CHAPTER 6

HYDROTREATING

Source: China Petroleum & Chemical Corp. (SINOPEC)

A catalytic hydrodesulfurization unit

INTRODUCTION

Hydroconversion is a term used to describe all different processes in which hydrocarbon reacts with hydrogen.

Hydrotreating	To describe the process of the removal of sulphur, nitrogen and metal impurities in the feedstock by hydrogen in the presence of a catalyst.
Hydrocracking	The process of catalytic cracking of feedstock to products with lower boiling points by reacting them with hydrogen.
Hydrogenation	aromatics are saturated by hydrogen to the corresponding naphthenes.

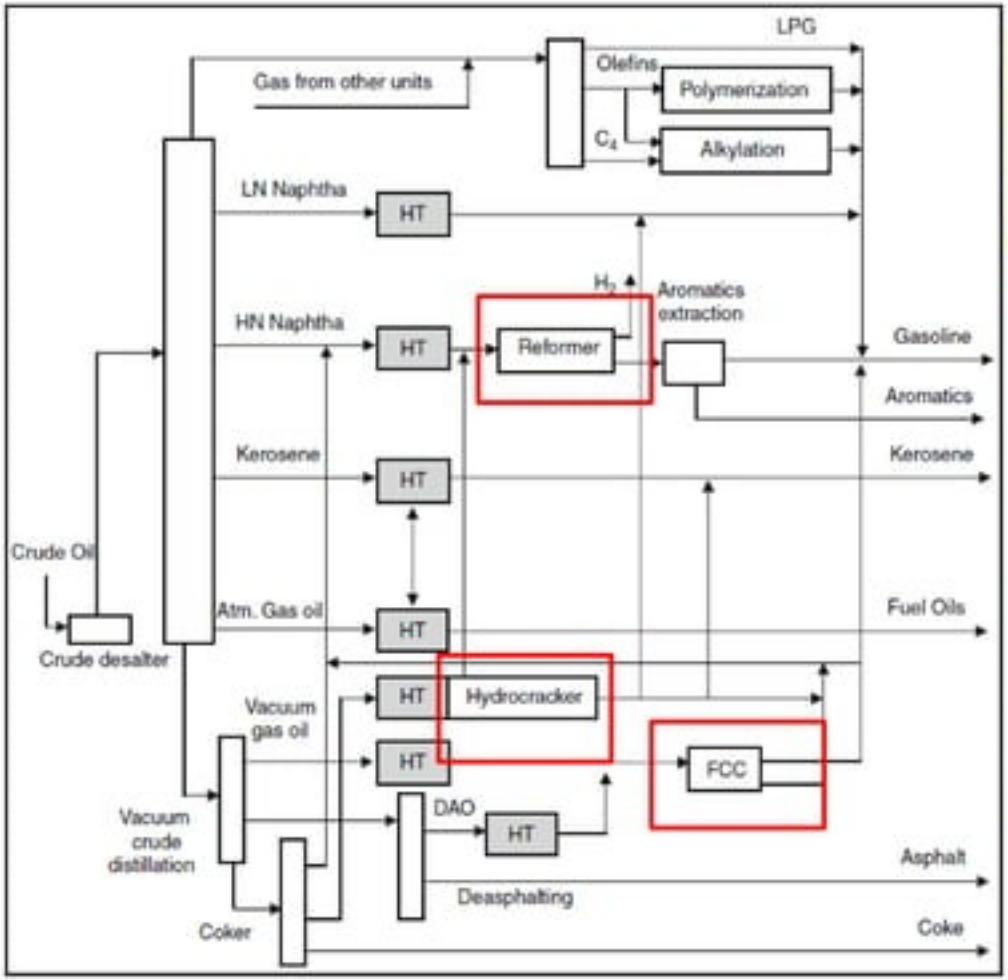
OBJECTIVES OF HYDROTREATING

1. Removing impurities, such as sulphur, nitrogen and oxygen for the control of a final product specification or for the preparation of feed for further processing.

2. Removal of metals, usually in a separate guard catalytic reactor when the organo-metallic compounds are hydrogenated and decomposed, resulting in metal deposition on the catalyst pores.

3. Saturation of olefins and their unstable compounds.

ROLE OF HYDROTREATING



HT are located before the reformer, hydrocracker and FCC

They are also needed to adjust the final product specification for various streams, such as light naphtha, kerosene and low sulphur fuel oils (LSFOs).

MAIN ROLE OF HT

1. Meeting finished product specification.

- Kerosene, gas oil and lube oil desulphurization.
- Olefin saturation for stability improvement.
- Nitrogen removal.
- De-aromatization for kerosene to improve cetane number.

Cetane number is the percentage of pure cetane in a blend of cetane and alpha-methyl-naphthalene. The latter matches the ignition quality of kerosene sample.

MAIN ROLE OF HT

2. Feed preparation for downstream units:

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

HT REACTIONS

1. Desulphurization

a. Mercaptanes:

$$RSH + H_2 \rightarrow RH + H_2S$$

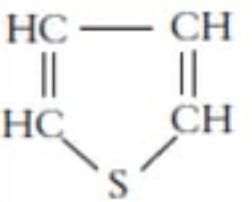
b. Sulphides:

$$R_2S + 2H_2 \rightarrow 2RH + H_2S$$

c. Disulphides:

$$(RS)_2 + 3H_2 \rightarrow 2RH + 2H_2S$$

d. Thiophenes:



$$+ \ 4H_2 \rightleftharpoons C_4H_{10} + H_2S$$

HT REACTIONS

2. Denitrogenation

a. Pyrrole:

$$C_4H_4NH + 4H_2 \rightarrow C_4H_{10} + NH_3$$

b. Pyridine:

$$C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$$

HT REACTIONS

3. Deoxidation

a. Phenol:

$$C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$$

b. Peroxides:

$$C_7H_{13}OOH + 3H_2 \rightarrow C_7H_{16} + 2H_2O$$

HT REACTIONS

4. Hydrogenation of chlorides

$$RCl + H_2 \rightarrow RH + HCl$$

5. Hydrogenation of olefins

$$C_5H_{10} + H_2 \rightarrow C_5H_{12}$$

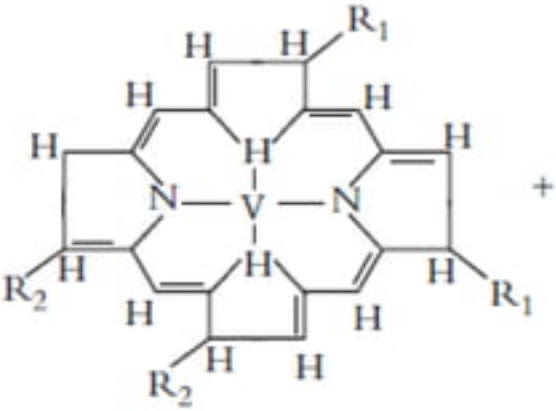
6. Hydrogenation of aromatics

$$C_6H_6 + 3H_2 \rightarrow \text{Cyclohexane}$$

$$\text{Naphthalene} + H_2 \rightarrow \text{Tetraline}$$

HT REACTIONS

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

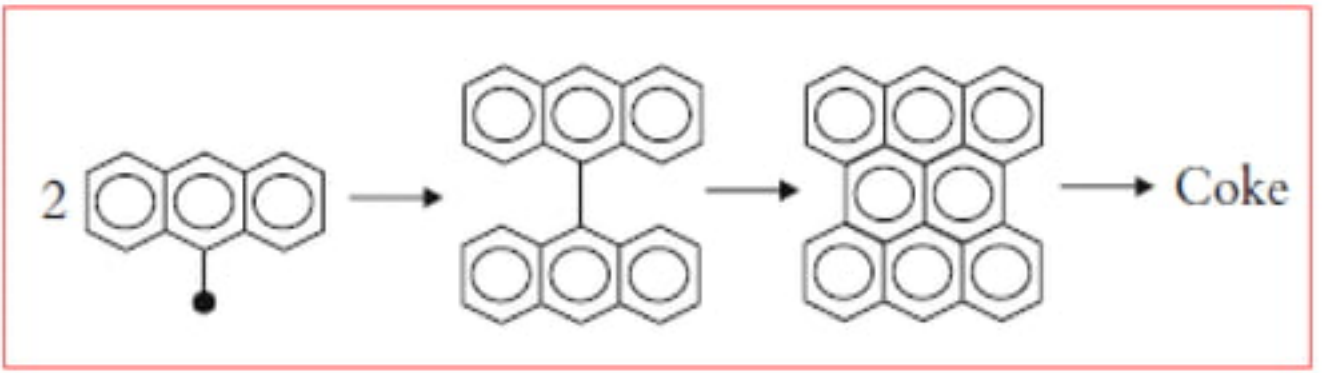


$$+ \quad H_2 \longrightarrow 2NH_3 + 2R_1H_4 + 2R_2H + V$$

Vanadium deposited as vanadium sulphide (V_2S_3)

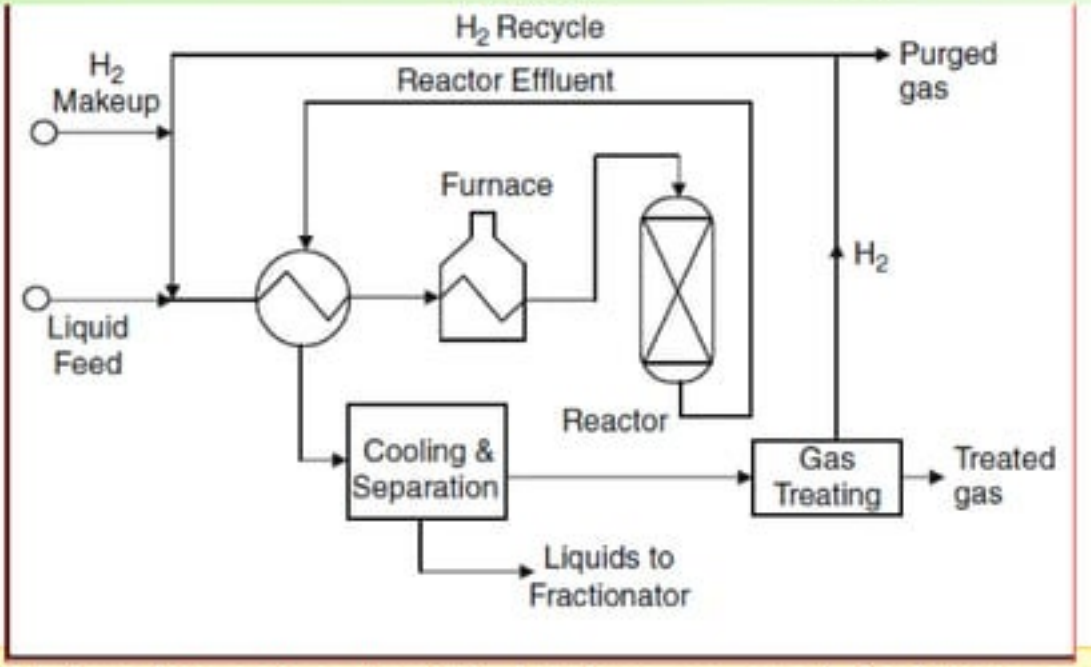
HT REACTIONS

8. Coke formation by the chemical condensation of polynuclear radicals

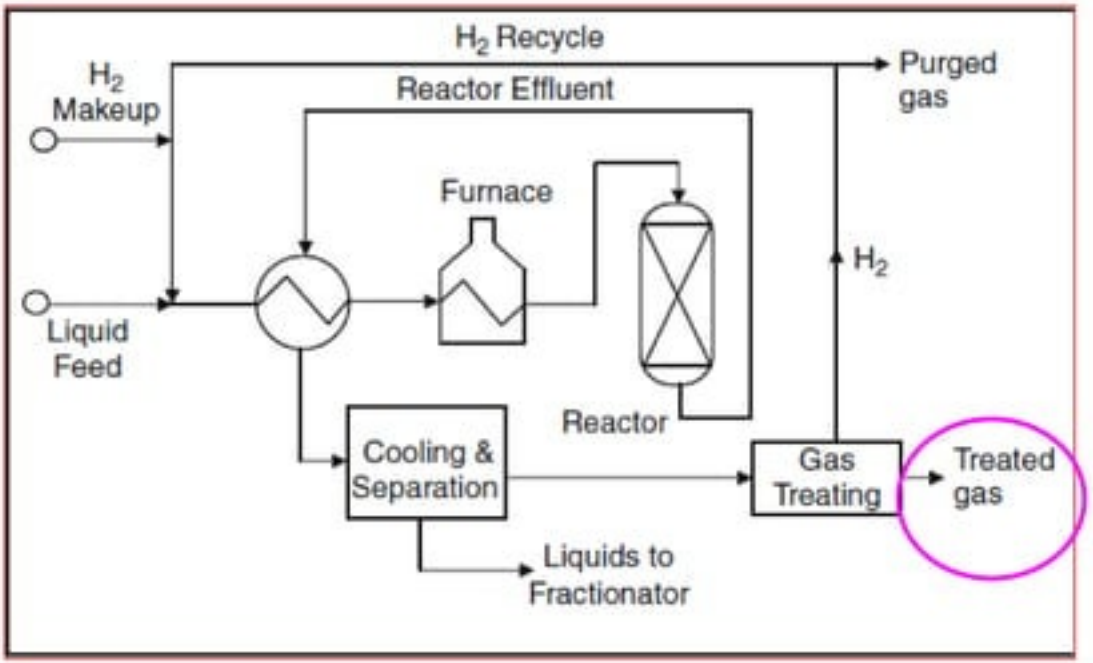


HT PROCESSES

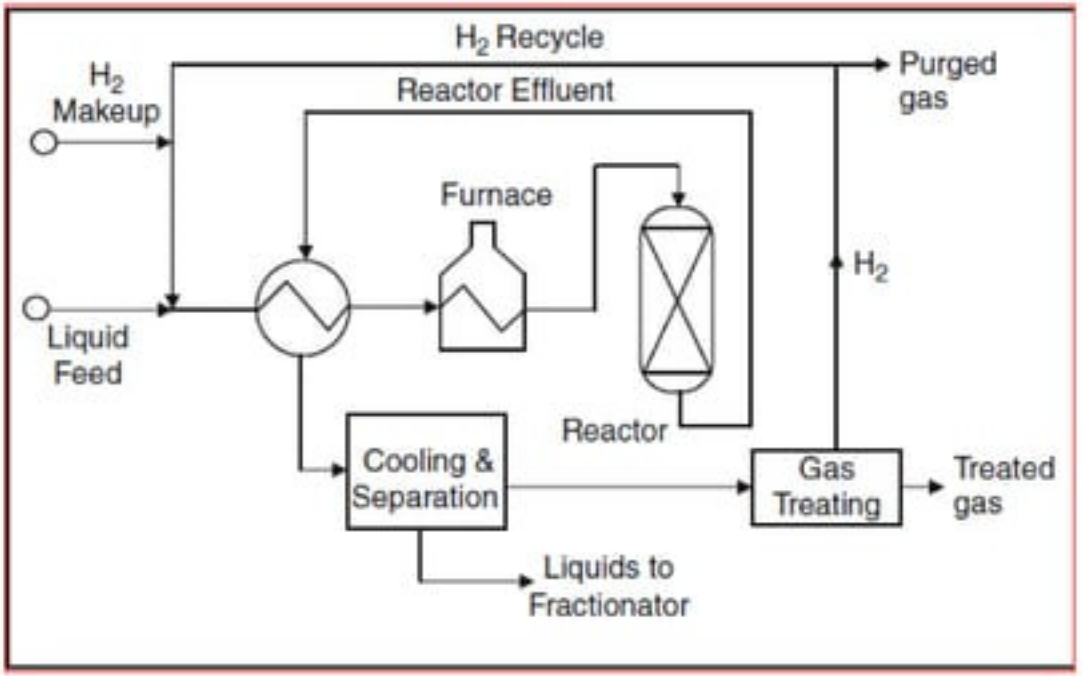
The main elements of a hydrotreating process



1. The liquid feed is mixed with hydrogen and fed into a heater and then fed into a fixed bed catalytic reactor.
2. The effluent is cooled and hydrogen-rich gas is separated using a high pressure separator.



3. Before the hydrogen is recycled, hydrogen sulphide can be removed using an amine scrubber.
4. Some of the recycle gas is also purged
   - To prevent the accumulation of light hydrocarbons (C1–C4)
   - To control hydrogen partial pressure.

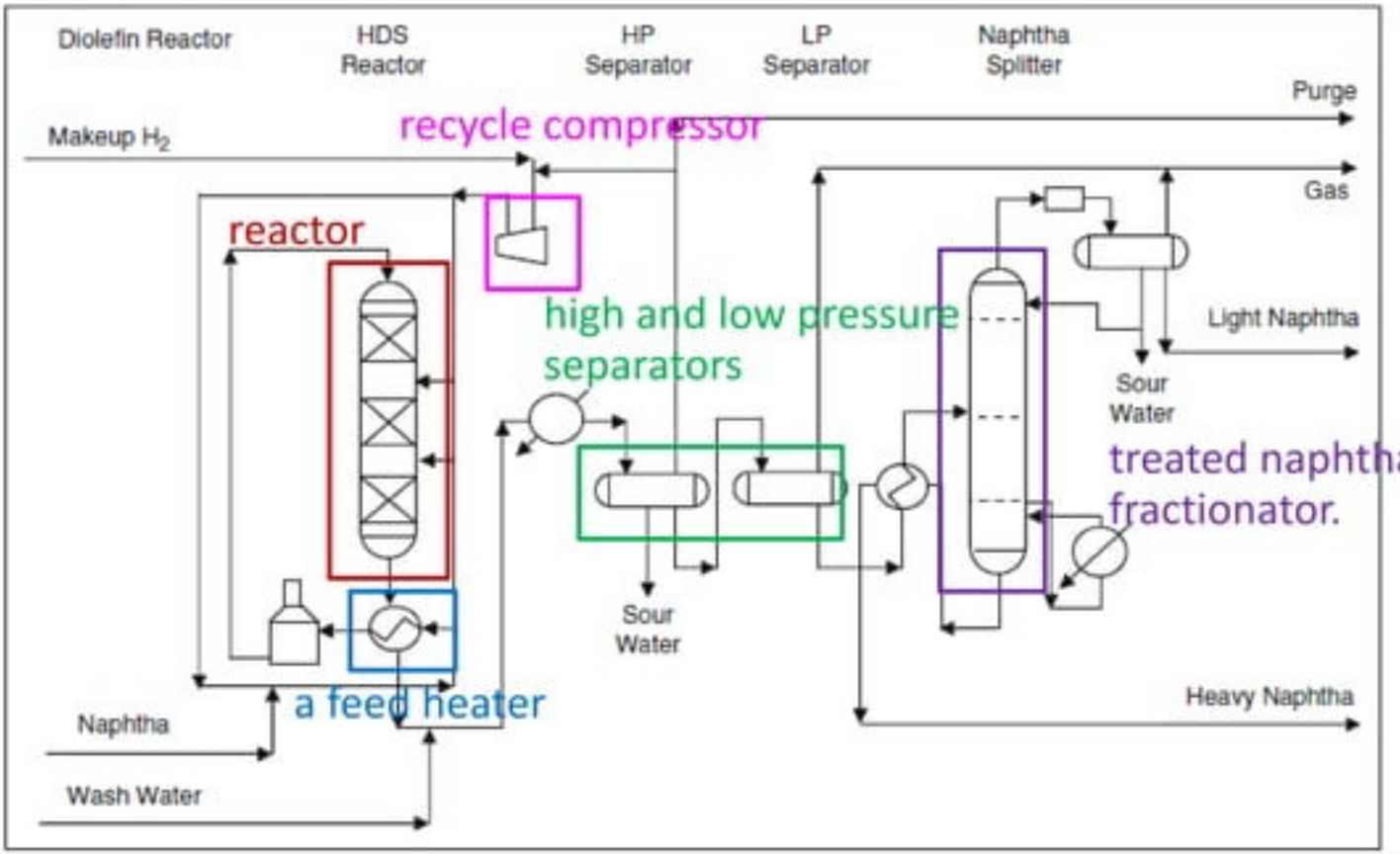


5. The liquid effluent for the reactor is introduced to a fractionators for product separation.

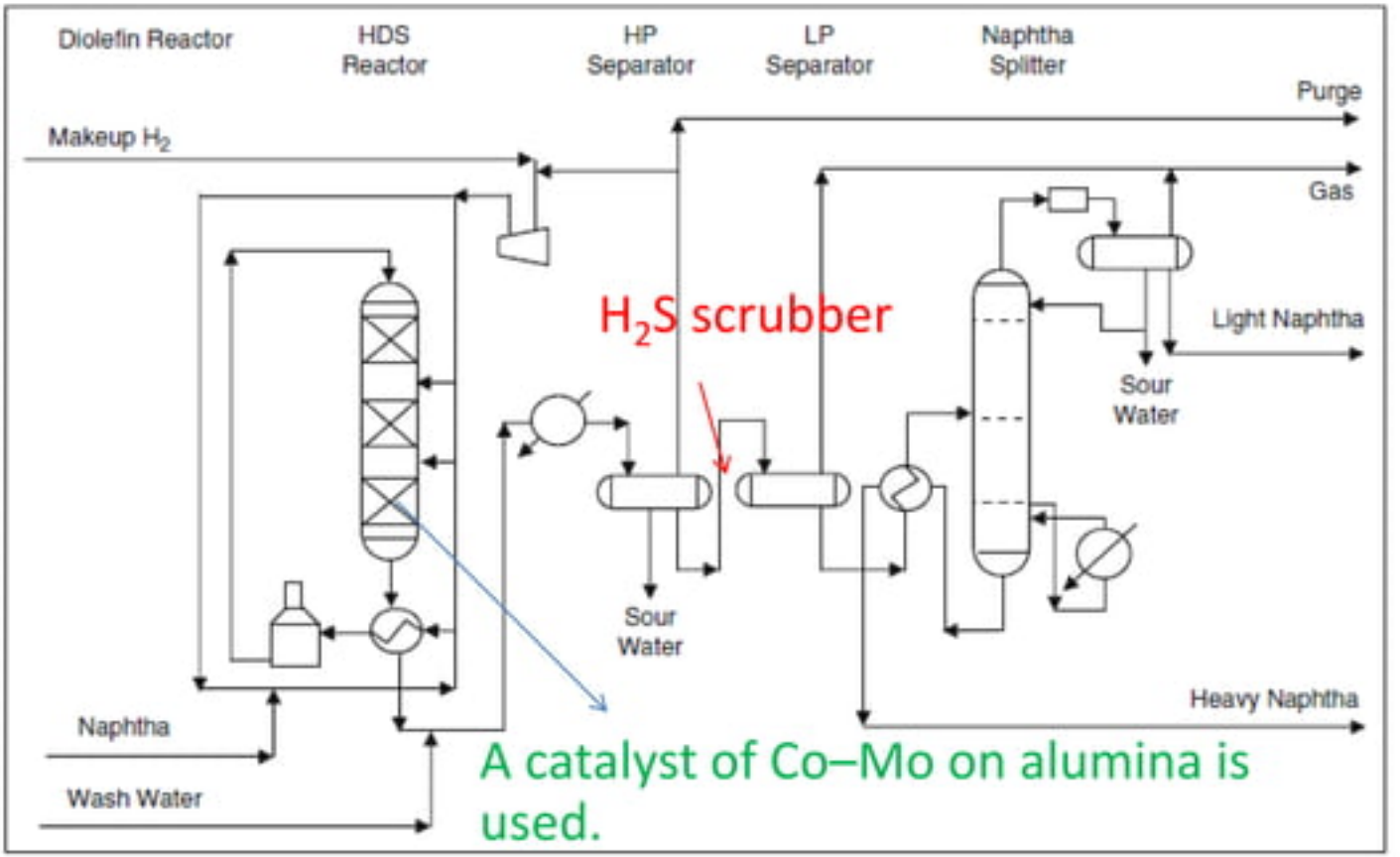
1. Naphtha Hydrotreating

- To remove the impurities so that the hydrotreated naphtha can be introduced to the catalytic reformer.
- The expensive platinum based catalyst used in the reformer is sensitive to poisoning by such impurities.

1. Naphtha Hydrotreating



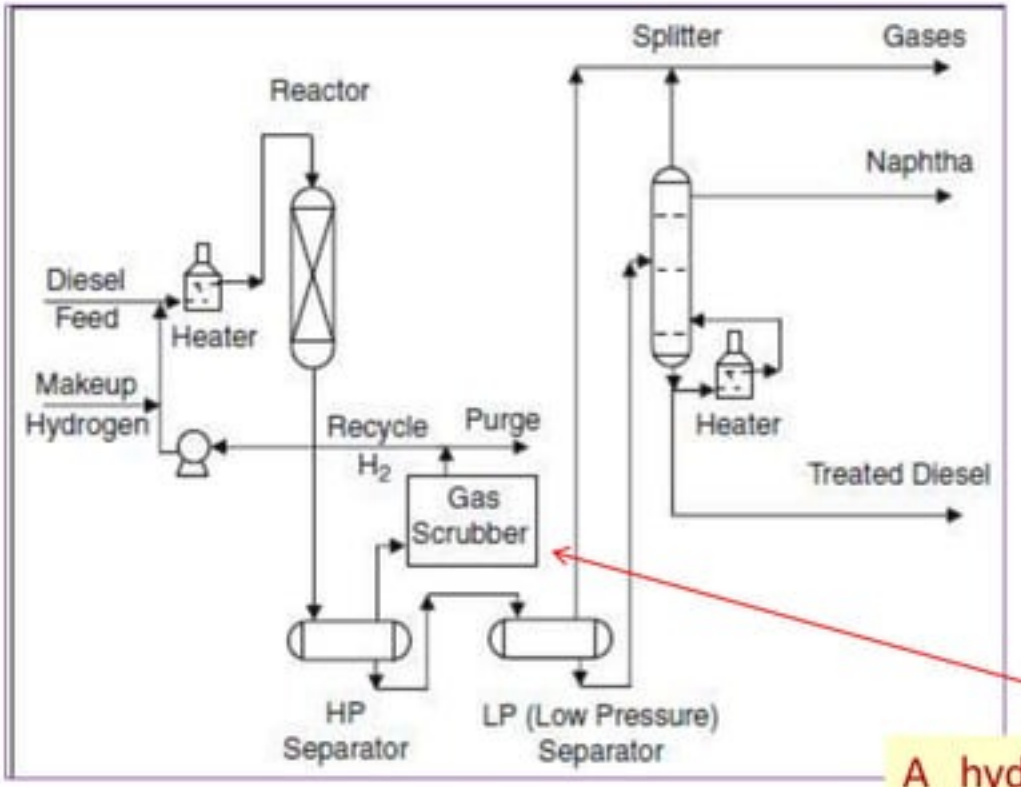
1. Naphtha Hydrotreating



2. Middle Distillates Hydrotreating

- Middle distillate is mainly composed of saturated paraffins and also some aromatics which include simple compounds with up to three aromatic rings.
- Kerosene, jet fuel oil and diesel fuel are all derived from middle distillate fractions.

2. Middle Distillates Hydrotreating

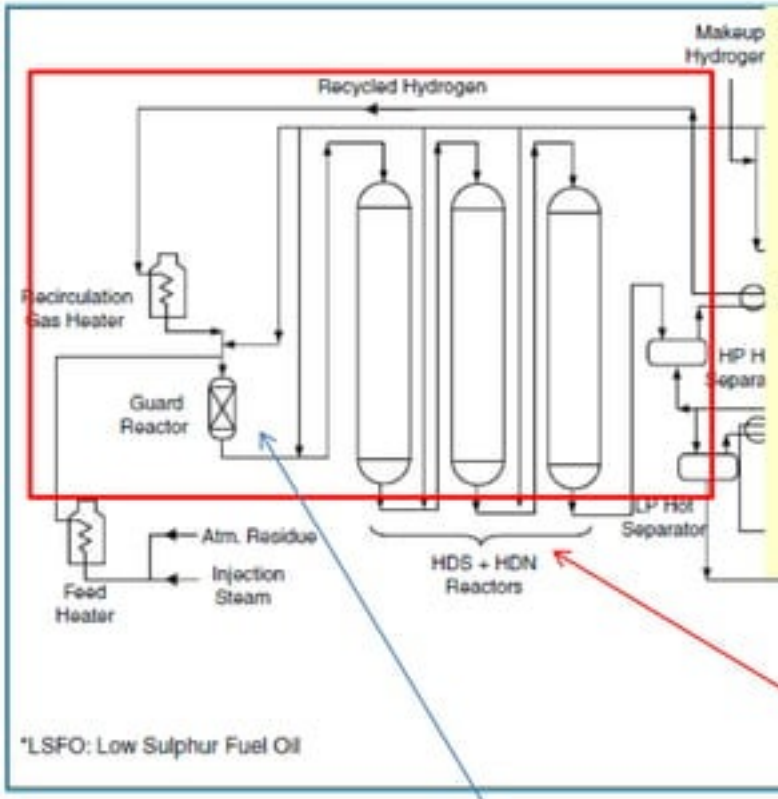


A hydrogen sulphide scrubber and a gas purging are usually used to improve the quality of recycled hydrogen.

3. Atmospheric Residue Desulphurization

- Atmospheric residue has a sulphur content and metals (Ni + V).
- The purpose of this process is to remove most of the metals and reduce sulphur content in the product to less than 0.5 wt%.

3. Atmospheric Residue Desulphurization



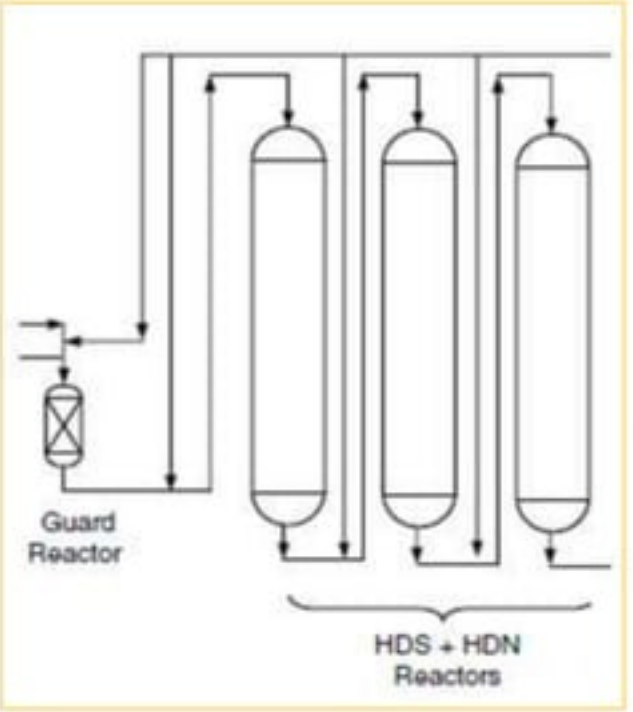
2. The heated recycled hydrogen is mixed with feed and together, they are introduced into a guard reactor.

3. The stream leaving the guard reactor is quenched with cold recycle hydrogen and introduced to the first of the three fixed bed reactors.

The main reactions of hydrodemetallization, hydrodesulphurization, denitrogenation and aromatic hydrogenation take place in the reactors.

contains a hydrogenation catalyst similar to that in the main reactor but usually cheaper.

Reactor



- The catalyst should have wide pores to avoid plugging due to metal deposition.
- Due to the fast deactivation of this catalyst, usually two reactors are used and the catalyst is changed in one of them while the other reactor is still online.
- Three to four reactors are usually used with different combinations of catalysts to achieve desired objectives.

Hydrogen requirements for hydrotreating are classified into:

(1) Chemical requirement:

- This is the amount of hydrogen required to remove impurities such as sulphur, oxygen, nitrogen, olefins and organometalic compounds, according to the stoichiometry of these reactions.

- Sometimes, it might be required to convert aromatics and naphthenes to corresponding paraffins.

Hydrogen requirements for hydrotreating are classified into:

(2) **Hydrogen lost** due to the dissolution of hydrogen in the hydrocarbons treated.

(3) **Amount of hydrogen lost with the purging** of light hydrocarbons (C1–C4) and hydrogen sulphide (if not removed by amine treatment).

Add more comparison – at least five more

Hydrotreating	Hydrocracking
Minimal conversion 10% to 20%	>50% conversion