

University of Diyala

College of Engineering

Chem. Eng. Dept.

# **Properties of Petroleum and Natural Gas**

## **Second stage**

**Lecturer**

**Mohammed Hamzah Msaed**

## **Topics**

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Chapter 1 : Classification of Crude Oil.

Chapter 2: Physical and Chemical Properties of Crude Oil.

Chapter 3: Crude Oil Preparation for Refining.

Chapter 4: Refining ( Distillation ) of Crude Oil.

Chapter 5: Petroleum Products.

Chapter 6: Gases Production from Petroleum Products.

Chapter 7: Chemical Processes in Petrochemicals Industrials.

### References:

- 1- Petroleum Refinery Engineering , by W.L.Nelson.
- 2- Petrochemicals , by Hazim.K.Yahya. & Faaz.A.Jameel.
- 3- Industrial Chemistry for third stage, by Jewad. Al-Khafagy.
- 4- اساس الكيمياء الصناعية , by Mohammed.A.Ameen.

## **Chapter 1 : Classification of Crude Oil**

### **1- Introduction:**

Petroleum has been defined as Gaseous, liquid and solid mixture of hydrocarbon and non hydrocarbon components which are derivatives that occur naturally in the earth.

Gaseous hydrocarbon is composed of lighter fractions, of which the more common is methane ( CH<sub>4</sub> ) that refer to as natural gas. Liquid petroleum consists of the liquid hydrocarbon but also contain varying proportion of dissolved gases and bituminous materials , it is most commonly called crude oil. Solid and semisolid petroleum is consists of heavier fraction from hydrocarbon and bituminous materials and had been refer to as bituminous or asphalt.

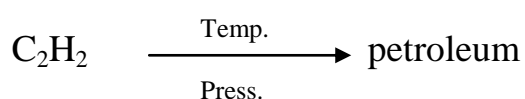
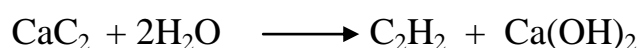
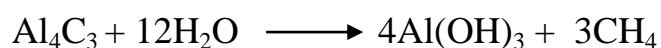
### **2- Definition of Petroleum :**

It is a mixture of hydrocarbon compounds and relatively small quantities of other materials such as oxygen, nitrogen, sulphur, salt , water, dissolved gases such as hydrogen sulphide ( H<sub>2</sub>S ) and trace amounts of metals such as iron, nickel, copper and vanadium.

**3- Origin of Petroleum :** Tow assumptions are explaining the formation of petroleum as follows:

#### **A- Inorganic hypothesis :**

This hypothesis 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:



## **B- Organic hypothesis :**

This hypothesis assume that the petroleum is formed from the decomposition of the animals and plants dead which converted to liquids and gases hydrocarbon by effect the high temperature, Pressure and catalyst ( as a small microscopic beings ) . Some sources suggest this hypothesis to explain the formation of the Arabian Gulf's petroleum.

## **4- Importance of petroleum :**

- a - It represent the major sources for energy in the world ( 45% crude oil and 15% natural gases).
- b – Electrical power generation.
- c – Fuel for cars, ships and airliners.
- d – Fuel for heating and cooking.
- e – It is used in petrochemicals industrials to produce various materials useful such as clothes, plastics, drugs, pipes, .....etc .
- f – It used for lubrication engines of different types.

## **5- Chemical analysis of crude oil :**

The proportion of hydrocarbons in the mixture is highly variable and ranges from as much as 97% by weight in the lighter oils to as little as 50% in the heavier oils and bitumen.

The exact molecular composition varies widely from formation to formation but the proportion of chemical elements vary over fairly narrow limits as follows:

<b>Element</b>	<b>Wt %</b>
C ( Carbon )	83 - 88
H <sub>2</sub> ( Hydrogen )	11 – 14
S ( Sulphur )	0.05 – 8
N <sub>2</sub> ( Nitrogen )	1 – 2
O <sub>2</sub> ( Oxygen )	0.05 – 1.5
Metals ( Fe , Ni , Cu , V , ..... )	< 0.03

## **6- Chemical composition of crude oil :**

The hydrocarbons in crude oil are mostly paraffin , naphthene, olefin and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium as follows :

### **A- Hydrocarbons components :**

All the petroleums contains the same hydrocarbons groups such as normal, branch, cyclic paraffins, olefins and aromatic. They generally have from 1 to 60 carbon atoms per molecule.

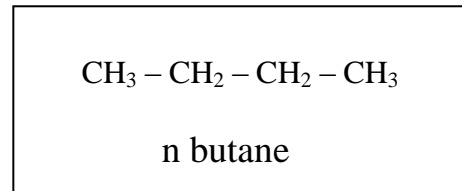
#### **I- Paraffins :**

The paraffins, also known as alkanes, are saturated hydrocarbons with straight, branched or cyclic chains which contain only carbon and hydrogen. It is found in different formula as follows:

**i- Normal /or series paraffins:**

The hydrocarbon chain is straight , the general formula  $C_nH_{2n+2}$  , example n butane mean  $n = 4 =$  carbon atoms (  $C_4H_{10}$  ). The properties of branch paraffins are:

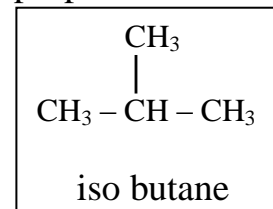
- High molecular weight.
- High boiling point.
- Low octane number.



**ii- Branch /or iso paraffins:**

The hydrocarbon chain is branched, the general formula  $C_nH_{2n+2}$  , example iso butane mean  $n = 4 =$  carbon atoms (  $C_4H_{10}$  ). The properties of branch paraffins are:

- Low boiling point.
- High octane number therefore is favorite in cars fuel.
- The common in crude oil is one branch and less tow branches.



**iii- Cycloparaffins ( Naphthenes ):**

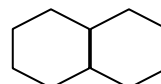
The cycloalkanes, also known as naphthenes, are saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula  $C_nH_{2n}$ . Cycloalkanes have similar properties to alkanes but have higher boiling points.



Cyclopentane



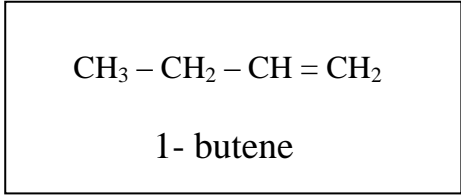
Cyclohexane



Decalin

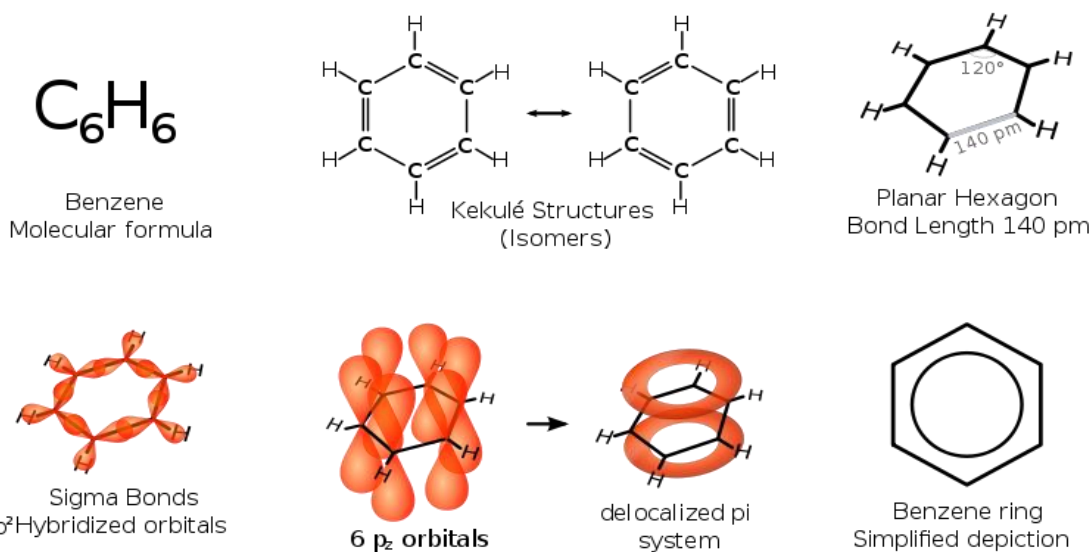
## II- Olefins:

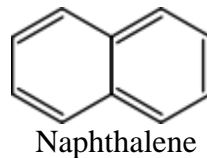
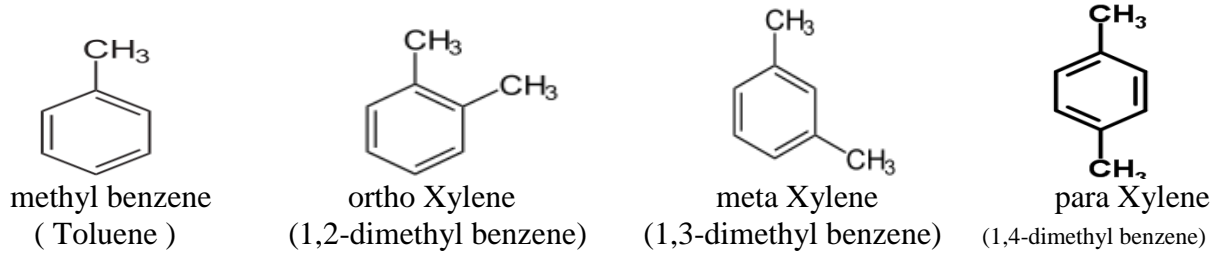
The olefins, also known as alkenes, are unsaturated hydrocarbons with general formula (  $C_nH_{2n}$  ). The low boiling olefins are probably not present in crude petroleum, but they are found in cracked products.



## III- Aromatics:

The aromatic hydrocarbons are unsaturated hydrocarbons which have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula (  $C_nH_n$  ) and many have a sweet aroma and a carcinogenic.





**B- Non hydrocarbons components :**

The non hydrocarbon components are caused :

- 1- Corrosion.
- 2- Break down in the refinery operation.

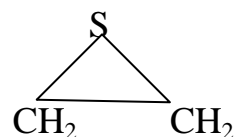
the non hydrocarbon components are divided to :

**I- Sulphur components :**

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

- i- Hydrogen Sulphide H- S- H ( or H<sub>2</sub>S )
- ii- Mercaptance : H- S- R , where R is Alkyl ( H- S- CH<sub>3</sub> ) .
- iii- Sulphides :

- \* Aliphatic sulphide : R- S- R
- \* Cyclo sulphide :



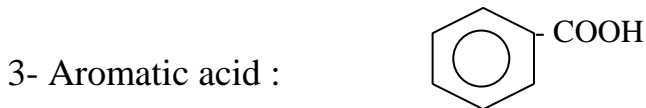
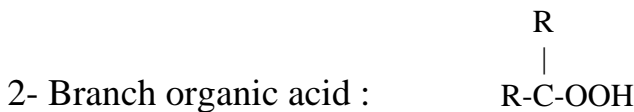
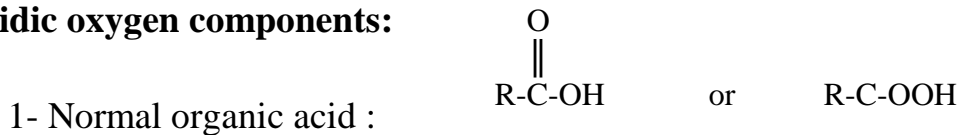
Disadvantages of Sulphur components:

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

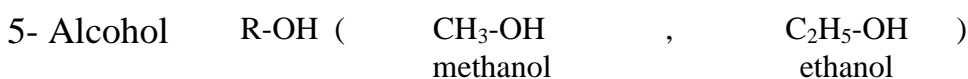
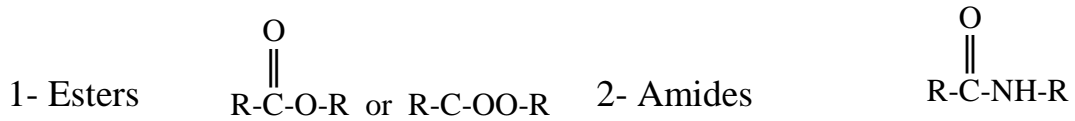
**II- Oxygen components :**

These compounds increase with increasing the ( b.p. = boiling point ) of the fraction. The types of oxygen components in the petroleum are :

**i- Acidic oxygen components:**



**ii- Non acidic oxygen components:**



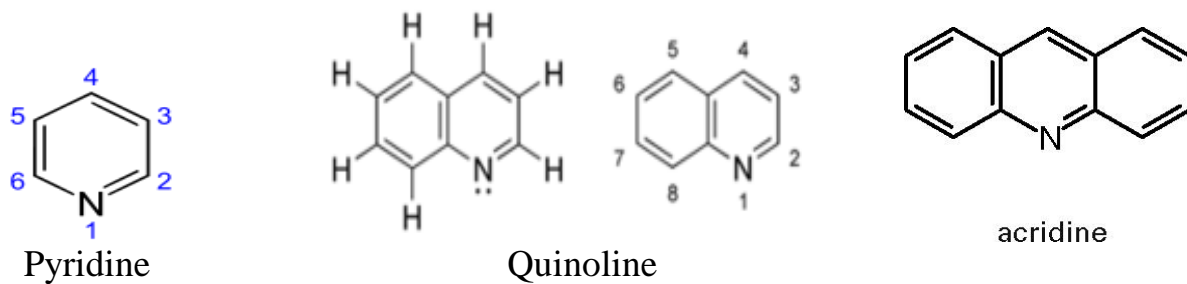
### III- Nitrogen components :

More asphaltic crudes will contain  $N_2$  compounds. They usually tolerate up to 0.25 wt%.

Disadvantages:

- 1- Can poison catalysts.
- 2- Increased carbon residue .
- 3- Decreased API.

Types of nitrogen components in the petroleum :



### IV- Metallic components :

Disadvantages :

- 1- Affected on catalyst activity.
- 2- Coke formation.
- 3- Reduced the yield of the gasoline.
- 4- Form ash deposits-power generation plants.
- 5- Corrosion.

Types of metallic components in the petroleum :

- 1- Organic metallic ( Iron Fe , Nickel Ni , Vanadium V , Cadmium Cd,...).
- 2- Soap metallic ( Magnesium Mg , Calcium Ca , ..... ).
- 3- Salt metallic ( Na<sup>+</sup> , Ba<sup>2+</sup> , .... ).

## **VI- 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<sup>+</sup> , Ba<sup>2+</sup> , Mg<sup>2+</sup> , Al<sup>3+</sup> , ..... ).
- 2- Negative ions ( Cl<sup>-</sup> , Br<sup>-</sup> , SO<sub>4</sub><sup>2-</sup> , I<sup>-</sup> , ..... ).

## **7- Classification of crude oil :**

Classification of crude oil refers to natural and type of crude oil ( type of hydrocarbons in crude oil ) by simplified tests. Four mainly methods are used:

### **A- Watson characterization factor ( K<sub>w</sub> ) :**

Watson characterization factor ( k) can be calculated from following equation :

$$K_w = \frac{\sqrt[3]{T_{av.bo.po.}}}{Sp.Gr.60 / 60^{\circ}F}$$

Where :

$K_w$  = Watson characterization factor.

$T_{av.bo.po.}$  = average boiling point temperature =  $T_{av. volume} - \Delta t$

$T_{av. volume}$  = average volume temperature.

$\Delta t$  = correction factor = slope of distillation curve.

Correction factor ( $\Delta t$ ) is calculating as a slope of distillation curve for distillation crude oil sample experiment data according ASTM method.

ASTM = American Society for Testing and Materials.

Sp.Gr. 60/60 °F = Specific Gravity at 15°C (60 °F)

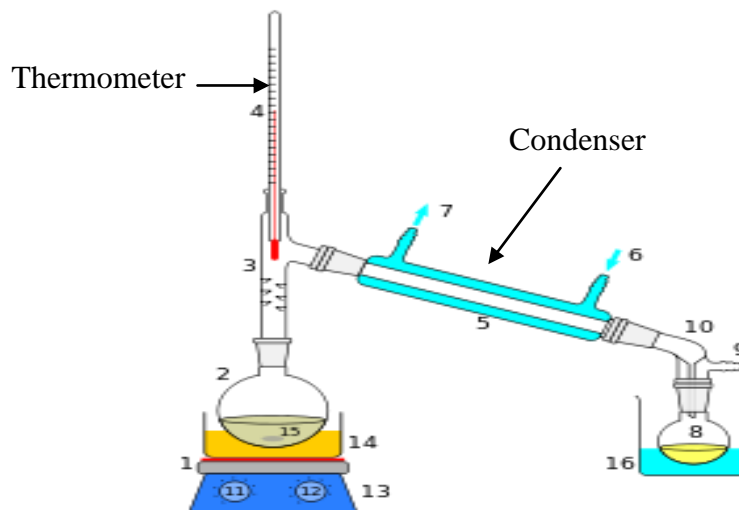
$$Sp.Gr.60/60 \text{ } ^\circ F = \frac{\text{Crude oil density at } 60 \text{ } ^\circ F}{\text{Water density at } 60 \text{ } ^\circ F}$$

Note :

Temperature in Rankin unit ( °R ).

Temperature convertor relationships :

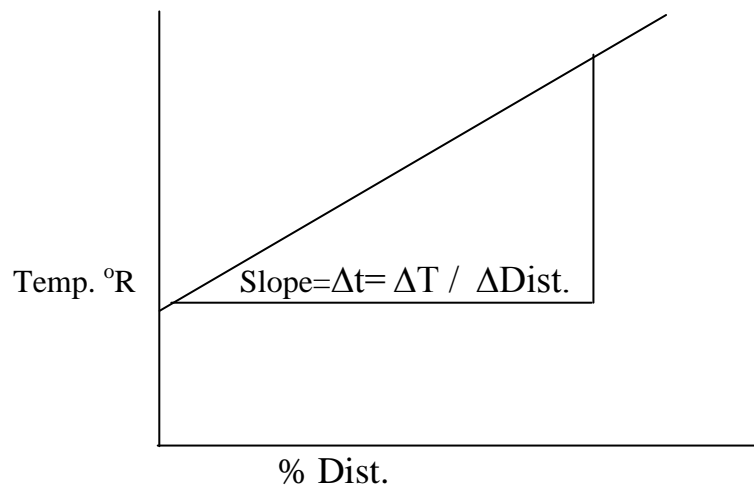
From	To	Formulae
Celsius	Fahrenheit	$F = C \times 1.8 + 32$
Celsius	kelvin	$K = C + 273.15$
Celsius	Rankin	$Ra = C \times 1.8 + 32 + 459.67$



Crude oil 100ml

Distillate %

% Distillate	Temp. °F
0	T <sub>0</sub> = IBP
10	T1
20	T2
30	T3
40	T4
50	T5
60	T6
70	T7
80	T8
90	T9
95	T10=FBP



IBP=Initial Boiling Point at 0% distillate.

FBP=Final Boiling Point at stop distillate.

$$T_{av. volume} = ( T1+T2+T3+T4+T5+T6+T7+T8+T9 ) / 9$$

$$\Delta t = slope = ( T9 - T1 ) / ( 90 - 10 ) = ( T9 - T1 ) / 80$$

Crude oil classified by Watson characterization factor as follows :

- 1- K = 12.15 – 12.9            paraffinic ( or light ) based crude oil
- 2- K = 11.5 – 12.1            mixed ( or intermediate ) based crude oil
- 3- K = 10.5 – 11.45           naphthenic ( asphaltic or heavy ) based crude oil

**B- Key Fraction ( API gravity ) :**

API = American Petroleum Institute

The formula to obtain API gravity of petroleum liquids, from specific gravity is:

$$APIgravity = \frac{141.5}{Sp.Gr_{60/60^\circ F}} - 131.5$$

Crude oil classified by API gravity according to distillate pressure as follows:

1- when the distillate at atmospheric pressure ( Press. = 1 atm ) as follows :

- 1- API gravity > 40                      paraffinic ( or light ) based crude oil
- 2- API gravity = 33 - 40              mixed ( or intermediate ) based crude oil
- 3- API gravity < 33                  naphthenic ( asphaltic or heavy ) based crude oil

2- when the distillate at vacuum pressure ( Press. = 40 mmHg ) as follows :

- 4- API gravity > 30                      paraffinic ( or light ) based crude oil
- 5- API gravity = 20 - 30              mixed ( or intermediate ) based crude oil
- 6- API gravity < 20                  naphthenic ( asphaltic or heavy ) based crude oil

**C - Sulfur Content :**

Crude oil naturally contains sulfur compounds. Crudes are classed as sweet or sour depending on their sulfur content. If a crude has less than 0.5% sulfur in it, it is considered to be " sweet crude oil ". If has greater than 2.5% sulfur, it is " sour crude oil ". A crude with a sulfur content between these two endpoints is called " intermediate ".

**D – Correlation Index ( C.I. ) :**

This method based on the percentages of various hydrocarbons types in the crude oil which are classified into paraffinic or aromatic according to following formula :

$$C.I. = \frac{48640}{T_{av.bo.po.}} + 473.3 * Sp.Gr.(60/60)^{\circ} F - 456.8$$

Where :

$T_{av.bo.po.}$  = average boiling point temperature , in Kelvin unit (  $^{\circ}K$  ).

Sp. Gr. ( 60/60) $^{\circ}F$  = specific gravity of crude oil at 60 $^{\circ}F$ .

The crude oil can be classify as follow as :

- i) C.I. = 0 ( normal paraffinic based crude oil ).
- ii) C.I = 0-15 ( predominance of n-paraffinic crude oil ).
- iii) C.I = 15 – 50 ( paraffinic and aromatic mixture ).
- iv) C.I > 50 ( predominance of aromatic crude oil ).
- v) C.I = 100 benzene ( Aromatic )

## 8 - Crude oil and gas reservoirs:

Three conditions must be present for oil reservoirs to form:

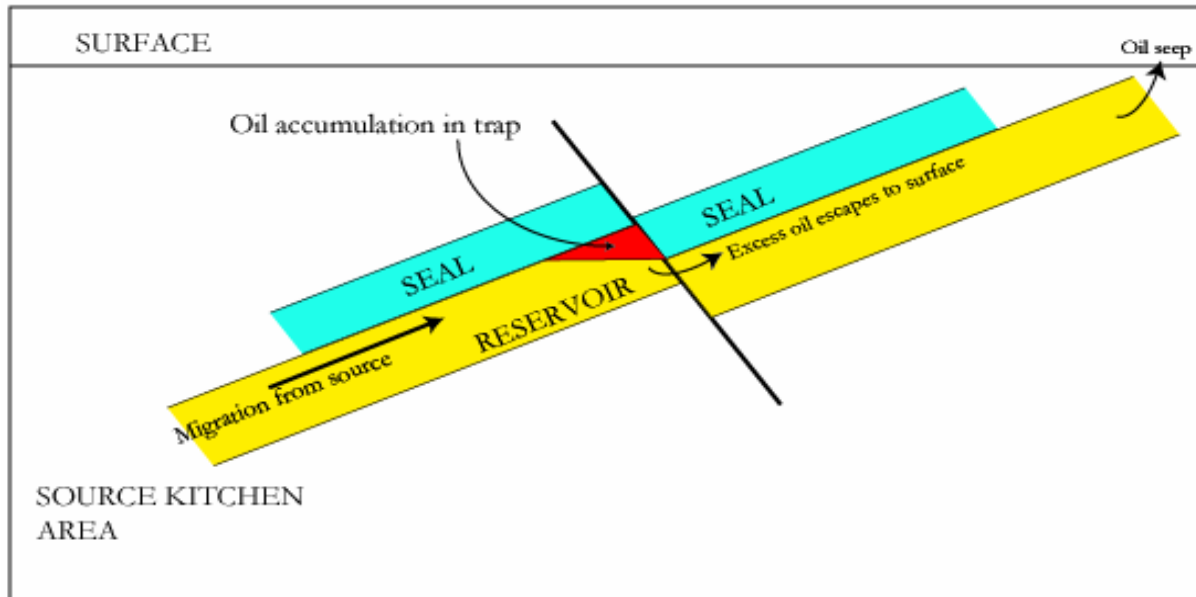
I- A source rock rich in hydrocarbon material buried deep enough for

subterranean heat to cook it into oil.

II- A porous and permeable reservoir rock for it to accumulate in.

III-A cap rock (seal) or other mechanism that prevents it from escaping to

the surface.

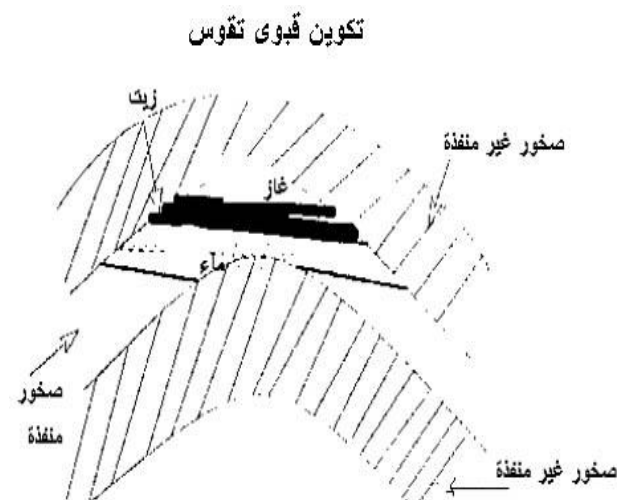


Within these reservoirs, fluids will typically organize themselves like a three-layer cake with a layer of water below the oil layer and a layer of gas above it, although the different layers vary in size between reservoirs.

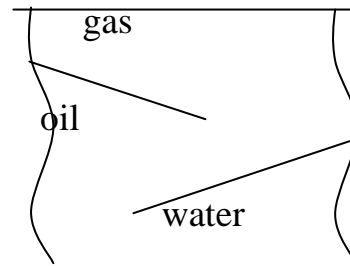
Most reservoir rocks are sedimentary rocks, including sandstone , limestone and dolomite (  $Mg CO_3$  ). Typical cap rocks are clay, shale and dense limestone.

Types of traps :

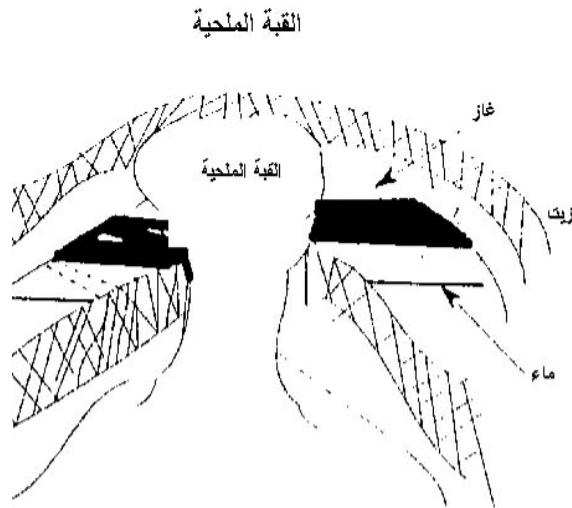
- 1- Folds ( anticline ).



2- Fault and wedge out traps.



3- Salt dome.



## Chapter 2: Physical and Chemical Properties of Crude Oil.

### A- Mechanical properties : ( Density , Viscosity , Surface tension )

**1- Density :** Density is defined as mass per unit volume. Density is a state function depends on both temperature and pressure . Liquid densities decrease as temperature increases but the effect of pressure on liquid densities at moderate pressures is usually negligible. Liquid density for hydrocarbons is usually reported in terms of specific gravity (SG) or relative density defined as

$$SG = \frac{\text{density of liquid at temperature T}}{\text{density of water at temperature T}}$$

Since the standard conditions adopted by the petroleum industry are 60 °F (15.5 ° C) and 1 atm, specific gravities of liquid hydrocarbons are normally reported at these conditions. At a reference temperature of 60°F (15.5°F) the density of liquid water is 0.999 g/cm<sup>3</sup> (999 kg/m<sup>3</sup>). Therefore, for a hydrocarbon or a petroleum fraction, the specific gravity is defined as :

$$SG (60^{\circ}F/ 60^{\circ}F) = \frac{\text{density of petroleum at } 60^{\circ}F \text{ in } g/cm^3}{0.999 g/cm^3}$$

Water density at 60°F is 0.999 or almost 1 g/cm<sup>3</sup>; therefore, values of specific gravities are nearly the same as the density of liquid at 15.5°C in g/cm<sup>3</sup>. The specific gravity is useful in terms of API gravity, characterization factor and indication of fluid flow of petroleum.

### Coefficient of thermal expansion (γ) :

The density of any liquid is of course a function of the temperature, there being expansion as the temperature rises therefore a reduction in the density. The

quantity relevant to this is the coefficient of thermal expansion, ( symbol  $\gamma$  ) defined by :

$$SG \text{ at } T_F = SG (60^\circ F / 60^\circ F) - \gamma ( T_F - 60 )$$

Where :

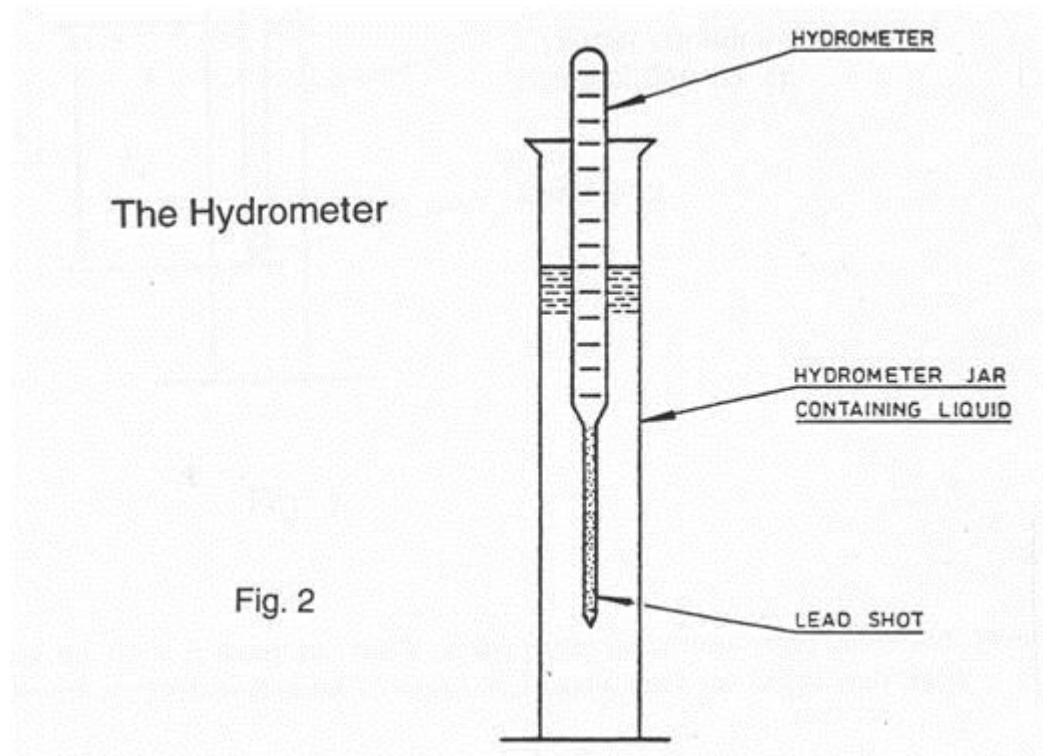
$SG ( 60^\circ F / 60^\circ F )$  : Specific Gravity at standard temperature (  $60^\circ F$  ).

$SG \text{ at } T_F$  : Specific Gravity at any temperature (  $^\circ F$  ).

$\gamma$  : Coefficient of thermal expansion = 0.000517 – 0.000897

$T_F$  = Any temperature (  $^\circ F$  ).

The Specific Gravity at any temperature can be also determine approximately from Figure ( 5-14) in Nelson. The density can determinate by hydrometer method.



## 2- Viscosity:

Is a measurement for internal friction coefficient for two liquid ( oil ) layers each areas are  $1 \text{ m}^2$ . It is needed in calculation of power required in mixers or to transfer a fluid, the amount of pressure drop in a pipe or column, flow measurement devices.

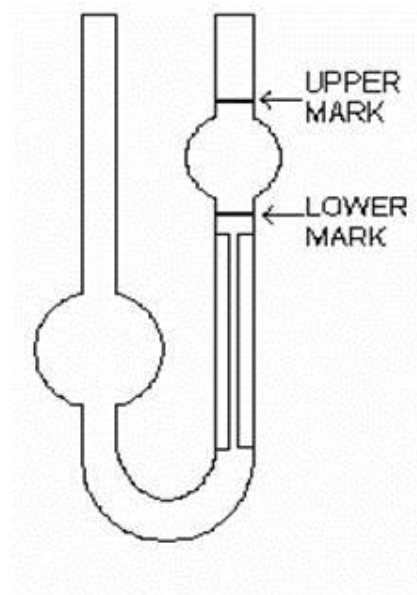
Types of viscosity:

- 1- Dynamic viscosity ( $\mu$ ) with units ( *poise* or  $\text{g} / (\text{cm} \cdot \text{s})$  ).
- 2- Kinematic viscosity ( $\nu$ ) with unit ( *stoke* or  $\text{cm}^2 / \text{s}$  ).

Kinematic viscosity is defined as the ratio of absolute viscosity (dynamic) to absolute density ( $\rho$ ) at the same temperature in the following form:

$$\nu = \mu / \rho$$

The kinematic viscosity can be measurement by viscometer ( U-tube device ) by following equation :



U- tube viscometer

$$v = c \cdot t$$

where :

v : kinematic viscosity ( St. )

c : viscometer constant (  $\text{mm}^2/\text{s}^2$  ) .

t : time required to passing the oil through the limited marks in viscometer ( s ) .

**Viscosity Index :**

The viscosity index is a number indicating the effect of change of temperature on the kinematic viscosity of an oil. A high viscosity index signifies a relatively small change of kinematic viscosity with temperature. Viscosity index increasing with paraffin and decreasing with naphthene.

VI=100 (best oil, paraffinic)

VI=0 (lowest VI oil, naphthenic)

Viscosity index calculated as the following cases :

**I – For VI = 0 – 100 :**       $VI = \left( \frac{L - U}{L - H} \right) * 100$

**II – For VI > 100 :**       $VI = \left( \frac{\text{anti log } N - 1}{0.00715} \right) + 100$

$$N = \frac{\log H - \log U}{\log Y}$$

Where:

Y = kinematic viscosity of oil in centistokes at 100 °C.

$U$  = kinematic viscosity of oil in centistokes at 40 °C .

$L$  = kinematic viscosity in centistokes at 40 °C of an oil of 0 viscosity index and

having the same kinematic viscosity at 100 °C as the oil whose viscosity

index is to be calculated.  $L$  determinate from table until  $Y=70$  cSt and from the following equation for  $Y$  above 70 cSt :

$$\mathbf{L = 0.8353 Y^2 + 14.67 Y - 216.25}$$

$H$  = kinematic viscosity in centistokes at 40 °C of an oil of 100 viscosity index,

and having the same kinematic viscosity at 100 °C as the oil whose viscosity

index is to be calculated.  $H$  determinate from tables or from the following

equation :

$$\mathbf{H = 0.1684 Y^2 + 11.85 Y - 96.95}$$



TABLE 1 Basic Values for L and H for Kinematic Viscosity in 40–100°C System

Kinematic Viscosity at 100°C, mm <sup>2</sup> /s (cSt)	L		H		Kinematic Viscosity at 100°C, mm <sup>2</sup> /s (cSt)	L		H		Kinematic Viscosity at 100°C, mm <sup>2</sup> /s (cSt)	L		H		Kinematic Viscosity at 100°C, mm <sup>2</sup> /s (cSt)	L		H		
	L	H	L	H		L	H	L	H		L	H	L	H		L	H			
2.00	7.994	6.394	7.00	78.00	48.57	12.0	201.9	108.0	17.0	369.4	180.2	24.0	683.9	301.8	42.5	1935	714.9			
2.10	8.640	6.894	7.10	80.25	49.61	12.1	204.8	109.4	17.1	373.3	181.7	24.2	694.5	305.6	43.0	1978	728.2			
2.20	9.309	7.410	7.20	82.39	50.69	12.2	207.8	110.7	17.2	377.1	183.3	24.4	704.2	309.4	43.5	2021	741.3			
2.30	10.00	7.944	7.30	84.53	51.78	12.3	210.7	112.0	17.3	381.0	184.9	24.6	714.9	313.0	44.0	2064	754.4			
2.40	10.71	8.496	7.40	86.66	52.88	12.4	213.6	113.3	17.4	384.9	186.5	24.8	725.7	317.0	44.5	2108	767.6			
2.50	11.45	9.063	7.50	88.85	53.98	12.5	216.6	114.7	17.5	388.9	188.1	25.0	736.5	320.9	45.0	2152	780.9			
2.60	12.21	9.647	7.60	91.04	55.09	12.6	219.6	116.0	17.6	392.7	189.7	25.2	747.2	324.9	45.5	2197	794.5			
2.70	13.00	10.25	7.70	93.20	56.20	12.7	222.6	117.4	17.7	396.7	191.3	25.4	758.2	328.8	46.0	2243	808.2			
2.80	13.80	10.87	7.80	95.43	57.31	12.8	225.7	118.7	17.8	400.7	192.9	25.6	769.3	332.7	46.5	2288	821.9			
2.90	14.63	11.50	7.90	97.72	58.45	12.9	228.8	120.1	17.9	404.6	194.6	25.8	779.7	336.7	47.0	2333	835.5			
3.00	15.49	12.15	8.00	100.0	59.60	13.0	231.9	121.5	18.0	408.6	196.2	26.0	790.4	340.5	47.5	2380	849.2			
3.10	16.36	12.82	8.10	102.3	60.74	13.1	235.0	122.9	18.1	412.6	197.8	26.2	801.6	344.4	48.0	2426	863.0			
3.20	17.26	13.51	8.20	104.6	61.89	13.2	238.1	124.2	18.2	416.7	199.4	26.4	812.8	348.4	48.5	2473	876.9			
3.30	18.18	14.21	8.30	106.9	63.05	13.3	241.2	125.6	18.3	420.7	201.0	26.6	824.1	352.3	49.0	2521	890.9			
3.40	19.12	14.93	8.40	109.2	64.18	13.4	244.3	127.0	18.4	424.9	202.6	26.8	835.5	356.4	49.5	2570	905.3			
3.50	20.09	15.66	8.50	111.5	65.32	13.5	247.4	128.4	18.5	429.0	204.3	27.0	847.0	360.5	50.0	2618	919.6			
3.60	21.08	16.42	8.60	113.9	66.48	13.6	250.6	129.8	18.6	433.2	205.9	27.2	857.5	364.6	50.5	2667	933.6			
3.70	22.09	17.19	8.70	116.2	67.64	13.7	253.8	131.2	18.7	437.3	207.6	27.4	869.0	368.3	51.0	2717	948.2			
3.80	23.13	17.97	8.80	118.5	68.79	13.8	257.0	132.6	18.8	441.5	209.3	27.6	880.6	372.3	51.5	2767	962.9			
3.90	24.19	18.77	8.90	120.9	69.94	13.9	260.1	134.0	18.9	445.7	211.0	27.8	892.3	376.4	52.0	2817	977.5			
4.00	25.32	19.56	9.00	123.3	71.10	14.0	263.3	135.4	19.0	449.9	212.7	28.0	904.1	380.6	52.5	2867	992.1			
4.10	26.50	20.37	9.10	125.7	72.27	14.1	266.6	136.8	19.1	454.2	214.4	28.2	915.8	384.6	53.0	2918	1007			
4.20	27.75	21.21	9.20	128.0	73.42	14.2	269.8	138.2	19.2	458.4	216.1	28.4	927.6	388.8	53.5	2969	1021			
4.30	29.07	22.05	9.30	130.4	74.57	14.3	273.0	139.6	19.3	462.7	217.7	28.6	938.6	393.0	54.0	3020	1036			
4.40	30.48	22.92	9.40	132.8	75.73	14.4	276.3	141.0	19.4	467.0	219.4	28.8	951.2	396.6	54.5	3073	1051			
4.50	31.96	23.81	9.50	135.3	76.91	14.5	279.6	142.4	19.5	471.3	221.1	29.0	963.4	401.1	55.0	3126	1066			
4.60	33.52	24.71	9.60	137.7	78.08	14.6	283.0	143.9	19.6	475.7	222.8	29.2	975.4	405.3	55.5	3180	1082			
4.70	35.13	25.63	9.70	140.1	79.27	14.7	286.4	145.3	19.7	479.7	224.5	29.4	987.1	409.5	56.0	3233	1097			
4.80	36.79	26.57	9.80	142.7	80.46	14.8	289.7	146.8	19.8	483.9	226.2	29.6	998.9	413.5	56.5	3286	1112			
4.90	38.50	27.53	9.90	145.2	81.67	14.9	293.0	148.2	19.9	488.6	227.7	29.8	1011	417.6	57.0	3340	1127			
5.00	40.23	28.49	10.0	147.7	82.87	15.0	296.5	149.7	20.0	493.2	229.5	30.0	1023	421.7	57.5	3396	1143			
5.10	41.99	29.46	10.1	150.3	84.08	15.1	300.0	151.2	20.2	501.5	233.0	30.5	1055	432.4	58.0	3452	1159			
5.20	43.76	30.43	10.2	152.9	85.30	15.2	303.4	152.6	20.4	510.8	236.4	31.0	1086	443.2	58.5	3507	1175			
5.30	45.53	31.40	10.3	155.4	86.51	15.3	306.9	154.1	20.6	519.9	240.1	31.5	1119	454.0	59.0	3563	1190			
5.40	47.31	32.37	10.4	158.0	87.72	15.4	310.3	155.6	20.8	528.8	243.5	32.0	1151	464.9	59.5	3619	1206			
5.50	49.09	33.34	10.5	160.6	88.95	15.5	313.9	157.0	21.0	538.4	247.1	32.5	1184	475.9	60.0	3676	1222			
5.60	50.87	34.32	10.6	163.2	90.19	15.6	317.5	158.6	21.2	547.5	250.7	33.0	1217	487.0	60.5	3734	1238			
5.70	52.64	35.29	10.7	165.8	91.40	15.7	321.1	160.1	21.4	556.7	254.2	33.5	1251	498.1	61.0	3792	1254			
5.80	54.42	36.26	10.8	168.5	92.65	15.8	324.6	161.6	21.6	566.4	257.8	34.0	1286	509.6	61.5	3850	1270			
5.90	56.20	37.23	10.9	171.2	93.92	15.9	328.3	163.1	21.8	575.6	261.5	34.5	1321	521.1	62.0	3908	1286			
6.00	57.97	38.19	11.0	173.9	95.19	16.0	331.9	164.6	22.0	585.2	264.9	35.0	1356	532.5	62.5	3966	1303			
6.10	59.74	39.17	11.1	176.6	96.45	16.1	335.5	166.1	22.2	595.0	268.6	35.5	1391	544.0	63.0	4026	1319			
6.20	61.52	40.15	11.2	179.4	97.71	16.2	339.2	167.7	22.4	604.3	272.3	36.0	1427	555.6	63.5	4087	1336			
6.30	63.32	41.13	11.3	182.1	98.97	16.3	342.9	169.2	22.6	614.2	275.8	36.5	1464	567.1	64.0	4147	1352			
6.40	65.18	42.14	11.4	184.9	100.2	16.4	346.6	170.7	22.8	624.1	279.6	37.0	1501	579.3	64.5	4207	1369			
6.50	67.12	43.18	11.5	187.6	101.5	16.5	350.3	172.3	23.0	633.6	283.3	37.5	1538	591.3	65.0	4268	1386			
6.60	69.16	44.24	11.6	190.4	102.8	16.6	354.1	173.8	23.2	643.4	286.8	38.0	1575	603.1	65.5	4329	1402			
6.70	71.29	45.33	11.7	193.3	104.1	16.7	358.0	175.4	23.4	653.8	290.5	38.5	1613	615.0	66.0	4392	1419			
6.80	73.48	46.44	11.8	196.2	105.4	16.8	361.7	177.0	23.6	663.3	294.4	39.0	1651	627.1	66.5	4455	1436			
6.90	75.72	47.51	11.9	199.0	106.7	16.9	365.6	178.6	23.8	673.7	297.9	39.5	1691	639.2	67.0	4517	1454			
													40.0	1730	651.8	67.5	4580	1471		
													40.5	1770	664.2	68.0	4645	1488		
													41.0	1810	676.6	68.5	4709	1506		
													41.5	1851	689.1	69.0	4773	1523		
													42.0	1892	701.9	69.5	4839	1541		
																70.0	4905	1558		

**Note :**

If we need to obtain the intermediate value can be used interpolation method as follows :

Ex:

Y	L	H
20.4	510.8	236.4
20.5	L	H
20.6	519.9	240.1

$$\frac{(20.4) L}{(20.5)(510.8)} = \frac{(20.5)(519.9)}{(20.6) L}$$

$$420.24 L^2 = 111603657.6 \rightarrow \boxed{L = 515.3}$$

$$\frac{(20.4) H}{(20.5)(236.4)} = \frac{(20.5)(240.1)}{(20.6) H}$$

$$\boxed{H = 238.2}$$

### **3 - Surface tension or interfacial tension ( IFT ) :**

Is a measurement of a tensile force between molecules at the separator surface between two states of substance ( solid – liquid , liquid – gas ). Volatility of petroleum fractions is increasing with surface tension decreasing. So the gasoline is highly volatility because low surface tension.

### **B - Thermal properties :**

#### **1- Cloud Point ( T<sub>c</sub> ) :**

The cloud point is the lowest temperature at which wax crystals begin to form by a gradual cooling under standard conditions. As temperature decreases below the cloud point, formation of wax crystals is accelerated. Therefore, low cloud point products are desirable under low-temperature conditions.

#### **2- Pour Point ( T<sub>p</sub> ):**

The pour point of a petroleum fraction is the lowest temperature at which the oil will pour or flow when it is cooled without stirring under standard cooling conditions. Pour point is one of low temperature characteristics of heavy fractions. When temperature is less than pour point of a petroleum product it cannot be stored or transferred through a pipeline.

Presence of wax and heavy compounds increase the pour point of petroleum fractions. Can be estimate the pour point of petroleum fractions from viscosity, molecular weight, and specific gravity in the following form:

$$T_p = 130.47[ SG^{2.97} ] \times [ M^{(0.61- 0.47SG)} ] \times [ \nu_{38(100)}^{(0.31- 0.33SG)} ]$$

Where:

$T_p$  : pour point temperature in kelvin.

SG : specific gravity at standard temperature .

M : molecular weigh.

$U_{38(100)}$ : kinematic viscosity at 38°C(100°F) in cSt.

### **3- Freezing Point:**

Freezing point is the temperature at which liquid solidifies at 1 atm pressure.

### **4- Melting Point ( $T_M$ ) :**

Melting point is the temperature that a solid substance liquefies at 1 atm. The melting point increases with molecular weight increases. A pure substance has the same freezing and melting points.

## **C- Optical properties:**

### **1- Boiling point :**

The boiling point of a pure compound at a given pressure is the temperature at which vapor and liquid exist together at equilibrium. If the pressure is 1 atm, the boiling point is called the normal boiling point . At this temperature the vapor pressure will equal to atm pressure.

### **2- Vapor Pressure ( $P^{vap}$ ) :**

In a closed container, the vapor pressure of a pure compound is the force exerted per unit area of walls by the vaporized portion of the liquid. Vapor pressure can also be defined as a pressure at which vapor and liquid phases of a

pure substance are in equilibrium with each other. Vapor pressure increases with temperature. The vapor pressure is also called saturation pressure,  $p^{\text{sat}}$ .

### **3- Flash Point ( $T_F$ ) :**

Flash point of petroleum fractions is the lowest temperature at which vapors arising from the oil will ignite, i.e. flash, when exposed to a spark or flame under specified conditions. Therefore, the flash point of a fuel indicates the maximum temperature that it can be stored without serious fire hazard.

A simple relation for estimation of flash point of hydrocarbon mixtures from vapor pressure was proposed by the below formula :

$$T_F = 231.2 - 40 \log P^{\text{vap}}$$

Where :  $p^{\text{vap}}$  is the vapor pressure at 37.8°C (100°F ) in bar.

$T_F$  : is the flash point in kelvin

### **4- Fire Point :**

Fire point of petroleum fractions is the lowest temperature at which vapors arising from the oil will ignite, i.e. fire, when exposed to a spark or flame under specified conditions. Therefore, the fire point of a fuel indicates the maximum temperature that it must not arrival to it to prevent the combustion of the petroleum fractions.

### **5- Autoignition Point :**

This is the minimum temperature at which hydrocarbon vapor when mixed with air can spontaneously ignite without the presence of any external source. Values of autoignition temperature are generally higher than flash point, Values of autoignition temperature for gasoline it is about 350 °C ( 660 °F ) and

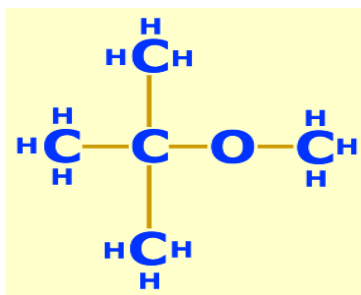
for alcohol is about 500 °C ( 930 °F ). With an increase in pressure the autoignition temperature decreases.

### 6- Octane number:

Octane number defined is a measure of fuel's ability to resist auto-ignition during compression and prior to ignition to prevent the anti-knock characteristic.

Higher octane number fuels have better engine performance so high octane number fuels are more desirable. Generally iso paraffins have higher octane number than do normal paraffins. Naphthenes have relatively higher octane number than do corresponding paraffins and aromatics have very high octane numbers.

The octane number of a fuel can be improved by adding tetraethyl- lead (TEL) (CH<sub>3</sub>CH<sub>2</sub>)<sub>4</sub>Pb ) or methyl-tertiary-butyl-ether (MTBE)



methyl-tertiary-butyl-ether (MTBE).

### REASERCH OCTANE NUMBER OF PURE HYDROCARBONS

Paraffins	ON	Iso Paraffins	ON	Olefins	ON	Naphthenes	ON	Aromatics	ON
n-butane	94	Iso butane	102	n-butene	99				
n-pentane	62	i-pentane	92	n-pentene	90	Cyclo pentane	100		
n-hexane	25	i-hexane	76	n-hexene	90	Cyclo hexane	91	benzene	103

**A > N > O > Iso P > P**

## 7- Aniline point ( AP ) :

Aniline point of a petroleum fraction is defined as the minimum temperature at which equal volumes of aniline and the oil are completely miscible. The higher aniline point with the lower aromatic content and the higher paraffin content. Aniline is an aromatic compound with a structure of a benzene molecule where one atom of hydrogen is replaced by the  $-NH_2$  group ( $C_6H_5-NH_2$ ).

The aromatic content in petroleum fraction may be calculated from aniline point by the following formula :

$$\%A = 692.4 + 12.15 (SG) (AP) - 794 (SG) - 10.4 (AP)$$

Where: %A is the percent aromatic content, SG is the specific gravity, and AP is the aniline point in °C.

## 8- Diesel index ( DI ) :

Diesel index is a number indicate to favours auto-ignition of diesel engines. The diesel fuel considered is best with high diesel index. Diesel index calculated from the following formula :

$$DI = ( API ) ( 1.8 AP + 32 ) / 100$$

Where: AP is the aniline point in °C.

## 9- Specific Heat

Specific heat is definition as the quantity of heat required to raise the temperature of a unit weight of petroleum fraction through a temperature

difference of one degree, measurement in ( KJ/Kg .°C or Kcal/Kg .°C or Btu / lb.°F ). Specific heat of petroleum fractions lies in the range of ( 0.3 to 0.85 ) and depends upon temperature and gravity. Lighter fractions have higher values. With increasing density the specific heat decrease. Specific Heat calculated from standard formula :

$$Sp.heat = \frac{1}{SG(60/60)^o F} (0.4024 + 0.00081T)$$

Where:

Sp.heat is the specific heat in kj / kg. °C .

SG is the specific gravity of petroleum fraction at (60/60) °F.

T is a temperature in °C.

## **10- volatility**

The volatility of a liquid is its tendency to change from the liquid to the vapor or gaseous state at any given temperature.

## **11- Refractive index**

Refractive index is an indicator used for light and medium petroleum fractions, usually it is higher for aromatics, lower for paraffins and medium for naphthenes. It is increasing with increase the molecular weight.