

An overview of Indian Petroleum Refining Industry



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What is Crude Oil ?

Crude oil, also known as black gold, is a thick, dark brown or greenish flammable liquid, which is found in the upper strata of some regions of the Earth's crust.

It is a complex mixture of various hydrocarbons, along with traces of other non-hydrocarbons and metals in traces.

When extracted from underground, it ranges in density from **very light to very heavy and in color, from yellow to black**

Crude oil can be categorized as either "**sweet crude**" (where the sulphur content less than 0.5 wt. %) or "**sour crude**," (where the sulphur content is more than 0.5 wt.%).

“The foundation of modern society”

“The lifeblood of modern civilization”

“The Prize”

20th and 21st century = “The Oil Century”

Petroleum is a non-renewable resource that took millions of years to form.

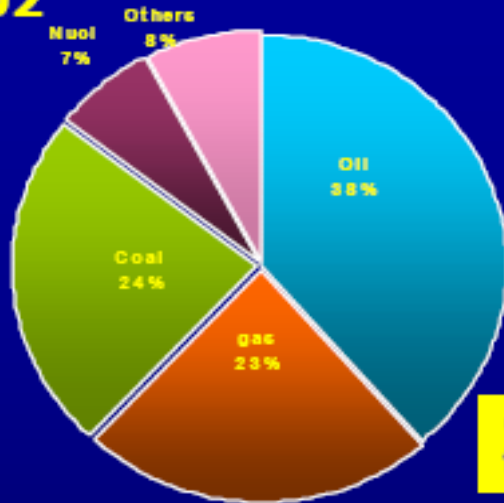
Our use of it has been unsustainable.

The inescapable fact: Modern developed societies depend on petroleum in innumerable ways. **We are a petroleum-dependent society.**

“No civilization can survive the destruction of its resource base.” Bruce Sterling

ENERGY SCENARIO

2002



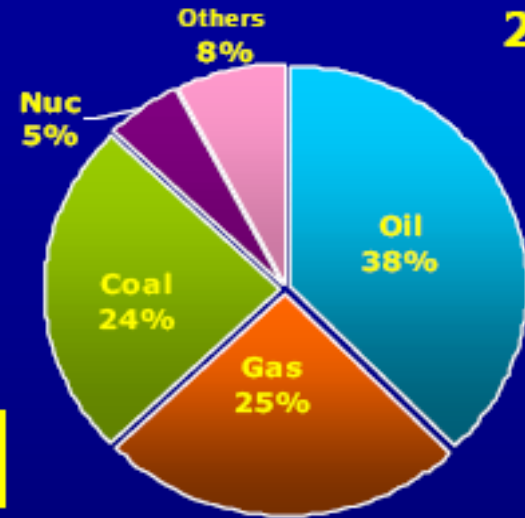
World



Oil & Gas continue to play major role

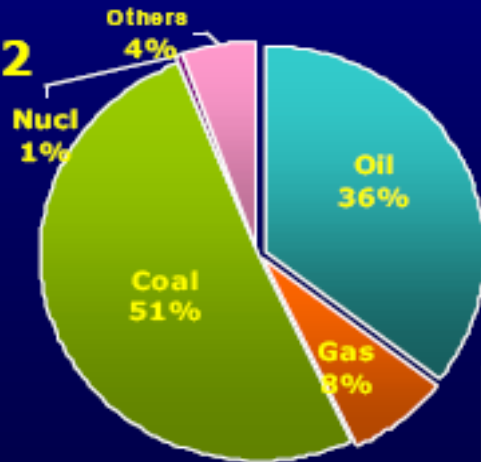
(10275 MTOE)

2025



(16115 MTOE) 2% Growth

2002



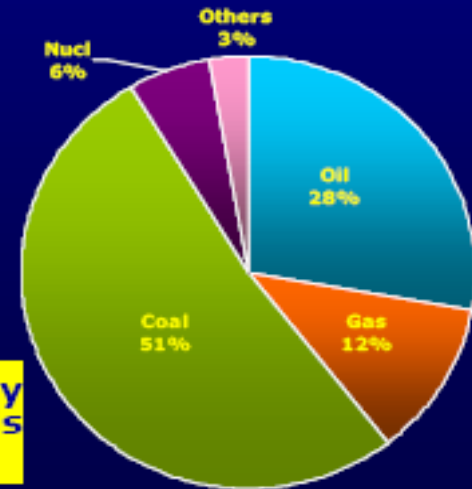
India



Coal & Oil continue to play major role, and Gas is emerging

(309 MTOE)

2025



(1168 MTOE) 5.95% Growth

India's position on world's petroleum map

5th largest energy consumer in the world

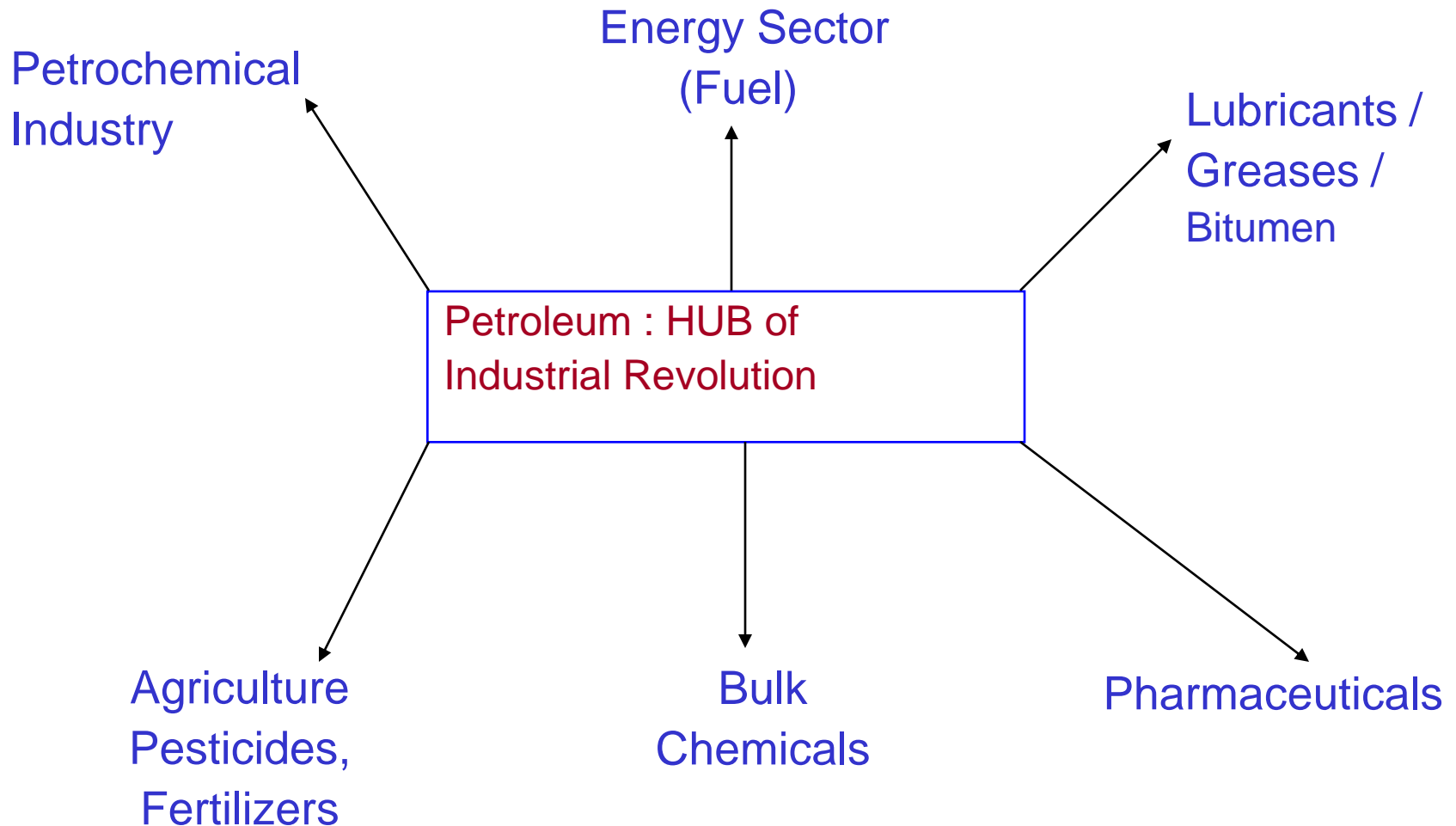
4th largest crude oil consumer

9th largest crude oil importer

6th in refining capacity

Out of 6 Indian companies figuring in Fortune Global 500 list, 5 are from petroleum sector

Petroleum – Precious natural source of energy & mother of industrial revolution world wide



History of Petroleum:

- Mankind has known crude oil or petroleum for more than 6000 years through the **seepages** that occur naturally along the earth's surface.
- The Middle East was the site where some of the earliest civilizations used surface deposits of asphalt formed by the **natural evaporation of crude oil** which oozed out in the form of oil seepage.
- In Sumerian, circa **6000 B.C.**, shipbuilding Industry, used Asphalt
- **Ittu** – by Sumerians - name for bitumen
- Sumerian city of Nimrud (now Mosul in Iraq)

History of oil contd.

- Egyptians used asphalt as a **water proofing material** as early as 2600 B.C. They also found it good for **embalming mummies**.
- Early Mediterranean civilizations used to dig shallow pits around seepages in order to collect oil.
- Used this as mortar to cement bricks & stones in buildings and as caulking compound in **wooden ships including Prophet Noah's ark**.
- The basket, in which the **baby Moses was hidden, made water proof with bitumen**.

➤ Christopher Columbus used bitumen to make his ship seaworthy.

Babylonians, Egyptians & Romans found useful as ointment, water proofing agent, to light lamps.

➤ It is said that when Alexander the great visited Persia, the inhabitants sprinkled the street with oil & set it a light. while passing through Kirkuk in 331 B.C., he was impressed by seeing a continuous flame issuing from the earth, probably a natural gas fire. Such fires were probably the basis of the fire worship prevailed than in the M. East.

➤ **India:** Makum (Assam) in **1867**, On the 26th March, oil was struck at a depth of 118 feet. The gusher rose to 74 feet.

This yielded about 300 gallons (about 1300 lits) & stopped.

➤ In Nov. 1890, the Assam Railway & Trading Co. drilled a well in Digboi. It struck oil, at a depth of 662 feet (220m) with a production of 200 gallons (900lits). This Digboi well No. 1 is the real harbinger of oil in India.

HYDROCARBON VALUE CHAIN



Exploration & Production



Crude Oil



Refining & Blending



QC

Upstream

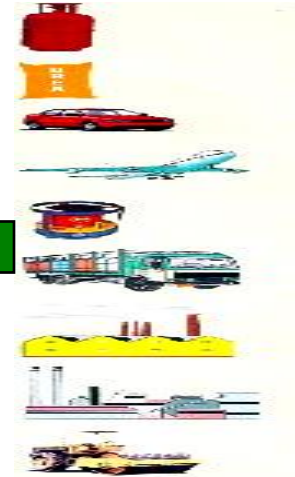
Downstream



Marketing



Transportation



Products

Origin of Petroleum

Theories broadly classified into non-biogenic & biogenic :

- **Non-biogenic : from inorganic sources**

Metal carbides + H₂O.....> Hydrocarbons

**CaCO₃ + alkali metal ---->CaC₂ + H₂O ---->Acetylene---->Petroleum
hydrocarbons**

Reaction of CO₂ with water, in presence of alkali and alkaline earth metals, is also postulated to form hydrocarbons

Theory did not receive much recognition

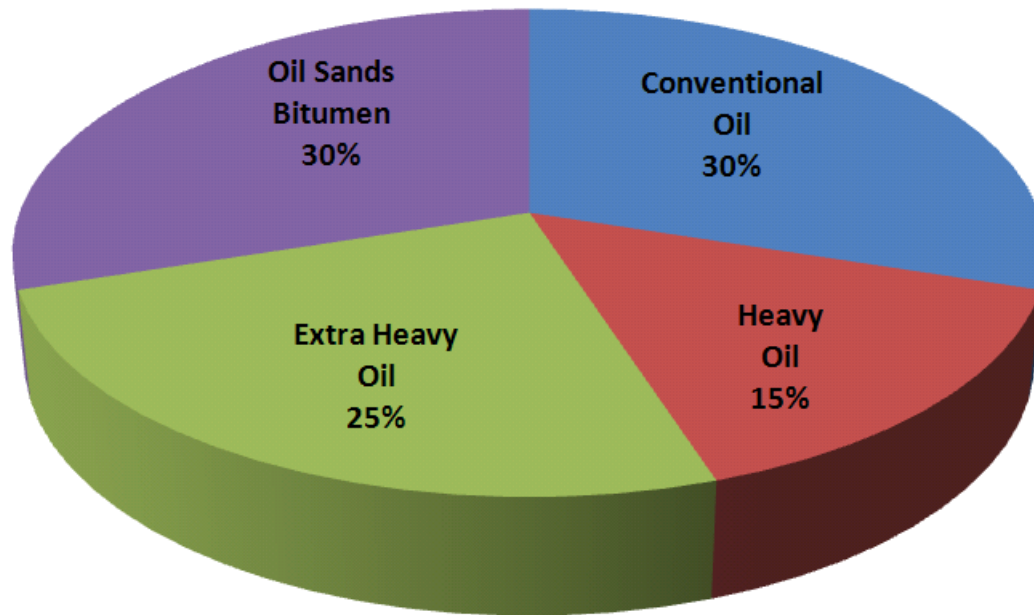
Origin of Petroleum

- **Biogenic : from organics, by bacterial transformation :**
Organic matter (carbohydrates/proteins//lipid/ lignin both from plant & animal origin ----->Decay in presence and/or absence of air into HC rich sediments which in presence of micro organism undergoes biological/physical and chemical alterations to form Kerogen (geopolymer) which may be coaly or sapropelic
Sapropelic Kerogen under high pressure and temperature further gets converted into Oil & Gas.

Widely accepted theory

Structure of Oil Reserves

Total World Oil Reserves



- Total worldwide reserves of crude oil is estimated to be 1028 bn. Barrels.
- Out of this, 814 bn. Barrels belong to OPEC.
- Total M. East share is 683 bn. Barrels.
- S. Arabia has 259.2 bn. Barrels.
- Iraq – 112.5
- Kuwait – 94
- India's share is only 4.7 bn. Barrels.

Total worldwide refining capacity is 81.3m barrels / day.

Total refineries 742 – operate all over the world.

Exxon Mobil – refines 5432×10^3 barrels/day – 34 refineries.

Shell – 3999×10^3 barrels/day – second, operates 39 refineries.

Individual Large refineries

Paraguana refining centre at Falcon, Venezuela having a refining capacity of 94×10^4 barrel / day – SK corp. of South Korea – 81.7×10^4 barrel /day

RIL-- 610×10^3 barrels/day

Annual crude oil consumption

Country	Kg per capita
N. America	3150
Japan	2010
N. Europe	1520
Asia-Australia	240
China	110
India	70

Crude Oil Chemistry

A very complex mixture consisting of paraffins, naphthenes (cyclo paraffins), and aromatic hydrocarbons as well as nitrogen-, oxygen-, sulfur- containing compounds and traces of a variety of metal-containing organic and inorganic compounds.

Hydrocarbons:

- **Saturated alkanes: (n-alkane and i-alkanes)**
 - **General formula C_nH_{2n+2}**
 - **Boiling point and density increase with increasing # of C atoms.**
 - **Branched alkanes (iso-alkanes) in relatively small quantities**
 - **Boiling point of straight chains > iso-alkanes with the same # of C**
- **Naphthenes or Cyclo paraffins (saturated cyclic hydrocarbons)**
 - General formula C_nH_{2n} for one ring compounds**
- **Alkenes or Olefins – unsaturated aliphatic hydrocarbon (i.e. ethylene or propylene)**
 - **Very small amounts in crude oil – produced during refining**
- **Aromatics hydrocarbon (cyclic and polyunsaturated hydrocarbons containing conjugated double bonds) – $C_nH_{2n-6}...$**

Crude Oil Chemistry

- **Alkyl aromatics have very high octane # - content in gasoline is limited by environmental regulations – health effects due to high toxicity.**
- **Di & polyaromatic Hydrocarbons – aromatics containing more than 2 and more aromatic ring**
- **Naphthalene – 2 rings**
- **Anthracene – 3 rings**
- **Pyrene – 4 rings (very toxic)**
- **Hydroaromatics or naphthenoaromatics – partially saturated PAHs**
- **Heteroatom compounds**
- **Nitrogen compounds**
 - **carbazole (2 benzene rings separated by 1 N atom) – neutral**
 - **Quinoline (2 benzene rings with 1 N atom on 1 ring) - basic**

Crude Oil Chemistry

- **Sulfur compounds might be present in inorganic and organic forms. In crude oils sulfur concentration can range from 0.1 to more than 8 weight percent. Such as dibenzylthiophene (2 benzene rings separated by 1 S atom) – is most difficult to release the Sulfur**
- **Oxygen compounds are responsible for petroleum acidity in particular.**
- **Carboxylic (OH-C=O bonded to a benzene ring)**
- **Phenolic (OH bonded to a benzene ring)**
- **Metal Compounds**
 - **Porphyryns contain Ni, V, or Fe**

Crude oil chemistry- sulphur compounds

Sulphur compounds are present primarily in aromatic rings

- **Thiols**
- **Sulphides**
- **Cyclic sulphides**
- **Disulphides**
- **Thiophenes**
- **Benzothiophenes**
- **Dibenzothiophenes**
- **Naphthobenzothiophenes**

Crude Oil Chemistry

- Sulphur Compounds

- **H₂S (CO, SRP, CP)**
- **Aliphatic / mercaptans RSH(CO, SRP,CP)**
- **Aromatic thiols/mercaptans (CP)**
- **Sulphides R-S-R (CO,SRP,CP)**
- **Disulphides R-S-S-R (SRP)**
- **Cyclic : sulphides (SRP,CP) / disulphides (CP)**
- **Thiophenes & homologs: (CP)**
(benzothiophenes, dibenzothiophenes,
naphthobenzothiophenes)

NB CO- crude oil: SRP- straight run product; CP- cracked product

Crude Oil Chemistry

Why sulphur compounds are not desirable in crude/fuels?

- **Great environmental concern, contribution to particulate matter, emission of obnoxious odoring sulphur oxide gases**
- **Reduction of sulphur level in all petroleum products mandated**
- **As a result refining technology focus shifted to sulphur removal from hydrocarbons**

Crude Oil Chemistry
- Oxygen compounds

May be present in different forms such as :

- **Alcohols**
- **Ether**
- **Cyclic ether/furan**
- **carboxylic acids**
- **Naphthenic acids :**

American crude oils : 0.006 to 0.35%wt

Russian crudes oils : 0.2 to 1.05 %wt

North Gujarat crude oil mix : 0.2%wt

Effect: Corrosion

Crude Oil Chemistry

- Nitrogen Compounds

Non-basic

Pyrroles

Indoles

Carbazoles

Benzocarbazoles

Effects:

Nitrogen oxide emissions & Catalysts poison

Basic

Pyridines

Quinolines

Indolines

Benzoquinolines

Crude Oil Chemistry - Metals

- Present as inorganic salts of organic acids and also as metallic Porphyrins (Ni, V, Fe) in ppm
- Salts mostly removed in desalting operation
- Ni & V Porphyrins are catalyst poisons

Crude Oil Composition- ultimate analysis

- **Carbon** **83.0 to 87.0%**
- **Hydrogen** **10.0 to 14.0 %**
- **Sulphur** **0.05 to 6.0 %**
- **Nitrogen** **0.1 to 2.0 %**
- **Oxygen** **0.05 to 1.5 %**
- **Metals** **0.00 to 0.14 %**

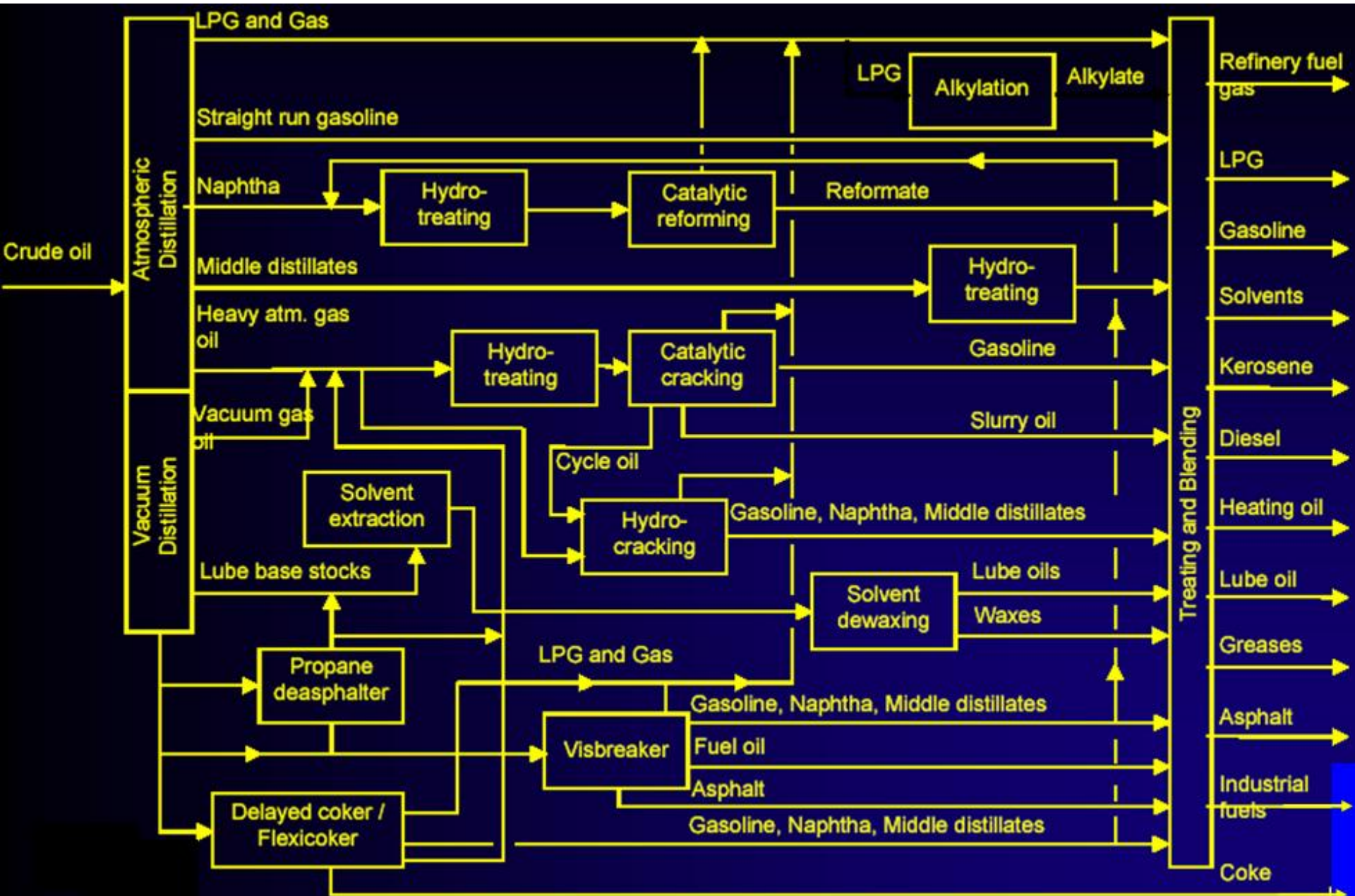
(Fe, Cu, Ni, V, Mg, Al, Cu)

PHYSICAL & CHEMICAL PROCESSES IN A TYPICAL PETROLEUM REFINERY

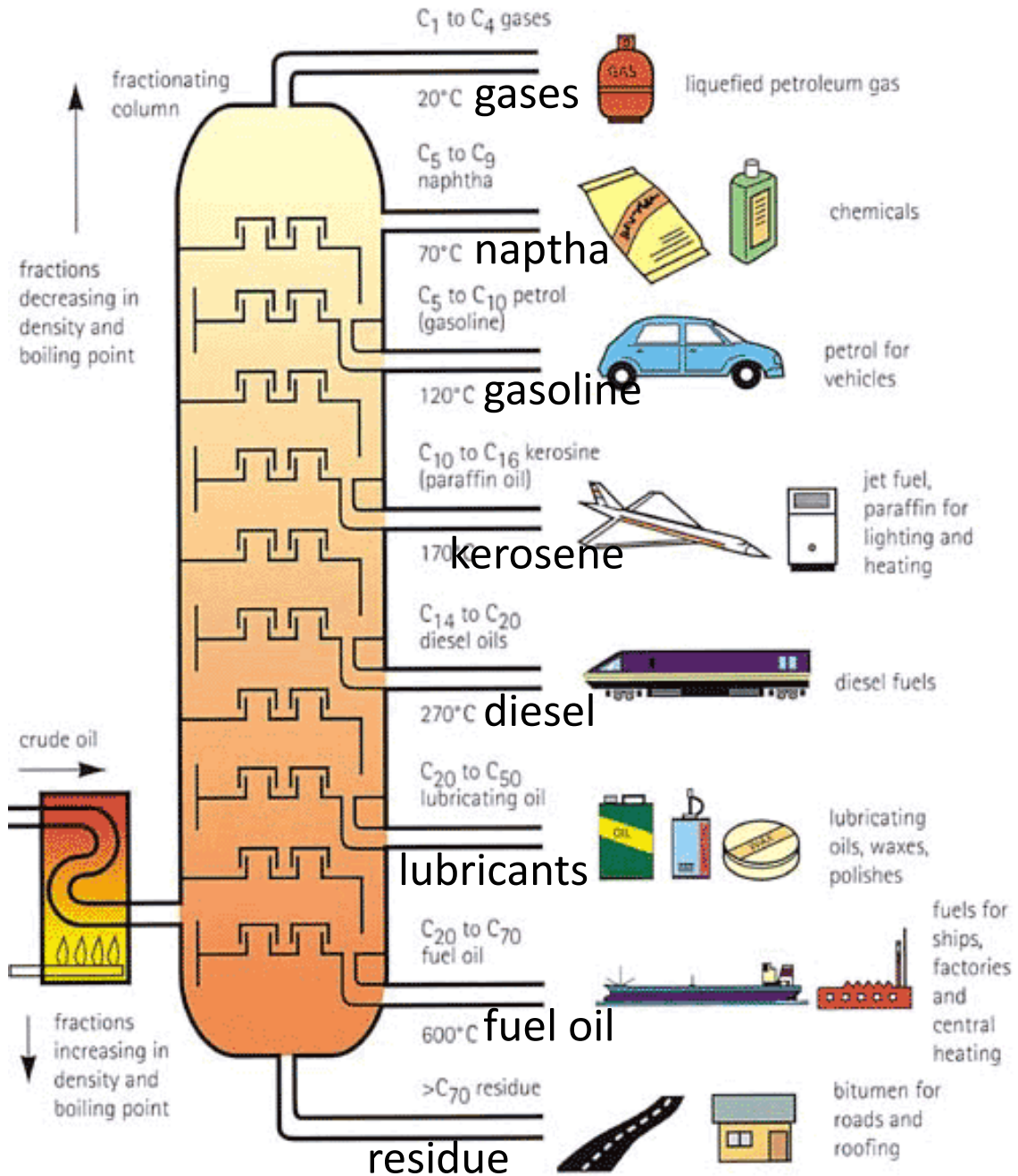
Physical Processes

- **Desalting/Dehydration (Extraction)**
- **Crude Distillation (Atm. & Vac.)**
- **Solvent Extraction**
- **Solvent (Propane) Deasphalting (Extraction)**
- **Solvent Dewaxing (Extraction)**
- **Adsorptive Separation**
- **Membrane Separation**
- **Blending (Mixing)**

Block Flow Diagram of a Modern Petroleum Refinery



Fractional distillation in a refinery



Fractions of Crude Oil & Their Properties

Name	Number of Carbon Atoms	Boiling Point (°C)	Uses
Refinery Gas	3 or 4	below 30	Bottled Gas (propane or butane).
Gasoline	7 to 9	100 to 150	Fuel for car engines.
Naphtha	6 to 11	70 to 200	Solvents and used in gasoline.
Kerosene (paraffin)	11 to 18	200 to 300	Fuel for aircraft and stoves.
Diesel Oil	11 to 18	200 to 300	Fuel for road vehicles and trains.
Lubricating Oil	18 to 25	300 to 400	Lubricant for engines and machines.
Fuel Oil	20 to 27	350 to 450	Fuel for ships and heating.
Greases and Wax	25 to 30	400 to 500	Lubricants and candles.
Bitumen	above 35	above 500	Road surface and roofing.

Thank
You

