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Chemistry of Crude Oils

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ABSTRACT

The word Petroleum is derived from the Petra-Rock and Oleum-Oils. Hence it can be define as Natural occurring material composed of mainly by hydrocarbons, in gaseous and liquid state and residual mass which cannot be distilled without decomposition.

Keywords: *Hydrocarbons; Alkanes; Paraffins; Naplnenes.*

1.0 Introduction

ORIGIN: Regarding the origin of crude oil the following probabilities were given.

I. Water + Metallic Carbides or H_2O + CO_2 + Alkali or Alkaline Earth Metals

⇓

Hydrocarbons

Because in some meteorites and in the atmosphere of certain planets, hydrocarbons were detected.

II. Organic matter on decay ⇒ Oil + Gas

III. (Animal + Vegetable) + Heat + Anaerobic Bacteria + Radio Activity

⇓ Low temperature

Crude oil

Low temperature is favored because in crude oil and its fractions no olefins were detected. This is also confirmed by the study of Maier and Zimmerly.

Oil Shale ⇒ Oil (but this oil has no similarity with crude oil)

(275- 365^0 C)

ß Carotene ⇒ Toluene

(at 119 & 150^0 C)

Also caretonoids on degradation under mild conditions produced Toluene.

1.1 Crude oils

Crude oil is a complex mixture of hydrocarbons, (i.e. Paraffins, Naphthenes & Aromatics) which is brownish black in colour and colloidal in nature. The impurities present in the oils are in the form of water, inorganic electrolytes, inorganic gases like (CO2, H2S) and siliceous debris of the hetero compounds of oxygen, sulphur, nitrogen and some trace metals like Ni, V, Fe, Cr.

Physically crude oils can vary from light, mobile, strain coloured liquids containing large proportion of easily fractions to highly viscous, semi solid black substances with very little distillable material before decomposition occurs. Crude oil compositions vary widely from oil field to oil field and even from well to well in the same oil field.

Elemental Composition of Crude Oils (% Wt)

Carbon	83.9-86.8
Hydrogen	11.0-14.0
Sulphur	0.06-8.00 (5% in Heavy Missisippi or Mexican crudes)
Nitrogen	0.02-1.70 (0.1-0.9% in Californian & South American Crudes)
Oxygen	0.08-1.82
Metals	0.00-0.14

Main Constituents of crude oil are Hydrocarbons (Compounds composed of C & H account for 75% of the material.

Heavy crudes of the younger formations like Vanezuelan crudes have low hydrocarbon content of the order of 35-38%, the remainder of the crude oil

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being compounds containing at least one hetero atom in the organic molecule.

Carbon No. distributions in distillates

Natural Gas	Paraffins	C_1-C_4
Gasoline	Paraffins, Aromatics & Naphthenes	C_5-C_{10}
Kerosine	---------do----------	C_{11}-C_{18}
Gas Oil	---------do----------	C_{18}-C_{28}
VGO	---------do----------	C_{28}-C_{40}
Residue	Asqhaltic	C_{40} Onwards

Hydrocarbons

The compounds of Carbon and Hydrogen are known as Hydrocarbons. It is generally represented by a general formula CnH2n+z

n=1, 2, 3……

z=0, 2,-4,-6,-8,-10,-12 etc…..... upto-30

Hydrocarbons are homologues series of hydrogen numbers.

C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}……..upto-30

In Petroleum there are only four classes of hydrocarbons usually present:

- N-ALKANES (n-PARAFFINS, Z=+2)
- I-ALKANSES (ISO PARAFFIN, Z=+2)
- ALKYL NAPHTHENES (CYCLO PARAFFIN, Z=0,-2,-4 etc.)
- AROMATICS (Z=-6,-8,-10 etc.)

Alkanes

Alkanes are the saturated aliphatic normal or branched chain compounds constituting homologues series of general formula CnH2n+2.

In crude oils alkane ranges from methane to molecule C60 or more with molecule weight 16-850

- Alkanes are present in all crude oils and natural gas.
- There ranges are from C1 to about C100.
- They relatively non reactive and non polar.
  - Uniquely described by the molecular formula upto C3 and C4 onwards are also occurs as isomers.

CARBON NUMBERS	n-ALKANES, B.Pt (Atm. Eq.)	NUMBER OF ISOMERS
5	36	3
8	125.6	18
10	174.0	75
12	216.0	355
15	270.6	4347
20	343.9	36.6 X 104
25	401.7	36.7 X 10^6
30	449.0	41.1 X 10^8
35	488.9	49.3 X 10^{10}
40	522	62.4 X 10^{12}
45	550	82.2 X 10^{14}
60	615.0	221.5 X 10^{20}
80	672.9	1056.4 X 10^{28}
100	707.8	5920 X 10^{36}

Reference. M.M. Boduszynsky, Energy & Fuels 2, (5) 597-613, 1988

n-ALKANES: (Normal Paraffins)

Normal alkanes or Paraffins are the saturated aliphatic straight chain compounds constituting homologues series of general formula CnH2n+2.

Except methane which is the parent paraffin, they are globular in shape and have the cylindrical symmetry in stretched form.

These paraffins are gases from C1-C4, liquids from C5-C16 and solid waxes from C17 onwards.

Compounds	Formula	Boiling Point 0C
e.g. Ethane	(C2H6)	-88.6
Propane	(C3H8)	-42.1
n-Butane	(C4H10)	-0.5
n-Pentane	(C5H12)	36.1
n-Hexane	(C6H14)	68.8
n-Heptane	(C7H16)	98.4
n-Octane	(C8H18)	125.7
n-Nonane	(C9H20)	150.9
n-Decane	(C10H22)	174.0
n-Undecane	(C11H24)	195.8
n-Dodecane	(C12H26)	216.3
n-Tridecane	(C13H28)	234.0
Etc		

The compounds above (C16H34) i.e. n-Cetane are solid at room temperature and similar in nature to paraffin wax.

In crude oil n-alkanes were observed of the order of C1-C42 with molecular weight about 590. Generally in crude oil 15 to 20% of all these normal paraffins are present upto (C40H82) i.e. tetracontane and in few cases beyond upto (C100). It is important constituent of light crude oil or paraffin wax.

- Paraffins are low in Heavy graded oils
- Upto 35% in light crudes (Paraffinic in nature)
- Relatively non reactive & non polar
- Usually the normal paraffins have the hightest melting point for the same carbon number isomers.

Normal alkanes are preferentially separated from Hydrocarbon mixtures by

- UREA ADDUCTION
- MOLECULAR SIEVES (5AO) (Molex Process UOP)

SIGNIFICANCE

- Feed stocks for straight chain Paraffins
- Oxidation of (C8 – C30) n-paraffins resulting fatty acids for soap industries
- Oxidation of (C12 – C14) n-paraffins resulting secondary alcohols
- Mono-chloroparaffins (C10- C30) as cutting oil additives, plasticizers and fire
- Retardant chemicals.
- Sulphonated n-paraffins (C16 – C17) for biodegradable detergents
- Paraffin wax
- Freezing point in ATF
- Cold flow properties of diesel and Lubes
- Ignition quality of gasoline and diesel fuels.

ISO PARAFFINS

Iso paraffins are the branched paraffins hydrocarbons having the same general formula of n-paraffins (Cn –H2n+2).

E.g. Iso butane
Iso pentane
Etc.

- (C4 –C33) have been isolated in petroleums
- Predominant members carry the simplest type of side chain i.e. CH3
- 2-methy1 alkanes are most prominent in (C6 – C8) range.
- di and Tri substituted are les abundant and are mainly present in higher boiling fractions.

Branched chain alkanes (isoprenoid hydrocarbons) having a methy1 group on every fourth carbon resumed to be derived from higher terpenes,

Most abundant iso-paraffins are

PRISTANE	(C19 – H40)
PHYTANE	(C20 –H42)

SIGNIFICANCE

- Iso paraffins are the most valuable components for the
- Gasoline (due to high Octane No.)
- ATF (Melt significantly below the corresponding n-Alkanes, except when Symmetrical compact structures like Neo-pentane etc.)
- Lubricating Oil.

Highly branched isomers are undesirable in diesel fuel.

NAPHTHENES (Cyclo Alkanes)

This is also a kind of saturated compounds which appears as a ring structures and also known as close chain or cyclic saturated compounds. The general formula of this series is

(Cn-H2n+2)-2RN

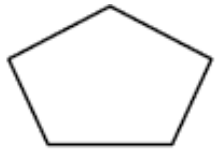
Where as RN is number of napthenic rings in the molecule.

In crude oil naphthenes are present about 50% by weight and its quantity is higher in heavier fractions.

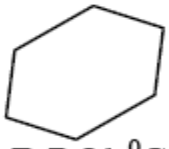
They occur in naphtha and predominated in most of the gas oils and in lubricating oils. They are chemically highly stable hydrocarbons.

Naphthenes present in the crude oils are cyclopentane.cvclohexane and their alkylated derivatives however cycloheptane (B.P 1180 C) has also been identified in petroleum products.

One Ring

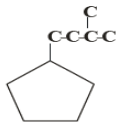


B.P 49^{0}CB.P,
M.P – 94 ^{0}C

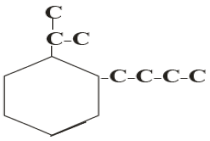


B.P 81 ^{0}C
M.P 7 ^{0}C
Cyclohexane

B.P 119°C
M.P – 8 °C
Cycloheptane

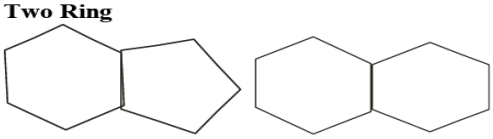


Alkyl Cyclopentane

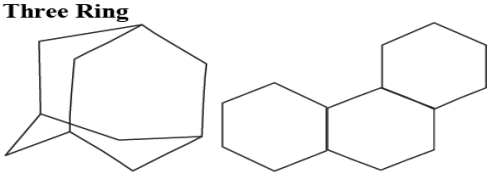


Alkyle Cyclohexane

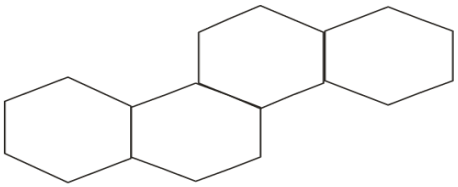
Two Ring



Three Ring

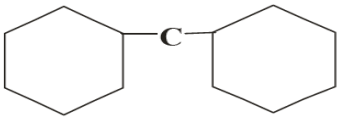


Four Ring

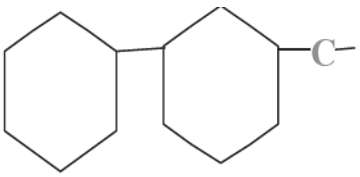


Naphthenes are classified into three classes.

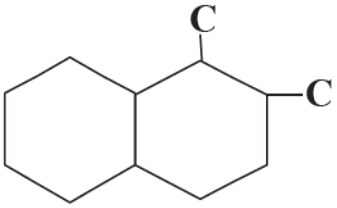
(A) Isolated Rings Type: When rings are separated by paraffinic chain e.g Dicyclohexyl alkane



(B) Conjugated Rings Type: When rings are linked each other by carbon ring to carbon ring bond. e.g Alkyl dicyclo hexyl



(C) Condensed Rings Type: When two rings have at least two vicinal carbon atom in common e.g condensed bycyclic or Alkyl decalin



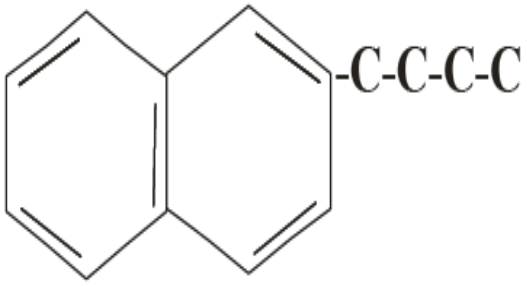
Bicyclic naphthenes are important constituent of the kerosene and gas oil fractions. Tetra & Pentacyclic occurs in lube oils. Even 10 rings naphthenes are observed in some fractions of lubricating oil.

Aromatic Hydrocarbons

Aromatics are unsaturated cyclic hydrocarbons having the general formula (Cn-H2n-6) & (C2n-H2n-12). Aromatics are found about 15% by weight in crude oils and present as derivatives of benzene and polynuclear aromatic hydrocarbons (both condensed and non condensed types) and their homologues. These hydrocarbons are chemically reactive and can form both substitution and addition products, thus behave as saturated as well as unsaturated type of hydrocarbons.

High amount of polycyclic aromatics are present in heavy gas oil, lubricating oil and in residues.

Low molecular weight aromatics (monoaromatics) like Benzene, Toluene, Xylene & ethyl benzene etc. were observed in gasolines (Virgin from light crude oil)



Alkyl Naphthanlen

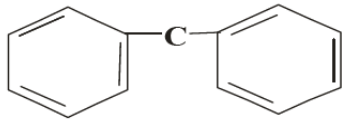
In Kerosene ⇒ With increasing number of alkyl substituents

In Diesel ⇒ Dinuclear- aromatics

In Lube oils ⇒ Mono, Di, & Tri nuclear aromatics aromatics with short alkyl chains and higher members upto 5 membered rings are also been identified.

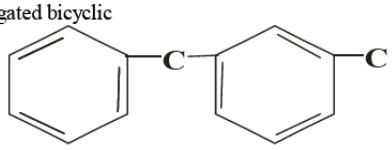
Aromatics are classified like naphthenes as follows

Isolated bicyclic



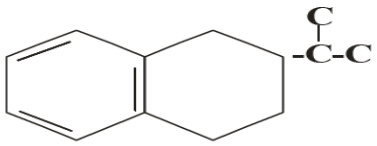
Diphenyl Alkene

Conjugated bicyclic

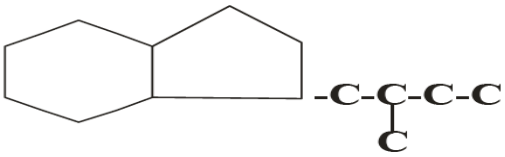


Alkyl Diphenyl

Condensed bicyclic

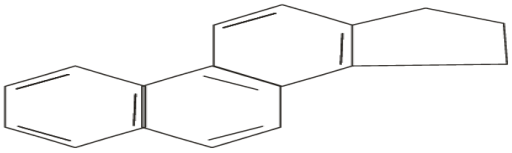


Alkyl teralene



Alkyl Indane

Heavier gasoils (Tetranuclear naphtheno-aromatics, e.g. Cyclopentenophenathrenes)



Cyclopenteno phenanthrenes Lubricating oils.

Significance

- Aromatics have the lower H/C ratio, higher refractive index, density and viscosity.
  The octane number of aromatic hydrocarbons are much higher than paraffins, isoparaffins and cycloparaffins of the same carbon number therefore as result of reforming the naphtha by increasing the concentration of aromatics octane number can be boosted.
- They are also having the poor cetane number and viscosity index.
- They have higher polarity and are extracted selectively by polar solvents.
- For the same carbon number volatility of aromatics is lower than its corresponding paraffins.
- They undergo readially for electrophillic substitution therefore they are used as good chemical feed stocks.
- They are also implicated in carcinogenesis.

Naphtheno Aromatics

These are also a kind of aromatic hydrocarbons in which aromatic ring is fused with a alicyclic ring with aliphatic chains.

Generally such type of compounds is present in middle distillates.

These types of the compounds start to appear from kerosene range and are classified according to total number of rings and the number of aromatic rings they contain. In polycyclic naphtheno-aromatic hydrocarbons the rings are mainly condensed.

Kerosene & Gas oil

Mixed molecules containing upto six membered rings. The aromatic portion contain several short chains (Mainly C1 & C2) while alkyl chains, more limited in numbers (one or two) are linked to cycloparaffin rings. The general formula (Consisting rings of six carbon atoms,)

Ortho condensed type is	CnH2n +2RN-6RA-2RAs
RN	Number of naphthenic rings.
RA	Number of aromatics rings.
RAs	Number of substantial aromatic rings.

Hetero Compounds

The hydrocarbon compounds containing nitrogen, oxygen & sulphur as a constituent with carbon and hydrogen are known as hetero hydrocarbons.

Sulphur Compounds

Sulphur is present in crude oils as hydrocarbon type as well as non hydrocarbon type. In

crude oils it varies from 0.1-3.0 percent by weight but values upto 7.0% sulphur content of crude (Maxican & Missiscippi & middle east) are also known. Indian crudes are sweet in nature, contain about (0.05 – 0.4% by Wt.) of sulphur. Generally higher the density of the crude greater the sulphur content. Distribution is not uniform in crude oil but it increases with increase in the molecular weight of the fractions, concentrating during distillation in residues.

Non Hydrocarbon Type Sulphur

Sulphur is also found in crude as elemental sulphur and as hydrogen sulphides. H2S is also associated with petroleum gases and is partically dissolved in oil. Elementary sulphur can be present dissolved in oil formed by the oxidation of H2S. Presence of elementary sulphur strongly indicate the low temperature processes involved in the formation and maturing of the oil, as it is well known that sulphur react with hydrocarbons formed H2S below 1000 C.

Hydrocarbon Type Sulphur

Sulphur is present with carbon & hydrogen.

It is found in the form of RSH

Cyclic sulphur compounds

Sulphides or Thio Ethers R-S-R

Disulphides RSSR

Sulfoxides

Sulphones

In low and medium molecular weight range (upto C_{25}) it is associated with carbon and oxygen where as in heavier fractions it is associated with polycyclic molecules which may also contain nitrogen and oxygen.

Sulphur Compounds Inentified in Crude Fraction (Ibp-100° C)

COMPOUNDS	BOILING POINT° C
1. Methane thiol	5.96
2. Ethane thiol	34.00
3. 2-Thiopropane	37.31
4. 2-Propanethiol	52.56
5. 2-Methyl 2-propanethiol	64.22
6. 2-Thiobutane	66.65
7. 1-Propanethiol	67.50
8. 3-Methyl-2-thiobutane	84.81
9. 2-Butanethiol	85.51
10. 2-methyl 1-propanthiol	88.72
11. 3-Thiopentane	95.52
12. 1-Butanethiol	98.40
13. 3,3 Dimethyl-2-thiobutane	99.00
14. 2-Methyl-2-Butanethiol	99.00

Mercaptans

In Gasolines

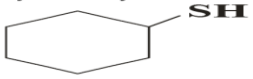
Thiophenes

MonomethylthiophemneC-C-S-C-C

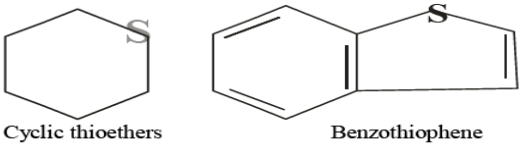
Diethylthioether 3-Thiapentane

In higher boiling fractions the —SH group attached to secondary carbon atom of an alkyl or isoalkyl chain

Cyclopentanethiol

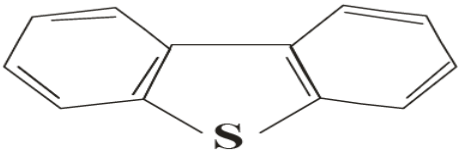


Cyclohexanethiol



Cyclic thioethers (With one or two CH_3 groups) Kerosenes Gas oils & lubricating oils

Benzothiophene



Dibenzothiophenes or Substituted thiophenes & higher polycyclic thiophenes Bitumen's Sulpur Compounds present in heavy distillates, bitumen & residual oils but very little is known about the composition of these sulphur compounds. In residues present with one or more naphthenic rings per molecule appear to be most abundant In the oily fraction of bitumen separated by solvents mono & di substituted benzo-thiophenes have been detected, but their complete structures is yet to known.

Condensed polycyclic structures with one or more naphthenic rngs per molecule are more common than isolated structures.

Effects of Sulphur Compounds in Crude Oil

Sulphur compounds are most undesirable constituent of crude oil.

- Corrosive in nature due to acidic nature.
- Acts as gum precursors during storage.
- Pollution (Toxic) due to emissions.
- Reduce lubricating oil life.
- Causes wear in engines.
- Increases deposits in engine.
- Acts as poison catalyst during reforming.
- Consumer acceptance.

Sulphur compounds (Mercaptans) can be converted into disulfides which is non corrosive in nature by the use of

- Sodium plumbite
- Cupric chloride
- Caustic solution with the addition of organic compounds solutizers.

Application of Sulphur Compounds

Sulphur compounds are not always harmful to the petroleum products. Some time sulphur compounds naturally presents or deliberately added to the petroleum fractions.

It acts as

- Anti-oxidants
- Additive for high pressure lubricants
- Diesel fuel ignition quality improver
- Centane no. improver
- Cutting oil improver
- Detergents
- Asphalt improver

Organo-Nitrogen Compounds

Nitrogen compounds are present in crude oil generally less than sulphur compounds in weight percent. Most of the crudes contain < 0.2% wt of total nitrogen. Nitrogen compounds present as basic as well as nonbasic in nature.

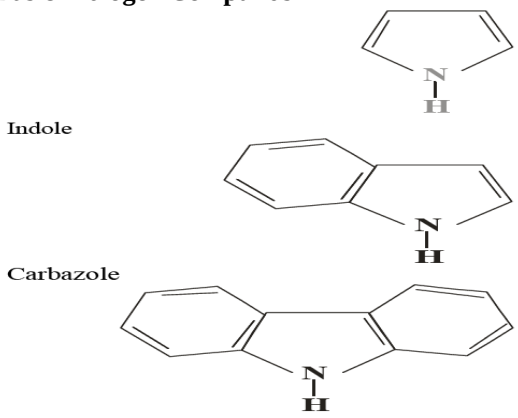
Generally their concentration is less upto 3000 C.

Increasing the boiling point nitrogen compounds increase and reaches a maximum in asphaltic residues. Nitrogen compounds are stable to heat and do not decompose during normal refinery

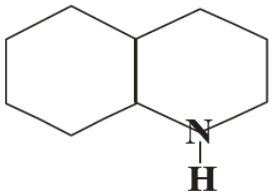
processes. However, even in traces amount in distillate products nitrogen containing compounds can create serious refining problems. High CCR of crude paralleled by high total nitrogen content.

High values of % N / % C are predominating in geologically young crudes and this ratio appears to correlate crudes of the same geological age in certain geographical areas.

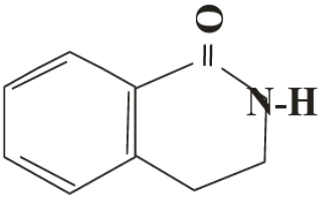
Basic Nitrogen Compunds



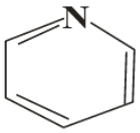
Amines $R\text{-}NH_2$



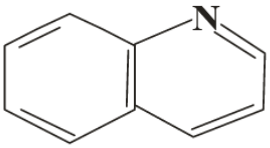
Amides



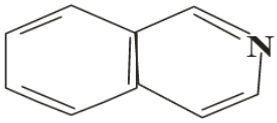
Pyridine



Quinoline



Iso-quinoline



Non Basic Nitrogen Compounds

Pyrrole

Porphyrines (Pyrrole nucleus)

The ratio between total nitrogen and basic nitrogen contents is almost constant (+ between 0.25 – 0.35). Although the amount of basic nitrogen content increases with boiling point, the ratio remain constant.

Effect of Nitrogen Compounds in Crude Oil

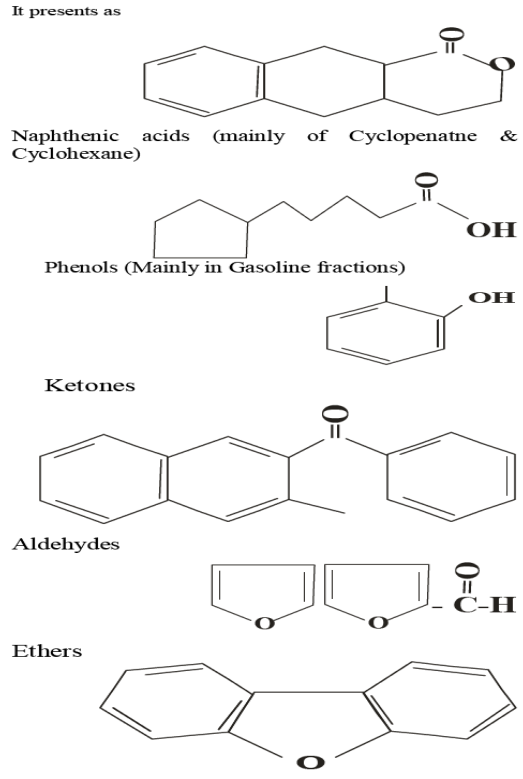
- Nitrogen compounds acts as poison to the catalyst due to basic nitrogenous compounds adsorption on the active centres of the catalyst. It is a temporary phenomenon. In which organic nitrogen compounds converted into ammonia under reforming conditions and this neutralizes acid sides on the catalyst and thus represses the activity for isomerization,

hydrocracking and hydrocyclisation reaction. Very small quantity (1-2 ppm) can have adverse effect. Normally straight run material do not present serious problems but feeds as coker naphtha may contain 50 ppm nitrogen. Removal of this quantity requires high pressure hydrogenation (800-1000 psig) over Ni/Co/Mo on alumina catalyst reported to be more efficient for nitrogen removal than Co/Mo. The compounds also impart on the dederioration of the colour of petroleum fractions.

- Quinoline & quinalidine do not decompose.
- Nitrogenous compounds like 2,5 Dimethyle pyrrole, Indoles etc. impart active role during the degradation of middle distillate fuels.

Oxygen Compounds

Oxygen present in the crude oil is relatively low varying from traces to maximum 2% by weight. Its concentration increasing the boiling point therefore oxygen content is found about 8% by weight in residual oils. These compounds have the molecular weight ranging between 700- 1400, in which polynuclear naphthenic acids and polynuclear carboxylic acids have been identified.



In Asphaltenes as bridge atom between polycyclic rings.

Oxygen content is determined by difference. In low and medium boiling range distillate fractions it is present as organic acids and to limited extent as phenols. Hence oxygen content can also replaced customarily by acidity of the fraction. It is observed that in paraffinic crudes oxygen content is less whereas in asphaltic crudes substantial amount of content (upto 0.6-1.0% wt.) is present in the form of acids. Acidity in the form of monocyclic & bicyclic carboxylic acids (derivatives of cyclopentane and cyclohexane) appears maximum in kerosene and oil fractions whereas in straight run gasoline, heavy fractions and residues contain only traces of acidic compounds. Under the name of naphthenic acids they are the products of industrial importance. e.g.

Extraction
Crude oil ⟹ regeneration and ⟹ metallic Soap used as

Varnish
NaOH Purification drier

- Manganese and Cobalt naphthenates as varnish dryers.
- Copper naphthenates as fungicides and wood preservatives.
- Calcium and Zinc naphthenates as lubricating oil dispersant additives.
- Aluminium Soap (Gelling agent as Napalm)

Effect:

- Naphthenic acids are corrosive in nature and can corrode the distillation unit.
- Water Tolerance.
- Peroxide formations.

High Molecular Weight Nitrogen & Sulphur Compounds These compounds present in the crude oil as a complex structures known as porphyrines. Generally they are present in the asphaltenes, resins. Asphlaltene molecules probably consist of sheet comprising of some 10-20 peri condensed aromatic rings linked with the naphthenic and paraffinic groups.

Asphaltene molecules form aggregates

Micelles, Molecular weight 30,000

Particle Molecular weight 3000-10000.

Where as resins possess lower molecular weight (500-1200).

Metallic Derivatives

Metals have been found in the ash of petroleum residue and petroleum fractions as such. They may be associated in the brines which is emulsified with or as such in contact with the crude oil, They may be salts of organic acids present in the crude oil, particularly in case of Ni, Cu & V may be present as organic porphyrins also, Metallic concentration in the crudes is very often less than 0.1 % wt.

- In refinery operation the deposition of inorganic salts suspended in crude oils can cause serious break downs; the thermal decomposition of deposited inorganic chlorides with evolution of free hydrochloric acids can give rise to serious corrosion problems in distillation equipment.
- Manganese and Cobalt naphthenates as varnish dryers.
- Copper naphthenates as fungicides and wood preservatives.
- Calcium and Zinc naphthenates as lubricating oil dispersant additives.
- Aluminium Soap (Gelling agent as Napalm)

Effect:

- The presence of organic acidic compounds i.e.mercaptans and acids can also promote metallic corrosion.
- In catalytic operation, passivation and/or poisoning of the catalyst can be caused by deposition of trace metals (Vanadium, Nickel) or by chemosorption of nitrogen containing compounds on the catalust, thus necessitating the frequent regeneration of the catalyst or its replacement.
- In finished products, the presence of non hydrocarbons may impart objectionable characteristics: discolouration or lack of stability on storage in distillate fuels caused by the presence of nitrogen compounds; the adverse effect on additives improvers, as in motor gasoline, where presence of traces of sulphur compounds reduces the effectiveness of organic lead antiknock additives. These compounds are also of fundamental interest in the elucidation of the origin of crude oils.Particularly importanl in this respect are the organomettalic compounds (porphyrins and related structures) found in crude oils and naturally occurring bitumens. Furthermore, a knowledge of their surface active characteristics is of the help in understanding problems related to migration of oil from source to actual reservoir.

2.0 Conclusion

Crude oil is a complex mixture of Hydrocarbons, Alkanes, n-Alkanes, isoparoffizis, and naphihenes. Aromatic hydrocarbons, Naphtheno aromaties, hetero compounds, sulphur compounds, hydrocarbons & non hydrocarbon Type sulphur, Mercaptans basic nitrogen compounds, oxygen ompounds high inofecular weigt of nitrogen & sulphur compounds metallic Derivatives.

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