasons:

- A pressure higher than the design favours not only the reactions but also the life of the catalyst, improving its performance, but it creates problems for the equipment (heater, reactor, exchangers).
- A pressure lower than the design has negative effects on the activity of the catalyst and accelerates its deactivation due to coke deposition.

Heavy feeds require higher pressures than lighter feeds. To increase the cetane number of a gas oil or to improve the smoke point of a kerosene, high pressures are needed, with a greater consumption of hydrogen.

**Space velocity**

The feed flow and type, and the degree of desulphurization desired, determine the quantity of catalyst to be placed in the reactor. The severity of the operation is in fact determined not only by the reaction temperature, but also by the relation between the volumes of hydrocarbon feed (on an hourly basis) and of the catalyst, which is termed the Liquid Hourly Space Velocity (LHSV):

\[
\text{LHSV} = \frac{\text{vol. of feed per hour (m}^3\text{/h)}}{\text{vol. of catalyst (m}^3\text{)}}
\]

This parameter has the dimensions of time\(^{-1}\) and is expressed in h\(^{-1}\); its inverse is practically the residence time.

### Table 3. Hydrogenation of a gas oil containing 1.3% sulphur and 26.7% aromatics

<table>
<thead>
<tr>
<th>PARTIAL PRESSURE OF HYDROGEN (MPa)</th>
<th>CONTENT OF AROMATICS IN EFFLUENT (weight %)</th>
<th>CONSUMPTION OF HYDROGEN FOR THE REACTION (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>25.7</td>
<td>0.4</td>
</tr>
<tr>
<td>4.0</td>
<td>20.0</td>
<td>0.6</td>
</tr>
<tr>
<td>6.5</td>
<td>10.0</td>
<td>0.9</td>
</tr>
<tr>
<td>8.5</td>
<td>5.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>
When the plant is in operation (and therefore the quantity and volume of the catalyst are constant), the LHSV depends on the feed volume. Operating with the LHSV far higher than the design value, and therefore with a high feed volume, requires a higher temperature, for the same product quality. Hence the possibility of coke formation and a shorter catalyst working cycle. Operating with the LHSV far lower than the design value causes a poor distribution on the catalyst. Usually the value of the LHSV is established (around 0.8-1.5 h⁻¹) in such a way as to guarantee a catalyst working cycle of at least one year for gas oil and a longer cycle for lighter feeds. To obtain deep desulfurization, if it is not possible to increase the quantity of catalyst, the space velocity has to be diminished.

**Hydrogen/hydrocarbon (H₂/HC) ratio**

Completion of the hydrodesulfurization reactions and the hydrogenation of the aromatics require high partial pressures of hydrogen, corresponding to gas quantities far greater than those required by the stoichiometry. To reduce hydrogen consumption, the majority of the gas is recycled, making up only the quantity consumed in the reactions or following solubilization. Recycled hydrogen can also be used, as seen, to control the temperature gradient of the reactor, by means of intermediate quenching.

The purity of the hydrogen introduced into the reactor depends both on the purity of the make-up gas (generally coming from reforming), and on the quantity of volatile hydrocarbons and of H₂S present in the recycled gas.

At constant pressure, an increase in the hydrogen/hydrocarbon ratio leads to a decrease in the partial pressures of the gaseous components and therefore to a lower partial pressure of the H₂S, which exercises a considerable inhibiting effect on the rate of desulfurization. The plant should not operate with lower values of the hydrogen/hydrocarbon ratio than the design value, in order to prevent the rapid deactivation of the catalyst which would otherwise occur.

The hydrogen/hydrocarbon ratio is calculated in the following manner:

\[
\text{H}_2/\text{HC} = \frac{\text{total gas capacity (Nm}^3\text{/h}) \times \text{H}_2 \text{ fraction}}{\text{total liquid flow (m}^3\text{/h})}
\]

As the quantity of gas that can be recycled is an inverse function of the total pressure, during a working cycle the flow of recycled gas (rich in H₂) diminishes due to the increased loss of feed in the reactor. The reduction in the recycle flow is acceptable all the time the value of the H₂/HC ratio does not go below the design value. When it is no longer possible to maintain this minimum value, the catalyst has to be regenerated or replaced, consequently reducing the loss of feed in the reactor. In all cases in which the H₂/HC ratio is too low, the feed volume has to be reduced so as to return to the desired value.

The hydrogen required, including what remains in solution in the product and that lost, is equal to about 0.3 kg/kg of sulphur removed, for a kerosene, and to about 0.4-0.5 kg/kg of sulphur removed for a gas oil.

The need to reach very deep desulfurization in middle distillates makes it necessary to purify both the recycled hydrogen and the make-up hydrogen.

**Partial pressure of H₂S**

Hydrogen sulphide has an inhibiting effect on desulfurization reactions. In the case of deep desulfurization, the recycled gas has to be purified from the hydrogen sulphide it contains (e.g. by washing with amines). A small quantity of H₂S, however, must in any case be present so as to maintain the catalyst in the form of sulphides.

**Optimization of variables**

**Table 4** sets out the indicative values of the main working parameters for the desulfurization of a number of oil fractions. We sum up below the main criteria to be adopted to achieve a deep desulfurization efficiency.

**Choice of catalyst and its regeneration.** The continued evolution of catalytic systems offers ever...
better possibilities of upgrading the catalyst to the specific needs, on the basis of the considerations already set out. Also the ways of regenerating the catalyst play an important role: regeneration carried out not in situ offers better guarantees of restoring activity and prolongs the time interval between one regeneration and the next.

Residence times. If the volume of the catalyst cannot be increased (the preferred solution), it is necessary to reduce the space velocity, i.e. to increase the residence time in the reactor.

Hydrogen. The increase in the partial pressure of hydrogen increases the efficiency of sulphur removal and at the same time prolongs the life of the catalyst. This can be achieved either by increasing the efficiency of recycling operations, or by using purer hydrogen.

Removal of H2S. The flow of recycled hydrogen has to be treated to remove the H2S, thereby reducing its inhibiting effect, increasing the desulphurizing activity.

Temperature. Increase in temperature influences the kinetics and hence the desulphurization capacity. This option is in contrast however with the thermodynamics of the desulphurization reactions, favoured by low temperatures. Control of the temperature by means of intermediate quenching is at all events advantageous.

Type of feed. The sulphur in heavy feeds is hard to convert. Reduction of the final boiling point of the feedstock helps to attain the objectives of deep desulphurization. Obviously, if other means are not available, recourse can be had to ‘easier’ feeds, such as straight-run distillates or crudes containing less sulphur.

Hydrogen/hydrocarbons ratio. Increasing the H2/oil ratio reduces the inhibiting effect of hydrogen sulphide and ammonia. It must be remembered that under the conditions in which deep desulphurization takes place, the reactions of nitrogen compounds are also favoured, with the formation of corrosive ammonium salts (sulphides), which can precipitate at low temperatures. It is therefore important to continuously inject water into the plant so as to keep these salts from being deposited.

3.1.8 Other hydrotreating processes

As already evidenced, the range of hydrotreating processes is vast and includes, apart from those already seen, a whole series of examples ranging from the simple olefin saturation reactor (sometimes used as a pretreatment) to the hydrogenation of aromatics. Conceptually the principles illustrated above hold good, and the schemes (with one or more reactors, with hydrogen recycling) are by and large similar to those already seen.

Saturation of fractions coming from cracking processes

Saturation of fractions coming from refinery catalytic or thermal cracking processes can become necessary to reduce the development of heat and the

---

**Fig. 16.** Selective hydrogenation in two stages of pyrolysis gasoline.
consumption of hydrogen in subsequent treatments, as well as to stabilize certain fractions and preserve octane quality. In the simplest case, adding a hydrogenation reactor upstream of the desulphurization unit is sufficient. Gasolines produced by pyrolysis coming from steam cracking units (used for the production of olefins) have to be treated before separation of the aromatics or use in fuels. This is done by means of hydrogenating the double bonds present in the aliphatic chains and in the lateral ones of cyclic compounds. The process can be carried out in two stages, as shown in Fig. 16: the first one consists in selective hydrogenation of the diolefins and the acetylenes (‘cold’ hydrogenation) and is applied to the entire fraction C₅-210 °C; in the second stage the remaining olefins and diolefins are thoroughly hydrogenated and the feedstock is desulphurized (only the fraction C₆-C₈). The combined process achieves both the stabilization of the feed portion, which ends up in motor gasoline (first stage), and the preparation of a concentrate rich in aromatics, particularly suitable for subsequent recovery of these (second stage). The conditions of the second stage require a temperature of 320-380 °C, Co/Mo based catalysts and a hydrogen pressure of between 2 and 3 MPa. The heat developed by the reaction is used for vaporizing the feed and for its preheating.

**Saturation of aromatics**

*Reduction of benzene content in gasolines.*

Saturation of the aromatics can become necessary to reduce the benzene content in the fractions intended for the formulation of commercial gasolines, in order to respect the limits in the specifications. The equilibrium of the reaction:

\[ \text{C}_6H_6 + 3\text{H}_2 \rightleftharpoons \text{C}_8H_{12} \]

can be shifted in the desired sense by acting on the working conditions. Thus, in the reforming process the endothermic reactions of aromatization (from right to left in the reaction shown above) are favoured by low pressures and high temperatures, whereas in saturation processes it is necessary to work at higher pressures and definitely lower temperatures.

In practice, to bring about saturation, a benzene-enriched intermediate fraction is separated (normally by means of distillation downstream of the reforming), which is then hydrogenated to saturate the benzene (Fig. 17). The column separates at the top the hydrocarbons with low boiling-points (≤C₈). With some C₇ isoparaffins, the benzene forms relatively volatile azeotropes, which pass into the distillate.

The benzene-rich fraction is separated over the feed tray and conveyed to the saturation reactor, containing a noble metal based catalyst. The effluent from the reactor, basically devoid of benzene, is again conveyed to the column. In the absence of benzene, the iso-C₇ are released and are extracted at the bottom of the column. The hydrogen is used in a more or less stoichiometric quantity. The reaction temperatures vary between 180 and 280 °C, with a difference between the reactor inlet and outlet that can exceed 100 °C. Given the characteristics of the catalysts, the hydrogen used must be H₂S-free.

**Saturation of aromatics in middle distillates.**

Saturation of the aromatics may be necessary in middle distillates to improve the smoke point of kerosenes and the cetane number of diesel fuels. The schemes of the relevant processes are similar to those of other hydrotreating plants, but with more severe working conditions, on the basis of the considerations set out earlier.

Very often these treatments are conducted downstream of desulphurization, with which they are combined. The HDS section works under the conditions and with the catalysts already seen for desulphurization;
Selective hydrogenation

In some cases it is necessary to hydrogenate selectively a number of unsaturated hydrocarbons, and not others; this occurs, for example, for the gaseous fractions of steam cracking, which contain acetylenic or allenic compounds (acetylene, propadiene, methylacetylene) in minimum quantities, which it is not worthwhile recovering. The reactivity of these compounds creates problems for a number of uses of ethylene and of propylene, such as the production of polymers.

For obvious reasons, acetylenic compounds have to be hydrogenated to give ethylene and propylene, without hydrogenating the ethylene and the propylene already present, which are the products of cracking. Butadiene, also present in the gases, tends to polymerize and to form rubbers; however, it is generally in sufficient quantities to justify recovery. Otherwise hydrogenation to butene is applied.

The hydrogenation of acetylene is normally carried out on the fraction C₃, after the separation of methane and hydrogen. The hydrogenation of acetylenic C₃ requires different conditions and is carried out in a second plant. If necessary, the butadiene is hydrogenated to butene in a subsequent phase. The main problem consists in managing to saturate all the acetylene without hydrogenating (and thus losing) the ethylene, the chief component of the fraction C₂; the same thing applies for propadiene and for methylacetylene, which have to be hydrogenated only in part, without losing the propylene.

Hydrogenation is complete in a vast interval of pressures and temperatures; there are therefore no particular thermodynamic limits, but on the other hand there are problems of selectivity. Considering the greater reactivity of highly unsaturated components, it is best to operate at low temperatures, using a selective catalyst. The hydrogen must be in a more or less stoichiometric quantity and very pure. As the affinity of hydrocarbons for hydrogenation with metallic catalysts decreases, passing from acetylene to olefins and to paraffins, it is advisable to use catalysts containing a low noble metal content (generally palladium, which is more selective for the hydrogenation of triple bonds than platinum and nickel); in practice the catalyst contains a much lower noble metal concentration than a typical alumina-supported hydrogenation catalyst (about 0.03-0.05%, instead of 0.3-0.4%); the use of a promoter such as silver further improves selectivity.

The excessive initial activity of the catalyst can be moderated with the addition of carbon oxide. Due to the exothermicity of the reaction, the temperatures vary from approximately 30°C to around 70°C between the reactor inlet and outlet (SoR). The formation of oligomerization compounds (green oils) on the catalyst is however difficult to avoid.

Hydrofinishing of lubricating oils

The purpose of treating with hydrogen the bases for lubricating oils is to improve their thermal stability, resistance to oxidation and colour (or in any case their organoleptic features). Catalytic hydrofinishing is conducted at medium hydrogen pressures and relatively moderate temperatures. The consumption of hydrogen depends on the type of feed and on the quality of the finished product. The scheme of the process is similar, as far as the hydrogenation section is concerned, to that of hydrodesulphurization.

Hydrotreating of residues

Before being sent for conventional hydrocracking treatments, oil residues, especially the heavy ones, have to be subjected to pre-hydrotreatment to reduce their content of sulphur, nitrogen, Conradson carbon and metals. These processes can also be used to make heavy fuel oils more ecocompatible, without any further treatment.

In general fixed-bed (two to four) catalytic reactors are used in two stages: the first one having a demetallizing function, and the second one to carry out a partial desulphurization. Depending on the working conditions (especially the hydrogen pressure), partial cracking can also take place, with the production of lighter products. This subject will be dealt with in the sections describing the conversion of residues.

References


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