*University of Baghdad*
*College of science*
*Department of chemistry*.

# *Industrial Chemistry*

# *for Third Year Chemistry*

## *الكورس الثاني*

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صناعية نفط

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# Fuel and energy

Fuel is a substance which, when burnt, i.e. on coming in contact and reacting with oxygen or air, produces heat. Thus, the substances classified as fuel must necessarily contain one or several of the combustible elements: carbon, hydrogen, sulphur, etc. In the process of combustion, the chemical energy of fuel is converted into heat energy. To utilize the energy of fuel in most usable form, it is required to transform the fuel from its one state to another, i.e. from solid to liquid or gaseous state, liquid to gaseous state, or from its chemical energy to some other form of energy via single or many stages. In this way, the energy of fuels can be utilized more effectively and efficiently for various purposes.

The main raw materials for the chemical industry are fossil fuels; there three major types of fossil fuel are coal, oil, natural gas. These are the most important sources of energy. The major source of energy is oil, accounting for about 40 % of the total energy consumption, while coal and natural gas account for 26 and 21 % respectively.

Conversion of coal into gas (coal gasification) and production of liquid fuels from both coal gas and natural gas is technically possible on a large scale. A lot of energy is used in the chemical industry; the amount of energy used is of same order as the quantity of hydrocarbon used as feedstock. Fuel is used in direct heaters and furnaces for heating process steams, and for generation of steam and electricity, the most important utilities.

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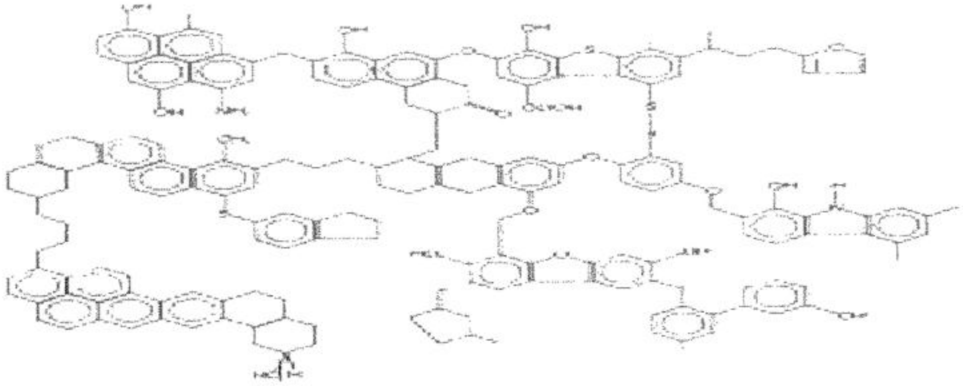
### Composition of Fossil Fuel

All three fossil fuels (coal, petroleum, natural gas) mainly consist of H and C, while also a small amount of hetero – atom like N, O, S, and metals are present. A characteristic feature of hydrocarbons is the C/H ratio. The relative amount of carbon in coal is much larger than in crude oil. Methane ($CH_4$) has the lowest C/H ratio of all hydrocarbons. The ratio for natural gas is very similar to that of methane

## Coal

Coal is composed primarily of carbon along with variable quantities of other elements, chiefly hydrogen, sulfur, oxygen, and nitrogen.

Throughout history, coal has been used as an energy resource, primarily burned for the production of electricity and/or heat, and is also used for industrial purposes, such as refining metals. Coal is the largest source of energy for the generation of electricity worldwide, as well as one of the largest worldwide anthropogenic sources of carbon dioxide releases. In 1999, world gross carbon dioxide emissions from coal usage were 8,666 million tons of carbon dioxide. In 2011, world gross emissions from coal usage were 14,416 million tons. Coal-fired electric power generation emits around 2,000 pounds of carbon dioxide for every megawatt-hour generated, which is almost double the approximately 1100 pounds of carbon dioxide released by a natural gas-fired electric plant per megawatt-hour generated.



Example chemical structure of coal

## Coal gasification

الغاز الفحمي

Coal gasification can be used to produce syngas, a mixture of carbon monoxide (CO) and hydrogen ($H_2$) gas. Often syngas is used to fire gas turbines to produce electricity, but the versatility of syngas also allows it to be converted into transportation fuels, such as gasoline and diesel, through the Fischer-Tropsch process; alternatively, syngas can be converted into methanol, which can be blended into fuel directly or converted to gasoline via the methanol to gasoline process,the hydrogen obtained from gasification can be used for various purposes, such as powering a hydrogen economy, making ammonia, or upgrading fossil fuels.

تعددية الاستعمال

بدلا من

مزجه

ترقيه

During gasification, the coal is mixed with oxygen and steam while also being heated and pressurized. During the reaction, oxygen and water molecules oxidize the coal into carbon monoxide (CO), while also releasing hydrogen gas ($H_2$). This process has been conducted in both underground coal mines and in the production of town gas.

3

$C \text{ (as Coal)} + H_2O \rightarrow H_2 + CO$

$C \text{ (as Coal)} + CO_2 \rightarrow 2CO$

$2C + O_2 \rightarrow CO_2$

$C + 2H_2 \rightarrow CH_4$

$CO + O_2 \rightarrow 2CO_2$

$CO + H_2O \rightarrow CO_2 + H_2$

In the past, coal was converted to make coal gas (town gas), which was piped to customers to burn for illumination, heating, and cooking.

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## Natural gas

Natural gas is a fossil fuel formed when layers of buried plants, gases, and animals are exposed to intense heat and pressure over thousands of years. Natural gas is a hydrocarbon gas mixture consisting primarily of methane, but commonly includes varying amounts of other higher alkanes and even a lesser percentage of carbon dioxide, nitrogen, and hydrogen sulfide. Natural gas is an energy source often used for heating, cooking, and electricity generation. It is also used as fuel for vehicles and as a chemical feedstock in the manufacture of plastics and other commercially important organic chemicals.

Natural gas can be "associated" (found in oil fields), or "non-associated" (isolated in natural gas fields), and is also found in coal beds (as coalbed methane). It sometimes contains a significant amount of ethane, propane, butane, and pentane—heavier hydrocarbons removed for commercial use prior to the methane being sold as a consumer fuel or chemical plant feedstock. Non-hydrocarbons such as carbon dioxide, nitrogen, helium (rarely), and hydrogen sulfide must also be removed before the natural gas can be transported.

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Landfill gas cannot be distributed through utility natural gas pipelines unless it is cleaned up to less than 3 per cent $CO_2$, and a few parts per million $H_2S$, because $CO_2$ and $H_2S$ corrode the pipelines.

$H_2S$ is often removed from natural gas by absorption to the liquid phase using alkanolamines like mono-ethanol amine (MEA) or di-isopropanolamine (DIPA).

$$\begin{tikzcd} \text{Natural gas} + \underset{\text{MEA}}{HO\text{-}CH_2\text{-}CH_2\text{-}NH_2} \arrow[r, "\text{absorption}"] & \text{Natural gas} + (RNH_2)_2S \arrow[l, bend left, "\text{Stripping Tower } (H_2O)"] \end{tikzcd}$$

Advantages of these amines are their high solubility in water and low volatility. Furthermore, their reaction with $H_2S$ is much faster than with $CO_2$ so that in case the gas to be treated contains both $H_2S$ and $CO_2$ the amount of absorbed $CO_2$ can be limited by choosing appropriate condition.

Natural gas can be used to produce hydrogen, with one common method being the hydrogen reformer. Hydrogen has many applications: it is a primary feedstock for the chemical industry, a hydrogenating agent, an important commodity for oil refineries, and the fuel source in hydrogen vehicles.

## Petroleum

Petroleum is a naturally occurring, yellow-to-black liquid found in geologic formations تحت beneath the Earth's surface, which is commonly refined into various types of fuels. It consists of hydrocarbons of various molecular weights and other liquid organic compounds. The name petroleum covers both naturally occurring unprocessed crude oil and petroleum products that are made up of refined crude oil. It is refined and separated, most easily by distillation, into a large number of consumer products, from gasoline (petrol) and kerosene to asphalt and chemical reagents used to make plastics and pharmaceuticals. Petroleum is used in manufacturing a wide variety of materials, and it is estimated that the world consumes about 90 million barrels each day.

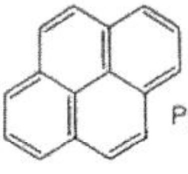
The use of fossil fuels, such as petroleum, has a negative impact on Earth's biosphere, releasing pollutants and greenhouse gases into the air and damaging ecosystems through events such as oil spills.

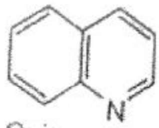
النفط [illegible]

## Composition

Petroleum includes only crude oil, but in common usage it includes all liquid, gaseous, and solid hydrocarbons. Under surface pressure and temperature conditions, lighter hydrocarbons methane, ethane, propane and butane occur as gases, while pentane and heavier ones are in the form of liquids or solids. However, in an underground oil reservoir the proportions of gas, liquid, and solid depend on subsurface conditions and on the phase diagram of the petroleum mixture.

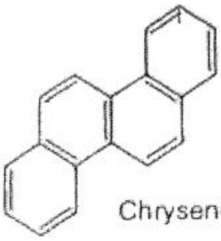
The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties, like color and viscosity.

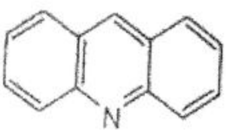

Pyrene



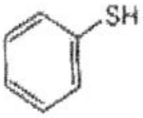
Quinolines

Alkylcyclopentanes

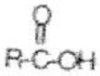

Chrysene



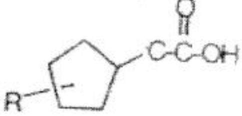
Acridines



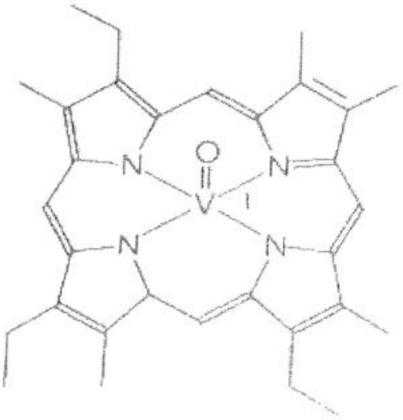
Aromatic

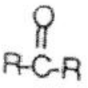

$R-\overset{O}{\overset{\|}{C}}-OH$

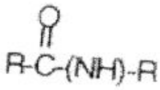
Aliphatic carboxylic acids



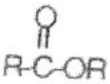
Monocyclic naphthenic acids




$R-\overset{O}{\overset{\|}{C}}-R$


$R-\overset{O}{\overset{\|}{C}}-(NH)-R$

Ketones


$R-\overset{O}{\overset{\|}{C}}-OR$

VO-ethioporphyrin I (VO-Etio-I)

Esters

Due to its high energy density, easy transportability and relative abundance, oil has become the world's most important source of energy since the mid-1950s. Petroleum is also the raw material for many chemical products.

# Processes in the oil refinery

## 1- Physical processes

### 1.1 Desalting / Dehydration

Crude oil often contains water, inorganic salts, suspended solids and water soluble trace metals. These contaminants can cause corrosion, plugging and fouling of equipment poisoning of catalysts in catalytic processes. Therefore, the first step in the refining process is desalting and dehydration. This can be accomplished by adding hot water with added surfactant to extract the contaminants from the oil. Upon heating, the salts and other impurities dissolve into the water or attach to it. The oil and water phase are then separated in a tank. The desalted crude is drawn from the top and sent to the crude distillation tower.

### 1.2 Crude Distillation

Crude oil consists of thousands of different compounds, and as a consequence, it is impossible and undesirable to separate crude oil in chemically pure fractions. The central separation step in every oil refinery is distillation of the crude, which separates the various fractions according to their volatility. The crude oil feed is heated to about 620 K in a furnace. It is discharged to the distillation tower as a foaming stream. The distillation column typically is 4 m diameter and 20-30 m in high. The stripping columns, which may be 3 m high with a diameter of 1 m, serve to remove the more volatile components from the side streams.

## 2- Thermal Processes

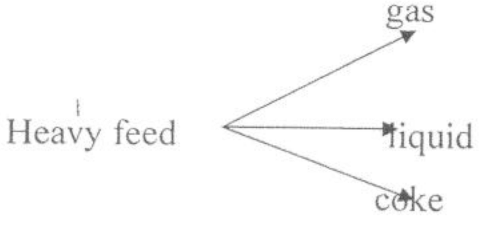
When heating a hydrocarbon to a sufficiently high temperature, thermal cracking takes place. Pyrolysis of coal yields a mixture of gases, liquids and solid residue (char). The same process is applied in oil conversion processes. Thermal processes are flexible but a disadvantage is that in principle large amount of low value products are formed.

### 2.1 Visbreaking

Visbreaking is a relatively mild thermal cracking process in which the viscosity of vacuum residue is reduced. The severity of the visbreaking process depends on temperature (710-760 K) and reaction time (1-8 min). Usually, less than 10% by weight of gasoline and lighter products are produced.

### 2.2 Delayed coking

Delayed coking is a thermal cracking process with long residence time, making it more severe than visbreaking. As a consequence, also solid residue (coke) is formed.



A good example is the production of coke for electrodes.

## 3. Catalytic processes

The most important catalytic processes in the oil refinery are fluid catalytic cracking (FCC), hydrotreating, hydrocracking, catalytic reforming and alkylation.

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The major part of the oil fractions is used in the transport sector, especially as diesel and gasoline. The octane number is a measure of quality of gasoline. Modern gasoline powered cars require a minimum octane number of 92.95 or 98. Gasoline with lower octane number can cause irreversible damage to the engine. The amount of gasoline obtained from simple distillation is too low. Therefore, either high octane number compounds have to be added or additional conversion steps such as catalytic cracking and hydrocracking, which convert heavy hydrocarbons into lighter ones, are required.

### 3.1 Catalysts Cracking

This process is needed to increase gasoline production. Feedtocks are heavy oil fractions, typically vacuum gas oil. Cracking is catalyzed by solid acids, which promote the rupture of C-C bonds. The crucial intermediates are carbocations (positively charged hydrocarbon ions). They are formed by action of the acid sites of the catalyst. In the following it will be described that they are "classical" carbenium ions and protonated cyclopropane derivatives.

Besides C-C bond cleavage a large number of order reactions occur.

- Isomerization
- Protonation, deprotonation

- Alkylation
- Polymerization
- Cyclization, condensation (eventually leading to coke formation)

## 3.2 Hydrotreating

Hydrotreating belongs to the class of conversions involving reaction with hydrogen. The term “hydrotreating” is limited to hydrogenolysis and hydrogenation reactions in which removed of “hetero-atoms” (especially S, N, and O) and some hydrogenation of double bonds and aromatic rings take place. Hydrogenation and hydrogenolysis both are reaction with hydrogen.

[illegible]

The major objectives of hydrotreating are protection of downstream catalysts (hetero-compounds often act as poisons), improvement of gasoline properties (odor, color, stability, corrosion), and protection of the environment.

# Corrosion

## Definition of Corrosion

Corrosion may be defined as a destructive phenomena, chemical or electrochemical, which can attack any metal or alloy through reaction by the surrounding environment and in extreme cases may cause structural failure. Corrosion can be also defined as the deterioration of material by reaction to its environment. The corrosion occurs because of the natural tendency for most metals to return to their natural state; e.g., iron in the presence of moist air will revert to its natural state, iron oxide. Metals can be corroded by the direct reaction of the metal to a chemical; e.g., zinc will react with dilute sulfuric acid, and magnesium will react with alcohols.

One of the fundamental factors in corrosion is the nature of the material. Materials are usually selected primarily for structural efficiency, and corrosion resistance is often a secondary consideration in design. The effective use of metals as materials of construction must be based on an understanding of their physical, mechanical, and chemical properties.

The nature and extent of corrosion depend on the metal and the environment. The important factors which may influence the corrosion process are:

a) Nature of the metal, nature of the environment and the corrosion products. b) Temperature. c) Concentration of electrolyte.

d) Electrode potential. f) Aeration. g) Agitation.

h) pH of the electrolyte.

## Theories of Corrosion

The corrosion of metals in aqueous solutions is an electrochemical process as established in the first half of the 19th century. Whitney gave the most acceptable electrochemical theory. The other theories such as acid theory, chemical attack theory, colloidal theory and biological theory were proved to form a part of electrochemical theory.

## Electrochemical theory of corrosion

Electrochemistry is a branch of chemistry dealing with relationships between electricity and chemical reactions. It involves oxidation and reduction (redox) reactions. Corrosion is an example of a type of electrochemical reaction, since a substance -oxidizing agent- oxidizes a metal in its environment. In the natural environment, oxygen gas is a good oxidizing agent. Most metals have lower reduction potentials than $O_2$; therefore they are easily oxidized in the presence of oxygen. Metals such as gold, silver and platinum are not so easily oxidized and are sometimes referred to as noble metals. One of the most familiar corrosion processes is the oxidation of iron (rust). Iron metal is spontaneously oxidized in the presence of $O_2$ and an aqueous electrolyte solution. Physical strains (scratches, dents, bends, etc…) present on the iron are more easily oxidized than other areas.

The result is that these regions are anodic (oxidation occurs) and simultaneously different areas are cathodic regions at which a reduction reaction (usually of $O_2$) occurs. The iron atom gives up two electrons to form the $Fe^{2+}$ ion:

$$Fe\,(s) \longrightarrow Fe^{2+}(aq) + 2e^- \quad \text{(anodic)}$$

The electrons that are released flow through the iron metal to the cathodic region where they react with oxygen:

$$O_2\,(g) + 2H_2O\,(l) + 4e^- \longrightarrow 4OH^-\,(aq) \quad \text{(cathodic)}$$

These two half reactions together give the overall reaction:

$$Fe\,(s) + 1/2O_2\,(g) + H_2O\,(l) \longrightarrow Fe^{2+}\,(aq) + 2OH^-\,(aq)$$

Common experience with this process (e.g., car fenders) tends to show that $Fe^{2+}$ is eventually oxidized further to $Fe^{3+}$, in the compound iron (III) oxide (rust):

$$4Fe^{2+}\,(aq) + O_2\,(g) + 4H_2O\,(l) \longrightarrow 2Fe_2O_3\,(s, \text{red colour}) + 8H^+\,(aq)$$

## Conditions necessary for corrosion

Electrochemical corrosion is the most important classification of corrosion. Four conditions must exist before electrochemical corrosion can proceed:

1- There must be something that corrodes (the metal anode).

2- There must be a cathode.

3- There must be continuous conductive liquid path (electrolyte and salt or other contaminations).

4- There must be a conductor to carry the flow of electrons from the anode to the cathode.

The elimination of any one of the four conditions will stop corrosion.

# Types of Corrosion

| Type | Characteristic | Examples |
|---|---|---|
| 1- General or uniform corrosion | All areas of the metal corrode at the same (or similar) rate<br>معدل | Oxidation and tarnishing; active dissolution in acids<br>تشوه<br>ذوبان<br>تآكل ذوبان |
| 2- Localized | Certain areas of the metal surface corrode at higher rates than others due to 'heterogeneities' in the metal, the environment or in the geometry of the structure as a whole.<br>تشابه | Crevice corrosion; filiform corrosion.<br>تآكل خيطي الشكل<br>فاصل |
| 3- Pitting<br>تنقر [illegible] | Highly localized attack at specific areas resulting in small pits that penetrate into the metal and may lead to perforation<br>اختراق<br>انثقاب | Pitting of passive metals such as the stainless steels, aluminum alloys |
| 4- Selective dissolution<br>الاذابة الانتقائية | One component of an alloy (usually the most active) is selectively removed from an alloy.<br>كسر | Dezincification; dealuminification<br>تعرية |
| 5-Conjoint action of corrosion and a mechanical factor<br>التأثير المشترك للتآكل والعامل الميكانيكي | Localized attack or fracture due to the synergistic action of a mechanical factor and corrosion<br>تعاون | Erosion – corrosion, cavitation damage<br>ضرر تجويفي |

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## The Consequences of corrosion

عواقب التآكل [illegible]

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarized as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown.

2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).

3. Loss of time in availability of profile-making industrial equipment.

4. Reduced value of goods due to deterioration of appearance.

5. Contamination of fluids in vessels and pipes.

6. Perforation of vessels and pipes allowing escape of their contents and possible harm to environment.

7. Loss of technically important surface properties of a metallic component. For example a leaky domestic radiator can cause expensive damage

8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.

9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

نفقة

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## Methods of Corrosion Protection

There are several ways that we use to try to control corrosion:

1- Protective Coatings 2- Inhibitors 3- Material Selection 4- Design
5- Cathodic Protection 6- Control of the Environment
7- Dehumidification

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طلاء، دهان

## Protective Coatings

This can be sub-divided into two main groups:

(a) Coating the metal, in order to interpose a corrosion resistant coating between metal and environment. The coating may consist of:

(i) another metal, e.g. zinc or tin coatings on steel,
(ii) a protective coating derived from the metal itself, e.g. aluminium oxide on "anodised" aluminium,
(iii) organic coatings, such as resins, plastics, paints, oils and greases.

The action of protective coatings is often more complex than simply providing a barrier between metal and environment. Paints may contain a corrosion inhibitor : zinc coating in iron or steel confers cathodic protection.

(b) Alloying the metal to produce a more corrosion resistant alloy, e.g. stainless steel, in which ordinary steel is alloyed with chromium and nickel. Stainless steel is protected by an invisibly thin, naturally formed film of chromium sesquioxide $Cr_2O_3$.

## Corrosion inhibitor

A corrosion inhibitor is a substance when added in a small concentration to an environment reduces the corrosion rate of a metal exposed to that environment. Inhibitors often play an important role in the oil extraction and processing industries where they have always been considered to be the first line of defence against corrosion.

### Anodic inhibitors

تكوين غشاء شديد مثل اكسيد واقي

Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors.

## Cathodic inhibitors

ابطاء تفاعل الكاثود [illegible]

Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface.

ترسيب انتقائي [illegible]
للحد من انتشار الانواع

## Organic Coating

Coating of inert organic materials like paints and lacquers on metallic surface to protect the metal usually thickness of the organic coating is less than 0.4 mm thickness.

The functions of organic coating are:

i- The organic coating serves as a barrier between the metal surface and corrosive environment.

ii- The pigment or drying oils present in the paint often exert and inhibitive action by electrochemical and other means.

There are certain requirements to have a good organic coating they are:

i- The organic coating should adhere tenaciously to the metal surface and should improve its physical appearance.

ii- The film formed should be uniform, continuous and act as a barrier to air and water.

iii- Should have reasonably long life.

iv- Should easily available, low cost, easy and properly applicable.

The performance of paint depends on the technique employed during application method.

The application of organic coating involves following steps

a- Surface preparation : it includes degreasing the surface and removing rust scale from it.

b- Priming : this is the first coat of primer like phosphate coating which must strongly adhere to the surface so that painting can properly done.

c- **Filling:** Fillers like nitrocellulose epoxides etc. are applied on well-dried surface in order to improve external appearance.

d- **Sanding:** The roughness and irregularities on the surface are smoothened by means of emery paper.

e- Final finishing coat of organic paints of two or three coat.

Organic coating usually applied such as brushing, spraying, dipping etc. Break of organic coating causes severe corrosion.

## Types Of Corrosion

**1.** Dry or chemical corrosion

**2.** Wet or electrochemical corrosion

## Dry Corrosion

This type of corrosion occurs by direct chemical attack of atmospheric gases like $O_2$ , halogens, hydrogen sulphide etc. on the metal surface. it is further of following types:

(a) Corrosion by $O_2$ or oxidation corrosion.

(b) Corrosion by other gases.

## Oxidation Corrosion

It is due to chemical attack of $O_2$ on the metal resulting the formation of metal oxide layer as:

- $2M + nO_2 \text{--------}\rightarrow 2MO_2$ (metal oxide)

This theory is called Wagner's Theory

**Nature of Metal oxide layer :**

(1) Stable: It acts as a barrier between metal and $O_2$, So prevents further corrosion.

(2) Unstable: It decomposes back to metal and $O_2$. Ag, Au and Pt are protected by this manner.

(3)Volatile: Layer volatiles and metal exposed for further corrosion.

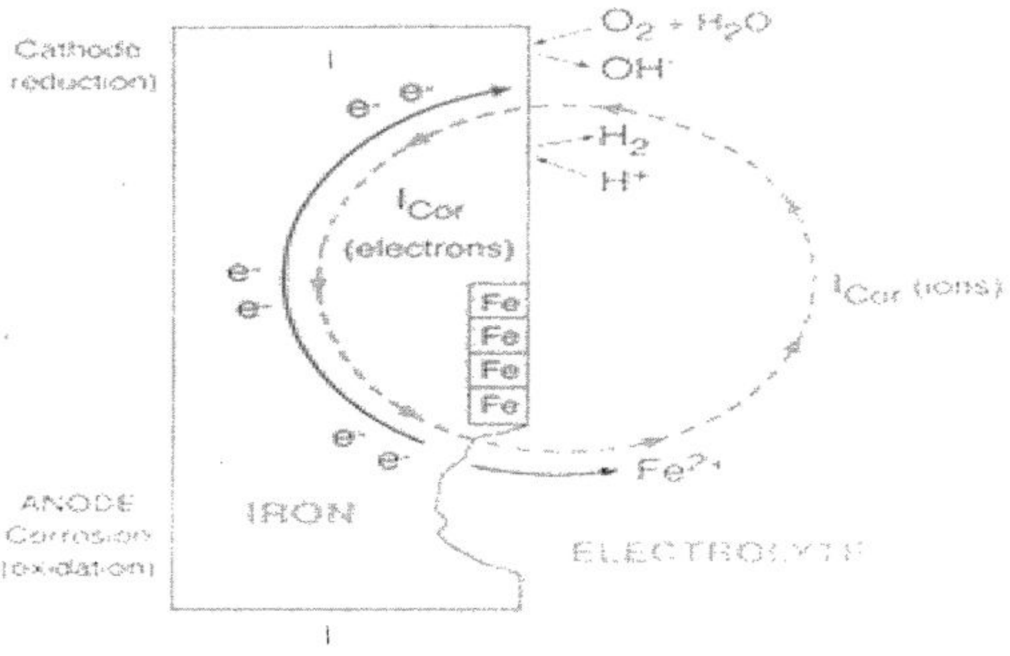
(4) Porous: Corrosion occur through pores and continues till entire metal gets corroded.

**Corrosion By Other Gases**

Corrosion is also caused by some other gases like $Cl_2$ ,$H_2S$, $SO_2$ etc. This type of corrosion depends on chemical affinity between metal and gas.

**Wet Corrosion**

This type of corrosion occurs when a liquid medium is involved. One part behaves as anode and undergoes oxidation and other part acts as cathode and undergoes reduction. Liquid medium involved acts as *electrolyte.* It is further of two types:



**Factors Affecting Rate Of Corrosion:**

Several factors affecting the rate of the corrosion, which can be divided into two parts

1. Factors affecting on metal (related to the metal)
2. Factors affecting on corrosive environment.

1- Nature of the metal: The tendency of the metal to undergo corrosion is mainly dependent on the nature of the metal. In general the metal with lower electrode potential have more reactive and more susceptible for corrosion and metal with high electrode potential are less reactive and less susceptible for corrosion for e. g.: metals like K, Na, Mg, Zn etc have low electrode potential are undergo corrosion very easily, whereas noble metals like Ag, Au, Pt have higher electrode potential, their corrosion rate are negligible but there are few exception for this general trend as some metals show the property of passivity like Al, Cr, Ti, Ta etc.

2. Surface state of the metal or nature of the corrosion product: The corrosion product is usually the oxide of the metal; the nature of the product determines the rate of further corrosion process. If the oxide layer which forms on the surface, is stoichiometric, highly insoluble and non-porous in nature with low ionic and electronic conductivity then that type of products layer effectively prevents further corrosion, which acts as a protective film. For e g : Al, Cr, Ti develop such a layer on their surface and become passive to corrosion and some metal like Ta, Zr and Mo not only forms such a protective layers but are capable of self-repairing oxide films when it is damaged. If the oxide layer forms on the metal surface is non-stochiometric, soluble, unstable and porous in nature and have an appreciable conductivity, they cannot control corrosion on the metal surface for egs: oxide layer formed on metals like Zn, Fe, Mg etc.

3. Anodic and Cathodic area:

The rate of the corrosion is greatly influenced by the relative sizes of cathodic and anodic areas. If the metal has smaller the anodic area and larger the cathodic area exposed to corrosive atmosphere, more intense and faster is the corrosion occurring at anodic area because at anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed. When anode is smaller and cathode region is larger all the liberated electrons at anode are rapidly consumed. This process makes the anodic reaction to takes place at its maximum rate thus increasing the corrosion rate. If the cathode is smaller and reverse process takes place decrease rate of corrosion.

For egs: If tin (Sn) coated on iron (Fe) and in that some area are not covered or some pin holes are left, there forms smaller anodic area and larger cathodic area because tin is cathodic with respect to iron so intense localized corrosion takes place. On the other hand if Zn coated to Fe then if there are some pin holes are there creates larger anodic area and smaller cathodic area because Fe is cathodic with respect to zinc so that rate of corrosion is very less.

4. Hydrogen over voltage:

A metal with low hydrogen over voltage on its surface is more susceptible for corrosion. When the cathodic reaction is hydrogen evolution type with low hydrogen over voltage, liberation of $H_2$ gas is more easier so that cathodic reaction is very fast, that makes anodic reaction faster hence overall corrosion process is very fast. If the $H_2$ over voltage is high so cathodic reaction is slow hence corrosion reaction also slower.

**Factors affecting on corrosive environment.**

1- Temperature: Rate of corrosion increases with increase in temperature.

2- Moisture: More the moisture, more is the rate of corrosion.

3- pH Value: Lesser the pH i.e. acidic conditions, more is corrosion.

4- Nature of electrolyte: Presence of salts in the electrolyte increases the rate of corrosion.

5- Presence of impurities in atmosphere: Impurities increase the rate of corrosion. Corrosion is more in industrial areas and sea. This is because of presence of gases like $CO_2$, $H_2S$, $SO_2$,

## Water treatment for industrial processes

Industries that produce metals, wood, paper, chemicals, gasoline, oils, and most other products all use water in some part of their production process. Industry depends on water, much like agriculture and domestic households. Industrial reliance (اعتماد) on water makes it essential to preserve water in every aspect possible and make sure water pollution is kept at minimal levels.

Water is a transparent fluid which forms the world's streams, lakes, oceans and rain, and is the major constituent of the fluids of living things. As a chemical compound, a water molecule contains one oxygen and two hydrogen atoms that are connected by covalent bonds. Water is a liquid at standard ambient temperature and pressure, but it often co-exists on earth with its solid state, ice; and gaseous state, steam (water vapor). It also exists as snow, fog, dew and cloud. Water covers 71% of the Earth's surface. It is vital for all known forms of life.

### Water Use in Industry

In industrial facilities, water is used in a wide range of activities. The value of water as a utility is illustrated by the following common uses:

- Incorporation in the final product.
  - Acetylene industry

    $CaO + 3C \longrightarrow CaC_2 + CO_2$

    $CaC_2 + 2H_2O \longrightarrow HC \equiv CH + Ca(OH)_2$

  - Also in H2SO4 industry

    $SO_3 + H_2O \longrightarrow H_2SO4$

- Washing or rinsing of raw materials, intermediates, or final products.
- Preparation of solvents or slurries.
- Cleaning of equipment.
- Removing or providing heat.
- Meeting hygienic and domestic needs.
- Generation of electric

## Water as Solvent

Pure water ($H_2O$) is colorless, tasteless, and odorless. Because water becomes contaminated by the substances with which it comes into contact, it is not available for use in its pure state. To some degree, water can dissolve every naturally occurring substance on the earth. Because of this property, water has been termed a "universal solvent." اثر 2 معنى

## Water Impurities

Water from surface sources is often contaminated by microbes; whereas groundwater is normally safer, but even groundwater can be contaminated by harmful chemicals from human activities or from the natural environment. Water impurities include dissolved and suspended solids. Calcium bicarbonate is a soluble salt. A solution of calcium bicarbonate is clear, because the calcium and bicarbonate are present as atomic sized ions which are not large enough to reflect light. Some soluble minerals impart a color to the solution. Soluble iron salts produce pale yellow or green solutions; some copper salts form intensely blue solutions. Although colored, these solutions are clear. Suspended solids are substances that are not completely soluble in water and are present as particles. These particles usually impart a visible turbidity to the water. Dissolved and suspended solids are present in most surface waters. Seawater is very high in soluble sodium chloride; suspended sand and silt make it slightly cloudy.

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بكثرة

As water moves through soil and rock, it dissolves very small amounts of minerals and holds them in solution. Calcium and magnesium dissolved in water are the two most common minerals that make water "hard." The degree of hardness becomes greater as the calcium and magnesium content increases and is related to the concentration of multivalent cations dissolved in the water as shown in table below.

| Classification | mg/l or ppm Ca$^{+2}$, Mg$^{+2}$) | grains/gal |
|---|---|---|
| Soft | 0 - 17.1 | 0 - 1 |
| Slightly hard | 17.1 - 60 | 1 - 3.5 |
| Moderately hard | 60 - 120 | 3.5 - 7.0 |
| Hard | 120 - 180 | 7.0 - 10.5 |
| Very Hard | 180 & over | 10.5 & over |

## Water Hardness

تسلل

Hard water is formed when water percolates through deposits of calcium and magnesium-containing minerals such as limestone, chalk and dolomite. Hard drinking water is generally not harmful to one's health, but can pose serious problems in industrial settings, where water hardness is monitored to avoid costly breakdowns in boilers, cooling towers, and other equipment that handles water. In domestic settings, hard water is often indicated by a lack of suds formation when soap is agitated in water, and by the formation of limescale in kettles and water heaters. There are two type of hardness:

### - Temporary hardness

Temporary hardness is a type of water hardness caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). When dissolved, these minerals yield calcium and magnesium cations ($Ca^{2+}$, $Mg^{2+}$) and carbonate and bicarbonate anions ($CO_3^{2-}$, $HCO_3^{-}$). The presence of the metal cations makes the water hard.

### Permanent hardness

2- Permanent hardness is hardness (mineral content) that cannot be removed by boiling. When this is the case, it is usually caused by the presence of calcium sulfate and/or magnesium sulfates or chlorides compounds in the water, which do not precipitate out as the temperature increases. Ions causing permanent hardness of water can be removed using a water softener, or ion exchange column.

Total Permanent Hardness = Calcium Hardness + Magnesium Hardness

The calcium and magnesium hardness is the concentration of calcium and magnesium ions expressed as equivalent of calcium carbonate.

## Disadvantage of hard water

1- With hard water, soap solutions form a white precipitate instead of producing lather, because the 2+ ions destroy the surfactant properties of the soap by forming a solid precipitate (the soap scum). A major component of such scum is calcium stearate, which arises from sodium stearate, the main component of soap:

$$2\ C_{17}H_{35}COO^{-}\ (aq) + Ca^{2+}\ (aq) \rightarrow (C_{17}H_{35}COO)_2Ca\ (s)$$

Hardness can thus be defined as the soap-consuming capacity of a water sample, or the capacity of precipitation of soap as a characteristic property of water that prevents the lathering of soap.

2- Hard water also forms deposits that block plumbing. These deposits, called "scale", are composed mainly of calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$, and calcium sulfate ($CaSO_4$). Calcium and magnesium carbonates tend تميل to be deposited as off-white solids on the inside surfaces of pipes and heat exchangers. This precipitation (formation of an insoluble solid) is

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principally caused by thermal decomposition of bicarbonate ions but also happens in cases where the carbonate ion is at saturation concentration. The resulting build-up of scale restricts the flow of water in pipes. يعيق يضعف تلف زيادة [illegible]

3- In boilers, the deposits impair the flow of heat into water, reducing the heating efficiency, and allowing the metal boiler components to overheat. The presence of ions in an electrolyte, in this case, hard water, can also lead to galvanic corrosion, in which one metal will preferentially corrode when in contact with another type of metal, when both are in contact with an electrolyte.

## Water testing

1- Testing for halides: the addition of $AgNO_3$ give white precipitate with $Cl^-$, cream ppt with $Br^-$ and pule yellow with $I^-$.

$$Ag^+_{(aq)} + X^-_{(aq)} \longrightarrow AgX_{(s)}$$

2- Testing for sulphate: using $BaCl_2$, sulphate ions give white ppt of $BaSO_4$.

3- Hardness of water can be calculated by titration with EDTA using EBT as indicator. [illegible]

4- Conductivity measurement for soft water equal to $1\times 10^{-6}$ mho.

5- Measurement of pH: pH for soft water equal to 7.

## Removal of water hardness

A- Removal of temporary hardness

1- By boiling: Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling. The insoluble carbonate can be removed by filtration.

$$Ca(HCO_3)_2 \xrightarrow{heat} CaCO_3 + CO_2 + H_2O$$

2- Clark's method: this process is used on a commercial scale. Calculated amount of lime (calcium hydroxide) [$Ca(OH)_2$] is added.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + H_2$$

B- Removal of permanent hardness

1- Washing soda method

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + NaCl$$

2- Ion exchange

In this method sodium zeolite is used as ion exchanger which is packed into the tank from the top. Hard water inters the bottom of the tank and slow rises through Na- zeolite layer. Na- zeolite is converted to Ca or Mg- zeolite. Water obtained is called deionized water. The resin requires regeneration.

$$\left.\begin{matrix}Ca\\ Mg\end{matrix}\right] \begin{matrix}(HCO_3)_2\\ SO_4\\ Cl_2\end{matrix} + Na_2Z \longrightarrow \left.\begin{matrix}Ca\\ Mg\end{matrix}\right] Z + Na_2 \left]\begin{matrix}(HCO_3)_2\\ SO_4\\ Cl_2\end{matrix}\right.$$

Regeneration by saturated NaCl

$Z=Al_2Si_2O_8.XH_2O$

$NaZ= NaAl_2Si_2O_8.XH_2O$

## Water purification techniques

Water purification is the process of removing undesirable chemicals, biological contaminants, suspended solids and gases from contaminated water. The goal is to produce water fit for a specific purpose. Most water is disinfected for human consumption (drinking water), but water purification may also be designed for a variety of other purposes, including fulfilling the requirements of medical, pharmacological, chemical and industrial applications. The methods used include physical processes such as filtration, sedimentation, and distillation; biological processes such as slow sand filters or biologically active carbon; chemical processes such as flocculation and chlorination and the use of electromagnetic radiation such as ultraviolet light.

### 1- Coagulation and flocculation

One of the first steps in a conventional water purification process is the addition of chemicals to assist in the removal of particles suspended in water. Particles can be inorganic such as clay and silt or organic such as algae, bacteria, viruses and natural organic matter. Inorganic and organic particles contribute to the turbidity and color of water. Chemical substances like aluminium sulphate (alum) and ferric sulphate were added to water at basic medium to prevent corrosion.

$$Al_2(SO_4)_3.18H_2O + 3Ca(HCO_3)_2 \longrightarrow CaSO_4 + 2Al(OH)_3 + 6CO_2 + 18H_2O$$

$$Fe_2(SO_4)_3.9H_2O + 3Ca(HCO_3)_2 \longrightarrow 3CaSO_4 + 2Fe(OH)_3 + 6CO_2 + 9H_2O$$

Flocculation is assisted by the addition of a polyelectrolyte several minutes after the alum is added to assist in the growth of particles (floc) to larger sizes. Particles in suspension are removed by subsequent processes of sedimentation and filtration.

2- Sedimentation process

Sedimentation processes a physical water treatment process using gravity to remove suspended solids from water. It is used to remove many particles including clay and silt based turbidity, natural organic matter, and other associated impurities. Sedimentation might occur in tanks of other shapes.

3- Filtration

It is used to remove solid substances by using:

1- Slow sand filters for drinking water.
2- Rapid sand filters for industrial water.
3- Granular activated carbon filters: in this type activated carbon adsorbs many toxic compounds, organic contaminates, taste and odor.

4- Ion Exchange: Ion exchange processes are used to remove inorganic contaminants if they cannot be removed adequately by filtration or sedimentation. Ion exchange can be used to treat hard water. It can also be used to remove arsenic, chromium, excess fluoride, nitrates, radium, and uranium.

5- Absorption: Organic contaminants, unwanted coloring, and taste-and-odor-causing compounds can stick to the surface of granular or powder activated carbon and are thus removed from the drinking water.

6- **Final Water Treatment** (water sterilization)

a- Boiling water is heated hot enough hot enough and long enough to inactivated or killed microorganisms that live in water.

b- Distillation involves boiling the water to produce water vapor then it condensed as a liquid 99.9% of pure water can be obtained by distillation.

c- Chlorine injection system to avoid the taste, odor and chemicals. The chlorination system consist of a tank filled with liquid chlorine (other types as tablets). But chlorine add an undesirable taste and chemical negative effects on body.

d- Ozone water sterilizers

Ozone is the most effective water sterilizing method. The technology employed generates a supply of ozone ($O_3$) electrically. The ozone is highly effective in decreasing pathogens and when it work is completed breaks down in $O_2$ which enhances the water's taste.

e- Ultra – violet water sterilizers

UV water sterilizers operate by generation UV light, which kill bacteria and viruses in water by passing through sterilizers. The treated water is completely unchanged as to taste, odor and mineral contents.

f- Reverse osmosis: it is a mechanical process pressure is applied to an impure water to force pure water through a semi permeable membrane.

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## Boilers water treatment

As water evaporates in the boiler, the concentration of sodium carbonate increases in the boiler. Sodium carbonate is used in softening of water by lime soda process, due to this some sodium carbonate may be left behind in the water. As the concentration of sodium carbonate increases, it undergoes hydrolysis to form sodium hydroxide.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

The presence of sodium hydroxide makes the water alkaline. This alkaline water enters minute cracks present in the inner walls of the boiler by capillary action. Inside the cracks, the water evaporates and amount of hydroxide keeps on increasing progressively. This sodium hydroxide attacks the surrounding material and the dissolves the iron of the boiler as sodium ferrate ($Na_2FeO_2$). This causes embrittlement of boiler parts like rivets, bends and joints, which are under stress.

Caustic embrittlement is the phenomenon in which the material of a boiler becomes brittle due to the accumulation of caustic substances. Caustic embrittlement can be prevented through several methods, including:

1- Controlling the temperature and potential.
2- Controlling the stress levels and hardness.
3- Use of materials that do not crack when used in given environments
4- Avoiding alkali where necessary.
5- Replacing sodium carbonates with sodium sulphates as softening reagents
6- Adding lignin, tannin or sodium sulphate that blocks hairline cracks as well as preventing infiltration of sodium hydroxide into the areas

# Boiler Operation

Boiler: A boiler is a closed vessel in which water is heated, steam is generated, superheated or any combination thereof under pressure or vacuum by the direct application of heat from combustible fuels or electricity. The steam produced is used for:

هو وعاء مغلق يتم تسخين الماء [illegible]
[illegible]

(a) Producing mechanical work by expanding it in steam engine or steam turbine.
(b) Heating the residential and industrial buildings
(c) Performing certain processes in the sugar mills, chemical and textile industries.

يتميز
[illegible]

Usually boilers are coal or oil fired. A boiler should fulfill the following requirements:

[illegible]

(1) Safety. The boiler should be safe under operating conditions.
(2) Accessibility. The various parts of the boiler should be accessible for repair and maintenance.
(3) Capacity. The boiler should be capable of supplying steam according to the requirements. [illegible]
(4) Efficiency. To permit efficient operation, the boiler should be able to absorb a maximum amount of heat produced due to burning of fuel in the furnace.
(5) It should be simple in construction and its maintenance cost should be low.
(6) Its initial cost should be low.
(7) The boiler should have no joints exposed to flames.
(8 ) The boiler should be capable of quick starting and loading.

## 1- Boiler Classifications

The boilers can be classified according to the following criteria.

**According to flow of water and hot gases:**

1. Water tube.
2. Fire tube.

In water tube boilers, water circulates through the tubes and hot products of combustion flow over these tubes. In fire tube boiler the hot products of combustion pass through the tubes, which are surrounded, by water. Fire tube boilers have low initial cost, and are more compacts. But they are more likely to explosion, water volume is large and due to poor circulation they cannot meet quickly the change in steam demand.

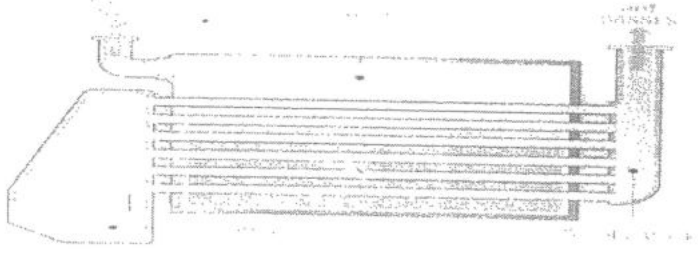
**According to position of furnace.**
(i) Internally fired (ii) Externally fired

**According to the position of principle axis.**
(*i*) Vertical (*ii*) Horizontal (*iii*) Inclined.

**According to steam pressure:**
(i) Low pressure (ii) Medium pressure (iii) Higher pressure

## 1-1 Fire-Tube Boiler

Operation of fire tube boiler is as simple as its construction. In fire tube boiler, the fuel is burnt inside a furnace. The hot gases produced in the furnace then passes through the fire tubes. The fire tubes are immersed in water inside the main vessel of the boiler. As the hot gases are passed through these tubes, the heat energy of the gasses is transferred to the water surrounds them. As a result steam is generated in the water and naturally comes up and is stored upon the water in the same vessel of fire tube boiler. This steam is then taken out from the steam outlet for utilizing for required purpose. The water is fed into the boiler through the feed water inlet. As shown in figure



Shape of fire-tube

## Advantages of Fire Tube Boiler

1) Compact in construction.

2) Fluctuation of steam demand can be met easily.

3) Cheaper than water tube boiler.

## Disadvantages of Fire Tube Boiler

1) Due to large water the required steam pressure rising time quite high.

2) Output steam pressure cannot be very high since the water and steam are kept in same vessel.

3) The steam received from fire tube boiler is not very dry.

4) In a fire tube boiler, the steam drum is always under pressure, so there may be a chance of huge explosion which resulting to severe accident.

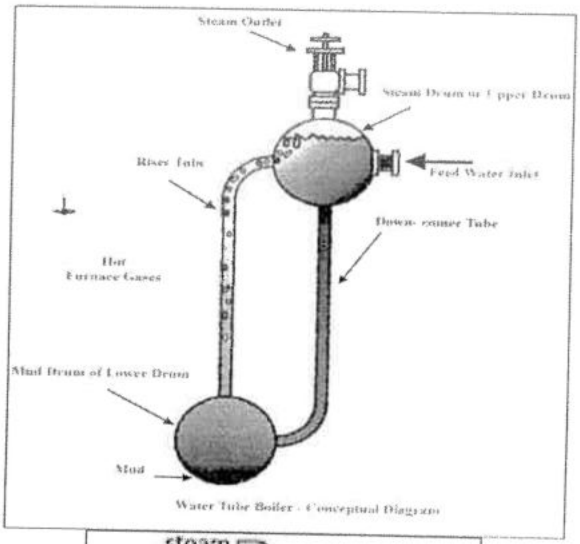
## 1-2 Water-tube boilers:

A water tube boiler is such kind of boiler where the water is heated inside tubes and the hot gasses surround them. This is the basic definition of water tube boiler. Actually this boiler is just opposite of fire tube boiler where hot gasses are passed through tubes which are surrounded by water.

## Working Principle of Water Tube Boiler

The working principle of water tube boiler is very interesting and simple. Let us draw a very basic diagram of water tube boiler. It consists of mainly two drums, one is upper drum called steam drum other is lower drum called mud drum. These upper drum and lower drum are connected with two tubes namely down-comer and riser tubes as shown in the picture. Water in the lower drum and in the riser connected to it, is heated and steam is produced in them which comes to the upper drums naturally. In the upper drum the steam is separated from water naturally and stored above the water surface.

steam outlet

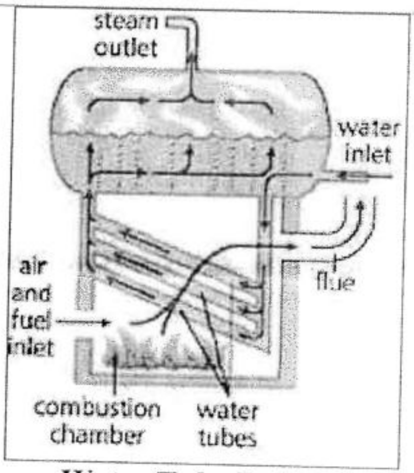


Riser tube

Feedwater inlet

Mud Drum of lower Drum

mud



Water Tube Boiler

## Advantages of Water Tube Boiler

There are many advantages of water tube boiler due to which these types of boiler are essentially used in large thermal power station.

1) Larger heating surface can be achieved by using more numbers of water tubes.

2) Due to convectional flow, movement of water is much faster than that of fire tube boiler, hence rate of heat transfer is high which results into higher efficiency.

3) Very high pressure in order of 140 kg/cm$^2$ can be obtained smoothly.

## 2- Industrial water tube boilers

The boilers are generally required in power station, chemical industries, paper industries, pharmaceutical industries and many others. Efficiency, reliability and cost are major factors in the design of industrial boilers. Boiler's capacity varies from of steam per hour.

## 3- Requirements of a Good Boiler

A good boiler must possess the following qualities:

1. The boiler should be capable to generate steam at the required pressure and quantity as quickly as possible with minimum fuel consumption.
2. The initial cost, installation cost and the maintenance cost should be as low as possible.
3. The boiler should be light in weight, and should occupy small floor area.
4. The boiler must be able to meet the fluctuating demands without pressure fluctuations.
5. All the parts of the boiler should be easily approachable for cleaning and inspection.
6. The boiler should have a minimum of joints to avoid leaks which may occur due to expansion and contraction.
7. The water and flue gas velocities should be high for high heat transfer rates with minimum pressure drop through the system.

## Pollution

Pollution is the introduction of contaminants into the natural environment that cause adverse change. Pollution can take the form of chemical substances or energy, such as noise, heat or light. Pollutants, the components of pollution, can be either foreign substances/energies or naturally occurring contaminants. Pollution is often classed as point source or nonpoint

## Forms of pollution

The major forms of pollution are listed below along with the particular contaminant relevant وثيق الصلة بالموضوع to each of them:

- Air pollution: the release of chemicals and particulates into the atmosphere. Common gaseous pollutants include carbon monoxide, sulfur dioxide, chlorofluorocarbons (CFCs) and nitrogen oxides produced by industry and motor vehicles. Photochemical ozone and smog are created as nitrogen oxides and hydrocarbons react to sunlight. Particulate matter, or fine dust is characterized by their micrometre size $PM_{10}$ to $PM_{2.5}$.
- Soil contamination occurs when chemicals are released by spill or underground leakage. Among the most significant soil contaminants are hydrocarbons, heavy metals, herbicides مبيدات الأعشاب, pesticides مبيدات حشرية and chlorinated hydrocarbons.
- Radioactive contamination, resulting from 20th century activities in atomic physics, such as nuclear power generation and nuclear weapons research, manufacture and deployment نشر.
- Thermal pollution, is a temperature change in natural water bodies caused by human influence الناجمة عن التأثير البشري , such as use of water as coolant in a power plant.
- Water pollution, by the discharge of wastewater from commercial and industrial waste (intentionally or through spills) into surface waters; discharges of untreated domestic sewage, and chemical contaminants, such as chlorine, from treated sewage; release of waste and contaminants into surface runoff flowing to surface waters (chemical fertilizers and pesticides) الأسمدة الكيماوية والمبيدات الحشرية.

## Industrial pollution

Industrial pollution is pollution which can be directly linked with industry, in contrast تباين to other pollution sources. The Industrial Revolution mechanized means of production, allowing for a much greater volume of production, and generating a corresponding increase in pollution. The problem was compounded اتفق، ضاعف by the use of fuels like coal, which is notoriously جهارًا، بطريقة علنية unclean, and a poor understanding of the causes and consequences of pollution.

There are a number of forms of industrial pollution. One of the most common is water pollution, caused by dumping إغراق السوق of industrial waste into waterways, ~~or~~ improper غير مناسب containment of waste, which causes leakage into groundwater and waterways. Industrial pollution can also impact تأثير، وقع تأثير air quality, and it can enter the soil, causing widespread environmental problems.

Industrial pollution hurts the environment in a range of ways, and it has a negative impact on human lives and health. Pollutants can kill animals and plants, imbalance ecosystems, degrade تتحلل air quality radically تتحلل نوعية الهواء بشكل جذري، damage buildings, and generally degrade quality of life.

## Types of water pollution

There are many types of water pollution because water comes from many sources. Here are a few types of water pollution:

1- Nutrients Pollution

Plant nutrients, such as phosphates and nitrates, enter the water through sewage صرف صحي , and livestock الماشية و and fertilizer runoff. Phosphates and nitrates are also found in industrial wastes// Though رغم أن these chemicals are natural, 80 percent of nitrates and 75 percent of phosphates in water are human-added. When there is too much nitrogen or phosphorus in a water supply, algae begin to develop. When algae blooms تزهر , the water can turn green and cloudy, feel slimy, and smell bad. This will make the water undrinkable, and even clog filters مرشحات تسد.

2- Heat can be a source of pollution in water. As the water temperature increases, the amount of dissolved oxygen decreases. Thermal pollution can be natural, in the case of hot springs and shallow ponds in the summertime البرك الضحلة في الصيف , or human-made, through the discharge of water that has been used to cool power plants or other industrial equipment. Fish and plants require certain temperatures and oxygen levels to survive, so thermal pollution often reduces the aquatic life diversity تنوع الحياة المائية in the water.

3- Oxygen Depleting المستنفدة

Water bodies المسطحات المائية have micro-organisms. These include aerobic and anaerobic organisms. When to much biodegradable matter (things that easily decay) end up in water, it encourages more microorganism growth, and they use up more oxygen in the water. If oxygen is depleted, aerobic organisms die, and anaerobic organism grow more to produce harmful toxins such as ammonia and sulfides.

4- Sediment is one of the most common sources of water pollution. Sediment consists of mineral or organic solid matter that is washed or blown في مهب from land into water sources. Sediment pollution is difficult to identify, because it comes from non-point sources, such as construction, agricultural and livestock operations, logging قطع الأشجار، و, flooding الفيضانات , and city runoff. Sediment can cause large problems, as it can clog municipal البلدية water systems, smother خنق aquatic life, and cause water to become increasingly turbid.

5- Hazardous and toxic chemicals are usually human-made materials that are not used or disposed of properly. Point sources of chemical pollution include industrial discharges and oil spills. Non-point غير المحددة sources of chemical pollution include runoff from paved roads الطرق المعبدة and pesticide runoff. Many people think industries produce the greatest amount of chemical pollution. But domestic and personal use of chemicals can significantly contribute to chemical pollution. Household cleaners, dyes, paints and solvents are also toxic. In fact, one drop of used motor oil can pollute 25 litres of water! And, people who use pesticides on their gardens and lawns المروج tend to use ten times more pesticide per acre فدان than a farmer would.

6- Radioactive pollutants include wastewater discharges from factories, hospitals and uranium mines، منجم . These pollutants can also come from natural isotopes, such as radon. Radioactive pollutants can be dangerous, and it takes many years until radioactive substances are no longer considered dangerous .

## Effects of water pollution

Water pollution is very harmful to humans, animals and water life. The effects can be catastrophic، فاجع , depending on the kind of chemicals, concentrations of the pollutants and where there are polluted. The effects of water pollution are varied and depend on what chemicals are dumped ملقاة مرمي and in which locations. Many water bodies near urban areas (cities and towns) are highly polluted. This is the result of both garbage القمامة dumped by individuals and dangerous chemicals legally or illegally dumped by manufacturing industries, health centers, schools and market places.

1- Death of aquatic (water) animals

The main problem caused by water pollution is that it kills life that depends on these water bodies المسطحات المائية .

2- Disruption of food-chains

Pollution disrupts the natural food chain as well. Pollutants such as lead and cadmium are eaten by tiny animals. Later, these animals are consumed by fish and shellfish, and the food chain continues to be disrupted at all higher levels.

3- Diseases

Eventually, humans are affected by this process as well. People can get diseases such as hepatitis by eating seafood that has been poisoned. In many poor nations, there is always outbreak outbreak of cholera and diseases as a result of poor drinking water treatment from contaminated waters.

تدمير الايكولوجية [illegible]

4- Destructionهدم of ecosystems

تعريف Ecosystems (the interaction of living things in a place, depending on each other for life) can be severely changed or destroyed by water pollution. Many areas are now being affected by careless human pollution, and this pollution is coming back to hurt humans in many ways.

[illegible]

## Liquid Waste (Sewage/Wastewater) Treatment

بالوعة حوض مغسلة

Wastewater (liquid waste) from flushing the toilet, bathing, washing sinks and general cleaning goes down the drain and into a pipe, which joins a larger sewer pipe under the road. The larger pipe also joins a major pipe that leads to the treatment center.

الأولى فحص [illegible] صحية [illegible]

1- STAGE ONE: SCREENING

Screening is first stage of the wastewater treatment process. Screening removes large objects like, diapers, nappies, sanitary items, cotton buds, face wipes and even broken bottles, bottle tops, plastics and rags that may block or damage equipment.

Special equipment is also used to remove grit that gets washed into the sewerأنبوبة مجاري .

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## 2- 2- STAGE TWO: PRIMARY TREATMENT

This involve the separation of organic solid matter (or human waste) from the wastewater. This is done by putting the wastewater into large settlement tanks for the solids to sink to the bottom of the tank. The settledثابت solids are called 'sludge'وحل لزج، راسب طيني . At the bottom of these circular tanks, large scrappers continuously scrape the floor of the tank and push the sludge towards the center where it is pumped away for further treatment. The rest of the water is then moved to the Secondary treatment.

يغوص

## 3- STAGE THREE: SECONDARY TREATMENT

The water, at this stage is put into large rectangular tanks. These are called aeration lanesممرات التهوية . Air is pumped into the water to encourage bacteria to breakdown the tiny bits of sludge that escaped the sludge scrapping process.

القطع

## 4- STAGE FOUR: FINAL TREATMENT

Next the 'almost' treated wastewater is passed through a settlement tank. Here, more sludge is formed at the bottom of the tank from the settling of the bacterial action. Again, the sludge is scrapped and collected for treatment. The water at this stage is almost free from harmless substances and chemicals. The water is allowed to flow over a wall where it is filtered through a bed of sand to remove any additional particles.

The filtered water is then released into the river.

*This description is not a standard for all treatment plants, but the principle is similar.

Now let us see some stunning ~~facts and disasters from water pollution~~ in recent time.

Troposphere 6-20 Stratosphere 50 km Mesosphere 85 km

Thermosphere 640 km.

**Air pollution** is the introduction of particulates, biological molecules, or other harmful materials into Earth's atmosphere, causing disease, death to humans, loss of breath, damage to other living organisms such as food crops, or the natural or built environment. Air pollution may come from anthropogenic or natural sources.

The atmosphere is a complex natural gaseous system that is essential to support life on planet Earth. Stratospheric ozone depletion due to air pollution has been recognized as a threat to human health as well as to the Earth's ecosystems.

Thermosphere
Mesosphere
Startosphere
Troposphere

## Pollutants

An air pollutant is a substance in the air that can have adverse effects on humans and the ecosystem. The substance can be solid particles, liquid droplets, or gases. A pollutant can be of natural origin or man-made. Pollutants are classified as primary or secondary. Primary pollutants are usually produced from a process, such as ash from a volcanic eruption. Other examples include carbon monoxidegas from motor vehicle exhaust, or the sulfur dioxide released from factories. Secondary pollutants are not emitted directly. Rather, they form in the air when primary pollutants react or interact. Ground level ozone is a prominent example of a secondary pollutant. Some pollutants may be both primary and secondary: they are both emitted directly and formed from other primary pollutants.

### Major primary pollutants produced by human activity include:

- Sulfur oxides ($SO_x$) - particularly sulfur dioxide, a chemical compound with the formula $SO_2$. $SO_2$ is produced by volcanoes and in various industrial processes. Coal and petroleum often contain sulfur compounds, and their combustion generates sulfur dioxide. Further oxidation of $SO_2$, usually in the presence of a catalyst such as $NO_2$, forms $H_2SO_4$, and thus acid rain. This is one of the causes for concern over the environmental impact of the use of these fuels as power sources. هذا احد اسباب القلق ازاء الاثر البيئي لاستخدام هذه الانواع من الوقود كمصادر للطاقة

- Nitrogen oxides ($NO_x$) - Nitrogen oxides, particularly nitrogen dioxide, are expelled طرد from high temperature combustion, and are also produced during thunderstorms by electric discharge. Nitrogen dioxide is a chemical compound with the formula $NO_2$. It is one of several nitrogen oxides. One of the most prominent بارز air pollutants, this reddish-brown بني محمر toxic gas has a characteristic مميزة sharp لاذعة, biting حادة odor.

- Carbon monoxide (CO) - CO is a colorless, odorless, toxic yet non-irritating gas. It is a product by incomplete combustion of fuel such as natural gas, coal or wood. Vehicular exhaust is a major source of carbon monoxide.

- Volatile organic compounds - VOCs are a well-known outdoor air pollutant. They are categorized صنفت as either methane ($CH_4$) or non-methane. Methane is an extremely efficient greenhouse gas which contributes to enhanced تعزيز global warming. The aromatic benzene, toluene and xylene are suspected carcinogens and may lead to leukemia with prolonged التعرض طويل exposure. 1,3-butadiene is another dangerous compound often associated with industrial use.

- Particulates, referred to atmospheric particulate matter, or fine particles, are tiny particles of solid or liquid suspended in a gas. In contrast, aerosol refers to combined particles and gas. Some particulates occur naturally, originating ناشئة from volcanoes, dust storms, forest and grassland fires, living vegetation, and sea spray. Human activities, such as the burning of fossil fuels in vehicles, power plants and various industrial processes also generate significant amounts of aerosols.

- Toxic metals, such as lead and mercury, especially their compounds.
- Chlorofluorocarbons (CFCs) - harmful to the ozone layer; emitted from products are currently banned from use. These are gases which are released from air conditioners, refrigerators, aerosol sprays, etc. CFC's on being released into the air rises to stratosphere. Here they come in contact with other gases and damage the ozone layer. This allows harmful ultraviolet rays to reach the earth's surface. This can lead to skin cancer, disease to eye and can even cause damage to plants.

  ممنوع

  بعد من
  tower sphere
  mesosphere
  12 km

- Ammonia ($NH_3$) - emitted from agricultural ~~processes~~. Ammonia is a compound with the formula $NH_3$. It is normally encountered as a gas with a characteristic pungent odor. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to foodstuffs and fertilizers. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals. Although in wide use, ammonia is both caustic and hazardous.

  واجه

  لاذعة، نفاذة

  الارضية

  مغذية

  مواد غذائية

  الاحتياجات الغذائية
  محفز

- Radioactive pollutants - produced by nuclear explosions, nuclear events, war explosives, and natural processes such as the radioactive decay of radon.

  تفجيرات

  متفجرات

**Secondary pollutants include:**

- Particulates created from gaseous primary pollutants and compounds in photochemical smog. Smog is a kind of air pollution. Classic smog results from large amounts of coal burning in an area caused by a mixture of smoke and sulfur dioxide. Modern smog does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by ultraviolet light from the sun to form secondary pollutants that also combine with the primary emissions to form photochemical smog.
- Ground level ozone ($O_3$) formed from $NO_x$ and VOCs. Ozone ($O_3$) is a key constituent of the troposphere. At abnormally high concentrations brought about by human activities (largely the combustion of fossil fuel), it is a pollutant, and a constituent of smog.
- Peroxyacetyl nitrate (PAN) - similarly formed from $NO_x$ and VOCs.

حتى ارتفاع
١٨-٢١
أو
6-10 Km

## Sources

There are various locations, activities or factors which are responsible for releasing pollutants into the atmosphere. These sources can be classified into two major categories.

**Anthropogenic (man-made) sources:**

These are mostly related to the burning of multiple types of fuel.

مداخن

معامل

محارق النفايات

- **Stationary sources** include smoke stacks of power plants, manufacturing facilities (factories) and waste incinerators, as well as furnaces and other types of fuel-burning heating devices/ In developing and poor countries, traditional biomass burning is the major source of air pollutants; traditional biomass includes wood, crop waste and dung.

- **Mobile sources** include motor vehicles, marine vessels, and aircraft.

مركبات + طرق النقل

- **Controlled burn** practices in agriculture and forest management. Controlled or prescribed burning is a technique sometimes used in forest management, farming, prairie restoration or greenhouse gas abatement. Fire is a natural part of both forest and grassland ecology and controlled fire can be a tool for foresters.

احراق ادارة استعادة المروج زراعة غازات الاحتباس الحراري

- **Fumes** from paint, hair spray, varnish, aerosol sprays and other solvents

ادخنة ورنيش بخاخات

- **Waste deposition** in landfills, which generate methane. Methane is highly flammable and may form explosive mixtures with air. Methane is also an asphyxiant and may displace oxygen in an enclosed space.

خانق

- **Military resources**, such as nuclear weapons, toxic gases, germ warfare and rocketry

الموارد العسكرية حرب صواريخ

**Natural sources:**

- Dust from natural sources, usually large areas of land with few or no vegetation
- Radon gas from radioactive decay within the Earth's crust. Radon is a colorless, odorless, naturally occurring, radioactive noble gas that is formed from the decay of radium. It is considered to be a health hazard. Radon gas from natural sources can accumulate in buildings, especially in confined areas such as the basement and it is the second most frequent cause of lung cancer, after cigarette smoking.
- Smoke and carbon monoxide from wildfires
- Vegetation, in some regions, emits environmentally significant amounts of VOCs on warmer days. These VOCs react with primary anthropogenic pollutants—specifically, $NO_x$, $SO_2$, and anthropogenic

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ضباب

organic carbon compounds — to produce a seasonal haze of secondary pollutants. Black gum, poplar, oak and willow are some examples of vegetation that can produce abundant VOCs.

صمغ الحور بلوط صفصاف

- Volcanic activity, which produces sulfur, chlorine, and ash particulates

## Industrial Pollution

The industrial sector is one of the most dynamic sectors of the economy and plays an essential role in economic development and the alleviation of poverty. Industries, in general, consume 37 per cent of the world's energy and emit 50 per cent of world's $CO_2$, 90 per cent of world's $SO_2$ and nearly all of its toxic chemicals. There has been a region-wide structural shift towards increased industrialisation. Developing economies with low levels of industrialisation are gradually shifting their dependence from agriculture to the industrial sector, while developed economies, with a high level of industrialisation, are shifting from the industrial to the service sector. Industry has increased its share of total output from 21 to 26 per cent in South Asia and this structural shift is expected to continue into the future.

التقليل من الفقر

هيكلي تحول

This shift has given rise to concern towards increasing carbon intensity in both local and regional environment. The $CO_2$ emission by industries in South Asia was estimated to be about 437 million tonnes in 2000-end and is estimated to increase by another 85 per cent by the year 2010.

قلق إقليمي

## Health effects

Air pollution is a significant risk factor for a number of health conditions including respiratory infections, heart disease, stroke and lung

الربو ونطاق [illegible]

تفاقم [illegible]

cancer. The health effects caused by air pollution may include difficulty in breathing, coughing, asthma and worsening of existing respiratory and cardiac conditions. These effects can result in increased medication use, increased doctor or emergency room visits, more hospital admissions and premature death. The human health effects of poor air quality are far reaching, but principally affect the body's respiratory system and the cardiovascular system. Individual reactions to air pollutants depend on the type of pollutant a person is exposed to, the degree of exposure, and the individual's health status and genetics. The most common sources of air pollution include particulates, ozone, nitrogen dioxide, and sulfur dioxide.

القلب

مبكرة

ردود الفعل الفردية

## Environmental Impact of Large Industries

Industries such as cement, glass, ceramic, iron and steel, paper and pulp, refineries, etc, exercise a wide range of environmental impacts. They emit large amounts of nitrogen, sulphur and carbon oxides into the air.

Emissions of lead, arsenic and chromium, both from glass and iron and steel industries, are extremely toxic. Waste disposal from such industries causes extensive water and soil contamination too. Extraction of raw materials causes large-scale surface disturbance and erosion.

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## Air Pollution Regulation

In the United States, the Environmental Protection Agency (US-EPA) has established air quality standards to protect public health, including the health of "sensitive" populations such as children, older adults, and people with asthma.

US-EPA also sets limits to protect public welfare. This includes protecting ecosystems, such as plants and animals, from harm, as well as protecting against decreased visibility and damage to crops, vegetation, and buildings. Under the Clean Air Act, the US-EPA has a number of responsibilities, including the following:

1- Ensuring that these air quality standards are met through national standards and strategies to control air pollutant emissions from vehicles, factories, and other sources.
2- Reducing emissions of $SO_2$ and $NO_X$ that cause "acid rain".
3- Reducing air pollutants such as PM, $SO_X$, and $NO_X$, which can reduce visibility across large regional areas, include many of the nation's parks and wilderness areas.
4- Ensuring that sources of toxic air pollutants that may cause cancer and other adverse human health and environmental effects are well controlled and that the risks to public health and the environment are substantially reduced.
5- Limiting the use of chemicals that damage the stratospheric ozone layer in order to prevent increased levels of harmful UV radiation.

## Industrial Production of Sulfuric Acid

Sulfuric acid (alternative spelling sulphuric acid) is a highly corrosive strong mineral acid with the molecular formula $H_2SO_4$. It is a pungent, colorless to slightly yellow viscous liquid which is soluble in water at all concentrations. Sometimes, it is dyed dark brown during production to alert people to its hazards. The historical name of this acid is oil of vitriol.

The main method used to produce sulfuric acid from elemental sulfur (or sulfur dioxide) consist four main steps. In summary:

1- $S_{(l)} + O_{2(g)} \longrightarrow SO_{2(g)}$

2- $SO_{2(g)} + 1/2O_{2(g)} \longleftrightarrow SO_{3(g)}\ \Delta = -99\ kJ/mol$

3- $SO_{3(g)} + H_2SO_{4(l)} \longrightarrow H_2S_2O_{7(l)}$

4- $H_2S_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2H_2SO_4(l)$

## Production of $SO_2$

If the process is started with elemental sulfur, it is first melted then sprayed into an excess of dry air at atmospheric pressure. The air is dried by passage through sulfuric acid, a dehydrating agent. This is done to avoid acid mist and corrosion in downstream pipes.

This reaction is described by the equation:

$$S_{(l)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

An excess of air (oxygen) ensures the sulfur reacts completely. The combustion of sulfur generates a lot of heat. It is necessary to cool the gas stream from 1000 °C to around 400 °C, it optimum temperature for the next step. Heat exchangers are used to remove the excess heat and recycle this heat energy so it can be used to remelt more sulfur or power turbines for electrical energy.

## Catalytic Oxidation of $SO_2$ and $SO_3$

Clean, dry sulfur dioxide is the feedstock for this stage. Electrostatic precipitators are used to remove any ash from the stream.

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This reaction is described by the equation:

$$SO_{2(g)} + 1/2O_{2(g)} \longleftrightarrow SO_{3(g)}\ \Delta = -99\ kJ/mol$$

The sulfur dioxide is mixed with air at pressure slightly higher than atmospheric, and is passed through a catalyst tower, called a converter. The tower contains 3 or 4 layers of vanadium oxide catalyst. Unreacted gases are recycled back into the gas stream.

In summary, the conditions for the conversion of $SO_2$ to $SO_3$ are:

- Pressure slightly higher than atmospheric.
- Excess of oxygen (1:1 ratio)

For $SO_2/SO_3$ systems, the following methods are available to maximize the formation of $SO_3$:

1- Removal of heat a decrease in temperature will favor the formation of $SO_3$ since this is an exothermic process.
2- Increased oxygen concentration in the input side.
3- Removal of $SO_3$ from the reaction zone.
4- Raised system input pressure.
5- Selection of the catalyst to reduce the working temperature.
6- Increased reaction time.
7- Increase in pressure of converter.

## Absorption of $SO_3$

The cooled sulfur trioxide from the final catalyst bed is dissolved in 98% sulfuric acid in the absorption tower. The acid is sprayed over the $SO_3$ and produces an oily liquid called fume (oleum).

This reaction is described by the equation:

$$SO_{3(g)} + H_2SO_{4(l)} \longrightarrow H_2S_2O_{7(l)}$$

This is preferable over directly dissolving sulfur trioxide in water as this forms sulfuric acid mists, due to the large heat of dissolution (130 kJ/mol), which are hard to control and difficult to coalesce. Also it is difficult to separate the sulfuric acid gas from others such as nitrogen.

The efficiency of the absorption depends on the following:

a- $H_2SO_4$ concentration of the absorbing liquid (98.3–98.7%).
b- Range of temperature of the liquid (normally 70 °C–120 °C).

c- The heat of absorption being removed by Plate Heat Exchanger (PHEs).
d- Temperature of incoming gas.
e- The device for separating $H_2SO_4$ aerosols.

## Conversion of fume (Oleum) to $H_2SO_4$

In the diluter, water is mixed with oleum to produce 98% sulfuric acid (18M). This reaction is described by the equation:

$$H_2S_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2\, H_2SO_4\ (l)$$

It is sold either as concentrated (98%) or diluted acid.

## Applications of Sulfuric acid

Sulfuric acid has a wide range of applications including

- Domestic acidic drain cleaner and various cleaning agents.
- Electrolyte in lead-acid batteries .
- A central substance in the chemical industry. Principal uses include mineral processing, fertilizer manufacturing, oil refining , wastewater processing, and chemical synthesis.

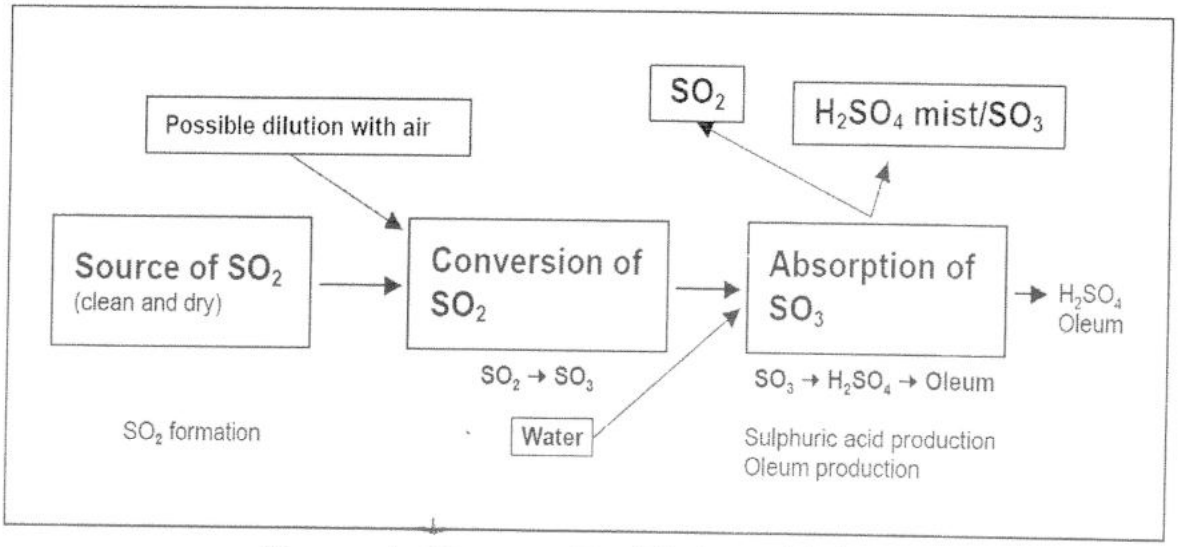


Figure 1. Stages of sulfuric acid formation.

## Ammonium Nitrate

Ammonium Nitrate is in the first place a nitrogenous fertilizer representing more than 10% of the total nitrogen consumption worldwide. It is more readily available to crops than urea. In the second place, due to its powerful oxidizing properties is used with proper additives as commercial explosive.

It is applied as a straight material or in combination with calcium carbonate, limestone, or dolomite. The combination is called calcium ammonium nitrate (CAN) or ammonium nitrate-limestone (ANL) or various trade names and in compound fertilizers including nitro phosphates. It is also a principal ingredient of most liquid nitrogen fertilizers. The nitrogen in ammonium nitrate is more rapidly available to some crops than urea or ammonium sulfate

### Ammonium Nitrate Properties

Ammonium nitrate is a white crystalline substance with a nitrogen content of 35% and a density of about 1.725 $kg/m^3$. The melting points depend on the content of the water, and it is practically impossible to obtain dry product in the industrial conditions.

In production and storage of ammonium nitrate, transformations of the crystal states that may affect the quality of the product occur.
Some additives such as $Mg(NO_3)_2$, $(NH_4)_2SO_4$, and some others can slightly change the critical relative humidities.

## Ammonium Nitrate Production

The production process comprises three main unit operations: neutralization, evaporation, solidification (prilling and granulation).

### *Neutralization*

Anhydrous liquid ammonia is evaporated in an evaporator using cooling water. The stoichiometic quantities of nitric acid (55% concentration wt/ wt) and gaseous ammonia are introduced by an automatic ratio controller to a neutralizer. The reaction between ammonia and nitric acid produces ammonium nitrate solution according to the following exothermic reaction.

$$NH_3 + HNO_3 \longrightarrow NH_4\,NO_3$$

Neutralization can be performed in a single stage or in two stages. The neutralizer can be carried out at atmospheric (either normal or low emission neutralizers where the temperature does not exceed 105°C and pH will be 6 and 3 respectively) or at elevated pressure of almost 4 atmospheres. The normal neutralizers are usually followed by flash evaporation in order to in crease the out let A.N concentration to 70%.

During evaporation some ammonia is lost from the solution. The steam which is boiled off is contaminated. The control of the neutralizer is important. The pH and the temperature must both be strictly controlled to limit the losses from the neutralizer. All installations must include pH and temperature controls.

The ammonium nitrate solution from neutralizer may be fed to storage without further processing but, if it is used in the manufacture of solid ammonium nitrate, it is concentrated by evaporation.

### 2. Evaporation to Concentrate the A.N

The outlet from the neutralizer is received in an intermediate tank. The solution should be made alkaline before being pumped to the evaporation section running under vacuum. The solution will be concentrated up to 97.5-99.5% (normally over 99 %) depending on whether ammonium nitrate will be granulated or prilled.

### 3. Mixing the Filling Material

In order to reduce the nitrogen content of A.N from 35% to 33.5%, the proper filling material is added (about 4% by weight of powdered limestone or dolomite).

### 4. Prilling or Granulation

The hot concentrated melt is either granulated or prilled. Ammonium nitrate is formed into droplets which then fall down a fall tower (prill tower) where they cool and solidify. Granulation requires more complicated plant than prilling and variety of equipment.

### 5. Drying, Screening

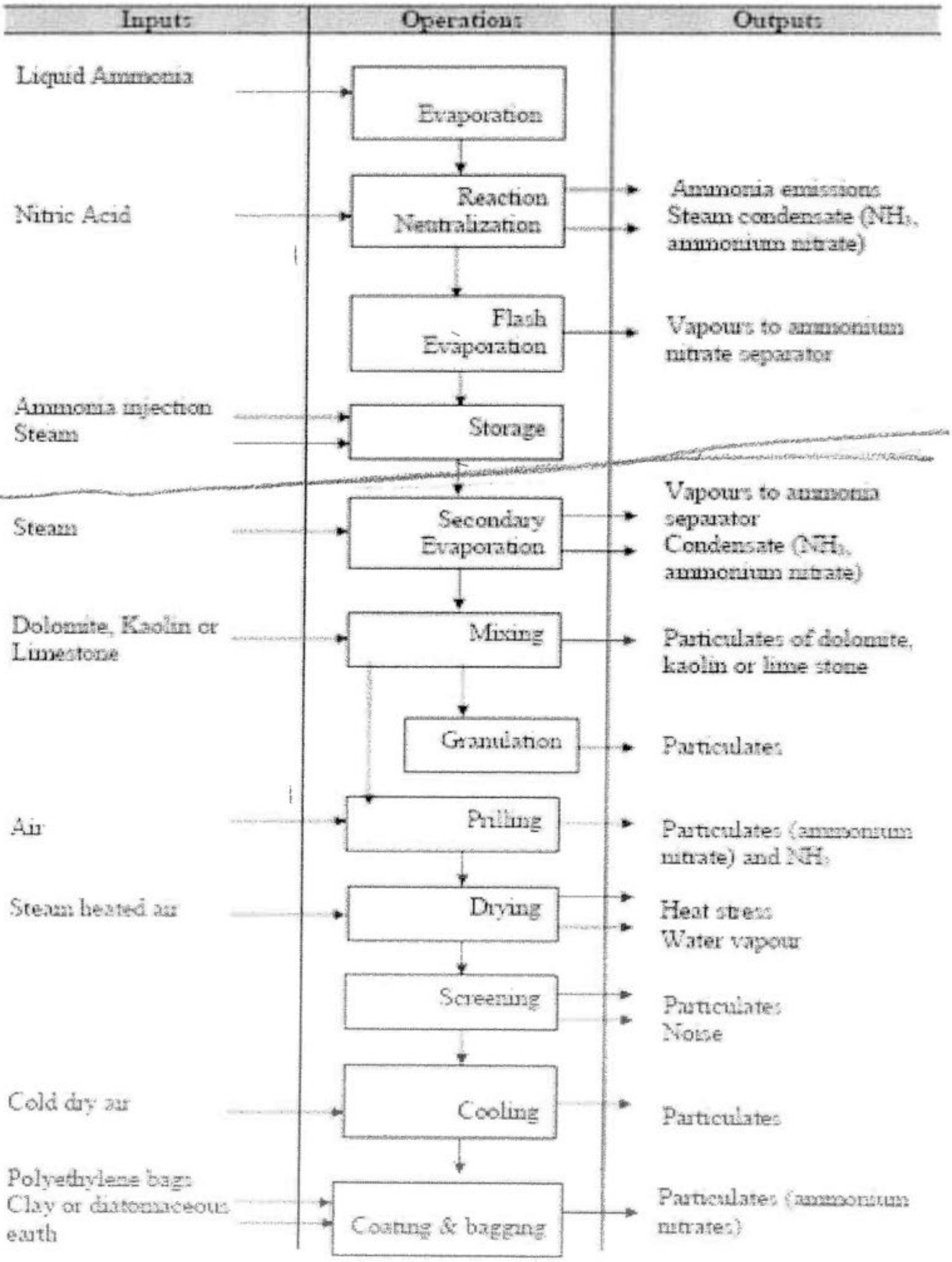
The ammonium nitrate (prills or granules) is dried (usually in drums) using hot air (steam heated), then screened to separate the correct product size. The oversize and undersize will be recycled either in the mixing tank (in case of prilling) or to the granulator.

### 5 Final Cooling

The hot proper size granules, are then cooled (against cooled and humid free air) down to 40°C and treated with anti-caking (usually amines) and then coated with an inert material (usually, kaolin, limestone or dolomite) and then conveyed to the storage.

Fig 8.1 illustrates the block flow diagram for ammonium nitrate production process.

**Fig 8.1 Process Flow Diagram for Ammonium Nitrate Manufacturing**



### *Major Hazards*

Ammonia, nitric acid and ammonium nitrate are the hazardous chemicals present in ammonium nitrate plants. A.N is an oxidizing agent and precautions must be taken in manufacturing, transport and storage.

The main chemical hazards associated with ammonium nitrate are fire, decomposition and explosion. Burns caused by hot AN solution should also be considered from a safety point of view.

Ammonium nitrate itself does not burn. Being an oxidizing agent, it can facilitate the initiation of a fire and intensify fires in combustible materials. Hot AN solution can initiate a fire in rags, wooden articles etc ,on coming into contact with them. Similarly, fertilizer products or dust contaminated with oil or other combustible materials can also start fires when left on hot surfaces.

Pure solid A.N melts at 169 $^{o}$C. On further heating it decomposes by way of a complex series of reactions. Up to about 250 $^{o}$C it decomposes primarily into $N_2O$ and $H_2O$. Above 300 $^{o}$ C reactions producing $N_2$, NO, $NO_2$ etc., become significant. These reactions are exothermic and irreversible.

A number of materials have a strong catalytic effect on the thermal decomposition of A.N. These include acids, chlorides, organic materials, chromates, dichromate, salts of manganese, copper and nickel and certain metals such as zinc, copper and lead. The decomposition of AN is suppressed or prevented by an alkaline condition. The release of toxic fumes is one of the main hazards associated with the decomposition of AN.

Strongly acidic conditions and the presence of contaminants should be avoided to counter the explosion hazard in AN solutions.

Lec/4 د. علي صناعية النظري

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ك ١

# Petroleum Processing

The term *petroleum* comes from the Latin stems *petra*, "rock," and *oleum*, "oil." It is used to describe a broad range of hydrocarbons that are found as gases, liquids, or solids beneath the surface of the earth. The two most common forms are natural gas and crude oil.

## *Natural gas:*

Natural gas which is a mixture of lightweight alkanes, accumulates in Porous rocks. A typical sample of natural gas when it is collected at its source contains about 80% methane ($CH_4$), 7% ethane ($C_2H_6$), 6% propane ($C_3H_8$), 4% butane and isobutane ($C_4H_{10}$), and 3% pentanes ($C_5H_{12}$). The $C_3$, $C_4$, and $C_5$ hydrocarbons are removed before the gas is sold. The commercial natural gas delivered to the customer is therefore primarily a mixture of methane and ethane. The propane and butanes removed from natural gas are usually liquefied under pressure and sold as liquefied petroleum gases (*LPG*).

## *Crude oil*

Is a composite mixture of hydrocarbons (50-95% by weight) occurring naturally. The first step in refining crude oil involves separating the oil into different hydrocarbon fractions by distillation. Each fraction is a complex mixture. For example, more than 500 different hydrocarbons can be found in the gasoline fraction.

Petroleum is found in many parts of the world which include the Middle East, southern United States, Mexico, Nigeria and the former Soviet Union.

## Uses of petroleum

Most of the crude oil is used in the production of fuels such as gasoline, kerosene, and fuel oil. Non-fuel uses include petroleum solvents, industrial greases and waxes, or as raw materials for the synthesis of *petrochemicals*. Petroleum products are used to produce synthetic fibers such as nylon and other polymers such as polystyrene, polyethylene and synthetic rubber. They also serve as raw materials in the production of refrigerants, aerosols, antifreeze, detergents, dyes, adhesives, alcohols, explosives and pesticides. The H2 given off in refinery operations can be used to produce a number of inorganic petrochemicals, such as ammonia, ammonium nitrate, and nitric acid from which most fertilizers as well as other 'agricultural chemicals are made.

## Oil Extraction

The vast majority of petroleum is found in oilfields or reservoirs below the earth's surface as shown in Fig 1.

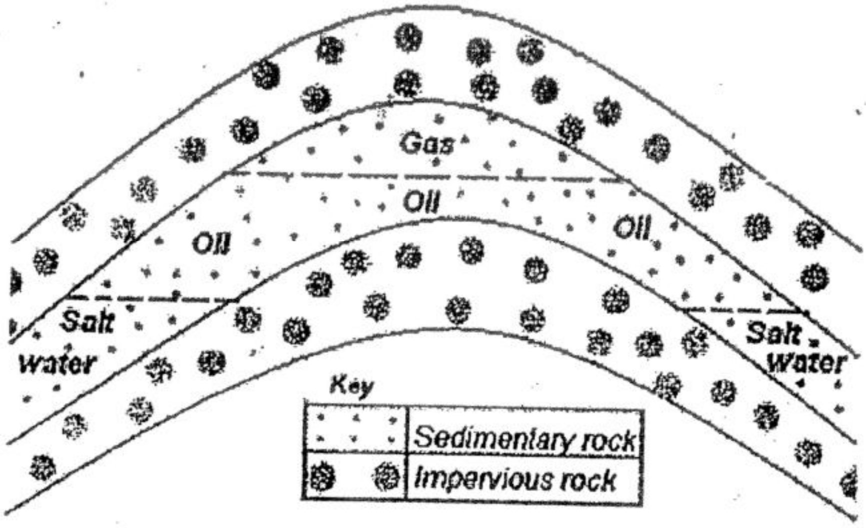

**Fig 1.** Schematic diagram of a crude oil reservoir

The oil is sometimes under high pressure and can flow to the surface on its own without pumping. However, most wells require induced pressure using water, carbon dioxide, natural gas or steam in order to bring the oil to the surface.

Petroleum refining has evolved continuously in response to changing consumer demand for better and different products. The original requirement was to produce kerosene as a cheaper and better source of light than whale oil. The development of the internal combustion engine led to the production of gasoline and diesel fuels.

The evolution of the airplane created an initial need for high-octane aviation gasoline and then for jet fuel, a sophisticated form of the original product, kerosene. Present-day refineries produce a variety of products including many required as feedstock for the petrochemical industry. Common petroleum products include gasoline, liquefied refinery gas, still gases, kerosene, aviation fuel, distillate fuel oil, residual fuel oil, lubricating oils, asphalt, coke and petrochemical feedstocks.

The history of petroleum refining is given in Table 1.

Lec/1 (Petroleum Processing) لحق كيمياء صناعية

| Year | Process | Purpose | By-Products, etc. |
|---|---|---|---|
| 1862 | Atmospheric distillation | Produce kerosene | Naphtha, tar, etc. |
| 1870 | Vacuum distillation | Lubricants originally, then cracking feedstocks (1930's) | Asphalt, residual, Coker feedstocks |
| 1913 | Thermal cracking | Increase gasoline yield | Residual, bunker fuel |
| 1916 | Sweetening | Reduce sulfur & odor | Sulfur |
| 1930 | Thermal reforming | Improve octane number | Residual |
| 1932 | Hydrogenation | Remove sulfur | Sulfur |
| 1932 | Coking | Produce gasoline basestock | Coke |
| 1933 | Solvent extraction | Improve lubricant viscosity index | Aromatics |
| 1935 | Solvent dewaxing | Improve pour point | Waxes |
| 1935 | Cat. polymerization | Improve gasoline yield and octane number | Petrochemical, feedstocks |
| 1937 | Catalytic cracking | Higher octane gasoline | Petrochemical, feedstocks |
| 1939 | Visbreaking | Reduce viscosity | Increased distillate, tar |
| 1940 | Alkylation | Increase gasoline octane & yield | High-octane aviation gasoline |
| 1940 | Isomerization | Produce alkylation feedstock | Naphtha |
| 1942 | Fluid catalytic cracking | Increase gasoline yield & octane Petrochemical feedstocks | |
| 1950 | Deasphalting | Increase cracking feedstock | Asphalt |
| 1952 | Catalytic reforming | Convert low-quality naphtha | Aromatics |
| 1954 | Hydrodesulfurization | Remove sulfur | Sulfur |
| 1956 | Inhibitor sweetening | Remove mercaptan | Disulfides |
| 1957 | Catalytic isomerization | Convert to molecules with high octane number | Alkylation feedstocks |
| 1960 | Hydrocracking | Improve quality and reduce sulfur | Alkylation feedstocks |
| 1974 | Catalytic dewaxing | Improve pour point | Wax |
| 1975 | Residual hydrocracking | Increase gasoline yield from residual | Heavy residuals |

## Characteristics and classification of Crude Oil

As has been mentioned, crude oils are complex mixtures containing many different hydrocarbon compounds that vary in appearance and composition from one oil field to another. Crude oils range in consistency from water to tar-like solids, and in color from clear to black.

An "average" crude oil contains about 84% carbon, 14% hydrogen, 1%-3% sulfur, and less than 1% each of nitrogen, oxygen, metals, and salts. Crude oils are generally classified as paraffinic, naphthenic, or aromatic, based on the predominant proportion of similar hydrocarbon molecules. Oils with low carbon, high hydrogen, and high API (American Petroleum Institute) gravity are usually rich in paraffins and tend to yield greater proportions of gasoline and light petroleum products; those with high carbon, low hydrogen, and low API gravities are usually rich in aromatics. The former category is known as light crudes and the latter as heavy crudes.

Crude oils that contain appreciable quantities of hydrogen sulfide or other reactive sulfur compounds are generally called "sour." while those with lower sulfur are called "sweet."

## Composition of petroleum

### Hyrocarbon compounds

***Paraffins*** - The paraffinic crude oil hydrocarbon compounds found in crude oil have the general formula $C_nH_{2n+2}$ and can be either straight chains (normal) or branched chains (isomers) of carbon atoms. The lighter, straight chain paraffin molecules are found in gases and paraffin waxes. The branched-chain (isomer) paraffins such as isobutene are usually found in heavier fractions of crude oil and have higher octane numbers than normal paraffins.

***Aromatics***: The aromatic series include **simple aromatic compounds such as benzene,naphthalenes and the most complex aromatics, the polynuclears** which have three or more fused aromatic rings. They have high anti-knock value and good storage stability.

***Naphthenes (Naphtha):*** **These** are saturated hydrocarbon groupings with the general formula CnH2n, arranged in the form of closed rings (cyclic) and found in all fractions of crude oil except the very lightest. Single-ring naphthenes (monocycloparaffins) with five and six carbon atoms such as cyclohexane predominate. Two-ring naphthenes (dicycloparaffins) are found in the heavier ends of naphtha.

***Alkenes (Olefins):*** Olefins such as ethylene, butene, isobutene are usually formed by thermal and catalytic cracking and rarely occur naturally in unprocessed crude oil.

They are unstable and also improve the anti-knock tendencies of gasoline but not as much as the iso-alkanes. When stored, the olefins polymerise and oxidize. This tendency to react is employed in the production of petrochemicals.

***Dienes and Alkynes:*** Examples of dienes or diolefins, are 1,2-butadiene and 1,3-butadiene. Acetylene is a typical alkyne. This category of hydrocarbons is obtainedfrom lighter fractions through cracking.

## Non-hydrocarbons

***Sulfur Compounds*:** Sulfur may be present in crude oil as hydrogen sulfide ($H2S$), asmercaptans, sulfides, disulfides, thiophenes, etc. or as elemental sulfur. Each crude oil has different amounts and types of sulfur compounds, but as a rule the proportion, stability, and complexity of the compounds are greater in heavier crude-oil fractions.

Sulphur is an undesirable component because of its strong offensive odour, corrosion, air pollution by some of its compounds and its effect of reducing tetraethyl lead (anti-knock agent). Hydrogen sulfide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulfur and mercaptans.

The corrosive sulfur compounds also have an obnoxious odor. The combustion of petroleum products containing sulfur compounds produces undesirables such as sulfuric acid and sulfur dioxide. Catalytic hydrotreating processes such as hydrodesulfurization remove sulfur compounds from refinery product streams. Sweetening processes either remove the obnoxious sulfur compounds or convert them to odorless disulfides, as in the case of mercaptans.

*Oxygen Compounds*: Oxygen compounds such as phenols, ketones, and carboxylic acids occur in crude oils in varying amounts.

*Nitrogen Compounds*: Nitrogen is found in lighter fractions of crude oil as basic compounds, and more often in heavier fractions of crude oil as nonbasic compounds.

Nitrogen oxides can form in process furnaces. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.

***Trace Metals*****:** Metals, including nickel, iron, and vanadium are often found in crude oils in small quantities and are removed during the refining process. Burning heavy fuel oils in refinery furnaces and boilers can leave deposits of vanadium oxide and nickel oxide in furnace boxes, ducts, and tubes. It is also desirable to remove trace amounts of arsenic, vanadium, and nickel prior to processing as they can poison certain catalysts.

***Salts:*** Crude oils often contain inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride in suspension or dissolved in entrained water (brine) in the form of an emulsion. These salts must be removed or neutralized before processing to prevent catalyst poisoning, equipment corrosion, and fouling.

Saltcorrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride(HCl) and the subsequent formation of hydrochloric acid when crude oil is heated.

Hydrogen chloride may also combine with ammonia to form ammonium chloride (NH4Cl), which causes fouling and corrosion. Salt is removed mainly by mechanical or electrical desalting

***Carbon Dioxide*****:** Carbon dioxide may result from the decomposition of bicarbonates present in or added to crude, or from steam used in the distillation process.

***Naphthenic Acids*****:** Some crude oils contain naphthenic (organic) acids, which may become corrosive at temperatures above 230°C when the acid value of the crude is above certain level.

## Petroleum Refining

The petroleum industry began with the successful drilling of the first commercial

oil well in 1859, and the opening of the first refinery two years later to process the crude into kerosene. Today, petroleum refinery products obtained include gasoline, kerosene, propane, fuel oil, lubricating oil, wax, and asphalt.

Refining crude oil involves two kinds of processes: First, there are physical processes which simply refine the crude oil (without altering its molecular structure) into useful products such as lubricating oil or fuel oil. Petroleum refining begins with **distillation**, or fractionation, which separates crude oil in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of differing boiling-point ranges called "fractions" or "cuts."

Second, there are **chemical conversion processes** which alter the size and/or molecular structure of hydrocarbon molecules to produce a wide range of products, some of them known by the general term petrochemicals. Conversion processes include:

- **Decomposition** (dividing) by thermal and catalytic cracking;
- **Unification** (combining) through alkylation and polymerization; and
- **Alteration** (rearranging) with isomerization and catalytic reforming.

As seen above, the major chemical conversions include cracking, alkylation, polymerisation, isomerisation and reforming. The converted products are then subjected to various treatment and separation processes.

**Treatment Processes** are intended to prepare hydrocarbon streams for additional processing and to prepare finished products. Treatment may include the removal or separation of aromatics and naphthenes as well as impurities and undesirable contaminants.

Treatment may involve chemical or physical separation such as dissolving,

absorption, or precipitation using a variety and combination of processes including hydrodesulfurizing and sweetening.

**Formulating and Blending** is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties. Integrated refineries incorporate fractionation, conversion, treatment, and blending operations and may also include petrochemical processing.

## Octane number and the development of cracking and reforming processes

About 10% of the product of the distillation of crude oil is a fraction known as **straight-run gasoline**, which served as a satisfactory fuel during the early days of the internal combustion engine. As the automobile engine developed, it was made more powerful by increasing the compression ratio. Modern cars run at compression ratios of about 9:1, which means the gasoline-air mixture in the cylinder is compressed

by a factor of nine before it is ignited. Straight-run gasoline burns unevenly in highcompression engines, producing a shock wave that causes the engine to "knock," The challenge for the petroleum industry was to increase the yield of gasoline from each barrel of crude oil and to decrease the tendency of gasoline to knock when it burned. It was found that:

- Branched alkanes and cycloalkanes burn more evenly than straight-chain alkanes.

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- Short alkanes ($C_4H_{10}$) burn more evenly than long alkanes ($C_7H_{16}$).
- Alkenes burn more evenly than alkanes.
- Aromatic hydrocarbons burn more evenly than cycloalkanes.

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The most commonly used measure of a gasoline's ability to burn without knocking is its **octane number**. Octane numbers compare a gasoline's tendency to knock against the tendency to knock of a blend of two hydrocarbons heptane and 2,2,4-trimethylpentane, (isooctane). Heptane produces a great deal of knocking while isooctane is more resistant to knocking. Gasolines that match a blend of 87% isooctane and 13%heptane are given an octane number of 87.

There are three ways of reporting octane numbers. Measurements made at high speed and high temperature are reported as *motor octane numbers* while measurements taken under relatively mild engine conditions are known as *research octane numbers*.

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The *road-index octane numbers* reported on gasoline pumps are an average of these two. Road-index octane numbers for a few pure hydrocarbons are given in the Table 2 below.

| Hydrocarbon | Road Index Octane Number |
|---|---|
| Heptane | 0 |
| 2-Methylheptane | 23 |
| Hexane | 25 |
| 2-Methylhexane | 44 |
| 1-Heptene | 60 |
| Pentane | 62 |
| 1-Pentene | 84 |
| Butane | 91 |
| Cyclohexane | 97 |
| 2,2,4-Trimethylpentane (iso-octane) | 100 |
| Benzene | 101 |
| Toluene | 112 |

Table 2. Hydrocarbon Road Octane Numbers

## Hydrocarbon Road Index Octane Number

By 1922 a number of compounds had been discovered that could increase the octane number of gasoline. Adding as little as 6 ml of tetraethyllead to a gallon of gasoline, for example, can increase the octane number by 15 to 20 units. This discovery gave rise to the first «ethyl» gasoline, and enabled the petroleum industry to produce aviation gasolines with octane numbers greater than 100.

Another way to increase the octane number is **thermal reforming**. At high temperatures (500-600°C) and high pressures (25-50 atm), straight-chain alkanes isomerize to form branched alkanes and cycloalkanes, thereby increasing the octane number of the gasoline. Running this reaction in the presence of hydrogen and a catalyst such as a mixture of silica ($SiO_2$) and alumina ($Al_2O_3$) results in **catalytic reforming**, which can produce a gasoline with even higher octane numbers.

The yield of gasoline is increased by "cracking" the long chain hydrocarbons into smaller pieces at high temperatures (500 °C) and high pressures (25 atm). A saturated $C_{12}$ hydrocarbon in kerosene, for example, might break into two $C_6$ fragments.

Because the total number of carbon and hydrogen atoms remains constant, one of the products of this reaction must contain a C=C double bond.

The presence of alkenes in thermally cracked gasolines increases the octane number (70) relative to that of straight-run gasoline (60), but it also makes thermally-cracked gasoline less stable for long-term storage.

Thermal cracking has therefore been replaced by **catalytic cracking**, which uses catalysts instead of high temperatures and pressures to crack long-chain hydrocarbons into smaller fragments for use in gasoline.

The flow diagrams Fig. 2 and 3 show the various processes undertaken to improve the yields and quality of petroleum products. Among them are catalytic cracking and catalytic reforming.

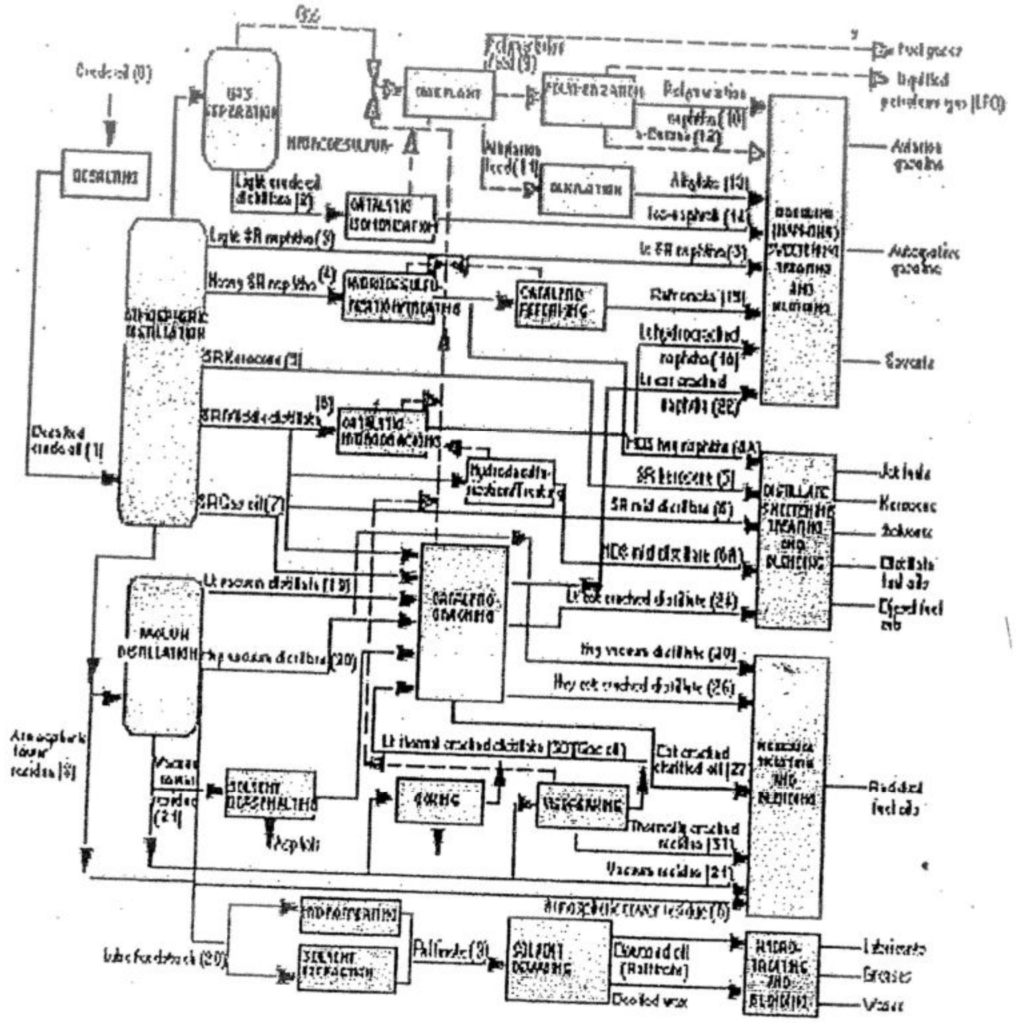


Fig. 2. Refining operations

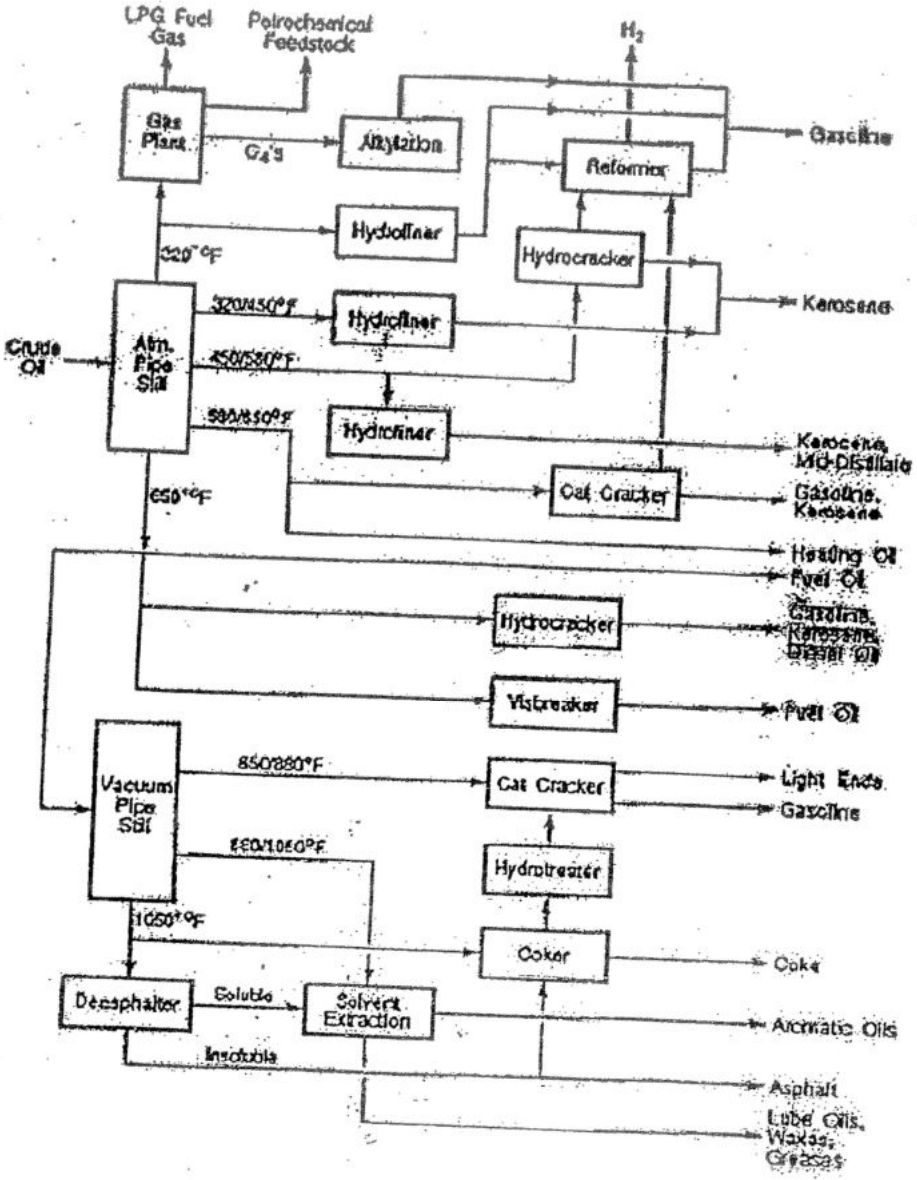


Fig 3 Petroleum refining

## Catalytic Cracking

Ethylene and propylene are the most important organic chemical feedstocks accounting for over 50-60% of all organic chemicals. But because of their relatively high reactivities, very few olefins are found in natural gas or crude oil. Therefore, they must be manufactured by cracking processes.

The purpose of cracking is to break complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. The heavy hydrocarbon feedstock is cracked into lighter fractions such as kerosene, gasoline, LPG, heating oil, and petrochemical feedstock. LPG gases are feedstock for olefins such as ethylene and propylene.

The decomposition takes place by catalytic action or heating in the absence of oxygen (pyrolysis). The catalysts used in refinery cracking units are typically zeolite, aluminum hydrosilicate, treated bentonite clay, fuller's earth, bauxite, and silica-alumina ($SiO_2$-$Al_2O_3$) all of which come in the form of powders, beads, or pellets.

The formation of gasoline (with low molecular weight) from heavy gas oil of high molecular weight is shown in the following equation:

$$\underset{\substack{\text{Heavy}\\ \text{gas oil}}}{(C_7H_{15})_2(CH_2)_{15}} \xrightarrow{\text{Heat}} \underset{\text{Gasoline}}{C_7H_{16}} + \underset{\substack{\text{Gasoline}\\ \text{(antiknock)}}}{C_6H_{13}:CH_2} + \underset{\substack{\text{Recycle}\\ \text{stock}}}{C_{14}H_{29}:CH_2}$$

There are three basic functions

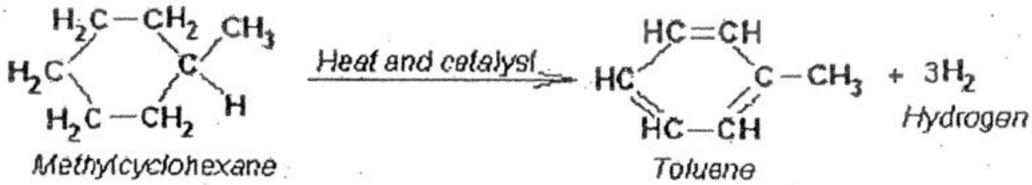
There are three basic functions in the catalytic racking process:

1- Reaction - Feedstock reacts with catalyst and cracks into different hydrocarbons
2- Regeneration - Catalyst is reactivated by burning off coke
3- Fractionation - Cracked hydrocarbon stream is separated into various products.

## Catalytic Reforming

Catalytic reforming is an important process used to convert low-octane naphthas into high-octane gasoline blending components called reformates. Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations

of toluene, benzene, xylene, and other aromatics useful in gasoline blending and petrochemical processing. Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes. Most processes use platinum as the active catalyst. Sometimes platinum is combined with a second catalyst (bimetallic catalyst) such as rhenium or another noble metal.
The conversion is illustrated by the following reaction in which a cycloalkane is converted to an aromatic compound, usually of higher octane number.



The naphtha feed is mixed with recycled hydrogen and introduced to the feed preheater to raise the temperature. The hot mixture of hydrogen and naphtha vapours is passed through a series of four reactors containing the catalyst. The working temperatures and pressures are usually between 150oC to 510oC and 1500kPa to 7000kPa respectively.
The products are cooled and about 90% of the hydrogen is compressed and recycled.
The main product is fractionated. The overhead product can be used as a fuel.
Some catalytic reforming systems continuously regenerate the catalyst while in other systems one reactor at a time is taken off-stream for catalyst regeneration, Some facilities regenerate catalysts from all of the reactors during shutdown.