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TABLE OF CONTENT

INTRODUCTION

Scope 4
General Design Consideration 5

DEFINITIONS 28

NOMENCLATURE 31

THEORY OF THE DESIGN 33

Prefractionation Section 34
Reactors Design and Operation 34
  A. Feed System 35
  B. Reactor System 35
  C. Wash Water System 36
  D. Separator System 36
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INTRODUCTION

Scope

This design guideline covers the basic elements in the field of hydrotreating in sufficient detail to allow an engineer to design a hydrotreater with the suitable process parameters; size of diameter, velocity, and pressure drop. This design guideline includes; design of reactor, catalyst, pressure drop and hydrogen consumption.

Hydrotreating or catalytic hydrogen treating removes objectionable materials from petroleum fractions by selectively reacting these materials with hydrogen in a reactor at relatively high temperatures and moderate pressures. The sizing of the unit and the choice of catalyst is important to give the optimum efficiency of hydrotreating.

The design of hydrotreating may be influenced by factors, including process requirements, economics and safety. All the important parameters used in the guideline are explained in the definition section which help the reader more understand the meaning of the parameters or the terms utilized.

In the application section of this guideline, three case studies are shown and discussed in detail, highlighting the way to apply the theory for the calculations. The theory section explains reactor sizing, hydrotreating catalyst, and common problems in hydrotreating.

Example Calculation Spreadsheets are part of this guideline. This Example Calculation Spreadsheets are based on case studies in the application section to make them easier to understand.

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INTRODUCTION

General Design Consideration

Oil and natural gas are the most important raw materials for the organic chemical industry. Oil is a complex mixture, its composition depends on the location where it is produced. The most important components are:

1. Hydrocarbons (alkanes, alkenes, cycloalkanes, aromatics)
2. Sulphur compounds
3. Nitrogen compounds
4. Oxygenates.

There are many methods that may be employed to remove acidic components (primarily H₂S and CO₂) and other impurities from hydrocarbon streams. The available methods may be broadly categorized as those depending on chemical reaction, absorption, adsorption or permeation.

Hydrotreaters are the most common process units in modern petroleum refineries. hydrotreating catalysts represent 10% of the annual sales of the total market of catalysts. In hydrotreating units, reactions that convert organic sulfur and nitrogen into H₂S and NH₃ also produce light hydrocarbons.

In hydrotreating catalytic hydrogenation takes place in which double bonds are hydrogenated and S, N, O and metals, are removed from molecules and aromatic molecules are hydrogenated using hydrogen as a reactant. These processes use catalysts based on transition metal sulfides.

The common objectives and applications of hydrotreating are listed below:

1. Naphtha (catalytic reformer feed pretreatment) : to remove sulfur, nitrogen, and metals that otherwise would poison downstream noble metal reforming catalysts
2. Kerosene and diesel : to remove sulfur and to saturate olefins and some of the aromatics, resulting in improved properties of the streams (kerosene smoke point, diesel cetane number or diesel index) as well as storage stability
3. Lube oil : to improve the viscosity index, color, and stability as well as storage stability
4. FCC feed: to improve FCC yields, reduce catalyst usage and stack emissions
5. Resids: to provide low sulfur fuel oils to effect conversion and/or pretreatment for further conversion downstream.

Table 1: Feeds and product objectives for different kinds of hydrotreaters

<table>
<thead>
<tr>
<th>Feed</th>
<th>Products from Hydrotreating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>Catalytic reformer feed</td>
</tr>
<tr>
<td>Straight-run light gas oil</td>
<td>Kerosene, jet fuel</td>
</tr>
<tr>
<td>Straight-run heavy gas oil</td>
<td>Diesel fuel</td>
</tr>
<tr>
<td>Atmospheric residue</td>
<td>Lube base stock, low-sulfur fuel oil, RFCC* feed</td>
</tr>
<tr>
<td>Vacuum gas oil</td>
<td>FCC feed, lube base stock</td>
</tr>
<tr>
<td>Vacuum residue</td>
<td>RFCC* feed</td>
</tr>
<tr>
<td>FCC light cycle oil</td>
<td>Blend stocks for diesel, fuel oil</td>
</tr>
<tr>
<td>FCC heavy cycle oil</td>
<td>Blend stocks for diesel, fuel oil</td>
</tr>
<tr>
<td>Visbreaker gas oil</td>
<td>Blend stocks for diesel, fuel oil</td>
</tr>
<tr>
<td>Coker gas oil</td>
<td>FCC feed</td>
</tr>
<tr>
<td>Deasphalted oil</td>
<td>Lube base stock, FCC feed</td>
</tr>
</tbody>
</table>

*RFCC = “residue FCC unit” or “reduced crude FCC unit,” which are specially designed to process feeds that contain high concentrations carbon-forming compounds.

The following chemical steps and/or reactions occur during the hydrotreating process (depending on the impurities present):

1. Sulfur removal, also referred to as desulfurization or hydro-desulfurization (HDS) in which the organic sulfur compounds are converted to hydrogen sulfide
2. Nitrogen removal, also referred to as denitrogenation or hydro-denitrogenation (HDN) in which the organic nitrogen compounds are converted to ammonia
3. (Organo-metallic) metals removal, also referred to as hydro-demetallation or hydrodemetalization, in which the organo-metals are converted to the respective metal sulfides

4. Oxygen removal, in which the organic oxygen compounds are converted to water

5. Olefin saturation, in which organic compounds containing double bonds are converted to their saturated homologues

6. Aromatic saturation, also referred to as hydro-dearomatization, in which some of the aromatic compounds are converted to naphthenes

7. Halides removal, in which the organic halides are converted to hydrogen halides

i. Sulfur removal

Sulfur removal occurs via the conversion to H₂S of the organic sulfur compounds present in the feedstock. This conversion is sometimes referred to as desulfurization or hydro-desulfurization (HDS). The hydrotreated naphtha sulfur content should be maintained well below the 0.5 weight ppm maximum. Commercial operation at 0.2 weight ppm sulfur or less in the hydrotreater product naphtha is common. In the naphtha to atmospheric residue range, can all be classified as belonging to one of the following six sulfur types: mercaptans, sulfides, di-sulfides, thiophenes, benzo-thiophenes, and di-benzo-thiophenes. The mechanism for the desulfurization reaction is shown below

Typical sulfur removal reactions are shown below.

a. (Mercaptan) \[ C-C-C-C-C-SH + H2 \rightarrow C-C-C-C-C + H2S \]

b. (Sulfide) \[ C-C-S-C-C-C + 2H2 \rightarrow 2 C-C-C + H2S \]

c. (Disulfide) \[ C-C-S-S-C-C-C + 3H2 \rightarrow 2 C-C-C + 2 H2S \]
.d. (Cyclic sulfide)

\[
\begin{align*}
\text{S} & + 2\text{H}_2 & \rightarrow & \text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2 + \text{H}_2\text{S}
\end{align*}
\]

Figure 2: Sulfur Removal

- Mercaptans sulphides: \( R - \text{SH} \)
  - Easy
- Dissulphides: \( R - \text{S} - R_2 \)
  - Moderate difficulty
- Thiophines
- Benzothiophenes
  - Difficulty
- Substituted dibenzothiophenes
  - Extremely difficult
- 4,6-Substituted dibenzothiophenes

Figure 2: Difficulty of desulphurization

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ii. Nitrogen removal

Nitrogen is mostly found in the heaviest end of petroleum fractions in five- and six member aromatic ring structures. Both the molecular complexity and quantity of nitrogen containing molecules increases with increasing boiling range, making them more difficult to remove. In denitrogenation, the aromatic is saturated first and then the nitrogen is removed. This is shown below.

(A) Aromatic hydrogenation

(B) Hydrogenolysis

(C) Denitrogenation

\[ H_3C-CH_2-CH_2-CH_2-NH_2 + H_2 \rightarrow H_3C-CH_2-CH_2-CH_2-CH_2NH_2 \]

Figure 3: Denitrogenation mechanism
iii. Oxygen removal

Most petroleum crudes contain low levels of oxygen. The oxygen-containing compounds are converted, by hydrogenation, to the corresponding hydrocarbon and water. The lower molecular weight compounds are easily hydrogenated, however, the higher molecular weight compounds such as furans can be difficult to remove. Shown below are typical examples of de-oxygenation.

(A) Phenols

\[
\text{Phenol} + \text{H}_2 \rightarrow \text{phenyl} + \text{H}_2\text{O}
\]

(B) Oxygenates

\[
(\text{CH}_3)_3\text{C-O-CH}_3 + 2\text{H}_2 \rightarrow (\text{CH}_3)_3\text{CH} + \text{H}_2\text{O} + \text{CH}_4
\]

(C) Naphthenic acids

\[
\text{Naphthenic acid} + 3\text{H}_2 \rightarrow \text{alkyl} + 2\text{H}_2\text{O}
\]

Figure 4: Oxygen removal mechanism
Oxygenate removal is favored by high pressure and high temperatures. For high feed concentrations, lower liquid space velocities are required. Processing of such compounds should be done with care. Complete oxygen removal is not normally expected and may only be 50%. However, MTBE has been shown to be essentially removed, but not completely, depending on the feed concentrations.

iv. Aromatic saturation

Saturation of aromatics is desirable for improvement of the properties of petroleum products e.g. smoke point, diesel index, etc. The aromatics found in the naphtha to gas oil boiling range are present as one, two, and three ring aromatics often referred to as mono, di, and tri aromatics. Typical reactions are shown below

(A) One ring – Toluene

\[
\begin{array}{c}
\text{苯} \quad + \quad 3\text{H}_2 \\
\text{+CH}_3 & \quad \text{→} & \quad \text{环} \quad + \quad \text{CH}_3
\end{array}
\]

(B) Two ring – Naphthalene

\[
\begin{array}{c}
\text{环} \quad + \quad 3\text{H}_2 \\
\text{+} & \quad \text{→} & \quad \text{环} \quad + \quad \text{环}
\end{array}
\]

(C) Three ring – Phenanthrene

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v. Metals removal

Most metallic impurities occur in naphtha and middle distillates at ppm or even ppb levels. They are present as organo-metallic compounds. In naphtha hydrotreating, the most commonly occurring metals are arsenic from certain crude sources, mercury from certain condensates and silicon from anti-foam agents used in visbreakers and cokers. These compounds decompose in the hydrotreater and the metal is deposited on the catalyst in the form of metal sulfide as shown below.

\[ R\text{-Me} + H_2S \rightarrow R\text{-H}_2 + \text{MeS} \]

Removal of metals is essentially complete, at temperatures above 315°C (600°F), up to a metal loading of about 2-3 weight percent of the total catalyst. Some Hydrotreating catalysts have increased capability to remove Silicon, up to 7-8 wt% of the total catalyst. Above the maximum levels, the catalyst begins approaching the equilibrium saturation level rapidly, and metal breakthrough is likely to occur. In this regard, mechanical problems inside the reactor, such as channeling, are especially bad since this results in a substantial overload on a small portion of the catalyst in the reactor.
vi. Olefin saturation

Hydrogenation of olefins is necessary to prevent fouling or coke deposits in downstream units. Olefins can polymerize at the Catalytic Reforming Unit combined feed exchanger and thus cause fouling. These olefins will also polymerize upstream of the naphtha hydrotreating reactor and cause heat transfer problems. A Naphtha Hydrotreating Unit must be approached with care because of the high exothermic heat of reaction. The olefin reaction is detailed below.

a. (Linear olefin) \[ \text{C-C-C-C} = \text{C-C} + \text{H}_2 \rightarrow \text{C-C-C-C} \] (and isomers)

b. (Cyclic olefin)

\[
\text{C-C-C-C-C-C (and isomers)} + \text{H}_2 \rightarrow \text{C-C-C-C-C-C}
\]

As a guide in the selection of the method of treating to be used, the following characteristics of each are given:

**A. Regenerated Caustic**

The regenerated caustic method of removing methyl and ethyl mercaptans from LP-gas or butane employs countercurrent contacting of the liquid with 10% sodium hydroxide solution in a packed column. The caustic is regenerated in a stripping column by the addition of open steam or by steam internally generated by a column heating element.

A condenser may be used to condense water vapors that go overhead with the liberated mercaptan vapors. The condensate is returned to the stripping column to maintain caustic concentration. An LP-gas stream containing 0.03% mercaptan sulfur can be treated doctor sweet with volume ratios of hydrocarbon to caustic as high as 33 to 1.
Approximately six pounds of process steam per gallon of caustic are required for regeneration at this hydrocarbon/ caustic volume ratio.

The diameter of the extractor is based upon the hydrocarbon throughput. A typical design uses flow rates of 10-15 GPM/ft² of cross-sectional area for a column packed with 1-1/4 in. raschig rings. Other tower packing may be used and, if so, the above throughput would be changed. The packed height is normally about 30 feet in two or three packed sections to optimize dispersion of the hydrocarbon phase. An additional 8 - 10 feet of column height is required for distribution and settling areas.

1. Can handle large volumes of hydrocarbon.
2. Primarily for removing methyl and ethyl mercaptans.
3. Capable of producing a doctor-sweet product.
4. Reduces the total sulfur content of treated product.

Figure 6: Non regenerative caustic

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B. Solid Copper Chloride

The copper chloride sweetening process can be used to sweeten natural gasoline. It is a continuous process in which the mercaptan sulfur in the gasoline is converted to disulfides in a reaction with copper chloride. To maintain the reactivity of the bed, water should be added by injecting a small quantity of steam into the gasoline feed stream to the treater, or bubbling a sidestream of gasoline through a small pot containing water and returning it to the main stream.

Any hydrogen sulfide in the gasoline must be removed by a caustic wash before contact with the bed. The "standard" bed depth is 7 feet with a maximum of 9 feet and a minimum of 4 feet.

Air is added to the sour charge by means of a diffusing disc at the rate of 1 cu ft of air (STP)/bbl of charge for each 0.01% mercaptan sulfur. If the mercaptan content of the gasoline is high, the operating pressure must be increased to hold the additional air in solution. The rate of air injection should be maintained as near to this figure as practical since insufficient air will prevent complete reactivation of the reagent and excess air may result in air binding of the treater vessel — an extremely hazardous condition.

1. Can treat gasoline streams with relatively high mercaptan content.
2. Suited for small flow rate.
3. Sulfur content not reduced.
4. Water content must be only that of saturation.
5. Hydrogen sulfide must be removed ahead of contact with bed.
6. Excess regeneration oxygen may cause corrosion downstream of bed. Gasoline with components that may be affected by oxygen, such as olefins, should not be treated with this process.
7. Capable of producing doctor-sweet product.
Table 2: Standard solid copper reagent towers

<table>
<thead>
<tr>
<th>Charge rate Bbl/day</th>
<th>Tower size ft</th>
<th>Bed volume Ft³</th>
<th>Reagent lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>187</td>
<td>2 x 10</td>
<td>21.9</td>
<td>1090</td>
</tr>
<tr>
<td>424</td>
<td>3 x 10</td>
<td>49.5</td>
<td>2475</td>
</tr>
<tr>
<td>752</td>
<td>4 x 10</td>
<td>88</td>
<td>4400</td>
</tr>
<tr>
<td>1177</td>
<td>5 x 10</td>
<td>137.5</td>
<td>6870</td>
</tr>
<tr>
<td>1500</td>
<td>5 x 12</td>
<td>176.5</td>
<td>8830</td>
</tr>
</tbody>
</table>

C. Batch Caustic Wash

Caustic wash can be used to remove hydrogen sulfide and/or lighter mercaptans from LP-gas and gasoline. Liquid hydrocarbon and recirculated caustic (Ratio 1:0.5) are mixed by means of a pump or static mixer and discharged to a settling tank where the liquids separate. The size of the tank required is based on the retention time necessary for complete separation of the gasoline-caustic emulsion. The retention time varies from 1-1/2 hours for heavy gasolines to 30 minutes or less for propane. A coalescing element on the settling tank inlet can reduce the required retention time.

1. Can use a single wash.
2. Best suited for streams with low mercaptan content (if mercaptan removal is important).
3. Primarily for removing trace amounts of hydrogen sulfide and methyl and ethyl mercaptans.
4. Disposing of spent caustic can be a major consideration.
5. Relatively high caustic consumption per gallon of product.
D. Solid Potassium Hydroxide

1. Low installation and operation costs.
2. Acts as a desiccant as well as removing the sulfur compounds.
3. Suitable for removing trace amounts of H2S.

E. Molecular Sieve

1. Can handle large or small streams.
2. Reduces total sulfur content by removing hydrogen sulfide, mercaptans, and partially removing organic sulfur in the same adsorber vessel.
3. Will produce 1A copper-strip, doctor-sweet product.
4. Will dry in the same step with additional equipment.
5. Requires that the regeneration gas be made slightly sour by use of this stream to strip sulfur compounds from the molecular sieve.

F. Merox

Sour product is treated with caustic containing Merox catalyst to extract the mercaptans. The Merox solution is regenerated by mixing with air and oxidizing. Disulfides and excess air are removed overhead. Existing extraction equipment with steam regeneration can be adapted to the Merox process. The Merox solution gives a very high degree of removal of mercaptans in a liquid stream. If more complete removal is desired, Merox also provides a fixed-bed catalytic conversion of mercaptans to disulfides.

1. Can handle large or small streams.
2. Eliminates problem of disposal of spent caustic.
3. Product is sweet when it leaves unit; no holding period is required.
4. Adds problems of sulfur compounds in regeneration air leaving the regenerator.
5. Low operating cost and investment requirement.
6. Ease of operation
7. Limited Mercaptan treating not less than 5ppm

G. Other Processes

Others offer several processes for the removal of Na2S and/or mercaptans from light hydrocarbon liquids. In all of these the key technology is use of a patented Fiber Film bundle to achieve intimate contact between the hydrocarbon feed and the caustic solution. The bundle is comprised of long continuous small diameter fibers placed in a pipe. The caustic solution preferentially wets the fibers, creating a large interfacial area for contact with the hydrocarbon liquid. The fiber bundles can be installed easily into existing systems.

1. Can handle large or small streams of light hydrocarbon liquids.
2. Removes mercaptans and organic acids.
3. Uses a bundle of fibers to increase interfacial area between caustic and hydrocarbon.
4. Sulfur compounds are present in regeneration air

The gas treating process can affect the design of the entire gas processing facility including methods chosen for acid gas disposal and sulfur recovery, dehydration, liquids recovery, liquids fractionation and liquid product treating. Some of the factors to be considered in making a gas treating process selection are:

1. Air pollution regulations regarding sulfur compound disposal and/or Tail Gas Clean Up (TGCU) requirements.
2. Type and concentration of impurities in the sour gas.
4. Specifications for the acid gas.
5. Temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered.
6. Volume of gas to be processed.
9. Capital cost and operating cost.
10. Royalty cost for process.
11. Liquid product specifications.
12. Disposal of byproducts considered hazardous chemicals.

A. Naphtha hydrotreating

Naphtha hydrotreating process is catalytic refining process employing a selected catalyst and a hydrogen-rich gas stream. It decomposes organic sulfur, oxygen and nitrogen compounds contained in hydrocarbon fractions. In addition, hydrotreating removes organometallic compounds and saturates olefinic compounds.

The feed stream and the hydrogen gas stream are pre-heated by exchange with the hot reactor effluent stream. The feed then enters the fired heater which brings it up to the reactor temperatures (about 450 F) and leaves the heater to enter the reactor which operates at about 400–450 psig. Sulfur is removed from the hydrocarbon as hydrogen sulfide in this reactor and the reactor effluent is cooled to about 100 F by heat exchange with the feed. The cooled effluent is collected in a flash drum where the light hydrogen rich gas is flashed off. This gas enters the suction side of the booster compressor which delivers it to other hydrotreaters. The liquid phase from the drum is pumped to a reboiled stabilizer. The overhead vapor stream from the stabilizer is routed to fuel while the bottom product, cat reformer feed, is pumped to the cat reformer.

1. Naphtha hydrotreated primarily for sulfural removal. Mostly mercaptans (R-SH) and sulfides (R-S-R’), some disulfides (R-S-S-R’) and thiophenes.
2. Cobalt molybdenum on alumina most common catalyst
3. Chemical hydrogen consumption typically 50 – 250 scf/bbl. For desulfurization containing up to 1 wt% sulfur typically 70 – 100 scf/bbl. For significant nitrogen and sulfur removal typically 250 scf/bbl.
Naphtha Hydrotreating Process

1. Reactor typically at 200 psig and 700 F. Temperature increases to compensate for decrease in catalyst activity.

2. Hydrogen recycle typically 2000 scf/bbl

3. Acid gas removal may not be directly incorporated into recycle gas loop. Overhead vapor from fractionators to saturates gas plant to recover light hydrocarbons and remove H2S.

4. Product fractionation: pentane/hexane overhead either to blending or isomerization, bottoms to reformer.

Table 3: Catalysts for naphtha hydrotreating

<table>
<thead>
<tr>
<th>Designator</th>
<th>Base</th>
<th>Form</th>
<th>Size (in)</th>
<th>ABD lb/ft³</th>
<th>Metals</th>
<th>Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-6</td>
<td>Alumina</td>
<td>Sphere</td>
<td>1/16</td>
<td>36</td>
<td>Ni/Mo/Co</td>
<td>Steam/Air</td>
</tr>
<tr>
<td>S-9</td>
<td>Alumina</td>
<td>Sphere</td>
<td>1/16</td>
<td>38</td>
<td>Mo/Co</td>
<td>Steam/Air</td>
</tr>
<tr>
<td>S-12</td>
<td>Alumina</td>
<td>Extrudate</td>
<td>1/16</td>
<td>45</td>
<td>Mo/Co</td>
<td>Inert Gas</td>
</tr>
<tr>
<td>S-15</td>
<td>Alumina</td>
<td>Extrudate</td>
<td>1/16</td>
<td>45</td>
<td>Ni/Mo</td>
<td>Inert Gas</td>
</tr>
<tr>
<td>S-16</td>
<td>Alumina</td>
<td>Extrudate</td>
<td>1/16</td>
<td>45</td>
<td>NVMo</td>
<td>Inert Gas</td>
</tr>
<tr>
<td>S-18</td>
<td>Alumina</td>
<td>Sphere</td>
<td>1/16</td>
<td>45</td>
<td>Mo/Co</td>
<td>Inert Gas</td>
</tr>
<tr>
<td>S-19</td>
<td>Alumina</td>
<td>Extrudate</td>
<td>1/16 — 1/16</td>
<td>41-45</td>
<td>Ni/Mo</td>
<td>Inert Gas</td>
</tr>
<tr>
<td>S-120</td>
<td>Alumina</td>
<td>Cylinder</td>
<td>1/16</td>
<td>47</td>
<td>Mo/Co</td>
<td>Inert Gas</td>
</tr>
<tr>
<td>N-108</td>
<td>Alumina</td>
<td>Quadlobe</td>
<td></td>
<td>40</td>
<td>Mo/Co</td>
<td>Inert Gas</td>
</tr>
<tr>
<td>N-204</td>
<td>Alumina</td>
<td>Extrudate</td>
<td>1/20</td>
<td>46</td>
<td>Ni/Mo</td>
<td>Inert Gas</td>
</tr>
<tr>
<td>HC-K</td>
<td>Alumina</td>
<td>Quadlobe</td>
<td>1/20</td>
<td>57</td>
<td>Ni/Mo</td>
<td>Inert Gas</td>
</tr>
</tbody>
</table>
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Figure 7: Naphtha hydrotreater
B. Distillate Hydrotreating

1. All liquid distillate streams contain sulfur compounds that must be removed
2. Saturate olefins in diesel to improve the cetane number
3. Hydrogenation at the high pressure produces small amounts of naphtha from hydrocracking. It required to get at the embedded sulfur
4. Diesel hydrotreater stabilizer will have an upper sidestream draw producing the naphtha which is recycled to motor gasoline processing.

Distillate Hydrotreating Process

1. Reactor typically at 800 F
2. Hydrogen recycle starts at 2000 scf/bbl, consumption 100 to 400 scf/bbl
3. Condition highly dependent upon feedstock.
4. Distillate (jet fuel and diesel) with 85% - 95% sulfur removal typically pressure about 300 psig, hydrogen consumption 200 – 300 scf/bbl.
5. Saturation of diesel for cetane number improvement has over 800 scf/bbl hydrogen with pressure up to 1000 psig
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Figure 8: Distillate hydrotreater
C. Gas Oil Hydrotreating

This process uses a recycled hydrogen stream to desulphurise a gas oil feed. A hydrogen rich stream is introduced at the coil outlet prior to the mixed streams entering the reactor. The reactor contains a bed of cobalt molybdenum on alumina catalyst and desulfurization takes place over the catalyst with 70 - 75% of the total sulfur in the oil being converted to \( \text{H}_2\text{S} \).

The reactor effluent is cooled by the cold feed stream, water or air. This cooled effluent enters a flash drum where the gas phase and liquid phase are separated. The gas phase rich in \( \text{H}_2\text{S} \) and hydrogen enters the recycle compressor. The gas stream then enters an amine contactor where the \( \text{H}_2\text{S} \) is absorbed into the amine and removed from the system.

1. Catalytic cracker feedstocks (atmospheric gas oil, light vacuum gas oil, solvent deasphalting gas oil) hydrotreated severely sulfur removal, opening of aromatic rings, and removal of heavy metals
2. Desulfurization of gas oil can be achieved with a relatively modest decomposition of structures
3. Gas oil can be contaminated with resins and asphaltenes. They deposited in hydrotreater. Thus require catalyst replacement with a shorter run length than determined by deactivation.
4. Guard chamber may be installed to prolong bed life
5. Nickel molybdenum catalyst system for severe hydrotreating
6. Gas oil units more expensive beause of more intensive hydrogenation, and required more equipment such as quench, multi stage flash and more complex strippers.

Gas Oil Hydrotreating Process

1. Normally two reactor beds, so the temperature is rise
2. Hydrogen partial pressure requirements related to ring saturation and amount of sulfur and other heteroatoms
   a. For low ring saturation 300 psig may be sufficient
b. 1200 psig will convert 25% ring saturation and somewhat less than 95% sulfur removal.

c. Pressure as high as 1500 psig can achieve saturation of 30% of aromatic rings.

3. Hydrogen absorption of 300 scf/bbl could give about 80% sulfur removal and only require 300 psig.

---

**Figure 9: Oil hydrotreater**
Below is design guideline for hydrotreating

1. Hydrotreating reactions are carried out at temperatures of 290 to 430°C and pressures ranging from 7 barg for naphtha to 140 barg for gas oils.
2. Two catalysts can be used on alumina; Co/Mo is more effective for S removal, Ni/Mo is more effective for N removal and aromatics saturation
3. When hydrotreating heavier fractions a “guard” reactor is required
4. Metals (particularly nickel and vanadium) are generally bound in large molecules requires catalyst with large pores.
5. Removed nickel and vanadium are bound up with sulphur and remain on the catalyst surface
6. Guard reactors have layers of catalyst starting with large pore size and decreasing pore size through the reactor
7. The hydrogen consumption increases depending on the severity and feedstock. Table 1 show the hydrogen consumption for typical feedstock
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Table 5: Hydrogen consumption for typical feedstock

<table>
<thead>
<tr>
<th>Application</th>
<th>Typical H2 use (Nm3/bbl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desulphurization of SR naphtha</td>
<td>1.5 → 4</td>
</tr>
<tr>
<td>Desulphurization of cracked naphtha</td>
<td>3 → 9</td>
</tr>
<tr>
<td>Desulphurization of kerosene</td>
<td>8 → 11</td>
</tr>
<tr>
<td>Light desulphurization of diesel</td>
<td>8 → 11</td>
</tr>
<tr>
<td>Deep desulphurization of diesel</td>
<td>9 → 18</td>
</tr>
<tr>
<td>Desulphurization of heavy gas oil</td>
<td>14 → 28</td>
</tr>
</tbody>
</table>
 DEFINITIONS

Absorption: A separation process involving the transfer of a substance from a gaseous phase to a liquid phase through the phase boundary.

Acid Gases: Impurities in a gas stream usually consisting of CO2, H2S, COS, RSH, and SO2. Most common in natural gas are CO2, H2S and COS.

Adsorption: The process by which gaseous components adhere to solids because of their molecular attraction to the solid surface.

Alkanolamine: An organic nitrogen bearing compound related to ammonia having at least one, if not two or three of its hydrogen atoms substituted with at least one, if not two or three linear or branched alkanol groups where only one or two could also be substituted with a linear or branched alkyl group (i.e. methyl diethanolamine MDEA). The number of hydrogen atoms substituted by alkanol or alkyl groups at the amino site determine whether the alkanolamine is primary, secondary or tertiary.

Antifoam: A substance, usually a silicone or a long-chain alcohol, added to the treating system to reduce the tendency to foam.

Aromatic molecules - Any of a large class of organic compounds whose molecular structure includes one or more planar rings of atoms, usually but not always six carbon atoms. The ring's carbon-carbon bonds (bonding) are neither single nor double but a type characteristic of these compounds, in which electrons are shared equally with all the atoms around the ring in an electron cloud.

Catalyst - A substance, usually used in small amounts relative to the reactants, that modifies and increases the rate of a reaction without being consumed in the process.

Catalytic - Causing a chemical reaction to happen more quickly

Cetane number - The performance rating of a diesel fuel, corresponding to the percentage of cetane in a cetane-methylnaphthalene mixture with the same ignition performance. A higher cetane number indicates greater fuel efficiency. Also called cetane rating.
Chelate: An organic molecule in which a central metallic ion is held in a coordination compound.

Claus Process: The process in which one third of the H₂S is burned to SO₂ which is then reacted with the remaining H₂S to produce elemental sulfur.

Deasphalting - The process of removing asphalt from petroleum fractions.

Degradation Products: Impurities in a treating solution that are formed from both reversible and irreversible side reactions.

Denitrogenation - Removal of nitrogen dissolved in the bloodstream and body tissues by breathing 100% oxygen for an extended period.

Desulfurization - The process of removing sulfur from a substance, such as flue gas or crude.

Furans - One of a group of colorless, volatile, heterocyclic organic compounds containing a ring of four carbon atoms and one oxygen atom, obtained from wood oils and used in the synthesis of furfural and other organic compounds.

Grain: A unit of mass where one pound is equivalent to 7,000 grains and a specification of 0.25 grain of H₂S per 100 SCF is equivalent to an H₂S concentration of 4.0 ppmv.

Hydrotreating - Oil refinery catalytic process in which hydrogen is contacted with petroleum intermediate or product streams to remove impurities, such as oxygen, sulfur, nitrogen, or unsaturated hydrocarbons.

LHSV (Liquid hourly space velocity) - Usually feed flow rate divided by catalyst mass or volume in heterogeneous catalysis

Maldistribution - Non-uniform liquid/gas flow leads to poor catalyst utilization, resulting in lower than expected activity and cycle length.

Mercaptans - A group of sulfur-containing organic chemical substances. They smell like rotting cabbage, and are, for the most part, what make pulp mills smell like pulp mills. If mercaptans are in the air, even at low concentrations, they are very noticeable.
Naphtha - Normally refers to a number of flammable liquid mixtures of hydrocarbons, i.e., a component of natural gas condensate or a distillation product from petroleum, coal tar or peat boiling in a certain range and containing certain hydrocarbons.

Physical Solvent: A liquid capable of absorbing selected gas components by solubility alone without associated chemical reactions.

Polythionic acid - an oxoacid which has a straight chain of sulfur atoms and has the chemical formula $H_2S_nO_6$

ppmv: A volume concentration of a species in a bulk fluid measured in parts per million. 
Residence Time: The time period for which a fluid will be contained within a specified volume.

Selective Treating: Preferential removal of one acid gas component, leaving at least some of the other acid gas components in the treated stream.

Sour Gas: Gas containing undesirable quantities of hydrogen sulfide, mercaptans and/or carbon dioxide.

Space velocity - The relationship between feed rate and reactor volume in a flow process; defined as the volume or weight of feed (measured at standard conditions) per unit time per unit volume of reactor (or per unit weight of catalyst).

Threshold Limit Value: The amount of a contaminant to which a person can have repeated exposure for an eight hour day without adverse effects.
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NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Deactivation rate, °F/bpp</td>
</tr>
<tr>
<td>A_{bed}</td>
<td>Cross-sectional area of bed, m²</td>
</tr>
<tr>
<td>A_C</td>
<td>Catalyst area, cm²</td>
</tr>
<tr>
<td>A_C/V_S</td>
<td>Outer surface / unit volume solid, cm²/cm³</td>
</tr>
<tr>
<td>D^0_S</td>
<td>Initial desulfurization activity</td>
</tr>
<tr>
<td>d_c</td>
<td>Diameter of catalyst, cm</td>
</tr>
<tr>
<td>d_R</td>
<td>Diameter, m</td>
</tr>
<tr>
<td>D_s</td>
<td>Desulfurization activity</td>
</tr>
<tr>
<td>Eff</td>
<td>% S &amp; N removes, %</td>
</tr>
<tr>
<td>F</td>
<td>Feed rate, bbl/day</td>
</tr>
<tr>
<td>F_{H2}</td>
<td>H₂ rate, scf/bbl</td>
</tr>
<tr>
<td>G_{H2}</td>
<td>Feed rate H₂, scf/hr</td>
</tr>
<tr>
<td>H₂cons</td>
<td>H₂ Consumption, kg/hr</td>
</tr>
<tr>
<td>H₂purity</td>
<td>Mole fraction of hydrogen purity</td>
</tr>
<tr>
<td>H₂S</td>
<td>H₂S formed, kg moles/hr</td>
</tr>
<tr>
<td>L_{bed}</td>
<td>Length bed, m</td>
</tr>
<tr>
<td>L_R</td>
<td>Reactor length, m</td>
</tr>
<tr>
<td>%N</td>
<td>% wt nitrogen in feed, %</td>
</tr>
<tr>
<td>M_F</td>
<td>Molar weight feed rate, kg moles/hr</td>
</tr>
<tr>
<td>M_{H2}</td>
<td>Molar feed rate H₂, Kg moles/hr</td>
</tr>
<tr>
<td>M_{mix}</td>
<td>Molar mix feed rate, kg moles/hr</td>
</tr>
<tr>
<td>MW</td>
<td>Feed Molecular weight of Feed, kg/kg moles</td>
</tr>
<tr>
<td>MW_{avg}</td>
<td>Avg molecular weight H₂ in stream, kg/kg moles</td>
</tr>
<tr>
<td>P</td>
<td>Reactor operating pressure, atm</td>
</tr>
<tr>
<td>ΔP</td>
<td>Pressure drop reactor, bar</td>
</tr>
<tr>
<td>Purity</td>
<td>H₂ purity, %</td>
</tr>
<tr>
<td>Recycle</td>
<td>Recycle gas to reactor, Nm³/hr</td>
</tr>
<tr>
<td>%S</td>
<td>% wt sulfur in feed, %</td>
</tr>
<tr>
<td>S_{CV}</td>
<td>Space velocity at standard condition (gas feed)/LHSV, hr⁻¹.</td>
</tr>
<tr>
<td>S_{CL}</td>
<td>Space velocity at standard condition (liquid feed)/GHSV, hr⁻¹.</td>
</tr>
<tr>
<td>t</td>
<td>Residence time, min</td>
</tr>
<tr>
<td>T</td>
<td>Temperature, K</td>
</tr>
<tr>
<td>T_c</td>
<td>Catalyst life, bpp</td>
</tr>
<tr>
<td>V_{bed}</td>
<td>Bed volume, m³</td>
</tr>
</tbody>
</table>
## HYDROTREATING

(ENGINEERING DESIGN GUIDELINES)

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_F )</td>
<td>Volume feed rate</td>
<td>m³/hr</td>
</tr>
<tr>
<td>( v_S )</td>
<td>Superficial velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>( V_{VS} )</td>
<td>Volumetric flow rate at standard condition</td>
<td>m³/hr</td>
</tr>
<tr>
<td>( W_C )</td>
<td>Catalyst mass</td>
<td>kg</td>
</tr>
<tr>
<td>( W_F )</td>
<td>Weight of feed</td>
<td>kg/hr</td>
</tr>
<tr>
<td>( W_{H2} )</td>
<td>Weight of ( H_2 )</td>
<td>Kg/hr</td>
</tr>
<tr>
<td>( W_{mix} )</td>
<td>Weight of combination feed</td>
<td>kg</td>
</tr>
</tbody>
</table>

### Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_{Feed} )</td>
<td>Density of Feed</td>
<td>kg/m³</td>
</tr>
<tr>
<td>( \rho_G )</td>
<td>Molar gas density</td>
<td>kg moles/m³</td>
</tr>
</tbody>
</table>