PETROLEUM REFINERY & PETROCHEMICAL ENGINEERING

UNIT-I

1. Introduction:

Modern refinery operations are very complex. The refinery has as a **goal** the **conversion of as much of the barrel of crude oil into transportation fuels** as is economically practical. Although refineries produce many profitable products, the **high-volume profitable products are the transportation fuels gasoline, diesel and turbine (jet) fuels, and the light heating oils, No. 1 and No. 2.**

- These transportation fuels have boiling points (**BP**) between **30 to 650°F** (0 and 345°C).
- Light heating oils are not properly transportation fuels but the hydrocarbon components are interchangeable with those of diesel and jet fuels, only the additives are different.
- Although products such as **lubricating oils, refrigeration and transformer oils, and petrochemical feedstocks** are profitable, they amount to **less than 5 percent (<5%)** of the total crude oil.
- Crude oils with **low API gravities (high specific gravities)** and **high sulfur contents require additional hydrotreating equipment.**
- **The greater densities crude oil** means more of the crude oil **will boil above 566°C (1050°F).**
- Historically this **high-boiling material or residua** has been used as **heavy fuel oil** but the demand for these heavy fuel oils has been decreasing because of stricter environmental requirements.
- This will require refineries to process the entire barrel of crude rather than just the material boiling below 1050°F (566°C).

1.OVERALL REFINERY OPERATIONS

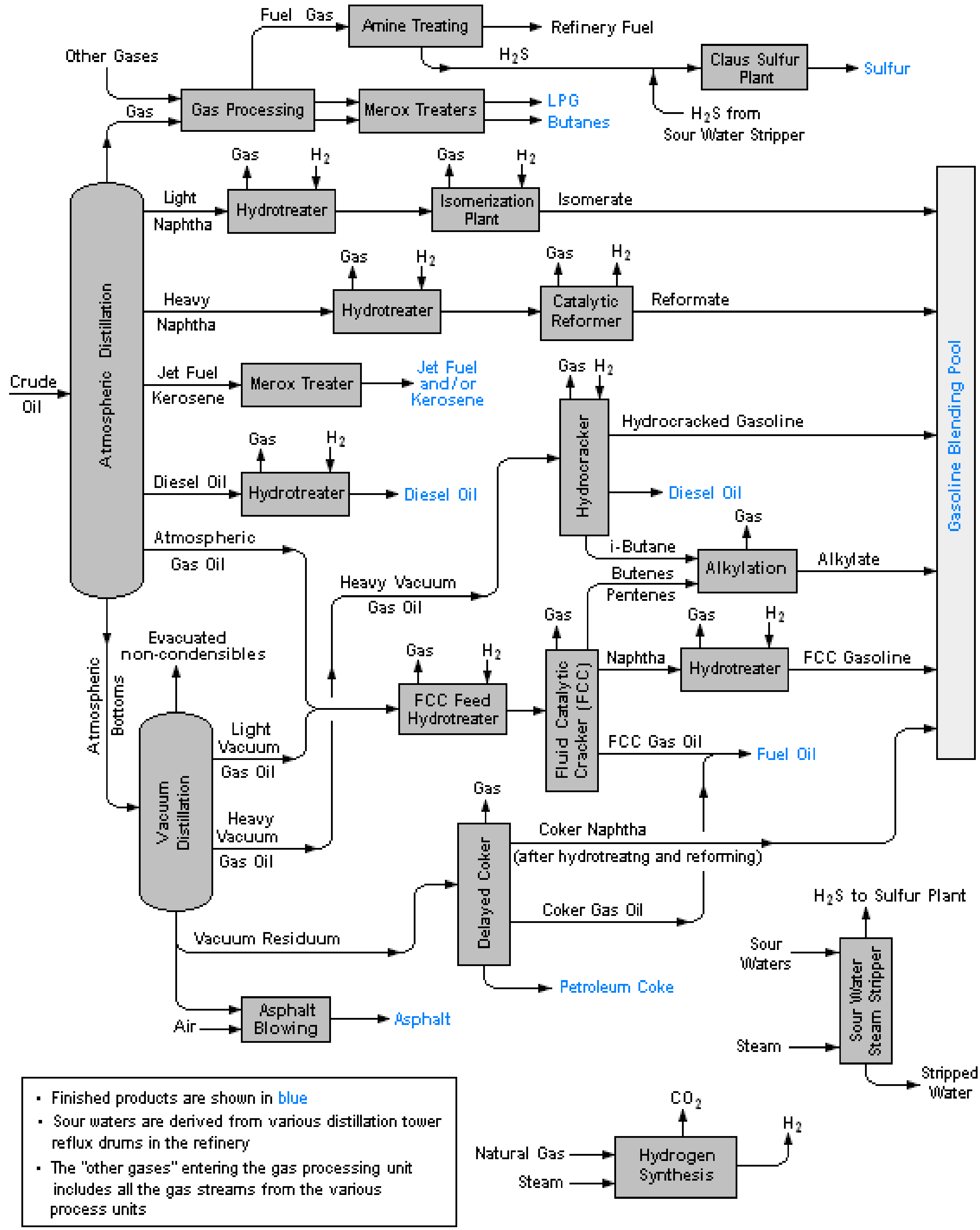


Figure 1.1 shows the processing sequence in a modern refinery indicating major process flows between operations.

The crude oil is heated in a **furnace** and charged (sent) to an **atmospheric distillation tower (ADU)**, where it is separated into

1. lighter wet gas,butanes (NOTE: A **wet gas** is any gas with a small amount of liquid present.)
2. light naphtha (unstabilized)
3. heavy naphtha
4. kerosine
5. atmospheric gas oil and
6. topped (reduced) crude (ARC).

The **reduced crude** is sent to the **vacuum distillation tower (VDU)** and separated into **vacuum gas oil stream** and **vacuum reduced crude bottoms** (residua, resid, or VRC).

The reduced crude bottoms (VRC) from the vacuum tower is then thermally cracked in a **delayed coker** to produce **wet gas, coker gasoline, coker gas oil, and coke**. **Without a coker**, this heavy resid would be sold for **heavy fuel oil or (if the crude oil is suitable) asphalt**. Historically, these heavy bottoms have sold for about 70 percent of the price of crude oil.

The atmospheric and vacuum crude unit **gas oils and coker gas oil are (almost all gas oils)** used as **feedstocks for the catalytic cracking or hydrocracking units**. These units **crack the heavy molecules into lower molecular weight compounds** boiling in the gasoline and distillate fuel ranges. The products from the hydrocracker are saturated.

The unsaturated catalytic cracker products are saturated and improved in quality by hydrotreating or reforming.

The light naphtha streams from the crude tower, coker and cracking units are sent to an **isomerization** unit to convert **straight-chain paraffins into isomers** that have higher octane numbers.

The heavy naphtha streams from the crude tower, coker, and cracking units are fed (sent) to the **catalytic reformer to improve their octane numbers**. The products from the catalytic reformer are blended into regular and premium gasolines for sale.

The **wet gas streams** from the crude unit, coker, and cracking units are separated in the **vapor recovery section (gas plant) into**

1. fuel gas,
2. liquefied petroleum gas (LPG),
3. unsaturated hydrocarbons (propylene, butylenes, and pentenes),
4. normal butane, and isobutane.

The fuel gas is burned as a fuel in refinery furnaces and the normal butane is blended into gasoline or LPG. The unsaturated hydrocarbons and isobutane are sent to the alkylation unit for processing.

The **alkylation unit** uses either sulfuric or hydrofluoric acid as catalyst to react **olefins with isobutane to form isoparaffins boiling in the gasoline range**. The product is called **alkylate, and is a high-octane** product blended into premium motor gasoline and aviation gasoline.

The **middle distillates** from the crude unit, coker, and cracking units are **blended into diesel and jet fuels and furnace oils.**

In some refineries, the heavy vacuum gas oil and reduced crude from **paraffinic or naphthenic base crude oils are processed into lubricating oils.**

After **removing the asphaltenes in a propane deasphalting unit**, the reduced crude bottoms is processed along with the vacuum gas oils to produce **lubeoil base stocks.** The vacuum gas oils and deasphalted stocks are first **solvent-extracted to remove the aromatic** compounds and then **dewaxed to improve the pour point.** They are then **treated with special clays or high-severity hydrotreating** to improve their color and stability before being blended into lubricating oils.

NOTE:

Each refinery has its own unique processing scheme which is determined

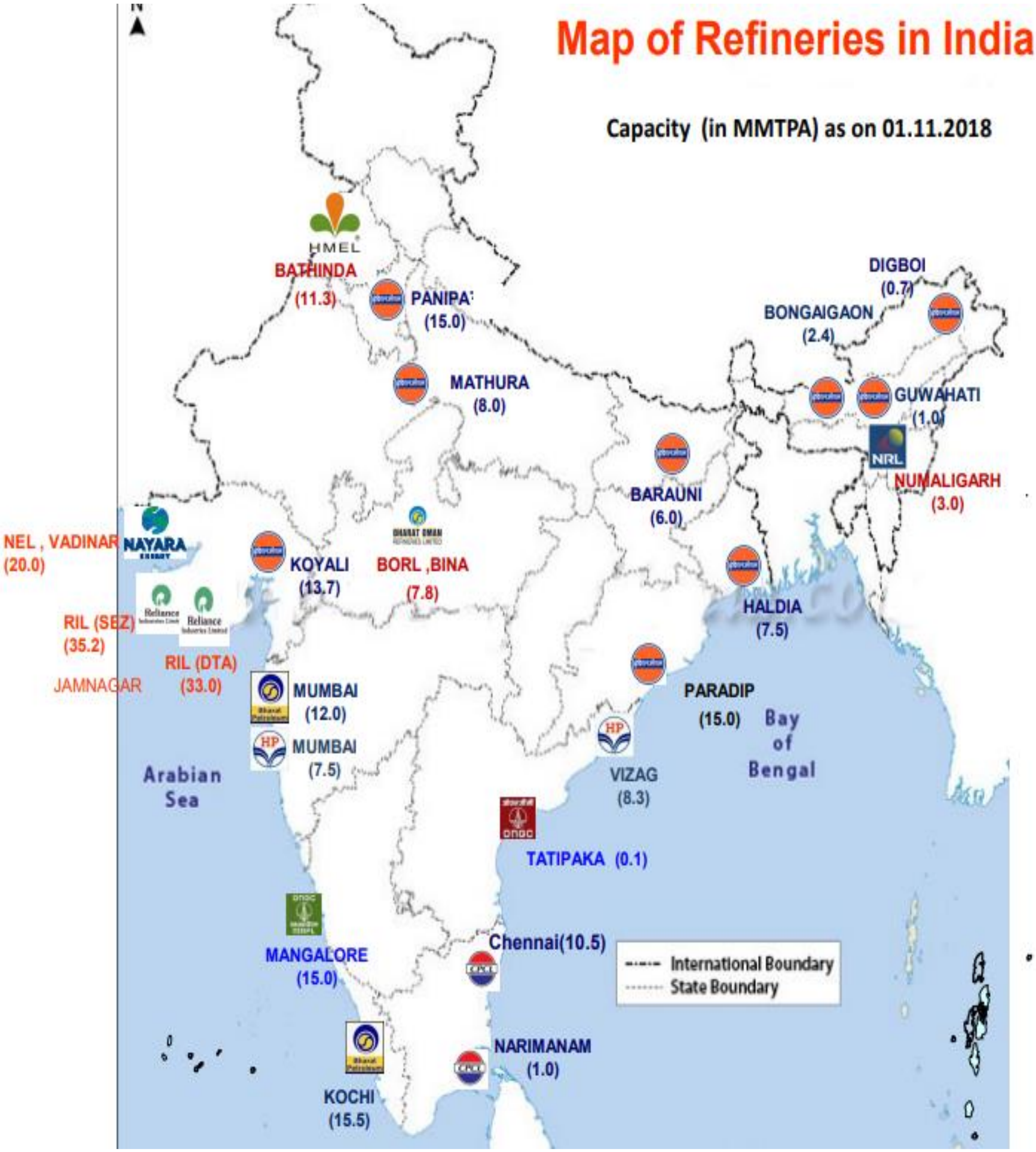
by the process equipment available, crude oil characteristics, operating costs, and

product demand. The optimum flow pattern for any refinery is dictated by economic considerations and no two refineries are identical in their operations.

2. Indian refinery scenario

Refineries have grown from 1 to 22 since Indian independence.

Overall Processing capacity increasing from 0.25 MMTPA at the time of independence to 249.4 MMTPA in Yr. 2017.



Map of Refineries in India
Capacity (in MMTPA) as on 01.11.2018
N
HMEL
BATHINDA
(11.3)
PANIPAT
(15.0)
MATHURA
(8.0)
DIGBOI
(0.7)
BONGAIGAON
(2.4)
GUWAHATI
(1.0)
NRL
NUMALIGARH
(3.0)
BARAUNI
(6.0)
NEL , VADINAR
(20.0)
NAYARA
KOYALI
(13.7)
BORL ,BINA
(7.8)
HALDIA
(7.5)
RIL (SEZ)
(35.2)
RIL (DTA)
(33.0)
JAMNAGAR
MUMBAI
(12.0)
MUMBAI
(7.5)
PARADIP
(15.0)
Bay of Bengal
VIZAG
(8.3)
Arabian Sea
TATIPAKA (0.1)
MANGALORE
(15.0)
Chennai(10.5)
International Boundary
State Boundary
NARIMANAM
(1.0)
KOCHI
(15.5)

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		**69.2**
10	HINDUSTAN PETROLEUM CORPORATION LIMITED (HPCL)	MAHARASTRA	MUMBAI	7.5
11		ANDHRA PRADESH	VISAKH	8.3
12	HPCL-HINDUSTAN MITTAL ENERGY LIMITED (HMEL) (JV)	PUNJAB	BATHINDA	11.3
		HPCL-TOTAL		**27.1**
13	BHARAT PETROLEUM CORPORATION LIMITED (BPCL)	MAHARASTRA	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	CAUVERY 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		**161.2**
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			**249.4**

PSU : PUBLIC SECTOR UNDERTAKING JV :JOINT VENTURE (JV) PVT :PRIVATE

Development of Indian refinery sector

At the time of Independence, India had only 1 very small capacity refinery at Digboi. With a total capacity of

0.25 MMTPA

First decade of Independence (1947-57) saw the establishment of 3 Coastal Refineries by Multinational oil companies operating in India at that time i.e Burmah Shell, Stanvac and Caltex**. Burmah Shell and Stanvac set up their refineries in Bombay while Caltex did so at Vizag**. Total Refining capacity in India raised to 4.8 MMTPA

Second decade (1957–67) witnessed the commissioning of 3 fully owned public sector oil Refineries – **at Barauni, Guwahati & Koyali Period**

(1977-97) saw the commissioning of 2 more Refineries in Public sector : one at Bangangaion; which was the first Refinery-cum-Petrochemical unit in India

3. REFINERY FEED STOCKS

The basic raw material for refineries is petroleum or crude oil. The elementary composition of crude oil usually falls within the following ranges.

Element	Percent by weight
Carbon	84–87
Hydrogen	11–14
Sulfur	0–3
Nitrogen	0–0.6

4. CRUDE OIL CLASSIFICATION

Crude oils are classified as

1. Paraffin Base,
2. Naphthene Base, Asphalt Base, Or
3. Mixed Base.

The U.S. Bureau of Mines has developed a system which classifies the crude according to two key fractions obtained in distillation:

No. 1 from 482 to 527°F (250 to 275°C) at atmospheric pressure and

No. 2 from 527 to 572°F (275 to 300°C) at 40 mmHg pressure.

5. CRUDE OIL PROPERTIES

API Gravity

1. The **density** of petroleum oils is **expressed in terms of API gravity** rather than specific gravity.
2. Increase in API gravity corresponds to a decrease in specific gravity. (API **inversely** related to Sp.gravity)
3. The units of API gravity are **°API.**

4. Crude oil gravity may range from less than 10°API to over 50°API. (most crudes fall in the **20 to 45°API** range). API gravity always refers to the **liquid sample at 60°F (15.6°C).**
5. °API and can be calculated from specific gravity by the following:

$$°\mathrm{API} = \frac{141.5}{\text{specific gravity}} - 131.5$$

Sulfur Content

1. Sulfur content and API gravity are two properties which have had the greatest influence on the value of crude oil The sulfur content is expressed as percent sulfur by weight.
2. It varies from less than 0.1% to greater than 5%.
3. Crudes with greater than 0.5% sulfur generally require more extensive processing. ''sour'' crudes contains dissolved hydrogen sulfide.
4. There is no sharp dividing line between sour and sweet crudes, but 0.5% sulfur content is frequently used as the criterion.

Sweet crude < 0.5 wt% Sulphur < Sour crude

Pour Point, °F (°C)

1. The pour point of a liquid is the temperature below which the liquid loses its flow characteristics.
2. It is rough indicator of the relative paraffinicity and aromaticity of the crude.
3. In crude oil a high pour point is generally associated with a high paraffin content.
4. The lower the pour point, the lower the paraffin content and the greater the content of aromatics.
5. The pour point of the crude oil, in °F or °C.

Carbon Residue, wt%

1. Carbon residue is determined by distillation to a coke residue in the absence of air.
2. The carbon residue is roughly related to the asphalt content of the crude and to the quantity of the lubricating oil fraction that can be recovered. In most cases the lower the carbon residue, the more valuable the crude.
3. This is expressed in terms of the weight percent carbon residue by either the Ramsbottom (RCR) or Conradson (CCR) ASTM test procedures (D-524 and D-189).

Salt Content, lb/1000 bbl

1. salt content of the crude expressed as NaCl. If it is greater than 10 lb/1000 bbl, it is generally necessary to desalt the crude before processing.
2. If the salt is not removed, severe corrosion problems may be encountered.
3. If residues are processed catalytically, desalting is desirable at even lower salt contents.
4. Salt content also can be expressed in ppm.

Characterization Factors

There are several correlations between yield and the aromaticity and paraffinicity of crude oils, but the two most widely used are the UOP or Watson ‘‘characterization factor’’ (KW) and the U.S. Bureau of Mines ‘‘correlation index’’ (CI).

(a) Watson characterization factor ranges from less than 10 for highly aromatic materials to almost 15 for highly paraffinic compounds. Crude oils show a narrower range of K_W and vary from 10.5 for a highly naphthenic crude to 12.9 for a paraffinic base crude.

$$K_W = \frac{T_B^{1/3}}{G}$$

where

TB ---- mean average boiling point, °R

G ----- specific gravity at 60°F.

(b) Correlation index is useful in evaluating individual fractions from crude oils. The CI scale is based upon straight-chain paraffins having a CI value of 0 and benzene having a CI value of 100. The CI values are not quantitative, but the lower the CI value, the greater the concentrations of paraffin hydrocarbons in the fraction; and the higher the CI value, the greater the concentrations of naphthenes and aromatics .

$$CI = \frac{87{,}552}{T_B} + 473.7G - 456.8$$

TB ---- mean average boiling point, °R

G ----- specific gravity at 60°F.

Nitrogen Content, wt%

A high nitrogen content is undesirable in crude oils because organic nitrogen compounds cause severe poisoning of catalysts used in processing and cause corrosion problems such as hydrogen blistering. Crudes containing nitrogen in amounts above 0.25% by weight require special processing to remove the nitrogen.

Distillation Range

1. The boiling range of the crude gives an indication of the quantities of the various products present.
2. The most useful type of distillation is known as a true boiling point (TBP) distillation and generally refers to a distillation performed in equipment that achieves a reasonable degree of fractionation. There is no specific
3. test procedure for TBP distillation (ASTM D-285 distillation method most commonly used.). Neither of
4. these specify either the number of theoretical plates or the reflux ratio used.

5. The crude distillation range also has to be correlated with ASTM distillations because product specifications are generally based on the simple ASTM distillation tests D-86 and D-1160.

Metals Content, ppm

1. The metals content of crude oils can vary from a few parts per million to more than 1000 ppm.
2. Minute quantities of some of these metals (nickel, vanadium,and copper) can severely affect the activities of catalysts and result in a lowervalue product distribution.
3. Vanadium concentrations above 2 ppm in fuel oils can lead to severe corrosion to turbine blades and deterioration of refractory furnace linings and stacks.
4. Distillation concentrates the metallic constituents of crude in the residues, and they appear in the higher-boiling distillates.
5. The metallic content may be reduced by solvent extraction with propane or similar solvents as the organometallic compounds are precipitated with the asphaltenes and resins.

6. COMPOSITION OF CRUDE OIL

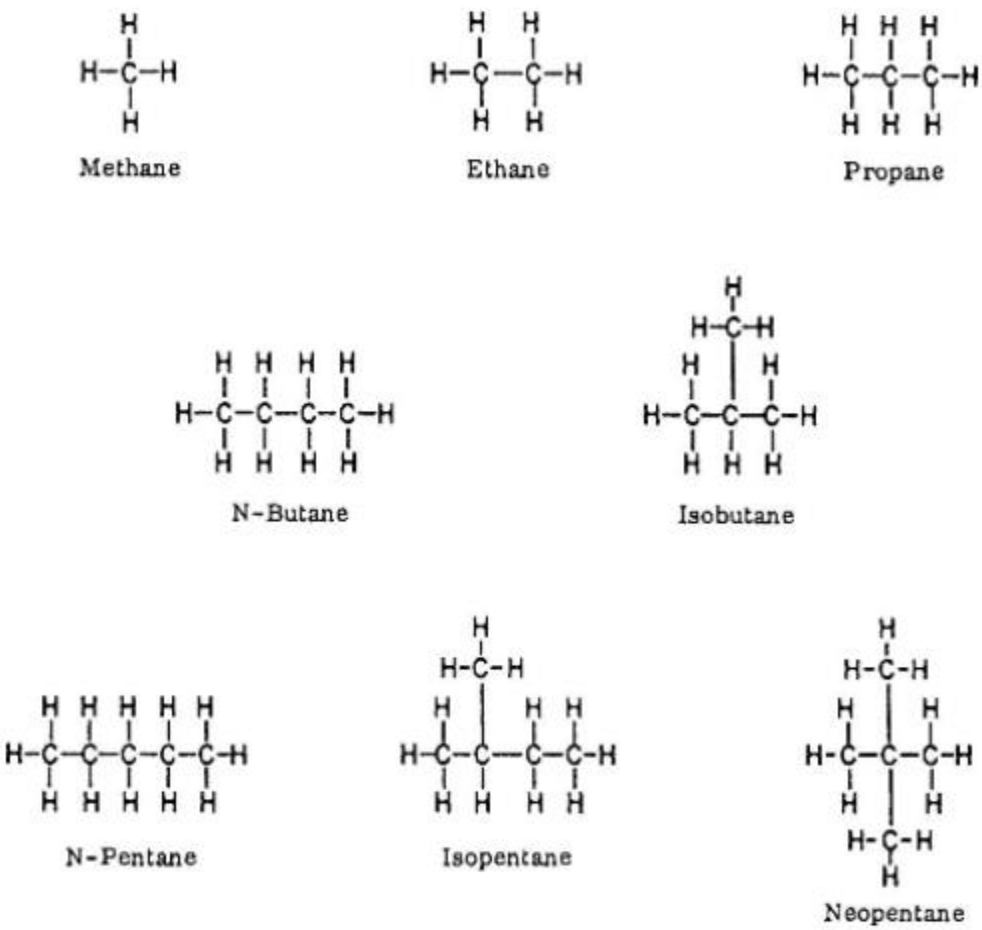
- Crude oils and high-boiling crude oil fractions are composed of many members of a relatively few homologous series of hydrocarbons.
- small differences in composition can greatly affect the physical properties
- Petroleum is essentially a mixture of hydrocarbons, and even the non-hydrocarbon elements.
- it also contains small quantities of oxygen, sulfur, nitrogen, vanadium, nickel, and chromium.

The hydrocarbons present in crude petroleum are classified into three general types: paraffins, naphthenes, and aromatics. In addition, there is a fourth type, olefins, that is formed during processing by the dehydrogenation of paraffins and naphthenes.

Paraffins

1. The paraffin are hydrocarbons characterized by the rule that the carbon atoms are connected by a single bond and the other bonds are saturated with hydrogen atoms.
2. The general formula for paraffins is C_nH_{2n+2}.
3. The simplest paraffin is methane, CH_4, followed by the homologous series of ethane, propane, normal and isobutane, normal, iso-, and neopentane, etc.
4. When the number of carbon atoms in the molecule is greater than three, several hydrocarbons may exist which contain the same number of carbon and hydrogen atoms but have different structures. carbon is capable of forming branched chains which give rise to **isomers** that have significantly different properties.
5. Example, the motor octane number of n-octane is 17 and that of isooctane (2,2,4-trimethyl pentane) is 100.

6. Crude oil contains molecules with up to 70 carbon atoms, and the number of possible paraffinic hydrocarbons is very high.



Paraffins in crude oil.

Olefins

Olefins do not naturally occur in crude oils but are formed during the processing.

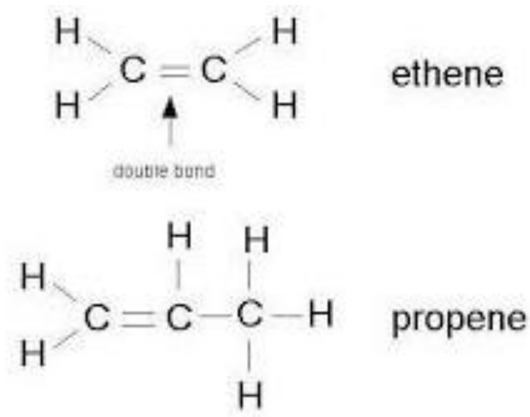
They are very similar in structure to paraffins but at least two of the carbon atoms are joined by double bonds.

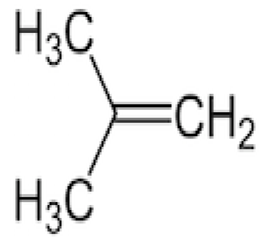
The general formula is CnH2n.

Olefins are generally undesirable finished products (even though they have high octane number) because the double bonds are reactive.

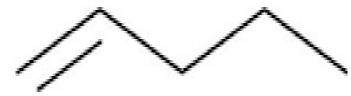
Olefins containing five carbon atoms have high reaction rates with compounds in the atmosphere that form pollutants.

Some diolefins (containing two double bonds) are also formed during processing which are also undesirable reactive as they polymerize and form filter and equipment plugging compounds.





Isobutylene



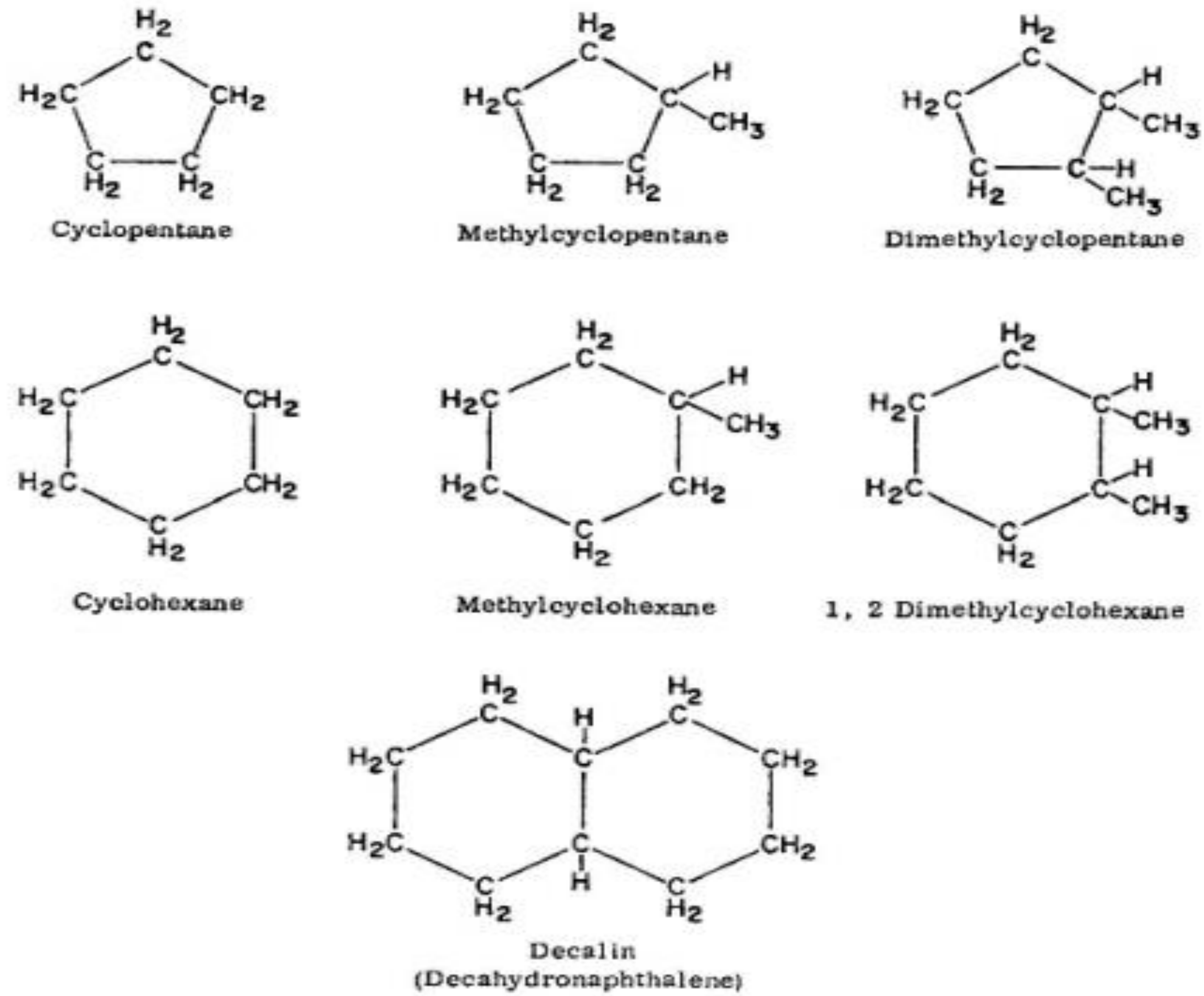
1-pentene

Naphthenes (Cycloparaffins)

Cycloparaffin hydrocarbons in which all of the available bonds of the carbon atoms are saturated with hydrogen are called naphthenes.

There are many types of naphthenes present in crude oil

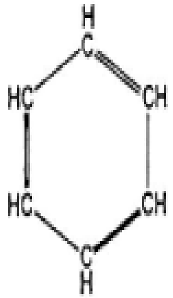
They are classified according to boiling range and their properties determined with the help of correlation factors such as the K_W factor or CI.



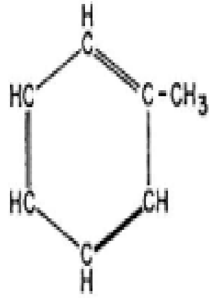
Naphthenes in crude oil.

Aromatics

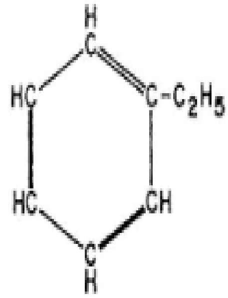
1. The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes).
2. Aromatic hydrocarbons contain a benzene ring which is unsaturated but very stable.
3. The cyclic hydrocarbons, both naphthenic and aromatic, can add paraffin side chains in place of some of the hydrogen attached to the ring carbons and form a mixed structure.
4. These mixed types have many of the chemical and physical characteristics of both of the parent compounds, but generally are classified according to the parent cyclic compound.



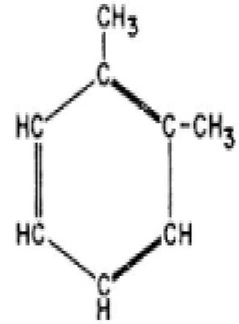
Benzene



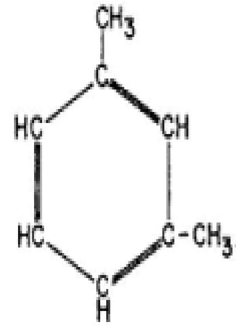
Toluene



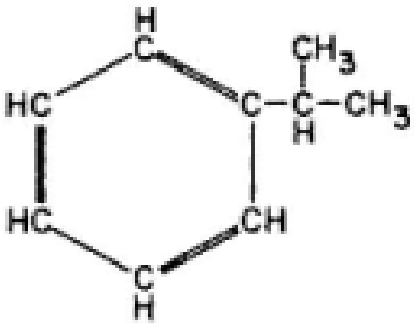
Ethylbenzene



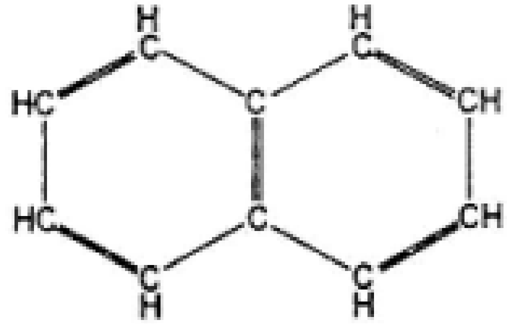
Ortho-xylene



Meta-xylene



Cumene



Naphthalene

7. CRUDES SUITABLE FOR ASPHALT MANUFACTURE

- It is not possible to predict with 100% accuracy whether or not a particular crude will produce asphalts without running the tests.
- Certain characteristics of crude oils indicate possible sources of asphalt.
- If the crude oil contains a residue [750°F (399°C)] mean average boiling point having a Watson characterization factor of less than 11.8 and the gravity is below 35°API, it is usually suitable for asphalt manufacture.
- If, however, the difference between the characterization factors for the 750°F and 550°F fraction is greater than 0.15, the residue may contain too much wax to meet most asphalt specifications.