

Lecture: 01

Petroleum Refining



**Dharmsinh Desai University, Nadiad
Gujarat - India**

Petroleum (or Rock oil)

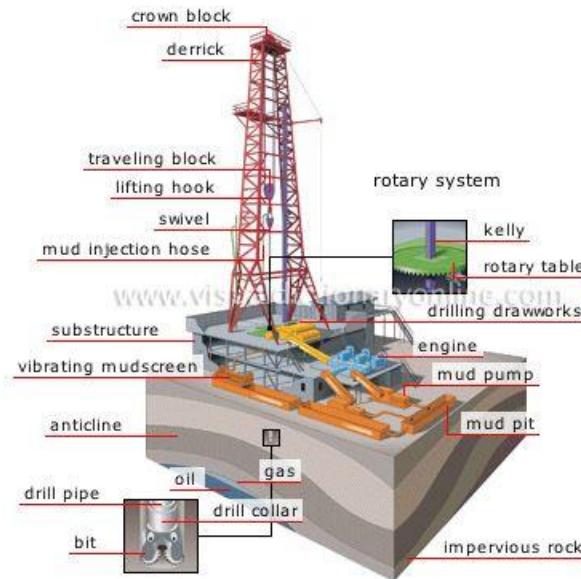
- Latin name: Petra (**Rock**) and Oleum (**Oil**).
- Petroleum is mainly a mixture of organic compounds called hydrocarbons
 - made of hydrogen and carbon.
 - Impurities: combined sulphur, nitrogen, oxygen, salts, metals etc..
- Also known as **crude oil**.
- “A naturally occurring mixture consisting predominantly of hydrocarbons and/or sulphur, nitrogen, and/or oxygen derivatives of hydrocarbons which is removed from earth in liquid state or is capable of being removed.”
- These days it is often called “**liquid gold**” or “**black gold**”

□ Hydrocarbons may be gaseous, liquid, or solid at normal temperature and pressure, depending on the number and arrangement of the carbon atoms in their molecules.

Those with up to **4** carbon atoms are **gaseous**; those with **20 or more** are **solid**; those **in between** are **liquid**.

Petroleum (or Rock oil)

- Petroleum or Rock oil is a naturally occurring brown to black oil comprising mainly of Hydrocarbon found under the crust of the earth on shore or off shore.
- It is obtained from the ground either by natural seepage or by drilling wells to various depths.
- Either petroleum oil flows out it self due to underground gas pressure or these are mechanically pumped out.





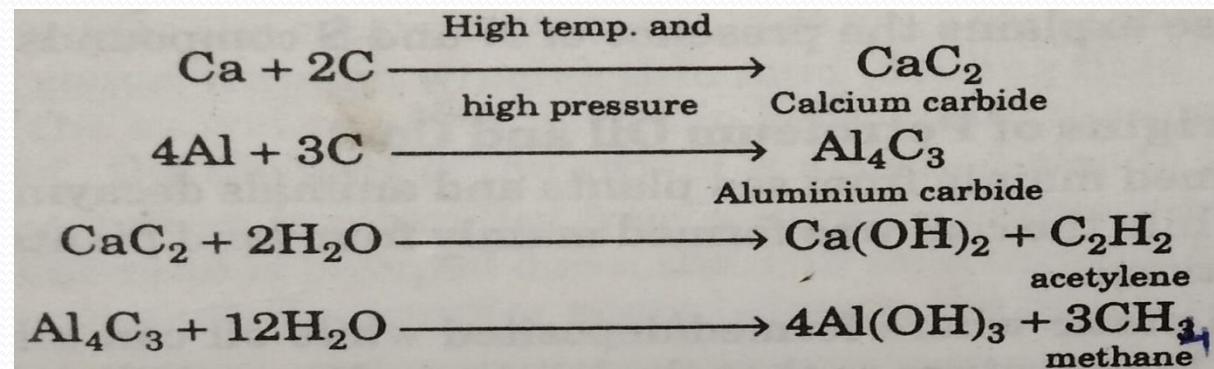


Origin of Petroleum

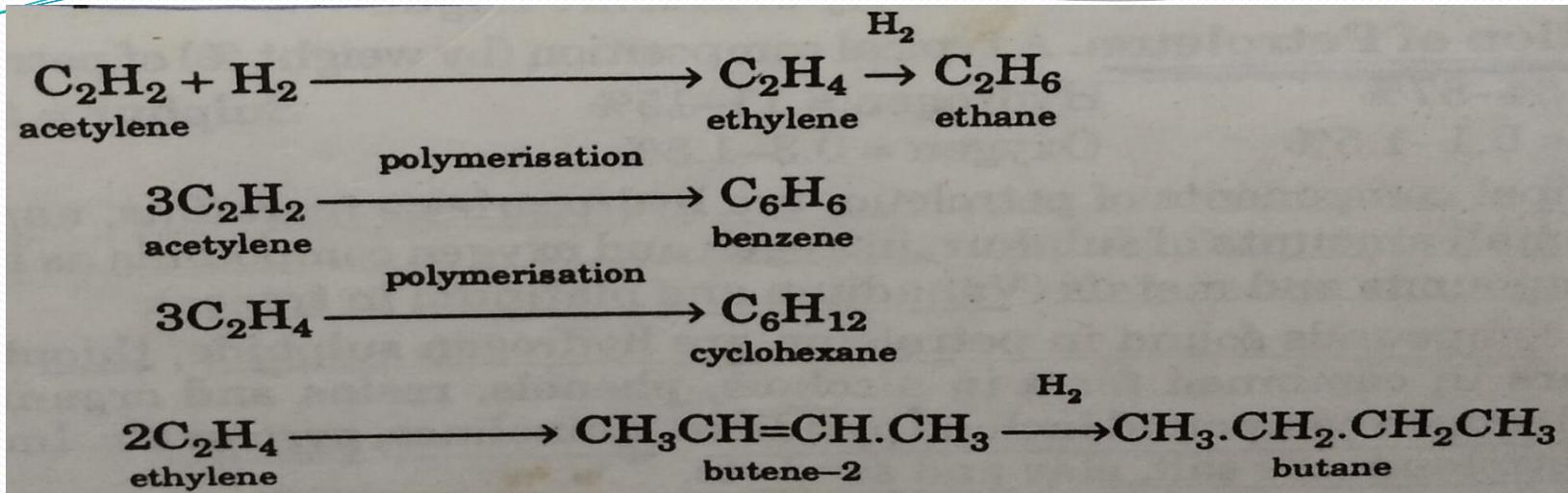
□ Although several theories were put forward to explain the formation of Petroleum, only **THREE** widely accepted are explained here:

1. Carbide theory:

Hydrocarbons present in petroleum are formed by the action of water on inorganic carbides. Inorganic carbides, in turn are formed by the reaction of metal and carbon under High Temperature and Pressure inside the earth.



These lower Hydrocarbons then undergo Hydrogenation and Polymerization to give various types of Hydrocarbons (Paraffins, Aromatic and Cycloparaffins)



This theory fails to explain the following facts:

- Presence of Nitrogen and Sulphur compounds.
- Presence of Chlorophyll and Haemin.
- Presence of optically active compounds.

2. Engler theory: Petroleum is of Animal origin.

Engler suggested that Petroleum is formed by the decay and decomposition of Marine Animals under High pressure and temperature.

- The sulphur dioxide gas given out by the volcanoes beside the sea-side kills the fish and other sea animals which go on piling beside the volcano.
- After hundreds of years, these animals starts decomposing under the influence of high pressure and temperature to form Petroleum.

This theory is supported by the following facts:

- Experimental destructive decomposition of fish oil and other animal fats under high pressure and temperature gives a product similar to natural petroleum.
- Presence of brine or sea water together with petroleum.
- Presence of Nitrogen and sulphur compounds.
- Presence of optically active compounds.
- Presence of fossils (the remains of animals which died long ago) in the petroleum area.

This theory fails to explain the following facts:

- Presence of Chlorophyll (green-colouring matter of plants) in petroleum.
- Fails to explain the presence of coal deposits in the vicinity of the oil fields.

3. Modern theory:

Petroleum is believed to be formed by the decay and decomposition of marine animals as well as that of vegetable organism of the prehistoric forests means it is of Animal as well as plant origin.

- It is thought that due to some upheavals or earthquakes, these prehistoric forests and sea animals got buried under the crust of earth.
- Due to action of prolonged action of high temperature and pressure in the interior of earth for ages, the biological matter decomposed into Petroleum.

This theory is supported by the following facts:

- Presence of brine is explained on the basis of Animal origin.
- Presence of coal is explained by plant origin.
- Presence of Nitrogen and sulphur compounds.
- Presence of optically active compounds.

- Theories on the origin of petroleum have been proposed and are normally classified into two general groups.
 - Abiogenic Origin or Inorganic Origin
 - Biogenic Origin or Organic Origin

Abiogenic Origin or Inorganic Theory

- A number of scientists adhere to the concept that inorganic oil and gas have originated in the earth's interior as a result of chemical reactions between hydrogen and carbon under conditions of high temperature and high pressures in the absence of organic matter.

Organic Theory

- Most accepted theory- maintains that the hydrogen and carbon source for petroleum was organic material from decaying plants and animals forming and accumulating in oceanic sediment.
- Acceptance of the organic theory of the origin of petroleum dictates that the search for oil be directed to areas underlying by thick sections of sedimentary rock.

Difference between origins of Petroleum oil and Coal

- Petroleum oil was formed mainly from sea plants and animal decaying under strongly reducing conditions .
- Petroleum oil can migrate under the effects of pressure and temperature so that the location of the existing deposits may not be the location of the initial accumulation of oil forming debris.
- Coal was formed mainly from land plants decaying under mildly reducing conditions.
- The coal seems remained static .

Composition of Petroleum

- A typical composition (by weight %) of petroleum is given below:
Carbon (84-87%), Hydrogen (11-15%), Sulphur (0.1-3%), Nitrogen (0.1-1.5%) Oxygen (0.3-1.8%)
- The principal components of petroleum are hydrocarbons (paraffins, naphthenes, aromatics, olefins etc.).
- Small amounts of sulphur, nitrogen and oxygen compounds as impurities.
- Some inorganic compounds and metals (Vanadium and platinum in traces).
- Sulphur compounds found in petroleum are ***Hydrogen sulphide, Thiophenes, Mercaptans.***
- Oxygen occurs in combined form in ***Alcohols, Phenols, Resins and Organic acids present in petroleum.***
- Nitrogen compound include ***Pyridines, Quinolines, Pyroles etc.***
- Inorganic compounds present in petroleum are ***Salt, Clay and Sand etc.***

- **Resins:** Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Molecular weights vary between 500 – 1500. Also contain sulphur, nitrogen, oxygen , vanadium and nickel.
- **Asphaltenes:** Polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffininc and naphthenic chains.
- **Salts:** Crude oil often contain inorganic salts
 - Sodium chloride
 - Magnesium chloride
 - Calcium chlorideIn suspension or dissolved in entrained water (brine).
- **Carbon dioxide:**
 - From the decomposition of bicarbonates present in or added to crude
 - From steam used in the distillation process

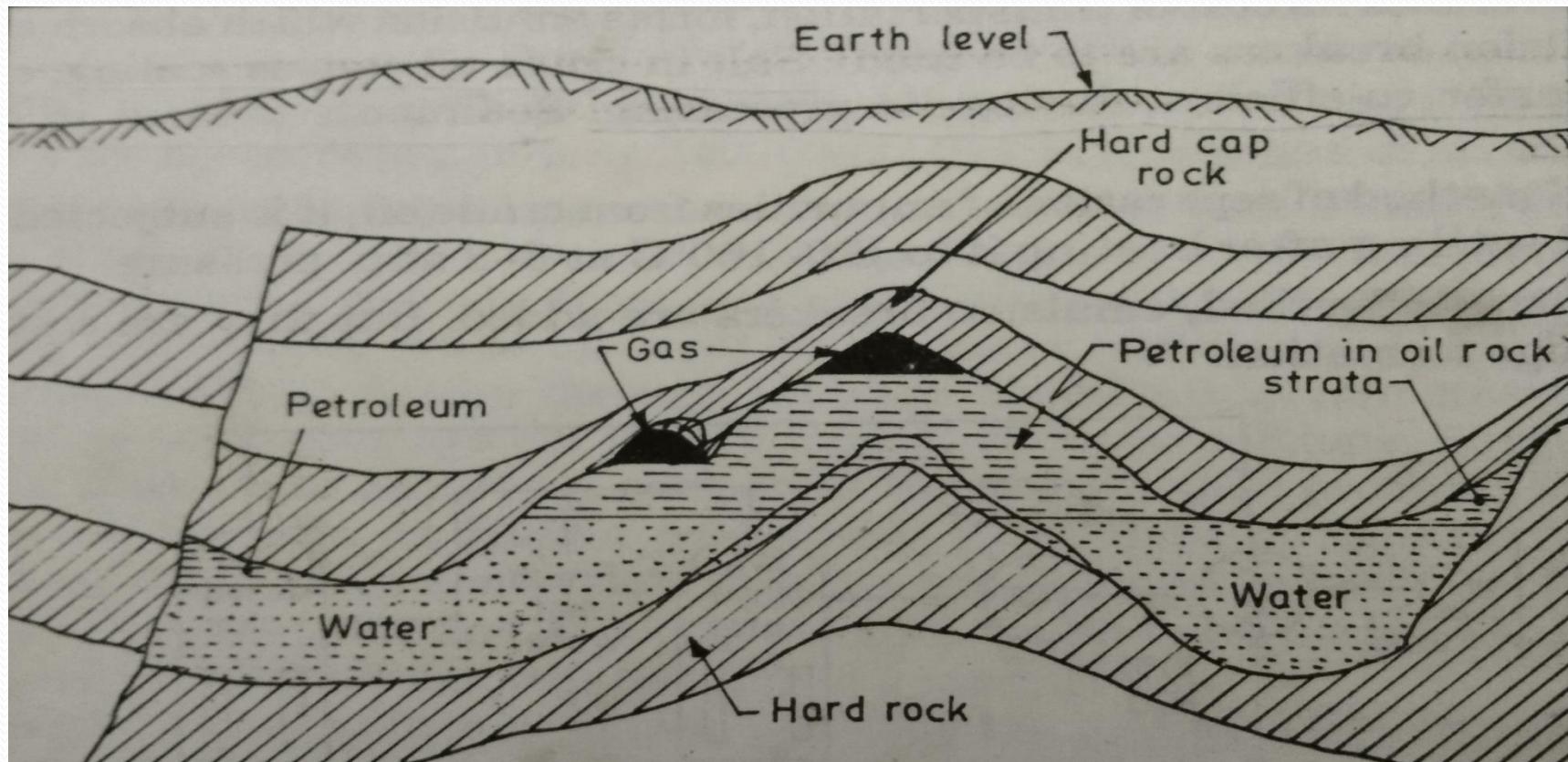
Note: Crude having high quantities of Resins and Asphaltenes(heavy crude) is usually targeted for coke production.

Detection of Petroleum Deposit

- Petroleum deposits are detected by following methods:
 - **Visual method:** It includes oil seepages at the surface of the earth.
 - **Geophysical method:** It includes the measurement of density, elasticity, magnetic and electrical properties of the rock in the crust of the earth from which the inference are drawn whether the petroleum deposit occurs there or not.
 - **Geological method:** It includes the measurement of age and nature of rocks inside the earth's crust which gives an idea of oil deposit.
 - **Drilling method:** Drilling in the crust of earth is the final test when the petroleum deposits have been proved by either of the earlier methods.

Production of Petroleum

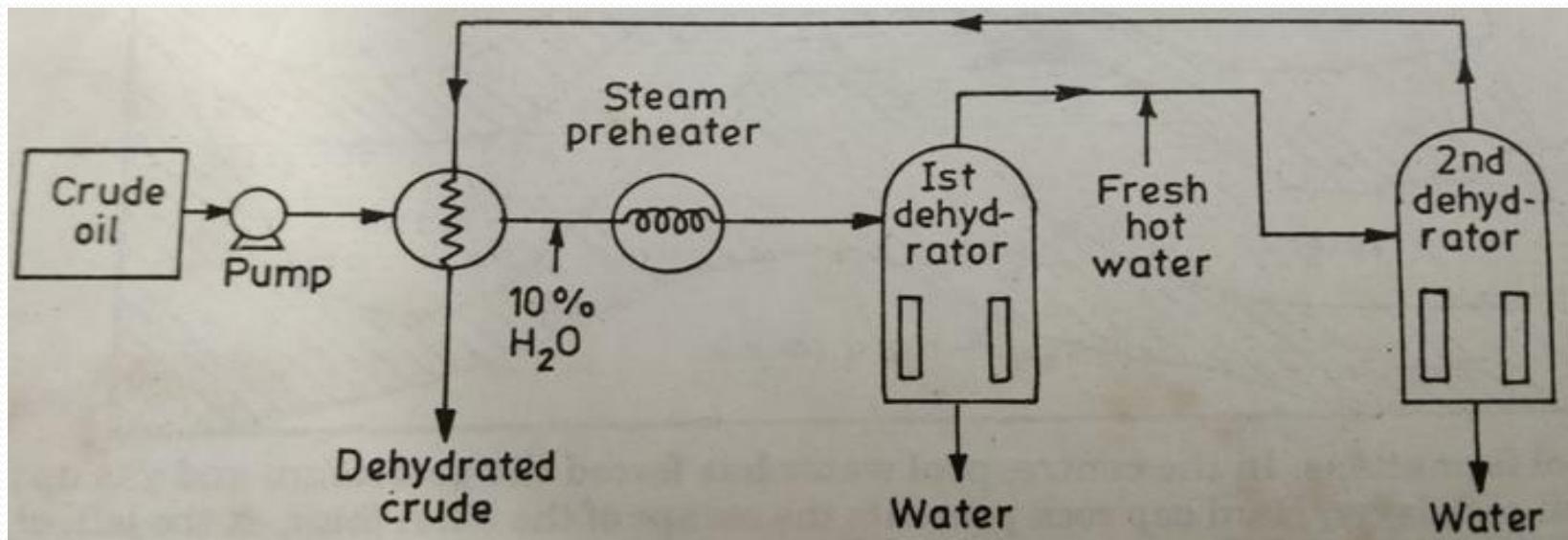
- Petroleum almost always occurs along with gas called **Natural gas**.
- After drilling in the crust of earth both **Natural gas and Oil** flow up through pipe under pressure initially.
- When the oil well contains both Oil and Gas it is called **Wet well** and if it contains only gas then it is called a **Dry well**.



Pre-treatment of crude oil at oil field before refining

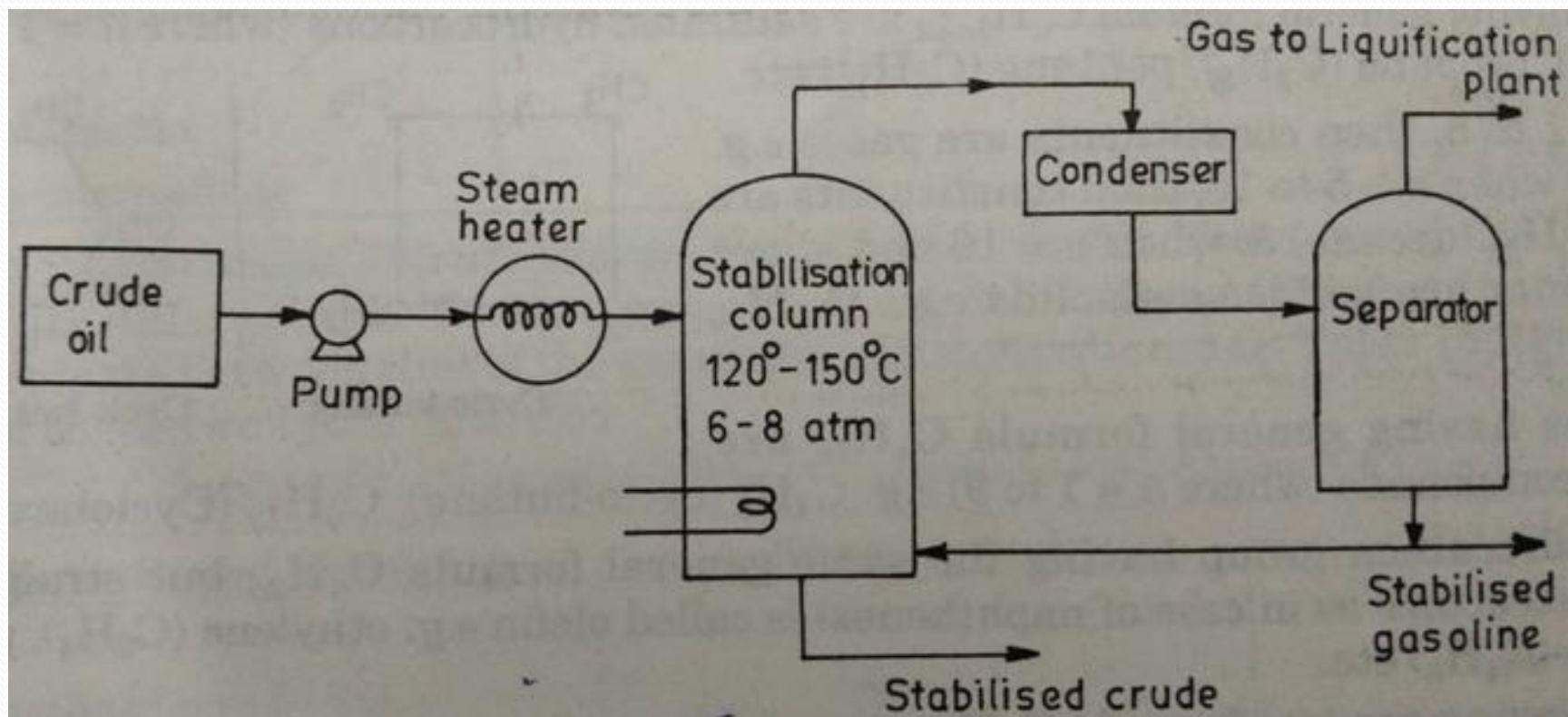
- Crude oil as it comes out of well may contain:
Water = upto 25%.
Salts (MgCl₂, CaCl₂, NaCl etc.) = upto 2000-5000 mg/litre
Sediments = upto 1-1.5%.
- For refining crude oil, the salt content in it should be <50 mg/lit and water <0.3%.
- **Excessive water** in crude require extra heat for its distillation, increase its cost of transportation, forms emulsion which absorb materials like resin.
- **Salt** in crude oil causes scaling, corrosion and reduces heat transfer coefficient during its processing.
- **Sediments** present in crude causes erosion and scaling.

1. **Mechanical method:** It is subjected to centrifuging, filtration and settling after heating it to 120-160 °C at 6-8 atm. pressure.
2. **Physico-chemical method:** Emulsion breaker are added and this is costly and cause corrosion and sludge formation.
3. **Electrical dehydration method:** 10% water is added to crude and it is heated before passing it through an electrical dehydrator which has two concentric metal plates as electrodes in which 30000 volts is supplied thereby separating water from crude.



Stabilisation of Crude Oil

- Removal of dissolved gases from crude oil by heating is called its ***Stabilisation***.
- Gas accompanied with crude oil must be removed to avoid breathing loss (loss of gasoline, if gas is not removed from oil during pre-refining).
- Breathing loss is about 0.4 – 0.75 kg/m³ of tank per month.



Classification of Petroleum

□ Depending on the Nature of hydrocarbons present:

- Paraffinic crude petroleum oil.
 - Naphthenic crude petroleum oil.
 - Asphaltic (aromatic) crude oil.
 - Mixed crude oil containing all paraffinic, naphthenic, and aromatic constituents.
- **Paraffinic crude petroleum oil :** Paraffins having general formula C_nH_{2n+2} are saturated hydrocarbons (where n = 1 to 35).
Examples: Methane (CH_4), Propane (C_3H_9), Pentane (C_6H_{12}) etc.

(n)	Physical state	Example
1-5	Constituents are gases	C_4H_{10} (butane)
5-15	Constituents are liquids	$C_{10}H_{22}$ (decane)
16 above	Constituents are solids/semi-solids	$C_{17}H_{36}$ (wax)

➤ **Naphthenic crude petroleum oil:** having general formula C_nH_{2n} are saturated ring compounds (where n = 1 to 9).

Examples: C_4H_8 (cyclo-butane), C_6H_{12} (Cyclohexane) etc.

Note: Another hydrocarbon group having the same general formula C_nH_{2n} but straight chain (instead of ring structure as in case of naphthenes) is called olefin e.g. ethylene (CH_4), propylene (C_2H) butylene (CAH) etc.

➤ **Asphaltic (aromatic) crude oil:** Aromatics having general formula C_nH_{2n-6} ($n \geq 6$) contain 6 carbon atoms in the form of a hexagon shaped ring and are unsaturated ring compounds.

Examples: Benzene (C_6H_6), Toluene ($C_6H_5-CH_3$), Naphthalene ($C_{10}H_8$), Anthracene ($C_{14}H_{10}$).

➤ **Mixed crude oil :** Indian crudes are mostly mixed crude oil. Naharkatia (Assam) crude contains 40% paraffins, 25% naphthenes and 35% aromatics.

□ Lane and Garton classification: On the basis of **Boiling range** ;

Key Fraction 1: 250-275 °C at 1 atmosphere pressure .

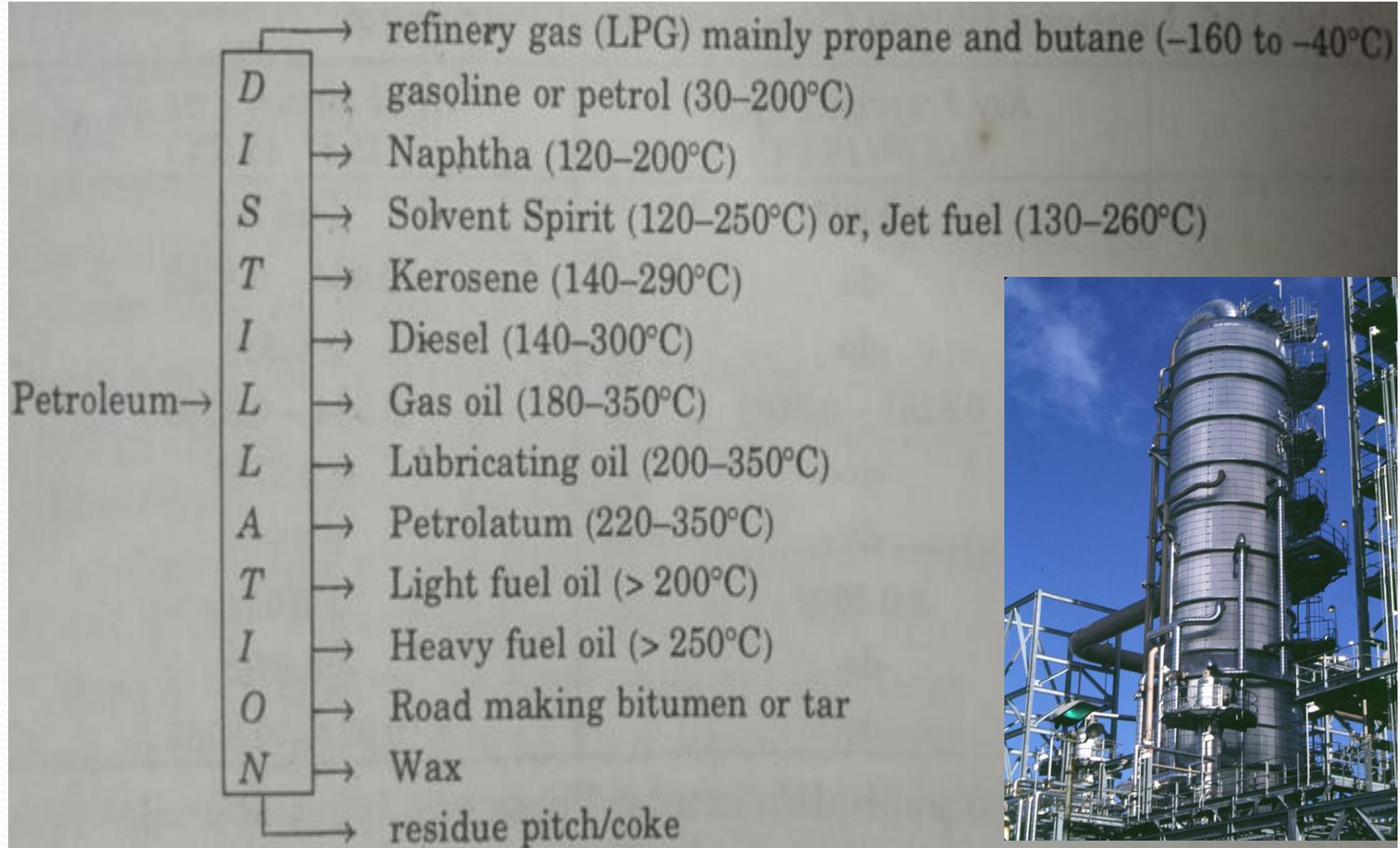
Key Fraction 2: 275-300 °C at a pressure of 40 mm of mercury.

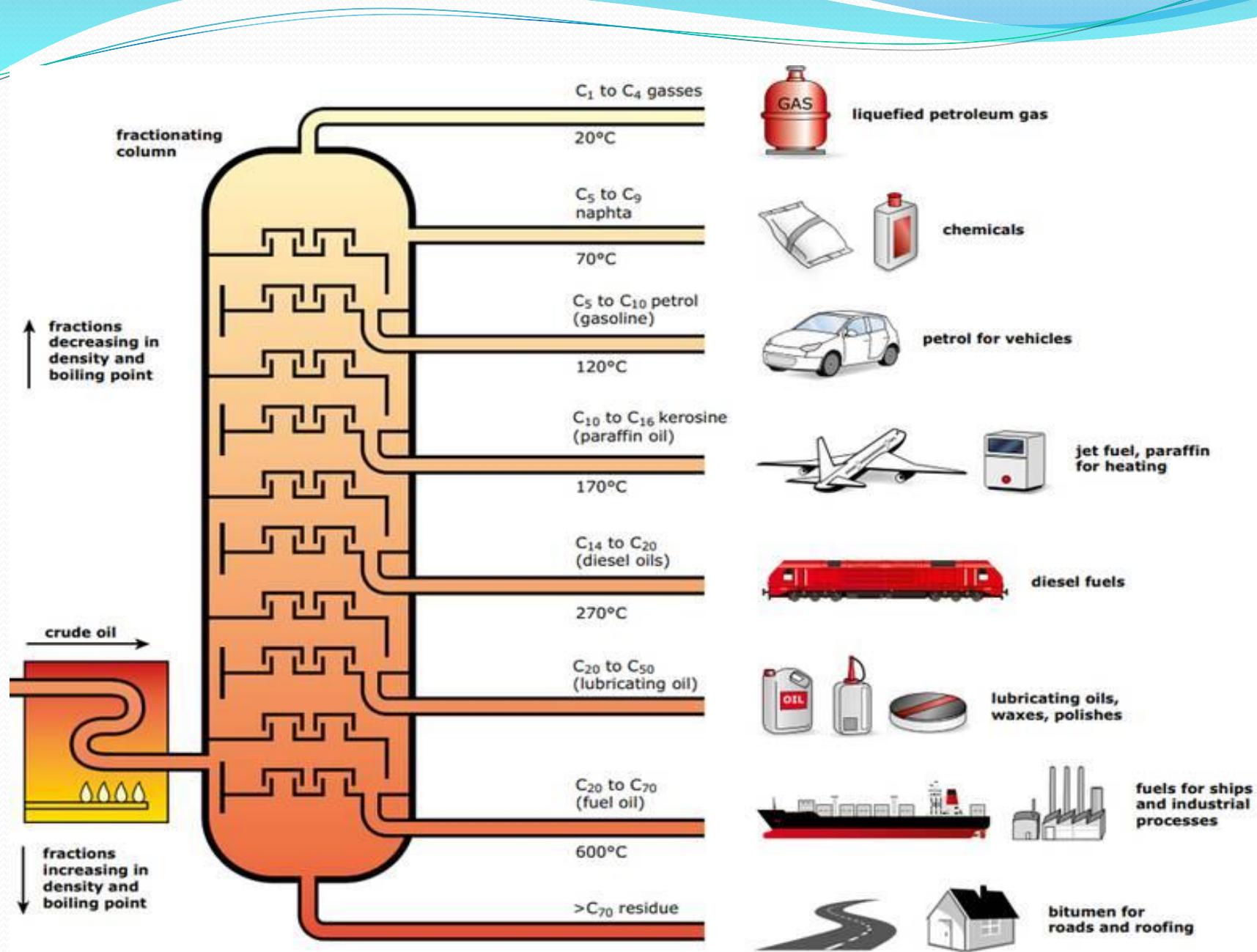
<i>Class</i>	<i>Key Fraction 1 Sp.gr. (15.5° / 15.5°C)</i>	<i>Key Fraction 2 Sp.gr. (15.5° / 15.5°C)</i>
Paraffin	≤ 0.8251	≤ 0.8762
Paraffin-intermediate	-do-	0.934 – 0.8762
Paraffin-naphthene	-do-	≥ 0.934
Intermediate	0.8251 – 0.8602	0.934 – 0.8762
Intermediate-paraffin	-do-	≤ 0.8762
Intermediate-naphthene	-do-	≥ 0.934
Naphthene	≥ 0.8602	≥ 0.934
Naphthene-paraffin	-do-	≤ 0.8762
Naphthene-intermediate	-do-	0.934 – 0.8762

➤ Characteristics of Paraffinic and Asphaltic crude:

<i>Properties and yields</i>	<i>Paraffinic crude</i>	<i>Asphaltic crude</i>
Density	low	high
Yield of gasoline (petrol)	high	low
Octane No. (quality) of petrol	low	high
Sulphur content	low	high
Hydrogen/carbon ratio	high	low
Smoke point (quality) of Kerosene	high (better)	low
Cetane No. (quality) of diesel	high	low
Freezing point of fuel oil	high	low (better)
Yield of lubricants	high	low
Viscosity index of lubricating oil	high (better)	low
Yield of wax	high	low
Yield of bitumen/asphalt	low	high
Odour	sweet	pungent
Colour	light	dark

Refining of Petroleum





□ Resources: Quantities of petroleum naturally occurring on or within the Earth's crust, discovered and undiscovered (recoverable and unrecoverable), plus those quantities already produced.

□ Reserves: RESERVES are those quantities of petroleum expected to be commercially recoverable.

Oil reservoirs are pools of hydrocarbons, located beneath the earth's surface in porous rock structures.

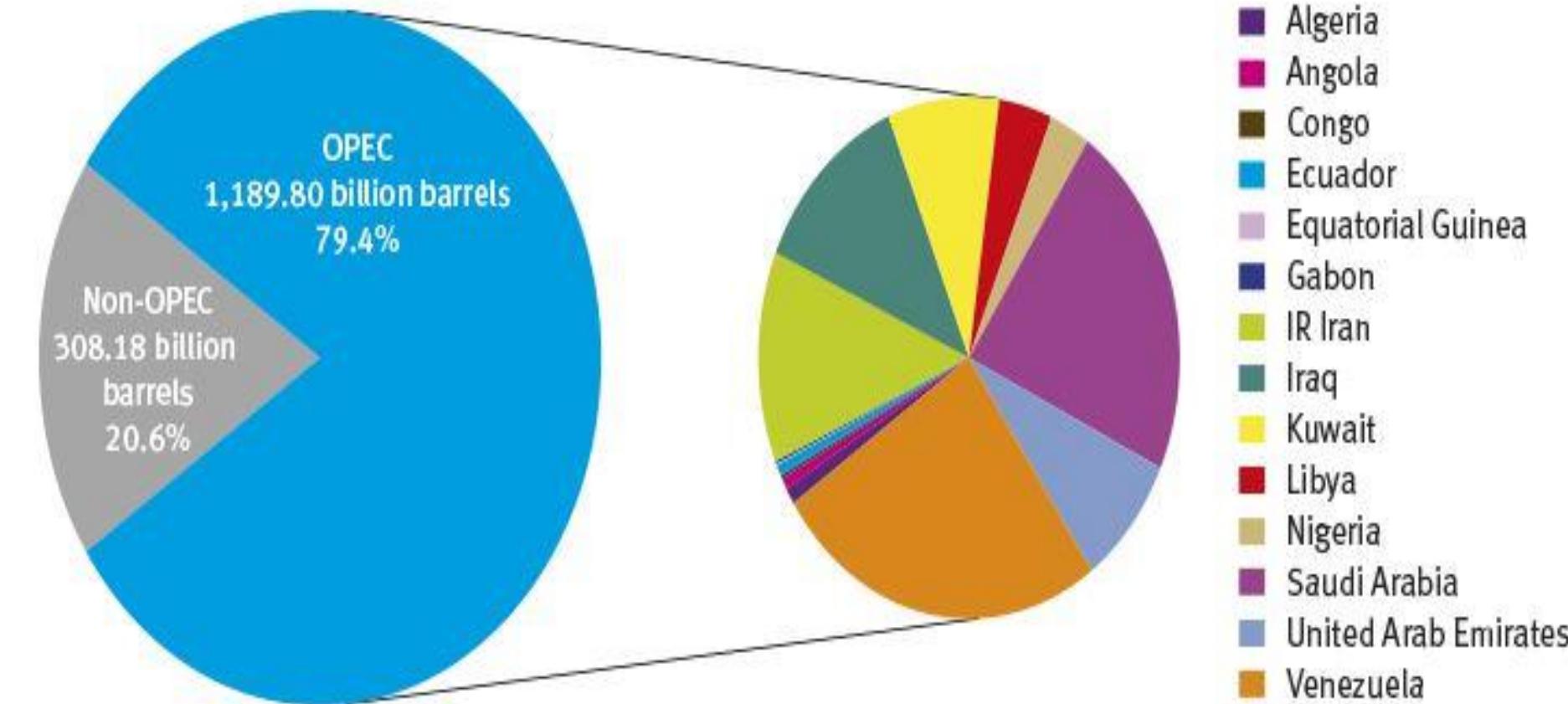
Total estimate of petroleum reservoirs includes the total quantity of oil that can be recovered and that which cannot be recovered.

Fraction of crude oil reservoirs that can be extracted from the oil field is classified as reserves.

Resources vs. Reserves

- Resources
 - Petroleum believed to exist on the basis of geological parameters.
- Reserves
 - Petroleum known to exist and which can be produced economically.

OPEC share of world crude oil reserves, 2018



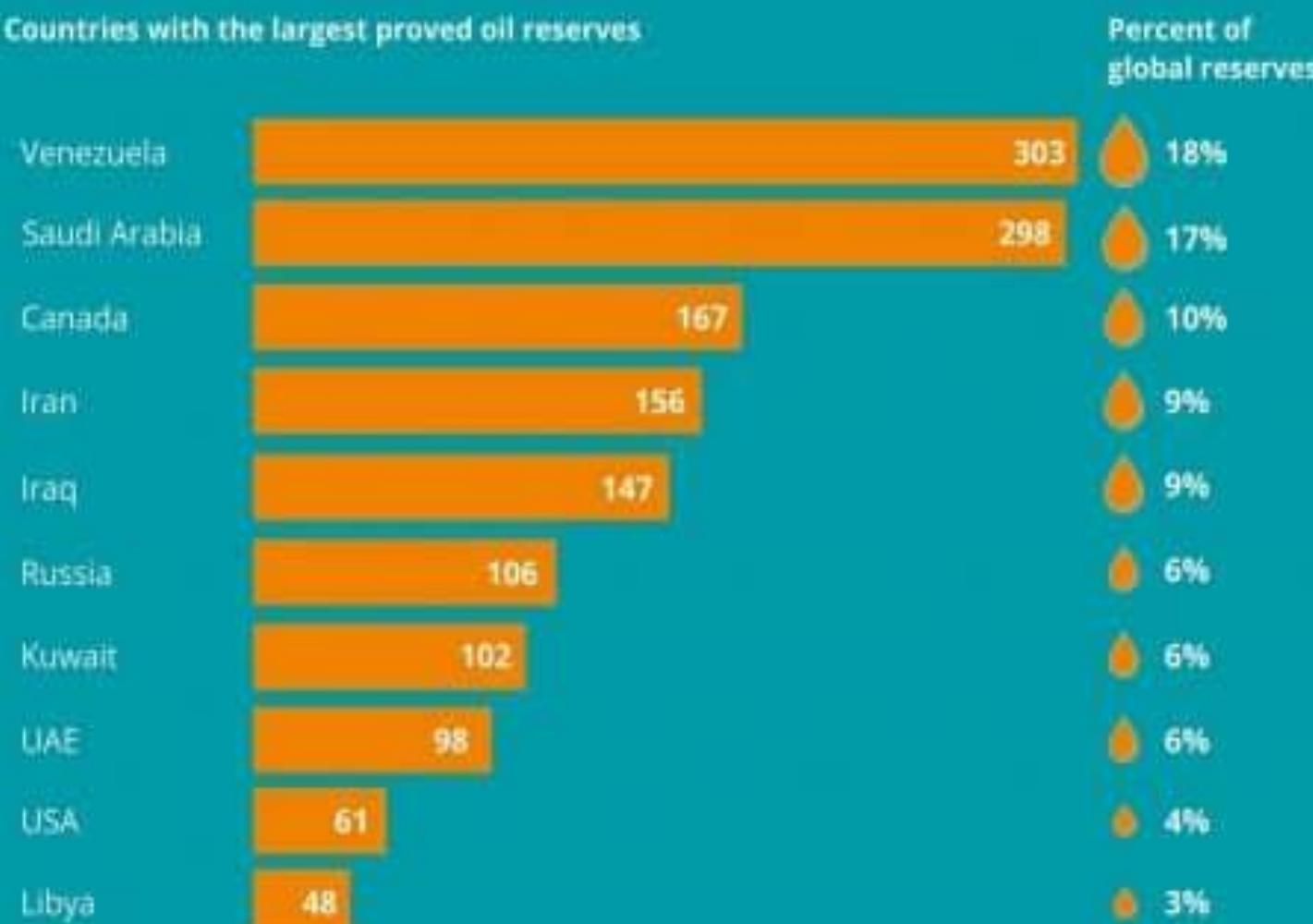
OPEC proven crude oil reserves, at end 2018 (billion barrels, OPEC share)

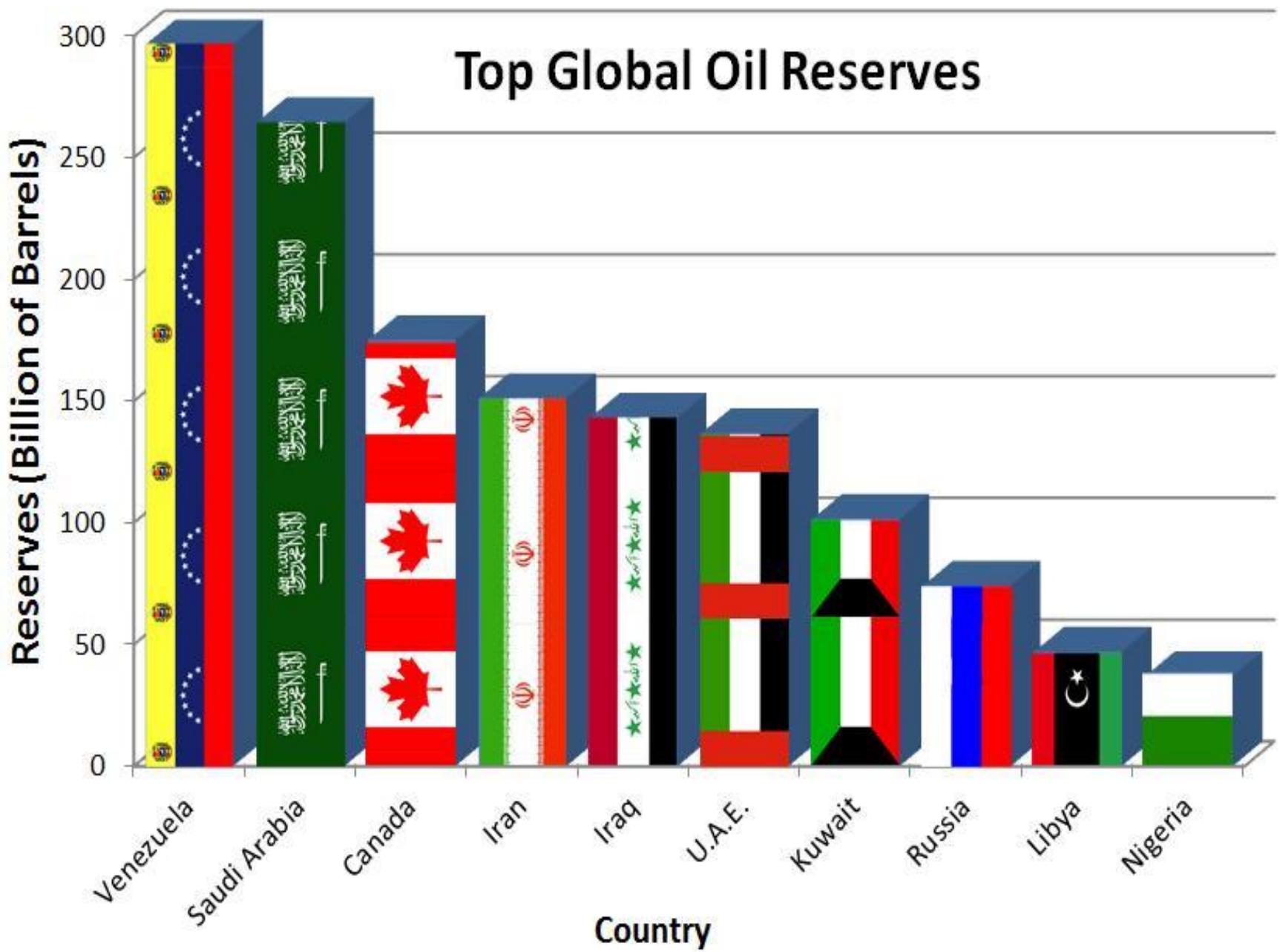
Venezuela	302.81	25.5%	Kuwait	101.50	8.5%	Algeria	12.20	1.0%	Gabon	2.00	0.2%
Saudi Arabia	267.03	22.4%	UAE	97.80	8.2%	Ecuador	8.27	0.7%	Equatorial Guinea	1.10	0.1%
IR Iran	155.60	13.1%	Libya	48.36	4.1%	Angola	8.16	0.7%			
Iraq	145.02	12.2%	Nigeria	36.97	3.1%	Congo	2.98	0.3%			

Source: OPEC Annual Statistical Bulletin 2019.

The Countries with the Largest Oil Reserves

Countries with the largest proved oil reserves



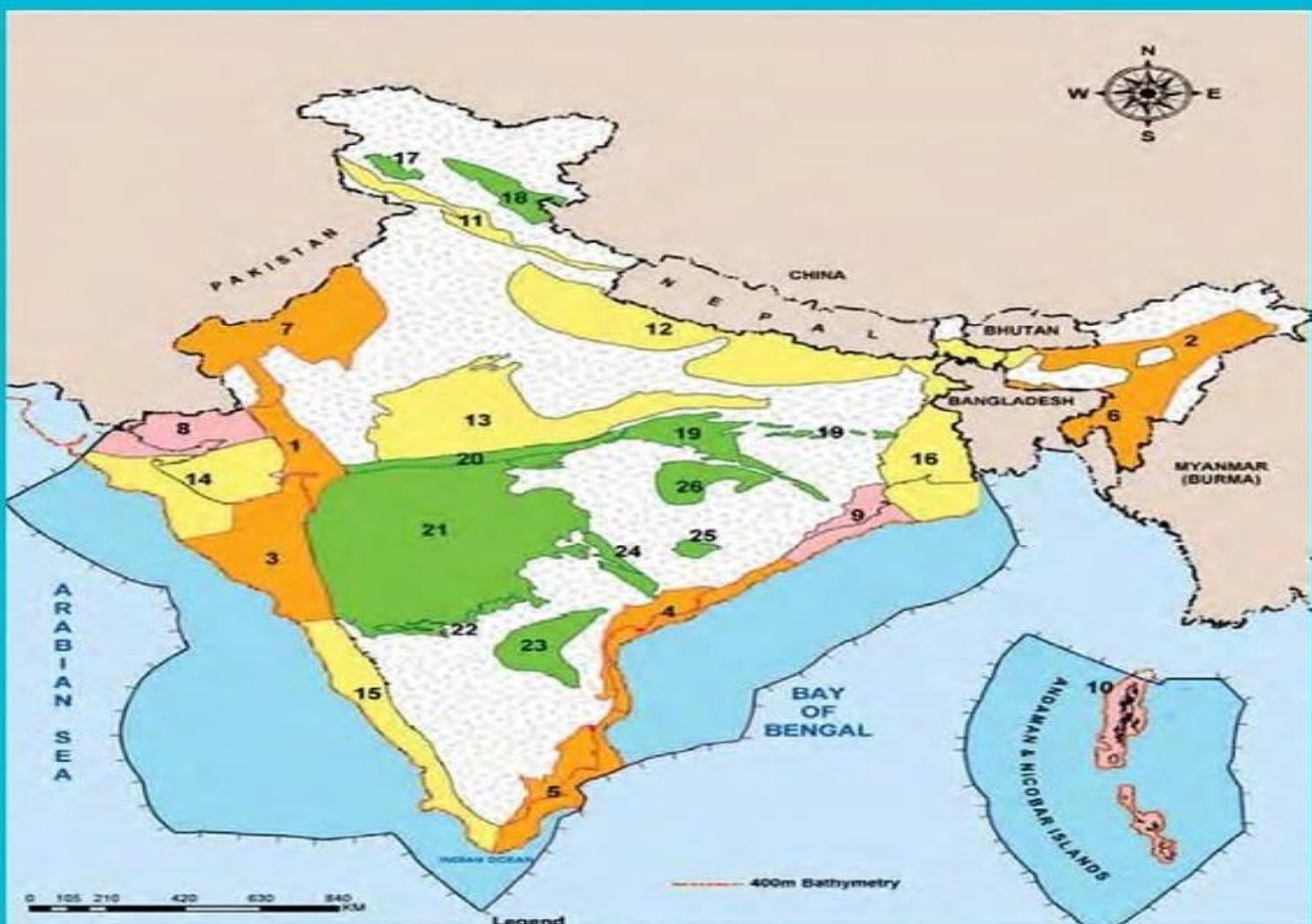


SIGNIFICANCE

- Oil refining is a key activity in the CPI.
- Over 600 refineries worldwide have a total annual capacity of more than 4200×10^6 tonnes.
- India has installed refining capacity of 245 Million Tonnes per Annum (MTPA)
- Goal of oil refining:
 - i. production of fuels for transportation, power generation and heating.
 - ii. production of raw materials for the Petrochemicals.
- Oil refineries are complex plants but are relatively mature and highly integrated.

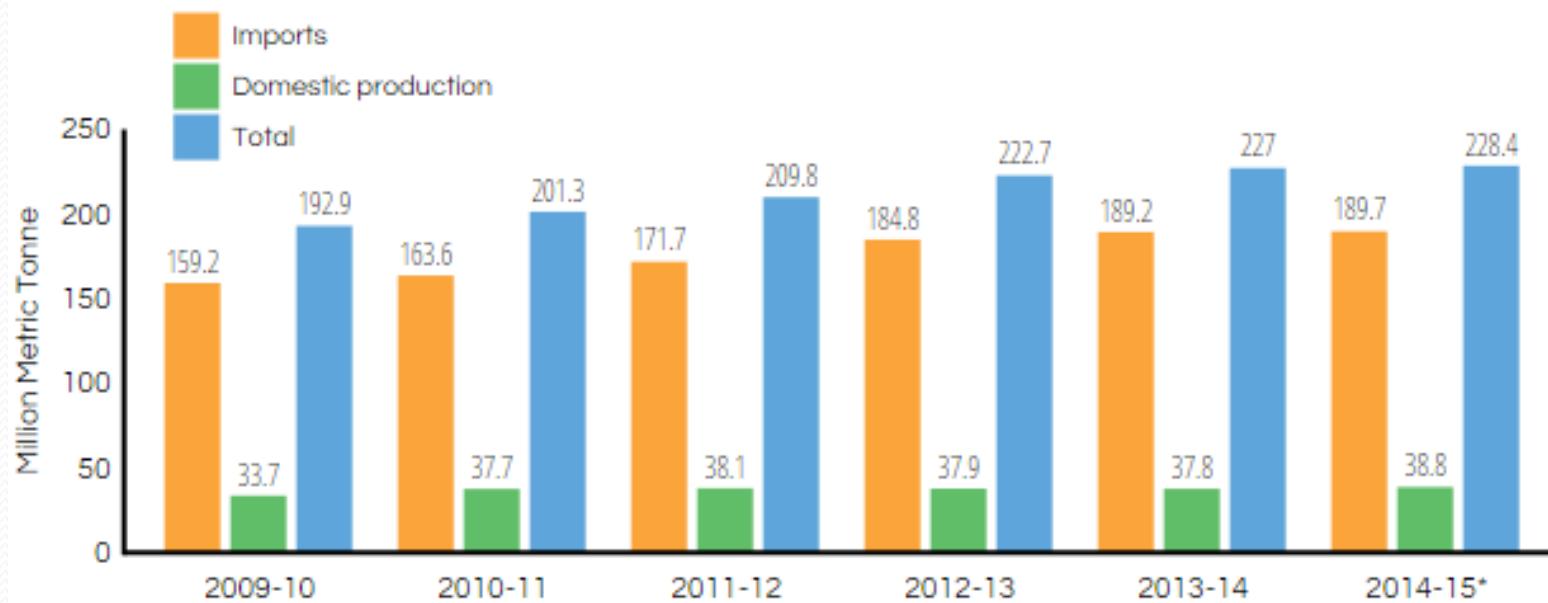
India's oil reserves

- Found in Bombay High off the coast of Maharashtra, Gujarat, Rajasthan and in eastern Assam meet 25% of the country's demand.

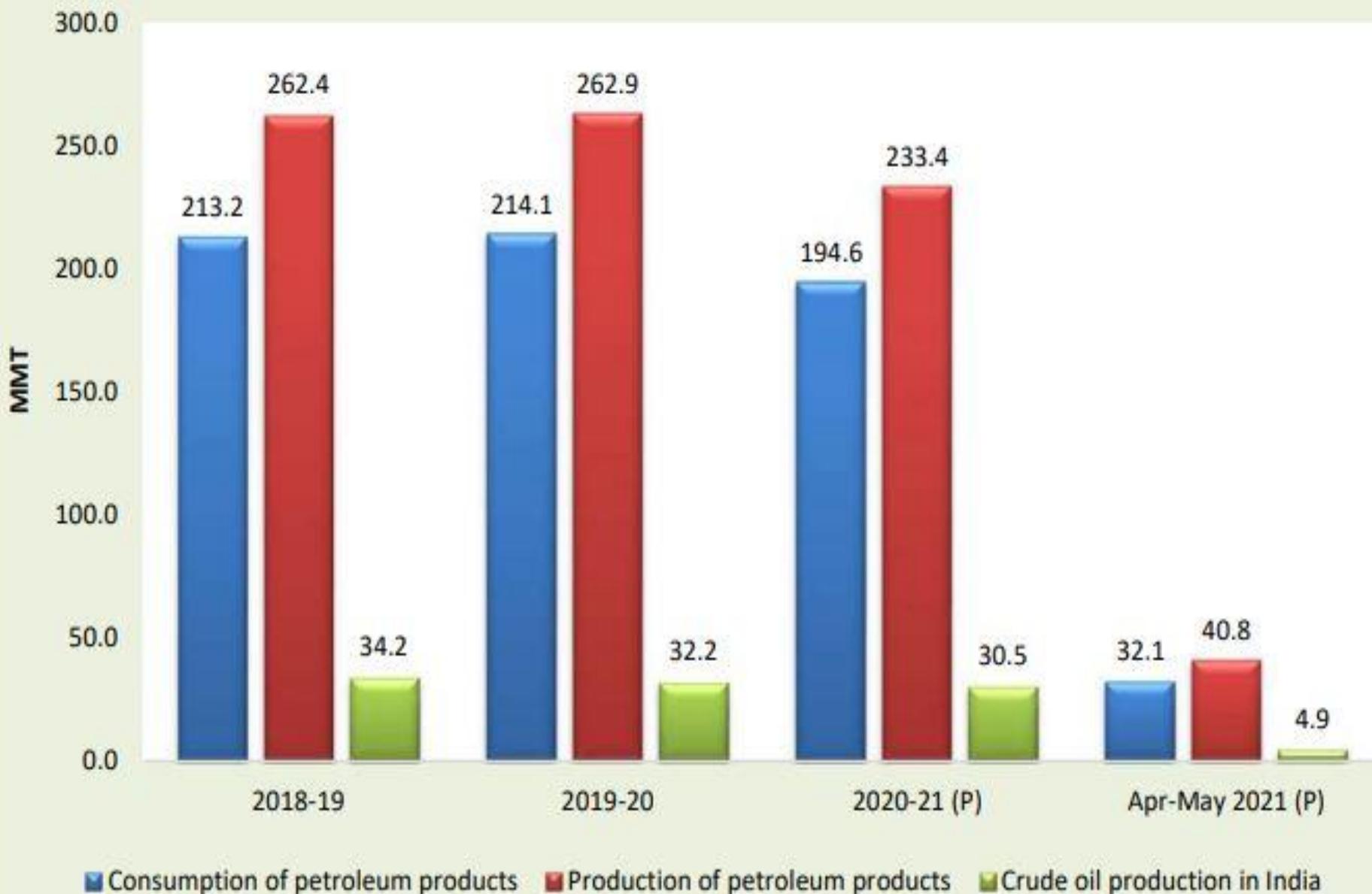


CATEGORY-I (Proven commercial productivity)	CATEGORY-III (Prospective Basins)	DEEP WATER AREAS WITHIN EEZ
CATEGORY-II (Identified prospectivity)	CATEGORY-IV (Potentially Prospective)	PRE-CAMBRIAN BASEMENT / TECTONISED SEDIMENTS
Categories I	Category II	Category III
1. Cambay Basin	8. Kutch Basin	17. Karwa Basin
2. Assam Shelf Basin	9. Mahanadi Basin	18. Spiti-Zanskar Basin
3. Mumbai Offshore Basin	10. Andaman-Nicobar Basin	19. Satpura-South Rewa-Damodar Basin
4. Krishna-Godavari Basin		20. Narmada Basin
5. Cauvery Basin		21. Deccan Synclise Basin
6. Assam-Arakan Fold Belt		22. Bhima-Kaladgi Basin
7. Rajasthan Basin		23. Cuddapah Basin
		24. Pranhita-Godavari Basin
		25. Bastar Basin
		26. Chhattisgarh Basin

India's Oil Imports & Domestic Production, FY 2010 - FY 2015



Crude Oil & Petroleum Products (MMT)



Oil Industry in India

- 1866** - Oil discovery - Nahorpung, Assam
- 1893** - Oil discovery – Digboi
- 1901** - First Refinery in India
- 1954** - Indian Oil Expedition with the help of Russian Geologist
- 1956** - Formation of ONGC
- 1958** - Discovery Cambay Oil Field

Growth of Indian Petroleum Industry

Year	Growth
1962	First public sector refinery started at Guwahati by Indian Oil Refinery Ltd.
1962	Indian Oil Blending Ltd. (IOBL) was formed for manufacture of lube oil & greases (Joint venture between Indian Oil Company and Mobil Petroleum Corp.).
1964	IRL and Indian Oil Company merged to form Indian Oil Corporation Ltd.
1965	Engineers India Ltd. started.

Growth of Indian Petroleum

Year	Growth
1967-77	Discovery of oil and gas at Dabka, Santhal and Balol in , Amguri, Charali; and Borholla in , and Baramura in Tripura.
1977-87	Discovery of oil in large quantity at Bombay High.
1974	IOBL became part of IOCL.
1977-87	Discoveries of oil & gas in the offshore area (Panna field, Bassein field Mumbai offshore, Heera, Ratna, South and Mid Tapi). Oil and gas reserves discovered at Gandhar and Dahej (Cambay basin).
1981	Oil & Gas found in Krishna-Godavari-Cauvery basin.
1995	Oil was found in Cachar () and Nagaland.

Growth of Indian Petroleum

Year	Growth
1998	Assam Oil Co. vested in IOCL as Assam Oil Division.
1999	First joint sector refinery MRPL commissioned.
2000	Panipat Refinery of Indian Oil Corporation commissioned. Reliance Petroleum Refinery commissioned at , Numaligarh refinery in commissioned.
2006	Indian oil first linear alkyl benzene plant commissioned at IOC Vadodara
2006	Indian oil first terephthalic acid plant commissioned at IOC Panipat refinery

Growth of Indian Petroleum

Year	Growth
2006	ONGC entered in Petroleum & refinery sector by acquiring MRPL
2008	HPCL Bhatida refinery
2009	BPCL Bina refinery commissioned
2009	ONGC to start mega petrochemical complex at Dahej Gujrat to be commissioned in 2012
2009	HPCL Mittal energy to set up Petrochemical hub to produce 400tpd polypropylene at
2009-10	IOC Panipat Refinery commissioned Naphtha cracker, polyethylene and poly propylene plnt



Map of Refineries in India

Capacity (in MMTPA) as on 01.11.2018



S. No.	NAME OF THE OIL COMPANY	STATE	LOCATION OF REFINERY	CAPACITY (MMTPA)
1	 INDIAN OIL CORPORATION LIMITED (IOCL)	BIHAR	BARAUNI	6.0
2		GUJARAT	KOYALI	13.7
3		WEST BENGAL	HALDIA	7.5
4		UTTAR PRADESH	MATHURA	8.0
5		HARYANA	PANIPAT	15.0
6		ASSAM	GUWAHATI	1.0
7		ASSAM	DIGBOI	0.7
8		ASSAM	BONGAIGAON	2.4
9		ODISHA	PARADIP	15.0
		IOCL TOTAL		60.2
10	 HINDUSTAN PETROLEUM CORPORATION LIMITED (HPCL)	MAHARASHTRA	MUMBAI	7.5
11		ANDHRA PRADESH	VISAKH	8.3
12	 HPCL-HINDUSTAN MITAL ENERGY LIMITED (HMEL) (JV)	PUNJAB	BATHINDA	11.3
		HPCL-TOTAL		27.1
13	 BHARAT PETROLEUM CORPORATION LIMITED (BPCL)	MAHARASHTRA	MUMBAI	12.0
14		KERALA	KOCHI	15.5
15	 BPCL-BHARAT OMAN REFINERIES LIMITED (BORL) (JV)	MADHYA PRADESH	BINA	7.8
		BPCL-TOTAL		35.3
16	 CHENNAI PETROLEUM CORPORATION LIMITED (CPCL)	TAMIL NADU	MANALI	10.5
17		TAMIL NADU	CALVERY BASIN	1.0
		CPCL-TOTAL		11.5
18	 NUMALIGARH REFINERIES LIMITED (NRL)	ASSAM	NUMALIGARH	3.0
19	 OIL & NATURAL GAS CORPORATION LIMITED (ONGC)	ANDHRA PRADESH	TATIPAKA	0.1
20	 ONGC-MANGALORE REFINERIES & PETROCHEMICALS LIMITED (MRPL)	KARNATAKA	MANGALORE	15.0
		ONGC TOTAL		15.1
		PSU/JV Total		181.2
21	 RELIANCE INDUSTRIES LIMITED (RIL)	GUJARAT	JAMNAGAR (DTA)	33.0
22		GUJARAT	JAMNAGAR (SEZ)	35.2
23	 NAYARA ENERGY LIMITED (NEL)	GUJARAT	VADINAR	20.0
		PVT Total		88.2
		ALL INDIA		240.4

PSU: PUBLIC SECTOR UNDERTAKING

JV: JOINT VENTURE (JV)

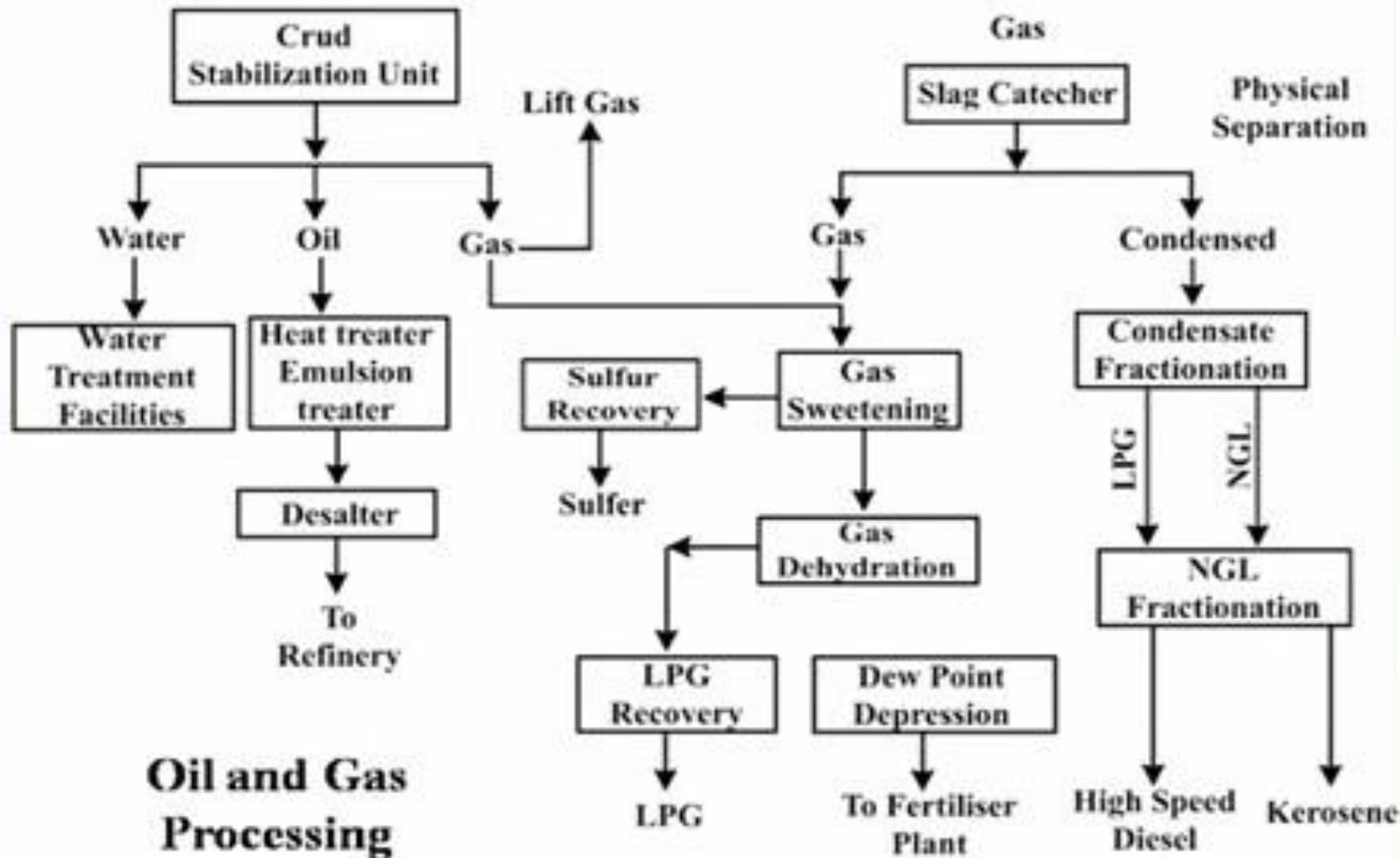
PVT: PRIVATE

SEZ: SPECIAL ECONOMIC ZONE

DTA: DOMESTIC TARIFF AREA

MMTPA: Million Metric Tonne Per Annum

Crud oil



Imported Crude Sources

Middle East	Gulf – Kuwait, Dubai, Arabian, Iraq, Abu Dhabi; Neutral Zone-between Iraq & Kuwait : Ratawai ; Egypt - Gulf of Suez
Mediterranean	Libya - Es Sider
West Africa	Nigeria-Bonny Lt, Escravos, Forcados, Penington, Quioiboe ; Angola, -Cabinda, Palanca, Girassol ; Eq. Guinea-Ceiba, Zaffiro ; Congo-Nikossa, Kitina
Far East	Malaysian, -Labuan, Miri Light; Australia-Barrow Island, Cooper Basin; Brunei-Seria Light

Crude Oil Quality:

- **Light Crude**: API gravity higher than 30 degrees
- **Medium Crude**: API gravity between 20 and 30 degrees.
- **Heavy Crude**: API gravity below 20 degrees.

$$API = \frac{141.5}{Sp.gr.} - 131.5$$

or

$$Sp.gr. = \frac{141.5}{API. + 131.5}$$

Characteristics of Some Indian basin Crude Oil

Basin	°API	Sulphur	Pour Point	Distillate Yield	Salient Features
Assam Crude Nahorkatia/ Moran	30	0.3%	+30 °C	65%	High Aromatics
ONGC, Lawkwa, Rudrasagar	27	0.3%	-	57%	High Aromatics
Ankleshwar Crude	48	0.1%	+18 °C	80-82% LD-24%; MD-47%	

LD-Light Distillate; MD-Middle Distillate; NA-Not Available;

Source: Mishra & Unnikrishnan, 1996, p.22

Changing Gasoline Specification

Specification	BIS	BIS-	Euro-III Eqv.		Euro-IV Eqv.	
	2000	II	Regu- lar	Prem- ium	Regu- lar	Prem- ium
Sulphur, ppmw (max)	1000	500	150	150	50	50
RON,Min	88	88	91	95	91	95
MON,Min	No spec.	No spec.	81	85	81	85
AKI,Min	84	84	81	85		
Benzene vol%(max)	5	3	1	1	1	1
Aromatics vol%(max)	No spec.	No spec.	42	42	42	35
Olefins vol%(max)	No spec.	No spec.	21	18	21	81

Fuels norms For High Speed Diesel

Specification	BIS2000	BS-II	Euro-III Equ.	Euro III Equiv.
Density@15°C Kg/m ³	820-860	820-860	820-845	820-845
Sulphur content ppmw(max)	2500	500	350	50
Cetane number(min)	48	48	51	51
Distillation 99% Vol (°C max)	370	370	360	360
Polycyclic aromatics hydrocarbons (PAH),% massmax	No spec.	No spec	11	11
Specification	BIS2000	BS-II	Euro-III Equ.	Euro III Equiv.

Source : Rajgopal,S " Refining challenges and Trends.6th summer School on " Petroleum refining and petrochemicals" June 6,2012, Organised by New Delhi.



Thank You