

Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering

Department

Petroleum Refining Processes

Fourth Class

Lecture 10

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Hydrotreating Units (HTU)

- ✚ HTU is used to remove about 90% of contaminants such as nitrogen, sulfur, oxygen, and metals from liquid petroleum products.
- ✚ Mild catalytic process done by selectively reacting these contaminants with hydrogen in a reactor at relatively high temperatures at moderate pressures.
- ✚ Hydrotreating is done prior to **processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock.**
- ✚ Hydrotreating is also used prior to **catalytic cracking to reduce sulfur and improve product yields, and to upgrade middle distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils.**

Feeds and Products:

- ✚ The feed ranges from Naphtha to reduced crude (residue).
- ✚ The heavier the feed the more severe the process is (higher T & P).

2- Feed preparation for downstream units

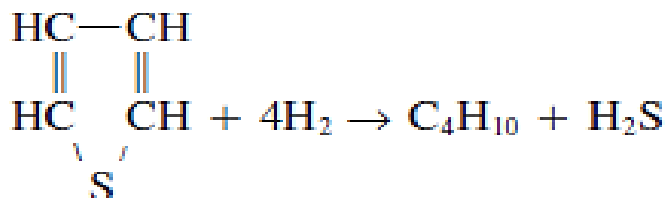
- ✚ Naphtha is hydrotreated for removal of metal and sulphur.
- ✚ Sulphur, metal, polyaromatics and carbon removal from vacuum gas oil (VGO) to be used as FCC feed.
- ✚ Pretreatment of hydrocracking feed to reduce sulphur, nitrogen and aromatics.

Chemistry of HT

Desulphurization, Denitrogenation, Deoxidation, Hydrogenation of chloride, Hydrogenation of olefins, Hydrogenation of aromatic, Hydrogenation of organometallic compounds, and Coke formation by chemical condensation of polynuclear radicals.

1. Desulfurization

- a. Mercaptans: $\text{RSH} + \text{H}_2 \rightarrow \text{RH} + \text{H}_2\text{S}$
- b. Sulfides: $\text{R}_2\text{S} + 2\text{H}_2 \rightarrow 2\text{RH} + \text{H}_2\text{S}$
- c. Disulfides: $(\text{RS})_2 + 3\text{H}_2 \rightarrow 2\text{RH} + 2\text{H}_2\text{S}$
- d. Thiophenes:



2. Denitrogenation

- a. Pyrrole: $\text{C}_4\text{H}_4\text{NH} + 4\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{NH}_3$
- b. Pyridine: $\text{C}_5\text{H}_5\text{N} + 5\text{H}_2 \rightarrow \text{C}_5\text{H}_{12} + \text{NH}_3$

3. Deoxidation

- a. Phenol: $\text{C}_6\text{H}_5\text{OH} + \text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{H}_2\text{O}$
- b. Peroxides: $\text{C}_7\text{H}_{13}\text{OOH} + 3\text{H}_2 \rightarrow \text{C}_7\text{H}_{16} + 2\text{H}_2\text{O}$

4. Dehalogenation



5. Hydrogenation:



6. Hydrocracking: $\text{C}_{10}\text{H}_{22} + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{C}_6\text{H}_{14}$

The naphtha HTU consists of:

A feed heater, reactor, high- and low-pressure separators, recycle compressor and treated naphtha fractionator. Some of the recycled gas is purged to lower the concentration of light hydrocarbon (C1– C4). A catalyst of Co–Mo on alumina is used.

Reactivity of HT catalyst

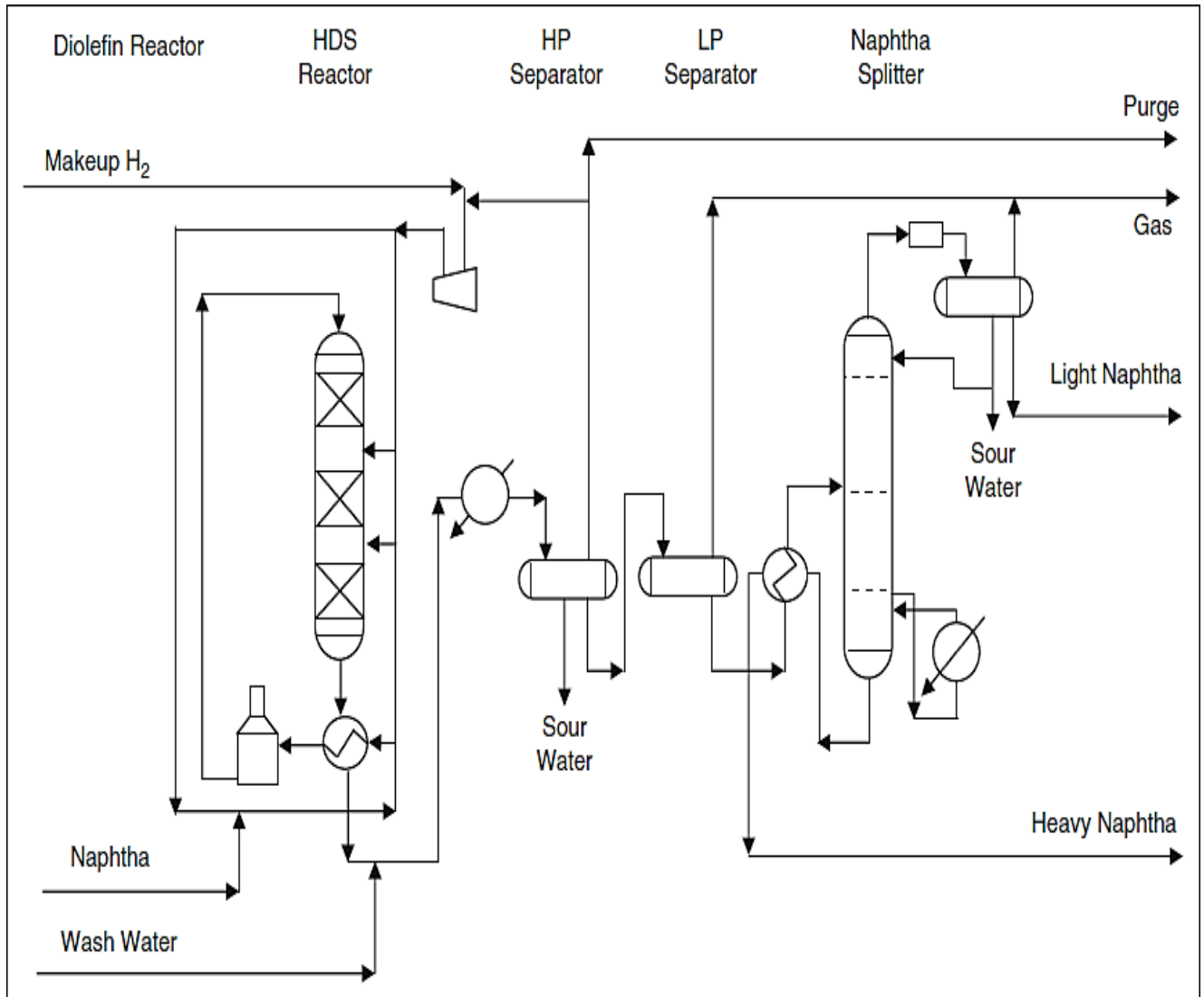
Catalyst	Hydro- desulphurization	Hydro- denitrogenation	Aromatics hydrogenation
Co–Mo/Alumina	Excellent	Good	Fair
Ni–Mo/Alumina	Very good	Very good	Good
Ni–W/Alumina	Good	Good	Excellent

Process description:

- ✚ The liquid feed is mixed with hydrogen and fed into a heater and the mixture is brought to the reaction temperature in a furnace and then fed into a fixed bed catalytic reactor.
- ✚ The effluent is cooled and mixed with wash water. the water mixed reactor stream is further cooled and sent to a phase separator.
- ✚ The phase separator splits the feed stream to three separate streams namely a gas phase stream, an organic stream and an aqueous stream.
- ✚ hydrogen-rich gas is separated using a high-pressure separator.
- ✚ The aqueous stream is rich of H₂S and NH₃ and will be sent out to a sour water processing unit to recover H₂S and NH₃.

- Some of the recycle gas is also purged to prevent the accumulation of light hydrocarbons (C1–C4) and to control hydrogen partial pressure.
- The liquid effluent for the reactor is introduced to a fractionator for product separation.

Naphtha Hydrotreating unit:



Process variables and operation conditions of HTUs

- ✚ Pressure, temperature, catalyst loading, feed flow rate and hydrogen partial pressure.
- ✚ The hydrogen partial pressure must be greater than the hydrocarbon partial pressure.
- ✚ Increasing hydrogen partial pressure improves the removal of sulphur and nitrogen compounds and reduces coke formation.
- ✚ Higher temperatures will increase the reaction rate constant and improve the kinetics.
- ✚ However, excessive temperatures will lead to thermal cracking and coke formation.
- ✚ The space velocity is the reverse of reactor residence time.
- ✚ High space velocity results in low conversion, low hydrogen consumption and low coke formation.

Feedstock	Naphtha	Kerosene	Gas oil	Vacuum gas oil	Residue
Boiling range, °C	70–180	160–240	230–350	350–550	>550
Operating temperature, °C	260–300	300–340	320–350	360–380	360–380
Hydrogen pressure, bar	5–10	15–30	15–40	40–70	120–160
Hydrogen consumption, wt%	0.05–0.1	0.1–0.2	0.3–0.5	0.4–0.7	1.5–2.0
^a LHSV, hr ⁻¹	4–10	2–4	1–3	1–2	0.15–0.3
H ₂ /HC ratio, std m ³ /m ³	36–48	36–48	36–48	36–48	12–24