CRUDE REFINING

Shrishti Lahoti
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Introduction of the Process Plant

Shrishti Lahoti

What is Petroleum?

A complex mixture containing thousands of different organic hydrocarbon molecules

83-87% Carbon

11-15% Hydrogen

1-6% Sulfur

Importance :

- Most important natural resource
- Generates heat, drive machinery and fuel vehicles and airplanes.
- Manufactures chemical products, such as plastics, detergents, paints,medicines.

IMPORTANT PETROLEUM PRODUCTS AND THEIR CRITICAL QUALITY PARAMETERS

Sl.no	Product	Key Quality parameters
1.	LPG	Evaporation Temperature at 95 % Volume =2 deg C, Max Cu Corrosion =not worse than No.1 RVP =1050 KPa, Max
2.	Motor Spirit	Density =720-775 Kg/M3 RON =91 Min Sulphur =150 ppm, Max Benzene =1 Vol. %, Max
3.	ATF	Density =775-840 Kg/M3 Flash Point = 38 deg c, Min Sulphur =0.25 wt %,Max Smoke Point =20 mm, Min
4.	SKO	Density =790-820 Kg/M3 Flash Point =35 deg c, Min Sulphur = 0.25 wt %, Max Smoke point = 18 mm, Min

Sl.no	Product	Key Quality parameters
5.	Diesel	Density =820-845 Kg/M3 Sulphur = 350 ppm Cetane Number = 51 Min Recovery at 360 deg C =95 Min
6.	Fuel Oil	Kinematic Viscosity@ 50 deg c =125 , Max (Winter) =180 , Max (Summer) Sulphur = 4 wt %, Max Ash = 0.1 wt %, Max
7.	Bitumen	Penetration at 25 deg c =60 (1/10mm) , Min Flash Point =175 deg C,Min Softening Point =45-55 deg C

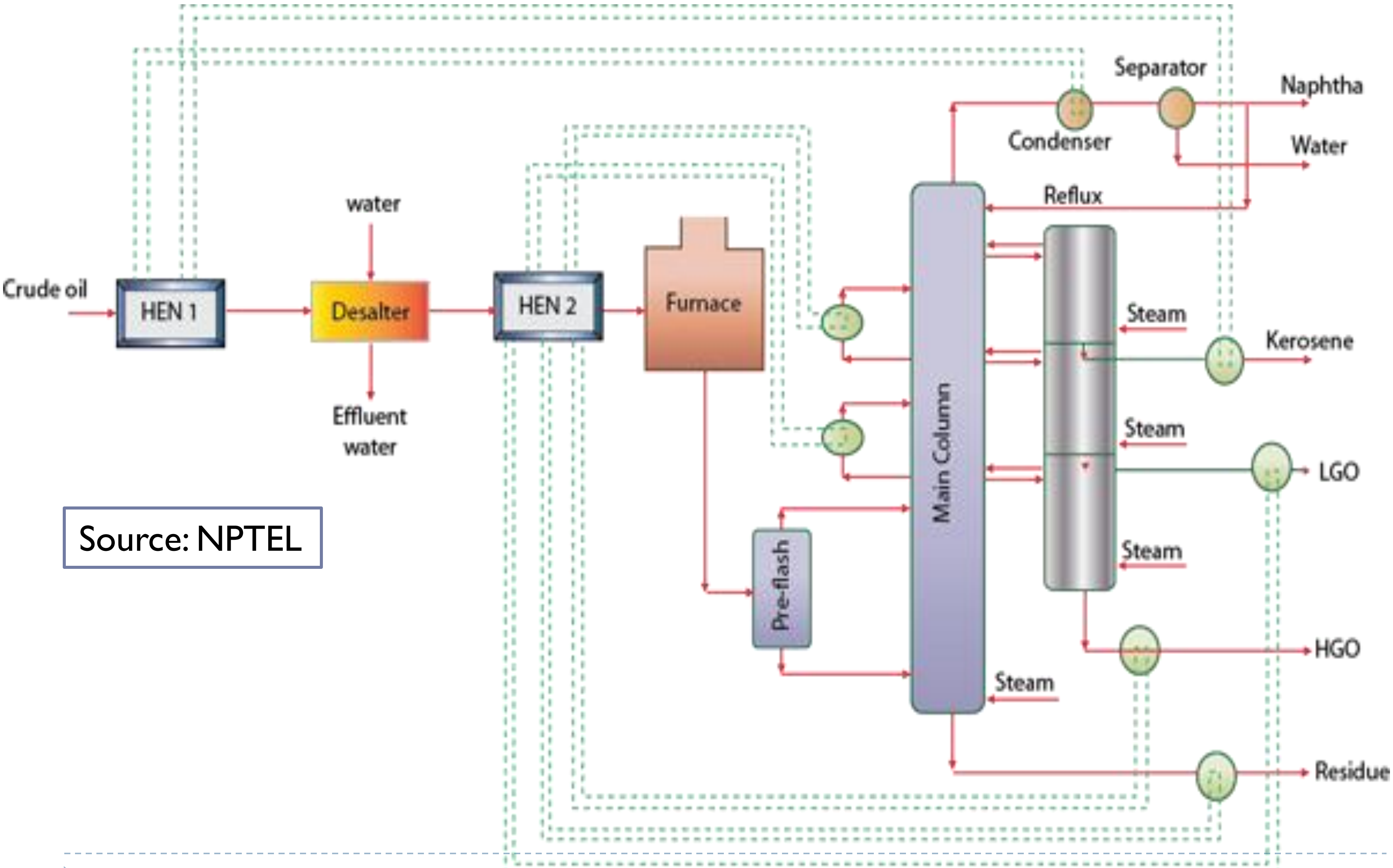
MAJOR SECTORS

UPSTREAM

MIDSTREAM

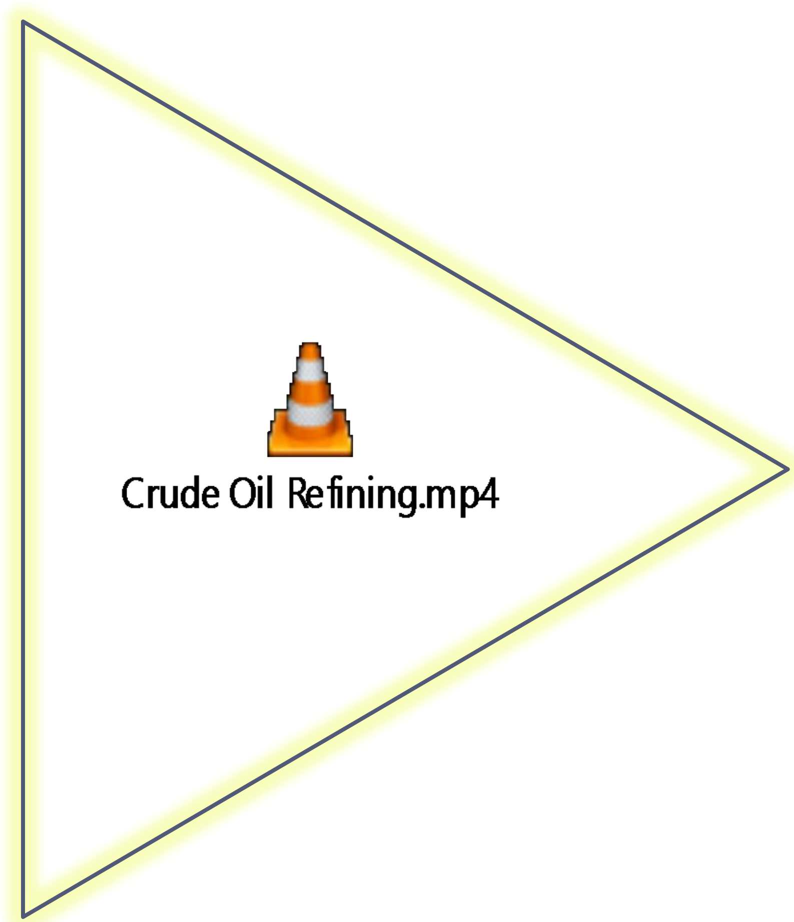
DOWNSTREAM

CRUDE DISTILLATION UNIT(ATMOSPHERIC DISTILLATION)



Source: NPTEL

Video Time!



Source: www.e-learning.com

IMPORTANT SUB- PROCESSES

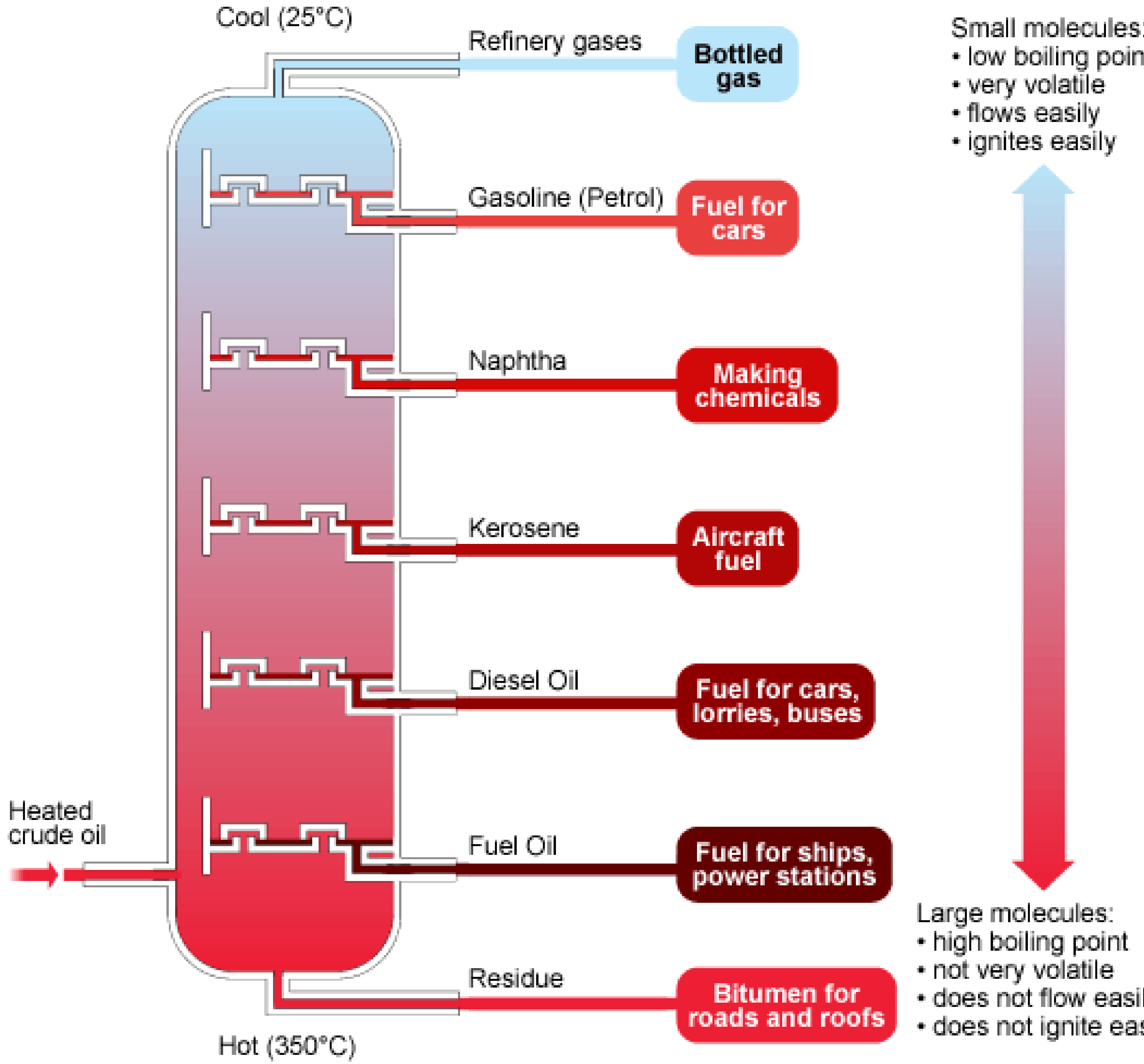
- CRUDE DESALTING
- FURNACE
- PRE -FLASH COLUMN
- MAIN DISTILLATION COLUMN
- HEAT EXCHANGER NETWORKS

Categories of General Refining Processes and Associated Operation

1. Separation Process
    a. Atmospheric Distillation
    b. Vacuum Distillation
    c. Light End Distillation (Gas Processing)
2. Petroleum Conversion Processes
    a. Cracking (Thermal /Catalytic)
    b. Reforming’
    c. Alkylation Polymerization
    d. Isomerization
    e. Coking
    f. Visbreaking
3. Petro Treating Processes
    a. Hydro-desulfurization
    b. Hydro-treating
    c. Chemical Sweetening
    d. Acid Gas Removal
    e. De-asphalting

REFINERY SCHEME

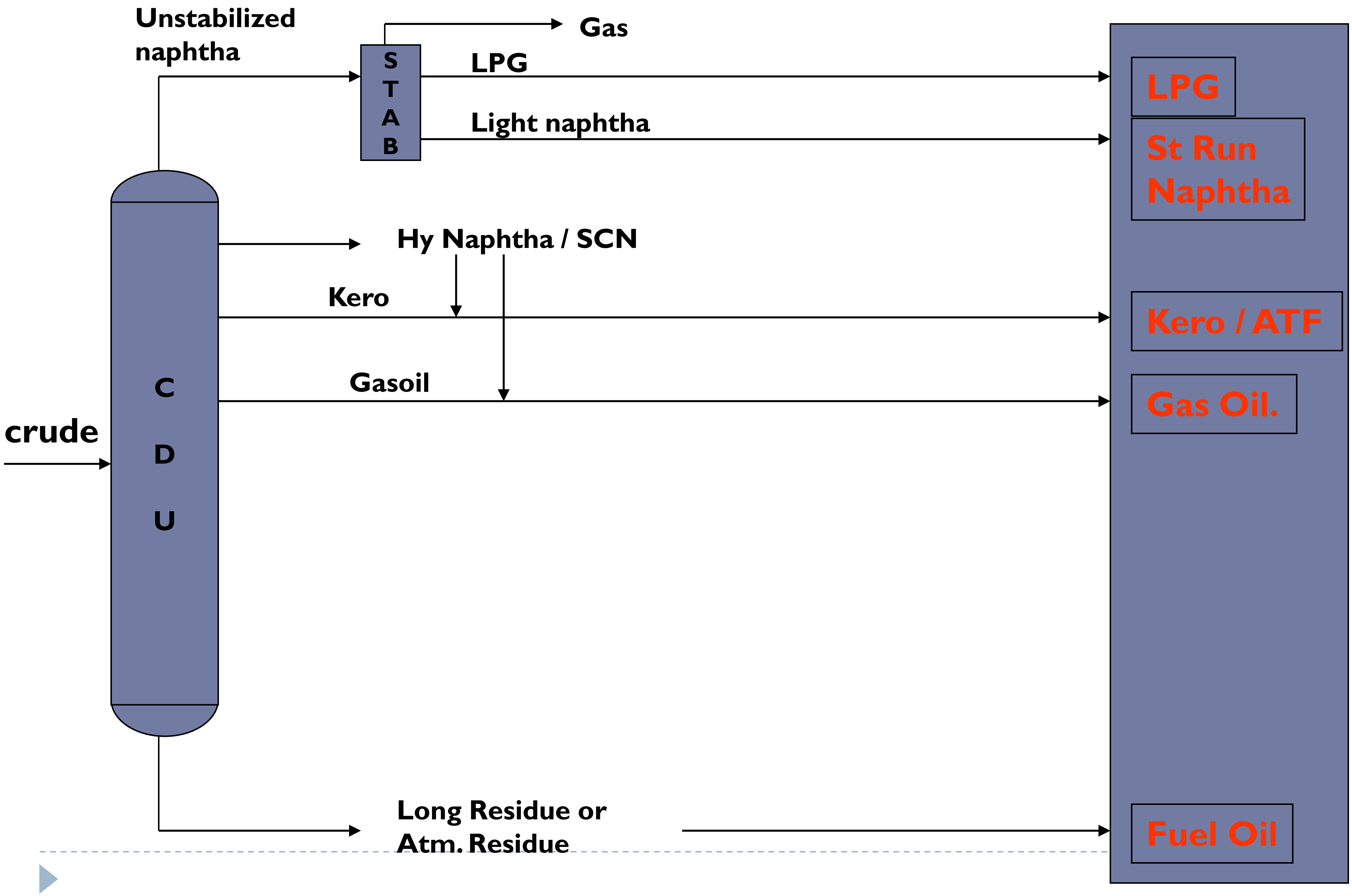
- Crude Pretreatment
- Desalting
- Fractionation
- Atmospheric & Vacuum
- Distillation
- Conversion
- Fluidized-bed Catalytic Cracking
- Hydro-cracking
- Delayed Coking
- Visbreaking /Coking
- Treatment
- Diesel Hydrodesulphurization
- Diesel Hydro-treatment
- Solvent Extraction (e.g. FEU)
- Catalytic Reforming

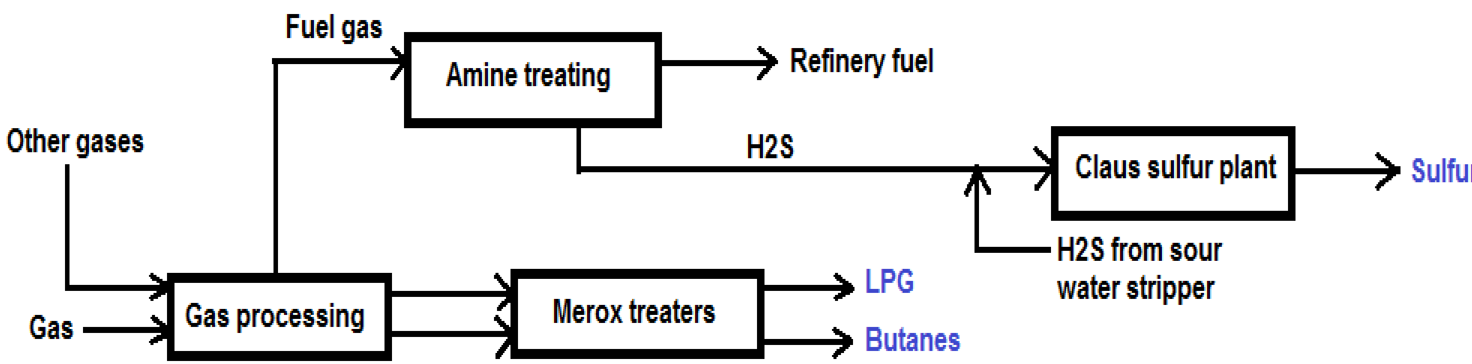

Cool (25°C)
Refinery gases
Bottled gas
Gasoline (Petrol)
Fuel for cars
Naphtha
Making chemicals
Kerosene
Aircraft fuel
Diesel Oil
Fuel for cars, lorries, buses
Heated crude oil
Fuel Oil
Fuel for ships, power stations
Residue
Bitumen for roads and roofs
Hot (350°C)
Small molecules
• low boiling poin
• very volatile
• flows easily
• ignites easily
Large molecules:
• high boiling point
• not very volatile
• does not flow easi
• does not ignite eas

Complex Refining

- Topping Refinery
- Cracking Refinery
- Hydro cracking Refinery
- Full conversion Refinery

TOPPING REFINERY



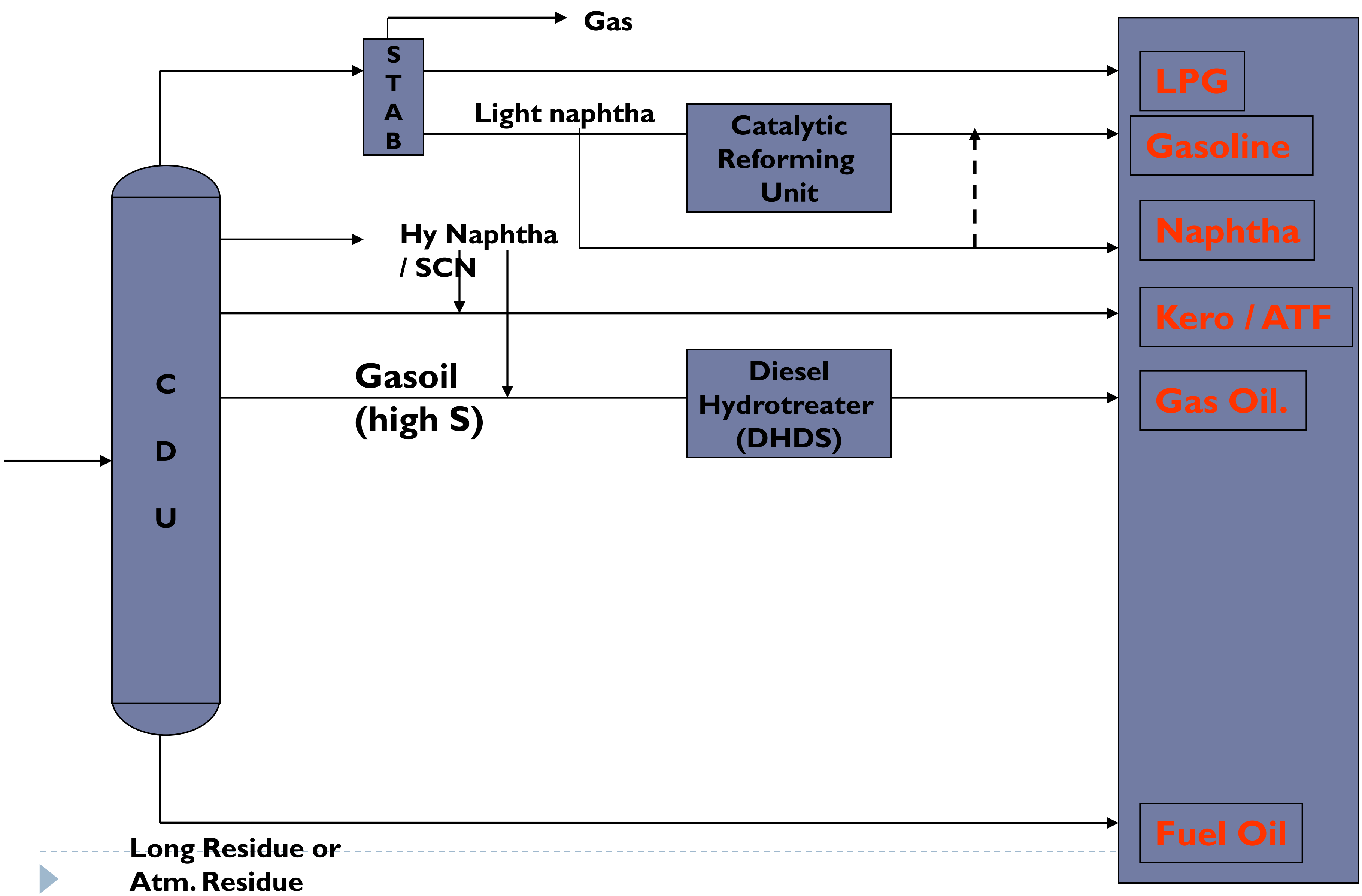


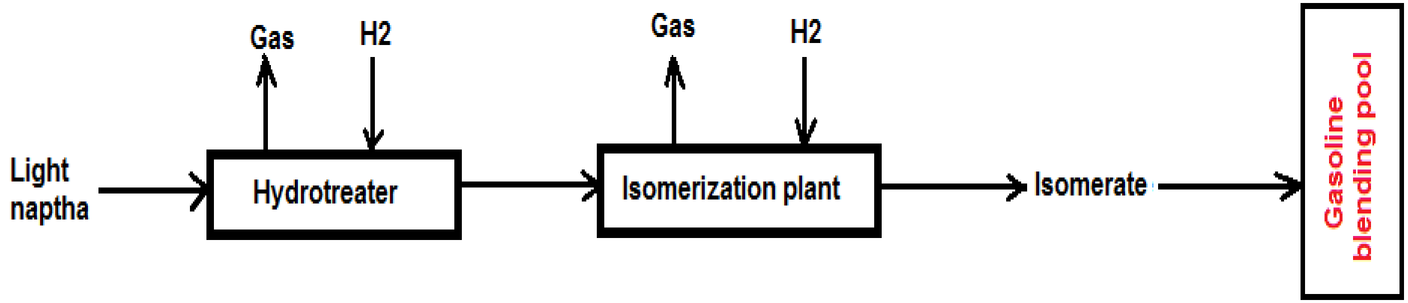
Amine Treating:

<u>Process objective</u>:

Refers to a group of processes that use aqueous solutions of various amines to remove H2S and CO2 from gases (sour gases/ acid gases)

HYDROSKIMMING REFINERY





Hydro-treating process:

Process Objective:

•Removal contaminants (Sulfur, Nitrogen, metals) and saturated olefins and aromatics to produce a clean product for further processing or finished product sales.

•Enhancing the cetane number,density and smoke point

Reaction And Chemistry:

It's a Hydrogenolysis process wherein the C-X clevage takes place leading to the formation of CH and HX.

Ethanethiol + Hydrogen → Ethane + Hydrogen Sulphide

$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$

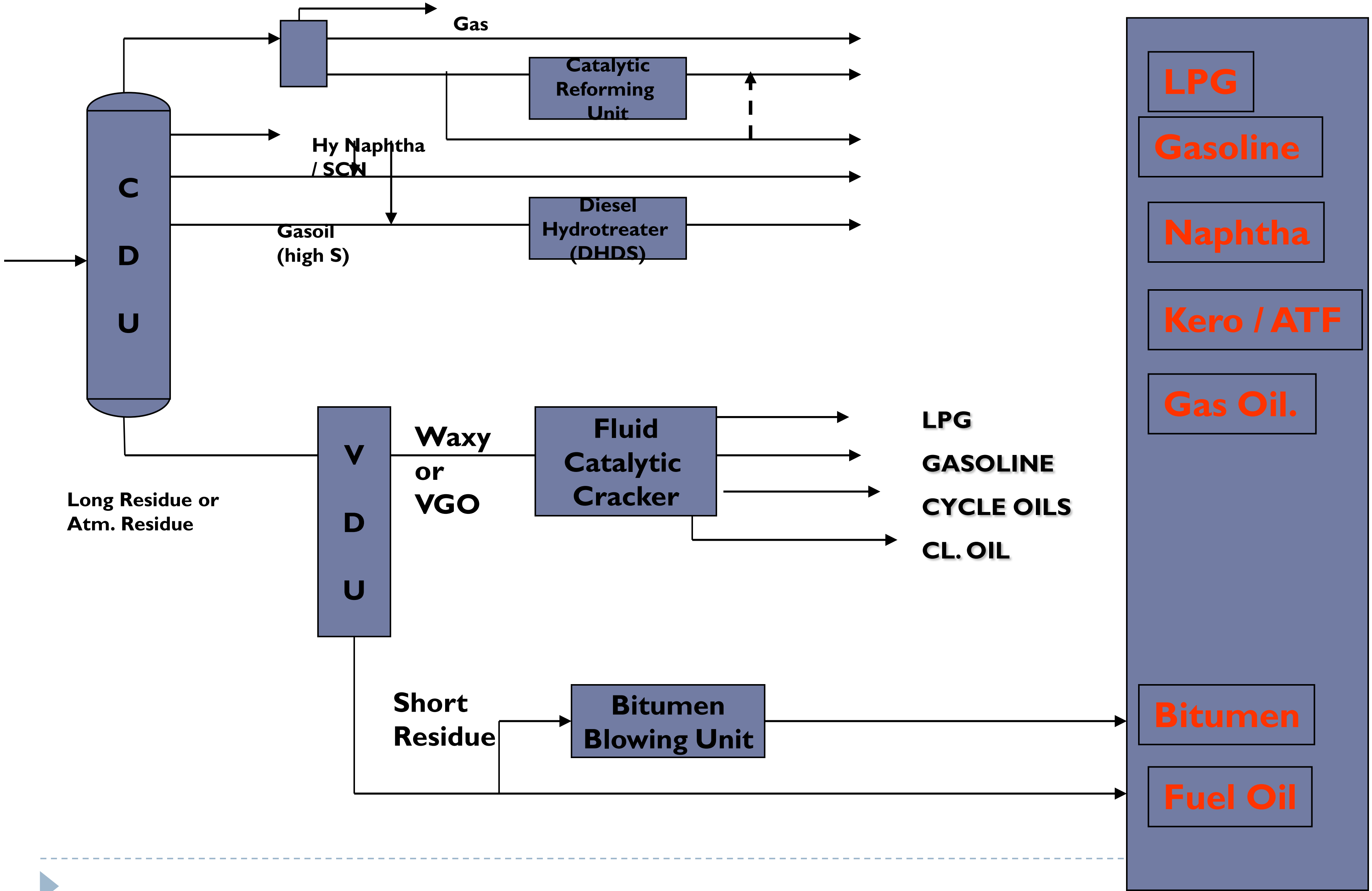
Process Description And Conditions:

•Use of trickle bed reactors.(PBR)

•T :300 to 400 °C; P :30 to 130 atm

•Catalyst: alumina based impregnated with cobalt and molybdenum(CoMo) ,at times a combination of nickel and molybdenum (called NiMo) is used, in addition to the catalyst, for specific difficult-to-treat feed stocks, such as those containing a high level of chemically bound nitrogen.

CRACKING REFINERY



Isomerization process:

<u>Process Objective</u>:

To convert low-octane n-paraffins to high-octane iso-paraffins

<u>Process Description:</u>

•Fixed Bed Reactors used.

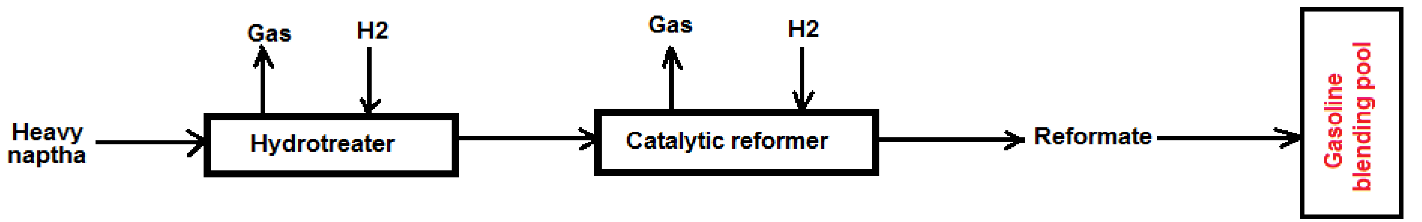
•Chlorine Promoted.

•Catalyst: Co-Mo for Hydrotreator Reactor

Pt for Penex Reactor

Ni Based for Methanation

• T: 126-145̊ C; P: 33.5 kg/cm2(g)



Catalytic reformer:

<u>Process objective</u>:

Conversion of low octane linear hydrocarbons (paraffins) into branched alkanes (isoparaffins) and cyclic napthenes which are then partially dehydrogenated to produce high octane aromatic hydrocarbons.

<u>Process Description/Condition:</u>

•Moving Bed Reactor with Catalyst Regeneration

•Catalyst: NiMo, Pt-Sn T:490-540℃ P: 2-30 kg/cm2

DHDS:
Diesel Hydro De-Sulphurization Unit

- Process Objective:

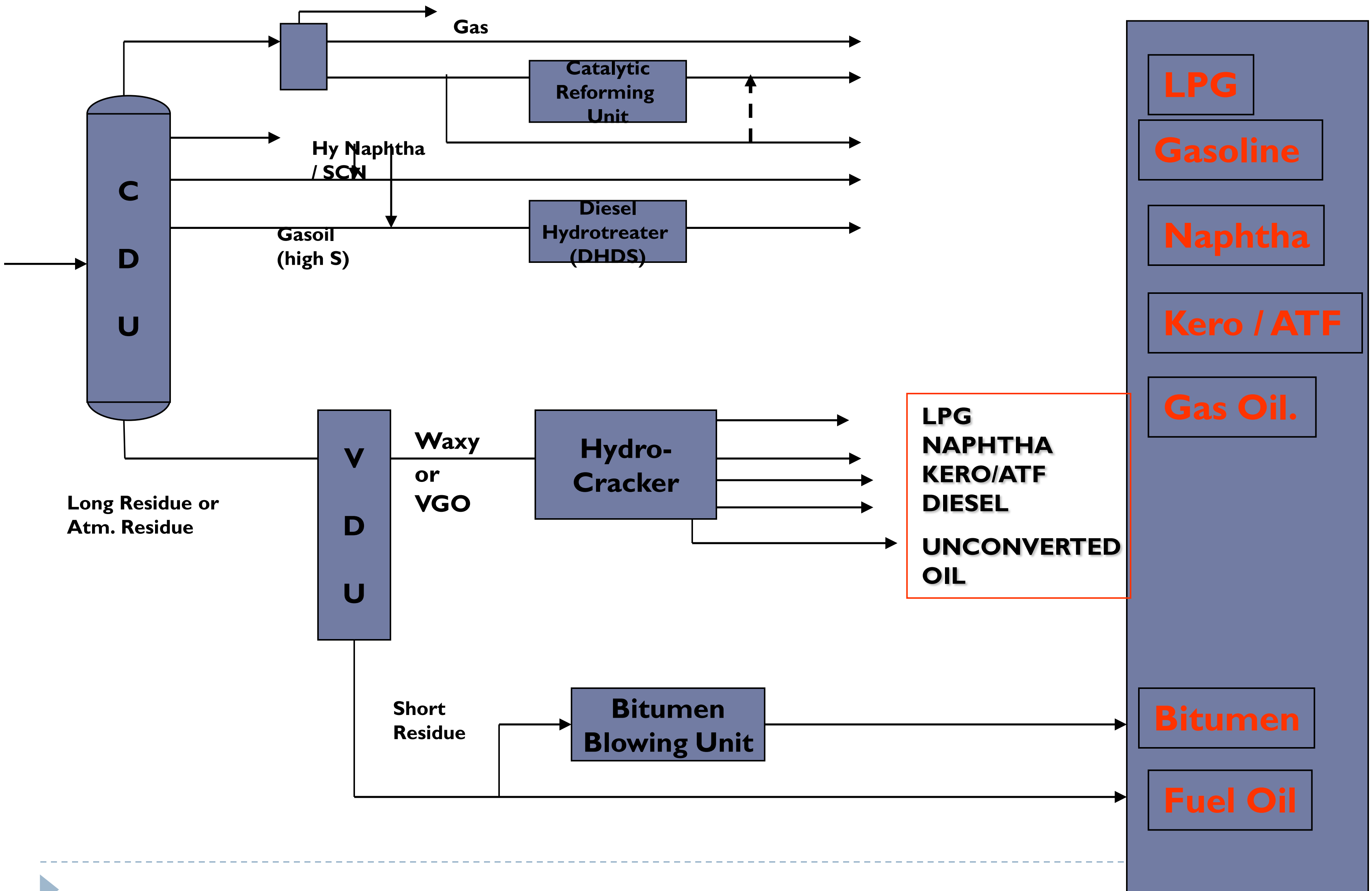
  To meet the EURO diesel quality requirement (<500 ppm S)

- Reactions:

  Desulphurization, Denitrification

- Process Description/Conditions:
  - Reactor: Pa
  - Catalyst: Ni-Mo oxides
  - T: 320-380 ℃
  - P:100-105 kg/cm2

HYDROCRACKING REFINERY



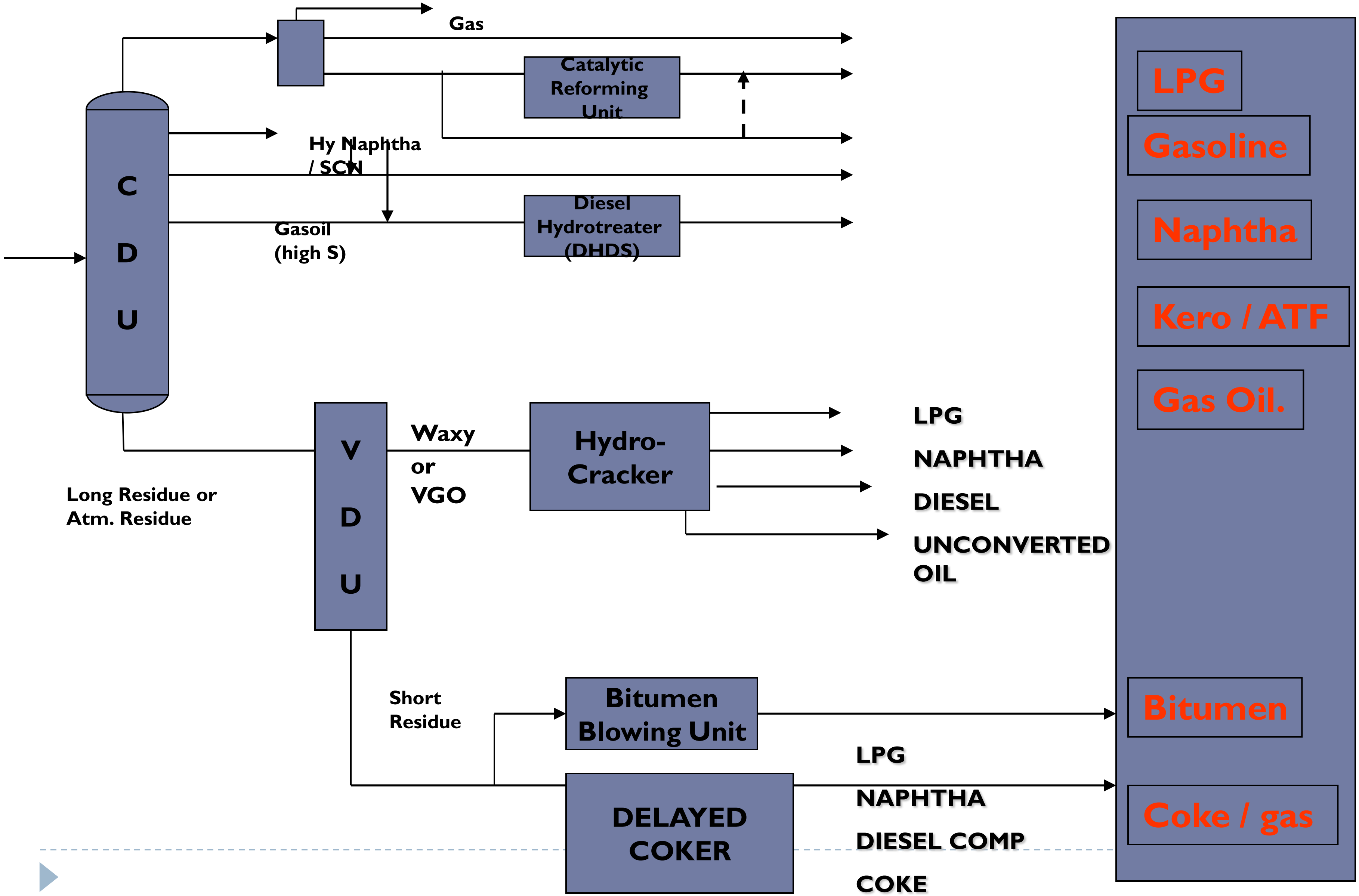
HYDROCRACKER UNIT

- Process Objective:

  To convert Heavy Vacuum gas oil to valuable distillates like LPG, Naphtha, ATF, Kerosene and Diesel.

- Process Description/Conditions:
  - Reactor: Pa
  - Catalyst: Ni-Mo oxides , Ni/Mo/W
  - T: 370-420 ℃
  - P:160-170 kg/cm2
  - Feed: VGO/Coker Products

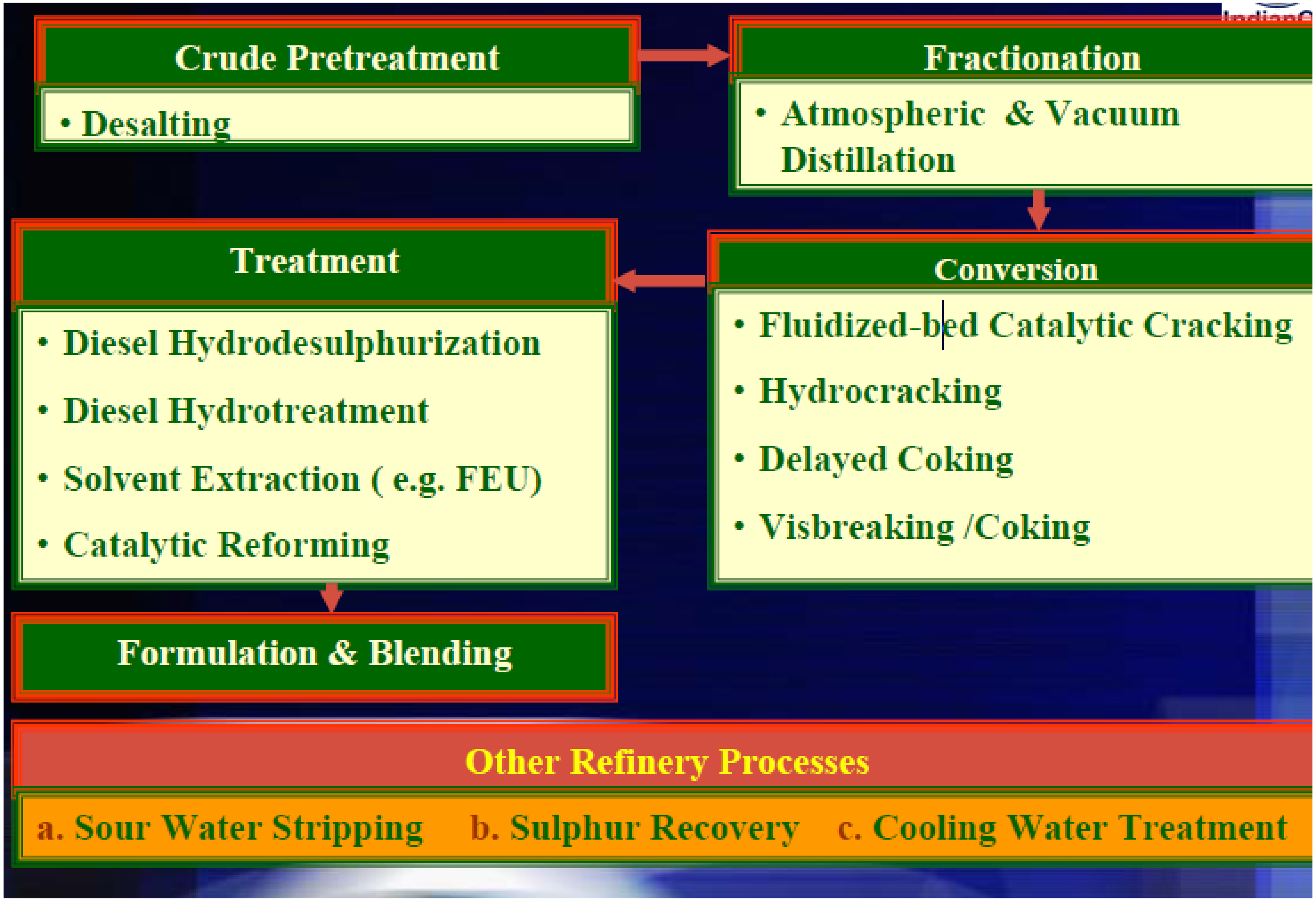
FULL CONVERSION REFINERY

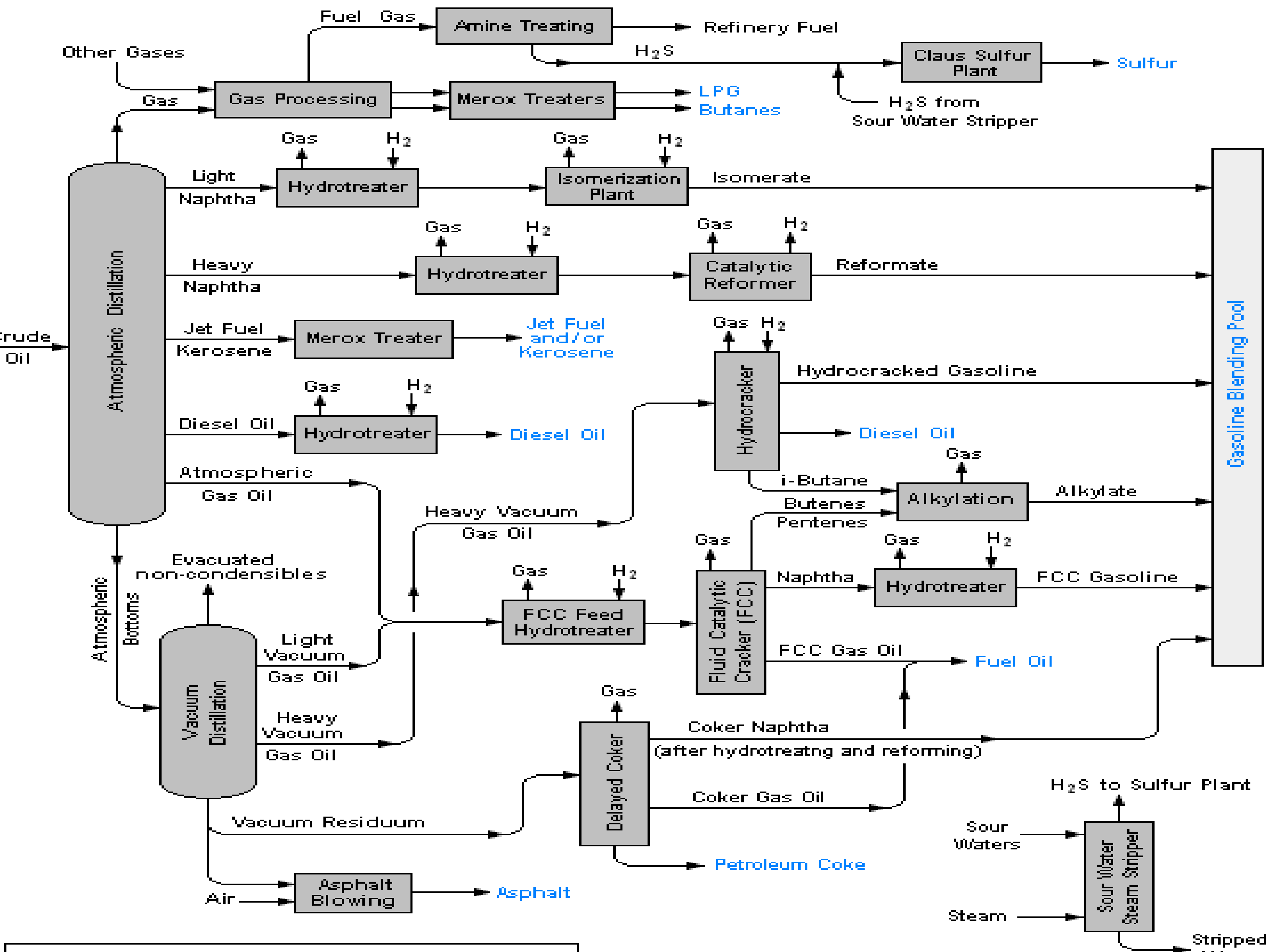


PROCESS EQUIPMENTS OF FLOW SHEETS

Priyanka Tata

SIMPLE SCHEME




Fuel Gas
Amine Treating
Refinery Fuel
H_2S
Claus Sulfur Plant
Sulfur
Other Gases
Gas
Gas Processing
Merox Treaters
LPG
Butanes
H_2S from Sour Water Stripper
Gas
H_2
Gas
H_2
Light Naphtha
Hydrotreater
Isomerization Plant
Isomerate
Gas
H_2
Gas
H_2
Heavy Naphtha
Hydrotreater
Catalytic Reformer
Reformate
Oil
Atmospheric Distillation
Jet Fuel Kerosene
Merox Treater
Jet Fuel and/or Kerosene
Gas
H_2
Hydrocracker
Hydrocracked Gasoline
Gas
H_2
Diesel Oil
Hydrotreater
Diesel Oil
Diesel Oil
Gasoline Blending Pool
Gas
Atmospheric Gas Oil
i-Butane
Alkylation
Alkylate
Butenes
Pentenes
Heavy Vacuum Gas Oil
Gas
Gas
H_2
Evacuated non-condensibles
Gas
H_2
Naphtha
Hydrotreater
FCC Gasoline
Atmospheric Bottoms
FCC Feed Hydrotreater
Fluid Catalytic Cracker (FCC)
Light Vacuum Gas Oil
FCC Gas Oil
Fuel Oil
Vacuum Distillation
Gas
Heavy Vacuum Gas Oil
Coker Naphtha
(after hydrotreatng and reforming)
Delayed Coker
Coker Gas Oil
H_2S to Sulfur Plant
Vacuum Residuum
Sour Waters
Sour Water Steam Stripper
Petroleum Coke
Asphalt Blowing
Asphalt
Air
Steam
Stripped

Distillation tower

Manufacturers:
J.D.Cousins and Sons
Excel Manufacturers, Mumbai

Furnaces

Manufacturers:
Petrotech
Linde India

De-salter

A desalter is a process unit in an oil refinery that removes salt from the crude oil. The salt is dissolved in the water in the crude oil, not in the crude oil itself. The desalting is usually the first process in crude oil refining.

Manufacturers:
Nalco
Baker Hughes (Baker Petrolite)
Champion Technologies
GE Water

Pre Flash Drum

if the crude has some light ends we normally have a preflash drum/tower and we only send the flashed liquid to the fired heater before it goes to the Crude Distillation Unit (CDU)

Manufacturers:
Magnetrol.inc

Hydro-treater

There are also compounds that contain sulfur, nitrogen, dissolve metals or oxygen that must be removed for environmental reasons and to keep them from damaging catalyst used in the refinery.
The unit within the refinery that performs this chemical treatment is the **hydrotreater**.

Manufacturers:
Shell
Haldor Topsoe India Pvt. Ltd.

Delayed Coker

To produce valuable distillate from Heavy Ends by Thermal Cracking

<u>Conditions:</u>

Reactor: Pa

Catalyst: Ni-Mo oxides , Ni/Mo/W

T: 495-505 ℃

P:2-3kg/cm2

Feed: RCO/Vaccum Residue/ Other Heavy Ends

Designed by Engineers India Limited and outsourced to local vendors

Fluidized catalytic cracking

Fluid catalytic cracking (FCC) is one of the most important conversion processes used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases, and other products.

Manufacturers:
Shell
Haldor Topsoe India Pvt. Ltd.

Merox treater

Removes mercaptans from LPG, propane, butanes, light napthas, kerosene and jet fuel by converting them to liquid hydrocarbon disulphides.

Manufacturers: Honeywell UOP
Haldor Topsoe India Pvt. Ltd.

Catalytic reformer

Catalytic reforming is a major conversion process in petroleum refinery and petrochemical industries. The reforming process is a catalytic process which converts low octane naphthas into higher octane reformate products for gasoline blending and aromatic rich reformate for aromatic production.

Manufacturers: Honeywell UOP
Haldor Topsoe India Pvt. Ltd.

Hydrocracker

To convert Heavy Vacuum gas oil to valuable distillates like LPG, Naphtha, ATF, Kerosene and Diesel.

Manufacturers:
XYTEL
Larsen & Turbro
Haldor Topsoe India Pvt. Ltd.

OPTIMIZING THE REFINING PROCESS:SCOPE OF IMPROVEMENT

Narayani Kelkar

MARKET DEMANDS

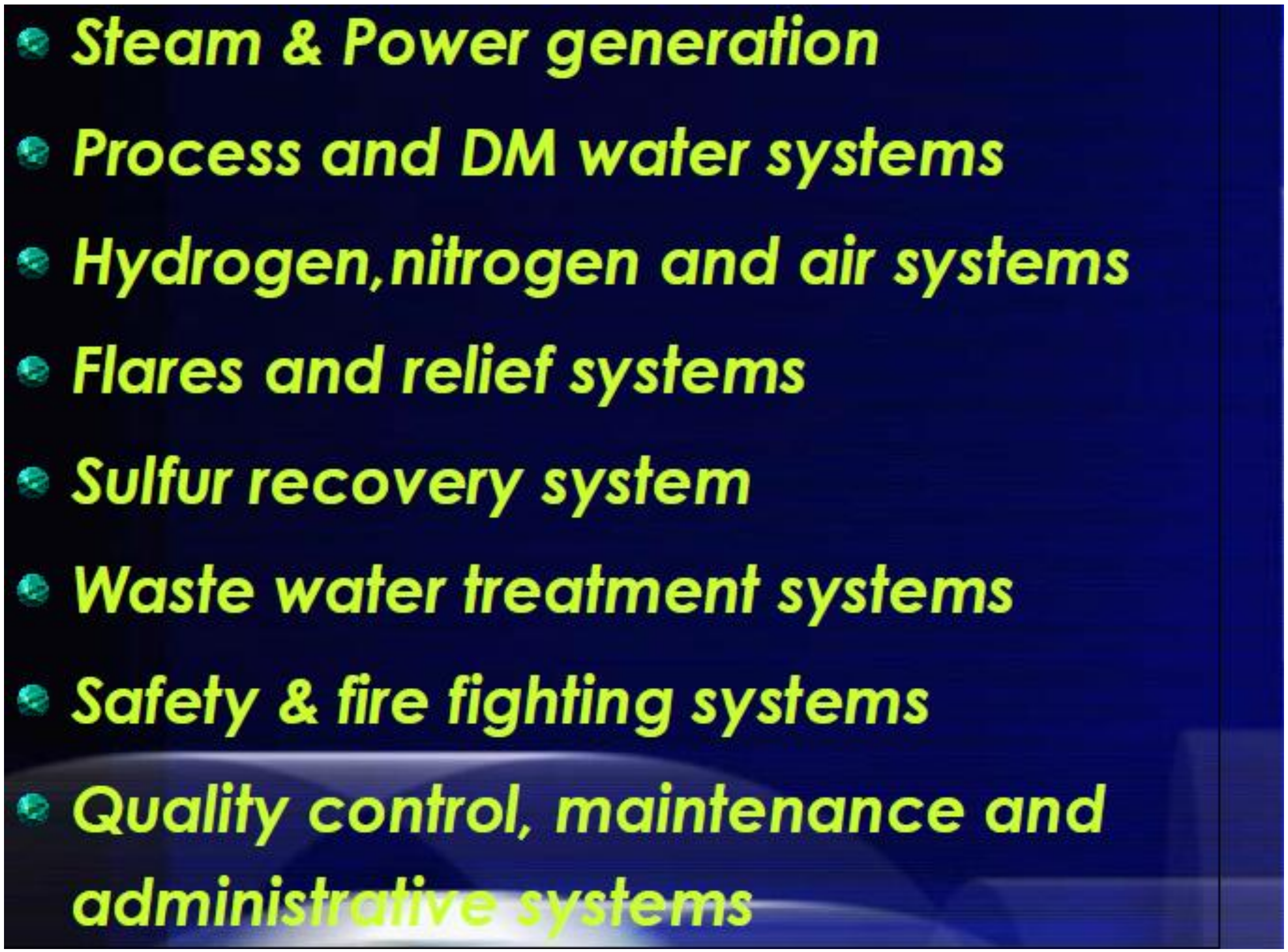
- Clean Products(Devoid of S,N,O, metals etc)
- More Gasoline(high octane number)
- More Diesel(high cetane number)
- Specific Products(Aromatics, Alkenes etc)
- Less Residue

CHALLENGES TO OIL INDUSTRY

CONSTRAINTS

- Crude oil sourcing - Indigenous production is only about 30% of the total requirement.
- Sharp fall in the availability of low Sulfur crude oil and even to the extent lighter crude oil.
- Hence refineries are forced to process wide variety of crude oil including high sulfur crude.
- Selection of suitable technology having enough flexibility.

OTHER SIDE PROCESSES THAT NEED TO BE INCORPORATED



RECOVERABLES

- Hydrogen : Recovered can be used to make the plant self sustained
- Sulphur: Can be used as raw material for the production of Sulphuric Acid.
- Heat : From Flue Gases, can be used for preheating.
- Waste Water Recovery: It can be re-used as Utilities.

Hydrogen Generation Unit

- Process Objective:

  To Meet the Hydrogen requirement for DHDS/DHDT/OHCU/ISOM/ Reforming Units and Other Hydrotreaters.

- Process Description/Conditions:
  - Reformer
  - Catalyst: Co-Mo for Hydrotreater

    ZnO/K2Co3 for H2S and Chloride adsorber

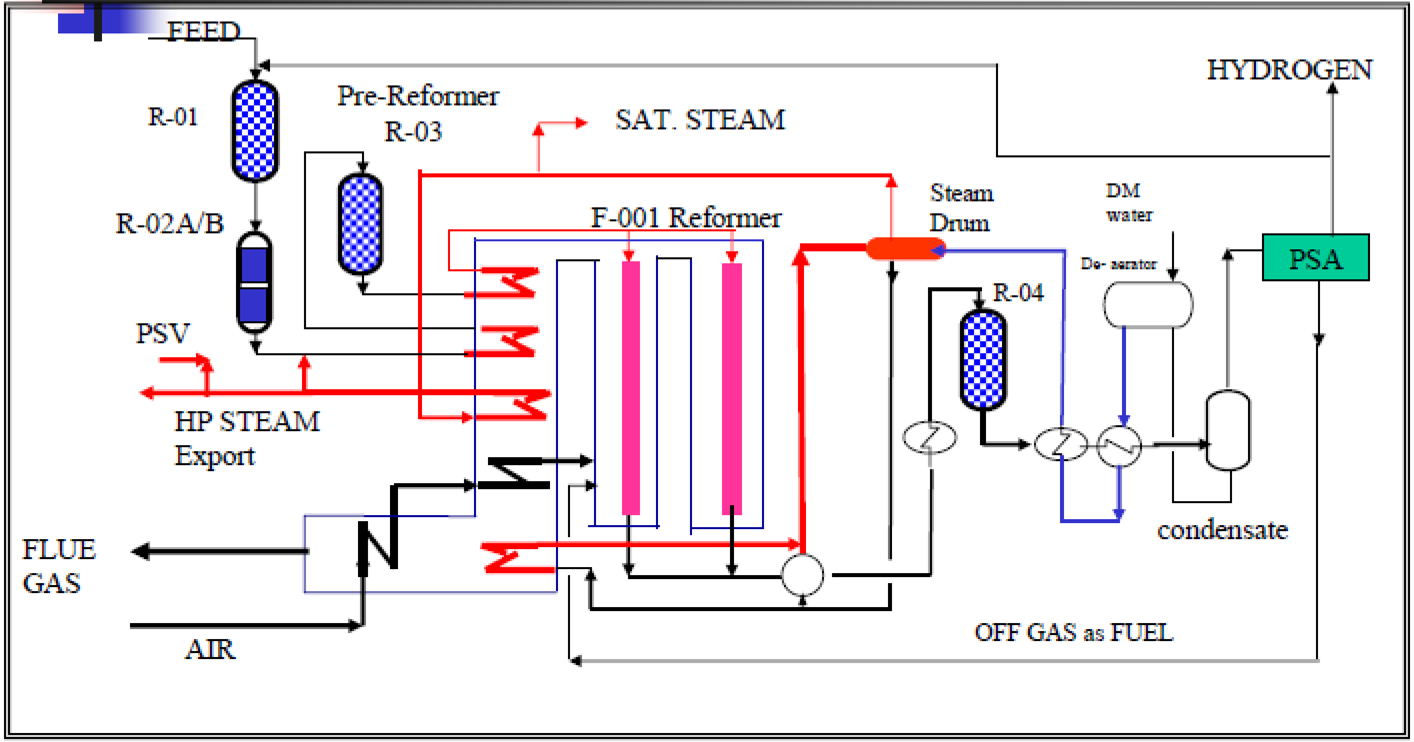
    NiO for Preformer

    Ni for Reformer

    CuO for HT/LT Shift reactors

    Adsorbents for PSA Adsorbers
  - T: 860-870℃
  - P:23-26 kg/cm2
  - Feed: Naptha /Natural Gas

Hydrogen Generation Unit Flow Diagram



Sulphur Recovery Unit

- Process Objective:

  To Reduce the SO2 emission from the Refinery by recovering Sulphur from Amine Acid and Sour Gases produced during various Hydrotreating Process.

- Process Description/Conditions:
  - Reformer
  - Catalyst: Co-Mo for Hydrotreater

    ZnO/K2Co3 for H2S and Chloride adsorber

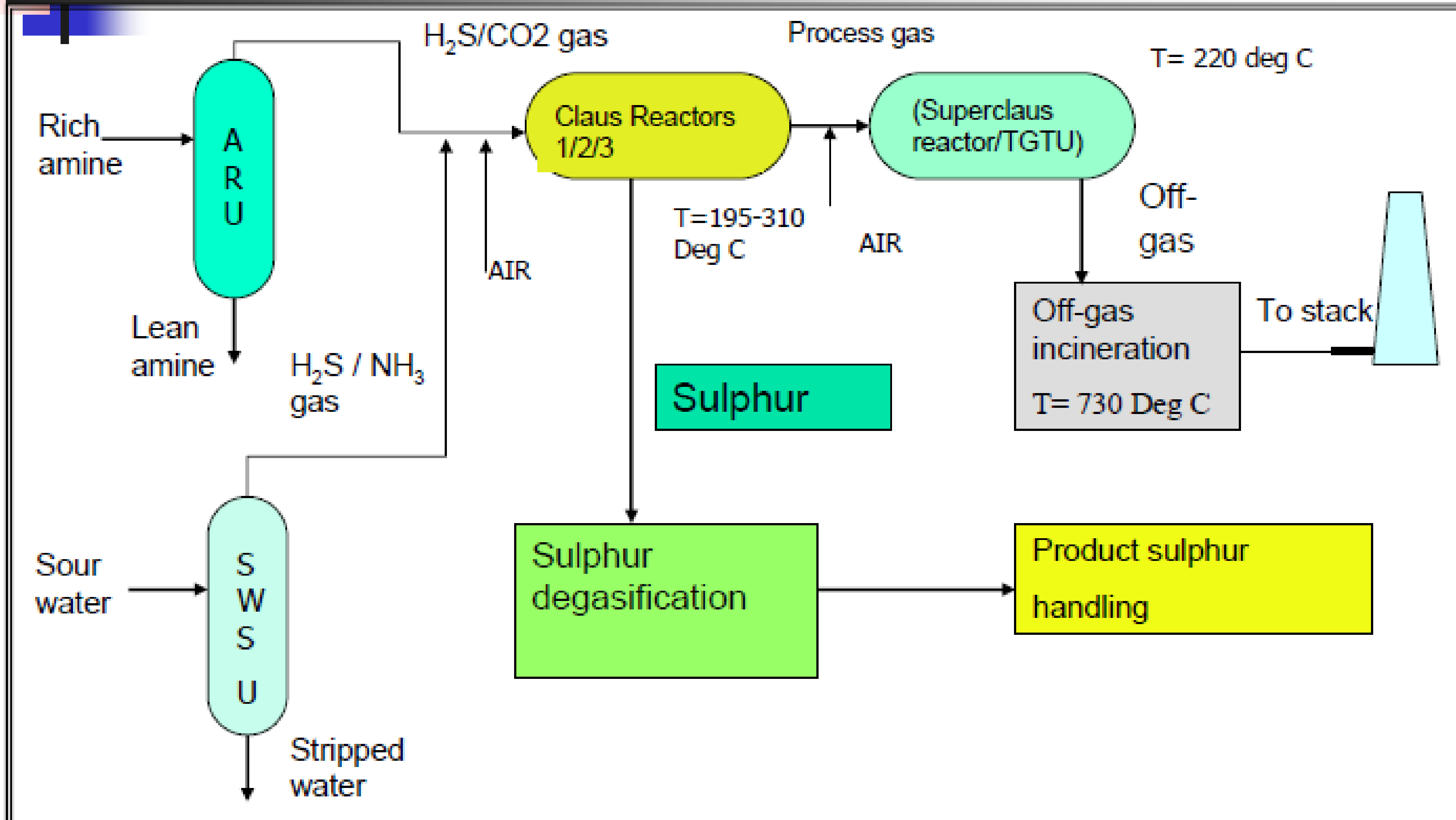
    NiO for Preformer

    Ni for Reformer

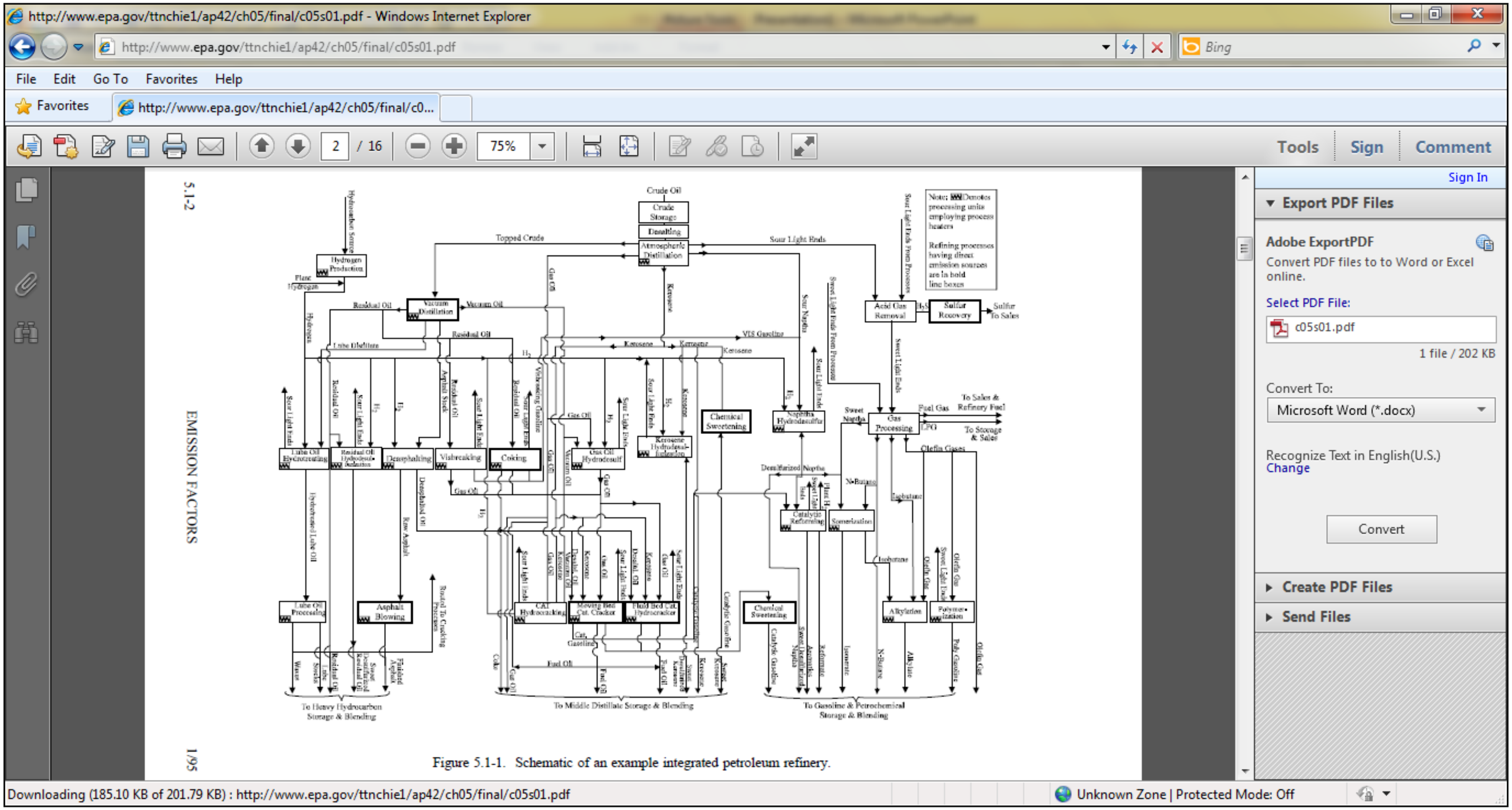
    CuO for HT/LT Shift reactors

    Adsorbents for PSA Adsorbers
  - T: 195-320 ℃
  - P:0.56 kg/cm2
  - Feed: Amine Acid gases and Sour acid gases

Sulphur Recovery Unit Flow Diagram



Schematic of an Integrated Petroleum Refinery



Future scope, Economy issues , technology roadmaps, Pollution control Board reports

Saee Mandlekar

Because of the high market demands and growing environmental concerns the petroleum industry needs to optimize its refining processes

REFINING ECONOMICS

While considering the economic performance of a petroleum refiner, several characteristics should be noted:

1. Feedstock costs (primarily crude oil)
2. Fuel costs and other operational costs for the refinery
3. Costs of complying with emissions regulations (Particularly NOx)
4. Market prices for the products produced

EVALUATING ECONOMIC PERFORMANCE

- Complicated by the fact that many refineries can use crude oil of lower quality
- Crude oil- lighter or heavier density/ low or high sulfur content
- Depending on the quality investment costs differ
- Profitability- gross refinery margin/ net refinery margin

ENVIRONMENTAL ISSUES

- Air emissions
- Waste water
- Hazardous materials
- Wastes
- Noise

1. AIR POLLUTION

- Exhaust gases: CO2, Nox and CO result from the combustion of gas and fuel oil or diesel in turbines, boilers, compressors and other engines for power and heat generation
- Venting and flaring: Petroleum hydrocarbons are emitted from emergency process vents and safety valves discharges
- Fugitive emissions: These are associated with vents, leaking tubes, flanges, packings, open-ended lines, storage tanks, pump seals etc
- Sulfur oxides: Sox may be emitted from boilers, heaters, etc based on the sulfur content of the processed crude oil
- Greenhouse gases: CO2 released in large quantities during combustion

WATER POLLUTION

- Industrial process waste water: Largest volume effluents in petroleum refining include ‘sour’ process water and non-oily/non-sour but highly alkaline process water
- Oil spills: Oil spills in the ocean during import/export cause immense damage to marine life and the hydrosphere in general
- Hydrostatic testing: Chemical additives are often added to water to prevent internal corrosion

CHALLENGES ON THE HORIZON

Key Drivers Affecting the Industry

- Environmental regulations
- Increasing cleanliness of fuels
- Globalization
- Increasing yields from crudes of decreasing quality
- Uncertainty about future consumer fuels of choice
- Pressure to reduce emissions of CO_2
- Attaining adequate profit margins
- Proactively dealing with public scrutiny, environment, global warming and other issues

In order to respond to these challenges the Petroleum Industry has come up with a Technology Vision 2020

Challenges contd.

- Environmental requirements
- Capital investment
- Production and growth
- Imports
- Permits and regulatory uncertainties

A TECHNOLOGY VISION 2020

- By 2020 it is envisioned that the petroleum industry will exhibit a number of desirable
- characteristics that represent continuous improvements to current practices

These include:

1. Environmentally sound
2. Energy efficient
3. Safe and simpler to operate
4. Completely automated
5. Operate with minimal inventory
6. Use processes that are fundamentally more understood

Process Unit	Product Energy Requirement	Still Gas	LRG	Gasoline	Jet Fuel/ Kero	Dist Fuel Oil	Resid Fuel Oil	Asphalt	Coke	Other
Crude Distillation:										
Atmospheric	658	1	1	295	54	180	38	30	49	12
Vacuum	242	0	0	61	0	33	39	45	64	0
Reformer	339	13	5	322	0	0	0	0	0	0
Hydrotreating	382	14	11	230	22	105	0	0	0	0
Alkylation	102	0	0	102	0	0	0	0	0	0
FCC	377	24	20	296	0	37	0	0	0	0
TOTAL	**2,101**	51	37	1,305	76	355	77	75	113	12
% of Total	**100%**	2.4 %	1.7%	62.1%	3.6%	16.9%	3.7%	3.6%	5.4%	0.6%

Improve energy and process efficiency

- Use cost effective technology with lower energy intensity (eg, better catalysts)
- Use the deregulation of utilities to improve their ability to generate electricity on-site
- Optimization of engines and fuels will result in better efficiency
- New sources of energy for transportation (fuel cells for car) will continue to be developed and implemented

Table 2: Energy content-based process energy allocation by final product: 1 kg of crude feed

Final Product	Mass (kg)	Fuel (kJ)	Allocated Energy Use				Allocated Energy Use Share (%)				Energy Intensity (%)
			Elec. (kJ)	Steam (kJ)	Total (kJ)	Mass (%)	Fuel	Electricity	Steam	Total	
Residual oil	0.004	3.1	0.1	1.6	4.8	0.4	0.1	0.1	0.2	0.2	41.3
Fuel (still) gas	0.044	92.9	6.2	42.1	141.2	4.4	4.2	6.1	6.5	4.8	110.0
Naphtha	0.001	0.5	0.1	0.9	1.5	0.1	0.0	0.1	0.1	0.1	50.9
Diesel	0.094	147.6	9.4	39.9	196.9	9.3	6.7	9.3	6.1	6.7	71.8
Kerosene	0.137	192.5	11.5	45.6	249.6	13.6	8.8	11.4	7.0	8.5	62.4
Gasoline	0.465	1334.7	53.6	184.4	1572.6	46.0	60.7	53.2	28.4	53.3	115.9
LPG	0.058	28.4	5.1	44.8	78.3	5.7	1.3	5.0	6.9	2.7	46.2
Gas oil	0.045	126.6	2.9	18.6	148.1	4.5	5.8	2.9	2.9	5.0	112.7
Heavy fuel oil	0.040	58.9	3.1	12.8	74.8	4.0	2.7	3.0	2.0	2.5	64.0
Lube stocks	0.070	111.4	5.3	202.1	318.8	6.9	5.1	5.3	31.1	10.8	156.0
Asphalt	0.020	46.8	1.5	23.5	71.8	2.0	2.1	1.5	3.6	2.4	123.0
Waxes	0.009	14.7	0.7	26.6	42.0	0.9	0.7	0.7	4.1	1.4	160.0
Coke	0.005	12.1	0.3	3.6	16.0	0.5	0.6	0.3	0.6	0.5	109.6
H_2 gas	0.005	21.2	0.8	1.4	23.4	0.5	1.0	0.8	0.2	0.8	160.3
H_2S gas	0.013	6.2	0.3	1.6	8.2	1.3	0.3	0.3	0.2	0.3	21.5
Total	1.010	2197.8	100.7	649.4	2947.9	100.00	100.0	100.0	100.0	100.0	100.0

Because of such high energy requirements petroleum refineries always use fluids as energy resources and not electrical supplies since it makes the entire process very cost ineffective.

Improve environmental performance

- Lower emissions with no harm to human health or the environment
- Manufacture, storage and delivery of fuels will be subject to engineering controls
- Sophisticated sensor technology

Materials and inspection technology

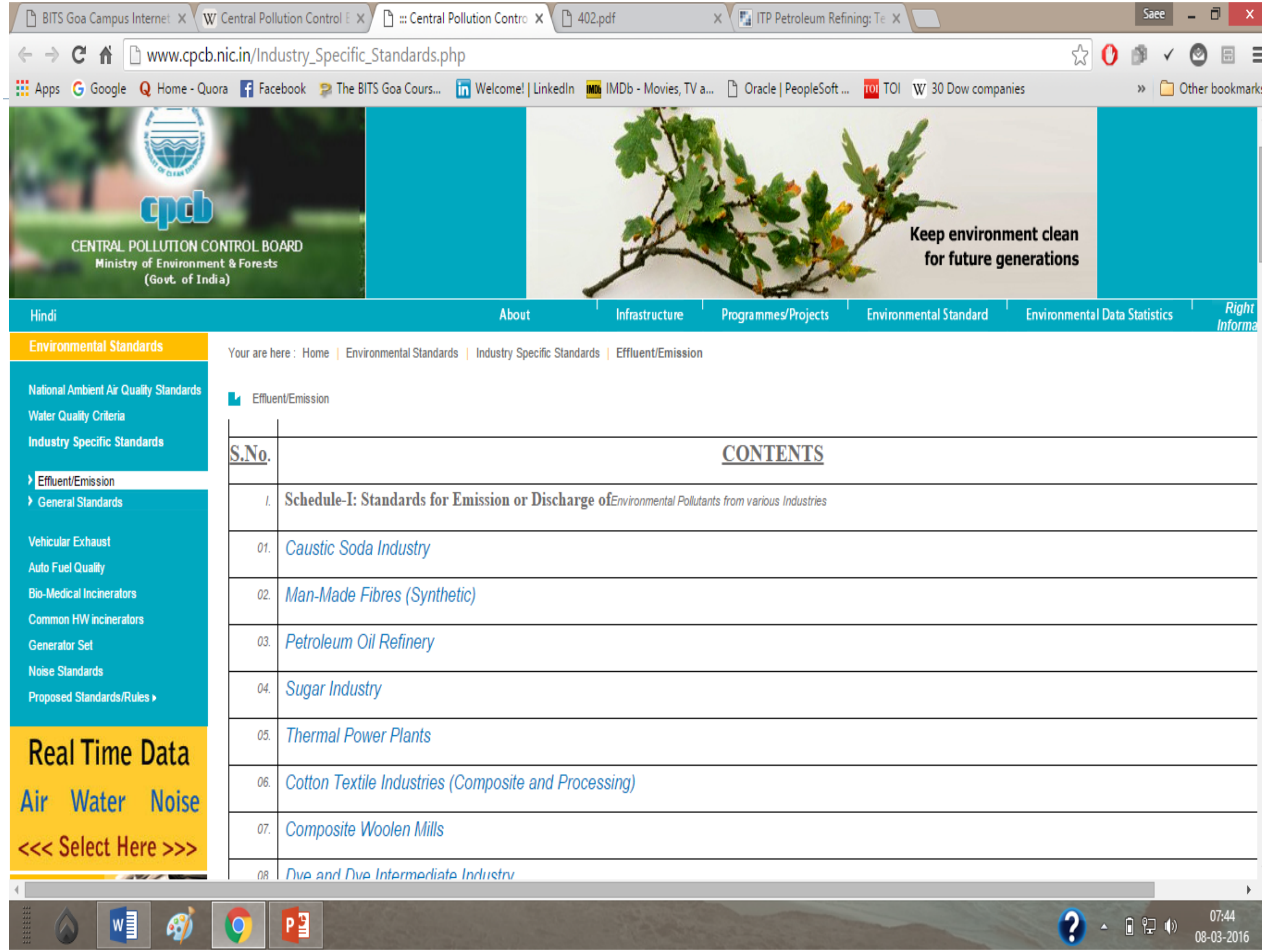
- Reduce the cost of maintenance
- Increase plant safety
- Extend useful life of equipment
- Equipment will be highly instrumented to monitor structural integrity (no boundary releases that significantly impact safety)

Refinery distribution system and retail delivery services

- Flexible- to handle various feedstocks and a variety of fuels for conventional and emerging alternative-fuelled transportation
- Service stations will be larger and more convenient
- Fueling processes and underground storage systems will be improved (eg, automated fuel dispensing systems)

CENTRAL POLLUTION CONTROL BOARD

- Under the Ministry of Environment and Forests



S.No.	CONTENTS
I.	Schedule-I: Standards for Emission or Discharge of Environmental Pollutants from various Industries
01.	Caustic Soda Industry
02.	Man-Made Fibres (Synthetic)
03.	Petroleum Oil Refinery
04.	Sugar Industry
05.	Thermal Power Plants
06.	Cotton Textile Industries (Composite and Processing)
07.	Composite Woolen Mills
08.	Dye and Dye Intermediate Industry

[3][3. **PETROLEUM OIL REFINERY**

A. EFFLUENT	
1. pH	6.0-8.5
2. Oil & Grease	5.0
3. $BOD_{3\ days,\ 27^{0}C}$	15.0
4. COD	125.0
5. Suspended Solids	20.0
6. Phenols	0.35
7. Sulphides	0.5
8. CN	0.20
9. Ammonia as N	15.0
10. TKN	40.0
11. P	3.0

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[1] The Environment (Protection) Rules, 1986 are referred to as principal rules in all subsequent Notifications beginning with S.O. 32(E), dated 16.2.1987 published in the Gazette no. 66, dated 16.2.1987. The Schedule to be principal rules was renumbered as Schedule-I vide S.O. 32(E) supra.

** Standards notified at Sl. No. 60 may also be referred.

[2] Substituted by Rule 2 of the Environment (Protection) Amendment Rules, 1996 notified by G.S.R.176(E), dated 2.4.1996 may be read as BOD (3 days at 27°C) wherever BOD 5 days 20°C occurred.

[3] Substituted by Rule 2 (i) of the Environment (Protection) Amendment Rules, 2008 notified by G.S.R.186(E), dated 18.3.2008.

Thank you