The Atmosphere

Introduction to the Atmosphere

The atmosphere is a layer of gas and suspended solids extending from the Earth's surface up many thousands of miles, becoming increasingly thinner with distance but always held by the Earth's gravitational pull.

The atmosphere surrounds the Earth and holds the air we breathe; it protects us from outer space; and holds moisture (clouds), gases, and tiny particles. In short, the atmosphere is the protective bubble in which we live.

This protective bubble consists of several gases (listed in the table below), with the top four making up 99.998% of all gases. Of the dry composition of the atmosphere, **nitrogen** by far is the most common. Nitrogen dilutes oxygen and prevents rapid burning at the Earth's surface. Living things need it to make proteins.

Oxygen is used by all living things and is essential for respiration. It is also necessary for combustion (burning). **Argon** is used in light bulbs, in double-pane windows, and to preserve museum objects such as the original Declaration of Independence and Constitution. Plants use **carbon dioxide** to make oxygen. Carbon dioxide also acts as a blanket that prevents the escape of heat into outer space.

The exact amounts of each gas vary slightly from day to day. The NOAA Global Monitoring Lab updates trends in the 4 main Greenhouse Gases in the atmosphere daily.

Chemical makeup of the atmosphere EXCLUDING water vapor

Gas	Symbol	Content
Nitrogen	N_2	78.084%
Oxygen	O_2	20.946%
Argon	Ar	0.934%
Carbon dioxide	CO_2	0.042%

Chemical makeup of the atmosphere EXCLUDING water vapor

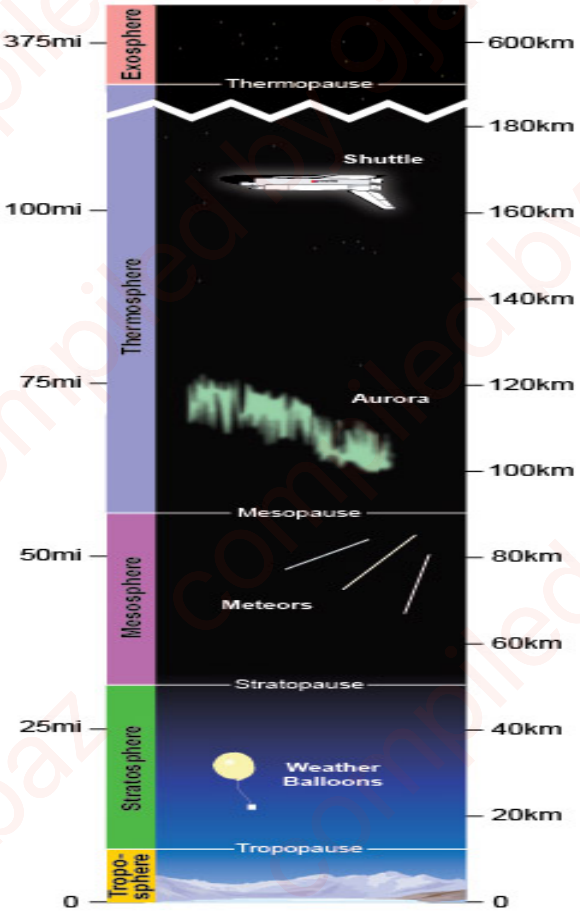
Gas	Symbol	Content
Neon	Ne	18.182 parts per million
Helium	He	5.24 parts per million
Methane	CH_4	1.92 parts per million
Krypton	Kr	1.14 parts per million
Hydrogen	H_2	0.55 parts per million
Nitrous oxide	N_2O	0.33 parts per million
Carbon monoxide	CO	0.10 parts per million
Xenon	Xe	0.09 parts per million
Ozone	O_3	0.07 parts per million
Nitrogen dioxide	NO_2	0.02 parts per million
Iodine	I_2	0.01 parts per million
Ammonia	NH_3	trace

These percentages of atmospheric gases are for a completely dry atmosphere. The atmosphere is rarely, if ever, dry. **Water vapor** (water in a gas state) is nearly always present, up to about 4% of the total volume.

Chemical makeup of the atmosphere INCLUDING water vapor

Water Vapor	Nitrogen	Oxygen	Argon
0%	78.084%	20.947%	0.934%
1%	77.30%	20.70%	0.92%
2%	76.52%	20.53%	0.91%
3%	75.74%	20.32%	0.90%
4%	74.96%	20.11%	0.89%

In the Earth's desert regions (30°N/S), when dry winds are blowing, the water vapor contribution to the composition of the atmosphere will be near zero. Water vapor contribution climbs to near 3% on extremely hot/humid days. The upper limit, approaching 4%, is found in tropical climates.


375mi
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Exosphere
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Tropo-sphere
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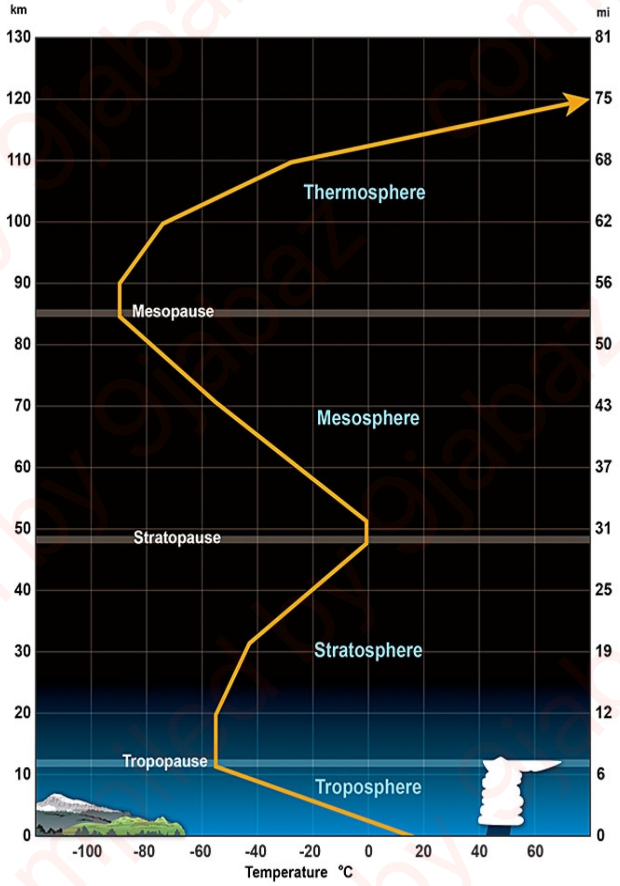
km
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70
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mi
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62
56
50
43
37
31
25
19
12
6
0
Thermosphere
Mesopause
Mesosphere
Stratopause
Stratosphere
Tropopause
Troposphere
-100
-80
-60
-40
-20
0
20
40
60
Temperature °C

01 Prof. Olubari

⇒ * Read the assignment - It is part of the note

The Atmosphere

The atmosphere is a layer of gas and suspendal solid extending from the earth surface. protective bubbles consists of several gases.

Nitrogen diffuse the O_2 and prevent rapid burning at the earth surface

NO_2 and NO are oxides of nitrogen where nitrogen mixed up - to prevent rapid burning of the earth surface

Oxygen is useful for respiration. Argon as a gas is also useful for protecting the museum object. CO_2 serve as a shield for the earth surface. The exact amount of these gases depend on the exact amount today. The chemical make up of atmosphere under water vapour. Water vapour contains up to 4% in the tropical region and lesser of those gases.....

The percentage of the atmosphere gases for completely dried atmosphere

* There is no way we can have a dry atmosphere, there will always be Water vapour

Layers of the Atmosphere

There are five layers by their thermal composition, density.

① Exosphere: Outermost layers of atmosphere, extends ~~600~~ 600kilometers to 10,000km above the earth. Atoms and molecules escapes into space in this layer

(ii) ~~85~~ 85km - 600km lies the thermosphere known as the uppermost layer. Incoming UV and sun radiation are absorbed in this layer. The temperature increases with height due to this absoption, from as low as -120°c at the bottom to as high as 3600F (2000°c at the top. But despite the high temperature, ~~the~~ still feels cold to the skin.

At the bottom of the thermosphere is the mesopus which links the thermosphere to

(iii) It mesosphere extends from 31 miles above the earth surface to 83 miles. The gases becomes denser as one descends because of the availability of water vapour, therefore temperature increases as one descends

Stratosphere

(iv) Both the mesophere and the stratosphere are referred to the midder of the layer. The transition boundary which seperates the mesophere and stratisphere ~~is~~ called stratopus

This layer holds 19% of earth atmosphere gases and little ~~percent of~~ water vapour. In this region, the temperature increases with height, heat is produced in the generation of ozone. This heat produced is responsible for the temperature increase and the very little amount of water vapour.

This increase in temperature means warmer air. There is no upward vertical movement of gases

(iii) troposphere

The transition layer below the stratosphere is called the tropopus

Almost all wheather occurs in this region

Exosphere.
Termospher
Mesosphere
Stratosphere
Troposphere

} layers of the atmosphere

CO_2, NO_x → Causes of pollution

Environmental pollution

In pollution, all the component causing pollution have exceeded the allowed limit

In contamination, the component causing the impurity is being introduced in a smaller amount; it has not exceeded the allowable limit. E.g water containing 0.05mg/g of pb.

pollution is the introduction of waste matter (Generated from somewhere) in the environment (which could air, land, water etc) by man, so that it causes damage or deterioration to living systems and/or the environment

e.g acid anhydride affecting stomata of plants

% of cement → $CaCO_3$

A pollutant is any substance produced by human activities ~~[illegible]~~ in a unacceptable level that causes damage.

Many pollutants are Chemicals.

It is only chemicals that can form reactions. pollutants don't cause problem if reactions are not taking place

- Types of

① Noise pollution
(II) Air pollution
(III) Water pollution
(IV) Land pollution

Air pollutant : CO_2, NO_x, ozone, hydrocarbons, SO_2, Particulates

CO_2 → generated from hydrocarbons

CO_2

It is generated from hydrocarbons

$CO + O_2 \longrightarrow CO_2 + O^{\cdot} \rightarrow$ w

It causes depletion of ozone layer

* Write equations, like five, on depletion of ozone layer. you can start with ~~any~~ formation of any of the gases. The conditions of the reactions must be specified.

~~CO, NO2,~~ S

SO_2

$SO_2 + H_2O \longrightarrow H_2SO_4$

$N_2 + O_2 \longrightarrow NO_2$

$NO_2 \xrightarrow{h\nu} NO$

21/04/26

Air Pollution

① Burning of fossil fuel and other material sources.
Every contaminant in the environment can be traced ultimately in the chemical reaction. The amount of contaminant is linked by a chemical equation to a resource consumed or some other substance chemically altered.

The chemical equation with associated atomic masses serves as quantitative bridge connecting pollution, resources and the level of man's activity.

$$C + O_2 \longrightarrow CO_2$$

Many organic materials including organic waste are largely carbon. So, the same equation expresses the most central features of their oxidation. In terms of mole ratio $C : CO_2$ is 1:1 (from the above equation). However the mass 44g of CO_2 produced (gained) is more than the mass 12g of C consumed. So, the mass ratio of CO_2 to C is $\frac{44}{12}$

$$\text{Mass ratio} = \frac{44}{12} = \frac{11}{3} //$$

Thus, for every three units of mass of carbon consumed in an environment. There are 11 units of mass of CO_2 produced This is pollution. With this 11/3 ratio, we can calculate the amount of CO_2 that is associated with any mass of carbon bonds. Thus, if 6×10^9 tons of fossil carbon are burnt, the mass of CO_2 produced will be; ~~6×10^9 tons of carbon x 11 packs of~~

$$\frac{6\times10^9 \text{ tons of carbon} \times 11 \text{ parts of } CO_2}{3 \text{ parts of } C}$$

$$= 22\times10^9 \text{ tons of } CO_2$$

Similarly, by using masses of oxygen which is 32g and C which is 12g, we can obtain the mass ratio of the consumed oxygen to carbon

$$\text{mass ratio} = \frac{32}{12} = 8/3$$

Thus if 6×10^9 tons of fosil carbons are burnt, the amount of oxygen consumed (removed) from the atmospher will be;

$$\frac{6\times10^9 \text{ tons} \times 8 \text{ packs of oxygen}}{3 \text{ packs of carbon}} = 16\times10^9 \text{ tons of oxygen.}$$

The atmosphere presently reservod ~~some~~ of oxygen is 10^{15} tons.

The fractional depletion of oxygen brought about is

$$\frac{16\times10^{9}\text{ tons}}{10^{15}} = 1.6\times10^{-5} = 0.002\%$$ has been removed from the reserved oxygen of the atmosphere

The problem can be solved by afforastation.

② Burning of Sulphur and sulphur containing compound

$$S + O_2 \longrightarrow SO_2$$

~~The ratio of SO_2 to S is 16 : 32 = 2 : 1~~

The ratio of SO_2 to S is 64.1 : 32 = 2 : 1

The Sulphur in SO_2 has it origin in certain ore, such as chalcocite (Cu_2S) and Chalcopyrite ($CuFeS_2$)

$$\underset{159.1}{CuS} + \underset{32.0}{O_2} \longrightarrow \underset{127}{2Cu} + \underset{64.1}{SO_2}$$

In this equation, we can determine the mass of SO_2 and Cu_2S $\frac{64.1}{127} = 0.505$

$SO_2 : Cu_2S = \frac{64.1}{159.1} = 0.423$

For each of tons of Chalcocite that is smelted, 0.423 tons of SO_2 is released to the atmosphere

③ Burning of Nitrogen and Oxides of Nitrogen ~~(NO2)~~$_x$

There are at least 5 kinds of nitrogen containing as molecules in the atmosphere, i.e N_2, NO, N_2O, NO_2, NH_3.

Nitrogen (N_2) dominates them all and their environmental role is to provide a large reservour from which nitrogen containing compound ~~in which~~ including some essential of life originates.

Upon raising air to a high temperature, NO is produced.

~~Such heating oc~~ $N_2 + O_2 \rightarrow 2NO$

Such heating occurs in flames and therefore, most NO comes from combustion of fuel, i.e, Coal petrol, oil etc

After formation of NO, it is oxidized by atmospheric ozone. The resultant NO_2 is partly absorbed by vegation, water and soil, and some converted trigonitrate acid

$$NO + O_3 \longrightarrow NO_2$$

by hydrolysis with air borne water, i.e, NO_2

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$ - formation of acid rain

The acid may be brought down by rain or first combined with NH_3 to form Ammonium nitrate

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

*yan

This is washed to the earth, where it becomes nutrients to the plants

④ Industrial Emission.

Industries emits smokes and various gases of various magnitude into the atmosphere, this leads to formation of smog ~~fog~~

Fog consists of a collidal dispersion of liquid in the air. Fog produced from photochemical reaction is commonly referred to as photochemical smog.

The term Smog originated from the term smoke and fog

⑤ Automobile Exhaust Emission

Combustion of gasoline or petrol

$$2C_8H_{18} + 2CO_2 \rightarrow 16CO_2 + 18H_2O$$

CO may be formed due to incomplete combustion

⑥ Particulate from construction sites, burners eg house lanterns, refuse, industrial burners, incinerators

Health Effects of Air-pollution

① Haemoglobin in the blood carries oxygen round to cells and tissues for suvival

$$Hb + O_2 \rightleftharpoons HbO_2$$

When CO is released into the atmosphere and inhaled

$$Hb + CO \longrightarrow HbCO$$ (not reversible)

~~When~~ It immobilizes the Hb and leads to acute shortage of oxygen in the blood which leads to headache, dizziness and eventually death

② Nitrogen oxides leads to formation of acid rain, photochemical smog, damage to lung, tissues and blood vessels to result.

③ Sulphur oxides form acid rain, H_2SO_4. It increase asthmatic attack and damage to respiratory system

④ Hydrocarbons leads to photochemical smog and cancer

⑤ Particulate matter inhaled can cause, asthma

Bronchitis and lung cancer ~~Lead containing particulates fr~~

⑥ Lead containg particulates from automobiles exhaust transmit toxic lead to lungs and hence to blood streams affect ~~CN~~ central nervous system, damage brain, kidney, liver and reproductive system

22/04/26

Green House Effect

The so called green house effect describes the trapping of heat near Earth surface by gases in the atmosphere particularly CO_2. The Sun hits the earth's surface by its UV light and reflects back to the upper atmosphere, but the presence of CO_2 in the atmosphere traps the heat and ~~its~~ emits back to the air, the Earth is heated up.

E.g in a green house, the glass roof transmits visible light and absorbs some of the outgoing ~~rad~~ IR radiation thereby trapping the heat.

CO_2 acts somewhat as a glass roof except that the temperature rises in the green house is due mainly to the restricted air circulation inside.

* which of the following do you consider as a green house gas and why?

The green house gases e.g CO_2, CH_4, water vapour plays crucial role in regulating the temperature of the Earth and its atmosphere
In the absence of these gases, the average surface temperature will be -19°C. There is concern of the rising of atmospheric temperature called global warming or green house warming, due to steady increase in CO_2 in the atmosphere.

Climate Change

Global warming jeopardize full security for world's poorest people arising from extreme climate condition
(i) Drought
(ii) flood
(iii) Area that are normally dry will be dryer with increased overgrazing, there would be desertification
Area that are normally wet will be wetter
Melting of ice cap
Rising in sea level

Solution

(i) Reduction ~~of~~ emission of green house gases, hydrocarbon & CO_2
(ii) Planting trees or aforestation
(iii) Reduction in the use of fossil fuels
(iv) Building against sea rise
(v) Resulting in ocean surge

Ozone formation

The formation of ozone in the stratosphere begins with photo dissociation of oxygen by solar radiation

$$O_2 \xrightarrow[<240nm]{UV} O^{\cdot} + O^{\cdot}$$

~~At~~ At wavelength below 240nm leading to cleavage of molecules and formation of very reactive oxygen. The high reacting oxygen atom, combines with oxygen molecules to form ozone.

eq^n $O^{\cdot} + O_2 \longrightarrow O_3$

$$\underset{\text{Inert}}{\underset{\downarrow}{M}} + O^{\cdot} + O_2 \longrightarrow O_3 + M$$

The energy that is not absorbed by M is given off as heat, as molecules becomes dexcited, they release more

CHLT3

heat to the surrounding

In addition, Ozone itself absorb UV light between 200nm – 300nm

$$O_3 \xrightarrow{UV} O^{\cdot} + O_2$$

The process continues when oxygen radical $O^{\cdot}$ and oxygen O_2 recombines to form ozone, it acts as protective shield against UV radiation, and prevents skin cancer

The formation and destruction of ozone by natural processes is a dynamic equilibrium and maintain at constant temperature of ozone in the stratospher

Freon

The harmful effect of freon $CFCl_3$ on ozone layer has become worrisome

$CFCl_3$, CF_2Cl_2, $C_2F_3Cl_3$, $C_2F_4Cl_2$

They are non toxic, inert, and non-combustible, and thus, used as coolant in referator and air conditione

Because of their reactive inertness, the CFCS slowly diffuse to the stratosphere where UV radiation of λ between 175nm – 220nm causes them to decompose

$$CFCl_3 \longrightarrow CFCl_2 + {}^{\cdot}Cl$$

$CF_2Cl_2 \longrightarrow CF_2Cl + {}^{\cdot}Cl$

In the Earth's atmosphere the ˙Cl produced in this way reacts to destroy ozone, in the manner of NO

$NO + O_3 \longrightarrow NO_2 + O_2$

${}^{\cdot}Cl + O_3 \longrightarrow ClO^{\cdot} + O_2$

$O_2 \longrightarrow O^{\cdot} + O^{\cdot}$

$ClO^{\cdot} + O^{\cdot} \longrightarrow ClO_2$

* Account for how ozone serves as pollutant and as screen

~~Smog~~ PAN

Photochemical smog is a type of smog formed under the influence of sunlight. It is actually a mixture of pollutant including particulate matter, nitrogen oxide, aldehyde, peroxy acetyl nitrates and unreacted hydrocarbon

Pan is peroxyl acetyl nitrate

A brownish haze that irritates our eyes is indicative of photochemical smog. Nitrogen dioxide is responsible for the brownish colour of the haze.

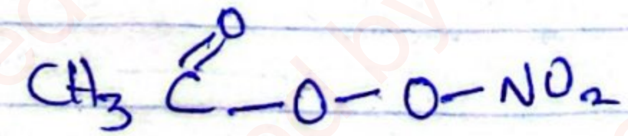
The reactions that leads to the formation of photochemica smog are initiated by sunlight and involves hydrocarbon and nitrogen oxides emitted from automobiles. Combination of sunlight catalyzed by particulate matter and abundant pollutant present in modern cities provide favourable conditions for smog formation

Nitrogen oxide from automobile exhaust first absorbs light and breaks down into NO (nitrogen mono oxide)

$$NO_{2(g)} \xrightarrow{UV\ Light} NO_{(g)} + O^{\cdot}_{(g)}$$

The oxygen radical then reacts with other component of automobile exhaust e.g unburnt hydrocarbons and those of the atmosphere e.g O_2 and H_2O (wate upon

In a series of complex reactions, ~~to~~ produce ~~a~~ varieties of compound and toxic chemicals such as Pan.



$$CH_3\overset{\overset{O}{\|}}{C}-O-O-NO_2$$

Very much simplified, Some principal reactions in the formation of photochemical smog are illustrated as;

$$\dot{O} + O_2 + M \longrightarrow O_3 + M$$

$$O + \text{hydrocarbons} \longrightarrow \text{aldehyde} + RCOOH$$

$$O_3 + \text{hydrocarbons} \longrightarrow \text{aldehyde} + ROOH$$

$$HC + O_2 + NO_2 — PAN$$

Measures of Improving Air Quality

(i) The use of un leaded petrol
(ii) Installation of catalytic converter in car exhaust system
(iii) Desulphurization of flue gas through the use of wet limestone gypsum scrubbing process which is capable of improving 90% of SO_2
(iv) Installation of electrostatic precipitation in power plants
(v) Installation of low nitrogen oxide burners in power plants

Concentration of Air pollutants

Concentation of pollutants can be expressed in ppm, that is the number of molecules of pollution per million (10^6) molecules of air, it is a ratio without unit. Based on avogado law, ppm is also equal to the number of volumes of pollutiant per million volume of air.

$$ppm = \frac{\text{number of molecules of pollutants}}{10^6 \text{ molecules of air}}$$

$$= \frac{\text{NO of volumes of pollutant}}{10^6 \text{ volume of air}}$$

50ppm of CO means there are $50cm^3$ of pollutant for every 1 million cm^3 of air. Percentage by volume concentration can also be converted to ppm by multiplying with a factor of 10,000

hence 0.1% by volume concencentratiom is equivalent to 1000ppm

i.e, $0.1\% = \frac{0.1}{100} \times 10^6 = 1000ppm$

Air concentration can also be expressed in mg/m^3 or $\mu g/l$

$$mg/m^3 = \text{concentration in ppb} \times \frac{\text{molecular weight}}{\text{molar volume in L}}$$

molar volume at 1atm at 25°c is 24.45L for every gas.

using gas law

$$PV = nRT, \quad V = \frac{nRT}{P} = \frac{1mole \times 8.314\ J/K/mol \times 298}{101325N/m}$$

$$= 0.02445m^3$$

1 Cubic metre = 1000L

$0.02445m^3 = 24.45L$

For SO_2 measured to be 1ppm in the atmosphere express in mg/m^3

no solution

$$mg/m^3 = \text{concentration in ppm} \times \frac{\text{molecular weight}}{\text{molar volume}}$$

Albedo is a measure of ~~water~~ how much sunlight (solar radiation) reflect on the earth surface

Mirage is an optical illusion caused by the bending of light (i.e refraction) through the air, layers of different temperature.

Water Quality

- Dissolved oxygen can be used to measure saturated oxygen amount in water, when water small, it means the microorganisms in the water has reduced the amount of oxygen in the water

* If water has high bod it means it is polluted with organic waste and much oxygen is required to break down the waste
* bod is determined in water by incubating a sample of water for 5 days at 20°c and measuring the amount of O_2 consumed

Noise Pollution

Noise is unwanted sound. What is pleasant to some ears may be extremely unpleasant to others.

Natural environment contains many sources of noise, Wind, oceans, volcanoes, animal sounds. Noise is an inescapable by product of industrial environment, which is increasing with advances in industrialization and urbanization.

Even in a non-industrial environment, noise from such activities such as auto repair, grinding affects those living in the immediate environment

Noise cause irritation or annoyance but also constricts the arteries, it reduces the flow of blood, and increases the flow of adrelaline, and forces the heart to work faster

Continuous noise causes an increase in the cholesterol level resulting in the permanent constriction of blood levels making on prone to heart attack or stroke

WHO fixed 45dB as the safe noise level for a city

Solid Waste Management

The term solid waste is often used with refuse

Literature often describe refuse as putriscible and non-putriescible, except dead bodies of human body.

Similarly solid waste is defined as non-gaseous and non-liquid waste that results from the daily activity of a community, residential, commenicial and agricultural sector.

This two definition can be seen to be similar in all material respect. Therefore, the term solid waste and refuse may be used interchangably, the former being more current in usage (Ogedengbe 1990). Solid waste can be subdivided into its component part, namely; gabbage, trash or rubbish and ashes.

Gabbage is the putrescible or biodegradable component of waste resulting from handling, preparation, cooking and Serving of foods and also of cleaning of food product and dishes. Gabbage is generated from homes, cafetaria, bukateria etc and

Trash or Rubbish refers to all non-putrescibles except ashes. It includes combustible wastes such as paper, plastics, rags, cardboard, boxes, wood, leaves, weeds, rubber etc as well as non-combustible such as metal & glass materials in the form of tiny cans, unservicables or abandoned.

What is flue gas? components!?

auto mobiles, television sets, refrigerator, stoves and beddings, ceramic

Solid Waste Management

By Incinerator

It involves the combustion of organic substances contained in waste materials. It is a thermal treatment in which waste is converted to ash, flu-gas and heat at a high temperature. The ash is mostly from inorganic constituent of the waste and may take the form of solid lump or particulate carried by the flue gas. The flue gases must be cleared of gaseous or particulate pollutant before they are dispersed into the atmosphere. Some are built with energy recovery system and are termed waste-to-energy technologies such as gasification, plasma arc, Pyrolysis and anaerobic digestion and could also be without energy recovery or [illegible]

Advantages

(i) Incinerator reduces the solid mass of the original waste by 80 – 85%, ~~rate~~ Materials such as metals recovered could be recycled.

(ii) It has a strong benefit of treating wastes and hospital and clinical waste and certain hazardous wastes where pathogen and toxins can be destroyed by high temperatures

(iii) The heat produced in incinerators can be used to generate steam which may then be used to drive turbines inorder to produce electricity.

Disadvantage

(1) It causes pollution: The output such as the ash and emission to atmosphere of flue gase.

Before the flue gas cleaning system, flue gases may contain significant amount of particulate matters, heavy metals, dioxins, furans, sulfur dioxide, SO_2 and HCl gas. The complete combustion processes make nearly all the carbon content in the waste to be emitted as CO_2 leading to green house effect, earth warming, climate change, and depletion of ozone layer, there is also odour pollution, caused by H_2S

(2) By Land filling:

It has major disposal method for municipal solid waste in many contries and cities. In land filling, the wastes are compressed

The potential environmental problem associated with land filling ~~is got~~ results mainly from the generation of land fill gas mostly methane ~~The poten~~ and leachate, which are highly polluting water percolating through decaying waste in land fill.

To ensure there are no harmful discharges to the environment, land fill gas and leachate are collected are treated.

~~Disadvantage~~ Advantantages

Methane has been used as an energy source in some countries.

Leachate is treated in sewage treatment plant, it is viable and other source of materials and energy

Provides jobs for waste pickers scavenging for usable materials, however because of the high concentration of gases and the unprodictability of the land fill contents which often includes sharp objects. Land fill escavation is generally considered dangerous

Other Alternative Methods

③ Waste reduction

④ Waste recycling

⑤ Anaerobic digestion

⑥ Composting

⑦ Mechanical biological treatment

⑧ Pyrolysis

A what is waste water management??

Waste Water Treatment

Characteristics/component of Waste Water

(i) Alkalinity
(ii) Chloride
(iii) COD - Chemical Oxygen Demand
(iv) Suspended solid
(V) Settable solid (vi) phosphorus
(vii) Total dissolved solid, (viii) Nitrogen component
(ix) Total organic component

Sedimentation: It is also ~~known~~ "settling" It is defined as the removal of solid particle from a suspension by settling under gravity

Clarification: It usually refers specifically to the function of sedimentation term in removing suspended matter to give a clarified water

In a broad sense; it could include flooding and filteration

Tickening in sendimentation term is the process whereby the settled impurities are concentrated and compacted on the floor of the term and the ~~slug~~ Slurred collected hoppers

Concentrated impurities withdrawn from the bottom of a Sendimentation tank is ~~called~~ Slurred

Materials that floats to the top of the tank is called Scum

Waste Water Management

What is waste water management?
Why is it called " " ??

Waste Water Treatment

① pretreatment/ preliminary treatment: It requires regulatory agency because it involves treatment of materials that won't be treated by municipher ingredients because these ingredients may be harmful.

It removes materials that inhibit biological impurities
(ii) ~~Secondary treatment~~ that could kill the microbes in
(iii) ~~Tertiary treatment~~. biological treatment.

Materials that cannot be treated by municipher ingredients but can be treated with preliminary treatment e.g Ag^+ are removed

Equilization Basins balances the ~~collective~~ colloidal materials and water

Primary treatment removes 65% of solids and 35% of BOD

*List out microbes/bacteria that can be used for the biological treatment of wastewater.

Secondary ~~treatment~~ system: It mainly biological treatment, when ~~Flow rate~~ there is introduction of microbe
Regulator detects the flow rate from
A way to measure the concentration of the water
Waster water slows do

Primary treatment: It is the 2nd Step, it allows filteration of solid and greases in the waster. The screened waste water flows ~~into the~~ primary settling tank where it is head for severa hours allowing solid particle to settle at the bottom of the tank and greases and oils to float ~~to~~ the top of the tank.

~~*Where to~~ the

(debris, microbes, greases, etc)
* Note where each materials are removed in waste water

~~Secondary tre.~~

Secondary treatment: It is a biological treatment process that removes dissolved organic substance from waste water. The partially treated wastewater from the settling tank

Question

You are sent to a village, no tap and no well water, only stream, how will you take it and make it a portable water?

* Allow it settle, you can add alum to enhance coagulatio use a moderate quantity, then filter after filteration, boil, and then allow it to cool down and then expose it to sun light, sunlight destroys all the microbes, it is called ozonization.

Solid processing

Primary solids from the primary settling tank and Secondary solids from the Clarifier are sent to a digester

Digestion results in 90% reduction in Pathogens and production of a wet soil like material called bio solids that contain 95-97% water.

Table 30-2 Possible alternatives for CFCs and some of their properties

Compound	Toxicity	Boiling point (°C)	Flammability	Ozone Depletion Potential
$CH_3CH_2CH_3$	Low	−42	Yes	0
$CH_3CH_2CH_2CH_3$	Low	0	Yes	0
CH_2Cl_2	High	40	No	< 0.05
CH_3OCH_3	Low	−24	Yes	0
CH_3CHF_2	Low	−24	Yes	0

Check Point 30-5

(a) Give some methods for reducing the depletion of the ozone layer.

30.3 Water Pollution

Water pollution is the degradation of the quality of water by the introduction of chemical, physical or biological wastes into rivers, streams, lakes and oceans.

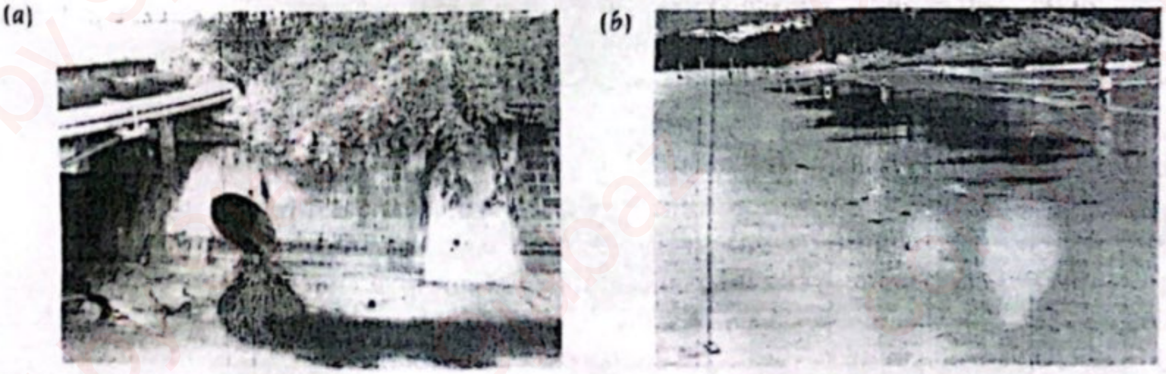


Fig.30-19 The (a) river and (b) beach are seriously polluted.

The Causes and Effects of Water Pollution on the Environment

Deterioration in **water quality** may be caused by livestock waste, oil spillages, residues of pesticides, detergents in the sewage and industrial effluents.

Industrial effluents containing inorganic and organic wastes are often discharged into rivers and the sea. Although they are often treated before discharge, they still contain toxic substances. Domestic sewage contains mainly organic waste and suspended particles. It also contains synthetic detergents that cause the foaming of water. Agricultural runoff contains fertilizers, livestock waste and pesticides. Accidental oil spillages cause the death of aquatic organisms and damage the marine ecosystem.

The adverse effects, caused by different factors, on water quality include:

1. *Livestock waste*
   When there is an excessive amount of organic matter discharged into water, the existing micro-organisms will grow and multiply rapidly. Oxygen is rapidly depleted and competition for space and food takes place. Because of the lack of oxygen, anaerobic micro-organisms begin to partially break down the organic matter, releasing noxious gases like methane, ammonia and hydrogen sulphide. As a result, aquatic organisms will die *(Fig. 30-20)*.

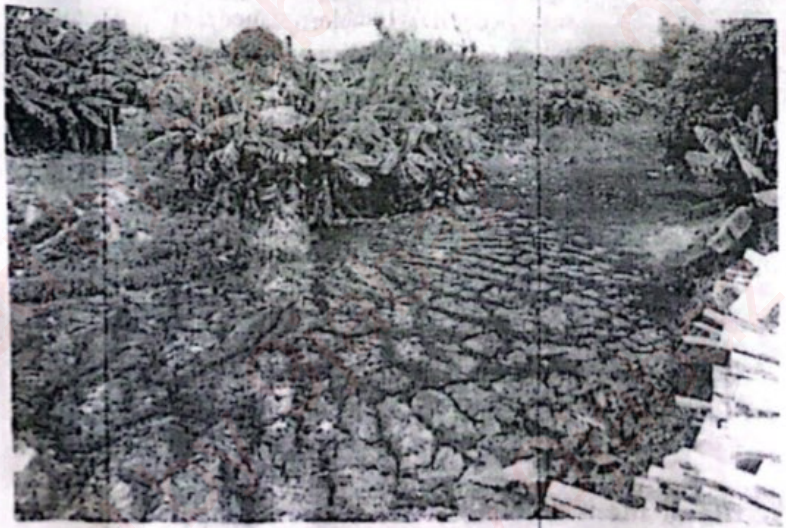


Fig.30-20 *The river is seriously polluted by livestock waste, causing the death of aquatic organisms.*

2. *Oil spillages*

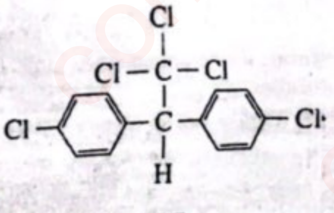
Oil may clog the feathers of sea birds and prevent them from flying or swimming. It also interferes with the insulation provided by the feathers, so affected birds may die of cold or pneumonia. When birds try to clean their feathers with their beaks, they may be poisoned through ingestion of the oil. Furthermore, oil floating on water prevents the dissolution of oxygen. Therefore, aquatic organisms may die due to depletion of oxygen. Oil kills marine life directly.

Besides, oil deposited on beaches may drive away holiday-makers and spoils recreational resorts.

Fig.30-21 *Oil spills are difficult to clean up because oil is not soluble in water.*

3. *Residues of pesticides*

Pesticides are synthetic organic compounds used to eliminate flying and crawling insect pests. On entry into water pathways, pesticides cause immediate toxic effects on aquatic life. They are non-biodegradable and may accumulate along the food chain until a toxic level is reached. DDT (dichlorodiphenyltrichloroethene), an organochlorine insecticide, was previously widely used.



DDT

However, it causes much ecological damage because

(a) it resists degradation and remains in the environment;
(b) it is very soluble in fat, including the fat of milk and the body fat of animals, with the potential for damaging internal organs;
(c) it affects the reproduction of birds, fish, etc., especially weakening the shells of eggs;
(d) many species of insects are developing resistance to this insecticide.

Its use has been banned in many parts of the world including Nigeria.

4. *Detergents in sewage*

Sewage is domestic wastewater. A major pollutant present in sewage is synthetic detergent. Discharge of detergents causes eutrophication (massive growth of algae in the water body resulting in death of other plants and animals due to depletion of oxygen, space and food) brought about by phosphates found in some detergents *(Fig. 30-22)*. It also causes foaming in rivers and lakes. Ingestion of detergents by aquatic organisms can cause death.

5. *Industrial effluents*

The toxic materials present in industrial effluents vary with the types of industries involved. They may contain heavy metals (e.g. Cd, Cr, Cu, Hg, Ni, Pb, Zn), cyanides, polychlorinated hydrocarbons, etc. Heavy metals may also accumulate in animal bodies along the food chain.

Fig.30-22 *Eutrophication produces a mat of algae on the surface of water.*

Fig.30-23 *Industrial effluents discharged into the sea cause serious water pollution.*

Table 30-3 summarizes the causes and effects of water pollution.

Table 30-3 *The causes and effects of water pollution*

Pollutant	*Harmful Effect*
Livestock wastes	1. Release noxious gases 2. Lead to the death of aquatic organisms
Oil spillages	1. Clog the feathers of sea birds and prevent them from flying or swimming 2. Interfere with the insulation of the feathers of birds 3. Poison birds by ingestion 4. Prevent dissolution of oxygen 5. Spoil recreational resorts
Residues of pesticides	1. Toxic 2. Accumulate along food chains 3. Potential for damaging internal organs 4. Harmful on reproduction of animals
Detergents in sewage	1. Cause eutrophication 2. Foaming in rivers and lakes 3. Lead to the death of aquatic organisms
Industrial effluents	1. Toxic 2. Accumulate along food chains

Water Quality

☐ Dissolved Oxygen

Oxygen dissolved in water is necessary for aquatic life. **Dissolved oxygen** (DO) can be used as an indicator of oxygen content in water. It is measured in mg of oxygen per dm^3 of water or percentage saturation of dissolved oxygen. The maximum concentration of dissolved oxygen in water at 16°C is 10 mg dm^{-3}. If a water sample contains 6 mg dm^{-3} of dissolved oxygen at 16°C, the percentage saturation of DO is then:

$$\frac{6}{10} \times 100 = 60$$

The sample is said to be 60% saturated with oxygen.

Fishes normally require 4 – 6 mg dm^{-3} of oxygen for survival. A minimal DO is also needed for reducing odour due to anaerobic degradation of organic matter. Depletion of oxygen may be caused by biological degradation of waste matter (anaerobic respiration of aquatic micro-organisms). Oxygen may be replenished by aeration.

❑ Biochemical Oxygen Demand

Biochemical oxygen demand (BOD) is the amount of oxygen required to break down the organic matter present in a water sample.

It is commonly used as an indicator of the extent of organic pollution in water. If water has a high BOD, a lot of organic waste is present and much oxygen is required to break down the waste. A low BOD indicates the presence of only a small amount of organic matter and there is little organic pollution. Natural clean water has a BOD of about 1 to 4 mg dm^{-3}. If BOD is greater than the amount of oxygen replenished, then some fishes and aquatic life may die. Organic debris will accumulate and anaerobic micro-organisms begin to multiply, producing unpleasant odours and tastes.

BOD is determined in the laboratory by incubating a sample of water for five days at 20°C and measuring the amount of oxygen consumed. The BOD determined in this way is also known as five-day BOD, or BOD_5. If a sample has an initial DO of 8 mg dm^{-3} and in five days this has dropped to 2 mg dm^{-3}, the BOD_5 is then

$$(8 - 2)\ \text{mg dm}^{-3} = 6\ \text{mg dm}^{-3}$$

The BOD_5 value is commonly used to indicate the relative oxygen requirements of treated effluents and polluted waters.

Table 30-4 The degree of pollution indicated by biochemical oxygen demand (BOD)

BOD (mg dm^{-3})	*Degree of Pollution*
< 30	No
30 – 80	Mild
> 80	Severe

Check Point 30-6

(a) The solubility of oxygen in water is 9 mg dm^{-3} at 20°C and 1 atm. In a stream, the water is found to be 40% saturated with oxygen. List some uses of the stream water.

(b) **(i)** What is the significance of BOD?
(ii) If the initial DO of a sample is 30 mg dm^{-3} and the value has dropped to 10 mg dm^{-3} in five days, calculate the BOD.

30.4 Solid Waste

Disposal of Solid Waste

Incineration and **landfilling** are two common disposal methods for solid waste.

☐ By Incineration

Incineration has the advantages of reducing the volume of the waste by approximately 85%, killing the disease-causing organisms at high temperature, and having no risk of causing water pollution. However, the main disadvantage of incinerating municipal waste is the potential danger of polluting the atmosphere with toxic chemicals, e.g. sulphur dioxide, carbon monoxide.

Fig.30-24 Solid waste can be disposed of by incineration.

☐ By Landfilling

Landfilling has now become the major disposal method for municipal solid waste in many cities. In landfilling, the wastes are compressed and covered with earth on landfill sites. The potential environmental problems associated with landfilling result mainly from the generation of landfill gas (mostly methane) and leachate (highly polluting water percolating through decaying waste in landfill). To ensure there are no harmful discharges to the environment, landfill gas and leachate are collected and treated. Methane has been used as an energy source in some countries. Leachate is treated in sewage treatment plants.

Fig.30-25 *Waste disposal at a landfill site*

Pollution Problems Associated with the Disposal of Plastics

The tremendous amount of plastic items used today creates waste disposal problems. The disposal of plastic waste by landfilling and incineration have both caused certain problems. As plastics are chemically tailored for long life, they do not generally undergo decomposition in landfill sites. Plastic waste can last for a long time, thus delaying the reuse of the landfill sites. Incineration of plastic waste produces air pollutants such as hydrogen chloride from polyvinyl chloride and other chlorine-containing polymers. The hydrogen chloride produced can cause acid rain which damages the environment.

Plastic waste in the sea poses direct danger to fishes. Small fishes have been found dead with their digestive tracts clogged by fragments of plastic foam they had ingested. Sea animals have been suffocated to death by plastic bags. The use of certain chemicals such as plasticizers and chlorofluorocarbons in the manufacture of plastics leads to further ecological and environmental problems.

Possible Solutions to Pollution Problems of Plastics

As plastics are indispensable in modern life, the associated pollution problems have to be solved. To tackle the problem of waste disposal, **degradable plastics** are being developed and processes for **recycling** plastic wastes are now underway.

☐ Development of Degradable Plastics

Plastics normally undergo extremely slow degradation because the enzymes in micro-organisms tend to attack only the ends of the polymer chains. Attempts have been made to develop plastics which are more degradable. There are several types of degradable plastics. They are biopolymers, photodegradable plastics and synthetic biodegradable plastics.

Biopolymers

Biopolymers are polymers made by living micro-organisms such as paracoccus, bacillus and spirullum *(Fig. 30-26)*. Poly(hydroxybutyrate), PHB, is a natural polyester made by certain bacteria. Micro-organisms found in soil and natural water sources are able to break down the polymer. Biodegradation of this polymer in the environment is usually complete within 9 months. PHB, however, is 15 times more expensive than poly(ethene).

Fig.30-26 *Micro-organisms producing biopolymers: (a) paracoccus, (b) bacillus and (c) spirullum*

Photodegradable Plastics

Light-sensitive functional groups such as the carbonyl group ($-C=O$) can be incorporated into the polymer chains. The long polymer chains will be broken down through the action of sunlight into shorter fragments which can then be biodegraded at a faster rate.

Synthetic Biodegradable Plastics

Synthetic biodegradable plastics are made by incorporating starch or cellulose into the polymer during production. As micro-organisms digest starch or cellulose, the plastic is broken down into tiny pieces. The very small pieces left over have a large surface area which greatly speeds up their biodegradation. The drawbacks of this method are that the products of biodegradation may cause water pollution, and the rate of biodegradation is still too slow for the large quantity of plastic wastes generated.

Degradable plastics have been used for making six-pack beverage rings, trash bags, and disposable diapers *(Fig. 30-27)*.

Fig.30-27 Products made of degradable plastics

☐ Recycling of Plastics

Since plastics are essentially derived from petroleum, which has limited reserves, disposal of plastics by landfilling or incineration is a waste of useful resources. Such wastage may be reduced by recycling them into one form or another.

Fig.30-28 A plastic bag made of recycled materials

Direct Recycling

This method applies only to thermoplastics. The plastics in the waste are separated, cleaned, pulverized, and remoulded into new plastic items. To do this successfully depends on the collection of clean and uncontaminated plastic wastes, which is the most difficult step. In 1988, the Society of the Plastics Industry (SPI) developed a uniform coding system that makes it possible to sort waste plastics. Once the waste plastics are separated, they can be reprocessed. The regenerated plastics usually have deteriorated properties due to repeated thermal and mechanical processing, and can only be used for articles which are not subject to high stress. Recent development on recycled plastics focuses on converting plastic products with short service lives, such as foam, wrappings and containers, to products with longer service lives, such as construction materials and plastic pipes.

Recycling of Energy

The energy values contained in plastics are quite high. The energy obtained from burning plastic wastes in incinerators can be used for heating or for generating electricity.

Table 30-5 Calorific values of plastics and various materials

Material	*Calorific Value* ($kJ\ kg^{-1}$)
Polystyrene	46 000
Poly(ethene)	46 000
Heating oil	44 000
Fats	37 800
Leather	18 900
Polyvinyl chloride (PVC)	18 900
Paper	16 800
Wood	16 000

Recycling of Chemicals

Plastic waste is pyrolysed (decomposed at high temperature in the absence of air), and the products fractionally distilled to give useful chemicals. These chemicals may be employed in the production of plastics or other purposes. *Table 30-6* shows some of the chemicals manufactured from the pyrolysis products.

Table 30-6 Chemicals manufactured from pyrolysis products

Pyrolysis Product	*Chemical Manufactured*
Ethene	Poly(ethene)
Propene	Poly(propene)
Methane	Town gas
Butadiene	Rubber
Benzene	Various plastics (e.g. polystyrene)
Miscellaneous	Chemical raw materials

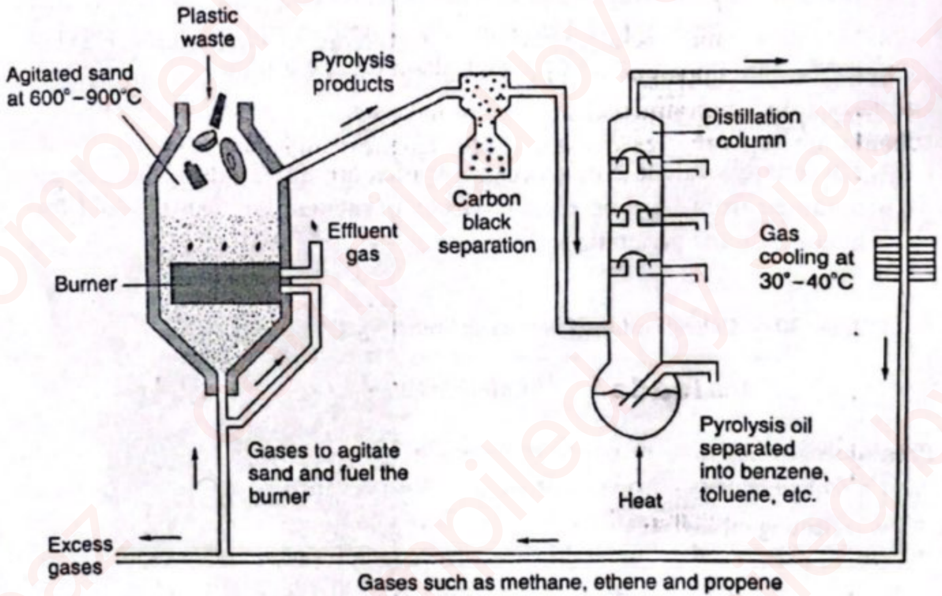


Fig.30-29 Recycling of chemicals from plastics by pyrolysis

Check Point 30-7

(a) What are the benefits of recycling plastics?

(b) What are the difficulties in recycling plastics?

Characteristics of Domestic Wastewater

Typical Composition of Untreated Domestic Wastewater

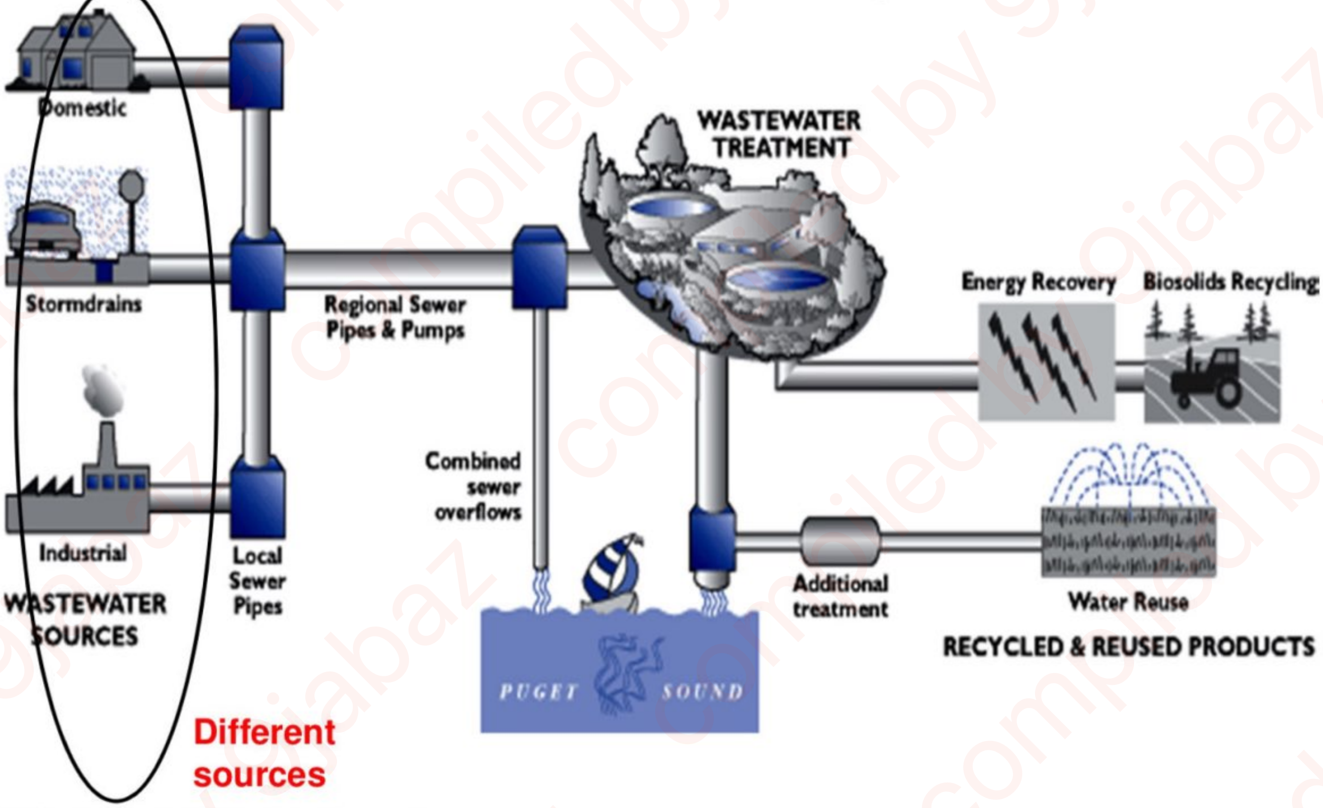
Constituent	**Weak**	**Medium**	**Strong**
		(all mg · L^{-1} except settleable solids)	
Alkalinity (as $CaCO_2$)[a]	50	100	200
BOD_5 (as O_2)	100	200	300
Chloride	30	50	100
COD (as O_2)	250	500	1000
Suspended solids (SS)	100	200	350
Settleable solids (in mL · L^{-1})	5	10	20
Total dissolved solids (TDS)	200	500	1000
Total Kjeldahl nitrogen (TKN) (as N)	20	40	80
Total organic carbon (TOC) (as C)	75	50	300
Total phosphorus (as P)	5	10	20

[a] This amount of alkalinity is the contribution from the waste. It is to be added to the naturally occuring alkalinity in the water supply. Chloride is exclusive of contribution from water-softener backwash.

Wastewater characteristics

- Compare wastewater (WW)characteristics of
  - Domestic WW
  - Industrial WW (for ex: tannery industry; distillery industry)

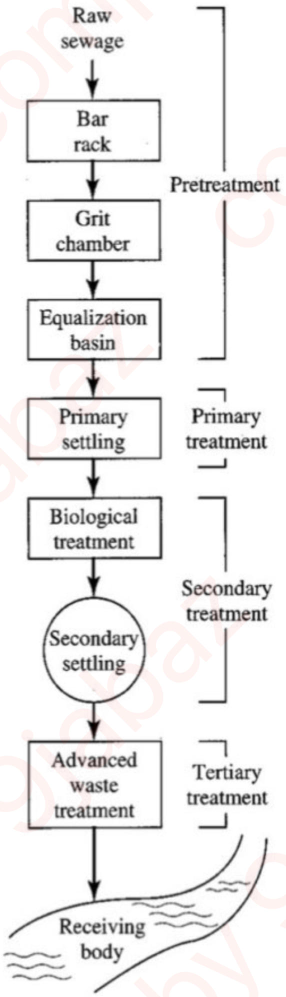
Wastewater Management



http://dnr.metrokc.gov/WTD/homepage/process.htm

Wastewater Management

www.oconomowocusa.com/ wastewater.gif



Municipal Wastewater Treatment Systems

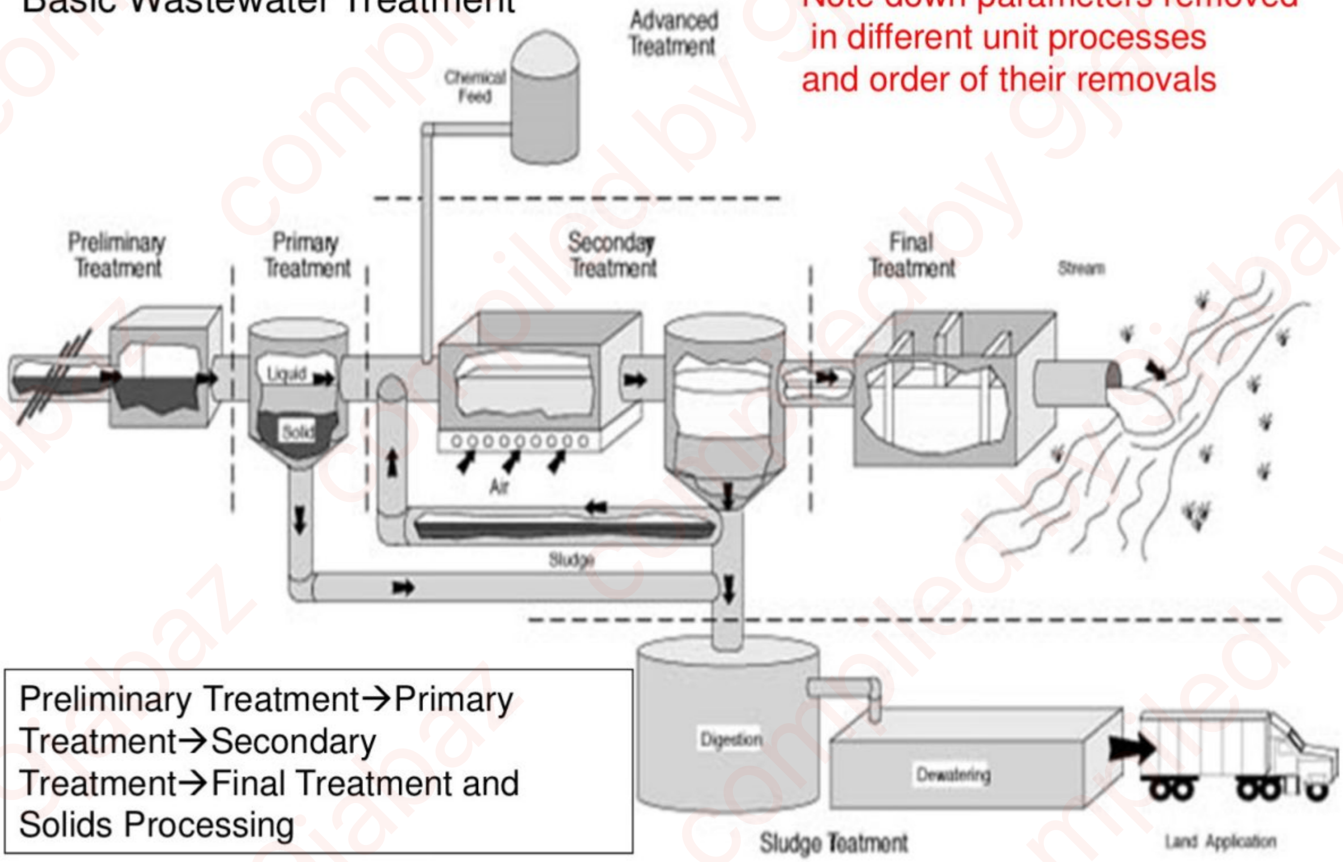
- Preliminary treatment (removes materials that can cause operational problems, equalization basins are optional)
- Primary treatment (remove ~60% of solids and ~35% of BOD)
- Secondary treatment (remove ~85% of BOD and solids)
- Advanced treatment (varies: 95+ % of BOD and solids, N, P)
- Final Treatment (disinfection)
- Solids Processing (sludge management)

Pre-Treatment of Industrial Wastewaters

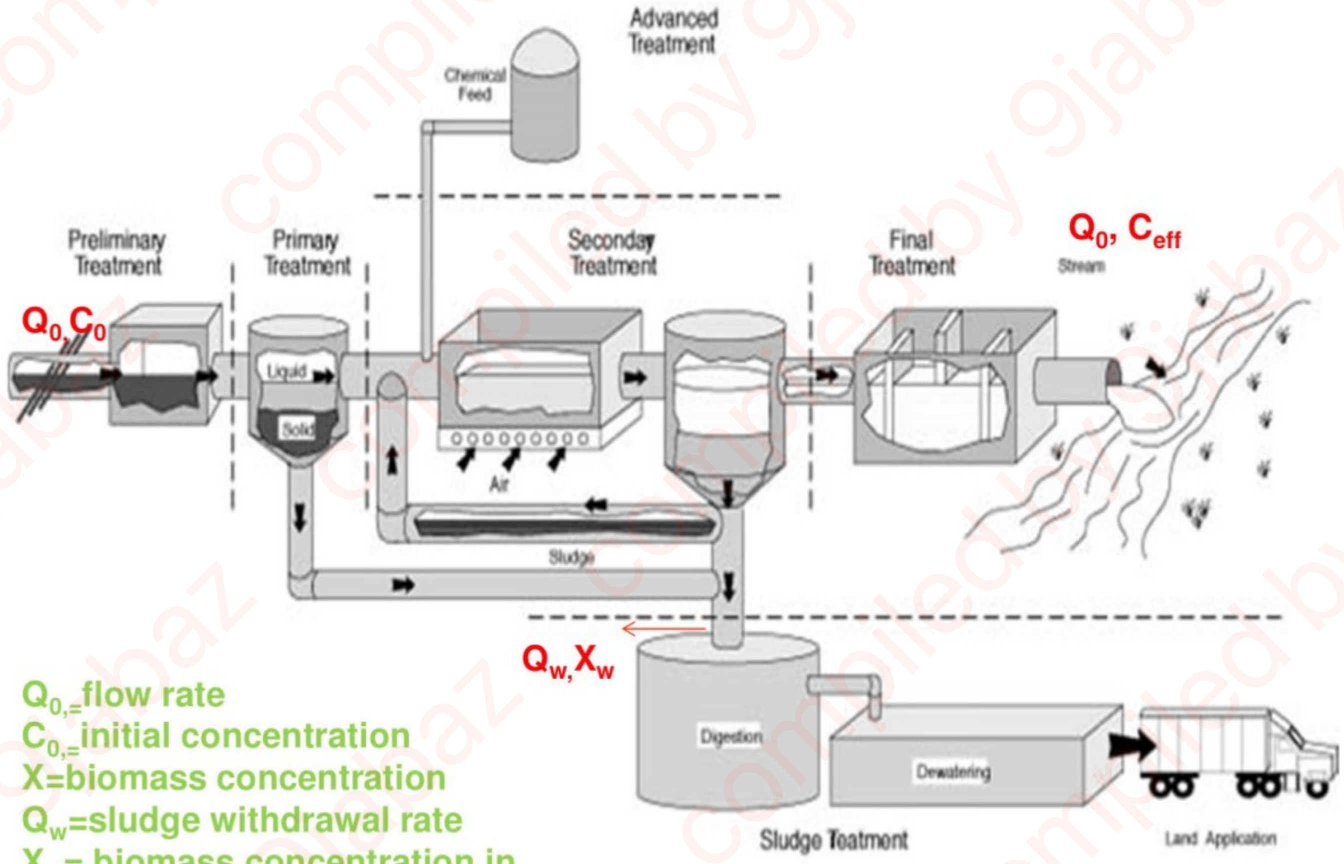
- Industrial wastewaters must be pretreated prior to being discharged to municipal sewer system
- Pretreatment requirements set by regulatory agencies
- Why: remove materials that will not be treated by municipal system, remove materials that inhibit the biological processes in secondary treatment
- For example: silver ions are toxic to bacteria which might affect biological process. Thus silver ions are removed at pre-treatment before biological process so that bacterial performance do not get affected.

Basic Wastewater Treatment

Note down parameters removed in different unit processes and order of their removals



Preliminary Treatment→Primary Treatment→Secondary Treatment→Final Treatment and Solids Processing



$Q_{0,=}$flow rate
$C_{0,=}$initial concentration
X=biomass concentration
Q_w=sludge withdrawal rate
X_w= biomass concentration in secondary settling tank

Preliminary treatment

Upon arrival via the sewer system, the wastewater is sent through a bar screen, which removes large solid objects such as sticks and rags.

Leaving the bar screen, the wastewater flow is slowed down entering the grit tank, to allow sand, gravel and other heavy material that was small enough not to be caught by the bar screen to settle to the bottom. All the collected debris from the grit tank and bar screen is disposed of at a sanitary landfill.

Primary treatment

Primary treatment is the second step in wastewater treatment. It allows for the physical separation of solids and greases from the wastewater. The screened wastewater flows into a <u>primary settling tank</u> where it is held for several hours allowing solid particles to settle to the bottom of the tank and oils and greases to float to the top.

Secondary treatment

-biological treatment process that removes dissolved organic material from wastewater. The partially treated wastewater from the settling tank flows by gravity into an aeration tank.

-mixing of water to solids containing that use oxygen to consume the remaining organic matter in the wastewater as their food supply (use of air bubble for mixing and oxygen supply)

-liquid mixture (i.e., solids with micro-organisms and water) is sent to the final clarifier.

-In clarifier, solids settle out to the bottom where some of the material is sent to the solids handling process and some is recycled back to replenish the population of micro-organisms in the aeration tank to treat incoming wastewater.

Final treatment

Treated water is disinfected and then it is send out for wastewater reuse activities or for discharging in river/streams. mostly chlorination and/or ultra violet irradiation is used for disinfection purposes.

Solids processing

The primary solids from the primary settling tank and the secondary solids from the clarifier are sent to a digester. Micro-organisms use the organic material present in the solids as a food source and convert it to by-products such as methane gas and water.

Digestion results in a 90% reduction in pathogens and the production of a wet soil-like material called “biosolids” that contain 95-97% water.

In order to remove some of this water, mechanical equipment such as filter presses or centrifuges are used to squeeze water from the biosolids to reduce the volume prior to being sent to landfill, incinerated or beneficially used as a fertilizer or soil amendment.

Wastewater Treatment

- **Preliminary Treatment (screening)**
- Primary Treatment (primary settling)
- Secondary Treatment (e.g. activated sludge)
- Advanced Treatment (e.g. P removal)
- Final Treatment (disinfection)
- Solids Processing (sludge treatment)

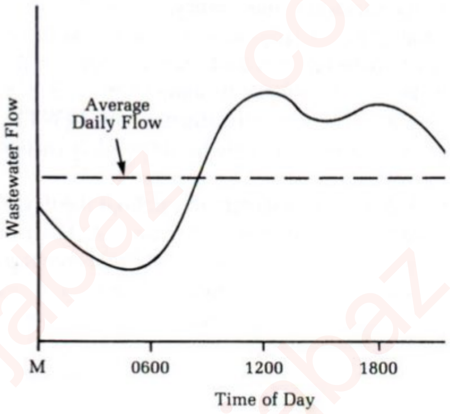
Bar racks

- Purpose: remove larger objects
- Solid material stored in hopper and sent to landfill
- Mechanically or manually cleaned

Grit Chambers

- Purpose: remove inert dense material, such as sand, broken glass, silt and pebbles
- Avoid abrasion of pumps and other mechanical devices
- Material is called “grit”

Equalization Basins



- Wastewater flow has daily fluctuations
- Purpose: To dampen the variation in wastewater flow into a WWTP
- Flow equalization is not a treatment process
- Improves effectiveness of primary & secondary treatment
- Usually achieved by large basins to collect wastewater and pumped to treatment plant at a constant rate
- Adequate aeration and mixing need to be provided to prevent odors and deposition of solids

Source: Davis and Cornwall, Introduction to Environmental Engineering, 2008

Wastewater Treatment

- Preliminary Treatment (screening)
- **Primary Treatment (primary settling)**
- Secondary Treatment (e.g. activated sludge)
- Advanced Treatment (e.g. P removal)
- Tertiary Treatment (disinfection)
- Solids Processing (sludge treatment)

Primary Treatment (settling)

- Primary treatment separates suspended solids and greases from wastewater. Wastewater is held in a tank for several hours allowing the particles to settle to the bottom and the greases to float to the top.
- The solids drawn off the bottom and skimmed off the top receive further treatment as sludge. The clarified wastewater flows on to the next stage of wastewater treatment.

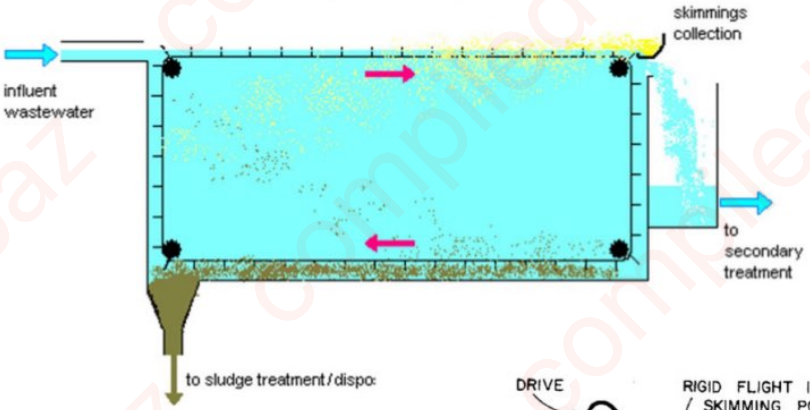
Settling/Sedimentation

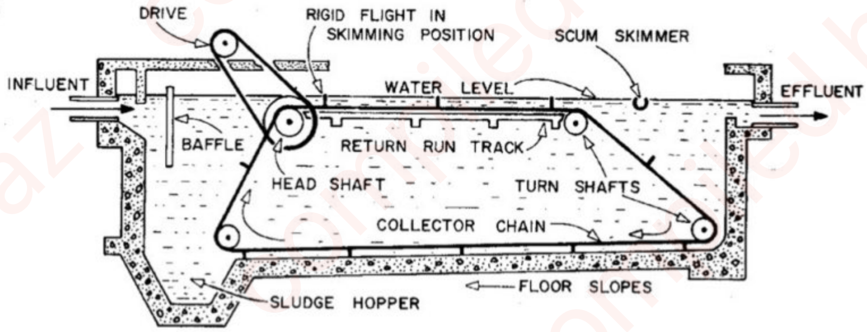
- Solid liquid separation process in which a suspension is separated into two phases –
  - Clarified supernatant leaving the top of the sedimentation tank (overflow).
  - Concentrated sludge leaving the bottom of the sedimentation tank (underflow).
- ***Purpose of Settling***
  - To remove coarse dispersed phase.
  - To remove coagulated and flocculated impurities.
  - To remove precipitated impurities after chemical treatment.
  - To settle the sludge (biomass) after activated sludge process / tricking filters

Some basic definitions

- ***Sedimentation****,* also known as *settling*, may be defined as the removal of solid particles from a suspension by settling under gravity.
- ***Clarification*** is a similar term, which usually refers specifically to the function of a sedimentation tank in removing suspended matter from the water to give a clarified effluent. In a broader sense, clarification could include flotation and filtration.
- ***Thickening*** in sedimentation tanks is the process whereby the settled impurities are concentrated and compacted on the floor of the tank and in the sludge-collecting hoppers.
- Concentrated impurities withdrawn from the bottom of sedimentation tanks are called ***sludge***, while material that floats to the top of the tank is called *scum*.

Primary Settling Basin





http://www.geocities.com/RainForest/5161/wwtps.htm

Primary Settling Basins

Primary Settling Tank Design Example

- Size:
  - rectangular: 3-24 m wide x 15-100 m long
  - circular: 3-90 m diameter
- Detention time: 1.5-2.5 hours
- Overflow rate: 25-60 $m^3/m^2 \cdot day$
- Typical removal efficiencies:
  - solids: 50-60%
  - BOD_5: 30-35%

Example 1

Question: A rectangular primary clarifier (2.4 m deep & 4.0 m wide) is designed to settle a flow of 2000 m^3/day and have an overflow rate of 32 m^3/m^2.day

I) How long should it be?

II) What detention time will it have?

Example 1

I) Length:

$$\text{Overflow rate} = \frac{\text{flow rate}}{\text{area}} = \frac{2000\,\frac{\text{m}^3}{\text{day}}}{4\ \text{m} \times \text{Length}} = 32\,\frac{\text{m}^3}{\text{m}^2 \cdot \text{day}}$$

Solve for length: $$\text{Length} = \frac{2000}{4 \times 32} = 15.6\ \text{m}$$

Example 1

II) Detention time:

$$\text{Detention time} = \frac{\text{volume}}{\text{flow rate}} = \frac{2.4\ \text{m} \times 4\ \text{m} \times 15.6\ \text{m}}{2000\ \frac{\text{m}^3}{\text{day}} \times \frac{\text{day}}{24\ \text{hr}}} = 1.8\ \text{hr}$$

Wastewater Treatment

- Preliminary Treatment (screening)
- Primary Treatment (primary settling)
- **Secondary Treatment (e.g. activated sludge)**
- Advanced Treatment (e.g. P removal)
- Final Treatment (disinfection)
- Solids Processing (sludge treatment)

Secondary Treatment

- Secondary treatment is a biological treatment process that removes dissolved organic matter from wastewater.
- Sewage microorganisms are cultivated and added to the wastewater. The microorganisms use organic matter from sewage as their food supply. This process leads to decomposition or biodegradation of organic wastes.

Secondary Treatment

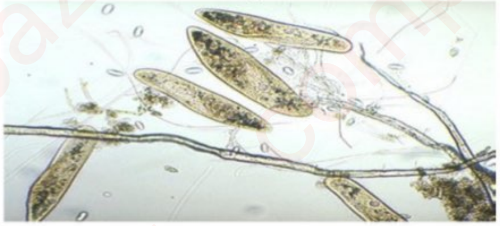
- Basic approach is to use <u>aerobic biological degradation:</u>

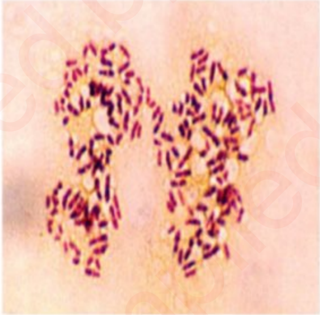
$$\text{organic carbon} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + \text{new cells}$$

- Objective is to allow the BOD to be exerted in the treatment plant rather than in the stream

How is this accomplished?

Create a very rich environment for growth of a diverse microbial community





Basic Ingredients

- High density of microorganisms (keep organisms in system)
- Good contact between organisms and wastes (provide mixing)
- Provide high levels of oxygen (aeration)
- Favorable temperature, pH, nutrients (design and operation)
- No toxic chemicals present (control industrial inputs)

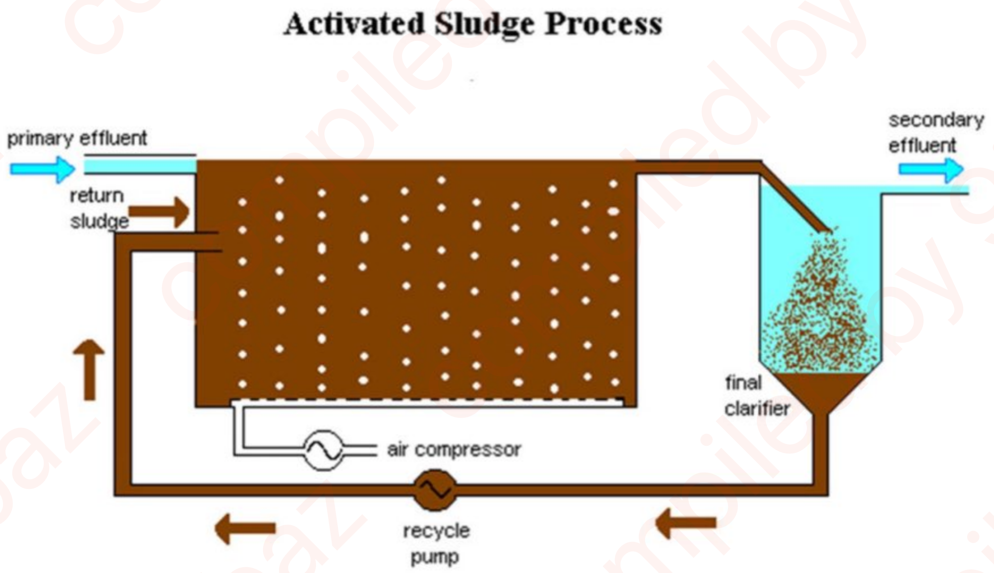
Dispersed (suspended) growth vs Fixed growth

- Two approaches of secondary treatment
  - fixed film, and suspended film systems
- Dispersed Growth (suspended organisms)
  - Activated sludge
  - Oxidation ditches/ponds
  - Aerated lagoons, stabilization ponds
- Fixed Growth (attached organisms)
  - Trickling filters
  - Rotating Biological Contactors

Activated Sludge

- Process in which a mixture of wastewater and microorganisms is agitated and aerated
- Leads to oxidation of dissolved organics
- After oxidation, separate sludge (mostly microbial cells, water, and other contaminants) from wastewater
- Induce microbial growth
  - Need food, oxygen
  - Want Mixed Liquor Suspended Solids (MLSS) of 3,000 to 6,000 mg/L

Activated Sludge Process



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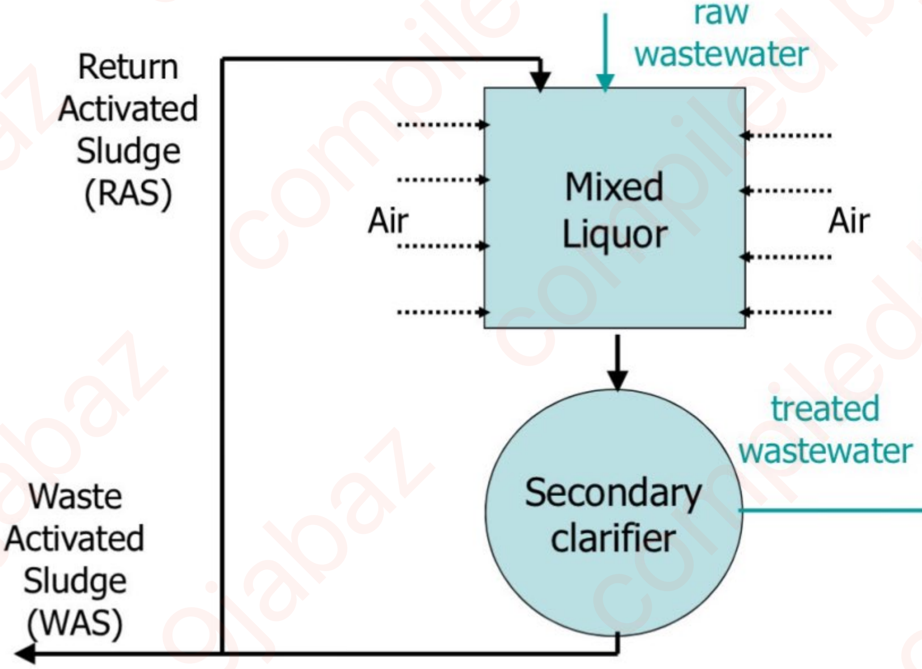
Activated Sludge Process



raw wastewater

Return Activated Sludge (RAS)

Air

Mixed Liquor

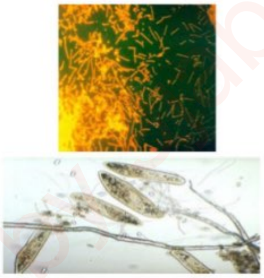
Air

Secondary clarifier

treated wastewater

Discharge to River or Land Application

Waste Activated Sludge (WAS)



Activated Sludge Process with secondary clarifier

East Lansing WWTP

East Lansing WWTP

F/M Parameter

- Low F/M (low rate of wasting)
  - – starved organisms
  - – more complete degradation
  - – larger, more costly aeration tanks
  - – more O_2 required
  - – higher power costs (to supply O_2)
  - – less sludge to handle
- High F/M (high rate of wasting)
  - – organisms are saturated with food
  - – low treatment efficiency

Activated Sludge Design

- Detention time: t_d = approximately 6 - 8 hr
- Long rectangular aeration basins
- Air is injected near bottom of aeration tanks through system of diffusers
- Aeration system used to provide mixing
- MLVSS and F/M controlled by wasting a portion of microorganisms

Other options

Low-tech solutions

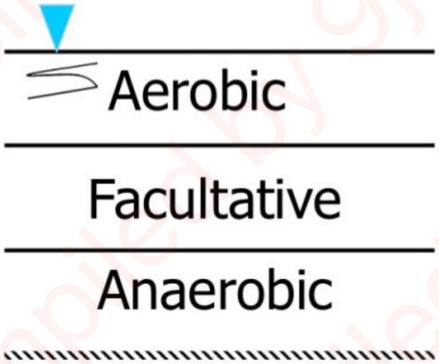
- Aerobic ponds
- Facultative ponds
- Anaerobic ponds

1. Aerobic ponds

- Shallow ponds (<1 m deep)
- Light penetrates to bottom
- Active algal photosynthesis
- Organic matter converted to CO_2, NO_3^-, HSO_4^-, HPO_4^{2-}, etc.

2. Facultative ponds

- ponds 1 - 2.5 m deep
- $t_d = 30 - 180$ d
- not easily subject to upsets due to fluctuations in Q, loading
- low capital, O&M costs



Aerobic

Facultative

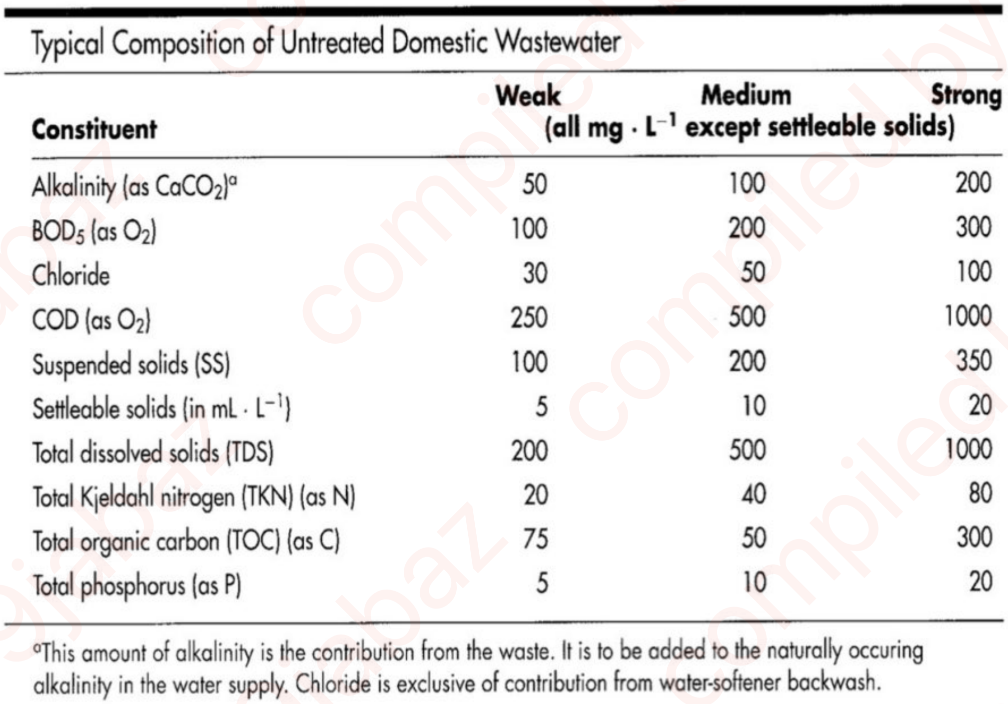
Anaerobic

3. Anaerobic Ponds

- Primarily used as a pretreatment process for high strength, high temperature wastes
- Can handle much high loadings
- 2 stage:
  - Acid fermentation: Organics → Org. acids
  - Methane fermentation Org. Acids → CH_4 and CO_2

Example 1: Performance of a “AA” WWTP

(Grit chamber→ PST→ Activated sludge unit→SST→ Nitrification unit→ Effluent)



Typical Composition of Untreated Domestic Wastewater

Constituent	Weak	Medium	Strong
	(all mg · L^{-1} except settleable solids)		
Alkalinity (as $CaCO_2$)[a]	50	100	200
BOD_5 (as O_2)	100	200	300
Chloride	30	50	100
COD (as O_2)	250	500	1000
Suspended solids (SS)	100	200	350
Settleable solids (in mL · L^{-1})	5	10	20
Total dissolved solids (TDS)	200	500	1000
Total Kjeldahl nitrogen (TKN) (as N)	20	40	80
Total organic carbon (TOC) (as C)	75	50	300
Total phosphorus (as P)	5	10	20

[a] This amount of alkalinity is the contribution from the waste. It is to be added to the naturally occuring alkalinity in the water supply. Chloride is exclusive of contribution from water-softener backwash.

Performance in a “AA” WWTP

Influent flow rate	1 MLD (million liters per day)
Influent parameters	Take highest value of parameters from previous slide
Remaining Suspended solids after primary sedimentation tank	100 mg/L (inf: 300mg/L)
remaining BOD5 after primary sedimentation tank	250mg/L(inf: 350mg/L)
BOD5 after activated sludge process	100mg/L
TKN after biological nitrification process	50 mg/L as N(inf: 80mg/L)

Question: Find out efficiency of different unit processes;
remaining conc. Of different parameters?
Is it meeting the standards of river?
How much is sludge generation? What information are required?

Performance in a “AA” WWTP

Influent flow rate	1 MLD (million liters per day)
Influent parameters	Take highest value of parameters from previous slide
Removal Suspended solids after primary sedimentation tank	=((350-100)/350)*100
Removal BOD5 after primary sedimentation tank	=(300-250)*100/300
Removal of BOD5 after activated sludge process	=(250-100)*100/250
Removal of TKN after biological nitrification process	??
Conc. Of bacteria in SST	10000mg/L
Sludge withdrawal rate from SST	0.1MLD

Performance in a “AA” WWTP

Influent flow rate	1 MLD (million liters per day)
Influent parameters	Take highest value of parameters from previous slide
Remaining Suspended solids after primary sedimentation tank	100 mg/L
remaining BOD5 after primary sedimentation tank	250mg/L
BOD5 after activated sludge process	100mg/L
TKN after biological nitrification process	50 mg/L as N

Question: Find out efficiency of different unit processes;
remaining conc. Of different parameters?
Is it meeting the standards of river?
How much is sludge generation? What information are required?

Dr. ore's part

HDA

Petroleum

Petroleum comes from the greek word potra which means "rock" and Oleum i.e Oil. Petroleum simply means rock oil.

It is a general term that covers naturally occuring for unprocessed crude oil, refined product and naturally occuring gas

Gasoline, Kerosene, diesel, lubricating oil

AGO - Automotive Gas Oil
DPK - Dual Purpose Kerosene
PMS - Premium Motor Spirit

We can get all the component of crude oil from bitumen but because it is more viscous than crude oil, so it requires Sophisticated

Sources of Petroleum in Nigeria

(i) Bitumen: found in three states in Nigeria, Ogun, Edo and Ondo state
(ii) Oil shale: found in Enugu state.
(iii) crude oil

Origin of petroleum

There are two origins of petroleum

(i) Abiogenic origin

(ii) Biogenic origin

Abiogenic origin: The theory says that there are chemical reaction occuring with metal under the earth crust

Biogenic origin: The theory say that the long time decay of algae; It is agreed on by many schlars

~~Chemical~~ Composition of Petroleum

(a) Elemental composition: It shows that petroleum contains C, H, N, O, S and it has ~~trace~~ some amount of transition element, Ni, V, Fe etc

Sometimes, we classify crude oil based on the composition of S. ~~There are~~ A crude is considered sweet if the % sulphur is < 5% and considered sour if is > ~~than~~ 5%

Nigerian crude oil is considered one of the sweetest crude oil in the world cos it contain very minimal % of Sulphur

When a crude oil has a high % of N or S, they will be generation of Noxious gases (NO_2, SO_2) which causes global warming, when they go to the atmosphere in large amount, it comes back as acid rain

Primary pollutants are emitted directly
Secondary " are caused by the oxidation of primary pollutant.

% of Sulphur can be reduced by HDS, hydrodesulphonati
Ni & V occurs in crude oil as Organometallic porphyrin complexes

* Draw the structure of a nickel porphyrin

② Chemical Composition: Petroleum contains total petroleum hydrocarbons which describes the total concentration of hydrocarbons that are contained in the petroleum.

Stages of Crude Oil Formation

There are three stages involved in the formation of petroleum

(i) Diagenesis: < 50°C

(ii) Catagenesis: occurs between ~~150~~ 50°C – 150°C

(iii) Metagenesis: occurs between 150°C – 200°C

These three stages can be identified by temperature associated with each of them.

Diagenesis: During sedimentation beneath the earth crust, the sediment organic metals is transformed to kerogen.

(ii) Catagenesis: cracking occurs, kerogen breaks down as temperature increase from ~~150~~ 50°C – 150°C. The oil molecules present in the kerogen begins to ~~transform~~ breaks down to gas; (naturally occuring gas

(iii) Metagenesis: It is the dry gas zone, predominantly gas.

Classification of Petroleum

Petroleum can be classified in different ways

(i) API gravity; API means American Petroleum Institute

$$API = \frac{141.5}{SG @ 15.6°C} - 131.5$$

SG = specific gravity = relative density

★ Classify the following oils Based on the API gravity

$$SG = \frac{\text{density of oil}}{\text{density of water}}$$

density ~~of~~ water = 0.997 g/cm³

If the density of oil = 0.886

$$SG = \frac{0.886}{0.997} = 0.8886$$

$$API = \frac{141.5}{0.888} - 131.5 = 27.84^{\circ}$$

~~When the~~ API gravity can be used to classify Petroleum as heavy, moderate, light etc

<10	extra-heavy
10 – 19	heavy
19 – 22	
22 – 30	
> 30	light

02/06/26

Classification of Petroleum Using Viscosity-Gravity Constant (VGC)

$$VGC = 10d - 1.0752\frac{\log(V-38)}{10-\log(V-38)}$$

d = specific gravity

V = Saybolt Viscosity

Questions

If two petroleum samples have densities of $0.82\,g/cm^3$ and $0.95\,g/cm^3$ as well as different Saybolt viscosities of 55s and 75s respectively at 100°F

(i) Compare their viscosity gravity constant values

(ii) Using their API gravities, state whether the petroleum samples are extra heavy, medium or light oils!

~~VGC = 10(0.82~~

$$VGC = 10d - 1.0752\frac{\log(V-38)}{10-\log(V-38)}$$

$$d = \frac{\text{density of oil}}{\text{density of water}} = \frac{0.82}{0.997} = 0.82247$$

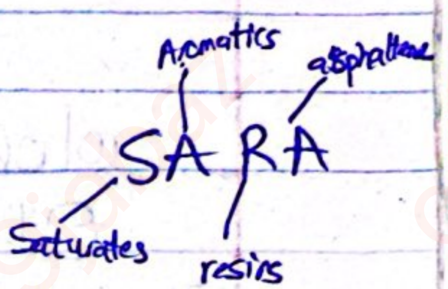
$$VGC = 10(0.82247) - 1.0752\left(\frac{\log(55-38)}{10-\log(55-38)}\right)$$

Classification of petroleum using UOP (not interested)

~~Petroleum~~ acid

To check the quality of petroleum, we check parameters like

(i) density
(ii) Specific gravity
(iii) ~~Asphaltine contents~~ Asphaltene contents.
(iv) sulphur contents
(v) Salt conten (vi) powerpoint (vi) flash point
vii) fire point viii) Aniline point



Distillation Test

It is another test that is used to estimate the quality of Petroleum. There are 7 products we get in distillation

(i) gas at < 15°C
(ii) gasoline between 15.5°C – 149°C
(iii) Kerosene between 149°C – 232°C
(iv) gas oil between 232°C – 343°C
(v) Light vaccum gas 343 – 371°C
vi Heavy vacuum gas 371 – 566
(vii) Residum 7 566°C

* Give the boiling point range of the seven fractions obtained in distillation test.

Degree of lightness;
Gasoline < Kerosene < diesel < lubricating oil.

10/06/26

Oil Refining

Possible crude material;
crude oil, oil sand bitumen, oil shale

Three process of oil refining

(i) Seperation
(ii) conversion: This where they produce sellable materials. It is the most important process.
(iii) Finishing: This process is to remove impurities which can be in form of metals

However, there are many conversion process, eg
(i) Thermal cracking
(ii) catalytic cracking
(iii) Coking: We are producing volatile products like gas, ~~it is similar~~ and coke
(iv) Reforming.
(v) Visbreaking: It is a mild form of thermal cracking

In cracking, we a picking a heavy molecule like crude oil. When

Subjected to thermal cracking, it produces lighter fuels

* Coke is like carbon. We are generating significant carbon in coking process

- Reforming is when we are trying to improve in the octane rating of the fuel. It can be thermal or catalytic

* Hydrocracking: It uses hydrogen for cracking, because we want to increase the hydrogen content of the fuel. The higher the hydrogen content of a fuel, the better the quality of the fuel. We can have
  - (i) Hydrotreatment
  - (ii) Hydrodesulphurization
  - (iii) Hydrodenitrogenation
  - (iv) Hydrodeoxygenation

Petrochemicals

They are chemicals obtained from petrol. Almost everything combustible are made from petrochemicals

Petrochemical Feedstock

(I) Olefins (II) Aromatics (III) Methanol

Petrochemical Intermediate.

They are usually produced by the conversion of 1° petrochemicals to form more complicated derivative products.

Petroleum pollution

*Petrochemical can constitute nuisance to the environment as useful as it is.

pollution is the introduction of an undesirable compound into a matrix at levels considered injurious to human health or ecosystem

The contamination of petroleum can arise from oil spills, ~~it do~~ oil spills don't make aquatic life comfortable

Biomagnification is a gradual build up of a contaminant overtime as it moves up the food chain.

Examples of contaminant; PCBs,

Compounds in petroleum are toxic, there are three primary exposure route

(I) Via skin or dermal contact

(II) Via inhalation

(III) Via oral ingestion

Practice Questions

① show the free radical chain reaction of butane

butane = C_4H_{10}

$CH_3CH_2CH_2CH_3$

chain Initiation step : generates two free radicals

$CH_3CH_2CH_2CH_3 \longrightarrow {}^{\bullet}CH_3 + {}^{\bullet}CH_2CH_2CH_3$ ✓

$\longrightarrow {}^{\bullet}CH_3CH_2 + {}^{\bullet}CH_2CH_3$ ✓ } both are correct

Chain propagation step: any of the free radicals recombines with the origanal molecule to produce a higher chain product with a radical

~~$CH_3CH_2 + {}^{\bullet}CH_2CH_3$~~

$CH_3CH_2CH_2CH_3 + {}^{\bullet}CH_2CH_3 \longrightarrow {}^{\bullet}CH_2CH_2CH_2CH_2CH_3 + CH_4$

~~Form~~

Termination Step: recombination of the free radicals

${}^{\bullet}CH_2CH_2CH_2CH_2CH_3 + {}^{\bullet}CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

The idea of this is that a longer chain is produced at the end than the original material

② Explain the following assays in estimatimate the quality of petroleum

(i) aniline point (ii) acid number (iii) refractive index

(iii) Boiling point ranges of distillation

(iv) Distinguish between the biogenic and abiogenic origin of petroleum

(v) Various exploration process that has been explored in the refining of petroleum e.g. thermal cracking, reforming...

CHM 404 – Petroleum Chemistry

Petroleum

The word petroleum is coined from the Medieval Latin, *petroleum* (rock oil), and was derived from two Latin words *petra* "rock or stone" and *oleum* "oil".

Petroleum is a mixture of naturally occurring hydrocarbon compounds and a trace quantity of heteroatoms compounds containing nitrogen, sulphur and oxygen, and some trace metals such as V, Ni, Cu and, Fe etc as impurities. It is a fossil fuel that includes oil in liquid (crude oil), semi-solid (heavy oil/bitumen), and hydrocarbon gaseous (natural gas) forms, depending on the conditions of pressure and the temperature it is subjected to. The term petroleum also covers both naturally occurring unprocessed petroleum and refined petroleum products.

Petroleum occurs broadly in geological formations beneath the earth's crust in gaseous, liquid, semisolid, or solid forms or mixtures in a single reservoir. Petroleum hydrocarbons occur in a vast number of isomeric arrangements so their separation and distinct identification are usually difficult and challenging.

It is, therefore, technically wrong to use hydrocarbon interchangeable with petroleum for any of its forms, since hydrocarbons are compounds containing hydrogen and carbon only, while petroleum consists of traces of many other substances as impurities apart from hydrocarbons.

Crude oil as a form of petroleum possesses a greasy appearance and texture; yellowish-black colour; composes primarily of liquid hydrocarbons. It is the supreme significant form of petroleum from an economic point of view. It usually occurs with substantial quantities of natural gas in the same reservoir as well as traces of other gases such as H_2S as impurities. Irrespective of disparities, most crude oil ranges from 82 - 87 % C by weight and 12 - 15 % H by weight. It is non-polar, making it insoluble in water but miscible with organic solvents like naphtha, carbon disulphide, ether, and benzene. The density of crude oil is usually less than that of water, while heavy oil or bitumen, or tar may be denser than water.

Origin of Petroleum

The theories of the origin of petroleum are generally divided into two groups based on their opinions of the principal source materials as abiogenic or biogenic. Early concepts supported the abiogenic sources, while the modern theories, with very limited exceptions, accept that the primary source materials were biogenic.

1. Abiogenic Origin

Abiogenic theories were basically the postulate of 19th century Chemists; they envisioned extensive chemical reactions taking place deep down the earth, producing basic petroleum hydrocarbons as the end products. These concepts were established in laboratory experiments and linked to reactions taking place in the deep interior of the terrestrial sphere.

The first definite theory was postulated by Berthelot in 1866, that when carbon dioxide reacts with free alkali metals at high temperature in the earth's interior, acetylides are produced, which in the presence of water change into hydrocarbons. A theory advocated a connection between the geographical distribution of oilfields and volcanoes as a result of the presence of traces of hydrocarbons in volcanic gas assumed that oil probably has a volcanic origin.

2. A *semi-abiogenic* theory was proposed by Gaedicke; his suggestion was that terrestrial water may disintegrate into its constituent hydrogen and oxygen gases through ϒ-rays originating from radioactive materials. The hydrogen so released will react with the carbon of either abiogenic or biogenic origin to form hydrocarbons.

$$(n + 1)\, H_2O \rightarrow 2(n + 1)H + (n + 1)O$$

$$nC + 2(n + 1)H \rightarrow C_nH_{2n+2}$$

Alkanes (paraffinic hydrocarbons)

All abiogenic theories have been rendered unauthentic due to the following listed facts:

a. The principal support for theories of abiogenic origin centers on the point that in the laboratory the hydrocarbons methane, ethane, acetylene, and benzene have been recurrently generated from abiogenic sources. *There has not been any field evidence recorded that the procedures have occurred naturally.*

b. Petroleum occurs *mainly in sedimentary, marine rocks*; if located in igneous rocks, it has evidently migrated there along obviously-distinct faults or shatter zones.

c. One of the physiognomies of petroleum is optical rotary power (optical activity), particularly of the intermediate boiling fractions (250-300ºF). It is evident that this occurrence is practically and exclusively limited to organic matter, and is usually detected only where biogenic activities had occurred. Petroleum possesses components such as pyridines and porphyrins which are the biogenic source.

d. Oil content of rocks of the earth's crust does not increase with depth. In fact, the opposite is the case because it is known that very ancient rocks contain no oil, but high-volume production is often found in tertiary sediments. This, therefore, ruled out any reactions purportedly occurring in the earth's interior to produce petroleum.

f. Unlike biogenic origin, abiogenic origin does not associate with activities that produce several homologous series of hydrocarbon compounds that are present in every period of petroleum.

g. The nonexistence of association between petroleum and volcanism or its products apart from rare and irregular incidences proves that there is any significant connection between the volcanic action and the origin of petroleum.

h. If petroleum were of cosmic origin, then it will be more uniformly distributed over the earth; and more plenteous in the older rocks.

i. There has been no abiogenic theory of oil origin that has gone beyond the generation of little simple hydrocarbons. None of the concepts can elucidate the high complexity of petroleum chemistry.

3. Biogenic Origin

The biogenic origin of petroleum hydrocarbons suggests that petroleum comes from a long time decaying of dead organisms such as planktons, zooplankton, and other forms of biological species under the subjection of high temperature and pressure. This hypothesis is currently accepted by many people around the world and it has many viable supporting grounds which fit well modern sciences. According to that hypothesis, a very long time ago, the organisms (marine living things, terrestrial) died and were buried and covered by silt in a sedimentary basin where they undergo a very slow and very long-lasting physical and chemical transformation which involves processes such as diagenesis and kerogen formation.

The more conventional view of petroleum formation is that it formed when selected aliquots of biomass from dead organisms were buried in a sedimentary basin and subjected to diagenesis through prolonged exposure to microbial decay followed by increasing temperatures and pressures. Oxygen-poor conditions, produced by exhaustion of local oxygen levels by biomass decay and often sustained by physical barriers to oxygen recharge, are obvious enhancers for fossil organic matter preservation and passage into the geosphere. The major organic components in life are large, high molecular weight entities and the most resistant of these units are preserved in sediments, augmented by cross-linking reactions that polymerize and incorporate smaller units into the complex network. The high molecular weight sedimentary organic matter is termed kerogen. It is worth noting that not all of life's organic matter is reflected in kerogen. Even under relatively favorable conditions less than 1% of the starting organism, representing the most resistant chemical constituents, may be preserved.

The hypothesis of biogenetic origin of petroleum has many possible evidences which can indeed allow scientists to simulate the production of petroleum (crude oil). Today advancements in science such as chemistry-knowledge about carbon and its compounds and geology make the hypothesis well understood and well useful. The most plausible evidence is the focus on the stage of what so-called "development of hydrocarbons", from peat to anthracite and equally from algae to oil.

Composition of Petroleum

a. Ultimate (Elemental) Composition

The constituent elements of petroleum are carbon, hydrogen, nitrogen, sulphur, oxygen and metals, while their percentages in the crudes with exception of few crudes are as stated.

C, 83.0 – 87.0 %; H, 10.0 – 14.0 %; N, 0.1 0.2 %; S, 0.05 – 6.0 %; O, 0.005 – 1.5 % and metals < 1000 ppm

b. Chemical Composition

The chemical constituents of a typical petroleum are hydrocarbons, N,S,O compounds and metallic constituents.

bi. Total petroleum hydrocarbon (TPH) is a term used to describe any mixture of hydrocarbons that occurs in petroleum. The hydrocarbon of petroleum which are in hundreds of various compounds may be as high as 97 % by weight in the paraffinic crude oils and as low as 50% in heavy crude oils. Generally, hydrocarbon components of petroleum comprise of the following:

Hydrocarbon	**Average**	**Range**
Paraffins	30%	15-60%
Naphthenes	49%	30-60%
Aromatics	15%	3-30%
Asphaltics	6%	remainder

Paraffinic Hydrocarbons (Alkanes)

The type of crude oils determines the quantity of paraffins constituents, but basically, crude's percentage of paraffinic hydrocarbons decreases with increasing molecular weight, while aromaticity and the relative proportion of heteroatoms (nitrogen, oxygen and sulphur) containing compounds increase.

Normal paraffins occur in varying amounts in most crude oil. In fact, and the constitute 20% to 50% of paraffinic petroleum by weight in the gas oil fraction. Though, naphthalene or asphaltic crude oils occasionally composes little quantity of normal paraffins.

Iso-paraffins which are the branched paraffins have the slightly branched paraffins predominate over the highly branched paraffins. Their 2- and 3-methyl derivatives occur in abundance than the 4-methyl derivative. The lower alkanes ($C – C_4$) are gases, while C_5 - C_{17} are liquids and $C_{16} – C_{78}$ are solids. The following compounds are the isomers of Hexane (C_6H_{14}).

Cycloparaffinic Hydrocarbons (Naphthenes)

The cycloalkanes (naphthenes), are saturated hydrocarbons with one or more carbon rings to which hydrogen atoms are attached according to the formula CnH2n. Cycloalkanes have similar properties to alkanes but possess higher boiling points. Naphthenes are derivatives of cyclohexane, cyclopentane and decahydronaphthalene as well as their polycyclic forms, and they occur in petroleum fractions at appreciable amount. Naphthene rings compose of a varying proportion of carbon atoms three to eight carbon atoms, but crude oils predominantly contain five and six carbon member rings which are the most thermodynamically stable forms. They occur in petroleum up to 60% of the total hydrocarbon constituents. The examples shown here are for three naphthenes of distinctive importance.

Aromatic Hydrocarbons

The aromatic hydrocarbons are unsaturated hydrocarbons which have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula CnHn. They tend to burn with a sooty flame, and many have a sweet aroma. Many of them are carcinogenic. Most of the aromatic hydrocarbons compose of paraffinic chains, naphthene rings and aromatic rings laterally and aromaticity increases with increased molecular weight. Aromatics devoid of naphthene rings or alkyl-substituted derivatives occur in significant quantity only in the light petroleum fractions and are comparatively rare in the heavier petroleum fractions. The following compounds are some of the aromatics present in crude oils.

Unsaturated Hydrocarbons

The occurrence of alkenes (olefins) in petroleum has been controversial for several years. Alkenes occur in crude oil is not common but only a few distinctive cases. Spectroscopic and chemical techniques indicated that the crude oils and all distillate fractions, contained up to 3 % w/w alkenes.

bii. Non-Hydrocarbon Components

Petroleum composes significant quantity of non-hydrocarbon organic constituents principally nitrogen, Sulphur and oxygen (NSO) containing compounds and little quantities of organometallic compounds in solution and inorganic salts in colloidal suspension. Their proportion in certain fractions may be rather small, nevertheless, their impact is significant.

biii. Metallic Constituents

Metallic constituents exist in all categories of crude oils and can cause catalytic poisoning. Even small quantities of Fe, Cu and principally Ni and V in the charging stocks for catalytic cracking can affect the activity of the catalysts and result in elevated gas and coke formation and decreased yields of gasoline.

biv. Porphyrins

Porphyrins usually occur in the non-basic portion of the nitrogen-containing concentrates. The porphyrin ring system contain four pyrrole rings linked by =CH- groups. The entire ring system is aromatic. Many metal ions can substitute the pyrrole hydrogens and form chelates. The chelate is planar around the metal ion and resonance results in four equivalent bonds from the nitrogen atoms to the metal. Virtually all crudes compose detectable quantities of vanadyl and nickel porphyrins. Porphyrin compounds and associated pigments are significant geochemical marker compounds in the genesis and characteristics of petroleum.

Crude oil classification

a. Based on location of its origin, example Nigeria Bonny crude, West Texas Intermediate etc.

b. Based on relative weight or viscosity e.g. light, intermediate and heavy crude.

c. Based on sulphur content (sweet" or 'sour). Sweet- for crude oil with little amount of sulphur, while sour crude oils are those containing substantial amount of sulphur.

Thus, sour crude requires further treatment/refining to meet certified products standards or specifications. The Sulphur content of Nigerian crude ranges between 0.1 and 0.3%. Most of Nigerian petroleum are then classified as light or sweet crudes because of the low sulphur contents and they are predominantly cyclic hydrocarbon and aromatics fractions.

Stages of crude oil formation

This process involves physical and chemical transformations of dead organic materials and it is controlled by biological activities, distribution of organic fluid phases, temperature, and pressure.

The four main phases involved in the formation of fossil fuels (petroleum and coal) are diagenesis, catagenesis, metagenesis and metamorphosis. The first three (diagenesis, catagenesis and metagenesis) involve the formation of petroleum.

a. Diagenesis

During sedimentation, organic matter is also deposited with fine sediments. As the thickness of the deposited sedimentation increases with depth, the organic matter under pressure and temperature converts into kerogen. These kerogens break down into hydrocarbon by various chemical processes known as cracking or catagenesis. At this stage, the dead organisms are submerged during sedimentation; the constituent of organic molecules or compounds i.e. Lipids, carbohydrates, amino acids, and lignin compounds will break down as a result of rising temperature and pressure. This transformation happens inside the first 100 m of the earth's crust. The resultant product is termed Kerogen. Sediment deposited in a sub-aquatic environment consists of H_2O (60% by weight of the total sediment), minerals, dead organic materials and living microorganisms. The mixtures came from different sedimentary processes and principal components of different origins. It is a heterogeneous system because it is out of equilibrium and unstable. Thus, diagenesis is the process through which the system tends to approach equilibrium under condition of burial with shallow overburden. In this process, the sediments become stabilized. In early diagenesis, the main agent of transformation is microbial activities which could be aerobic or anaerobic. The organic material within the sediment proceeds towards equilibrium. Previous biogenic polymers (carbohydrate, lipids etc) are degraded by microbial activities, while their constituents become progressively engaged in new poly condensed structures i.e. Geopolymers.

b. Catagenesis

This is the cracking process which converts organic kerogens into hydrocarbons.

This involves physical and chemical alteration of sediments and pore fluids at temperatures (50 to 150 ºC) and pressures higher than those of diagenesis. At these temperatures, chemical bonds break down in kerogen and clays within shale, generating liquid hydrocarbons. At the high end of this temperature range, secondary cracking of oil molecules can produce gas molecules.

Significantly, the process of catagenesis is catalyzed by the minerals that are deposited and persist through marine diagenesis. The conditions of catagenesis define the product, such that higher temperature and pressure lead to more complete "cracking" of the kerogen and progressively lighter and smaller hydrocarbons such as gases. Petroleum formation, then, requires a specific window of conditions; too hot and the product will favor natural gas (small hydrocarbons), but too cold and the plankton will remain trapped as kerogen.

c. Metagenesis

Metagenesis is the third and final stage of kerogen modification with the slow elimination of the residual kerogen consisting of two carbons or more out of three atoms. In terms of petroleum exploration, metagenesis occurs mainly in the dry gas zone. Metagenesis occurs at temperatures of 150 to 200 ºC. At the end of metagenesis, methane, or dry gas, is evolved along with nonhydrocarbon gases such as CO_2, N_2, and H_2S, as oil molecules are cracked into smaller gas molecules. At this stage, organic matter gives majorly methane gas and carbon residue, and the formation of coal commences.

d. Metamorphosis

This is apparently the last stage of the evolution of sediment, in this case, temperature and pressure reach very high values, and rocks are exposed to the influence of magma and hydrothermal effects. In the metamorphosis, coal transforms into meth-anthracite. The constituents of kerogen are converted to graphite carbon.

PETROLEUM POLLUTION

Contamination/pollution of hydrocarbon occurs as a result of toxic organic chemical substances and petroleum which are a serious concern for the environment. Contamination caused by petroleum hydrocarbon is a matter of concern because of its harmful effects on flora and fauna. Crude oil contamination is common due to its extensive use and its related dumping process and accidental spills. Complex mixture of a large range of high and low molecular weight hydrocarbons makes up the petroleum. The complex mixture of petroleum consists of saturated and branched alkanes, alkenes, and homo- and heterocyclic naphthenes; aromatics consisting of heteroatoms including heavy metal complexes and N, S, and O. Petroleum hydrocarbon consisting of different functional groups such as ethers, carboxylic acids, etc.; and large aromatic molecules such as asphaltenes, resins, and naptheno-aromatics.

Heavy metals are present in crude oil, and its heavy metal content is associated with porphyrins which is the pyrrolic structure. Lube oil waxes, light oil, asphaltenes, naphtha, diesel, kerosene, etc.

are the several fractions in which the petroleum is refined. Light ends is the term that is used for the light fractions which are distilled at atmospheric pressure, and heavy ends is used for heavy fractions such as lube oil. Light ends of petroleum consist of a lower percentage of aromatic compounds and lower molecular weight saturated and unsaturated hydrocarbons, while heavier ends consist of higher molecular weight saturated and unsaturated hydrocarbons, aromatic compounds with high molecular weight, and organometallic compounds. This part is relatively rich in metals and nitrogen, sulphur, and oxygen-containing compounds.

Oil Spillage

Oil spillage is accidental or intentionally discharges of oil. It is categorized into three main groups namely:

Minor oil spills: This takes place when the oil discharge is less than 25 barrels in inland waters or less than 250 barrels on land or coastal waters.

Medium oil spills: This takes place when about 250 barrels are discharged in inland water or 250 - 2,500 barrels are discharged on land or coastal water.

Major oil spills: This takes place when the discharge is in excess of 2,500 barrels in inland water or over 2,500 barrels on land or coastal waters.

Causes of oil spills

Causes of oil spillage include:

Well blow-out

Pipeline rupture

Storage failure

Overflow of drilling mud

Hose failure on tanker loading system

Offshore/onshore production activities/accidents

Washing of tankers

Shipping and terrestrial traffic accidents

Sabotage of well ends and pipe flow lines

Leakage at the depot and gas station, and

Disposal of petroleum waste etc.

Oil spillage from most of these sources could be prevented by proper engineering practices, equipment and procedures. Sporadic incidences of oil spills have been reported worldwide from time to time. In Nigeria, over the last two decades till date, the country has recorded several oil spill cases with net volume of up to 3 million barrels.

Due to the use of spill sensors and mechanisms for shutting down sections of pipeline, individual events are usually much smaller than can potentially be spilled by oceanic supertankers or by blowouts of offshore platforms.

Because the spread of spilled oil is much more restricted on land than on water, terrestrial spills usually affect relatively localized areas (unless the spilled oil reaches a watercourse).

Organic pollutants

Organic pollutants in petroleum and petroleum products that are responsible for environmental and health-related problems are as follow.

Polycyclic aromatic hydrocarbons (PAHs)

PAHs are considered to be universal contaminants. There are up to 100 diverse compounds of PAHs. PAHs are occasionally used for the industrial purposes such as the manufacturing of pesticides, dyes, and plastics and for the production of medicines. Polycyclic aromatic hydrocarbons are produced on partial burning of organic matters. Because PAHs are carcinogenic and mutagenic in nature thus, highly poisonous to organisms. The degradation of PAHs with high molecular weights is very slow due to low hydrophobicity and water solubility. They have a tendency to accumulate and persist in ecosystems. Sixteen individual PAHs have been classified as priority pollutants by the USEPA due to their poisonous, carcinogenic, and mutagenic natures.

Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are hazardous due to their carcinogenicity, toxicity, and slow biodegradation nature. They are well known to be the worst pollutants. About hundreds of thousands of metric tons of PCBs are persistent in the environments. PCBs are widely used in adhesives and lubricants, dielectric fluids in flame retardants, transformers, hydraulic fluids, and plasticizers. PCBs are as well released from disposal and spillage of petroleum and its products.

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) deposited decades ago are still present in deep sediment layers. Toward biotic and abiotic degradation processes, PCDD/Fs are often known to be persistent. PCDD/Fs are a set of notorious pollutants present in nature.

Movement of oil from a point source

The hydrophilic component of the oil tends to migrate into the aqueous phase of the soil and has the potential to contaminate ground water. Lateral flow of oil facilitates the evaporative removal of low molecules weight components, but increases contaminated area. Vertical flow minimizes this process but results in deep seated pollution of ground waters.

Movement of oil is influenced by the following factors:

Spill volume

Hydrocarbon viscosity

Temperature

Wind speed

Land contour topography

Vegetation

Soil composition or soil chemistry

When oil spills in water, it spreads across its surface, while wind and wave action may spread or blow the slick to one side. Persistent hydrocarbons finally settle on the sediments. Generally, oil found in water body has films, solution, emulsion or tar balls depending on the solubility.

Oil spill containment

Containment/inhibition is a process in which attempts are made to restrict the movement of oil so as to prevent it from further spreading. The dangerous nature of oil spills has led to the development of containment devices. The following devices are employed in oil containment.

i. Chemical dispersal: Dispersants are chemicals that are sprayed on a surface oil slick to break down the oil into smaller droplets that more readily mix with the water. Dispersants do not reduce the amount of oil entering the environment, but push the effects of the spill underwater. Some dispersant enhance hydrocarbon oxidation by microorganisms while others inhibit the oxidation process. This implies that some dispersant is harmful and toxic to the microbiota (microorganism). Furthermore, addition of chemicals to spilled oil to sink it into the bottom of the sea may put a threat to aquatic organisms and even subsequent biodegradation is retarded both by the lack of O_2 due limited surface area.

ii. Skimmers: A skimmer is a device for recovering spilled oil from the water's surface. Skimmers may be self-propelled, used from shore, or operated from vessels. The efficiency of skimmers is highly dependent upon conditions at sea. In moderately rough water, skimmers tend to recover more water than oil.

iii. Erection of earthen moat or channel around storage tanks

iv. Collection of oil by vacuum trucks or suction by foam

v. Booms: Booms are temporary floating barriers used to contain marine spills, protect the environment, and assist in oil recovery. A boom includes a containment partition that floats on and extends above the water's surface and a "skirt" or "curtain" that sinks into the water.

They are floating devices used to prevent oil from a spread in an aquatic environment and they are of various sizes. An excellent boom device used for oil containment must possess the following qualities: Integrity, Rapid and easy deployment, Durability, Easy to clean, Flexibility, wave resistant, and oil retention with no loss especially under the boom.

Environmental fate of crude oil or petroleum

Fuels are typically released into the environment when storage and delivery system leak or when a sudden accidental spill occurs. Storage tanks either above ground or underground are made of steel which is known to corrode and leak if not properly protected with anticorrosion devices. Fuel storage and delivering systems are in physical contact with air, soil, and/or ground H_2O. The environmental fate of sub-surface crude oil discharge/release is determined by a number of interrelated factors which include:

i. The type of crude oil released

ii. Rate of release

iii. Characteristics of the ground water surface

iv. Vertical distance to the ground water surface

v. Proximity to surface H_20 *body*

The fate of oil spill in the environment

An oil spill into the environment has the following fate:

i. Physical transport: The distribution of oil spills on the sea surface occurs under the influence of gravitational force, the viscosity of oil and surface tension of H_2O. During the first day after an oil spill, a considerable part of oil will be transformed into the gaseous phase. The oil slick will also lose H_2O soluble hydrocarbon rapidly. Further changes take place under the combined compact of meteorological and breakdown of oil into less harmful compounds, adsorption of hydrocarbon into or by organic matter in the environment will also occur. In the unsaturated soil, being above the ground water zone, fuel migrates downward under the force of gravity and is spread horizontally under other mechanical forces. Once the fuel reaches the ground H_2O, it will dissolve to a minor degree and accumulate at the ground H_2O surface where it will continue to volatilize into the dry soil above and the rest dissolves in the ground H_2O below.

Complex processes of oil transformation in the marine environment start developing when oil gets in contact with seawater.

ii. Dissolution: Most of the oil components are water soluble to a certain degree. Polar compounds formed as a result of oxidation of some oil fraction in the marine environment also dissolve in seawater.

Hydrodynamic and physico-chemical conditions in surface H_2O also strongly affect the rate of the dissolution process.

iii. Sedimentation and biosedimentation: These involve the adsorption of some oil components on suspended materials in the H_2O followed by deposition. This may happen in the narrow coastal zone and shallow water where particulates are abundant and water is subjected to intense mixing.

iv. Emulsification: An oil emulsion is a mixture of oil, water, and an emulsifying agent. It contains fine water droplets dispersed in oil. In a crude oil emulsion, the quantity of water droplets is usually less than 10%. In moderate to rough seas, most oils will take up water droplets and form water-in-oil emulsions under the turbulent action of waves on the sea surface. This process of emulsification significantly changes the properties of spilled oil.

Due to the absorption of water, the volume of the pollutant may be increased by a factor of up to four times. As the emulsion develops, the movement of the oil in the waves causes the droplets of water that have been taken up in the oil to become reduced, making the emulsion progressively more viscous and stable. This increase in viscosity can change original liquid petroleum into a semi-solid material. Emulsified oil is no longer dispersible.

v. Aggregation: Oil can aggregate in form of petroleum lumps and tar balls or pelagic tar and this can be found in both open coastal water as well as the beaches. Hydrological factors are mainly on the power and direction of wind waves and currents. An oil slick usually drifts in the same direction as the wind storms and active turbulence speed up the dispersion of the slick and its fragment.

vi. Microbial degradation: The fate of most petroleum hydrocarbons in the environment is ultimately defined by their transformation and degradation due to microbial activity. There are several known species of bacteria and fungi that are able to use petroleum hydrocarbons to sustain their growth and metabolism. Biochemical processes of oil degradation with microorganism participation include several types of enzyme (oxygenases, dehydrogenises, reductases, amidases) oxidation processes. These cause aliphatic and aromatic oxidation, hydroxylation, oxidative deamination, hydrolysis, and other biochemical transformation of the petroleum hydrocarbons and the intermediate products of their degradation.

The biodegradation of petroleum is essential to the elimination of oil spills, oil degraded by both marine bacteria and filamentous fungi. The physical form of crude oil makes a large difference in its degradability. Degradation in water occurs at water-oil interface. Therefore, thick layers of crude oil prevent contact with bacteria enzyme and oxygen.

vii. Oxidation and destruction: chemical transformation of oil in water starts not earlier than a day after oil enters the marine water. The chemical transformation often involves photochemical ion under the influence of UV waves. These processes are catalyzed by some trace elements e.g. vanadium and inhibited by compounds of Sulphur. The final products are usually hydroperoxide, phenol, carboxylic acid, ketone and aldehyde which are soluble in H_2O.

Toxicity of petroleum hydrocarbon

Hydrocarbons are the most commonly used substance in industries most especially in developing societies. Hydrocarbon products are usually a mixture of saturated, unsaturated rings, and straight chain molecules. The liquid form comprises molecules containing 5 -15 carbon atoms that are arranged in aliphatic, alicyclic, and aromatic structures with varying amounts of sulphur, nitrogen, and oxygen impurities.

Clinical health effects of hydrocarbon intoxication include

i. Respiratory diseases: These include burning sensation in the mouth, choking, gagging, cough, cyanosis, and fever.

ii. Central nervous system (CNS) diseases: These include lightheadedness, lethargy, dizziness, headache, visual disturbance, seizure, and coma.

iii. Direct skin contact: This may result in dermatitis or skin burn. Skin contamination has a particular affinity for nerve tissue.

iv. Cancer diseases: These are caused mainly by polycyclic aromatic hydrocarbons.

Chronic poisoning is much more common and may result in hematological abnormalities such as leukemia. anemia and acute myeloid.

This shows that the toxicity of petroleum varies according to its chemical composition. Thus, aromatic hydrocarbons are generally more toxic than other types of hydrocarbons.

Remediation techniques for Contamination due to petroleum

Contamination due to petroleum is widespread in the environment and contaminates surface and groundwater. Several operations in petroleum exploration, leaking of underground storage tanks, and its production and transportation are responsible for affecting the environment. Contamination causes threat to human health and safety and can affect nature by contaminating surface and groundwater.

Efforts are made both nationally and internationally in order to remediate the pollution caused by hydrocarbon contamination which can cause environmental and health risk. There are three methods involved in the remediation of sites contaminated due to petroleum hydrocarbons. These are Phytoremediation, Bioremediation and Chemical remediation

a. Phytoremediation

Phytoremediation is the process which involves the use of plants for the degradation, extraction, and elimination of the contaminants from the air, water, and soil. It includes various mechanisms which can lead to degradation of contaminants, dissipation, immobilization, and accumulation. Various phytoremediation applications with examples are given in Table below.

Application	Media	Contaminants	Typical plants that can be used
Phytotransformation	Soil, groundwater, landfill leachate, land application of wastewater	Herbicides, aromatics, chlorinated aliphatics, nutrients, ammunition waste	Phreatophyte trees (popular, willow, cottonwood, aspen) Grasses (rye, Bermuda, sorghum, fescue) Legumes (clover, alfalfa, cowpeas)
Rhizosphere bioremediation	Soil, sediments, land application of wastewater	Organic contaminants (pesticides, aromatics, and polynuclear aromatic hydrocarbons)	Phenolic releasers (mulberry, apple, Osage orange) Grasses with fibrous roots (rye, fescue, Bermuda) for contaminants 0.3 ft deep Phreatophyte trees for 0.10 ft Aquatic plants for sediments
Phytostabilization	Soil, sediments	Metals (Pb, Cd, Zn, As, Cu, Cr, Se, U), hydrophobic organics (PAHs, PCNBs, dioxins, furans, pentachlorophenol, DDT, dieldrin)	Phreatophyte trees to transpire large amounts of water for hydraulic control Grasses with fibrous roots to stabilize soil erosion Dense root systems are needed to sorb/bind contaminants

Application	**Media**	**Contaminants**	**Typical plants that can be used**
Phytoextraction	Soil, brown fields, sediments	Metals (Pb, Cd, Zn, Ni, Cu) with EDTA addition for Pb selenium (volatilization)	Sunflowers Indian mustard Rape seed plants Barley Hops Crucifers Serpentine plants Nettles Dandelions
Rhizofiltration	Groundwater, water and wastewater in lagoons or created wetlands	Metals (Pb, Cd, Zn, Ni, Cu), radionuclides (137Cs, 90 Sr, U), hydrophobic organics	Aquatic plants: emergents (bulrush, cattail, coontail, pondweed, arrowroot, duckweed); submergents (algae, stonewort, parrot's feather, Eurasian watermilfoil, hydrilla)

Mechanisms of phytoremediation

Contaminated land and water are remediated more feasibly by using plants involving a variety of pollutant attenuation mechanisms than physical and chemical remediation techniques. Plants due to their sedentary nature had developed various abilities for dealing with hazardous compounds. Plants serve as solar-driven pumping and filtering systems as they take up pollutants from the soil through the roots which is transported to various parts of the plant by the help of plant tissues where they can be volatilized, metabolized, or sequestered. Different types of mechanisms are used by the plant for removing the pollutants from the soil. They consist of biophysical and biochemical processes such as adsorption, translocation, and transport, as well as mineralization and transformation by plant enzymes are the mechanisms of phytoremediation. Halogenated substances like trichloro ethane are degraded by plants using oxidative degradation pathways, and it includes plant-specific dehalogenases. After the death of the plant, the dehalogenase activity is still maintained. Laccases, P450 monooxygenases, nitroreductases, dioxygenases, phosphatases, peroxidases, dehalogenases, and nitrilases are various contaminant-degrading enzymes which are present in plants. The basic physiological mechanisms involved in phytoremediation in higher plants and related microorganisms, such as mineral nutrition, photosynthesis, transpiration, and metabolism. The root of the plant is responsible for the uptake of the organic and inorganic compounds from the soil, and it can bind and stabilize substance on its external surfaces on interaction with microorganism in the rhizosphere. Uptake or release of molecules occurs through exchanging gases from the aerial plant's parts with the atmosphere.

b. Bioremediation

Bioremediation is a cost-efficient method used for the treatment of soil polluted with oil and wastes of petroleum consisting of biodegradable hydrocarbons and indigenous microbes.

The management of suitable levels of nutrient fertilizer addition, moisture control to optimize soil degradation by microorganisms, aeration and mixing, and pH amendment are required for the process of land treatment.

Enzymes attack on some inorganic compounds and on most of the organic compounds through the activities of living organisms. Bioremediation is the technique which involves the productive use of the biodegradative process for the elimination or detoxification of pollutants from the environment.

Bioremediation through microorganism is considered to be the most effective method in comparison to other biological methods, but the high molecular weight hydrocarbons with low adsorption and solubility limit their accessibility to microorganisms.

Principle of bioremediation

Composite mixture of diverse chemical substances makes up the crude oil. Oil and its component are recognized by microbes using bioemulsifiers and biosurfactants, and then they join themselves; hydrocarbon is used as the resource of carbon and energy. High molecular weight hydrocarbons due to their low adsorption and solubility limit their accessibility to microorganisms. Oil biodegradation rates are improved by the biosurfactant's addition which increases the elimination and solubility of these pollutants.

The oil constituents vary particularly in susceptibility, volatility, and volubility to biodegradation. A number of substances are easily degraded, some are non-biodegradable, and some oppose degradation. Diverse species of microbes preferentially attack diverse compounds due to this biodegradation of petroleum that occurs at different rates but concurrently. Enzymes produced by microorganisms in the presence of sources of carbon are accountable for attacking the hydrocarbon molecules. Hydrocarbon present in the petroleum is degraded by different enzymes and metabolic pathways. Hydrocarbon degradation is prevented by the lack of suitable enzyme.

Bioremediation process involves the utilization of natural microorganisms for the decontamination of atmosphere. This process converts pollutants into useful or nontoxic substances by using bacteria, fungi, and yeast which are the naturally occurring microorganisms. This is also a process in which microorganisms restore the quality of the environment by degrading and metabolizing the chemical substances. Table below represents the main microorganisms which are included in the remediation of hydrocarbons.

<u>List of microorganisms for bioremediation</u>

Bacteria	**Yeast and fungi**
Achromobacter	*Aspergillus*
Acinetobacter	*Candida*
Alcaligenes	*Cladosporium*
Arthrobacter	*Penicillium*
Bacillus	*Rhodotorula*
Brevibacterium	*Sporobolomyces*
Corynebacterium	*Trichoderma*
Flavobacterium	*Fusarium*

Bacteria	**Yeast and fungi**
Nocardia	
Pseudomonas	*Trichoderma*
Vibrio	

Microorganisms

1 Bacteria

Microbial species has efficient hydrocarbon degradation capability in natural environments. Various microbial species have been isolated from heavily polluted coastal areas, variety of oil spill, or soil contaminated by petroleum. These are isolated on the basis of their capability to metabolize different sources of carbon such as aliphatic and aromatic compounds and their chlorinated derivate. Enrichment culture procedures were used for obtaining the microorganisms, and for the selection criterion, maximum final cell concentration or maximum specific growth rate was used. Various microorganisms such as fungi, microalgae, bacteria, and yeast are used for degrading the petroleum hydrocarbons. Out of these microorganisms, bacteria play a significant role for hydrocarbon degradation. Rapid degradation of low molecular weight alkanes is reported by various studies. The capability of microorganisms to use hydrocarbons to assure the growth of cell and energy requirements by degrading hydrocarbon is the driving force for the petroleum biodegradation. Biodegradation of petroleum is carried out more extensively by mixed cultures in comparison to pure culture. Adequate indigenous microbial community in many ecosystems is capable of biodegradation of oil, but for oil degradation metabolic activity, environmental conditions should be favorable. Indigenous microorganisms have several advantages than adding microorganisms for hydrocarbon degradation.

2 Fungi

For the biodegradation of hydrocarbons in soils, fungi play a more vital role than bacteria. Filamentous fungi which are found in aquatic structures are mostly related with surface films and sediments. The enzymatic processes used by mammalian organizations are also used by fungi in polycyclic aromatic hydrocarbons (PAHs). Two major types of cytochrome P450 monooxygenases have been well characterized in yeasts and filamentous fungi. Several fungi have the ability to oxidize polycyclic aromatic hydrocarbons to phenols, dihydrodiols, and other metabolites and conjugates, but only some fungi such as Phanerochaete chrysosporium have the capability to catabolize them totally to CO_2.

Example are Mitosporic Ascomycota, Dothiorella aureobasidium and Saccharomycetales candida

3 Yeast

The biodegradability of various yeasts decreases from n-alkanes > branched alkanes > low molecular weight aromatic hydrocarbons > cycloalkanes > high molecular weight aromatic and polar compounds.

Bioremediation process involves the detoxification of pollutants due to the various metabolic capabilities of microorganisms which is the developing method for elimination of contaminants from nature together with the yields of the petroleum industry. Bioremediation technique is considered to be cost-effective and noninvasive. Petroleum and other hydrocarbon contaminants can be eliminated from the atmosphere by using microorganisms which is considered as primary mechanism, and it is the cheaper method in comparison to other remediation technologies. Microorganisms having suitable metabolic capabilities are the essential requirement.

Alkylaromatic degradation is carried out by various microorganisms such as Arthrobacter, Mycobacterium, Sphingomonas, Burkholderia, Rhodococcus,

and Pseudomonas.

Fungi, bacteria, and yeast are accountable for the biodegradation of hydrocarbons in the environment. Six percent to 82% is the reported efficiency of biodegradation for soil fungi, 0.003–100% for marine bacteria, and 0.13% to 50% for soil bacteria. Complex mixtures of hydrocarbons such as crude oil in freshwater, aquatic environments, and soil are degraded by mixed populations with overall wide enzymatic capacities.

Bioremediation involves two processes which are bioaugmentation and biostimulation

Bioaugmentation

Bioaugmentation process involves the degradation of the harmful hydrocarbons by the addition of microorganisms in order to achieve the pollutant reduction. It is also the injection of polluted water with microorganisms capable of hydrocarbon degradation. This process sometimes involves biodegradation of the hydrocarbon pollutants by adding the genetically engineered microorganisms into the polluted water. Bioaugmentation process is not often used for the hydrocarbon degradation because microorganisms responsible for hydrocarbon degradation naturally exist in the environment. Bioaugmentation process is not so much effective to be used in oil spill remediation sites, and nonindigenous microorganisms used in this process can cause competition with the microbes already present in the environment.

Biostimulation

Biostimulation is the process which involves degradation of the harmful compounds by adding the nutrients required by indigenous hydrocarbon-degrading microbes. The growth of microorganisms responsible for the degradation of oil during oil spillage is activated by the increase in carbon. The tendency of the microorganisms to degrade the hydrocarbons is enhanced by addition of suitable concentration of supplemental nutrients. Due to this reason, microorganisms are competent of achieving their utmost rate of growth and consequently the utmost rate of contaminant uptake. The maximum biostimulation is achieved by obtaining the ideal nutrient concentration which is required for the utmost growth of the microorganisms and maintaining concentration as long as possible for microorganisms.

c. Chemical remediation

This process requires the use of chemicals. Contaminants can be treated by using various chemicals. Chemicals usually have the capability of altering the contaminant's chemical and physical properties. Dispersants, solidifiers, and chemical oxidants are the three categories in which the chemical remediation are grouped.

Dispersants

Slick of oil can be broken down into smaller droplets by surfactants which are present in dispersants, and these droplets undergo rapid dilution by transferring it into the water and can be effortlessly degraded. Chemical dispersants can raise the oil droplet surface area which results in an increased rate of natural biodegradation, and this process makes the oil less sticky to the surface by slowing down the development of oil-water emulsions and allows fast treatment. This method makes oil spills less harmful for living organisms and the marine life. This is achieved by converting oil slicks into droplets which in turn can be degraded by bacteria. Some of the examples of chemical dispersants are Nokomis 3-F4, Slickgone NS, Finasol OSR 52, SPC 1000™, Neon AB3000, ZI-400, Corexit 9500, Corexit 8667, and Saf-Ron Gold.

Solidifiers

In this method oil is removed by physical method which involves the interaction of dry granular materials with the oil and converts its liquid state into rubberlike solid state. Dry particulate and semisolid substances such as balls, pucks, sponge, etc. are the various forms in which the solidifiers can be applied. Solidification can be enhanced by using the solidifiers in the seas because mixing energy is provided by the seawater. Solidifiers are difficult to recover after solidification, and it is less efficient, which are the major drawbacks for the use of the solidifiers.

Chemical oxidants

Chemical oxidation technique involves the usage of chemical agents which are capable of oxidizing the organic pollutants. These chemical agents are introduced by the help of the mixing apparatus and injection in water or soil at the contaminated site. The usefulness of the process is found to depend upon oxidant quality, efficient contact between pollutant and oxidant, geological conditions, and oxidant's residence time. This process is rapid and can be applied in all-weather situations which are some of the advantages of this process. Table below represents the details of major advantages and disadvantages.

Advantages and disadvantages of chemical treatment

Chemical treatment	Advantages	Disadvantages
Dispersants	Suitable in all-weather conditions and for a wide range of oils	No oil recovery Not effective on highly viscous, non-spreading, and waxy oil
	Accelerates by degradation of the oil by natural processes. Advanced formulations have been reduced. The previous concerns about toxicity. Less manpower is needed. Less expensive than mechanical methods.	The localized and temporary increase in the amount of oil in water concentration would have an effect on the surrounding marine life. If dispersion is not achieved, other response method's effectiveness may reduce less dispersed oil
Solidifiers	This process is rapid and can be applied in all-weather situations	Lack of practical application Large amount required Selected oil Not effective. No oil recovery

Chemical treatment	Advantages	Disadvantages
Chemical oxidation	This process is rapid and can be applied in all-weather situations	The process depends upon oxidant quality, efficient contact between pollutant and oxidant, geological conditions, and oxidant's residence time.

Methods used for the treatment of soil contamination

Pollution of soil occurs due to leakages from pipes and wellheads during offshore oil production and drilling operations, leakage from underground storage tanks of petroleum, overflow from gathering stations, petroleum yields, and inappropriate dumping of waste of petroleum. During the excavation, transport, and handling of polluted material, significant risk may be created by this method. For the final disposal of the substance, it is very hard to locate new landfill sites. There is continuous requirement of monitoring and maintenance of separation barriers since the pollutant remains on the site, and hence cap and containment technique is the temporary solution.

In situ and ex situ methods are used for the treatment of oil contaminated soils.

In situ method

This method involves physicochemical processes including air sparging (soil venting), soil air extraction, or by combinations of these two methods applied to the soil at the contaminated site. Vertical & horizontal fossil fuel drilling equipment's are used in-situ treatment. This technique is more efficient on sandy soil than on clay soils. Soil pollutant can be taken out by using air sparging. The growth of aerobic bacteria on oxygen feeding is accelerated by the help of this method. Air sparging can be also performed under the water table if the contamination takes place in the groundwater through extraction wells or to the surface by gravity segregation. The oil can be extracted from the oil saturated ground water or partially saturated soil by using a process called as slurping.

The volatile components which are trapped in the soil are extracted by injecting steam into the contaminated soil.

Ex situ method

This technique involves the elimination and transportation of polluted soil to off-site remediation ability. Various processes are used to perform the ex situ remediation which is as follows:

Land farming process is used in which soil polluted with oil is excavated and spread above a bed where it once in a while is tilled until the contaminants are degraded. Fifteen to 35 cm of soil surface is treated with the help of this technique.

Composting involves the increase in the development of the microbial species by mixing polluted soil with harmless organic compounds to contaminated soil.

Bioreactors are used for the bioprocessing of polluted soil, sediment, and water in which the three phases, gas, soil, and liquid, are mixed continuously in order to enhance the biodegradation rate. Before loading the contaminated soil to the bioreactors, the soil is pretreated. Contaminants undergo chemical reaction and convert harmful compounds into nontoxic compounds. **Dechlorination or UV** is used for the catalyzation of the oxidation reactions.

These techniques have a few limitations such as high cost due to the complication of the method required.

Bioremediation due to natural biological action is a choice which provides the chance to degrade the hydrocarbon contaminants.

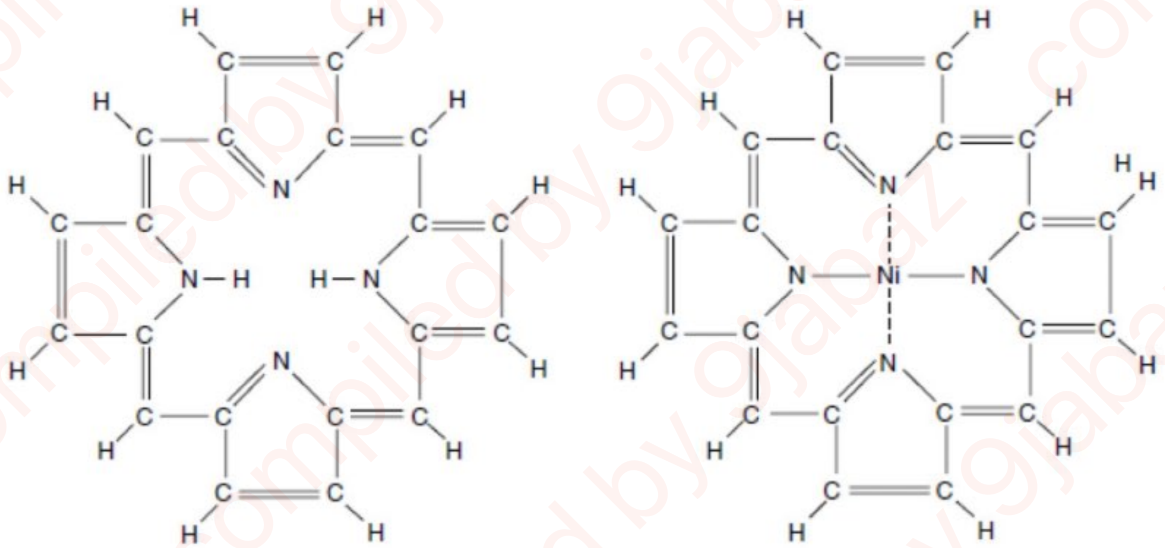


Figure: Porphyrin and the Nickel-containing derivative

CLASSIFICATION OF PETROLEUM USING API GRAVITY

Conventional crude oil and heavy oil have also been defined very generally in terms of physical properties. For example, heavy oils were considered those petroleum-type materials that had gravity somewhat less than 20° API, with the heavy oils falling into the API gravity range of 10° to 15° (e.g., Cold Lake crude oil = 12° API) and bitumen falling into the 5° to 10° API range (e.g., Athabasca bitumen = 8° API). Residua vary depending on the temperature at which distillation is terminated. Atmospheric residua are usually in the 10° to 15° API range of, and vacuum residua are in the range of 2° to 8° API. There have been several recent noteworthy attempts to classify crude oil using one or more of the general physical properties of crude oils. One method uses divisions by API gravity, which is already accepted by most workers, it also uses viscosity data. This method is essentially a more formal attempt in which specific numbers are applied without recognition of the implications of these numbers.

CLASSIFICATION OF PETROLEUM USING VISCOSITY-GRAVITY CONSTANT

This parameter, along with the Universal Oil Products characterization factor, has been used to some extent as a means of classifying crude oils. Both parameters are usually employed to give an indication of the paraffin character of the crude oil, and both have been used, if a subtle differentiation can be made, as a means of petroleum characterization rather than for petroleum classification.

Nevertheless, the viscosity–gravity constant (VGC) was one of the early indices proposed to characterize (or classify) oil types:

$$VGC = 10d - 1.0752\log(v - 38)/(10 - \log(v - 38))$$

Where d is the specific gravity 60°/60°F and v is the Saybolt viscosity at 39°C (100°F). For heavy oil, where the low-temperature viscosity is difficult to measure, an alternative formula has been proposed in which the 99°C (210°F) Saybolt viscosity is used, viz:

$$VGC = d - 0.24 - 0.022\log\frac{v - 35.5}{0.755}$$

The two do not agree well for low-viscosity oils. However, the viscosity–gravity constant is of particular value in indicating a predominantly paraffin or cyclic composition. The lower the index number, the more paraffin the feedstock; for example, naphthene lubricating oil distillates have VGC equal to approximately 0.876 and the raffinate obtained by solvent extraction of lubricating oil distillate has VGC equal to approximately 0.840.

CLASSIFICATION OF PETROLEUM USING UOP CHARACTERIZATION FACTOR

This factor is perhaps one of the more widely used derived characterization or classification factors and is defined by the formula:

$$K = \frac{(T_B)^{\frac{1}{3}}}{d}$$

where T_B is the average boiling point in degrees Rankine (°F + 460) and d is the specific gravity 60°/60°F. This factor has been shown to be additive on a weight basis. It was originally devised to show the thermal cracking characteristics of heavy oils; thus, highly paraffin oils have K in the range 12.5 to 13.0 and cyclic (naphthene) oils have K in the range 10.5 to 12.5.

Finally, all the classification systems mentioned here are based on the assumption that petroleum can be more or less characterized by the properties of one or of a few fractions. However, the properties of certain fractions of a crude oil are definitely not always reflected in those of other fractions of the same oil. Indeed, some crude oils have a different chemical character in low-boiling and high-boiling fractions, and any method of classification in which the properties of a certain fraction are extrapolated to the whole crude oil must be applied with caution, as serious errors can arise.

QUALITY CHARACTERISTICS OF PETROLEUM (PETROLEUM ASSAY)

1. Density and specific gravity

The density and specific gravity of crude oil are two properties that have found wide use in the industry for preliminary assessment of the character and quality of crude oil. Density is the mass of a unit volume of material at a specified temperature and has the dimensions of grams per cubic centimeter (a close approximation to grams per milliliter). On the other hand, specific gravity is the ratio of the mass of a volume of the substance to the mass of the same volume of water and is dependent on two temperatures, those at which the masses of the sample and the water are measured. When the water temperature is 4°C (39°F), the specific gravity is equal to the density in the centimeter–gram–second (cgs) system, since the volume of 1 g of water at that temperature is, by definition, 1 mL. Thus, the density of water, for example, varies with temperature, and its specific gravity at equal temperatures is always unity. The standard temperatures for a specific gravity in the petroleum industry in North America are 60/60°F (15.6/15.6°C).

The accurate determination of the API gravity of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperature of 60°F (15.56°C). Gravity is a factor governing the quality of crude oils. However, the gravity of a petroleum product is an uncertain indication of its quality. Correlated with other properties, gravity can be used to give approximate hydrocarbon composition and heat of combustion. This is usually accomplished through use of the API gravity, which is derived from the specific gravity:

$$API\ gravity\ (°) = \frac{141.5}{specific\ gravity\ at\ 15.6°C} - 131.5$$

2. Carbon residue and asphaltene content

The carbon residues of petroleum and petroleum products serve as an indication of the propensity of the sample to form carbonaceous deposits (thermal coke) under the influence of heat. Tests for Conradson carbon residue (ASTM D-189, IP 13), Ramsbottom carbon residue (ASTM D-524, IP 14), the microcarbon carbon residue (ASTM D4530, IP 398), and asphaltene content (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143) are sometimes included in inspection data on petroleum. The data give an indication of the amount of coke that will be formed during thermal processes as well as an indication of the amount of high-boiling constituents in petroleum.

The determination of the *carbon residue* of petroleum or a petroleum product is applicable to relatively nonvolatile samples that decompose on distillation at atmospheric pressure. Samples that contain ash-forming constituents will have an erroneously high carbon residue, depending on the amount of ash formed. All three methods are applicable to relatively nonvolatile petroleum products that partially decompose on distillation at atmospheric pressure. Crude oils having a low carbon residue may be distilled to a specified residue with the carbon residue test of choice then applied to that residue.

The asphaltene fraction (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143) is the highest molecular-weight, most complex fraction in petroleum. The asphaltene content gives an indication of the amount of coke that can be expected during processing.

3. Distillation test

The distillation tests give an indication of the types of products and the quality of the products that can be obtained from petroleum, and the tests are used to compare different petroleum types through the yield and quality of the 300°C (572°F) residuum fraction. For example, the waxiness or viscosity of this fraction gives an indication of the amount, types, and quality of the residual fuel that can be obtained from the petroleum. In this respect, the determination of the aniline point (ASTM D-611, IP 2) can be used to determine the aromatic or aliphatic character of petroleum. Although not necessarily the same as the wax content, correlative relationships can be derived from the data.

The basic method of distillation (ASTM D-86) is one of the oldest methods in use because the distillation characteristics of hydrocarbons have an important effect on safety and performance, especially in the case of fuels and solvents. The boiling range gives information on the composition, the properties, and the behavior of petroleum and derived products during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors. Several methods are available to define the distillation characteristics of petroleum and its various petroleum products. In addition to these physical methods, other test methods based on gas chromatography are also used to derive the boiling point distribution of a sample (ASTM D-2887, ASTM D-3710, ASTM D-5307, ASTM D-6352).

Usually, seven fractions provide the basis for a reasonably thorough evaluation of the distillation properties of the feedstock:

1. Gas, boiling range: <15.5°C (60°F)
2. Gasoline (light naphtha), boiling range: 15.5–149°C (60–300°F)
3. Kerosene (medium naphtha), boiling range: 149–232°C (300–450°F)
4. Gas oil, boiling range: 232–343°C (450–650°F)
5. Light vacuum gas oil, boiling range: 343–371°C (650–700°F)
6. Heavy vacuum gas oil, boiling range: 371–566°C (700–1050°F)
7. Residuum, boiling range: >566°C (1050°F)

4. Salt content

The salt content of crude oil is highly variable and results principally from production practices used in the field and, to a lesser extent, from its handling aboard the tankers bringing it to terminals. The bulk of the salt present will be dissolved in coexisting water and can be removed in desalters, but small amounts of salt may be dissolved in the crude oil itself. Salt may be derived from reservoir or formation waters or from other waters used in secondary recovery operations.Aboard tankers, ballast water of varying salinity may also be a source of salt contamination.

Salt in crude oil may be deleterious in several ways. Even in small concentrations, salts will accumulate in stills, heaters, and exchangers, leading to fouling that requires expensive cleanup.

More importantly, during flash vaporization of crude oil, certain metallic salts can be hydrolyzed to hydrochloric acid according to the following reactions:

$$2NaCl + H_2O \rightarrow 2HCl + Na_2O$$

$$MgCl_2 + H_2O \rightarrow 2HCl + MgO$$

The hydrochloric acid evolved is extremely corrosive, necessitating the injection of a basic compound, such as ammonia, into the overhead lines to minimize corrosion damage. Salts and evolved acids can also contaminate both overhead and residual products, and certain metallic salts can deactivate catalysts. Thus, knowledge of the content of salt in crude oil is important in deciding whether and to what extent the crude oil needs desalting.

5. Sulphur content

Sulphur is present in petroleum as sulphides, thiophenes, benzothiophenes, and dibenzothiophenes. In most cases, the presence of sulphur is detrimental to the processing because sulphur can act as catalytic poisons during processing. Sulphur compounds contribute to corrosion of refinery equipment and poisoning of catalysts, cause corrosiveness in refined products, and contribute to environmental pollution as a result of the combustion of fuel products. Sulphur compounds may be present throughout the boiling range of crude oils although, as a rule, they are more abundant in the higher-boiling fractions. In some crude oils, thermally labile sulphur compounds can decompose on heating to produce hydrogen sulphide, which is corrosive and toxic. The Doctor test measures the amount of sulphur available to react with metallic surfaces at the temperature of the test. The rates of reaction are metal type-, temperature-, and time dependent. In the test, a sample is treated with copper powder at 149°C or 300°F. The copper powder is filtered from the mixture. Active sulphur is calculated from the difference between the sulphur contents of the sample (ASTM D-129) before and after treatment with copper.

6. Viscosity and pour point

Viscosity and pour point determinations are performed principally to ascertain the handling (flow) characteristics of petroleum at low temperatures. There are, however, some general relationships of crude oil composition that can be derived from pour point and viscosity data. Commonly, the lower the pour point of a crude oil the more aromatic it is, and the higher the pour point the more paraffinic it is. Viscosity is usually determined at different temperatures (e.g., 25°C/77°F, and 100°C/212°F) by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer (ASTM D-445).

The *viscosity index* (ASTM D-2270, IP 226) is a widely used measure of the variation in kinematic viscosity due to changes in the temperature of petroleum between 40°C and 100°C (104°F and 212°F). For crude oils of similar kinematic viscosity, the higher the viscosity index the smaller is the effect of temperature on its kinematic viscosity. The accuracy of the calculated viscosity index is dependent only on the accuracy of the original viscosity determination.

The *pour point* of petroleum is an index of the lowest temperature at which the crude oil will flow under specified conditions. The maximum and minimum pour point temperatures provide a temperature window where petroleum, depending on its thermal history, might appear in the liquid as well as the solid state. The pour point data can be used to supplement other measurements of cold flow behavior, and the data are particularly useful for the screening of the effect of wax interaction modifiers on the flow behavior of petroleum.

7. Water and sediment content

Considerable importance is attached to the presence of water or sediment in petroleum because they lead to difficulties in the refinery, for example, corrosion of equipment, uneven running on the distillation unit, blockages in heat exchangers, and adverse effects on product quality. The water and sediment content of crude oil, like salt, results from production and transportation practices. Water, with its dissolved salts, may occur as easily removable suspended droplets or as an emulsion. The sediment dispersed in crude oil may be comprised of inorganic minerals from the production horizon or from drilling fluids and scale and rust from pipelines and tanks used for oil transportation and storage. Usually, water is present in far greater amounts than sediment, but, collectively, it is unusual for them to exceed 1% of the crude oil on a delivered basis. Like salt, water and sediment can foul heaters, stills, and exchangers and can contribute to corrosion and to deleterious product quality. Also, water and sediment are principal components of the sludge that accumulates in storage tanks and must be disposed of periodically in an environmentally acceptable manner. Knowledge of the water and sediment content is also important in accurately determining net volumes of crude oil in sales, taxation, exchanges, and custody transfers.

The Karl Fischer test method (ASTM D-1364, ASTM D-6304) covers the direct determination of water in petroleum. In the test, the sample injection in the titration vessel can be performed on a volumetric or gravimetric basis. Viscous samples can be analyzed with a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry, inert carrier gas.

Water and sediment in petroleum can be determined simultaneously (ASTM D-96, ASTM D-4007, IP 359) by the centrifuge method. Known volumes of petroleum and solvent are placed in a centrifuge tube and heated to 60°C (140°F). After centrifugation, the volume of the sediment and-water layer at the bottom of the tube is read. For petroleum that contains wax, a temperature of 71°C (160°F) or higher may be required to completely melt the wax crystals so that they are not measured as sediment.

8. Wax content

Petroleum with a high wax content presents difficulties in handling and pumping as well as producing distillate and residual fuels of high pour point and lubricating oils that are costly to dewax. On the other hand, the wax appearance point (ASTM D-3117) may be determined by cooling of a sample under prescribed conditions with stirring. The temperature at which the wax first appears is the wax appearance point.

9. Other tests

The *Reid vapor pressure* test method (ASTM D-323, IP 69) measures the vapor pressure of volatile petroleum. The Reid vapor pressure differs from the true vapor pressure of the sample because of some small sample vaporization and the presence of water vapor and air in the confined space.

The *acid number* is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample in this solvent to a green/green-brown end point, using *p*-naphtholbenzein indicator solution.The *strong acid number* is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading to a meter reading corresponding to a freshly prepared nonaqueous acidic buffer solution or a well-defined inflection point as specified in the test method (ASTM D-664, IP 177).

The *aniline point* (or *mixed aniline point*) (ASTM D-611, IP 2) has been used for the characterization of crude oil, although it is more applicable to pure hydrocarbons and in their mixtures and is used to estimate the aromatic content of mixtures. Aromatics exhibit the lowest aniline points and paraffins the highest aniline points. Cycloparaffins and olefins exhibit values between these two extremes. In any hydrocarbon homologous series, the aniline point increases with increasing molecular weight.

The *refractive index* is the ratio of the velocity of light in a vacuum to the velocity of light in the substance. The measurement of the refractive index is very simple (ASTM D1218), requires small quantities of material, and, consequently, has found wide use in the characterization of hydrocarbons and petroleum samples. For closely separated fractions of similar molecular weight, the values increase in the order: paraffin, naphthene, and aromatic. For polycyclic naphthenes and polycyclic aromatics, the refractive index is usually higher than that of the corresponding monocyclic compounds. For a series of hydrocarbons of essentially the same type, the refractive index increases with molecular weight, especially in the paraffin series. Thus, the refractive index can be used to provide valuable information about the composition of hydrocarbon (petroleum) mixtures; as with density, low values indicate paraffinic materials and higher values indicate the presence of aromatic compounds.

The *cloud point* of petroleum or a petroleum product is the temperature at which paraffin wax or other solidifiable compounds present in the oil appear as a haze when the sample is chilled under definitely prescribed conditions (ASTM D2500, ASTM D3117, IP 219, IP 444, IP 445, IP 446).

The *flash point* of petroleum or a petroleum product is the temperature to which the product must be heated under specified conditions to give off sufficient vapor to form a mixture with air that can be ignited momentarily by a specified flame (ASTM D56, D92, and D93). The flash point of a petroleum product is also used to detect contamination. A substantially lower flash point than expected for a product is a reliable indicator that a product has become contaminated with a more volatile product, such as gasoline. The flash point is also an aid in establishing the identity of a particular petroleum product.

The *fire point* is the temperature to which the product must be heated under the prescribed conditions of the method to burn continuously when the mixture of vapor and air is ignited by a specified flame (ASTM D92).

Surface tension is a measure of the force acting at a boundary between two phases. If the boundary is between a liquid and a solid or between a liquid and a gas (air) the attractive forces are referred to as surface tension, but the attractive forces between two immiscible liquids are referred to as *interfacial tension*.

OIL REFINING

Petroleum refining is the separation of petroleum into fractions and the subsequent treating of these fractions to yield marketable products. In fact, a refinery is essentially a group of manufacturing plants which vary in number with the variety of products produced. Refinery processes must be selected and products manufactured to give a balanced operation in which petroleum is converted into a variety of products in amounts that are in accord with the demand for each.

To convert crude oil into desired products in an economically feasible and environmentally acceptable manner, refinery process for crude oil are generally divided into three categories:

1. Separation: division of crude oil into various streams (or fractions) depending on the nature of the crude material
2. Conversion: production of saleable materials from crude oil, usually by skeletal alteration, or even by alteration of the chemical type of the crude oil constituents
3. Finishing: purification of various product streams by a variety of processes that essentially remove impurities from the product; for convenience, processes that accomplish molecular alteration, such as reforming, are also included in this category

The separation and finishing processes may involve distillation or even treatment with a wash solution, either to remove impurities or, in the case of distillation, to produce a material boiling over a narrower range and the chemistry of these processes is quite simple. The inclusion of reforming processes in this category is purely for descriptive purposes rather than being representative of the chemistry involved. Reforming processes produce streams that allow the product to be finished, as the term applies to product behavior and utility.

Conversion processes are, in essence, processes that change the number of carbon atoms per molecule, alter the molecular hydrogen-to-carbon ratio, or change the molecular structure of the material without affecting the number of carbon atoms per molecule. These latter processes (isomerization processes) essentially change the shape of the molecule(s) and are used to improve the quality of the product.

Modern Processes

1. Thermal cracking

The term cracking applies to the decomposition of petroleum constituents that is induced by elevated temperatures (>350°C, >660°F), whereby the higher molecular weight constituents of petroleum are converted to lower molecular weight products. Cracking reactions involve carbon–carbon bond rupture and are thermodynamically favored at high temperature. Thus, cracking is a phenomenon by which higher boiling (higher molecular weight) constituents in petroleum are converted into lower boiling (lower molecular weight) products. However, certain products may interact with one another to yield products with higher molecular weights than the constituents of the original feedstock.

Thermal cracking is a free radical chain reaction; a free radical is an atom or group of atoms possessing an unpaired electron. Free radicals are very reactive, and it is their mode of reaction that actually determines the product distribution during thermal cracking. The free radical reacts with a hydrocarbon by abstracting a hydrogen atom to produce a stable end product and a new free radical. Free radical reactions are extremely complex, and it is hoped that these few reaction schemes illustrate potential reaction pathways. Any of the preceding reaction types are possible, but it is generally recognized that the prevailing conditions and those reaction sequences that are thermodynamically favored determine the product distribution.

2. Catalytic cracking

Catalytic cracking is the thermal decomposition of petroleum constituents' hydrocarbons in the presence of a catalyst. Thermal cracking has been superseded by catalytic cracking as the process for gasoline manufacture. Indeed, gasoline produced by catalytic cracking is richer in branched paraffins, cycloparaffins, and aromatics, all of which serve to increase the quality of the gasoline. Catalytic cracking also results in production of the maximum amount of butenes and butanes (C_4H_8 and C_4H_{10}), rather than ethylene and ethane (C_2H_4 and C_2H_6).

Although thermal cracking is a free radical (neutral) process, catalytic cracking is an ionic process involving carbonium ions, which are hydrocarbon ions having a positive charge on a carbon atom. The formation of carbonium ions during catalytic cracking can occur by:

(i) Addition of a proton from an acid catalyst to an olefin

(ii) Abstraction of a hydride ion (H^-) from a hydrocarbon by the acid catalyst or by another carbonium ion

However, carbonium ions are not formed by cleavage of a carbon–carbon bond. In essence, the use of a catalyst permits alternate routes for cracking reactions, usually by lowering the free energy of activation for the reaction. The acid catalysts first used in catalytic cracking were amorphous solids composed of approximately 87% silica (SiO_2) and 13% alumina (Al_2O_3) and were designated low-alumina catalysts. However, this type of catalyst is now being replaced by crystalline aluminosilicates (zeolites) or molecular sieves.

Catalytic cracking has a number of advantages over thermal cracking: (a) the gasoline produced has a higher octane number; (b) the catalytically cracked gasoline consists largely of iso-paraffins and aromatics, which have high octane numbers and greater chemical stability than monoolefins and diolefins which are present in much greater quantities in thermally cracked gasoline. Substantial quantities of olefinic gases suitable for polymer gasoline manufacture and smaller quantities of methane, ethane, and ethylene are produced by catalytic cracking. Sulfur compounds are changed in such a way that the sulfur content of catalytically cracked gasoline is lower than in thermally cracked gasoline. Catalytic cracking produces less heavy residual or tar and more of the useful gas oils than does thermal cracking. The process has considerable flexibility, permitting the manufacture of both motor and aviation gasoline and a variation in the gas oil yield to meet changes in the fuel oil market.

3. Visbreaking

Visbreaking (viscosity breaking) is essentially a process of the post-1940 era and was initially introduced as a mild thermal cracking operation that could be used to reduce the viscosity of residua to allow the products to meet fuel oil specifications. Alternatively, the visbroken residua could be blended with lighter product oils to produce fuel oils of acceptable viscosity. By reducing the viscosity of the residuum, visbreaking reduces the amount of light heating oil that is required for blending to meet the fuel oil specifications. In addition to the major product, fuel oil, mate rial in the gas oil and gasoline boiling range are produced. The gas oil may be used as additional feed for catalytic cracking units, or as heating oil.

4. Coking

Coking is a thermal process for the continuous conversion of heavy, low-grade oils into lighter products. Unlike visbreaking, coking involves complete thermal conversion of the feedstock into volatile products and coke. The feedstock is typically a residuum and the products are gases, naphtha, fuel oil, gas oil, and coke. The gas oil may be the major product of a coking operation and serves primarily as a feedstock for catalytic cracking units. The coke obtained is usually used as fuel but specialty uses, such as electrode manufacture, production of chemicals and metallurgical coke are also possible and increases the value of the coke. For these uses, the coke may require treatment to remove sulfur and metal impurities.

Delayed coking is a semi-continuous process in which the heated charge is transferred to large soaking (or coking) drums, which provide the long residence time needed to allow the cracking reactions to proceed to completion. The feed to these units is normally an atmospheric residuum, although cracked residua are also used.

Fluid coking is a continuous process which uses the fluidized- solids technique to convert atmospheric and vacuum residua to more valuable products. The residuum is coked by being sprayed into a fluidized bed of hot, fine coke particles, which permits the coking reactions to be conducted at higher temperatures and shorter contact times than can be employed in delayed coking. Moreover, these conditions result in decreased yields of coke; greater quantities of more valuable liquid product are recovered in the fluid coking process.

Flexicoking is also a continuous process that is a direct descendent of fluid coking. The unit uses the same configuration as the fluid coker, but has a gasification section in which excess coke can be gasified to produce refinery fuel gas.

5. Thermal Reforming

In carrying out thermal reforming, a feedstock such as 205°C (400°F) end-point naphtha or a straight-run gasoline is heated to 510°C to 595°C (950°F to 1100°F) in a furnace, much the same as a cracking furnace, with pressures from 400 to 1000 psi (27 to 68 atm). As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha. The material then enters a fractional distillation tower where any heavy products are separated. The remainder of the reformed material leaves the top of the tower to be separated into gases and reformate. The higher-octane number of the reformate is due primarily to the cracking of longer-chain paraffins into higher-octane olefins. The products of thermal reforming are gases, gasoline, and residual oil or tar, the latter being formed in very small amounts (about 1%). The amount and quality of the gasoline, known as reformate, is very dependent on the temperature. A general rule is: the higher the reforming temperature, the higher the octane number, but the lower the yield of reformate. Thermal reforming is less effective and less economical than catalytic processes and has been largely supplanted. As it used to be practised, a single-pass operation was employed at temperatures in the range of 540°C to 760°C (1000°F to 1140°F) and pressures of about 500 to 1000 psi (34 to 68 atm). The degree of octane number improvement depended on the extent of conversion, but was not directly proportional to the extent of crack per pass. However at very high conversions, the production of coke and gas became prohibitively high. The gases produced were generally olefinic and the process required either a separate gas polymerization operation or one in which C3 to C4 gases were added back to the reforming system. More recent modifications of the thermal reforming process due to the inclusion of hydrocarbon gases with the feedstock are known as gas reversion and polyforming. Thus, olefinic gases produced by cracking and reforming can be converted into liquids boiling in the gasoline range by heating them under high pressure.

Since the resulting liquids (polymers) have high octane numbers, they increase the overall quantity and quality of gasoline produced in a refinery.

6. Catalytic Reforming

The catalytic reforming process was commercially nonexistent in the United States before 1940. The process is really a process of the 1950s and showed phenomenal growth in the 1953 to 1959 time period. Like thermal reforming, catalytic reforming converts low-octane gasoline into high-octane gasoline (reformate). When thermal reforming could produce reformate with research octane numbers of 65 to 80 depending on the yield, catalytic reforming produces reformate with octane numbers on the order of 90 to 95. Catalytic reforming is conducted in the presence of hydrogen over hydrogenation–dehydrogenation catalysts, which may be supported on alumina or silica–alumina. Depending on the catalyst, a definite sequence of reactions takes place, involving structural changes in the feedstock. This more modern concept actually rendered thermal reforming somewhat obsolescent. The commercial processes available for use can be broadly classified as the moving-bed, fluid-bed and fixed-bed types. The fluid-bed and moving-bed processes used mixed nonprecious metal oxide catalysts in units equipped with separate regeneration facilities. Fixed-bed processes use predominantly platinum-containing catalysts in units equipped for cycle, occasional, or no regeneration. Catalytic reformer feeds are saturated (i.e., not olefinic) materials; in the majority of cases that feed may be a straight-run naphtha, but other byproduct low-octane naphtha (e.g., coker naphtha) can be processed after treatment to remove olefins and other contaminants. Hydrocracker naphtha that contains substantial quantities of naphthenes is also a suitable feed. Dehydrogenation is a main chemical reaction in catalytic reforming, and hydrogen gas is consequently produced in large quantities. The hydrogen is recycled through the reactors where the reforming takes place to provide the atmosphere necessary for the chemical reactions and also prevents the carbon from being deposited on the catalyst, thus extending its operating life. An excess of hydrogen above whatever is consumed in the process is produced, and, as a result, catalytic reforming processes are unique in that they are the only petroleum refinery processes to produce hydrogen as a byproduct.

Catalytic reforming is usually carried out by feeding a naphtha (after pretreating with hydrogen if necessary) and hydrogen mixture to a furnace, where the mixture is heated to the desired temperature, 450 °C to 520 °C (840 °F to 965 °F), and then passed through fixed-bed catalytic reactors at hydrogen pressures of 100 to 1000 psi (7 to 68 atm). Normally, pairs of reactors are used in series with heaters which are located between adjoining reactors in order to compensate for the endothermic reactions taking place. Sometimes as many as four or five reactors are kept on stream in series, whereas one or more is regenerated.

7. Hydrocracking

Hydrocracking is a thermal process (>350°C, >660°F) in which hydrogenation accompanies cracking. Relatively high pressure (100 to 2000 psi) is employed, and the overall result is usually a change in the character or quality of the products. The wide range of products possible from hydrocracking is the result of combining catalytic cracking reactions with hydrogenation. The reactions are catalyzed by dual-function catalysts in which the cracking function is provided by silica–alumina (or zeolite) catalysts, and platinum, tungsten oxide, or nickel provides the hydrogenation function.

8. Hydrotreating

It is generally recognized that the higher the hydrogen content of a petroleum product, especially the fuel products, the better is the quality of the product. This knowledge has stimulated the use of hydrogen-adding processes in the refinery. Thus, hydrotreating (i.e., hydrogenation without simultaneous cracking) is used for saturating olefins or for converting aromatics to naphthenes as well as for heteroatom removal. Under atmospheric pressure, olefins can be hydrogenated up to about 500°C (930°F), but beyond this temperature dehydrogenation commences. Application of pressure and the presence of catalysts make it possible to effect complete hydrogenation at room or even cooler temperature; the same influences are helpful in minimizing dehydrogenation at higher temperatures.

9. Alkylation Processes

The combination of olefins with paraffins to form higher iso-paraffins is termed alkylation. Since olefins are reactive (unstable) and are responsible for exhaust pollutants, their conversion to high-octane iso -paraffins is desirable when possible. In refinery practice, only isobutane is alkylated, by reaction with iso-butene or normal butene and iso-octane is the product. Although alkylation is possible without catalysts, commercial processes use aluminum chloride, sulfuric acid, or hydrogen fluoride as catalysts, when the reactions can take place at low temperatures, minimizing undesirable side reactions, such as polymerization of olefins.

Alkylate is composed of a mixture of iso-paraffins which have octane numbers that vary with the olefins from which they were made. Butylenes produce the highest octane numbers, propylene the lowest and pentylenes the intermediate values. All alkylates, however, have high octane numbers (> 87) which makes them particularly valuable.

10. Isomerization

The importance of isomerization in petroleum refining operations is twofold. First, the process is valuable in converting n-butane into iso -butane, which can be alkylated to liquid hydrocarbons in the gasoline boiling range. Second, the process can be used to increase the octane number of the paraffins, boiling in the gasoline boiling range, by converting some of the n-paraffins present into iso-paraffins. Catalytic reforming processes provide high-octane constituents in the heavier gasoline fraction but the normal paraffin components of the lighter gasoline fraction, especially butanes, pentanes and hexanes, have poor octane ratings. The conversion of these normal paraffins to their isomers (isomerization) yields gasoline components of high octane rating in this lower boiling range. Conversion is obtained in the presence of a catalyst (aluminum chloride activated with hydrochloric acid), and it is essential to inhibit side react ions such as cracking and olefin formation.

11. Polymerization

Polymerization is a process in which a substance of low molecular weight is transformed into one of the same composition, but of higher molecular weight while maintaining the atomic arrangement present in the basic molecules. It has also been described as the successive addition of one molecule to another by means of a functional group, such as that present in an aliphatic olefin. In the petroleum industry, polymerization is used to indicate the production of, say, gasoline components that fall into a specific (and controlled) molecular weight range, hence the term polymer gasoline.

PETROCHEMICALS

The petrochemical industry began in the 1920s, as suitable byproducts became available through improvements in the refining processes. It developed parallel with the oil industry and has rapidly expanded since the 1940s, with the oil refining industry providing plentiful cheap raw materials.

A petrochemical is any chemical (as distinct from fuels and petroleum products) manufactured from petroleum (and natural gas) and used for a variety of commercial purposes. The definition, however, has been broadened to include the whole range of aliphatic, aromatic, and naphthenic organic chemicals, as well as carbon black and such inorganic materials as sulfur and ammonia. Petroleum and natural gas are made up of hydrocarbon molecules, which are composed of one or more carbon atoms, to which hydrogen atoms are attached.

Currently, through a variety of intermediates, oil and gas are the main sources of the raw materials because they are the least expensive, most readily available, and can be processed most easily into the primary petrochemicals. Primary petrochemicals include: olefins (ethylene, propylene and butadiene) aromatics (benzene, toluene, and the isomers of xylene); and methanol. Thus, petrochemical feedstocks can be classified into three general groups: olefins, aromatics, and methanol; a fourth group includes inorganic compounds and synthesis gas (mixtures of carbon monoxide and hydrogen). In many instances, a specific chemical included among the petrochemicals may also be obtained from other sources, such as coal, coke, or vegetable products. For example, materials such as benzene and naphthalene can be made from either petroleum or coal, whereas ethyl alcohol may be of petrochemical or vegetable origin.

As stated earlier above, some of the chemicals and compounds produced in a refinery are destined for further processing and as raw material feedstocks for the fast-growing petrochemical industry. Such nonfuel uses of crude oil products are sometimes referred to as its nonenergy uses. Petroleum products and natural gas provide two of the basic starting points for this industry; methane from natural gas, and naphtha and refinery gases.

Petrochemical intermediates are generally produced by chemical conversion of primary petrochemicals to form more complicated derivative products. Petrochemical derivative products can be made in a variety of ways: directly from primary petrochemicals; through intermediate products which still contain only carbon and hydrogen; and, through intermediates which incorporate chlorine, nitrogen or oxygen in the finished derivative. In some cases, they are finished products; in others, more steps are needed to arrive at the desired composition. Of all the processes used, one of the most important is polymerization. It is used in the production of plastics, fibers and synthetic rubber, the main finished petrochemical derivatives.

Some typical petrochemical intermediates are: vinyl acetate for paint, paper and textile coatings, vinyl chloride for polyvinyl chloride (PVC), resin manufacture, ethylene glycol for polyester textile fibers, styrene which is important in rubber and plastic manufacturing. The end products number in the thousands, some going on as inputs into the chemical industry for further processing. The more common products made from petrochemicals include adhesives, plastics, soaps, detergents, solvents, paints, drugs, fertilizer, pesticides, insecticides, explosives, synthetic fibers, synthetic rubber, and flooring and insulating materials.

Hydrocarbon intermediates used in the petrochemical industry

Carbon number	**Hydrocarbon type**		
	Saturated	**Unsaturated**	**Aromatic**
1	Methane		
2	Ethane	Ethylene Acetylene	
3	Propane	Propylene	
4	Butane	n-Butene Iso-butene Butadiene	
5	Pentane	Iso-pentene	
6	Hexane Cyclohexane	Methylpentene	Benzene

7			Toluene
8			Xylene Ethylbenzene Styrene
18			Dodecylbenzene