Petroleum and Gas Chemistry

1st class/ Petroleum Reservoir Engineering Department

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Introduction:

The word petroleum originated from the Latin words, Petra, meaning rock and oleum, meaning oil. Literally it means 'Rock Oil,' and can also be defined as a non-renewable fossil fuel or oil that is found underground. This is any naturally-occurring flammable mixture of hydrocarbons found in geological formations such as rock strata.

Technically, the term petroleum refers to describe any solid, liquid or gaseous hydrocarbons. It's also known as 'crude oil' or 'mineral oil.'

Petroleum is one of the most important substances consumed by man at present time. It is used as a main source of energy for industry, heating, and transportation and it also provides the raw materials for the petrochemical plants to produce polymers, plastics, and many other products. The word petroleum, derived from the Latin words petra and oleum, means literally rock oil and a special type of oil called oleum

Petroleum is a complex mixture of hydrocarbons that occur in the sedimentary rocks in the form of gases (naturalgas), liquids (crude oil), semisolids (bitumen), or solids (wax or asphaltite). Liquid fuels are normally produced from liquid hydrocarbons, although conversion of nonliquid hydrocarbons such as coal, oil shale, and natural gas to liquid fuels is being investigated. In this book, only petroleum hydrocarbons in the form of gas or liquid, simply called petroleum fluids, are considered. Liquid petroleum is also simply called oil.

Hydrocarbon gases in a reservoir are called a natural gas or simply a gas. An underground reservoir that contains hydrocarbons is called petroleum reservoir and its hydrocarbon contents that can be recovered through a producing well is called reservoir fluid. Reservoir fluids in the reservoirs are usually in contact with water in porous media conditions and because they are lighter than water, they stay above the water level under natural conditions.

Occurrence of Petroleum

Petroleum occurs in the earth's crust, in all possible states and varies in color from light brown to dark brown or black, exhibiting luminescence in some cases. It is a mixture of various hydrocarbons, of homologous series namely paraffins, napthenes and aromatics.

The final result is a black viscous product of composition:

Carbon 80 to 89%

Hydrogen 12 to 14%

Nitrogen 0.3 to 1 %

Sulphur 0.3 to 3%

Oxygen 2 to 3%

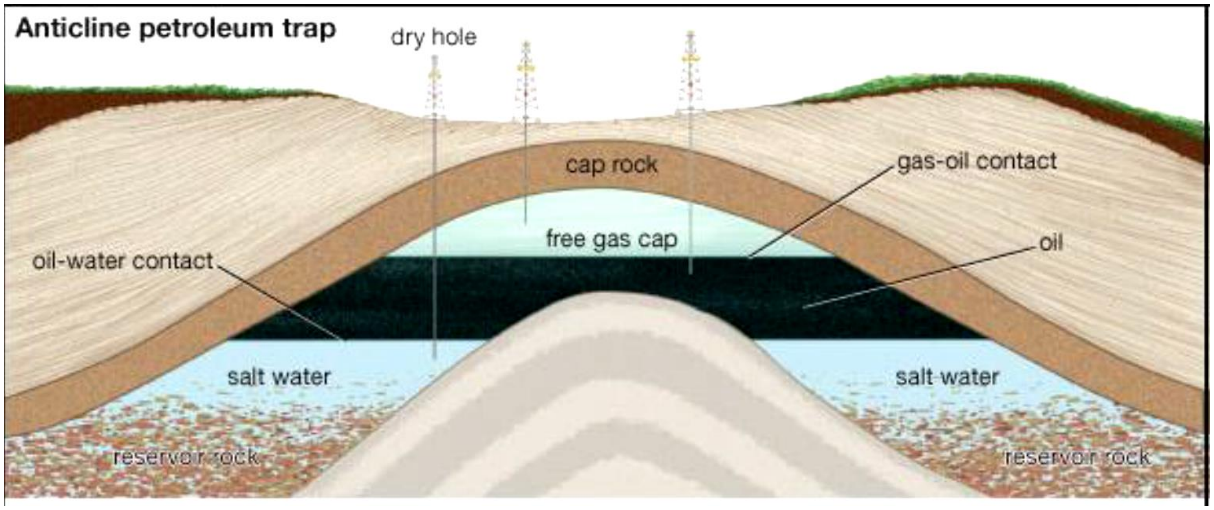
The main elements of petroleum are carbon (C) and hydrogen (H) and some small quantities of sulfur (S), nitrogen (N), and oxygen (O). There are several theories on the formation of petroleum.

Petroleum Formation.

There are basically two theories explaining the origin of oil,

1-**Organic Theory (Biotic Theory)**

- Oil developed millions of years from organic material remains of dead plants and animals (algae and planktons).
- The dead organisms sank to the bottom of water bodies (seas and lakes), where the environment tends to be anaerobic.
- They accumulated in the mud on the beds of the water bodies, partially decomposed.
- Sediment deposition on the bed of the water body, burying and compressing the organic matter under its weight.
- Increase in temperatures(100-160°c) and pressures resulted due to continued sediment deposition.
- With time the conditions broke down the organic compounds into shorter hydrocarbon chains, forming oil and natural gas.
- Oil and natural gas flowed from the source rock, accumulating in thicker more porous rock called a reservoir rock.
- Earth movements (faulting, folding) trapped the oil and natural gas in the reservoir rock between layers of impermeable rock or cap rock also called an oil trap.



Conditions necessary for biotic on formation.

1. Deep burial under sand and mud.

2. Pressure cooking.

3. Hydrocarbon migration from the source to the reservoir rock.

4. Impermeable rock to trap the oil.

2-Inorganic Theory:

This theory assume the oil hydrocarbon compounds produced from reaction hot water vapor with carbides which will form the hydrocarbon substances under high pressure and temperature as follows:

$$Al_4C_3 + 12H_2O \xrightarrow{\Delta \,\&P} 4Al(OH)_3 + 3CH_4$$

$$CaC_2 + H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

$$C_2H_2 \xrightarrow{\Delta \,\&P} \text{Petroleum}$$

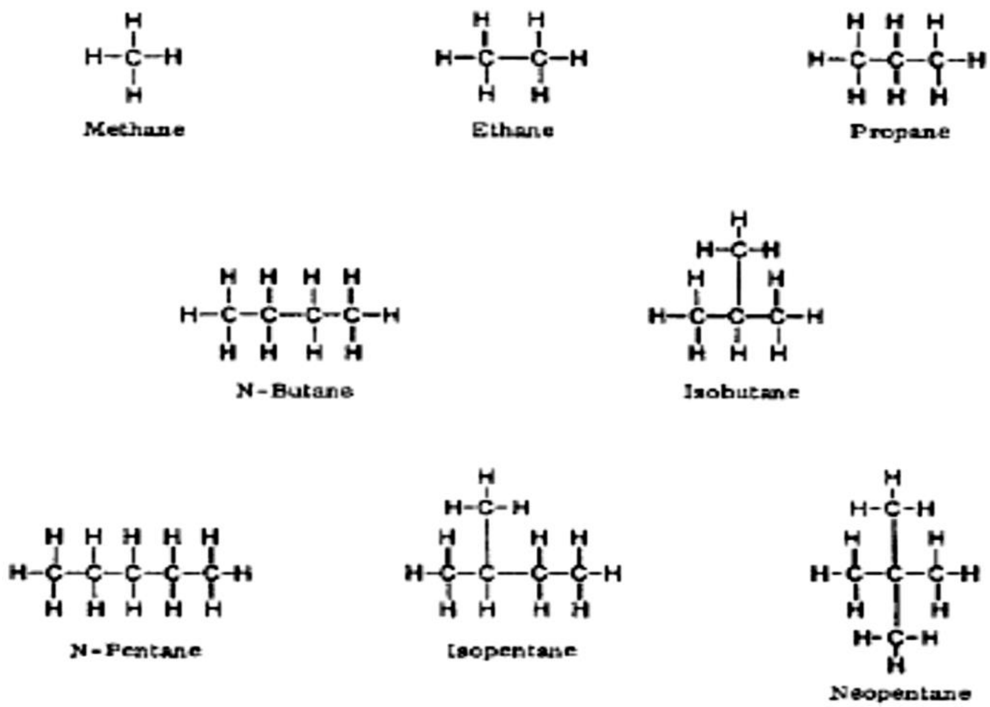
Chemical Composition of Petroleum

Petroleum is a mixture of hundreds of hydrocarbons of all type with water, salts, sulfur and nitrogen containing compounds and some metal complexes.

The three different types of hydrocarbons that crude has are paraffins, aromatics, cyclo-alyphatic or naphthenes and olefins.

Paraffins

The paraffin series of hydrocarbons is characterized by the rule that the carbon atoms are connected by a single bond and the other bonds are saturated with hydrogen atoms. The general formula for paraffins is C_nH_{2n+2}. The simplest paraffin is methane, CH_4, followed by the homologous series of ethane, propane, normal and isobutane, normal, iso-, and neopentane, etc. (Fig. 1).



Figure(1) Paraffins in crude oil.

Saturated alkanes: (n-alkane and i-alkane)

General formula CnH2n+2

Boiling point and density increase with increasing of C atoms.

Branched alkanes (iso-alkanes) is very small in quantity

Boiling point of straight chains > iso-alkanes with the same of C

Naphthenes or cycloparaffins

Cycloparaffin hydrocarbons in which all of the available bonds of the carbon atoms are saturated with hydrogen are called naphthenes. Typical examples of these are cyclopentane, cyclohexane, etc. (Figure 2).

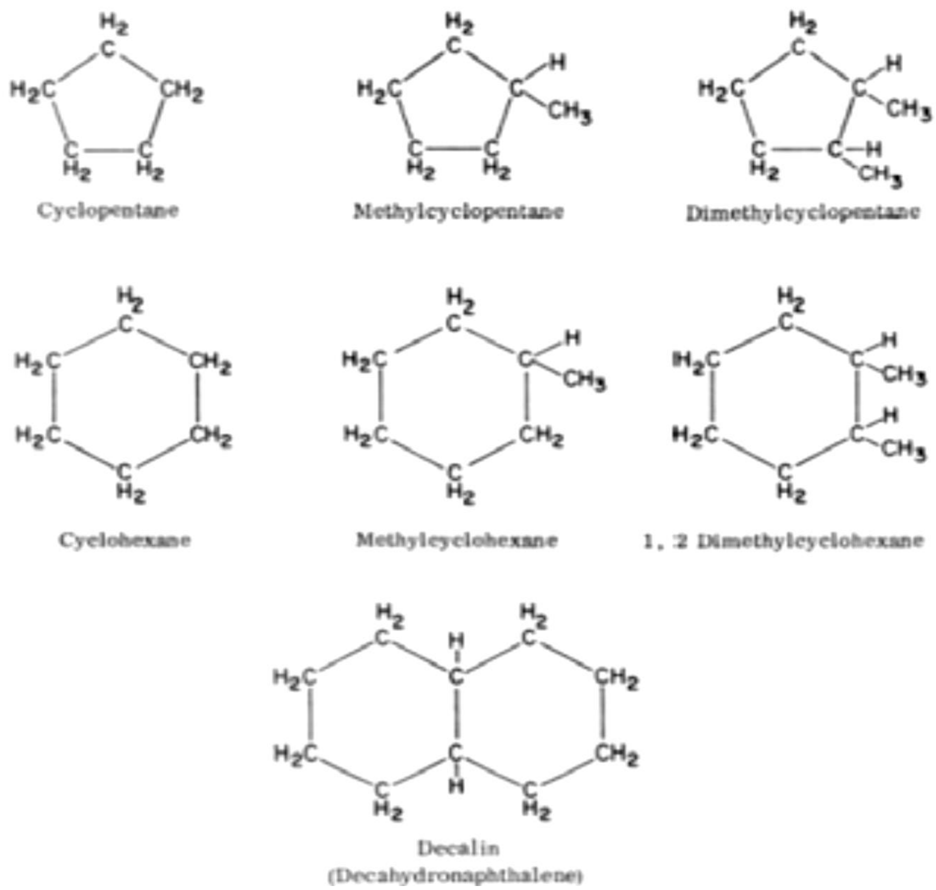


Figure 2: Naphthene compounds

General formula CnH_2n for one ring compounds

Aromatics

The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes). Aromatic hydrocarbons contain a benzene ring which is unsaturated but very stable and frequently behaves as a saturated compound. Some typical aromatic compounds are shown in (Figure 3).

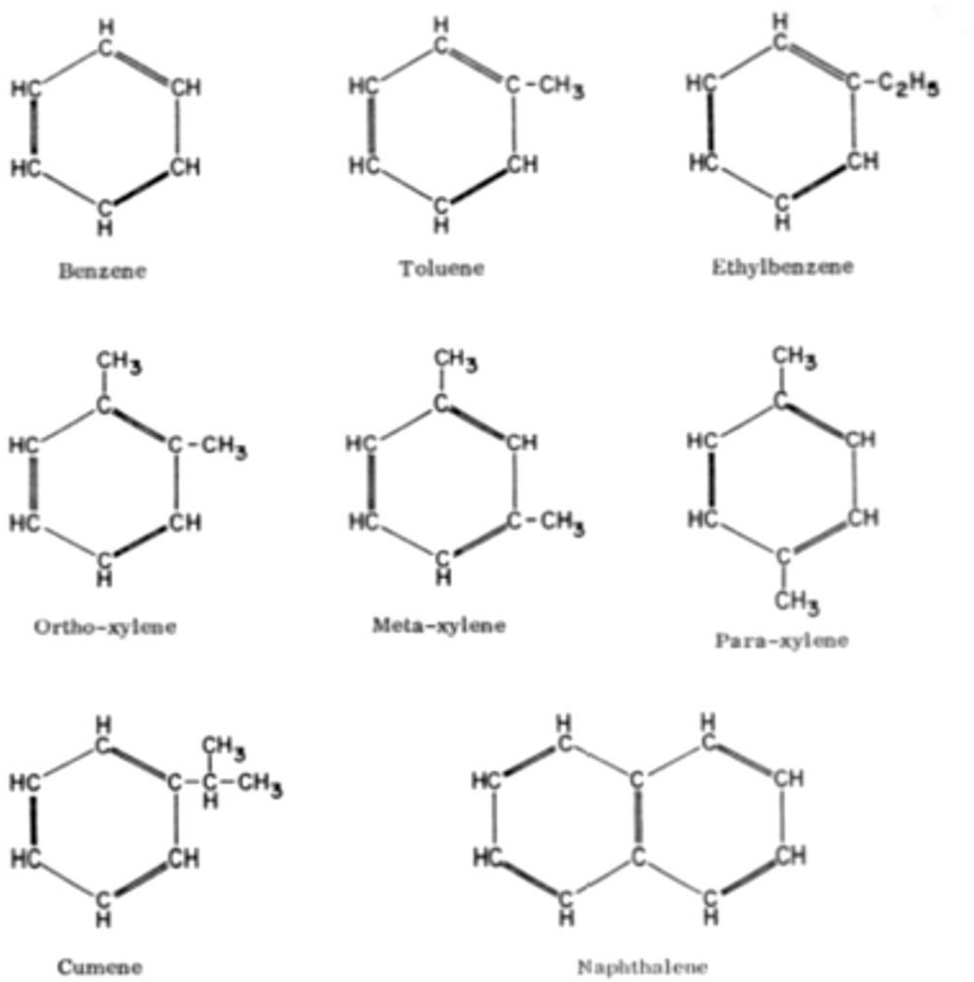


Figure 3: Aromatic compounds

Olefins

Olefins do not naturally occur in crude oils. However, they are formed during its processing. They are very similar to paraffins, but they exhibit double bonds, usually one per molecule (Figure 4), although some di-olefins (two double bonds in the same molecule, (Figure 5) can be found.

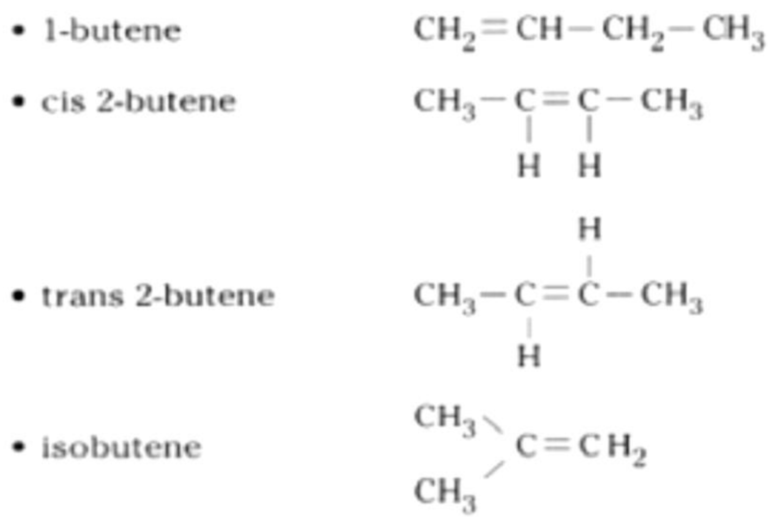


Figure 4: Olefin compounds

Figure 5: Di-olefin compounds

Heteroatom compounds (non hydrocarbon compounds):

Sulfur compounds:

It is the most important one that increase as the density increased. The types of sulfur components in the petroleum are:

- **a.** Hydrogen sulfide H-S-H (or H_2S).
- **b.** Mercaotance: H-S-R, where R is Alkyl (H-S-CH_3).
- **c.** Sufides: Aliphatic sulfide R-S-R, Cyclo sulfide.

Disadvantages of sulfur components:

1- Corrosion the metal parts of the engine.
2- Reduce O.N. (octane number).
3- Reduce oxidation resistance.
4- Solids deposition.

Nitrogen Compounds

Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C_5H_5N) and pyrrole (C_4H_5N), or in a complex structure as in porphyrin.

The nitrogen content in most crudes is very low and does not exceed 0.1 wt%.

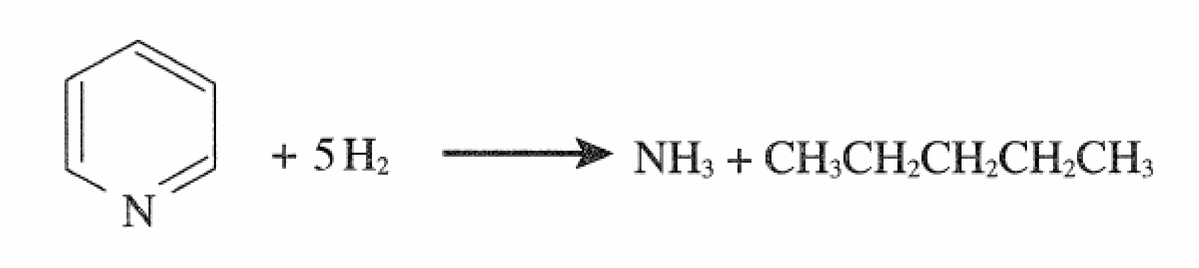
In some heavy crudes, however, the nitrogen content may reach up to 0.9 wt %.

Nitrogen compounds are more thermally stable than sulfur compounds and accordingly are concentrated in heavier petroleum fractions and residues.

Light petroleum streams may contain trace amounts of nitrogen compounds, which should be removed because they poison many processing catalysts.

During hydrotreatment of petroleum fractions, nitrogen compounds are hydrodenitrogenated to ammonia and the corresponding hydrocarbon.

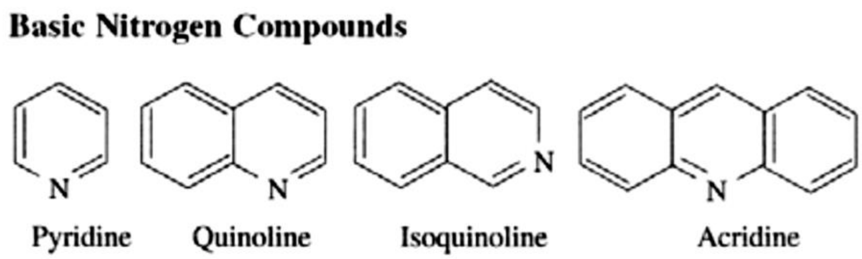
For example, pyridine is denitrogenated to ammonia and pentane:

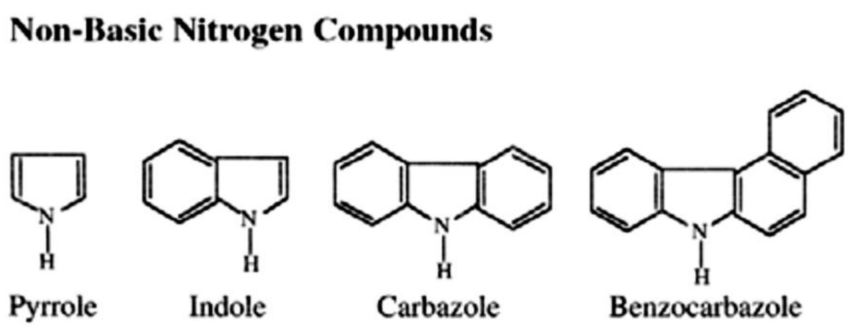


Nitrogen compounds in crudes may generally be classified into basic and non-basic categories.

Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic compounds have a pyrrole structure.

Both pyridine and pyrrole are stable compounds due to their aromatic nature.



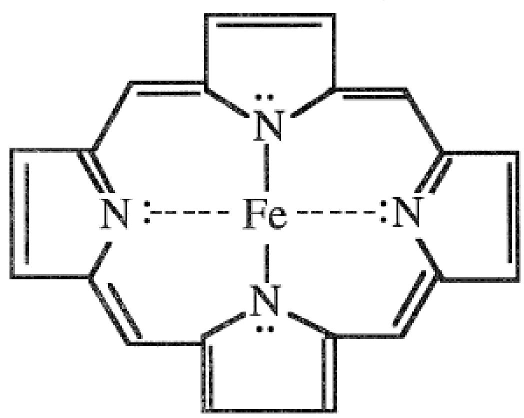


Porphyrins are non-basic nitrogen compounds.

The porphyrin ring system is composed of four pyrrole rings joined by =CH- groups.

The entire ring system is aromatic. Many metal ions can replace 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.

Almost all crude oils and bitumens contain detectable amounts of vanadyl and nickel porphyrins. The following shows a porphyrin structure:



Oxygen Compounds

Oxygen compounds in crude oils are more complex than the sulfur types. However, their presence in petroleum streams is not poisonous to processing catalysts.

Many of the oxygen compounds found in crude oils are weakly acidic. They are carboxylic acids, cresylic acid, phenol, and naphthenic acid. Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain.

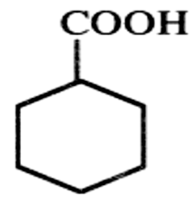
Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solutions. The total acid content of most crudes is generally low, but may reach as much as 3%, as in some California crudes.

Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds. They are of no commercial value.

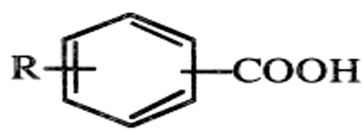
Acidic Oxygen Compounds

$CH_3(CH_2)_nCOOH$

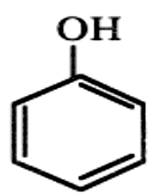
An aliphatic carboxylic acid



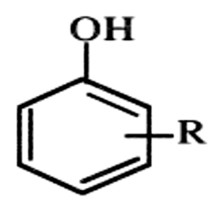
Cyclohexane carboxylic acid



Aromatic acids



Phenol



Cresylic acid

Non-Acidic Oxygen Compounds

R-COOR'

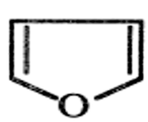
Esters

R-CONHR'

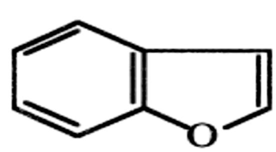
Amides

R-C(=O)-R

Ketone



Furan



Benzofuran

Metallic Compounds

Many metals occur in crude oils. Some of the more abundant are sodium (Na), calcium (Ca), magnesium (Mg), aluminium (Al), iron (Fe), vanadium (V), and nickel (Ni).

They are present either as inorganic salts, such as sodium and magnesium chlorides, or in the form of organometallic compounds, such as those of Ni and V (as in porphyrins).

Calcium and magnesium can form salts or soaps with carboxylic acids. These compounds act as emulsifiers, and their presence is undesirable.

Although metals in crudes are found in trace amounts, their presence is harmful and should be removed. When crude oil is processed, sodium and magnesium chlorides produce hydrochloric acid, which is very corrosive.

Desalting crude oils is a necessary step to reduce these salts.

Vanadium and nickel are poisons to many catalysts and should be reduced to very low levels.

Most of the vanadium and nickel compounds are concentrated in the heavy residues.

Solvent extraction processes are used to reduce the concentration of heavy metals in petroleum residues.

Brine water:

Water molecules are suspension in crude oil with extremely high concentrations of dissolved salt ions nearly 300-300,000 ppm. The ions are divided to types:

1- Positive ions (Na^+,Ba^{2+} , Mg^{2+}, Al^{3+},…….)
2- Negative ions (Cl^-, Br^-, SO_4^{2-}, I^-,………)

Table 2.2. General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	–161	–1	–259	31
Liquefied petroleum gas	C_3	C_4	–42	–1	–44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	–1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	

*Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.