Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering Department

Petroleum Refining Processes

Fourth Class

Lecture 14

By

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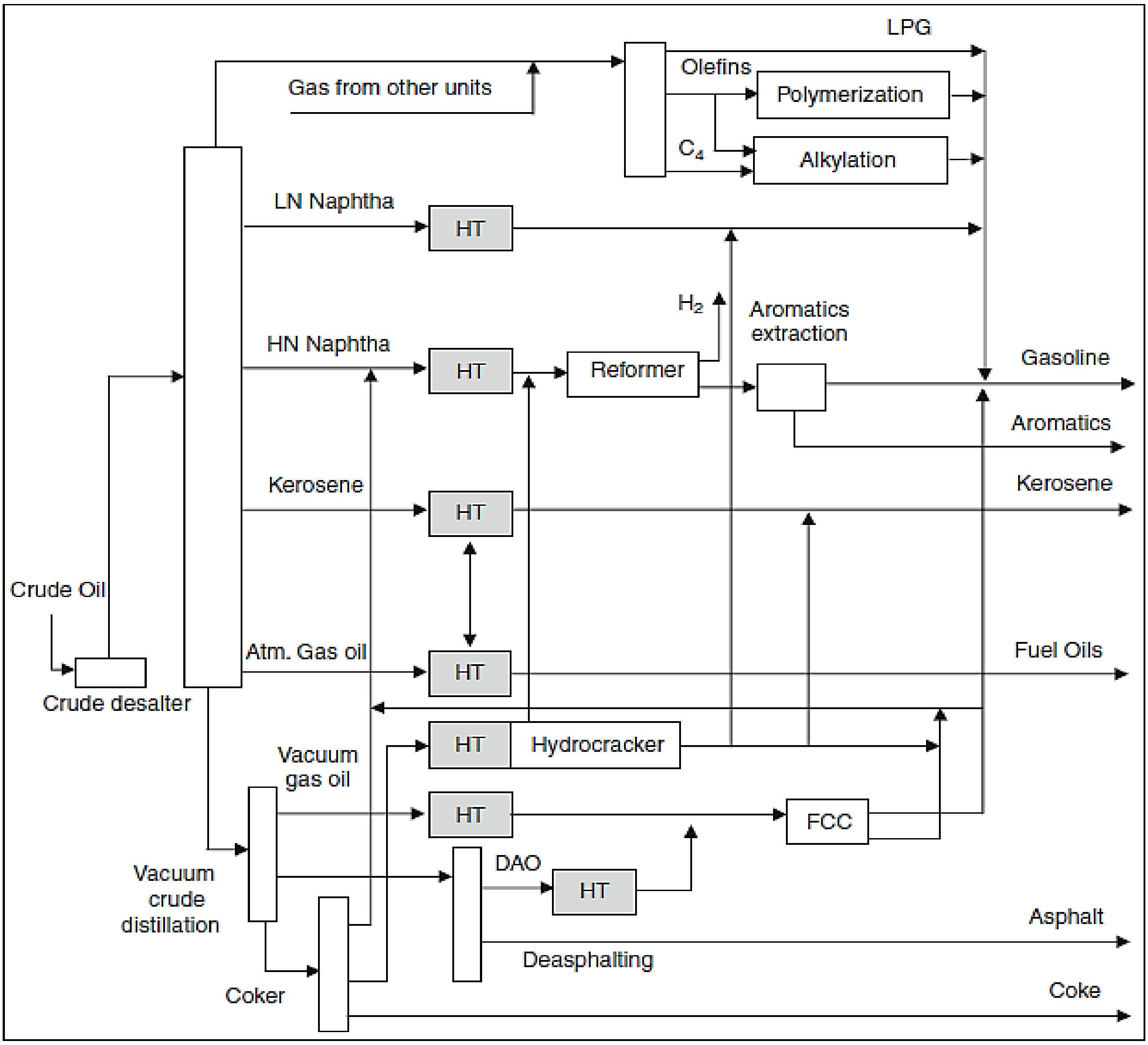
Hydrotreating Units (HTU)

- 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).



The main role of HTU is to

1- Meeting finished product specification:

- Olefin saturation for stability improvement.
- Reduce materials like sulfur and nitrogen, oxygen, halides, and trace metals content.
- De-aromatization for kerosene to improve smoke point and cetane number.
- It does not alter the initial and final boiling points.

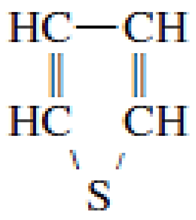
2- Feed preparation for downstream units:

- 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.

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: $RSH + H_2 \rightarrow RH + H_2S$
   b. Sulfides: $R_2S + 2H_2 \rightarrow 2RH + H_2S$
   c. Disulfides: $(RS)_2 + 3H_2 \rightarrow 2RH + 2H_2S$
   d. Thiophenes:



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

2. Denitrogenation
   a. Pyrrole: $C_4H_4NH + 4H_2 \rightarrow C_4H_{10} + NH_3$
   b. Pyridine: $C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$
3. Deoxidation
   a. Phenol: $C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$
   b. Peroxides: $C_7H_{13}OOH + 3H_2 \rightarrow C_7H_{16} + 2H_2O$
4. Dehalogenation
   Chlorides: $RCl + H_2 \rightarrow RH + HCl$.
5. Hydrogenation:
   Pentene: $C_5H_{10} + H_2 \rightarrow C_5H_{12}$
6. Hydrocracking: $C_{10}H_{22} + H_2 \rightarrow C_4H_{10} + C_6H_{14}$

Feed properties

Property	Feed	Naphtha	ATK[a]	Heavy kerosene
Aniline point (°F)	143			156.5
API	46.44	58.89	44.82	41.17
Density	0.7952	0.7432	0.8025	0.8195
Aromatics (vol%)	22	10.3	19.1	19.9
Cloud point (°F)				2
ASTM distillation (°F)				
(IBP)	192	124	384	452
5 vol%	306	178	396	464
10 vol%	324	202	400	472
20 vol%	346	232	404	478
30 vol%	362	256	406	484
50 vol%	396	292	412	500
70 vol%	440	316	422	518
90 vol%	504	348	440	544
95 vol%	526	360	448	556
(EBP)	556	394	470	576
Flash point (°F)			184	226
Freeze point (°F)			−65.2	
Pour point (°F)				Zero
Smoke point (mm)	24		26	25
Sulphur (ppm)	4500	1900	3.6	41.1
Kinematic viscosity at 122 °F (cSt)	1.1		1.32	2.2

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

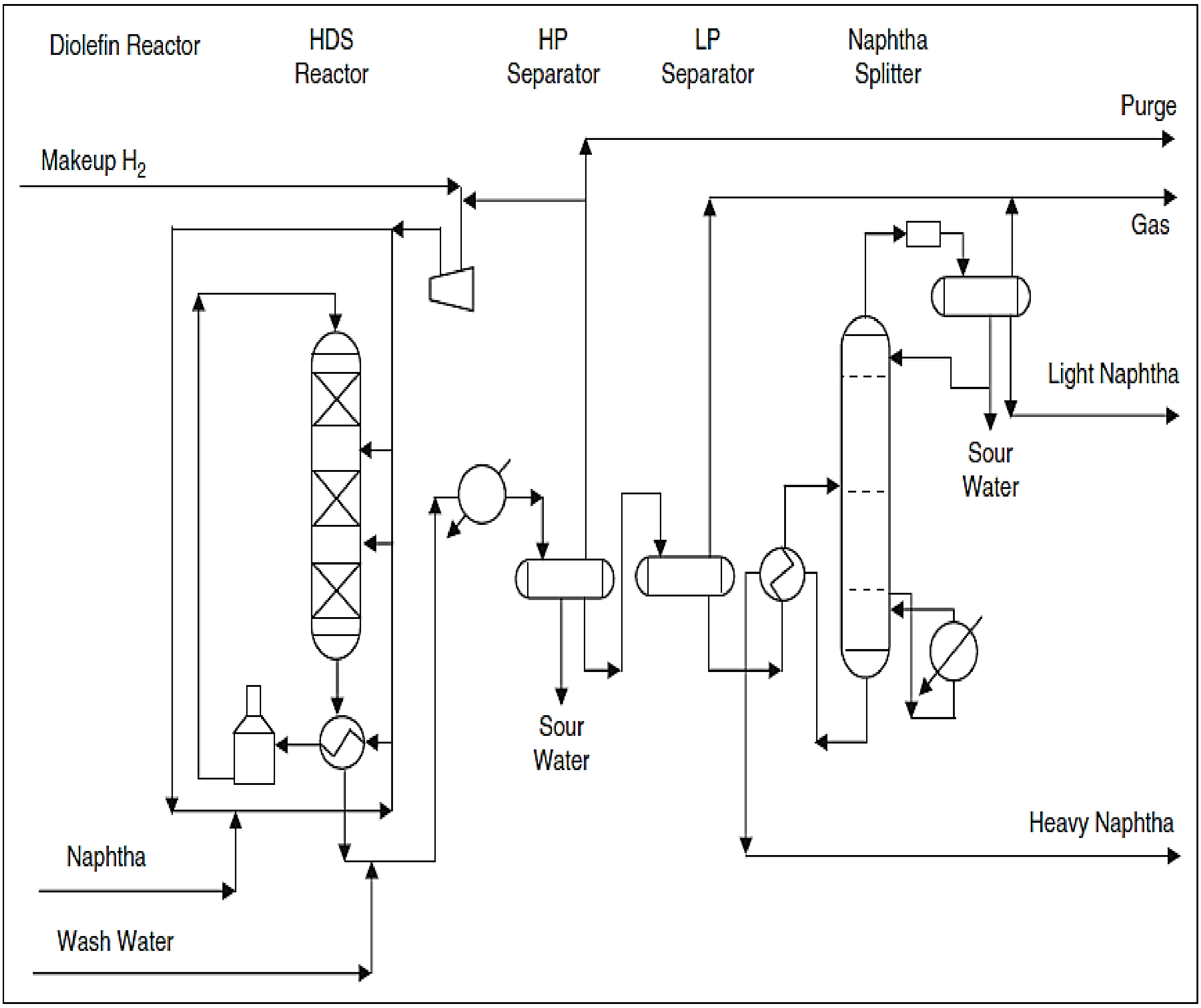
Catalyst	Hydro-desulphurization	Hydro-denitrogenation	Aromatics hydrogenation
Co–Mo/Alumina	Excellent	Good	Fair
Ni–Mo/Alumina	Very good	Very good	Good
Ni–W/Alumina	Good	Good	Excellent

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