



**PROSPECTS**

*Of*

**EM TECHNOLOGY**

*In*

**PETROLEUM INDUSTRY**



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# PROSPECTS OF EM TECHNOLOGY IN PETROLEUM INDUSTRY

## Summary

Crude petroleum is natural organic material composed principally of hydrocarbons (83–87% C and 11–15% H) and small quantities of non-hydrocarbons such as N (0 – 0.5%), S (0 – 6%) and O (0–0.5%). Besides this vanadium (up to 0.1%), Ni and Fe in comparatively less concentrations and other metallic elements like Al, Na, Ca, Cu, Mg, Mn, Cr, Sr, Pb, Ag, etc have also been reported in a variety of crude petroleum.

Hydrocarbons contain two types of covalent bonds, C–C and C–H. On the basis of structure, hydrocarbons may be open chain (acyclic) and closed chain (cyclic). Acyclic are further classified into two groups i.e. saturated and unsaturated. The saturated hydrocarbons contain single covalent bonds between the C atoms, e.g. alkanes. The unsaturated hydrocarbons contain atleast one double or triple covalent bonds between the carbon atoms, e.g. alkenes ( $C = C$ ) and alkynes ( $C \equiv C$ ). The cyclic hydrocarbons are further classified into two groups, namely cyclo-alkanes and arenes. Cyclo-alkanes are saturated hydrocarbons in which carbon atoms are joined by single covalent bonds to form a ring. These compounds are also called alicyclic compounds because of their similarity with aliphatic compounds. These compounds are also called polymethylene compound because they contain a number of methylene groups forming a closed ring, e.g. cyclo propane, cyclo butane, cyclo pentane etc. The arenes hydrocarbons contain one or more benzene rings, e.g. benzene, naphthalene etc. These compounds are aromatic and unsaturated.

In short the main types of hydrocarbons present in crude oils are alkanes, cycloalkens, arenes and hybrids involving combination of these types.

During the processing and production of useful products from the crude oil, wastes like air pollutants (sulphur compounds, hydrocarbons, nitrogen oxides, smoke, carbon monoxide, aldehydes, ammonia and odors) being emitted from refining operations, wastewater/ effluent (80 – 90% of the water supplied to the refinery comes out as wastewater) and sludge (suspension of solids in process waters and aqueous wastes) are produced. The sludge is formed in the petroleum refineries at nine places, which include: i) crude tank bottoms, ii) slop oil emulsion sludge, iii) cooling tower sludge, iv) lube oil filter cake, v) heat exchanger bundle cleaning sludge, vi) FCC catalyst fines, vii) API separator sludge, viii) dissolved air floatation sludge, and ix) waste biosludge.

Air emissions, wastewater and sludges are classified as dangerous to the environment. Their safe disposal is must in order to provide clean air and water and healthy environment to the human beings. In developed countries even expensive methods are being used to save the environments. In underdeveloped or

developing countries the pollution caused by the industrial wastes and sewage water have played havoc. Almost all the industries in these countries are throwing their gaseous emission partially treated into the air, effluent in the open drains or sewage system, which finally finds its way into the natural water bodies such as lakes and rivers, and the sludge, is being thrown openly in the nearby places or elsewhere on the land. Since the research has been carried out on sludge using EM Technology, described in detail in chapter 5, and summarized here.

Prof. Dr. Teruo Higa, Okinawa, Japan invented Effective Microorganisms (EM). EM is made up of 3 main genera: phototrophic bacteria, lactic acid bacteria and yeast. These Effective Microorganisms secrete beneficial substances such as vitamins, organic acids, chelated minerals and antioxidants when in contact with organic mater. Today, EM is produced in more than 50 countries around the world and has been successfully applied not only in agriculture, but also played magic in the field of environments and industries to control pollution. Recently its use has been extended in the field of health by manufacturing special type of EM, i.e. EM-X.

There exists microorganisms which derive their energy from waste products and other dead organisms and convert complex organic molecules into simpler inorganic forms. Microorganisms/microbes are the invisible scavenger force of Nature and provide a means to eliminate unwanted pollutants in the hazardous petroleum sludge. The prominent bacterial strains of *pseudomonas* sp of phototrophic bacteria contained in EM has been found capable of growing on alkanes, polycyclic hydrocarbons, salicylates, heterocyclics, phenolics and halogenated aliphatic and aromatic compounds. The bacteria *rhodopseudomonas palustris* can biodegrade benzene rings in the absence of oxygen. These bacteria secrete amino acids, nucleic acids, bioactive substances (hormones and enzymes) and sugars, which act as substrates for increasing beneficial microbial population. Lactic acid bacteria contain in the EM suppress harmful microorganisms and enhances decomposition of organic matter. The organic matter in the petroleum sludge provide food to the microorganisms, the production of many organic and inorganic acids increase the microbial population tremendously and hence hasten the bioremediation process.

The oxidation and reduction reactions carried out through bacteria detoxify the heavy metals by making them either more water-soluble and less toxic or less water soluble and precipitated or volatilized. Since most of the metals exist in the combined form as oxides, hydroxy carbonates, carbonates, chlorides, sulphides, silicates, their interaction with the gases being produced in the sludge convert them to respective oxides, sulphides, carbonates, hydroxides, sulphates or other compounds. Thus the properties of heavy metals are changed. Alkali metals and alkaline earth metals are oxidized at a quicker rate at low temperature and at high temperature all the metals are oxidized.

During an experiment [*Chapter-5*] the pure petroleum oily sludge was treated with various products of EM, anaerobic bioremediation was maintained and within a period of six weeks it was converted to biosludge. Finally mixing with equal quantity of dried soil material the biosludge was converted to biofertilizer. With EM treatment Ba was reduced up to 85%, Pb, Fe, Zn, Ni up to 50% in the biosludge while As, Cr, Cu and Mn showed no significant change.

The biofertilizer was applied to the soil on the bases of 10% by weight of the furrow-slice soil material keeping in view the higher content of organic matter of contained in the biofertilizer and to minimize the concentration of heavy metals. Onion crop was sown. EM solutions were applied with each irrigation in order to continue further decompose the organic matter and reduce the contents of heavy metals present in the biofertilizer.

The contents of heavy metals in the onions grown with this biofertilizer were comparable with those grown with FYM and these were far less than the limits given by FAO and Food Nutrition Laboratory. Thus, it can safely be concluded that EM Technology ensures not only the proper disposal of petroleum sludge but also its safe application in various fields of agriculture.

In short, the use of EM Technology for the proper disposal of petroleum oily sludge is safe to handle, easy to apply, cost effective and environment friendly. EM Technology converts the useless, wasteful petroleum sludge into useful and beneficial resource. Form environment protection point of view EM Technology is the future of the world as being “An Earth Saving Revolution”.

# PROSPECTS OF EM TECHNOLOGY IN PETROLEUM INDUSTRY

## 1. Petroleum

### 1.1 Occurrence

Petroleum means rock oil (Latin: Petra = rock & Oleum = oil). It occurs under the rocky strata of shale, limestone and clay below the surface of the earth at different depths varying from 150 – 4600 meters in many different parts of the world. The mining of the petroleum in recent years is done with airlift and hydraulic-rotary methods.

### 1.2 Crude petroleum or Crude oil

The liquid part of petroleum obtained after the removal of dissolved gasses is commonly called as crude petroleum or crude oil or simply crude.

### 1.3 Typical properties of Crude oil

Crude oils range widely in their physical and chemical properties, the range of typical properties is given in table -1.

### 1.4 Elemental composition of Crude oil

Petroleum is natural organic material composed principally of hydrocarbons (83 – 87% carbon, C, and 11 – 15% hydrogen, H) and small quantities of non-hydrocarbons such as nitrogen, N (0 – 0.5%), sulphur, S (0 – 6%) and oxygen, O (0 – 0.5%)\*.

[\* *Fuels and Petroleum Processing by B. K. Sharma, 1<sup>st</sup> Edition 1998.*]

#### 1.4.1 Hydrocarbons

The hydrocarbons present in the crude petroleum may be divided into two main classes:

##### a) Open chain or aliphatic compounds

These are comprised of n-paraffin series ( $C_nH_{2n-2}$ ), isoparaffin series ( $C_nH_{2n+2}$ ) and olefin series ( $C_nH_{2n}$ ). In general, n-paraffin straight chain series comprises a large fraction of most crude petroleum than any of the other individual classes; an n-alkane with  $C_{78}$  has actually been reported. Branched chain alkanes (isoparaffin series) occur to limited extent. Some naturally occurring members are 2 or 3 methyl pentanes, 2, 3 dimethylpentane, and 2 methyl hexane. The branched chain compounds are frequently manufactured by catalytic reforming, alkylation and isomerisation. The olefin series (ethylene, propylene, butylenes etc) is either absent or exists in very small quantities. Olefines have excellent antiknock properties and chemical reactivity and can be prepared by cracking.

**b) Ring compounds** These comprised of naphthalene series ( $C_nH_{2n}$ ) and aromatic or benzene series. The naphthene series is the second most abundantly occurring series of compounds (cyclohexene, methylcyclopentane, dimethyl cyclopentanes, methyl cyclohexane) in most crude petroleum. These naphthenes predominate in most gas oils and lubricating oils from all types of crudes. They have also been found to be present in residual products. Aromatic compounds (benzene, toluene, xylenes, ethylbenzene etc) may be present in small as well as in large amount. These compounds are produced by chemical processing, and like the olefins, have high antiknock properties [*Fuels and Petroleum and Processing by B. K. Sharma, 1<sup>st</sup> Edition 1998, P. F – 70 & 71*]. The details are given below:

Hydrocarbons are organic compounds composed solely of H and C. These contain two types of covalent bonds, C–C and C–H. On the basis of structure, hydrocarbons may be open chain (acyclic) and closed chain (cyclic). Acyclic are further classified into two groups i.e. saturated and unsaturated. The former contain single covalent bonds between the C atoms, e.g. alkanes, the later contain at least one double or triple covalent bonds between the carbon atoms, e.g. alkenes ( $C = C$ ) and alkynes ( $C \equiv C$ ). The cyclic hydrocarbons are further classified into two groups, namely cyclo alkanes and arenes. Cyclo alkanes are saturated hydrocarbons in which carbon atoms are joined by single covalent bonds to form ring. These compounds are also called alicyclic compound because of their similarity with aliphatic compounds. These are also called polymethylene compounds because they contain a number of methylene groups forming a closed ring, e.g. cyclo propane, cyclo butane, cyclo pentane etc.

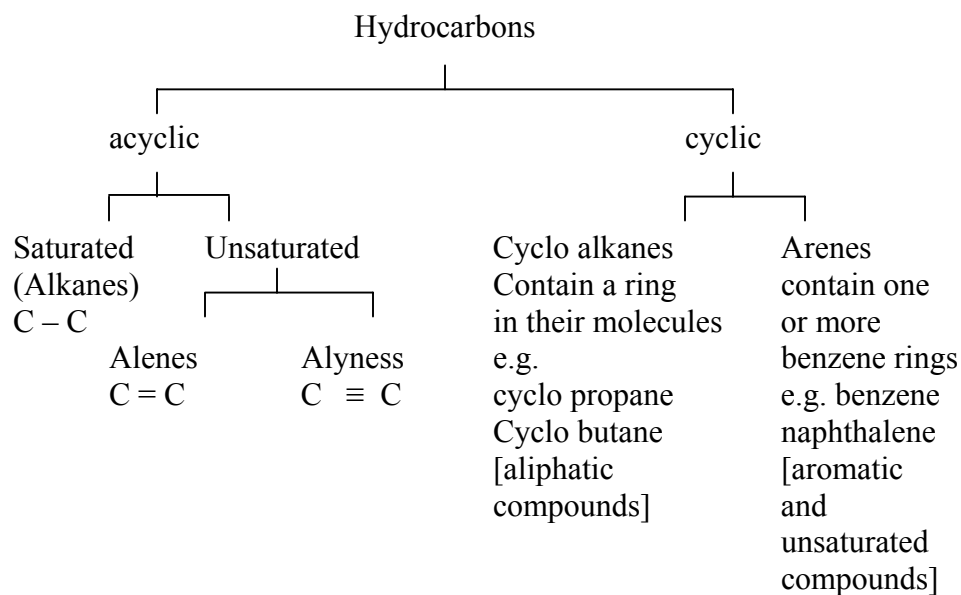
In short the main types of hydrocarbons present in crude oils are alkanes, cycloalkens, arenes and hybrids involving combination of these types. The classification of hydrocarbons is given in Fig –1 [*Organic Chemistry by Dr. J. N. Gurtu and Dr. H. C. Khera, 1<sup>st</sup> Edition 1987, p. 93*].

**Table -1 Range of typical properties of crude oil\***

Sr. No.	Property	Range in values
1	SP. Gravity at 15°C	0.788 to 0.886
2	Colour	Brown to brownish black/black
3	S (wt %) S (Vol %)	.13 to 1.9 .05 to .07
4	H <sub>2</sub> S (ppm)	Nil to 200
5	Pour point (°C)	-15 to 30
6	Flash point (°C)	<27 to 15
7	Kinematic viscosity At 37.8°C, (cSt)	2.02 to 5.9
8	Wax content (wt%)	6 to 12.5
9	Water content (vol%)	Nil to 1.5
10	Salt content (wt%)	1.5 to 35
11	Ash content (wt%)	.004 to .006
12	Consistency	Fluidity like that of petrol to like that of tar.

\* *Petroleum Refinery Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 16.*

**Fig -1 Classification of hydrocarbons**

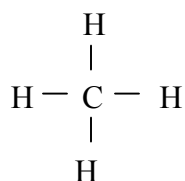


## Alkanes

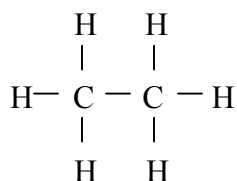
These are open-chain saturated hydrocarbons and contain only C – C single bonds in their molecules. They are also called paraffins (means less reactive). Alkanes are of two types:

- **Straight chain alkanes-normal:**  
C atoms are connected in a straight chain.
- **Branched chain alkanes-iso or neo:**  
C atoms are connected in a branched fashion. When methyl group is attached to carbon number 2 from either end and contain the group  $(\text{CH}_3)_2\text{CH}$ – is known as *iso-compound*. When 4 carbon atoms are attached to one carbon atom is known as *neo alkane* [*Organic Chemistry by Dr. J. N. Gurtu and Dr. H. C. Khera, 1<sup>st</sup> Edition 1987, p. 94*].

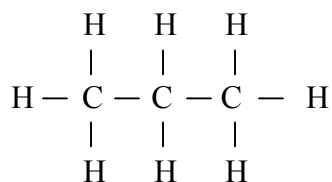
Alkanes have a general formula  $\text{C}_n \text{H}_{2n+2}$ , where  $n$  is the number of carbon atoms and  $n = 1, 2, 3, 4$ , etc. The 1<sup>st</sup> four alkanes have special names: methane, ethane, propane and butane [*Petroleum Refinery Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 17*].



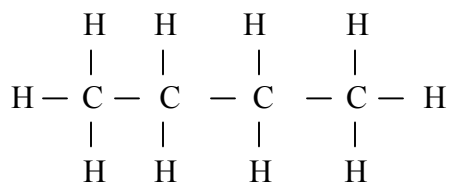
Methane  
 $\text{CH}_4$



Ethane  
 $\text{C}_2\text{H}_6$



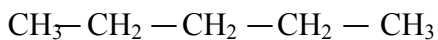
Propane  
 $\text{C}_3\text{H}_8$



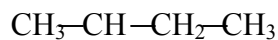
Butane  
 $\text{C}_4\text{H}_{10}$



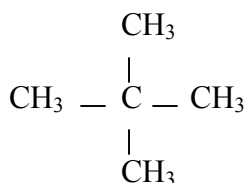
FROM pentane (C<sub>5</sub>H<sub>12</sub>) own words, Latin or Greek numerals are used to reveal the number of carbon atoms per molecule, e.g.



*n*-pentane

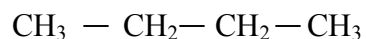


*Iso pentane*



*neo pentane*

From butane (C<sub>4</sub>H<sub>10</sub>) onwards, alkanes may exist in two or more forms (isomers) differing in structure. For example, butane may exist in two forms as follows:



*n*-butane

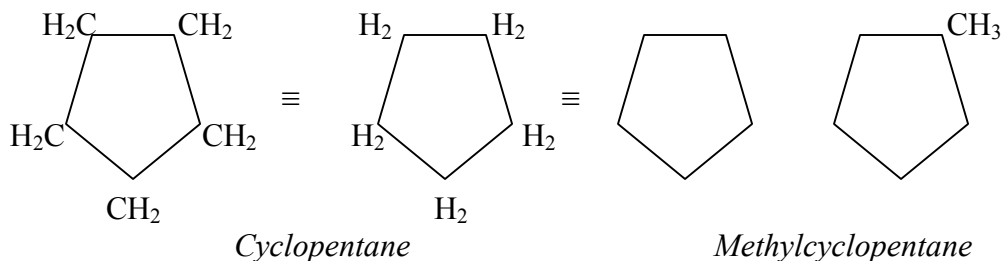


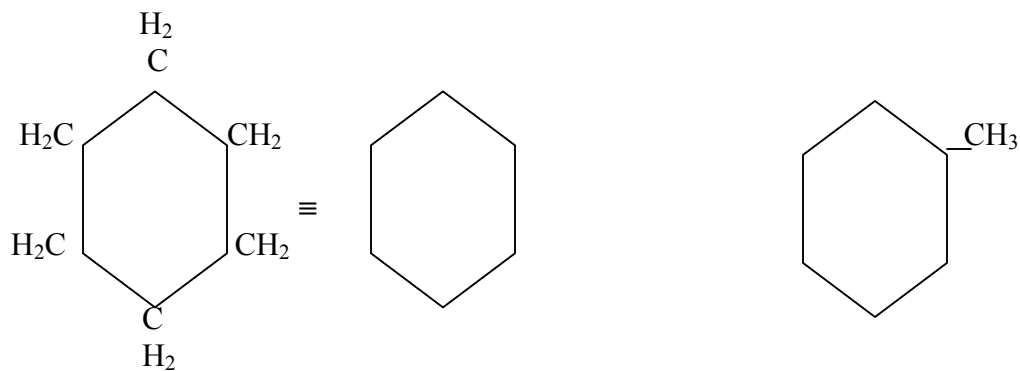
*iso butane*

### Cycloalkanes (cycloparaffins):

These are called naphthenes in petroleum industry. These are saturated hydrocarbons in which carbon atoms are joined by single covalent bonds to form a ring. The general formula of the cycloalkanes is C<sub>n</sub>H<sub>2n</sub>, where n is the number of carbon atoms.

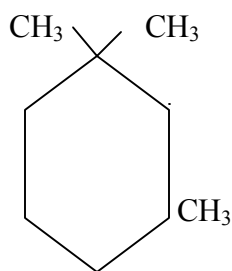
Cyclopentane and cyclohexane and their alkyl derivatives of low molecular weight (<C<sub>10</sub>) are important constituents of crude oils. It is uncommon in the crude oil to possess rings smaller than C<sub>5</sub> or large than C<sub>6</sub>. The structures of cycloalkanes are depicted below [*Petroleum Refinery Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 17*]:





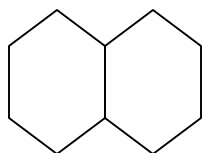
Cyclohexane

Methylcyclohexane

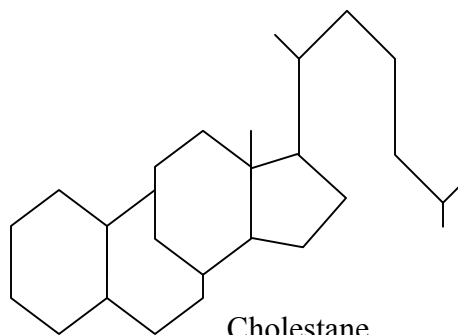


1,1,3- trimethylcyclohexane

The heavier fractions of crude oil contain the fused polycyclic type naphthenes, i.e. bicyclic  $C_{10}$  compounds (decalin,  $N = 2$ ,  $C_{10}H_{18}$ ) and tetracyclic  $C_{27}$  hydrocarbon (cholestane,  $N = 4$ ,  $C_{27}H_{48}$ ). Bicyclicnaphthenes are important constituents of the kerosene fraction. Tetracyclic and pentacyclic compounds appear in the lubricating oil fractions [*Petroleum Refinery Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 19*].



Decalin



Cholestane

## Arenes

These are called aromatic hydrocarbons in the petroleum industry. These are unsaturated cyclic compounds and hence very reactive chemically. The first compound in this series is the benzene ( $C_6H_6$ ).

In addition, alkyl derivatives of benzene, e.g. toluene, ethylbenzene, and ortho-, meta-, and para-xylenes, are present in crude oils. These mononuclear aromatics have a general formula  $C_nH_{2n-6}$ .

Crude oils also contain polynuclear aromatic hydrocarbon such as biphenyl, naphthalene, 2, 3, 6-methyl naphthalene, anthracene, phenanthrene etc. Many polycyclic aromatic hydrocarbons in petroleum are carcinogens.

## Alkenes

These are open chain unsaturated hydrocarbons containing C – C double bond. These contain the same carbon – hydrogen proportions as the monocyclic cycloalkanes. The first alkene,  $C_2H_4$ , is known as ethylene (or ethene:  $CH_2 = CH_2$ ). These are also called *olefins (means oil forming)*. Ethylene with chlorine forms an oily liquid, ethylene dichloride. This class has the general formula  $C_nH_{2n}$  [*Organic Chemistry by Dr. J. N. Gurtu and Dr. H. C. Khera, 1<sup>st</sup> Edition 1987, p. 121*].

## Alkynes

Alkynes are open chain hydrocarbon containing one carbon – carbon triple bond. The first member of this series is acetylene,  $C_2H_2$ , which appear in extended formula as the linear molecule:  $H - C \equiv C - H$ . Additional members of the alkyne series comprise open – chain molecule somewhat similar to the higher alkenes but with each double bond replace by a triple bond.

The boiling points and relative densities of the alkynes are slightly higher than those of the corresponding alkanes.

## Cycloalkanoarenes

These are also called naphthenoaromatics. These are mixed polycyclic hydrocarbons and possess structures involving fusion of aromatic with alicyclic rings, and may carry aliphatic side chain. These appear in the kerosine fraction [*Petroleum Refinery Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 21*].

## Natural Gas

Natural gas occurs as accumulations in underground, porous reservoirs, with or without petroleum oil. Natural gas is mainly composed of paraffin series of hydrocarbons from methane to pentane, carbon dioxide, nitrogen and sometimes helium. The most important products obtained from natural gas are fuel, natural gasoline, LPG, carbon black, helium, hydrogen, and petrochemicals [*Fuels and Petroleum Processing by B. K. Sharma, 1<sup>st</sup> Edition 1998, p. F – 118*].

### 1.4.2 Non-Hydrocarbons

In addition to hydrocarbons the crude oil contain small quantities of S, N and O. Some of these are associated with metals such as vanadium and nickel, i.e. they are organometallic in nature.

#### Sulphur compounds

S is the most abundant atomic constituent of crude oils. Crude oils vary considerably in their S content, ranging from a few hundredths by weight to as much as 8 – 13.95 % of S. Sulphur is present generally as alkylsulphides, hydrosulphides, hydrogen sulphide, thiophene and less frequently, as elemental sulphur

[1. *Petroleum Refinery Technology* by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 22].

[2. *Fuels and Petroleum Processing* by B. K. Sharma, 1<sup>st</sup> Edition 1998, p. F – 70].

#### Nitrogen compounds

Nitrogen occurs in crude oils to a lesser extent than sulphur, generally less than half of the sulphur content and frequently amounting to only about one-tenth. The N content is usually greater in heavier grades of crude oil. The N compounds may be divided into:

- i) **Basic nitrogen compounds** (Titratable with perchloric acid) are predominant in the lower boiling fraction of the crude oil, e.g. pyridine, quinoline, isoquinoline and acridine.
- ii) **Non-basic nitrogen compounds** are the most abundant and are found in the higher boiling fractions, e.g. pyrrole, indole and carbazole.

Additional N compounds such as anilines, phenazines and nitriles have also been found in petroleum fractions after catalytic cracking.

Among N compounds, porphyrins occupy a special place. They may be present in crude oil either in free state (four pyrrole rings) as complexes containing N compounds and organic derivatives of vanadium and nickel.

The N compound are relatively stable towards heat and do not decompose under refining condition.

#### Oxygen compounds

The total amount of combined oxygen is relatively low, varying from traces to a maximum of 2% by weight. The oxygen concentration increases from lighter fraction to heavier once; greater portion of oxygen containing constituents being concentrated in the residual oils, where values as high as 8% have been reported.

In the low-and medium- boiling range distillate fractions, O is mainly present in the form of carboxylic acids and to a limited extent, phenols. The carboxylic acids are very common organic acids characterized by the presence of the carboxylic group, i.e. – COOH, attached to carbons. A number of aliphathic monocarboxylic

acids, dicarboxylic acids, and alicyclic monocarboxylic acids have been found in crude oils.

The aliphatic acids range from formic acid to palmitic acid and include both the normal and isoalkyl chain structures. The dicarboxylic acids include dimethyl maleic acids and 1, 2, 2 – trimethylcyclopropane – 1, 3 – dicarboxylic acid. The alicyclic acids, otherwise referred to as naphthenic acids, that have been identified are mostly derivatives of cyclopentane, but cyclohexane structures also occur. Substituted phenols are also found in crude oils.

### **Metallic compounds**

A large number of metallic elements have been reported in a variety of crude oil. These include iron, vanadium, nickel, aluminium, sodium, calcium, copper, magnisum, manganese, barium, silicon, chromium, strontium, lead, molybdenum, cobalt, gold, silver, titanium.

The most abundant metal frequently found in crude oil is vanadium, its concentration going up by as much as 0.1% by weight, nickel and iron follow at comparatively concentrations. Other trace metals are encountered at still lower concentrations (<1ppb) and are present in the form of petroporphyrins and related complexes. They are undesirable in refining operation due to the fact that they produce undesirable reactions.

### **Asphaltenes and resins**

These are present in the asphaltic residuum, which remains after removal of distillable material from crude oil. Asphaltenes and resins contain in addition to carbon and hydrogen, some nitrogen, sulphur and oxygen. Some trace metals, such as nickel and vanadium are also present. About half of the total combined nitrogen and sulphur present in crude oils appears in the form of asphaltenes and resins. Most of these elements are present in the form of hetrocyclic groups. The probability of all molecular species present containing one or more heteroatoms (N, S or O) is high [*Petroleum Refinery Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 24 – 25*].

## 2. Processing of crude petroleum

### 2.1 Impurities in crude petroleum

Crude petroleum obtained from the oil wells consists of mainly hydrocarbons varying in boiling range from methane to asphalt along with gases, salt, water and mechanical impurities. The impurities in crude oils can be classified as:

- i) **Oleophobic:** These impurities are insoluble in crude oils and include:-
  - Salts-mainly chlorides and sulphates of sodium, calcium and magnesium
  - Sediments-silt, sand, drilling mud, iron oxide, iron sulphide, etc, and
  - Water-present as soluble, emulsified and / or finely dispersed water.
- ii) **Oleophilic:** These impurities are soluble in crude oils and include:-
  - Sulphur compounds
  - Organometallic compounds containing Ni, V, Fe, As, etc.
  - Naphthenic acids, and
  - Nitrogen compounds

These impurities have to be removed to avoid problems in subsequent processing operations. The removal of the oleophobic impurities in crude oils results in longer on-stream time, reduced maintenance, cost reduction and pollution abatement due to recycling of phenol bearing condensate water, and beside the removal of many harmful effects caused by these impurities [*Petroleum Refinery Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 177*].

### 2.2 Processing of petroleum

During the exploitation of petroleum deposit, the content of petroleum in crude product gradually decreases and that of water increases even up to 95 to 98%. Settled petroleum has even been found to contain great amount of salts, up to 6 g/lit. Due to reduction in pressure at the oil wells the dissolved gases evolve from the petroleum and are liberated. The gas liberated is known as *casing-head gas*, which is fed to the gasoline plants for further processing.

The crude petroleum obtained from the oil wells is usually a weak unstable emulsion of petroleum and water. The crude petroleum to be processed must contain not more than 2 mg/lit of salts and 0.2% of water. Hence deep purification is necessary at the oil well or at the nearest petroleum storage station Fig –2. Thus, all grades of petroleum must be demulsified in order to facilitate there processing in petroleum processing plants because presence of water in crude petroleum sharply impairs the productivity of plants and causes an excessive lose of power for evaporation and condensation of water. Salts and mechanically impurities present in it may cause erosion and clogging of pipes of furnaces and heat exchangers, lower the heat transfer coefficient, and increase the ash content in fuel oils and goudrons produced. In addition, dissolved salts in crude petroleum

cause the corrosion of the equipment by HCl, formed as a result of hydrolysis of some chlorides such as  $MgCl_2$ :-



### **Removal of water and destruction of petroleum emulsion**

Petroleum emulsions are hydrophilic (petroleum-in-water) and hydrophobic (water-in-petroleum). The stability of emulsions depends on the presence of *emulsifying agent* (substances soluble in one of the liquids which forms films on droplets and thus prevent these from coalescing). Emulsifying agents may also be hydrophilic or hydrophobic. Hydrophilic emulsifiers are readily soluble in water and insoluble in petroleum. These are sodium salts of naphthenic acids, sulphoacids etc. Hydrophobic emulsifying agents are soluble in petroleum but insoluble in water and include naphthenate, finely divided clay, metal oxides such as that of Ca, Mg, Fe, and Al, and tar asphaltene compounds etc.

Emulsions may be stable because water droplets and solid particles can store charges of static electricity. A hydrophilic emulsion is dissolved in water and settles to the bottom in gasoline, while an opposite effect has been observed in case of hydrophobic emulsion. Hydrophilic emulsion conduct electric current while hydrophobic emulsions are non-conductive.

Crude petroleum containing emulsions can not be processed directly and it is subject to demulsification, that is, emulsion is destroyed to separate petroleum from water and other impurities. Fresh emulsions are destructed more easily and hence demulsification should be performed as soon as possible. The removal of water from, and destruction of emulsions, in crude petroleum can be carried out by:-

- a) Mechanical methods
- b) Thermal methods
- c) Thermochemical methods
- d) Electrical methods

### **Dehydration and desalting**

Plants in which the process of dehydration and desalting is affected are known as electric dehydrators.

### **Distillation of crude petroleum**

Crude petroleum is a greenish red to black fluorescent emulsion with sandy oil and water as pumped out from wells. It also contains dissolved gases, liquids with low, medium and high boiling points and widely varying viscosities and solids as well as semi solids. The crude oil is pumped under pressure to cylindrical tanks through underground pipes. In these tanks the emulsion is allowed to settle as a result of which the emulsion is broken into two separate layers by heating which

also releases the dissolved gases with the crude oil. These gases are disposed off as wet natural gas. The oil separates as a top layer. While wet sand (sand + water) forms the lower layer. Both layers are separately withdrawn. Some gas is also separated during distillation. Electrostatic separation of oil and water has also been carried out by passing crude oil between electrically charged insulated plates.

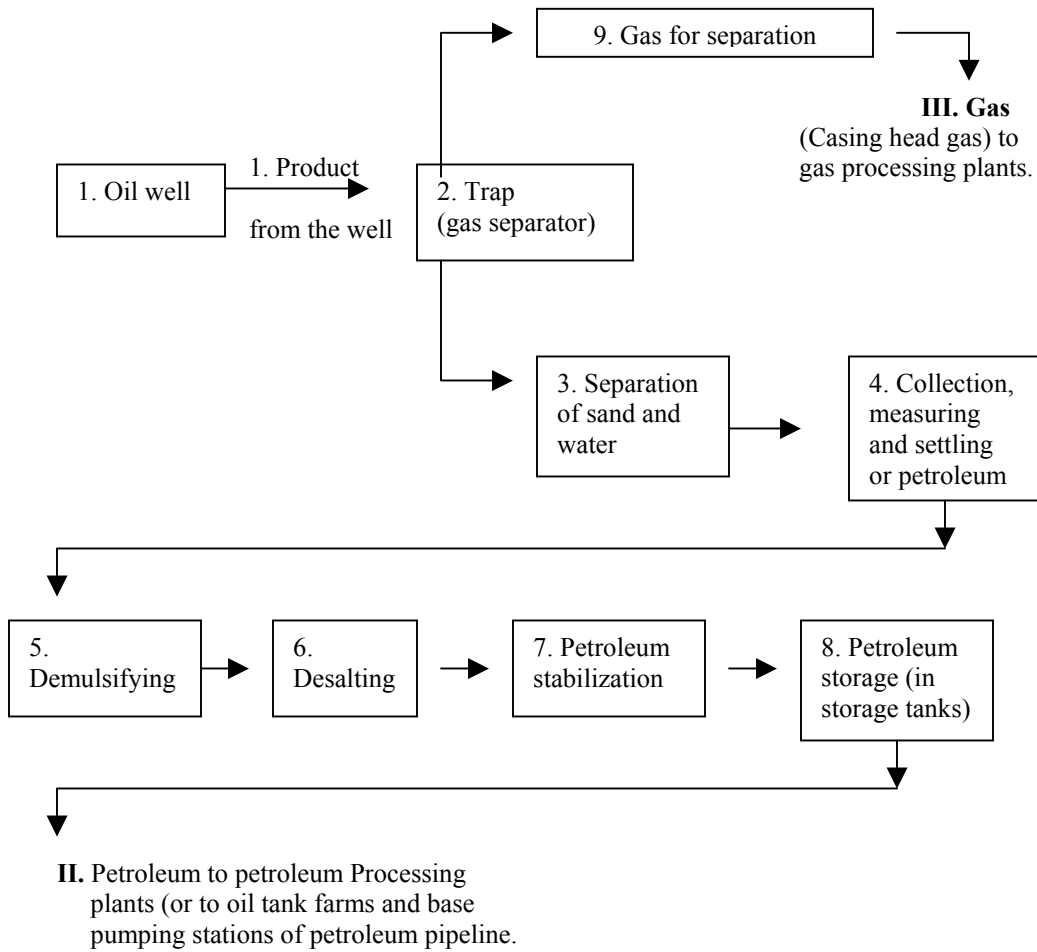
Excessive salt content of the crude oil is reduced by washing with water. Mineral salts are removed in a desalting process in which petroleum is repeatedly scrubbed with warm water to dissolve the salts. The emulsion so formed is separated from the petroleum during dehydration. Complete dehydration is only possible if the emulsion is destroyed by demulsifying agents such as sodium salts of naphthenic acids. Electrical dehydration is very effective method and consist in passing a film of petroleum at a high temperature between electrodes to which alternating current is fed at a voltage of 30,000 – 40,000 volts. As a result, emulsion is destroyed, water drops under go coagulation and then water is separated from petroleum by settling.

In most modern refineries the *pipe stills* are used to refine the petroleum by continuous distillation. The pipe stills are fitted with tubular furnace and tall fractionating column (a multiplate bubble cap tower). As a result of fractional distillation, a number of fractions viz., gas, gasoline/petrol, kerosene oil, gas oil and high boiling residue are obtained in a continuous process.

In fractionating column, high boiling fraction condense first and low boiling fractions last. The various products with their boiling ranges and uses are listed in table –2 [*Fuels and Petroleum Processing* by B. K. Sharma, 1<sup>st</sup> Edition 1998, p. F – 89 – 99].



**Fig -2: Principal diagram of petroleum and gas collection at oil wells\***



\* = *Fuels and Petroleum Processing by B. K. Sharma, 1<sup>st</sup> Edition 1998.*

**Table –2. Various products with their boiling ranges and uses\***

Fraction	Composition	Boiling range (°C)	Uses
Gas – Cymogene and Rhgolene		0 – 30	Liquid cymogene is used in the manufacture of ice. Rhigoline is used in medicine as local anaesthesia
Crude Naphta – on refractionation it further gives:	$C_5H_{12} - C_8H_{14}$	30 – 150	
a) Petroleum ether		30 – 70	As solvent in extraction of oils and fats and rubber industries for dry cleaning.
b) Gasoline or petrol	$C_6H_{14} - C_8H_{18}$	70 – 90	Motor fuel, dry cleaning etc.
c) Ligroin or light Petroelum	$C_6H_{14} - C_8H_{18}$	90 – 120	In dry cleaning, as a solvent
d) Benzene	$C_8H_{18} - C_{10}H_{22}$	120 – 160	In dry cleaning. In oil and paints industry as solvent.
Kerosene oil	$C_{10}H_{22} - C_{18}H_{38}$	150 – 300	As a fuel, as an illuminant and for making oil gas.
Gas oil or heavy oil	$C_{18}H_{38} - C_{42}H_{88}$	> 300	
Residue		> 400	As fuel in diesel engines, cracked to get more gasoline.
Further fractionated under reduced pressure to yield:			
a) Paraffin wax	$C_{20} - C_{30}$	On cooling	
b) Lubricating oil	$C_{16} - C_{22}$		For manufacture of candles and shoe polishes.
c) Vaseline			For lubrications
d) Pitch			In toilet goods and ointments.
e) Petroleum coke (on redistillation of tar)			In paints and varnish. As fuel.

\* = Fuels and Petroleum Processing by B. K. Sharma 1<sup>st</sup> Edition 1998, p. F – 99.

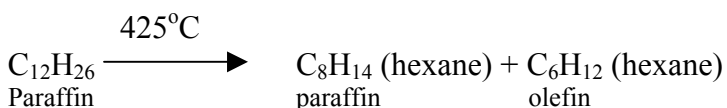
The high boiling residue is generally further fractionated under low pressure into lubricating oil, paraffin wax etc. More gasoline may also be recovered by subjecting the residue to catalytic cracking.

### Cracking

Cracking is the splitting of molecules of the initial material into smaller ones. Cracking not only causes decomposition, but also accompanied by secondary processes of synthesis of large molecules. The bonds between atoms and molecules of hydrocarbons are weakened at high temperatures and so they can break to form new compounds. The lighter is low boiling hydrocarbons split less readily than high boiling hydrocarbons. In addition to splitting into lighter hydrocarbons, other transformation can also take place, particularly the packing of molecules in which large molecules are formed. Under thermal processes heavier fractions are decomposed at elevated temperatures from preliminary petroleum processing. **The chemistry and mechanism of cracking of principal classes of hydrocarbons is given below:-**

#### a) Paraffin Hydrocarbons

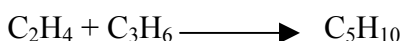
The breakdown of C – C bonds in cracking of commercial paraffin (C<sub>24</sub>H<sub>50</sub>, C<sub>25</sub>H<sub>52</sub> and C<sub>26</sub>H<sub>54</sub> hydrocarbons) of high molecular mass forms paraffin hydrocarbons and olefins, and it takes place in the middle of the molecule. The new paraffin hydrocarbon formed by cracking can then be broken down into simpler molecules, e.g.



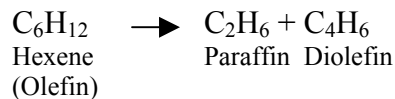
Olefin is the larger fragment of a broken molecule and gaseous paraffinic hydrocarbon or hydrogen is the smaller one. The rate of the reaction at a given temperature increases almost linearly with the molecular mass and this is true in the case of all groups of hydrocarbons.

#### b) Olefinic Hydrocarbons

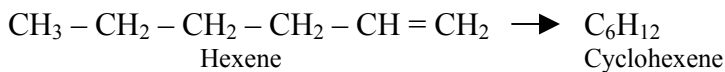
These hydrocarbons are the principal hydrocarbons among all unsaturated hydrocarbons formed by cracking. They prevail as gaseous compounds (from ethylene, C<sub>2</sub>H<sub>4</sub> to butylenes, C<sub>4</sub>H<sub>8</sub>) and liquid hydrocarbons (from amylenes, C<sub>5</sub>H<sub>10</sub> to penta decenes, C<sub>15</sub>H<sub>30</sub>). Olefins undergo appreciable more diverse primary reactions during cracking and the most important among them are the polymerization reactions and depolymerization reactions, especially at an early stage of the process. Polymerization is the principal reaction at moderately high as well as high pressure and can occur not only between like molecules but also between unlike molecules of olefins.



Olefins are dehydrated partially into diolefins at later stages of the process. The diolefins have two double bonds, and hydrogen. The olefins may also split into diolefins and paraffinic hydrocarbons.

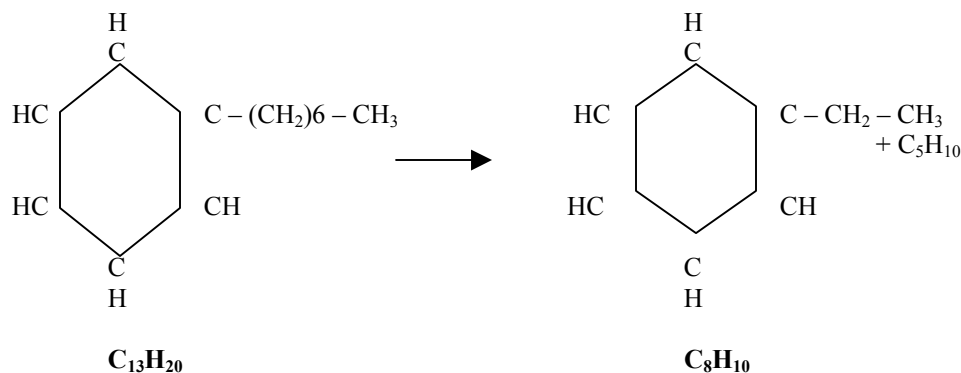


Secondary reactions may take place between olefins and diolefins forming cyclo-olefins, which are present in cracking products in very small quantities. Olefins may be converted into cyclic hydrocarbons, known as naphthenes



### c) Naphthenic Hydrocarbons

Dealkylation (splitting of paraffinic side chains) and the dehydrogenation of hexacyclic naphthenic hydrocarbons into benzene hydrocarbons are the main and principal reactions in cracking of these hydrocarbons and both of this reaction may occur simultaneously.



Naphthenic and benzene hydrocarbon lose most of their long side chains. The paraffinic side chains break to form gaseous and low boiling paraffinic hydrocarbons and olefins. Even naphthenic rings can break in high temperature processes. Thus hydrocarbons lose their cyclic structure and polycyclic structures and are partially decycled if they have many rings and in that case paraffinic, olefinic and naphthenic hydrocarbons are formed.

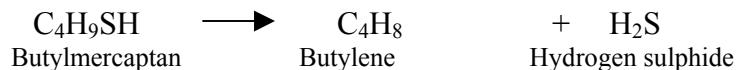
### d) Benzene Hydrocarbons

The cyclo-olefins or naphthenes formed at earlier stages of the cracking are dehydrogenated to form benzene hydrocarbons, which are quite stable at high

temperatures (especially benzene, toluene and xylenes). The principal reactions in cracking of benzene hydrocarbons with alkyl chains are dealkylation and condensation. Condensation may take place between the molecules of benzene hydrocarbons or between benzene and olefin hydrocarbons or some other unsaturated hydrocarbons. This provides polycyclic benzene hydrocarbons which condense further to asphaltenes and coke.

#### e) Sulphur Compounds

These compounds are decomposed during cracking and H<sub>2</sub>S gas is liberated.



Cyclic sulphur compound, such as thiophane and thiophene, are very stable against the composition. H<sub>2</sub>S and S which can be formed in cracking of sulphurous and high sulphurous petroleum grades cause serious corrosion of the process equipment.

#### f) Inert Tars and Asphaltenes

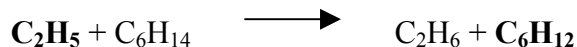
These include various heterocyclic compound (usually including oxygen, sulphur, nitrogen and some metals). In thermal cracking they form gases, liquid products and a large amount of coke. The yield of coke in cracking of asphaltenes may even go up to 60% and that in cracking of tars to 7 – 20%, depending on the molecular mass of tars.

Because the starting materials for industrial thermal cracking are usually mixture of many hydrocarbons of different and complicated structures, many reactions may take place simultaneously, as a result of which it is very difficult to explain the actual mechanism of thermal cracking. It has, however, been assumed that most reactions of thermal cracking can be described by the formation of free radicals.

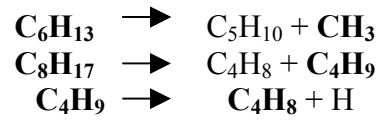
Under the conditions of thermal cracking, some compounds contained in the starting materials decompose to yield free radicals.



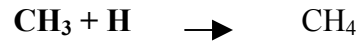
Free radicals are short lived but very reactive. So they can react with molecules of other hydrocarbons, decomposed to olefins and lower radicals, recombine with other free radicals, react with substances which deactivate the catalyst, and react with metals. Hydrogen, methyl and ethyl radicals are more stable than larger radicals such as propyl, butyl free radicals. They react with other hydrocarbons, detach hydrogen atoms and give rise to the formation of new radicals.



The larger radicals are unstable and decompose into olefins and lower free radicals.



A chain reaction of free radicals comes to its end when two free radicals undergo recombination, e.g.,



or on interaction of a radical with metal.

[*Fuels and Petroleum Processing* by B. K. Sharma, 1<sup>st</sup> Edition 1998, p. F – 154 – 156].

### 3. Petroleum Products

The products obtained from petroleum can conveniently be divided into four groups. These are:-

#### **(Group I) Fuels:**

This group includes liquefied hydrocarbon gases, fuels for carburetor engines (gasolines), fuels for jet (kerosene) and for turbojet engines, diesel fuels, boiler fuels etc.

Liquefied hydrocarbon gases mainly consist of propane and butane along with small quantities of propylene and butylenes.

#### **(Group II) Lubricating oils:**

This group includes various lubricating oils, paraffins, ceresins and petroleum.

#### **(Group III) Miscellaneous petroleum products**

This group includes plastic greases, bitumens, coke etc.

#### **(Group IV) Chemical and petrochemical products**

This group includes hydrocarbons of various classes which serve as starting products for organic and petrochemical synthesis [*Fuels and Petroleum Processing by B. K. Sharma, 1<sup>st</sup> Edition 1998, p. F – 120*].

#### **Natural gas and petrochemical**

Besides the above mentioned four groups **Natural gas** occurs as accumulation in underground, porous reservoirs, with or without petroleum oil. Natural gas is a mixture of lower hydrocarbons such as alkanes and alkenes and large amounts of hydrocarbons are obtained as by-products during cracking of heavy oil in petroleum refineries. These hydrocarbons are excellent **raw materials** for the manufacture of a large number of chemical compounds, called **petrochemicals**. Petrochemicals are those chemicals which are derived from petroleum, including natural gas. The petrochemical now form the basic raw materials in the manufacture of a large number of other materials, such as fertilizers (ammonia), plastics, fibers, rubbers (nylon, polyester, acetate etc) and paints. They have also been used in the manufacture of pesticides, lubricants, adhesives and solvents. Many important processes, such as production of ammonia, acetone, ethyl alcohol, acetic acid, acetic anhydride, glycerine and other are now based wholly or significantly upon petrochemical.

Some of the petrochemicals obtained from saturated and unsaturated hydrocarbons (obtained from petroleum) are given in table –3.

**Table –3. Petrochemical obtained from saturated and unsaturated hydrocarbons\***

<b>Hydrocarbons</b>	<b>Petrochemicals</b>
<b>Methane (CH<sub>4</sub>)</b>	Formaldehyde, formic acid, acetylene, ethylene-glycol, dimethyl ether, methyl amine, hexamethyl-tetramine, dichloro monofluoro methane, dichloro difluoro methane, mono, di-, tri- and tetra chloro methane etc.
<b>Ethylene (C<sub>2</sub>H<sub>4</sub>)</b>	Ethanol, ethylene oxide, ethylene glycol, ethylene chlorohydrin, vinyl chloride, acetic acid, acetaldehyde diethyl ether, ethyl acetate, ethyl chloride, tetra-ethyl lead, butyric acid, PVC and polyethene plastic etc.
<b>Ethane (C<sub>2</sub>H<sub>6</sub>)</b>	Ethyl chloride, ethylene, acetic acid, acetic anhydride, diethyl ether, ethyl acetate, acetaldehyde etc.
<b>Propane (C<sub>3</sub>H<sub>8</sub>)</b>	Propyne, ethylene, nitroethane, nitromethane, nitropropane, propionic acid, isopropylether, acetone, acetone cyanohydrin etc.
<b>Propene (C<sub>3</sub>H<sub>6</sub>)</b>	Allyl chloride, glycerol, allyl alcohol, isopropyl alcohol, acetone, propylene glycol, diacetone alcohol, propionic acid, acrolein, cumene, n-propyl alcohol, isopropyl ether etc.
<b>Butanes (C<sub>4</sub>H<sub>10</sub>)</b>	Butylenes, thiophene, butadiene etc.
<b>Butenes (C<sub>4</sub>H<sub>8</sub>)</b>	Butanol, tert, butyl alcohol, butyl rubber, iso-octane, ethyl butyl ketone, methyl ethyl ketone etc.
<b>Pentane (C<sub>5</sub>H<sub>12</sub>)</b>	Amyl chloride, amyl alcohol, amyl phenols etc.
<b>n-Hexane</b>	DDT, benzene, phenol, gammaxene, styrene, polystyrene, plastics etc.
<b>n-Heptane</b>	Toluene, benzaaldehyde, benzoic acid, TNT, benzyl chloride benzal chloride, benzo trichloride, terephthalic acid etc.
<b>Acetylene (C<sub>2</sub>H<sub>2</sub>)</b>	Vinyl acetylene, acetaldehyde, acetic acid, vinyl chloride, trichloro ethane, ethylene chloride, vinyl acetate, butadiene, acrylic fibres etc.
<b>Cyclo alkanes</b>	Toluene, sylene, benzene, adipic acid, hexamethylene diamine etc.

\* *Fuels and Petroleum Processing by B. K. Sharma, first Edition 1998, p. F – 282.*



## 4. Environmental Pollution in relation to Petroleum Industry

Air, water and soil are vital to life on this planet. Man, the custodian of all biodiversity and natural resources, has always indulged in trespassing the natural ecosystems under the guise of the so-called progress and prosperity. Profound scientific and innovative advancements and mushroom growth of industries have led to polluting the vast panorama of Nature. The industrial pollution has miserably affected the ecosystem of our Planet. The existence of the life is threatened. The wastes, effluents, smoke and heat emanating from the factories have polluted our land, air, water, wildlife, agriculture, forests and food resources.

### 4.1 Air pollution

In simple words air pollution means the contamination of the atmosphere with the airborne undesirable solids, liquids and gases. Major air pollutants that may be emitted from **refining operations** are sulphur compounds, hydrocarbons, nitrogen oxides, particulates including smoke and carbon mono-oxide. Other emissions are aldehydes, ammonia and odours. The gaseous emissions from petroleum refineries are summarized in table –4.

**Table –4. Emission\* from petroleum refineries per daily capacity of 17,000 m<sup>3</sup>**

Sr. No	Pollutants	Emission (ton/day)
1.	Carbon monoxide	13
2.	Hydrocarbons	7
3.	Aldehydes, organic acids	1
4.	Sulphur dioxide	5
5.	Nitrogen oxides	4

\* *Petroleum Refining Technology by Dr. Ram. Prasad  
1<sup>st</sup> Edition March 2000, p. 341.*

## 4.2 Water pollution

Water is used in petroleum refineries for a variety of purposes. Since water does not enter into the final product, it can be expected that 80–90 % of the water supplied to the refinery comes out as wastewater. The characteristics of wastewater from petroleum refineries and their accompanied pollutants are indicated in table –5.

**Table –5 Characteristics of wastewater and pollutants from petroleum refineries\***

Sr. No	Effluent characteristics	Value	Pollutants
1.	Flow (l/kg oil)	1.5	1- Free oil (2000 – 3000 mg/l) 2- Emulsified oil (80 – 120 mg/l) 3- H <sub>2</sub> S & RSH (10 – 220) 4- Phenols (12 – 30 mg/l) 5- Ammonia & Chromium if cooling water is also mixed with process water
2.	pH	6.8 – 7.2	
3.	Suspended solids (mg/l)	200 – 400	
4.	BOD (mg/l)	100 – 300	
5.	COD (mg/l)	-	
6.	BOD / COD	-	
7.	BOD load (g/unit product)	0.3	

\* *Petroleum Refining Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 347.*

Various types of water pollution encountered from industrial wastes can be classified as under:

### 1. Physical pollution

This is due to temperature, turbidity, suspended matter, color, foam & froth and radioactivity.

### 2. Chemical pollution

This can be due to inorganic and organic chemicals. Inorganic chemicals include acids, alkalies, heavy metals, soluble salts or inert insoluble substances. Acids & alkalies and salts of metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn etc are highly toxic to all aquatic organisms. Organic chemicals can be of either biodegradable or non-biodegradable type. Mineral oil and petrochemical are non-biodegradable.

### 3. Physiological pollution

Taste and odour constitute physiological pollution. Salts of iron and manganese, chlorine, hydrogen sulphide, phenols impart characteristic and unpleasant taste to water. Organic sulphides (mercaptans) give rise to odour problems. The presence of small amounts of sulphides gives rise to H<sub>2</sub>S at low pH.

#### **4. Biological pollution**

Biological pollution is the result of discharge of wastewater containing pathogenic forms of bacteria, fungi, algae, viruses, protozoa and helminthic parasites. The diseases related to biological pollution are cholera, typhoid, dysentery, gastro-enteritis, polio-myelitis and infectious hepatitis.

#### **4.3 Control of Water Pollution in Petroleum Refineries**

The uses of water in a refinery can be categorized as drinking, cooling, boiler feed, direct processing, sanitary and fire protection. The effluent water originated can be classified as under:

##### **a) Water free from oil**

It includes storm water from oil free catchments areas, water treatment plant effluent, boiler blowdown etc.

##### **b) Sanitary sewage**

It includes waste water coming from administrative buildings, canteens, toilets etc.

##### **c) Process effluents**

These are basically oily waters originating from different sources such as drainage from product storage tanks and loading facilities, storm water from oily areas, water from pump houses, blowdown from cooling systems, desalter water, overhead condensate water from process units, spent caustic etc.

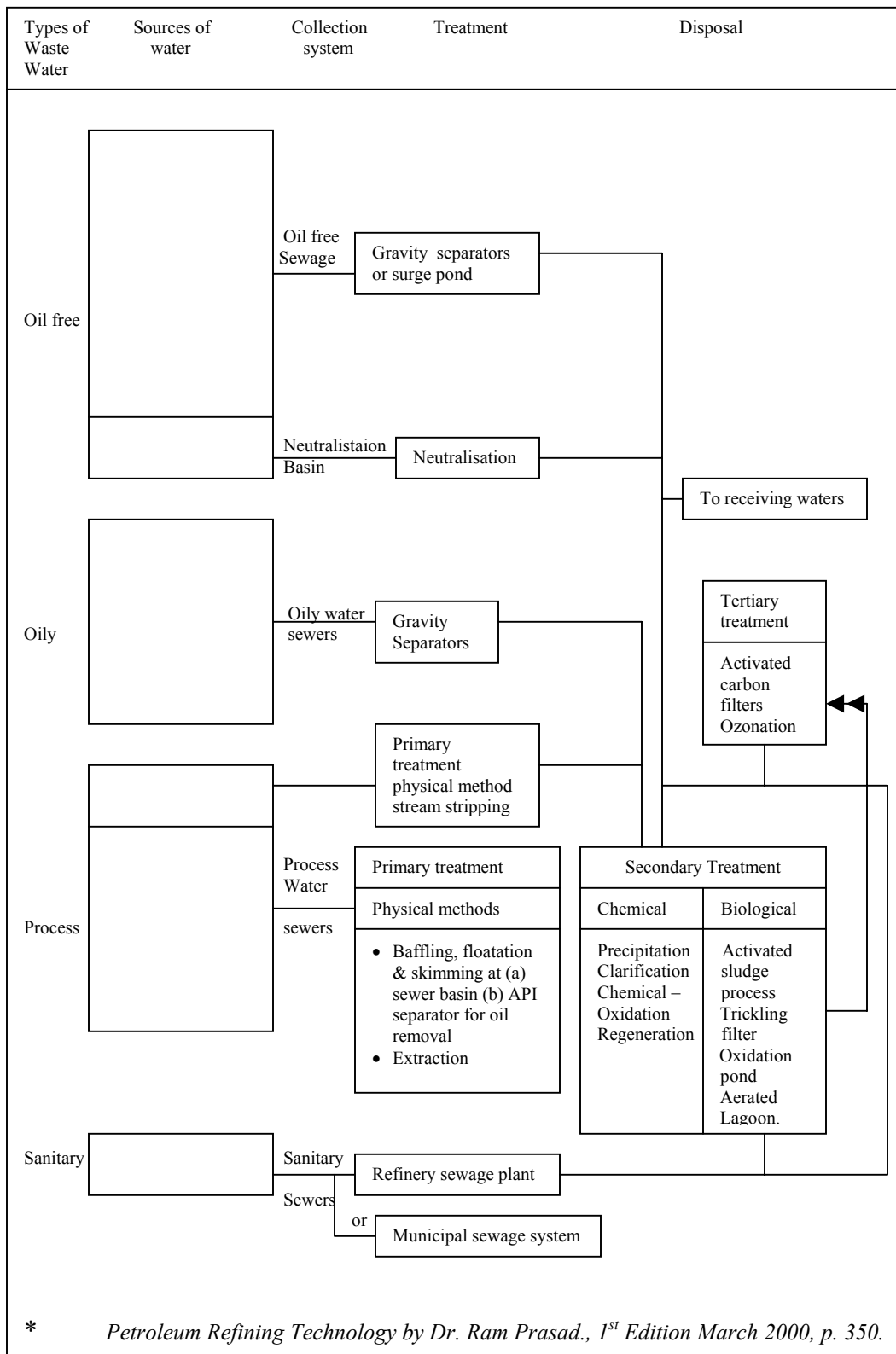
#### **Contaminants**

The major contaminant is oil. The other contaminants are sulphides, phenols, nitrogen compounds, sludge etc. Drainage water from product tanks, storm water from oily areas, cooling water blowdown are contaminated only by oil. Overhead condensates from process units contain oil, sulphides, phenol, ammonia. Desalter water and drainage from crude oil tanks contain salts, sulphides, phenols etc.

#### **Treatment of effluent**

For effective treatment of the effluent water, the streams are segregated through separate drainage systems and treated accordingly. The effluent treatment is usually divided into three categories, i.e. primary, secondary and tertiary (table-6).

**Table –6 General plan for Treatment, Disposal of Effluents of Petroleum Refineries\***



### **Primary treatment methods**

This treatment consist of oil removal in two stages physical methods (baffling, floatation, skimming, stripping and extraction).

The first stage of oil removal is done in small pond or basin where major portion of the oil is removed by using baffling, floatation and skimming methods. The second stage of oil removal is mainly by API (American Petroleum Institute) separators or other gravity separators, where the remaining oil is removed through aforementioned methods.

**Stripping** is another physical method. Stripping with the aid of steam is done to remove gases like hydrogen sulphide, mercaptans and ammonia and for some extent phenol.

**Extraction** is another physical method which is used to remove phenolic compounds which solvents like tricresyl phosphate and mixed organic esters in refinery operation.

### **Secondary treatment methods**

These are further classified into:

- **Chemical method** is used to remove emulsified oil with edition of flocculating agents and suspended solids and toxic substances by sedimentation and filtration using neutralization, precipitation & clarification, chemical oxidation and regeneration methods.
- **Biological method** aims at the removal of all oxidizable and organic matter from the wastewater by employing the use of activated sludge process, trickling filters, oxidation ponds and aerated lagoons.

### **Tertiary treatment methods**

It is limited to activated carbon filtration process and ozonation, which are effective in removal of the taste and odour and organics from biologically treated with wastewaters.

## **4.4 Standards for Discharge of Effluent Water**

Many countries have formulated policies and programs which ensure environmental protection without hampering fast economic growth. Environmental protection agency (EPA), USA, Occupational Safety and Health Administration (OSHA), USA, Environmental Agency, Japan, World Health Organization, etc are actively engaged in framing laws, regulations and suitable recommendation to prevent and control the pollution and finally in implementation of the recommendations in their respective countries. The tolerance limits as given in the relevant standards for the discharge of effluents to various receiving streams are given in table –7. The relevant standards are:

**IS: 2490 (part I) – 1974:** Prescribes the general limits for effluents discharged into inland surface waters.

**IS: 3307 – 1977:** It takes into account the fact that land can take more pollutant load than water streams. The limits of various parameters have been fixed so as not to impair the susceptibility of the land for irrigation purposes.

**IS: 4764 – 1973:** The stringent limits on TSS (30mg/l) and BOD (20mg/l) of sewage effluents discharged into inland waters have been given.

**IS: 3306 – 1974:** The limits have been given for small industries which can not put up their own treatment plants.

**IS: 2296 – 1974:** It prescribes the tolerance limits for inland surface waters subject to pollution which are used for the purposes of raw water for public water supply, bathing ghats, fish culture, and irrigation.

**IS: 7968 – 1976:** It lays down the tolerance limits for industrial effluents discharged into marine coastal areas. This standard is less stringent than IS: 2490 as marine areas can tolerate more pollutant load than in land waters.

**Table – 7. Standards for Liquid Effluents and Inland Surface Waters\***

Sr. No.	Effluent characteristics	Tolerance Limits					
		For inland surface waters subject to pollution		For effluents discharged on land for irrigation (IS: 2296–1974)	For effluents discharged into public sewers (IS : 3306 – 1974)	For effluent discharged into inland surface waters	For effluents discharged into marine coastal areas (IS : 7968 – 1976)
		For public water supply & for bathing ghats (IS : 2296 – 1974)	For irrigation (IS : 2296 – 1974)				
1.	2	3	4	5	6	7	8
1.	TSS, mg/l, Max.	-	-	-	600	100	100
2.	Particle size of TSS, micron, Max.	-	-	-	-	850	3000 (floatable solids) 850 (settleable solids)
3.	TDS, mg/l Max,	-	2100	2100	2100	-	-
4.	Temperature, °C, Max.	-	-	-	45	40	45
5.	pH	6.0 – 9.0	5.5– 9.0	5.5 – 9.0	55 – 9.0	5.5 – 9.0	5.5 – 9.0
6.	BOD, mg/l, Max.	3.0	-	500	500	30	100
7.	COD, mg/l, Max.	-	-	-	-	250	250
8.	Dissolved oxygen, mg/l, Min.	3.0	-	-	-	-	-
9.	Oils and grease, mg/l, Max.	0.1	-	10	100	10	20
10.	Ammoniacal nitrogen (as N), mg/l, Max.	-	-	-	50	50	50
11.	Free ammonia (as NH <sub>3</sub> ), mg/l, Max.	-	-	-	-	-	-
12.	Nitrates (as NO <sub>3</sub> ), mg/l, Max.	50	-	-	-	-	-
13.	Sulphates (as SO <sub>4</sub> ), mg/l, Max.	-	1000	1000	1000	-	-
14.	Phosphates (as P). mg/l, Max.	-	-	-	-	15	-
15.	Sulphides ( as S), mg/l, Max.	-	-	-	-	2.0	5

Continued

1	2	3	4	5	6	7	8
16	Fluorides (as F), mg/l, Max.	1.5	-	-	-	2.0	15
17	Chlorides (as Cl), mg/l, Max.	600	600	600	600	-	-
18.	Cyanides (as CN), mg/l, Max.	0.01	-	-	2	0.2	0.2
19.	Lead (as Pb), mg/l, Max.	0.1	-	-	1	0.1	1.0
20.	Selenium (as Se), mg/l, Max.	0.05	-	-	-	0.05	0.05
21.	Zinc (as Zn), mg/l, Max.	-	-	-	1.5	5	5.0
22.	Copper (as Cu), mg/l, Max.	-	-	-	3	3.0	3.0
23.	Nickel (as Ni), mg/l, Max.	-	-	-	2	3.0	5.0
24.	Cadmium (as Cd),	-	-	-	-	2.0	2.0
25.	Hexavalent chromium (as Cr <sup>6+</sup> ), mg/l, Max.	0.05	-	-	2	0.1	1.0
26.	Mercury (as Hg), mg/l, Max.	-	-	-	-	0.01	0.01
27.	Arsenic (as As),	0.2	-	-	-	0.2	0.2
28.	Sodium (as Na), percent, Max.	-	60	60	60	-	-
29.	Phenolic compounds (as C <sub>6</sub> H <sub>5</sub> OH),	0.005	-	-	5	1.0	
30.	Residual chlorine (as Cl), mg/l, Max.	-	-	-	-	1	1

\* *Petroleum Refining Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition. March 2000, p. 355.*



#### **4.5 Petroleum Sludge**

Sludge is the suspension of solids in process waters and aqueous wastes. Sludge produced in petroleum refineries include the following:

- i) Crude tank bottoms
- ii) Slop oil emulsion sludge
- iii) Cooling tower sludge
- iv) Lube oil filter cake
- v) Heat exchanger bundle cleaning sludge
- vi) FCC catalyst fines.

Sludge formed in primary & secondary treatments of wastewater include:

- a) API separator sludge
- b) Dissolved air floatation sludge
- c) Waste bio-sludge

For environmentally sound disposal, the sludge is to be treated. The oil content in the refinery sludge is high and it needs to be separated. Various hazardous constituents are needed to be removed, e.g. polychlorinated biphenyls (PCB).

##### **4.5.1 Sludge characteristics**

Sludge must be characterized for pathogenicity, toxicity and various rheological properties. Sludge need to be tested for pathogenicity. The pathogens (disease producing) organisms of most concern are some bacteria (particularly salmonella, califorms and other non-enteric species), protozoans and parasites, such as Taenia saginata (beef tapeworm), potato cyst nematodes and Ascaris (roundworm).

Sludge need to be tested for toxicity. A range of tests are available for specific toxicological effects, such as genotoxicity (such as reverse mutation assay and cytotoxicity), oral toxicity (*via* ingestion and inhalation), and dermal and ocular toxicities.

Hazardous characteristics that need to be considered include such characteristics as corrosivity, irritancy, flammability and explosivity.

##### **4.5.2 Sludge conditioning**

Sludge conditioning may be used to increase solids concentration, improve recovery or reduce thickening time. This can be achieved by chemical edition or thermal treatment.

The chemical conditioning involves the use of either inorganic or organic chemicals. The most commonly used inorganic chemicals for conditioning sludge include lime, ferrous and ferric sulphates, ferric chloride and alum. Organic polyelectrolytes (commonly termed polymer) have been used in sludge conditioning. This fall into three classes: non-ionic, anionic and cationic.

Thermal conditioning is to improve the dewaterability. The advantages of this process include reduced solids quantity, low or very low specific filtration resistance, sterilization and enhanced activated sludge digestion.

Lime stabilization is done to raise the pH to 12 or higher with the addition of lime. The alkaline conditions reduce microorganisms and control odors.

#### **4.5.3 Sludge Thickening**

The thickening of sludge removes excess water to reduce the volume of the sludge. The principal thickening methods are:

- Gravity thickening
- Centrifugal thickening
- Floatation thickening
- Gravity belt thickening

#### **4.5.4 Dewatering of sludge**

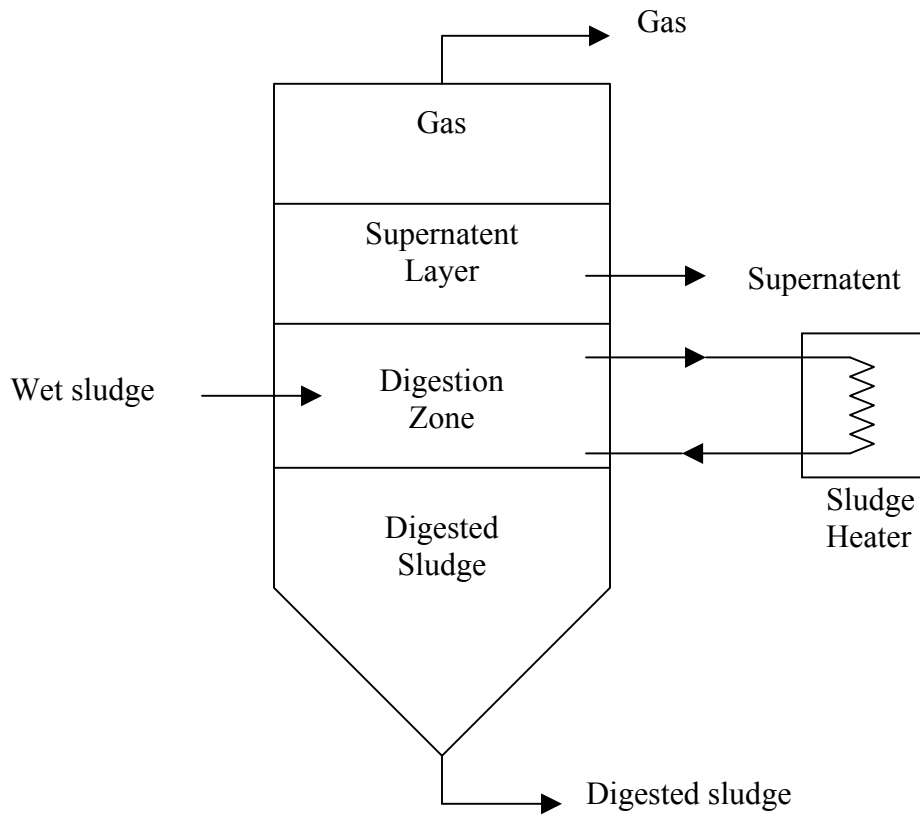
The thickened sludge is dewatered for efficient handling. This is achieved by centrifugation and filtration. The process of dewatering overlaps to some extent with sludge thickening. The selection of dewatering equipments depends on requirements for subsequent treatment or disposal or both.

Two non-mechanical systems use for the watering sludge are sludge drying beds and drying lagoons.

Dewatering of sludge is also done by evaporating water from sludge by thermal means. Usually the moisture contents of the dried sludge is < 10 %. Sludge drying occurs at a temperature of about 370°C, whereas incineration requires a temperature of up to 760°C.

After concentration sludge is digested usually under anaerobic conditions. Organic compounds produce methane and carbon-dioxide. Bound water is released from the sludge (Fig – 3).

**Fig – 3. Sludge digestion under anaerobic conditions\***



\* [*Petroleum Refinery Technology by Dr. Ram Prasad, 1<sup>st</sup> Edition March 2000, p. 364*].

#### 4.5.5 Sludge Disposal

Once the oil and hazardous organic and inorganic material are removed from the concentrated sludge, it is disposed of with incineration method or directly on land.

**Incineration** it is the combustion of a material in the presence of at least a stoichiometric quantity of air. It requires a temperature of up to 760°C. The principal products of incineration are CO<sub>2</sub>, water and ash. Incineration offers the benefits of reducing waste volume, completely eliminating harmful bacterial and viral constituents, destroying toxic organic compounds and it facilitates waste heat recovery. Several types of incinerators are:

- Multiple hearth furnace
- Fluidized bed incinerator
- Liquid waste incinerator
- Direct flame incinerator
- Rotary kiln
- Wet air oxidation

**Direct Disposal:** In developing countries almost more than 50% of the sludge is directly disposed of on agricultural systems, including forestes and land reclamation projects, making it the biggest and most important outlet. The presence of high concentration of **heavy metals** in some sludge limit the amount of sludge that can be applied to any section of land.

#### **Land farming with organic wastes:**

Land farming of organic wastes combines biological, chemical, physiological processes to breakdown the wastes into CO<sub>2</sub>, water and vary small percentage of solids with the help of microflora (bacteria, yeast) in the soil. Organic wastes are spread on the landfarm surface directly and filled into the top 6 to 12 inches of soil. Microorganisms in the presence of oxygen metabolize the waste. Non-degradables are bound to soil particles and migration is prevented. Land farms must be porous to prevent saturation of solids. When soil is saturated no waste is applied. For effective land farming, proper soil moisture content, pH, nutrient level, and aeration must be present. The advantages of land farming include the following:

- a) It costs less
- b) It can handle wastes over long period of time
- c) It is an environmentally safe method
- d) It can handle the sludge from API separator, slop oil sludge, tank bottom sludge, cooling water sludge, biological sludge.

## **5. EM Technology, Petroleum Sludge Bioremediation for Safe Disposal and Use of Bio fertilizer in Agriculture**

### **5.1 EM Technology**

EM stands for Effective Microorganisms. EM is a combination of various beneficial, naturally occurring microorganisms mostly used for or found in foods. It contains beneficial organisms from three main genera: phototrophic bacteria, lactic acid bacteria and yeast. These effective microorganisms secrete beneficial substances such as vitamins, organic acids, chelated minerals and antioxidants when in contact with organic matter. At first, EM was considered an alternative for agricultural chemicals, but its use has now spread to applications in environmental, industrial, and health fields. However, it must be stressed that EM is neither a synthetic chemical nor a medicine.

EM Technology can bio-treat wastes that are difficult to be treated chemically. The EM Technology de-ionizes all elements present in the sludge and their concentration is minimized extremely.

EM Research organization was founded in 1994 in Okinawa, Japan. EM Research Organization promotes and disseminates EM Technology all over the world through its regional branch/liaison offices, Joint venture companies, NGO, NPO affiliates and local governments. EM Research Organization has a team of more than 100 researchers around the globe conducting EM research in different fields to uncover viable solutions for existing environmental and health problems. EM bacteria environmentally friendly and does not pose problem of contamination.

#### **Establishment of EM Pakistan.**

EM PAKISTAN is headed by Dr. Syed Ali as Managing Director. The research activities are carried out with a team of qualified personnel having M.Sc and Ph.D degrees. EM PAKISTAN is responsible for:

- carrying out research using EM Technology in preparation of bio active organic manures to maintain the fertility of the land to increase yields of various crops,
- carrying out research to establish formulae to be applicable in the areas of agriculture, horticulture, floriculture, fisheries, poultry and animal husbandry,
- undertaking research to resolve problems relating to environmental pollution caused by sewage and all types of industrial effluent and solid wastes,
- demonstrating the application of EM for deodorization especially in tanneries as well as of sewage water, and.
- Carrying out research in reclaiming saline and alkali soil using EM Technology in combination with FYM + PM.

## **5.2 Petroleum Sludge Disposal Problem**

Petroleum refining industries are troubled by the problem of handling substantial quantity of sludge in one form or the other depending upon the nature of the crude, processing capacity, downstream capacities, design of effluent treatment plants, pollution abatement measures and the efficiency-cum-effectiveness of these plants. To fulfill all the legislative and environmental requirements oil refineries need a well-planned oily sludge management strategy to manage the oily sludge with more cost-effective alternative to traditional physical and chemical methods of disposal.

## **5.3 Petroleum Sludge Bioremediation Using EM Technology**

A trial on bioremediation (anaerobic) of pure petroleum oily sludge of Attock Refinery Limited (ARL), Rawalpindi, Pakistan within its premises using EM Technology was successfully completed with the collaboration of EMRO/NCPC/ARL within a period of six weeks (29<sup>th</sup> Oct to 10<sup>th</sup> December 2002).

The Effective Microorganisms (EM) transformed the undiluted oily sludge from ARL into bio-sludge. The mixing of equal quantity of dry soil with the bio-sludge eliminated the oily nature of the bio-sludge. The final mixture was named bio-fertilizer.

**For heavy metals** breakdown the trial data shows that Ba was reduced by 85% in the EM treated petroleum sludge as compared to original ARL sludge, and Pb, Fe, Zn, and Ni were reduced by about 50% in the EM treated bio-sludge. The contents of As, Cr, Cu and Mn showed no change (table –8).

The calculated quantity of bio-fertilizer was then applied to agriculture land and onion crop was grown. The bio-fertilizer was comparable with FYM as it was rich in macro and micronutrients. The concentration of heavy metals in soil samples taken from the field where bio-fertilizer was applied, and in onion samples grown in the plots where bio-fertilizer and EM irrigations were applied, was far less than the permissible limits prescribed by NEQS and Department of Plant & Sciences Laboratory, and FAO Standards (Table – 9 & 10).

**Table – 8 Analysis Of Pure Oily Sludge and \*Bio-Oily Sludge**

S. #	Test	Before Treatment	After Treatment
	pH	<b>HDIP</b> 6.7	<b>HDIP</b> 7.0
	Nitrogen Carbon Hydrogen Sulphur	<b>NIBGE</b> 0.83 81.5 9.25 3.61	<b>NARC</b>
	<u>Metals</u> Pb Mn Ba Fe Zn Ni As Cr Cu	<b>PINSTECH</b> <u>%</u> 0.020 0.022 0.257 3.443 0.144 0.009 0.0029 0.0024 0.005 <u>ppm</u> 200 220 2570 34430 1440 90 29 24 50	<b>PINSTECH</b> <u>ppm</u> 83 207 382 17373 765 52 36 26 42
	<b>QCL</b> TPH	65.10	76.2

**Table 9: Heavy metals content in Soil taken from EM treated area and FYM treated area:**

<i>Heavy metals</i>	<i>FYM soil ppm</i>	<i>Treated sludge (1:1) ppm</i>	<i>Permissible limit (ppm)*</i>
Chromium (Cr)	0. 04	0. 07	1. 0
Cadmium (Cd)	0. 17	0. 14	>1. 0
Copper ( Cu)	0. 03	1. 05	3. 0-5. 0
Nickle (Ni)	0. 45	0. 32	1. 0
Lead (Pb)	2. 0	1. 57	15–20

\* *Source for Permissible limits: NEQS and Department of Plant & Soil Sciences Laboratory.*

**Table 10: Conc. Of Heavy metals in onions grown using Biofertilizer and FYM.**

<b>Heavy metals</b>	<b>FYM onions (ppm)</b>	<b>Treated sludge (1:1) onions (ppm)</b>	<b>Permissible limit (ppm)</b>
Chromium (Cr)	0. 15	0. 21	1.0
Cadmium (Cd)	0. 05	0. 04	0.24
Copper ( Cu)	4. 11	8. 14	05-20
Nickel (Ni)	0. 14	0. 10	1.0
Lead (Pb)	1. 87	3. 30	>1.0

**Source:** *Pakistan Book Foundation, and FAO Standards.*



#### 5.4 Mechanism of Bioremediation

The application of biological methods for pollution reduction is referred to as bioremediation. Bioremediation repertoire is growing. In recent years the most significant breakthrough has been its success in treating petroleum oily sludge using Effective Microorganisms Technology, in which the useful microorganisms involved are known and definite formula can be evolved for each kind of petroleum sludge so as to dispose it off safely.

The crude oil mainly composed of compounds of C & H (chapter – 1, table – 1). The main types of hydrocarbons present in crude oil are alkanes (paraffins), cycloalkanes (naphthenes), arenes (aromatic), alkenes, alkynes and cycloalkanoarenes (naphthenoaromatics). The crude oil also contains sulphur compounds, nitrogen compounds and oxygen compounds along with metallic compounds of Fe, Ni, Al, Cr, Mo, Ca, Mg, Na, etc besides asphaltenes and resins (chapter –1).

The sludge is formed at nine places in the petroleum refineries (section 4.5), meaning thereby that the sludge also contains the aforementioned hydrocarbons and other compounds, the concentration/composition of these may vary at each point. These are classified as hazardous material from the view point of environment. It, therefore, necessitates the safe disposal of petroleum sludge. The sludge is being disposed of using methods (section 4.5.5.).

Taking all the factors into consideration, it is, therefore important to arrive at the **mechanism of bioremediation**. Recently the bioremediation of petroleum sludge with the help of EM Technology (anaerobic and partially aerobic) has been demonstrated successfully (section 5.1, 5.2 and 5.3), meaning thereby that the safe disposal of petroleum sludge at large scale is possible.

Microorganisms or microbes are the invisible scavenger force of Nature and provide a means to eliminate unwanted elements in the environmentally dangerous / hazardous petroleum sludge. The microorganisms have evolved extensive range of enzymes to degrade a wide variety of hydrocarbons.

The prominent bacterial strains of *Pseudomonas* sp has been found capable of growing on alkanes, polycyclic hydrocarbons, salicylates, heterocyclics, phenolics and halogenated aliphatic and aromatic compounds [Ribbons DW & William, PA 1982. In: *Genetic Engineering of Microorganisms for Chemicals* Plenum, New York 211; mentioned by K A. Dadarwal in his book *biotechnical Approaches in Soil Microorganisms for Sustainable Crop Production*, p. 248]. The bacteria *rhodopseudomonas palustris* is commonly found in many polluted environments. This bacterium, whose genome has been fully sequenced, can biodegrade benzene rings in the absence of oxygen [CEMP Materials: PSB, Technical Material, phototrophic bacteria, studies, uses, by Caroline Harwood, Ph. D., UI Prof. of Microbiology]. EM Technology (chapter –5) also comprised of these microorganisms under the name phototrophic bacteria.

To undertake bioremediation of petroleum sludge various products of EM are prepared as per requirements and arrangements are made to mix these with the pure undiluted petroleum oily sludge manually or mechanically depending upon the quantity of sludge being treated. The nutrients already present in the sludge, addition of Bokashi and decomposition products produced during bioremediation serve as food to the Effective Microorganisms for their efficient working. Even during the anaerobic bioremediation process the moisture content in the treated sludge is maintained at about 30% with EM solution. The activity of microorganisms is monitored at regular intervals and if needed the whole sludge is mixed again and various products of EM are added to accelerate the bacterial activity to complete bioremediation in time.

The microorganisms can transform toxic organic compound into non-toxic inorganic end products. Bioremediation has been deployed successfully to reclaim lands contaminated with compounds such as polyaromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) [Shannon JR & Unterman R 1993: Ann Rev Microbial 47:715].

Advances in technologies associated with molecular biology have resulted in the construction of organisms (tailored strains), which are capable of degrading chloroaromatic compounds like chlorosalicylate, chlorobenzoate and dichloronaphthalene to bring them to complete mineralization [Durham DR & Stewart DB 1987: J. Bacterial 169: 2889]. Thus the known species of microbes as in case of EM Technology in which the concentration of all the bacteria from three main genera are maintained, being a potential tool to combat pollution in the sludge and consequently in the environment, break down organic compounds into CO<sub>2</sub> and H<sub>2</sub>O. The microbial activities during the decomposition of organic matter and microbial production of many inorganic and organic acids tremendously increase the microbial population and hence hasten the bioremediation process.

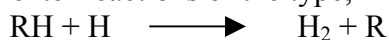
Complex organic material is broken down into smaller substances and decomposition is brought about by the action of living organisms, especially the useful and beneficial microorganisms contained in EM. These Effective Microorganisms secrete beneficial substances such as vitamins, organic acids, chelated minerals and antioxidants when in contact with organic matter contained in the sludge. These also secrete enzymes suitable to the process. Many complex chemical reactions are brought about by the microorganisms through the respective enzymes. Organic acids and nitrogenous compounds are attacked by bacteria and as a result are converted into acid carbonate and ammonia compounds.

Bacterial transformations of **heavy metals**, with the help of specific enzymes, lead to detoxification through oxidation and reduction reactions brought about by these specific enzymes, which act as catalysts for these complex reactions [Tyler G. 1981. In: Soil Biochemistry (Paul EA & JN Ladd eds), New York 371].

Chemical reactions of oxidation, reduction combination, elimination of atoms or groups etc take place with their active radicals. The radical OH and H<sub>2</sub>O<sub>2</sub> have oxidizing properties. The hydrogen atoms and hydrated electrons show oxidizing properties in an acid medium or in the presence of molecular oxygen. The hydrated electron in an acid medium i.e. in the presence of H<sup>+</sup> ions, form atomic hydrogen:



This atomic hydrogen can enter reactions of the type,



In the presence of oxygen, hydrogen atoms and hydrated electrons form hydrogen peroxide radicals, HO<sub>2</sub>, having oxidizing properties [*Industrial chemistry by P. K. Sharma 14<sup>th</sup> Edition 2004, p 195*].

The heavy metals are made either more water soluble and less toxic or less water soluble and precipitated, and or volatilized and are no more present in polluted matrix.

In nature most of the metals exist in combined forms as oxides, hydroxy carbonates, carbonates, chlorides, sulphides, silicates etc. The interaction of these within the sludge environment containing moisture and gases such as oxygen, halogens, sulphurdioxide, hydrogen sulphide, nitrogen etc, takes place and respective oxides, sulphides, carbonate, hydroxides, sulphates etc or other compound are formed and with this the properties of heavy metals are changed altogether. Alkali metals (Li, Na, K, Rb etc), and alkaline earth metals (Be, Mg, Ca, Sr etc) are oxidized at a quicker rate at low temperature. At high temperature almost all the metals are oxidized. Some examples of heavy metals are given here:

### **Chromium compounds**

These compounds exist in trivalent (chromite ion CrO<sub>3</sub><sup>-3</sup>, chromic ion Cr<sup>+3</sup>) and hexavalent (chromate ion, CrO<sub>4</sub><sup>-2</sup>, dichromate ion, Cr<sub>2</sub>O<sub>7</sub><sup>-2</sup>) forms. All chromium compound tend strongly to be oxidized to the chromic condition. Hexavalent chromium can be reduced to the trivalent form by heat, organic matter, or by reducing agents.

Salts of trivalent chromium are not considered to be physiologically harmful. Hexavalent chromium is generally considered to be harmful even in small doses. Chromium in refinery wastewaters is contributed by cooling water blowdown when chromium salts are used for cooling water treatment for deposit control.

In soils chromium exists in low redox forms: chromic (Cr<sup>3+</sup>) and chromate (Cr<sup>6+</sup>). Chromate is rapidly reduced to chromic in soils. Chromic is insoluble and also strongly sorbed. These reactions reduce its presence in the soil solution and reduces plant uptake. The inert nature of Cr compounds and chelates can be important in limiting the potential for oxidation of applied Cr<sup>3+</sup> and leaching of

Cr<sup>6+</sup>. This inert nature is an important source of environmental protection against adverse effects of Cr<sup>3+</sup> applied to soil by biofertilizer made from petroleum sludge treated with EM Technology [Land Application of Sewage Sludge and Biosolids by Eliot Epstein 2003].

Plant uptake of Cr is very limited because it is reduced in the roots to Cr<sup>3+</sup> and is not translocated to the above portion of the plant. Thus the food chain is protected against excess Cr in plant tissues. Plants grown on serpentine soils containing as much as 1% (10,000 mg Cr/Kg) do not exhibit Cr phytotoxicity.

### **Lead (Pb)**

The use of compounds like tetraethyl lead may contribute lead to refinery wastewater. A Pb content of 0.1 mg/l in water may cause chronic poisoning if the water is used continuously. Inorganic Pb salts in irrigation water may be toxic to plants. Among animals, chronic lead poisoning has been caused by 0.18 mg/l of Pb in soft water. The toxic concentrations of Pb towards various aquatic species range from 0.5 mg/l to 1.0 mg/l. Calcium in concentration of 50 mg/l destroys the toxic effect of 1.0 mg/l of Pb.

Pb does not readily move through the soil profile. It remains on or near the soil surface. Pb solubility decreases as the soil pH increases. In calcareous soils lead carbonate appears to be dominant.

Plants can take up Pb into the roots and insoluble Pb-phosphate is formed in the roots. Thus food chain is protected from excess lead.

### **Use of Biofertilizer**

Plant nutrients contained in the biofertilizer made from petroleum sludge treated with EM Technology are valued by the farmers for their macro nutrients (NPK) and micronutrients (Fe, Cu, Zn, Mn, B, etc). The addition of this very biofertilizer to the normal agricultural soils increases the organic matter content and the plant nutrient concentration. The application of this very fertilizer to the saline and alkali soils help in quicker reclamation of these soils. As this very biofertilizer contains Effective Microorganisms, the application of which increases the microbial population of the soil and with that the yield of various crops.

The application of biofertilizer made from petroleum sludge treated with EM Technology to agricultural lands can be quantified keeping in view the total quantity of the furrow slice soil and the amount of biofertilizer. In this way the quantity of heavy metals can also be regulated to such an extent which is no more deleterious /dangerous to soil and plant health.

### **Conclusion**

During the manufacturing of various useful products from crude petroleum at the refineries wastes like gas emission, effluent and sludge are produced. Their discharged to the atmosphere, natural water bodies and land has resulted in the

degradation of environment to such an extent that even human survival has been jeopardized. Major air pollutants emitted from refining operations are sulphur compounds, hydrocarbons, nitrogen oxides, smoke, carbon monoxide, aldehydes, ammonia and odors. Refinery air pollution control techniques exist, which should be followed strictly by the refineries without constituting a serious air pollution problem. The discharge of untreated wastewater into the drains and sewage system, which finally find their way into the natural water bodies such as lakes and rivers, has polluted the water resource badly. Wastewater of all types be treated chemically or biologically to reduce water pollution. The effluent can be treated biologically to reduce pollutant in the wastewater.

The sludge produced in the petroleum refineries was successfully converted into a useful resource with EM Technology. EM Technology invented by Prof. Dr. Teruo Higa, Okinawa, Japan has made it easy to solve environmental problems relating to effluent and sludge of various industries. The pure petroleum oily sludge was treated with various products of EM. Under anaerobic bioremediation it was converted to biosludge within a period of 6 weeks. By mixing with equal quantity of dried soil material it was converted to biofertilizer. The contents of heavy metals in the onions grown with this biofertilizer were comparable with those grown with FYM and these were far less than the limits given by FAO and Food Nutrition Laboratory. Thus, EM Technology ensures not only the safe disposal of petroleum sludge but also its safe application in various fields of agriculture.

In short, the petroleum oily sludge can be treated with EM Technology. The use of EM Technology is safe to handle, easy to apply, cost effective and environment friendly. EM Technology converts the useless and waste petroleum sludge into useful and beneficial resource. Simply EM from the point of view of environmental pollution control is the future of the world as being “An Earth Saving Revolution”.