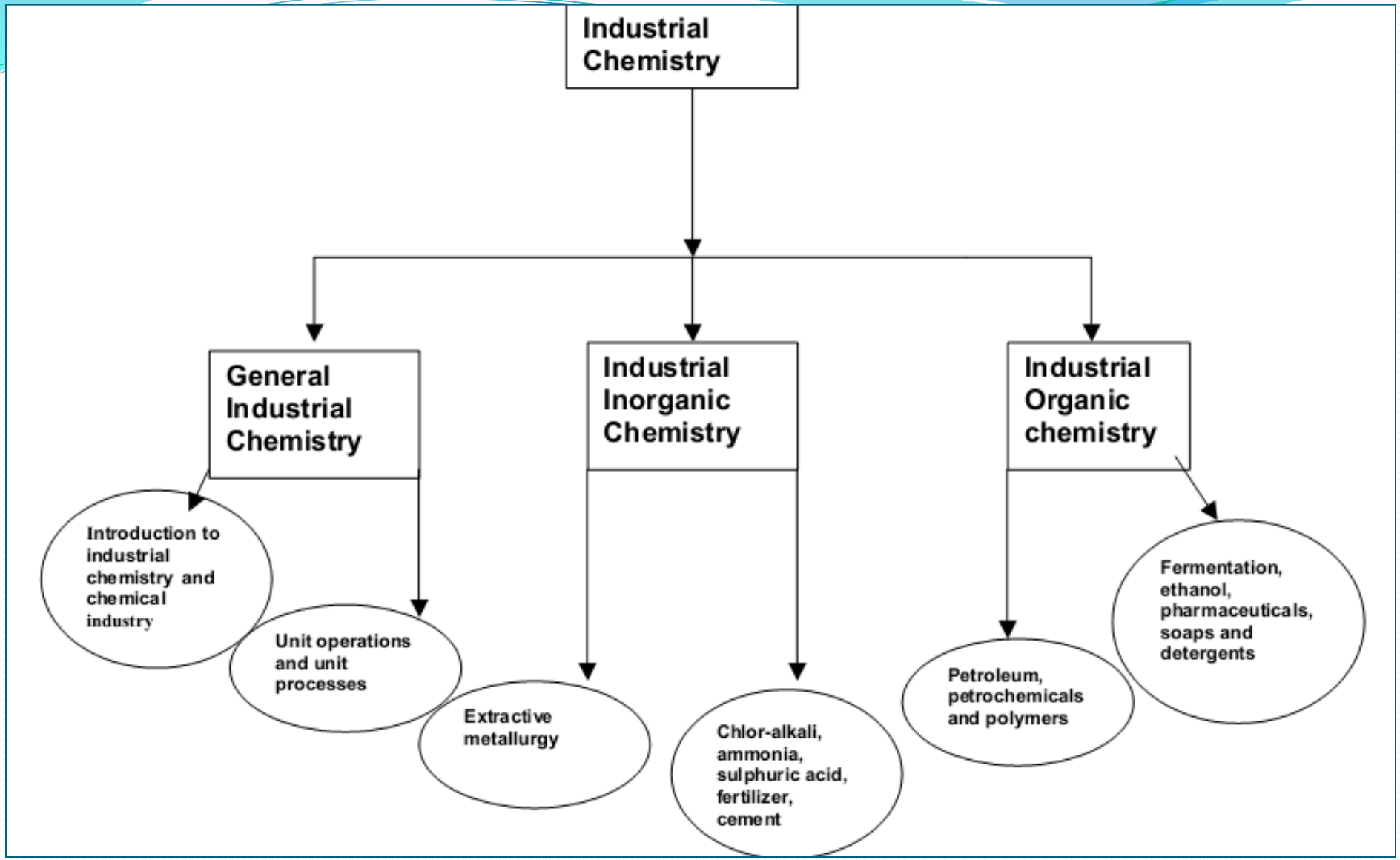
INDUSTRIAL CHEMISTRY II (CHEM3122)

CHAPTER ONE

COAL AND PETROLEUM PROCESSING

INTRODUCTION

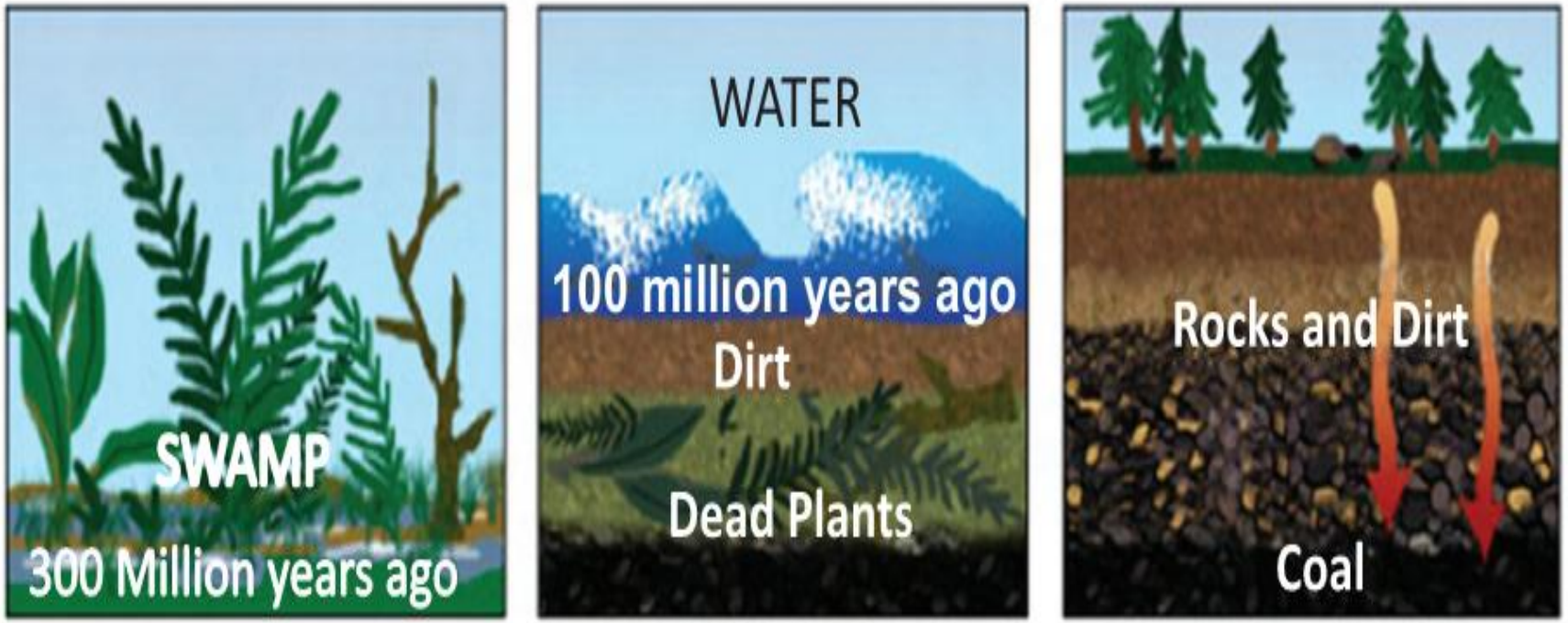
- **What is Industrial chemistry?**
- What are the main roles of Industrial chemistry?
- **Industrial Chemistry** is the branch of chemistry which applies physical and chemical processes towards the transformation of natural raw materials into products that are of benefit to humanity.
- This includes the manufacture of basic chemicals to produce products for various industries.
- It can be thought of as an industry that generates synthetic replacements for natural products.


Industrial Chemistry
General Industrial Chemistry
Industrial Inorganic Chemistry
Industrial Organic chemistry
Introduction to industrial chemistry and chemical industry
Unit operations and unit processes
Extractive metallurgy
Chlor-alkali, ammonia, sulphuric acid, fertilizer, cement
Petroleum, petrochemicals and polymers
Fermentation, ethanol, pharmaceuticals, soaps and detergents

- Substances that burn in air to give heat energy are **fuels.**
- **Fossil fuels** are formed from the buried remains of decayed plants & animals over millions of years, under the influence of heat & pressure in the absence of air.
  - Coal,
  - petroleum and
  - natural gas are called fossil fuels
- plants got buried into the bottom of the soil & were converted as fossil due to high temp. & pressure.

Coal

- The decaying plants were pressed and coal was formed.
- As coal contains mainly **C**, the slow process of conversion of dead vegetation into coal is called **carbonisation**.



1.1 Origin of Coal and Its Ranking

What is coal?

- **Coal** is a natural combustible rock composed of an organic heterogeneous substance contaminated with variable amounts of inorganic compounds.
- It is classified into different ranks according to the degree of chemical change that occurred during the decomposition of plant remains in the prehistoric period.
- It is formed by high pressure & temperature anaerobic decomposition of dead plants.

1.1 Origin of Coal and its Ranking

- **Coal** is a natural black mineral, which is a mixture of free C & compounds of **Carbon** containing Hydrogen, oxygen, nitrogen & sulphur.
- Coals are classified in a maturity rank according to age & fixed **C** content:

1.Peat: It is the 1st stage of coal.

- It is the most inferior variety of coal w/c

contains 10-15% of C. When it is burnt, it produces a lot of smoke.

2. **Lignite** : It is brown in colour .

- It contains 25-35% of carbon.
- Like peat it also produces a lot of smoke on

being ignited.

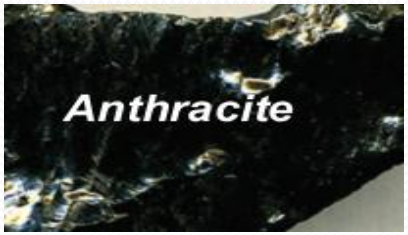
- It can be used for power generation.

Coal

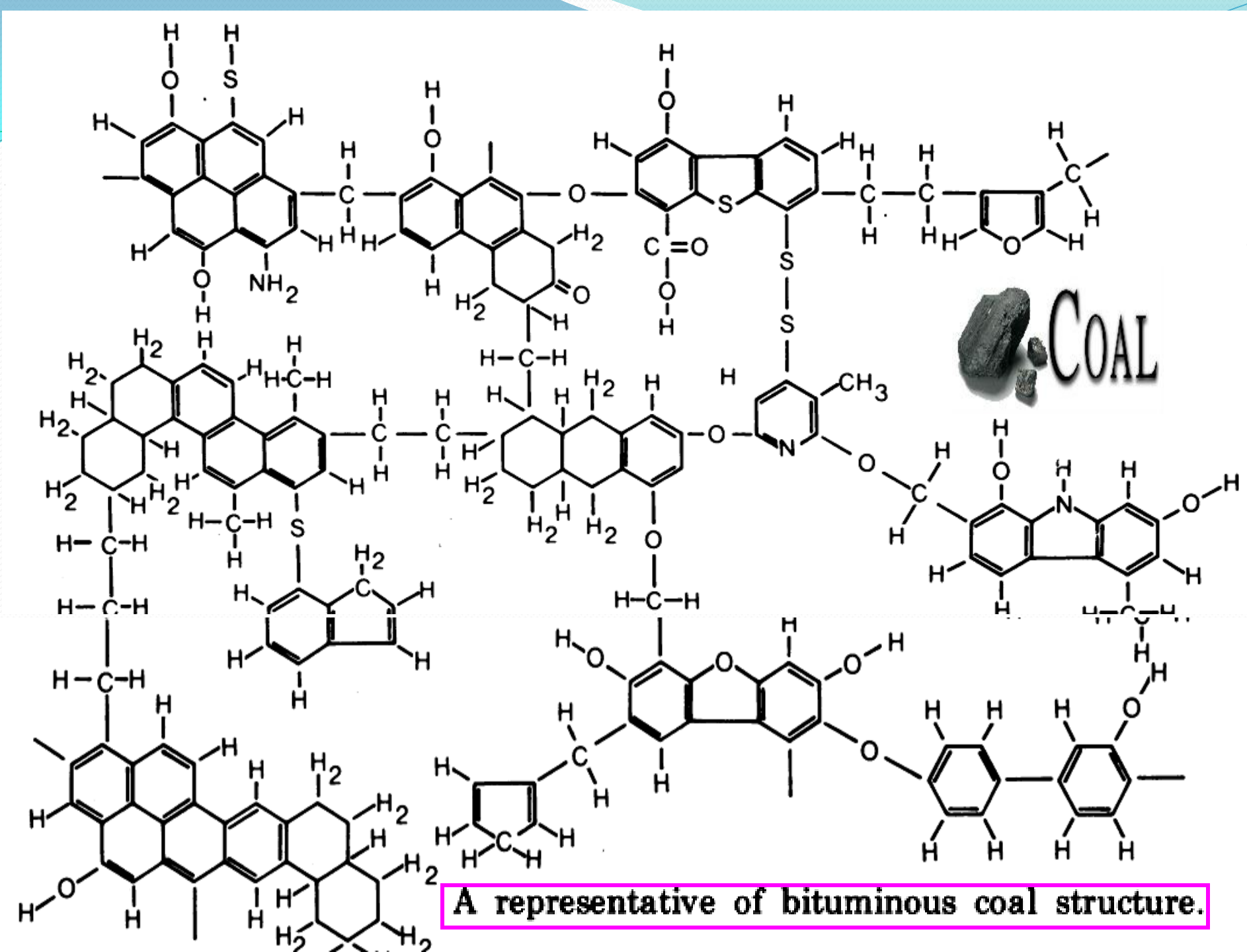
3. Bituminous Coal (soft coal)

✓ It contains **45-86%** of **C**. It is used as a common household fuel & industrial fuel

4. Anthracite Coal (called hard coal).



- ✓ It is one of the most superior variety.
- ✓ It contains **87-97% carbon**.
- ✓ It produces high heat energy.
- ✓ It is the hardest, purest, more brittle & scarce coal; too precious for a fuel (it is used for chemicals).



A representative of bituminous coal structure.

1.2 Carbonisation of coal

What is Carbonisation of coal?

- ✓ Carbonisation or pyrolysis is the heat treatment of bituminous coal in the absence of air (oxygen) in coke oven batteries to yield gas and liquid products plus solid product coke.

- ✓ 3 important methods to convert coal to useful coal chemicals.

These are :

- ☛ Carbonisation or Pyrolysis
- ☛ Gasification
- ☛ Hydrogenation/ solvent extraction

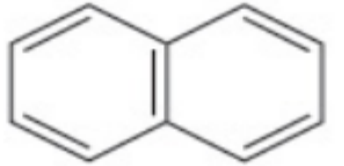
- ✓ In coal carbonization process, coal chemicals such as NH_3, crude tar, crude benzol & coke oven gas are generated along with solid mass i.e. coke.

Carbonisation of coal

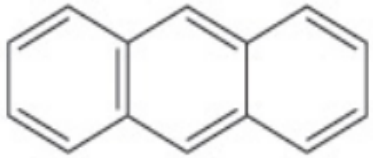
- Coal CZ chemicals mainly crude benzol & crude tar are used further, e.g., benzene, toluene & Xylenes (BTX) are the main constituents of crude benzol.
- Coal tar due to its inherent aromatic character it is more suitable source of poly-nuclear cpds. e.g. Naphthalene, alkylnapthalenes, anthracene, phenanthrene, carbazole, etc.
- So, coal tar is most important source of aromatic compounds.
- Carbonization (CZ) can be carried out at low temp. or high temp.
- Low temp. (450-750 ℃) CZ is used to produce liquid fuels while high temp (over 900 ℃). CZ is used to produce gaseous products.

Carbonisation of coal

- The major constituents of coal tar are the aromatics & heterocyclic cpds:

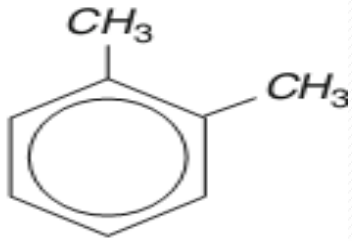


naphthalene

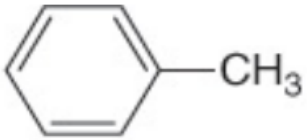


anthracene

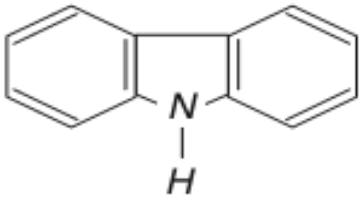
benzene



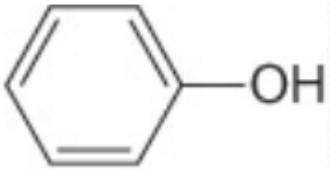
o-xylene



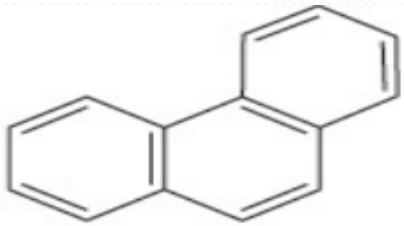
toluene



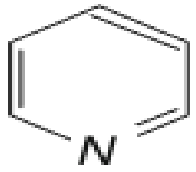
carbazole



phenol



phenanthrene



pyridine

1.3. Gasification of coal

What is Gasification of coal? Why Gasification?

- ✓ It is a conversion technology converts any **C**-containing material, coal for example, into synthesis gas.
- ✓ It is process w/c involves the complete cracking of residue into gaseous products.
- ✓ **C** reacts with H_2O in the form of steam & $\mathbf{O_2}$ at high pressure typically greater that 30 bar & at temp. 1,500 K to produce raw synthesis gas or syngas, a mixture composed primarily of **CO** & $\mathbf{H_2}$ & some minor byproducts.
- ✓ Gaseous product made from coal containing ≅ 50% $\mathbf{H_2}$, with the rest comprised of mostly $\mathbf{CH_4}$ & $\mathbf{CO_2}$ with 3-6% **CO**.

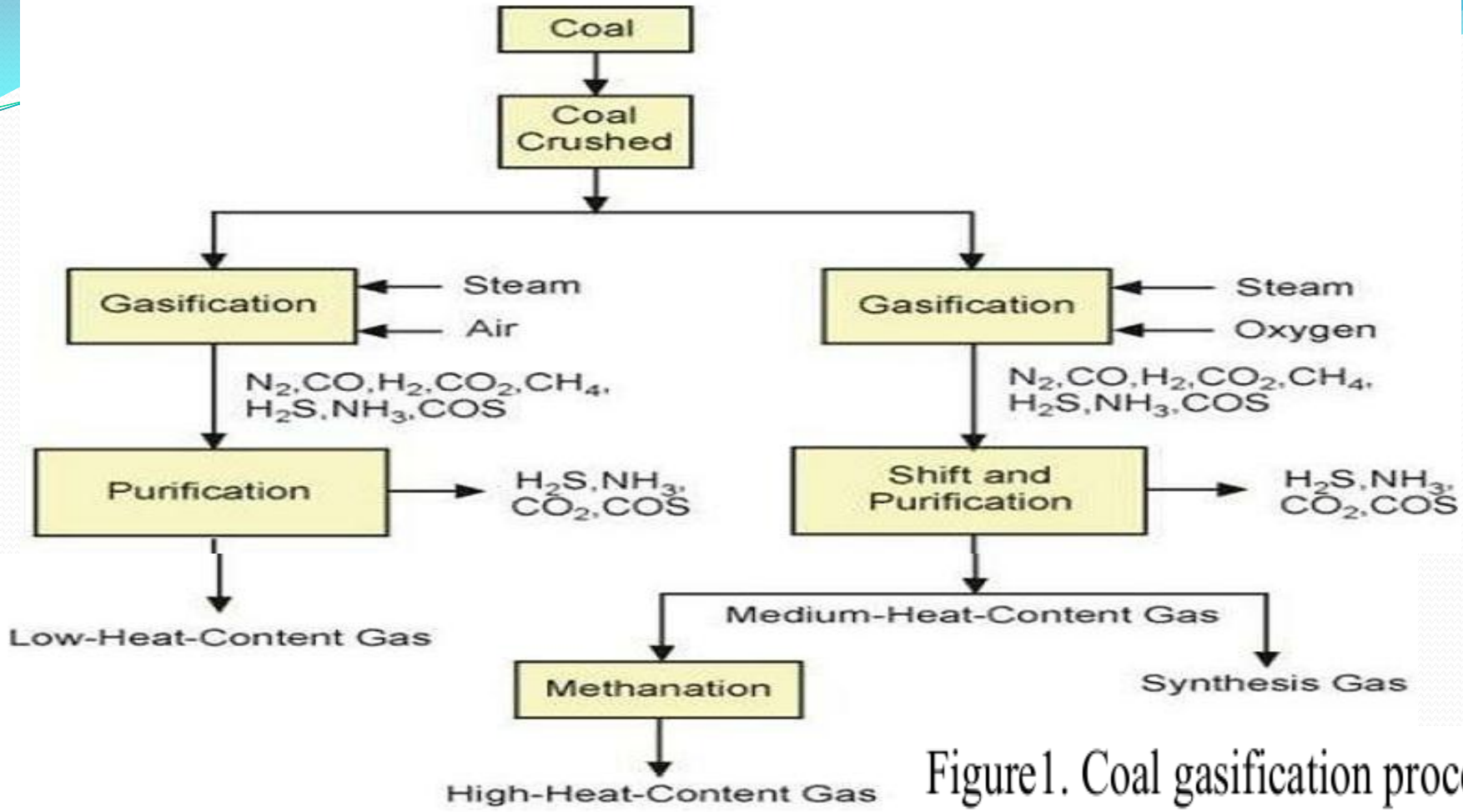


Figure1. Coal gasification process

- ✓ Coal is first crushed & dried, then fed into gasifier, in which coal reacts with steam & either air or oxygen.
- ✓ The gasification reaction usually occurs at high temp. from 800 to 1900°C.

Coal Gasification Reactions

When it is gasified under practical conditions of ff rxns occurs:

$$Coal \xrightarrow{Pyrolysis} Char(C) + \text{Coal volatiles(VM)}$$

$$VM + H_2 \xrightarrow{Hydrocracking} CH_4 - \Delta H$$

$$VM + H_2O \xrightarrow{Gasification} CO + H_2 + \Delta H$$

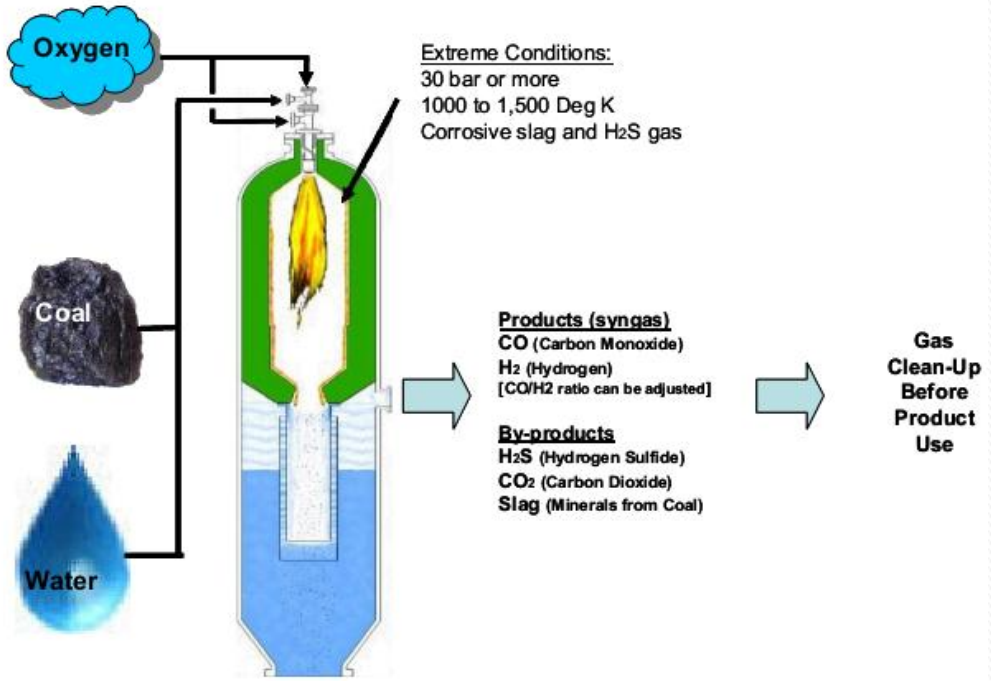
$$C + 2H_2 \xrightarrow{Hydrogasification} CH_4 - \Delta H$$

$$C + H_2O \xrightarrow{Gasification} CO + H_2 + \Delta H$$

$$C + CO_2 \xrightarrow{Gasification} 2CO + \Delta H$$

$$CO + H_2O \xrightarrow{Shift\ Conversion} CO_2 + H_2 - \Delta H$$

$$C + O_2 \xrightarrow{Combustion} CO_2 - \Delta H$$



Reaction Process	Chemical Formula	Change in Enthalpy
Gasification with Oxygen	$C + \frac{1}{2} O_2 \rightarrow CO$	–3,922 Btu/lb C
Combustion with Oxygen	$C + O_2 \rightarrow CO_2$	–14,111 Btu/lb C
Gasification with Carbon Dioxide	$C + CO_2 \rightarrow 2\ CO$	6,267 Btu/lb C
Gasification with Steam	$C + H_2O \rightarrow CO + H_2$	4,750 Btu/lb C
Gasification with Hydrogen	$C + 2\ H_2 \rightarrow CH_4$	–2,672 Btu/lb C
Water Gas Shift	$CO + H_2O \rightarrow CO_2 + H_2$	–650 Btu/lb CO
Methanation	$CO + 3\ H_2 \rightarrow CH_4 + H_2O$	–3,181 Btu/lb CO

1.3. Gasification of coal

Coal gasification: Its importance

- It is used to make up the shortage in liquid & gaseous fuels.
- It is primary way to produce liquid fuels for transportation & gaseous fuels for heating & chemical production.
- It is necessary to develop advanced power generation system.
- It is very important clean coal technology from the viewpoint of sustainable development.
- The most significant reason is the continuing high price of natural gas & highway transportation fuels.
- It is due to the need for energy independence.

1.3. Gasification of coal, Its advantage:

- It the key conversion step for converting coal to H_2,synthetic natural gas, liquid fuels, & the capture of CO_2 for sequestration.
- It is more efficient, has lower emissions and competitive capital cost compared to combustion.
- The byproducts are removed to produce a clean syngas w/c is used as a fuel to generate electricity, as a basic chemical building block for a large no of uses in the petrochemical & refining industries, & for the production of **H_2**

1.4. Hydrogenation of coal

- Most hydrogenation processes require energy addition at elevated temperature & pressures in order to breakdown the coal.
- It helps to get low-sulfur, refined fuels produced by such processes are much more acceptable.

1.5. Petroleum: Origin, Classification and Mining

What is petroleum?

- Petroleum (*petr* from Greek: **rock**; Latin: oleum mean oil) is a naturally occurring flammable liquid consisting of a complex mixture of hydrocarbons (HCs) of various molecular weight & other liquid organic compounds, that are found in geologic formations beneath the earth's surface.
- **Petroleum** (Crude oil) is a thick, flammable, yellow-to–black combustible mixture of gaseous, liquid, & solid hydrocarbons that occur naturally beneath the earth’s surface.

Petroleum origin, Classification and mining

- ✓ Millions of years ago, dead plants & animals were buried at the bottom of the sea.
- ✓ They got covered with layers of sand & clay.
- ✓ Due to high pressure & temp., they transformed into petroleum.

occurrence of Petroleum

- ✓ The chief petroleum producing countries are U.S.A, Kuwait, Iraq, Iran, Russia and Mexico.
- ✓ Table. Elemental composition of crude oils

Element	Composition (wt%)
Carbon	83.0–87.0
Hydrogen	10.0–14.0
Sulphur	0.05–6.0
Nitrogen	0.1–0.2
Oxygen	0.05–2.0
Ni	<120 ppm
V	<1200 ppm

Crude petroleum contain:

- ✓ Hydrocarbon compounds,
- ✓ non-Hydrocarbon compounds &
- ✓ Organometallic compounds & inorganic salts

Hydrocarbon compounds: Paraffins

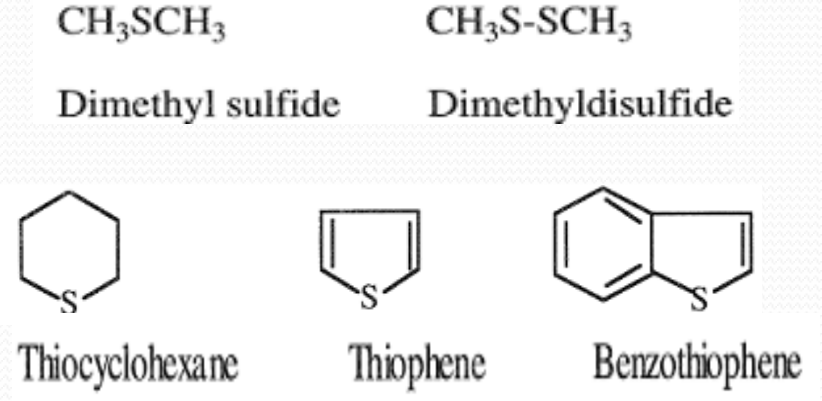
- ✓ The lighter, straight chain paraffin molecules are found in gases & paraffin waxes.
- ✓ Aromatics: include simple aromatic compounds such as benzene, naphthalenes & the most complex aromatics.

- ✓ Naphthenes (Naphtha): are saturated hydrocarbon groupings found in all fractions of crude oil except the very lightest.
- ✓ Alkenes (Olefins): such as ethylene, butene, isobutene are usually formed by thermal and catalytic cracking.
- ✓ Dienes & Alkynes: Example: 1,2-butadiene & 1,3-butadiene. Acetylene is a typical alkyne.
- ✓ This category of hydrocarbons are obtained from lighter fractions through cracking.

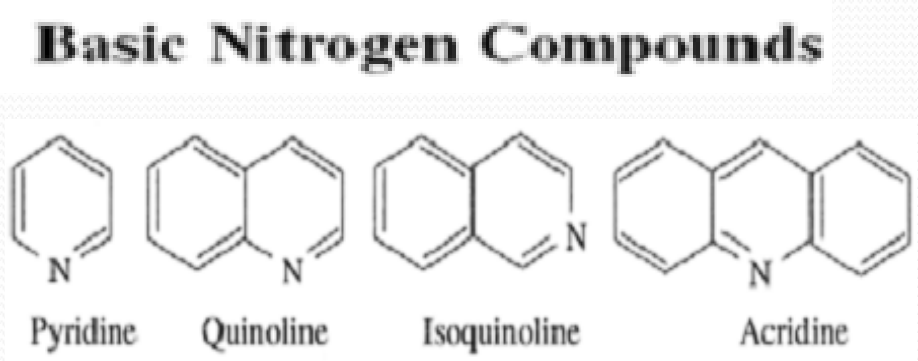
- **Non-hydrocarbons:** Sulfur (S) Compounds
- Sulfur in crude oils is mainly present in the form of organosulfur compounds.
- H_2S-is the only important inorganic **S** compound found in crude oil.
- However, its presence is harmful because of its corrosive nature.
- Organosulfur cpds may be classified as acidic & non-acidic.

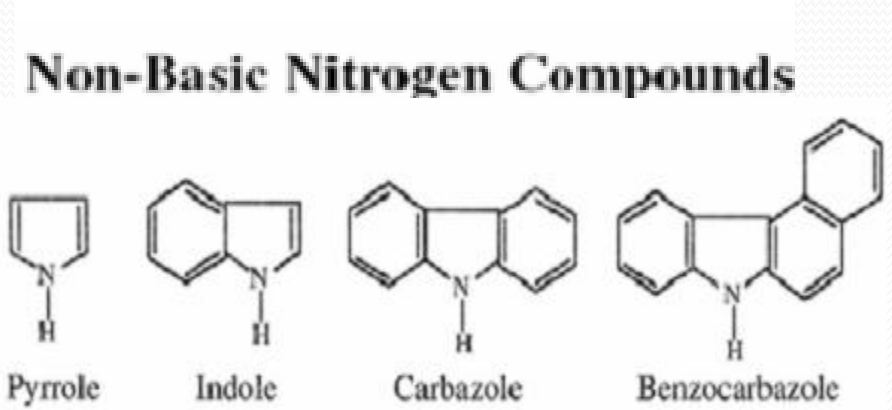
Acidic Sulfur Compounds

Non-acidic Sulfur Compounds



- **Non-hydrocarbons: Nitrogen (N) Compounds**
- Organic **N** compounds occur in crude oils either in a simple heterocyclic form as in pyridine and Pyrrole or in a complex structure as in porphyrin.
- **N** compounds in crudes may be classified into basic & non-basic.
- Basic **N** compounds are mainly those having a pyridine ring, & the non-basic compounds have a Pyrrole structure.





Petroleum Refining process

- **Petroleum** is obtained by drilling through the earth.
- The crude oil is pumped out from the well as a black liquid.
- It is a mixture of various constituents such as petroleum gas, petrol, diesel, kerosene, lubricating oil, paraffin wax, etc.
- The process of separation of the various constituents or fractions of petroleum by fractional distillation in fractionating columns is known as refining of petroleum.
- The process of heating a mixture of liquids having different boiling points & then separating them by cooling is called fractional distillation.
- As the basic elements of crude oil, **C** & **H** form the main input into a refinery.

Petroleum Refining process

- As the vapors of crude oil move up the tower, the various fractions condense according to their boiling point ranges.
- Petroleum refinery products obtained include: gasoline, kerosene, propane, fuel oil, lubricating oil, wax, and asphalt.

To convert crude oil into desired products in an economically feasible & environmentally acceptable manner.

Refinery processes for crude oil are divided into 3:

- 1) separation processes, e.g. distillation
- 2) conversion processes, e.g. catalytic cracking
- 3) finishing processes, e.g. hydro treating

- But, desalting and dewatering are carried out before separation process.

Fractional Distillation

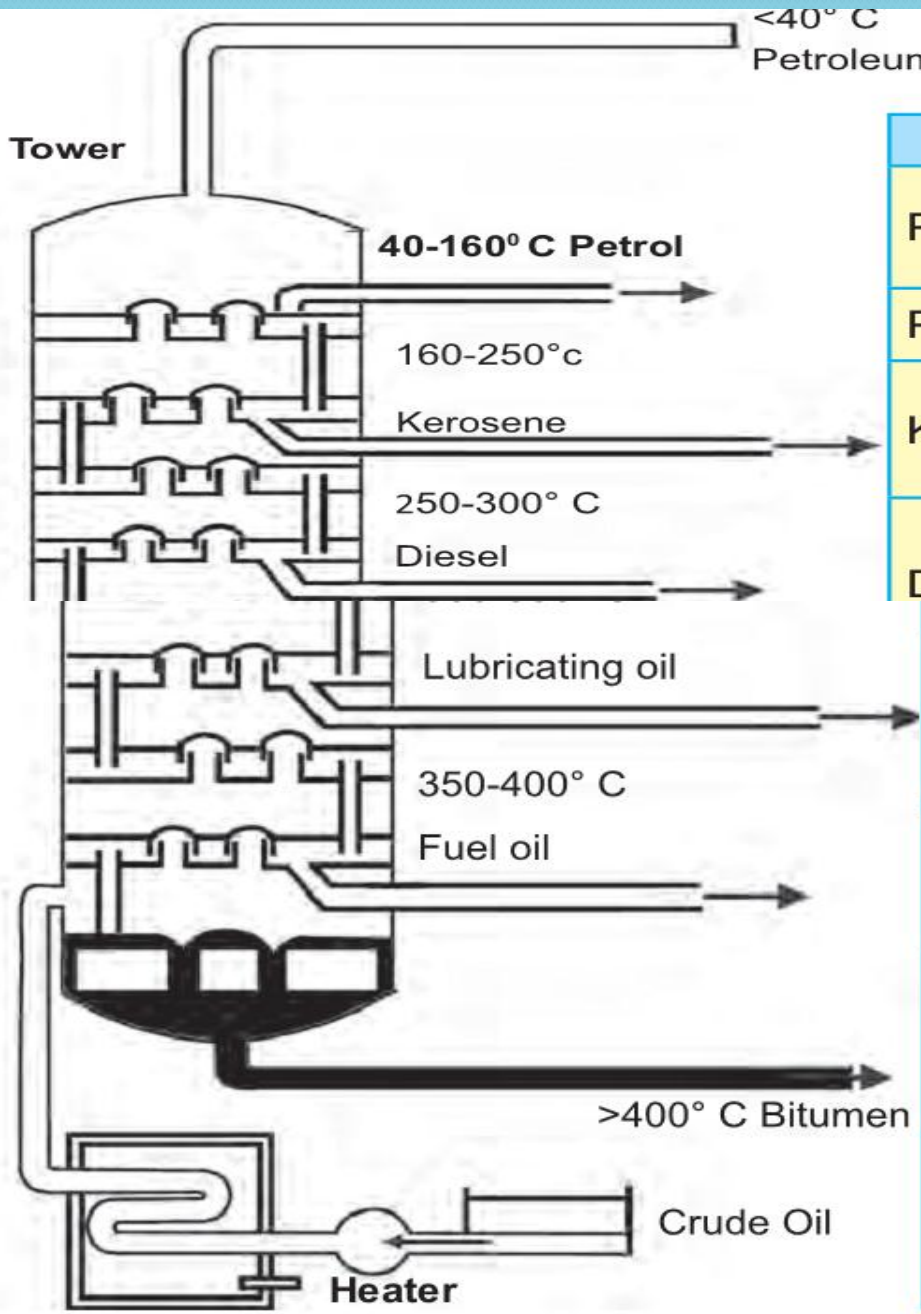
- Distillation is used to separate a mixture of miscible liquids which have different volatilities.
- Suppose a mixture with low concentration of the more volatile component is distilled and the vapor condensed.
- The condensate which we refer to as distillate will be more concentrated with this component than the feed.
- If we return the distillate to the distillation apparatus & distill it to a 2nd distillate, this distillate will be more richer in the more volatile component than the first distillate.

Fractional Distillation

- If we continue this process, we will approach a pure distillate of the more volatile component.
- The greater the relative volatility between the two components, the fewer the needed distillation stages. This is the concept of **fractional distillation**.
- It is used when:
  - Boiling points of mixture components are close
  - Volatilities of the components are close
- This is the case in petroleum refining.
- Industrially, fractional distillation is carried out in distillation columns also known as distillation towers.
- They are like many distillation stills stack together vertically.

Petroleum Refining process

- Distillation refine the crude oil into useful products such as lubricating oil or fuel oil.
- Petroleum refining begins with distillation, or fractionation, which separates crude oil in atmospheric & vacuum distillation towers into groups of hydrocarbon compounds of differing boiling point ranges called "fractions".
- conversion processes which alter the size &/or molecular structure of hydrocarbon molecules to produce a wide range of products.



Fraction	Uses
Petroleum Gas	Fuel for home (LPG)
Petrol	Motor fuel
Kerosene	Fuel for stove and jet aircrafts
Diesel	Fuel for heavy
Lubricating oil	Lubrication
Fuel Oil	Fuel for Power Stations and Ship
Paraffin wax	Candles, Vaseline
Bitumen	Paints, Road surfacing

Petroleum Refining process

Chemical Conversion processes include:

- ✓ Decomposition (dividing) by thermal and catalytic cracking;
- ✓ Unification(combining) through alkylation & polymerization;
- ✓ Alteration (rearranging) with isomerization & catalytic reforming.
- ✓ the major chemical conversions include cracking, alkylation, polymerization, isomerization and reforming.
- ✓ The converted products are then subjected to various treatment and separation processes.

1.7. Rating of Petrol and Diesel

Cetane number (CN) and Octane number (ON)

- ✓ Petroleum is refined to produce petrol and diesel.
- ✓ Petrol is produced at temperature between 35 -200 ^{o}C while diesel is produced at a boiling point of 250-350 ^{o}C, so, petrol is produced first.
- ✓ **CN** measures the ability for auto ignition & is essentially the opposite of the **ON**.
- ✓ **CN** is the percentage of pure cetane (n-hexadecane) in a mixture of cetane and alpha methyl naphthalene which matches the ignition quality of a diesel fuel sample.
- ✓ Octane number is a figure of merit representing the resistance of gasoline to premature detonation when exposed to heat and pressure in the combustion chamber of an internal combustion engine.
- ✓ Premature detonation is indicated by knocking or ringing noises that occur as the engine operates
- ✓ The ability of a fuel to resist auto-ignition during compression & prior to the spark ignition gives it a high **ON**.

Rating of Petrol and Diesel

- The quality of diesel fuels can be expressed as CN.
- CN is expressed in terms of the volume % of cetane ($C_{16}H_{34}$) which has high ignition (CN=100) in a mixture with alpha-methyl-naphthalene ($C_{11}H_{10}$) which has low ignition quality (CN=0).
- Diesel fuel includes No.1 diesel (Super-diesel) which has CN of 45 and it is used in high speed engines, trucks and buses.
- No. 2 diesel has 40 CN.
- Factors which can increase the octane number are more branching:
- 2-methylbutane is less likely to auto ignite than pentane.
- Shorter chains: pentane is less likely to auto ignite than heptane.

Rating of Petrol and Diesel

- ✓ Railroad diesel fuels are similar to the heavier automotive diesel fuels, but have higher boiling ranges up to 400 ℃ & lower CN (CN = 30).
- ✓ **ON** of a fuel is determined by measuring its knocking value compared to the knocking of a mixture of n-heptane & isooctane.
- ✓ Pure n-heptane is assigned a value of zero octane while isooctane is assigned 100 octane.
- ✓ Hence, an 80 % isooctane mixture has an **ON** of 80.

1.8. Cracking, Alkylation, Hydro treating & Reforming

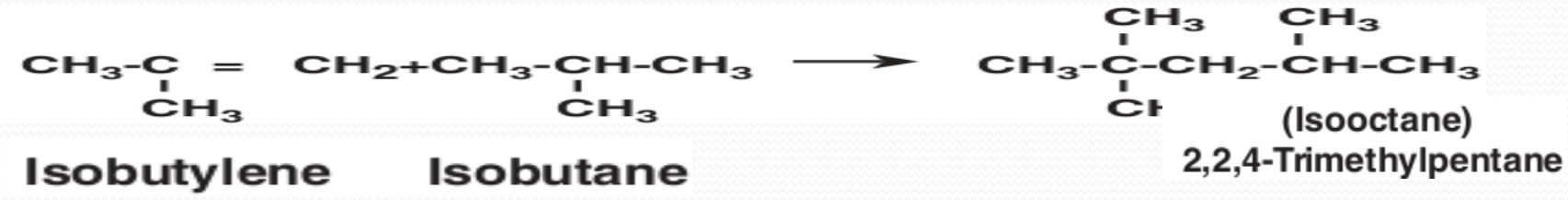
1.8. 1 Catalytic Cracking

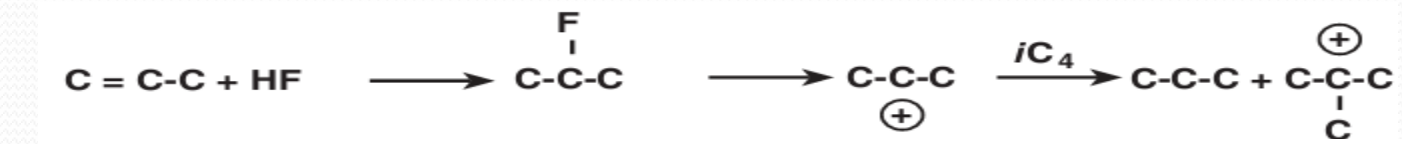
- ✓ Catalytic cracking is the most common cracking process, in which heavy feedstock or cuts are broken down or changed by being heated, & reacted with catalysts.
- ✓ Fluid catalytic cracking (FCC) is the main player for the production of gasoline.
- ✓ The catalyst in this case is a zeolite base for the cracking function.
- ✓ The main feed to FCC is vacuum gas oils (VGO) and the product is **gasoline**, but some gas oil & refinery gases are also produced.

1.8.2 Alkylation

- Alkylation is the introduction of an alkyl radical by substitution or addition into an organic compounds.
- In the presence of an acid catalyst such as HF or H_2SO_4, this reaction is used for the conversion of gaseous hydrocarbons to gasoline.
- The processes are usually exothermic.
- The industrial alkylation of aromatics with olefins is one of the major examples of development of environmentally friendly processes.
- The reactions include an initiation step and a propagation step and may include an isomerization step.

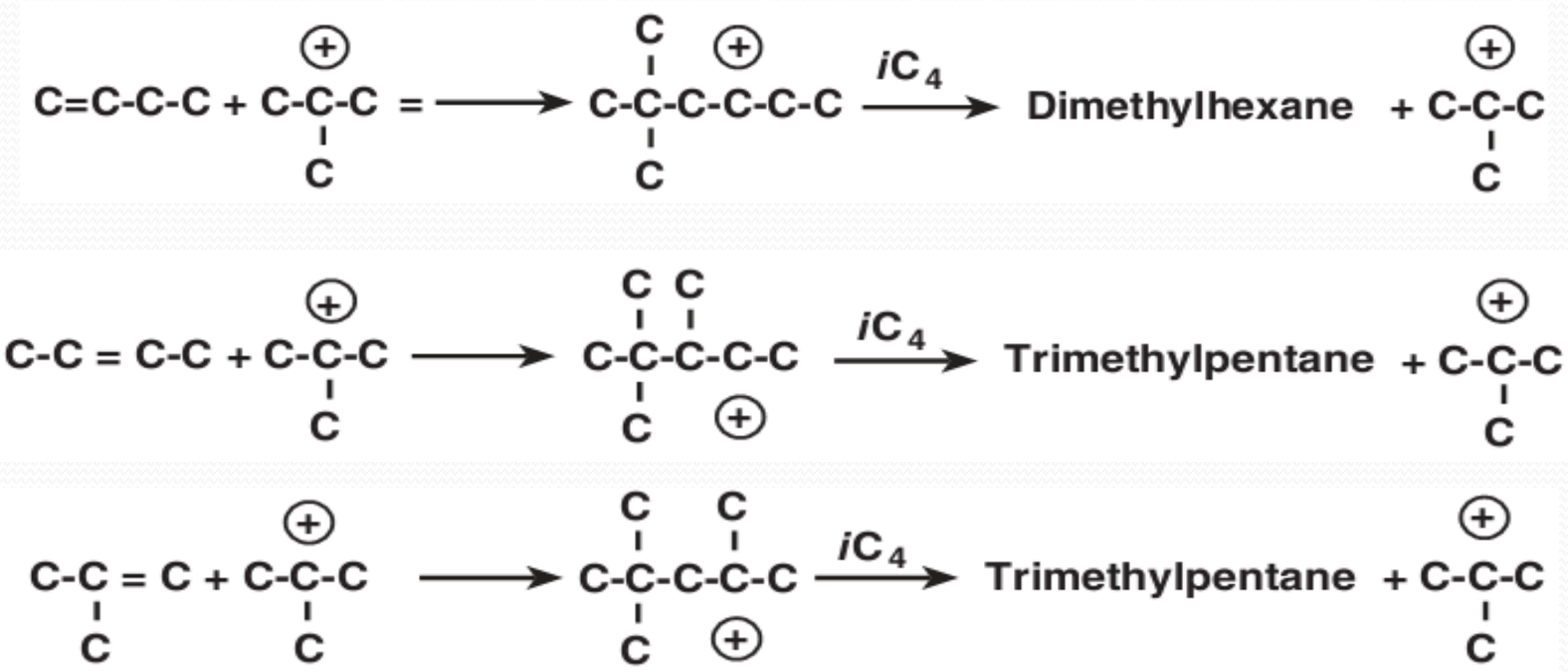
- The **initiation** step generates the tertiary butyl cations that will subsequently carry on the alkylation reaction.





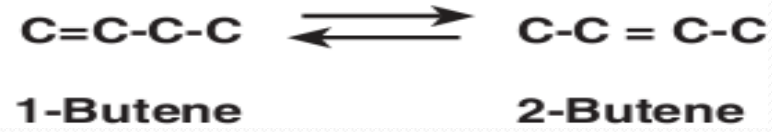
HF alkylation reaction mechanism—initiation reactions.

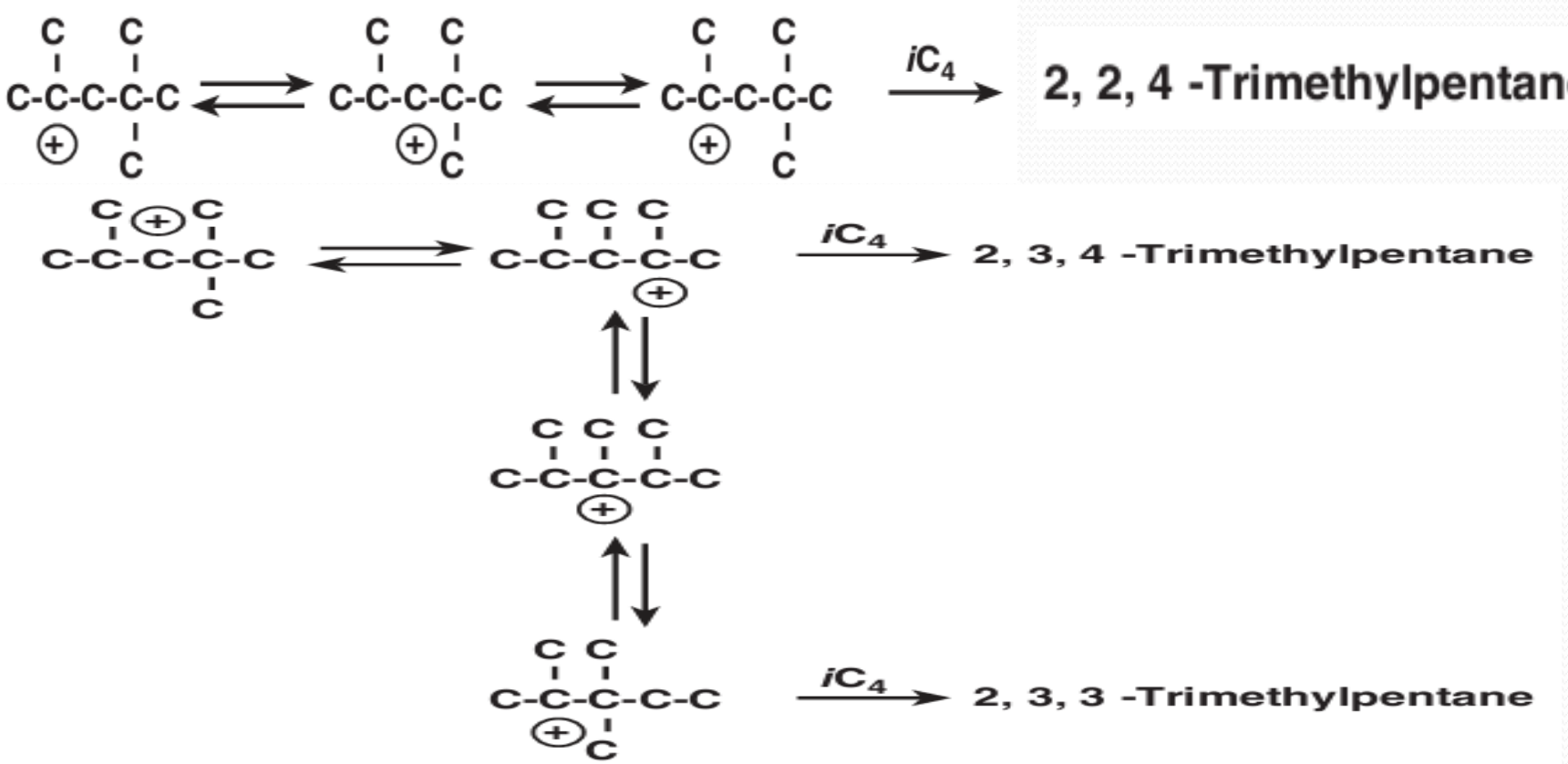
- **Propagation** reactions involve the tertiary butyl cation reacting with an olefin to form a larger carbenium ion, which then abstracts a hydride from an isobutane molecule.



HF alkylation reaction mechanism—propagation reactions

- **Isomerization** is very important in producing good octane quality from a feed that is high in 1-butene

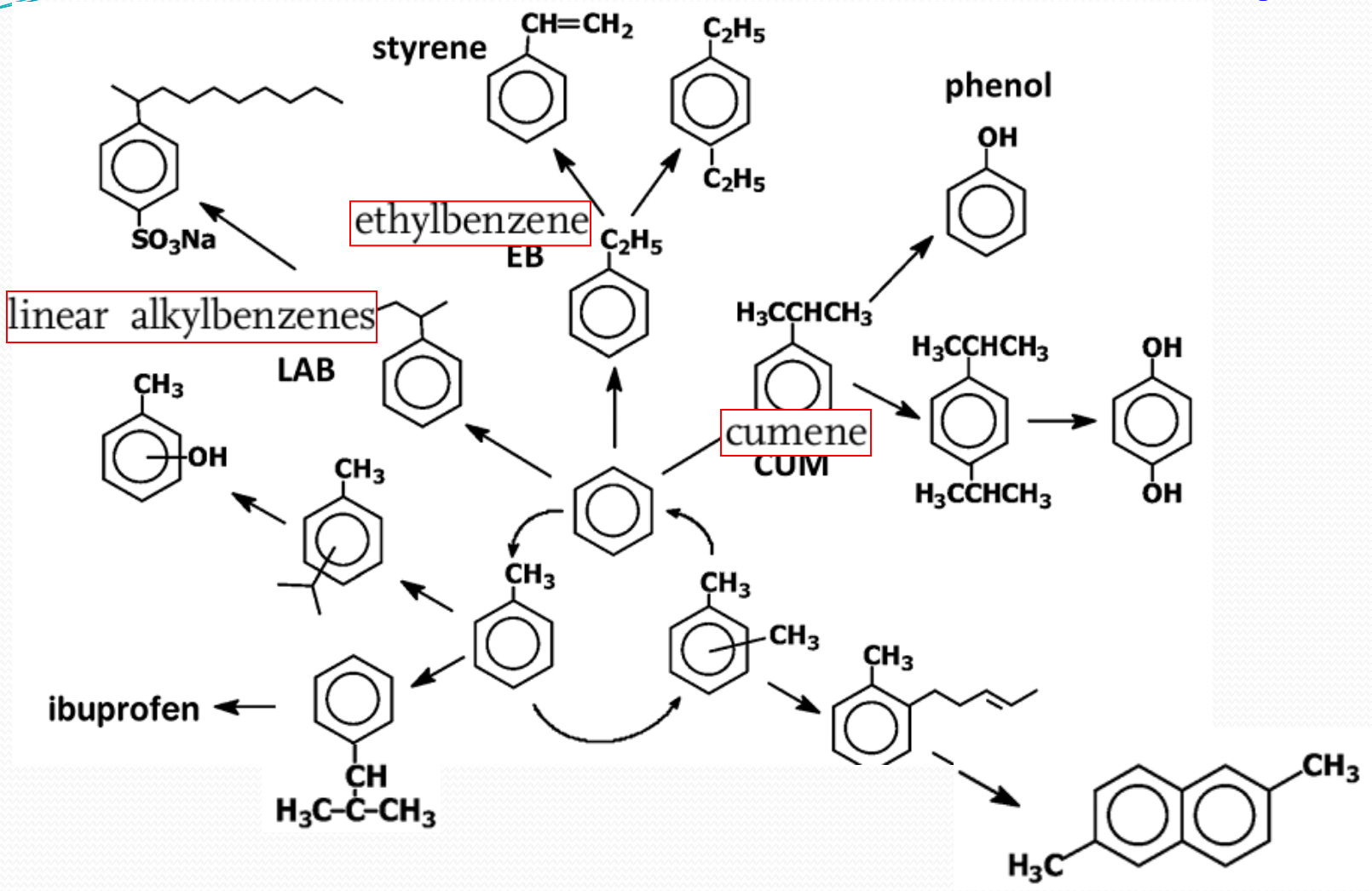




Alkylation

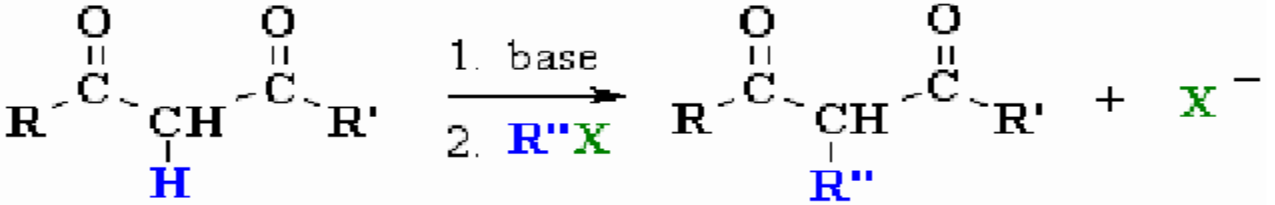
- The principal products obtained are ethyl benzene, cumene, p-diethylbenzene, p-diisopropylbenzene, and C_{10}–C_{14} linear alkylbenzenes.
- Aromatic alkylations industrially applied for the preparation of important chemical intermediates.
- These reactions include the most important aromatic substrates, benzene, toluene and xylene, & different olefins.
- two different kinds of alkylation: **electrophilic alkylation** on the aromatic ring catalyzed by acids & **side-chain alkylation** catalyzed by bases.

Alkylation


styrene
CH=CH2
C2H5
C2H5
phenol
OH
SO3Na
ethylbenzene
EB
C2H5
linear alkylbenzenes
LAB
H3CCHCH3
H3CCHCH3
OH
CH3
OH
cumene
CUM
H3CCHCH3
OH
CH3
CH3
CH3
CH3
CH3
ibuprofen
CH
H3C–C–CH3
CH3
H3C

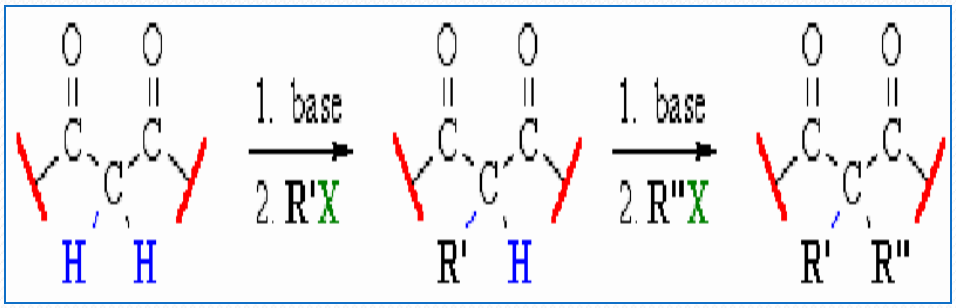
Alkylation

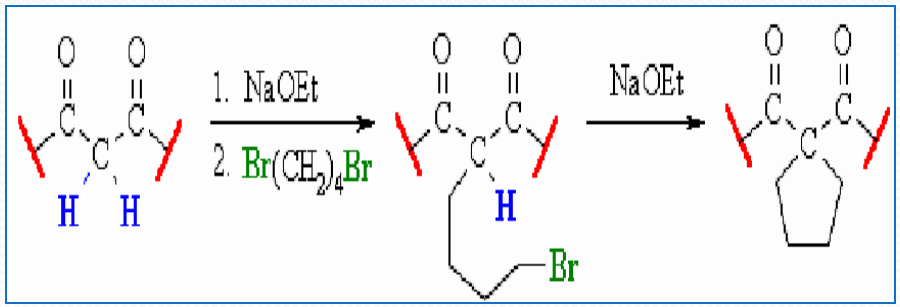
- other than gasoline, alkylation reactions include pharmaceuticals, detergents, disinfectants, dyes and plastics.
- Alkylates of active methylenes are easily prepared using a base such as ethoxide, EtO^-



R, R' = alkyl or alkoxy

- Methyl and primary halides are most suitable for alkylation reactions.





1.8. 3 Hydro treating

- **Hydro treating** of residual oils was a natural extension of hydro treating distillate oils and vacuum gas oils to remove sulfur.
- It is one of the major processes for the cleaning of petroleum fractions from impurities such as S, N, oxygen & chloro-compounds, aromatics, waxes & metals using hydrogen.
- The catalyst is selected to suit the degree of hydro treating & type of impurity.
- Catalysts, such as cobalt & molybdenum oxides on alumina matrix, are commonly used to change reaction rate.

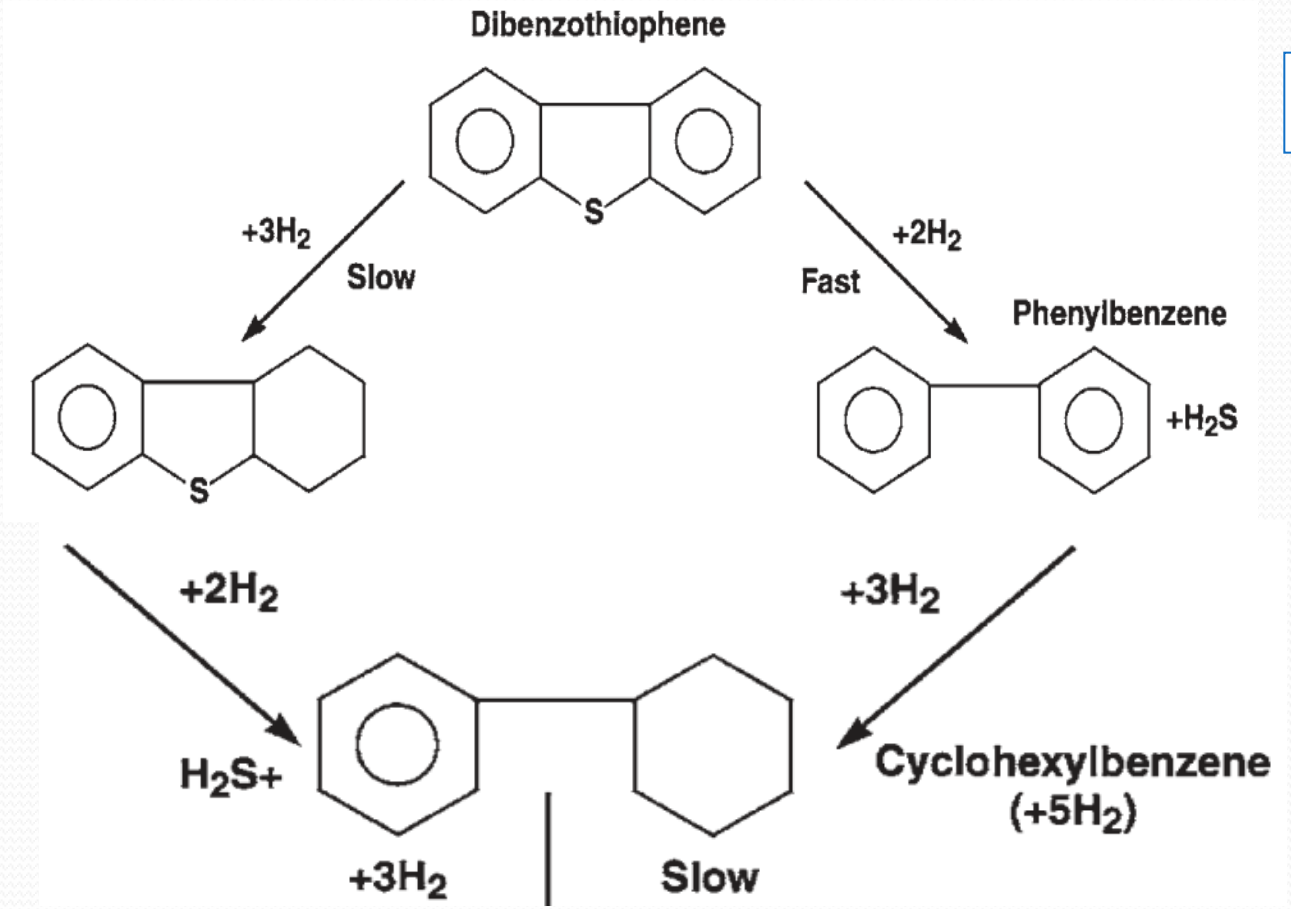
Hydro treating

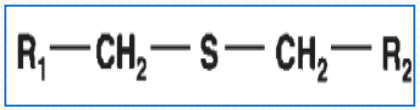
- Hydro treating is very exothermic.
- The heat produced by the reactions causes the gas & oil to increase in temp. as they pass down through the catalyst beds.
- Desulfurization is by far the most common of the hydro treating reactions.
- **S**-containing hydrocarbons come in a no of forms, & the ability to remove **S** from the d/t types of hydrocarbons varies from one type to the next.
- The degree to which **S** can be removed from the hydrocarbons varies from near-complete desulfurization for light straight-run naphthas to 50% to 70 % for heavier residual materials.

Hydro treating

- The temp. in the reactors is controlled by the addition of **H** quench gas b/n reactors & b/n catalyst beds within a reactor.
- **S** atoms tend to be bound in the oil as "**S** bridges" b/n two **C** atoms or to be contained in a saturated ring structure.
- Removal of these **S** atoms requires only the breaking of the two **S-C** bonds per **S** atom & the subsequent addition of four atoms of **H** to cap the ends of the bonds that were broken.
- The removed **S** is converted into H_2S gases.
- This diffuse out of the catalyst pore with the other reactants.
- The removed **Ni** & **V** are bound up with **S** & remain on the catalyst surface.

- When the part of the molecule that contains the **S** can access the catalyst surface, **S** removal is relatively easy.





Sulfide

1.8.4 Catalytic Reforming

- In this process, a special catalyst (Pt-metal supported on silica or silica base alumina) is used to restructure naphtha fraction (C_6–C_{10}) into aromatics & isoparaffins.
- The produced naphtha reformate has a much higher octane no than the feed.
- This reformate is used in gasoline formulation & as feedstock for aromatic production (BTX).

Steam Cracking

- Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons.
- It is the principal industrial method for producing the lighter alkenes (commonly olefins), including ethene (ethylene) and propene (propylene).