

Salahaddin university-College of science education
Chemistry department
Petrochemistry laboratory
Exp.1: Evaluation of petroleum and its products by distillation

Simple distillation:

Distillation, a method of separation, is the most commonly used method of purification for liquid samples. As part of the distillation process, you will obtain the boiling point range of both components of your mixture. The better your separation, the more accurate your boiling points will be.

Both boiling point and refractive index are physical properties that are used to characterize organic liquids and give some indication of their purity. You will use the boiling points and to assess how well the mixture was separated using each method of distillation.

Boiling point principles:

The boiling points of organic compounds can give important clues to other physical properties. A liquid boils when its vapour pressure is equal to the atmospheric pressure. Vapour pressure is determined by the kinetic energy of molecules. Kinetic energy is related to temperature and the mass and velocity of the molecules. When the temperature reaches the boiling point, the average kinetic energy of the liquid particles is sufficient to overcome the forces of attraction that hold molecules in the liquid state. Then these molecules break away from the liquid forming the gas state.

Molecules which strongly interact or bond with each other through a variety of intermolecular forces can not move easily or rapidly and therefore, do not achieve the kinetic energy necessary to escape the liquid state. Therefore, molecules with strong intermolecular forces will have higher boiling points. This is a consequence of the increased kinetic energy needed to break the intermolecular bonds so that individual

molecules may escape the liquid as gases. The boiling point can be a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors.

Simple fractional distillation:

Fractional distillation is a method to separate mixtures of liquids with boiling points that are close to each other. It uses the same principles as simple distillation, but it involves the separation of different liquids rather than the isolation of impurities or the most volatile component.

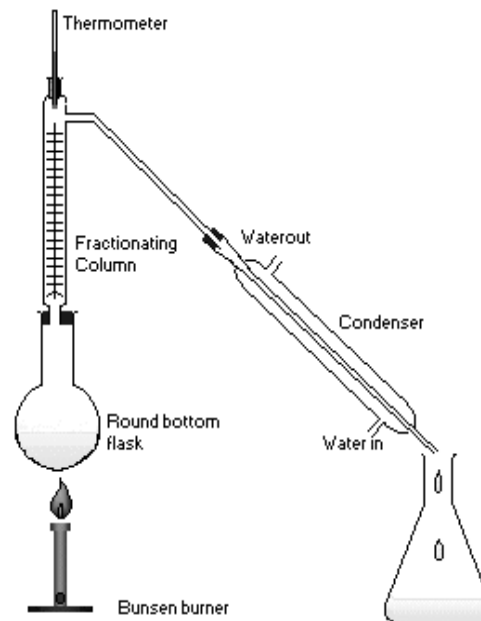
When a solution is distilled in fractions, it passes through a series of redistillations that increase the purity of the final products. The distillation column (condenser) used in a simple distillation is packed with a nonreactive material in order to increase the surface area. This is referred to as a fractionating column. As the liquid is heated, vapor will begin to rise. The vapors condense as they come in contact with the cooler surfaces in the fractionating column. Continued heating of the liquid causes more vapors to rise. The condensed vapors in the column re-vaporize and move up the column. As this process is repeated many times, the component which vaporizes the easiest (lowest boiling point) reaches the top of the column first and is collected in the collection vial. The other components will be collected in order of ascending boiling points.

This process is also useful in separating mixtures with many different liquids. Crude oil, for example, is separated in towers that are 150 feet high. One hundred different components are separated from 200,000 barrels of crude oil per day.

Apparatus:

Fractional distillation in a laboratory makes use of common laboratory glassware, as well as some single-purpose items like a fractionating column and "pigs" and "cows" used to cut fractions.

- 1- Heat source, such as a hot plate with a bath.
- 2- Distilling flask, typically a round-bottom flask.
- 3- Receiving flask, often also a round-bottom flask.
- 4- Fractionating column.
- 5- Distillation head.
- 6- Thermometer and adapter if needed.
- 7- Condenser.
- 8- Vacuum adapter (not used in upper right image).
- 9- Boiling chips, also known as anti-bumping granules.



The cut types of petrol can be illustrated as follows

<u>Cut</u>	<u>Boiling range</u>
Upper	25- 95
Part (light gasoline)	
Naphtha	95 -150
Kerosene	150 – 230
Oil gas	230 – 340

Fractional vacuum distillation:

Is similar to the normal or simple fractional distillation except in this type the fractional column used is big in diameter in order to stabilize the speed of the vapor at vacuum pressure; this pressure generated by using steam rejecters; i.e. the low volatile parts can be distilled without increasing the temperature to the range which leads to the thermal cracking reactions if the process taking part at normal atmospheric pressure, and temperature must not exceed 400C°.

Super fractionation: this type of distillation has fractional column of higher number of fractional plates to produce pure compounds, this type used for separation of isopentan in high pure percent 90% (aviation gasoline) as well as can be separate isohexane and isoheptane.

The aim of the experiment:

The crude oil can be evaluated by distillation; if the distillation volume percent is high at low temperature i.e this sample is very good economically while, is all distillate components distillate at high temperature 160C°, i.e. this sample contains heavy compounds or asphalt so it is not good economically and cannot be used as fuel.

<u>Boiling range</u>	<u>%volume</u>
60 – 70	6
70 – 80	19
80 – 90	22
90 – 100	25
100 – 130	30

Procedure:

- 1- Set up your fractional distillation apparatus as described above in the figure
- 2- Make sure that all of the joints of your distillation apparatus are tightly sealed.
- 3- Prepare a sample of 50 ml of crude oil and place it in the round bottom flask.
- 4- After preparing all the apparatus, begin to apply heat gradually using oil or sand bath.
- 5- Note the temperature when the first drop of the distillate begin to fall, that's mean the initial boiling point of the first component.
- 6- Collect the distillate volume form the initial boiling point to 50C°.
- 7- Continue the distillation and collect the volume for each 50C° until 400C°.
- 8- Calculate the volume percents according to this equation
- 9- $\text{Vol.\%} = (\text{volume} / 50) * 100$

Discussion:

- 1- Make a graph of your Temperature vs. Volume percent data and evaluate the quality of your distillation.

Petro chemistry laboratory

Exp.2: Normal paraffin separation

Petrol nowadays occupy a great part between the different energy sources in the world, that's because it contain several products in addition of large amounts of natural gas since it exist under earth and under pressure, also it's availability and simplicity of extraction from earth.

In addition of it characterized by high thermal efficiency in compare with solid fuel, also it's transportation is easy, for these reasons the production of petrol is developed from the last century.

Petrol contains mainly hydrocarbons in addition of small amounts of inorganic compounds which consist of sulfur, oxygen, nitrogen and other metals, mostly petrol composition specify it's physical and chemical properties also the quality of it's products, All hydrocarbon classes are present in the crude mixture, except alkenes and alkynes. This may indicate that crude oils originated under a reducing atmosphere. The following is a brief description of the different hydrocarbon classes found in all crude oils.

Paraffinic hydrocarbons:

It's formula is (C_nH_{2n+2}) and it is a saturated compounds exist in petrol beginning from methane is the principal constituent of natural gas. Methane, ethane, propane, and butane are gaseous hydrocarbons at ambient temperatures and atmospheric pressure. They are usually found associated with crude oils in a dissolved state. to the compounds of carbon atoms (C_{44}) or more, in normal temperature it will be gases ($C_1- C_4$) or liquids ($C_5- C_{15}$) or solids starting from hexadecane ($C_{16}- C_{44}$), . Normal alkanes (n-alkanes, n-paraffins) are straight-chain hydrocarbons having no branches. Branched alkanes are saturated hydrocarbons with an alkyl substituent or a side branch from the main chain. A branched alkane with the same number of carbons and hydrogens as an n-alkane is called an isomer. For example, butane (C_4H_{10}) has two isomers, n-butane and 2-methyl propane

(isobutane). As the molecular weight of the hydrocarbon increases, the number of isomers also increases. Pentane (C_5H_{12}) has three isomers; hexane (C_6H_{14}) has five.

Naphthenes (cycloparaffins) hydrocarbons:

Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils. Their ratio, however, depends on the crude type. The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds. They are normally present in the light and the heavy naphtha fractions. Cyclohexanes, substituted cyclopentanes, and substituted cyclohexanes like (methylcyclopentane, cyclopentane, methylcyclohexane) are important precursors for aromatic hydrocarbons.

If a naphtha fraction contains these compounds, the first two can be converted to benzene, and the last compound can dehydrogenate to toluene during processing. Dimethylcyclohexanes are also important precursors for xylenes.

Heavier petroleum fractions such as kerosine and gas oil may contain two or more cyclohexane rings fused through two vicinal carbons.

Aromatic hydrocarbons:

Lower members of aromatic compounds are present in small amounts in crude oils and light petroleum fractions. The simplest mononuclear aromatic compound is benzene (C_6H_6). Toluene (C_7H_8) and xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oils. Benzene, toluene, and xylenes (BTX) are important petrochemical intermediates as well as valuable gasoline components.

Separating BTX aromatics from crude oil distillates is not feasible because they are present in low concentrations. Enriching a naphtha fraction with these aromatics is possible through a catalytic reforming process.

Binuclear aromatic hydrocarbons are found in heavier fractions than naphtha. Trinuclear and polynuclear aromatic hydrocarbons, in combination with heterocyclic

compounds, are major constituents of heavy crudes and crude residues. Asphaltenes are a complex mixture of aromatic and heterocyclic compounds. The nature and structure of some of these compounds have been investigated. The following are representative examples of some aromatic compounds found in crude oils:

(Benzene, Toluene, Xylene, Naphthalene, 1,2-benzopyrene, Tetralin), Only a few aromatic-cycloparaffin compounds have been isolated and identified. Tetralin is an example of this class.

In this experiment an industrial method for n-paraffin separation from the other cycloparaffins, using urea with methanol as activation compound in addition to existence of a solvent like (cyclohexane, isopropanol), with agitating where the n-paraffins enters in the vacancies which is made by urea molecules as a result for the linkage between it's molecules by a hydrogen bonds, so there is no way for passage of isomers where it stay in the reaction media.

Crude oil contains (naphthenic, n-paraffins which no. of carbon atoms greater than 6, iso-paraffins) so the high percent of n-paraffins in crude oil increase it's importance.

the urea adduct (additional product) can form (hydrogen bonding) as result from channels related with n-paraffins (i.e inter to these channels) which can be then separated through their solubility in hot water to form two phases by using organic solvent to separate n-paraffins to the organic phase.

Iso-paraffins can be separated by using thio urea because of the formation channels is bigger as compared with urea because the outer shell of the sulfur is greater than oxygen which iso-paraffins can enter the channels separated as similar to urea adduct.

Procedure:

- 1- in a conical flask mixture 10g of urea with 1.5 ml methanol and 10ml of solvent with 10g of from petroleum.
- 2- Agitate the mixture for one hour in 25C°.

- 3- Filtrate the mixture on a Buchner funnel then wash the precipitate using the solvent, where the precipitate contains the n-paraffins.
- 4- Heat 150ml of distilled water at 60C° then add the separated urea with n-paraffins and let it until urea dissolves and n-paraffins separated.
- 5- Transfer them to a separation funnel and shake them well until the n-paraffins are separated from the aqueous solution of urea.
- 6- Weight the extracted results and determine the percentage.

Petrochemistry laboratory

Exp.3: Separation of aromatic and non aromatic compounds from the high boiling point oils using liquid - solid chromatography

Benzene, toluene, xylenes (BTX), and ethylbenzene are the aromatic hydrocarbons with a widespread use as petrochemicals. They are important precursors for many commercial chemicals and polymers such as phenol, trinitrotoluene (TNT), nylons, and plastics. Aromatic compounds are characterized by having a stable ring structure due to the overlap of the π -orbitals (resonance).

Accordingly, they do not easily add to reagents such as halogens and acids as do alkenes. Aromatic hydrocarbons are susceptible, however, to electrophilic substitution reactions in presence of a catalyst.

Aromatic hydrocarbons are generally nonpolar. They are not soluble in water, but they dissolve in organic solvents such as hexane, diethyl ether, and carbon tetrachloride.

Extraction of aromatics industrially

Benzene, toluene, xylenes (BTX), and ethylbenzene are obtained mainly from the catalytic reforming of heavy naphtha. The product reformat is rich in C₆, C₇, and C₈ aromatics, which could be extracted by a suitable solvent such as sulfolane or ethylene glycol.

These solvents are characterized by a high affinity for aromatics, good thermal stability, and rapid phase separation. The Tetra extraction process by Union Carbide (American company) uses tetra ethylene glycol as a solvent. The feed (reformat), which contains a mixture of aromatics, paraffinic, and naphthenic, after heat exchange with hot raffinate, is counter currently contacted with an aqueous tetra ethylene glycol solution in the extraction column. The hot, rich solvent containing BTX aromatics is cooled and introduced into the top of a stripper column. The aromatics extract is then purified by extractive distillation and recovered from the solvent by steam stripping.

Chromatography:

It is a separation process which depends on differential distribution of the components of the mixture between a mobile bulk phase and an essential thin film

stationary phase, the stationary phase may be either in the form of packed column (column chromatography) through which a mobile phase is allowed to flow, or in the form of a thin layer adhering to a suitable form of packing material (thin-layer chromatography) over which the mobile phase is allowed to ascend by capillary action.

Liquid-solid column chromatography:

Separations on a preparative scale employing this technique are generally accomplished by loading the substance on to a cylindrical column of the solid stationary phase, and developing the chromatogram by allowing the liquid mobile phase contained in a suitable reservoir to flow through the column under gravity or under pressure applied to the top of the solvent reservoir.

In this experiment there is a separation for oils which contains a mixture of hydrocarbons which boils between (230-538 C^o), using Liquid-solid column chromatography, where the aromatic part flows with the polar solvent like Ether and in addition to the aromatic compound, it contains compounds having sulphur, oxygen, and nitrogen atoms, while the non aromatic parts slips with the non-polar solvents like petroleum ether or pentane, and this part contains a mixture of paraffinic and naphthenec hydrocarbons.

The end point for the separation of aromatic compounds can be specified by using oil drop test or refractive index test for separated compounds.

Procedure:

- 1- Prepare a glass column and put in its end a little amount of glass wool then fill it by silica gel (100-200 mesh) which activated, in the oven at 160C^o for 8 hours then cover it by the glass wool and fix the column by stand.
- 2- Add to the column 30ml of petroleum ether at (40-60 C^o) for the saturation of the stationary phase with solvent, then weight 5g of oil and dilute it by 25ml of petroleum ether, add the solution to column.

- 3- Collect the displaced liquid from the end of column in weighted dry beaker then evaporate the solvent and weight the rest (A).
- 4- To specify the separation end point between the aromatic and non aromatic compounds, put a drop from the displaced liquid on a filter paper and note the spot after evaporation of solvent, this indicate that the separation of the non aromatic compounds in ended and it is the beginning of aromatic separation, or by the refractive index test where it is **1.474** for non aromatics, **(1.5-1.6)** for aromatics.
- 5- Removal of the rest oil (aromatics) from the column with 100ml of di-ethyl ether which collected in a weighted dry beaker, then solvent evaporated in a water bath and the rest is weighted (B).
- 6- Calculation:

Percent of aromatics & non aromatics = (gross weight (A+B) / sample weight)* 100

Percent of non-aromatics in extract= (weight of A / sample weight)*100

Percent of aromatics in sample = (weight of B / sample weight)*100

Petro chemistry laboratory
Exp.4: Determination of molecular weight of petroleum using viscosity
method

Viscosity is a measure of the resistance of a fluid to deform under either shear stress or extensional stress. It is commonly perceived as "thickness", or resistance to flow.

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction.

Viscosity is divided in to two types:

1- Dynamic (absolute) viscosity (μ):

It is the tangential force on unit area of either of two parallel planes at unit distance apart when the space between the planes is filled with the fluid and one of the planes moves relatively to the other with unit velocity in it's own plane.

The cgs (centimeter-gram-second) physical unit for dynamic viscosity is the poise (P), It is more commonly expressed, particularly in ASTM standards, as centipoise (cP).

The centipoise is commonly used because water has a viscosity of 1.0020 cP (at 20 °C).

$$1 \text{ P} = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} = \text{dyne s/cm}^2 = 1/10 \text{ Pa s}$$

2- Kinematic Viscosity (ν)

It is the ratio of absolute or dynamic viscosity to density - a quantity in which no force is involved. Kinematic viscosity obtained by dividing the absolute viscosity of a fluid with its mass density as

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

Where ν = kinematic viscosity μ = absolute or dynamic viscosity ρ = density

Kinematic viscosity has SI units ($\text{m}^2 \cdot \text{s}^{-1}$). The cgs physical unit for kinematic viscosity is the stokes (abbreviated S or St), It is sometimes expressed in terms of centistokes (cS or cSt). In U.S. usage, stoke is sometimes used as the singular form.

$$1 \text{ stokes} = 100 \text{ centistokes} = 1 \text{ cm}^2 \cdot \text{s}^{-1} = 0.0001 \text{ m}^2 \cdot \text{s}^{-1}$$

$$1 \text{ centistokes} = 1 \text{ mm}^2 / \text{s}$$

Viscometer:

A viscometer (also called viscosimeter) is an instrument used to measure the viscosity of a fluid. For liquids with viscosities which vary with flow conditions, an

instrument called a rheometer is used. Viscometers only measure under one flow condition, viscometer types are:

1- U-tube viscometers:

These are also known as Ostwald viscometers or glass capillary viscometers. They basically consist of a glass tube in the shape of a U held vertically in a controlled temperature bath.

2- Falling Sphere Viscometers:

In these the fluid is stationary in a vertical glass tube. A sphere of known size and density is allowed to descend through the liquid. If correctly selected, it reaches terminal velocity, which can be measured by the time it takes to pass two marks on the tube.

3- Vibrating viscometers:

Vibrating viscometers are rugged industrial systems used to measure viscosity in the process condition. The active part of the sensor is a vibrating rod. The vibration amplitude varies according to the viscosity of the fluid in which the rod is immersed.

4- Rotation viscometers:

Rotational viscometers uses the idea that the torque required to turn an object in a fluid, can indicate the viscosity of that fluid. The common Brookfield-type viscometer determines the required torque for rotating a disk or bob in a fluid at known speed.

5- Stormer viscometer:

The Stormer viscometer is a rotation instrument used to determine the viscosity of paints, commonly used in paint industries. It consists of a paddle-type rotor that is spun by an internal motor, submerged into a cylinder of viscous substance.

In this experiment the kinematic viscosity of oil is determined using U-tube viscometer at 100 and 210 F° (37.78 and 98.89 C°) a function H of the 100 F° viscosity is established by reference to a tabulation of H function versus 100 F° viscosity, the H value and the 210 F° viscosity are then used to estimate the mean relative molecular mass from a correlation chart.

Procedure

- 1- Prepare a U-tube viscometer and fix it in a temperature controlled water bath.
- 2- Take a sample of oil and put it inside the viscometer and adjust the bath thermometer to 100 F°.
- 3- Measure the time taken by the oil to move between the two marks of viscometer.
- 4- Apply the following equation to calculate the kinematic viscosity:

$$v = kt$$
 where k = viscometer constant t = time measured.
- 5- Repeat the above steps for temperature of 210 F°.
- 6- Look in table 1 for 100 F° viscosity and read the value of H correspond to the measured viscosity.
- 7- Read the viscosity-mean relative molecular mass chart for H and 210 F° viscosity, to find the accurate molecular mass value.

TABLE 1 Tabulation of H Function

Kinematic Viscosity, cSt at 100°F (37.78°C)	H				
	0	0.2	0.4	0.6	0.8
2	-178	-151	-126	-104	-85
3	-67	-52	-38	-25	-13
4	-1	9	19	28	36
5	44	52	59	66	73
6	79	85	90	96	101
7	106	111	116	120	124
8	128	132	136	140	144
9	147	151	154	157	160
10	163	166	169	172	175
11	178	180	183	185	188
12	190	192	195	197	199
13	201	203	206	208	210
14	211	213	215	217	219

TABLE 1 *Continued*

Kinematic Viscosity, cSt at 100°F (37.78°C)	<i>H</i>									
	<i>H</i>									
	0	100	200	300	400	500	600	700	800	900
1 000	569	574	578	583	587	591	594	597	600	603
2 000	605	608	610	612	614	616	618	620	621	623
3 000	625	626	628	629	631	632	633	634	636	637
4 000	638	639	640	641	642	643	644	645	646	647
5 000	648	649	650	651	652	652	653	654	655	656
6 000	656	657	658	658	659	660	660	661	662	662
7 000	663	664	664	665	665	666	666	667	667	668
8 000	668	669	670	670	671	671	671	672	672	673
9 000	673	674	674	675	675	676	676	677	677	677
	<i>H</i>									
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000
10 000	678	681	684	688	691	694	696	698	701	703

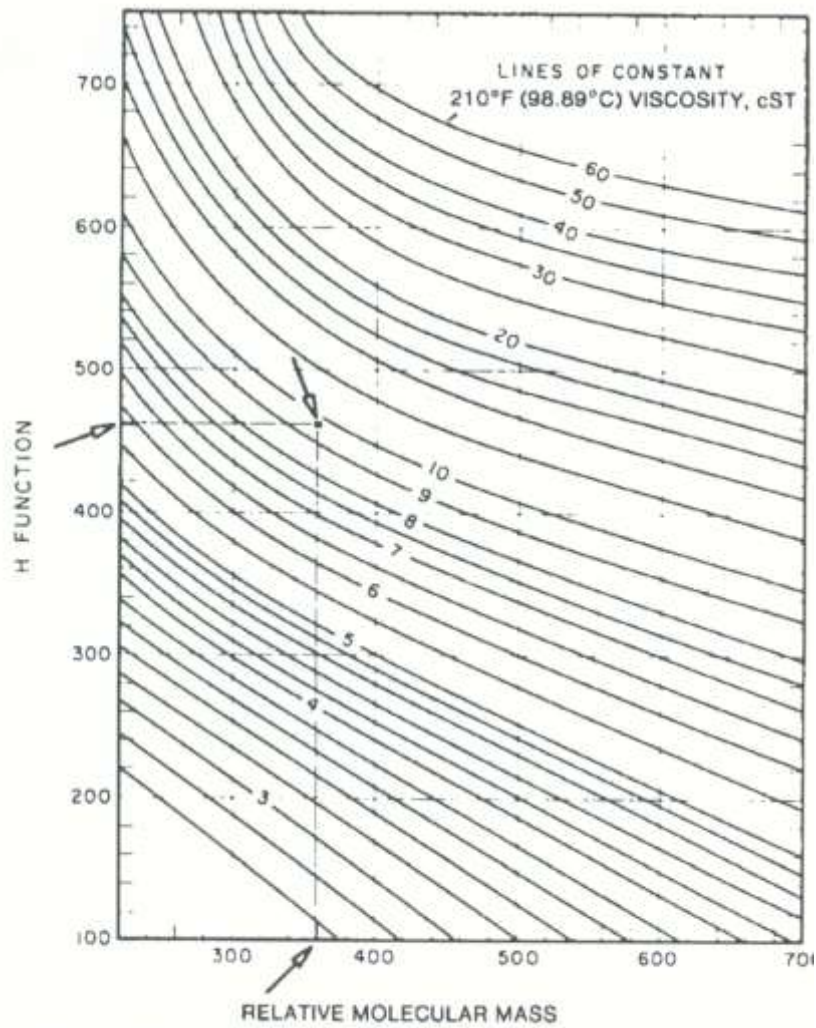


FIG. 1 Viscosity-Mean Relative Molecular Mass Chart

retrochemistry laboratory

**Exp.5: Analysis of compound group of petroleum using
(n-d-M) method**

This test method covers the calculation of the carbon distribution and ring content of olefin-free petroleum oils from measurements of refractive index, density and molecular weight (n - d - M).

The Refractive Index (n) - of a medium is a measure for how much the speed of light is reduced inside the medium. The speed of light in a medium can be expressed as $v = c / n$

Where v = speed of light in the medium

c = speed of light in air or vacuum - approximately 3×10^8 meters per second

n = refractive index

Density (d): is mass (m) per unit volume (V) — the ratio of the amount of matter in an object compared to its volume. A small, heavy object, such as a rock or a lump of lead, is denser than a larger object of the same mass, such as a piece of cork or foam. In the common case of a homogeneous substance, density is expressed as:

$$\rho = m/v$$

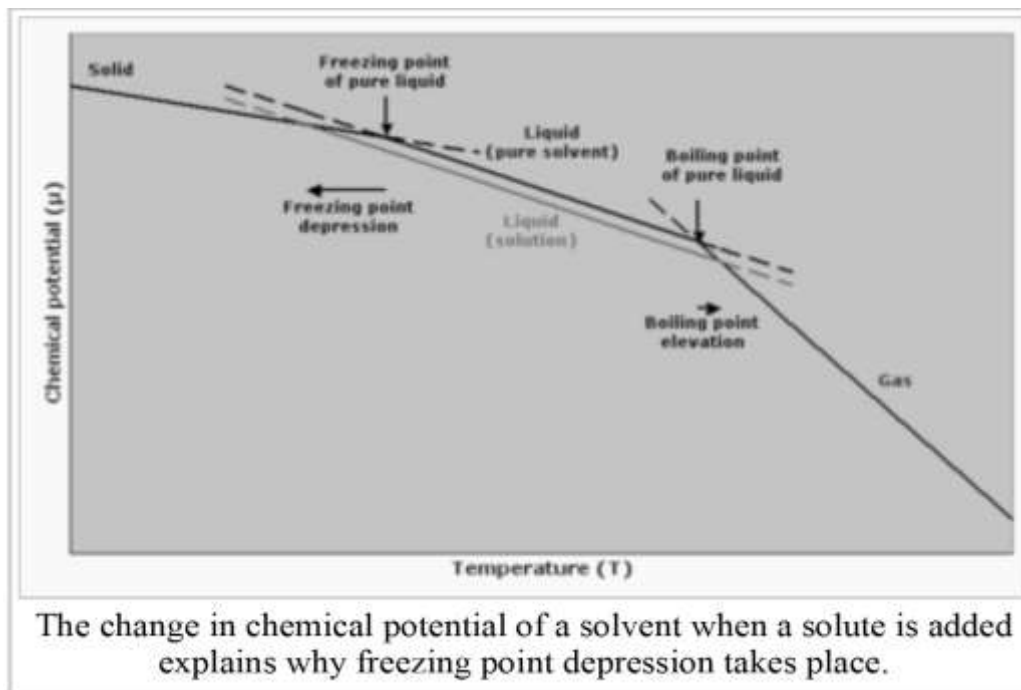
Where, in SI Units: ρ (rho) is the density of the substance, measured in $\text{kg} \cdot \text{m}^{-3}$

m is the mass of the substance, measured in kg

V is the volume of the substance, measured in m^3

Molecular weight calculation: it may be calculated in different methods like estimation it by viscosity measurement or by using freezing point depression, which it is described as phenomenon that the freezing point of a liquid (a solvent) is depressed when another compound is added, meaning that a solution has a lower freezing point than a pure solvent. This happens whenever a solute is added to a pure solvent, such as water. The phenomenon may be observed in sea water, which due to its salt content remains liquid at temperatures below 0°C , which it is the freezing point of pure water.

as illustrated in the following scheme



The composition of complex petroleum fractions is often expressed in terms of the proportions of aromatic rings (RA), naphthene rings (RN), and paraffin chains (CP) that would comprise a hypothetical mean molecule. Alternatively, the composition may be expressed in terms of a carbon distribution, that is, the percentage of the total number of carbon atoms that are present in aromatic ring structures (% CA), naphthene ring structures (% CN), and paraffin chains (% CP).

Significance of experiment:

The carbon distribution and ring content serves to express the gross composition of the heavier fractions of petroleum, these data can be used to as an adjunct to the bulk properties in monitoring the manufacture of lubricating oil base stock by distillation, and in comparing the composition of stocks from different crude sources.

Illustration for calculation purposes:

% C_A Percentage of Aromatic Carbon

% C_N Percentage of Naphthenic Carbon

% C_P Percentage of paraffinic Carbon

R_A Average Number of aromatic rings per Molecule

R_N Average Number of naphthene rings per Molecule

R_T Average Number of rings per Molecule

The mass % Sulfur must be determined in order to calculate values for R_T and R_N. The n-d-M and Sulfur content are determined by the following:

Refractive Index at 20°C (n)

Density at 20°C (d)

Average Molecular Weight (M)

Sulfur Content (mass %)

Procedure:

- 1- Determine the refractive index and density of the oil sample at 20 C°.
- 2- Determine the molecular weight experimentally using freezing point depression or estimate it from the viscosity measurement at 100 and 210 F°.
- 3- Calculate the carbon distribution (% C_A, % C_N, % C_P) or the ring analysis R_A, R_N using these data as described in the calculation section.

Calculation:

- 1- Calculate the factors ν and w from the observed density (d) and the observed refractive index (n) using the following equations:

$$\nu = 2.51(n_D^{20} - 1.475) - (d_4^{20} - 0.851)$$

$$w = (d_4^{20} - 0.851) - 1.11(n_D^{20} - 1.475).$$

- 2- Calculate the percentage of aromatic carbons (%C_A) from ν and the molecular weight (M) using one of the following equations:

If ν is positive: %C_A = 430 ν + 3660/M

If ν is negative: %C_A = 670 ν + 3660/M

3- Calculate the percentage of carbon in total (aromatic and naphthenic) ring structures ($\%C_R$) from w and the molecular weight.

If w is positive $\%C_R = 820 w - 3S + 10000/M$

If w is negative $\%C_R = 1440 w - 3S + 10600/M$

Where **S = mass % sulphur. (m of S=0.001)**

4- Calculate the percentage of naphthenic carbon ($\%C_N$) and the percentage of paraffinic carbon ($\%C_P$) as follows:

$$\%C_N = \%C_R - \%C_A$$

$$\%C_P = 100 - \%C_R$$

5- Calculate the average number of aromatic rings per molecule (R_A) from v and the molecular weight.

If v is positive $R_A = 0.44 + 0.055 M v$

If v is negative $R_A = 0.44 + 0.080 M v$

6- Calculate the average total number of rings per molecule (R_T) from w and the molecular weight.

If w is positive $R_T = 1.33 + 0.146 M (w - 0.005 S)$

If w is negative $R_T = 1.33 + 0.180 M (w - 0.005 S)$

7- calculate the average number of naphthene rings per molecule (R_N) by difference

$$R_N = R_T - R_A$$

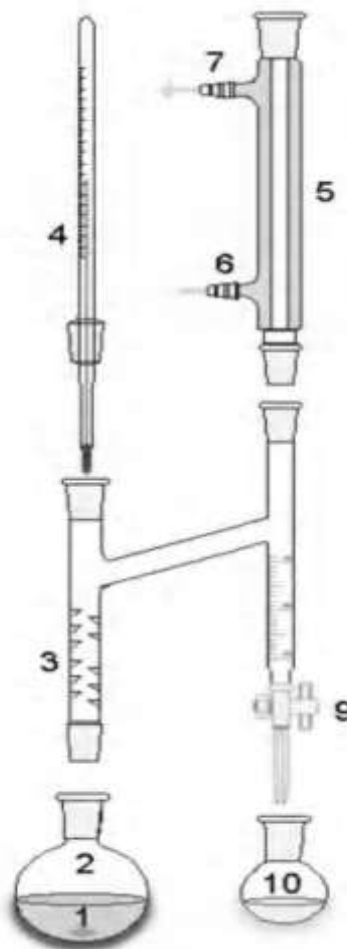
Petrochemistry laboratory

Exp.6: Determination of water content of petroleum and petroleum products

This method determines the water content of crude petroleum, greases, cutback bitumen, asphalt, and of petroleum products whose final boiling points are not less than 300 C° by distillation using **Dean and Stark** apparatus.

The Dean-Stark apparatus or Dean-Stark receiver or distilling trap is a piece of laboratory glassware used in synthetic chemistry to collect water (or occasionally other liquid) from a distillation flask. It is used in combination with a reflux condenser and a batch flask for continuous removal of the water.

- 1: Stirrer bar/anti-bumping granules
- 2: Still pot
- 3: Fractionating column
- 4: Thermometer/Boiling point temperature
- 5: Condenser
- 6: Cooling water in
- 7: Cooling water out
- 8: Burette
- 9: Tap
- 10: Collection vessel



The Dean-Stark apparatus in the laboratory typically consists of vertical cylindrical piece of glass (the trap, above (9) in figure), often with a volumetric graduation on its full length and a precision tap on the bottom very much like a burette. The top of the cylinder is a fit with the bottom of the reflux condenser (5). Protruding from the top the cylinder has a side-arm sloping toward the distillation flask (2). At the end the side-arm makes a

sharp turn so that the end of the side arm (3) is vertical as well. This end connects with the reactor.

The material to be tested is heated under reflux with a water-immiscible solvent, which is co-distilled with the water in the sample, condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still.

Significance of experiment:

Knowledge of the water content of petroleum products is important in the refining, purchase, sale, and transfer of products.

The amount of water as determined by this test method may be used to correct the volume involved in the custody transfer of petroleum products and bituminous materials, also it is specified in the contracts.

Solvent carrier liquid

A solvent – carrier liquid appropriate to the material being tested shall be used, different types of solvent – carrier liquid are used in this test like:

1. aromatic solvent like xylene, toluene and mixture of xylene and toluene
2. petroleum distillates, available from most chemical companies under the name of Stoddard solvent or ligroine.
3. volatile spirits solvent, like petroleum spirit, iso-octane

Procedure:

1. Measure 100 ml of the sample into the distillation flask and add 100 ml of solvent – carrier liquid.

2. when testing solid or semi-solid materials, weight 100g of the sample or 50g if it is a lubricating grease, and place it in the distillation vessel together with 100ml of solvent – carrier liquid.
3. assemble the apparatus as described in the above figure.
4. heat the flask and regulate the heating so that the condensate falls from at a rate of (2-5)drops per second.
5. continue heating the sample until the volume of water in the receiver remains constant for 5 minuets.
6. when the volume of water remains constant remove the heat source and allow cooling to room temperature, record the total volume of water.
7. calculate the percent of water by:

volumetric percent of water = (volume of condensed water)/(total volume of sample) * 100

Petrochemistry laboratory
Exp.7: Determination of specific gravity of petroleum and petroleum
Products using pyknometer method

This method covers the determination of the specific gravity or density crude petroleum and petroleum products using pycnometer, it is used when great accuracy is required, or when as for solids or viscous liquids the hydrometer is not suitable.

Specific gravity: it is the ratio of the mass of a given volume of liquid at 60 °F to the mass of an equal volume of pure water at the same temperature.

Pycnometer or Pyknometer

a device used for measuring fluid density, also known as a specific gravity bottle. Uses an appropriate working fluid such as water or mercury to find a volume for use in laboratory principle.

It consist of flask with a close-fitting ground glass stopper with a fine hole through it, so that a given volume can be accurately obtained. This enables the density of a fluid to be measured accurately, by reference to an appropriate working fluid such as water or mercury, using an analytical balance.

If the flask is weighed empty, full of water, and full of a liquid whose specific gravity is desired, the specific gravity of the liquid can easily be calculated.

The particle density of a powder, to which the usual method of weighing cannot be applied, can also be determined with a pycnometer. The powder is added to the pycnometer, which is then weighed, giving the weight of the powder sample. The pycnometer is then filled with a liquid of known density, in which the powder is completely insoluble. The weight of the displaced liquid can then be determined, and hence the specific gravity of the powder.



Procedure

- 1- Weight the clean and dry pycnometer.
- 2- Fill the pyknometer with the sample, bring the pyknometer and it's content to the test temperature (T_1) by immersing the pyknometer up to it's neck in the constant temperature bath for (20) minute in order to stabilize the temperature, assist filling and permit air bubbles to rise to the surface.
- 3- When the temperature is constant, firmly insert the capillary stopper, which has also been brought to the test temperature taking care to avoid trapping air bubbles below the stopper.
- 4- Remove the pyknometer from the bath and cool it to the room temperature.
- 5- Clean the pyknometer from outside and weigh it.
- 6- Calculate the specific gravity using the following equation.

$$\text{Specific gravity } T_1/60 \text{ }^\circ\text{F} = (W_2 - W_1)/W + C$$

Where:

W_1 = weight of empty pyknometer.

W_2 = weight of pyknometer with sample.

W = water equivalent of pyknometer at 60 $^\circ\text{F}$.

C = air buoyancy correction, obtained from table I.

- 7- calculate the API gravity using the following equation:

$$\text{API}_{\text{gravity}} = (141.5/\text{sp.gr } 60/60 \text{ }^\circ\text{F}) - 131.5$$

Table I

BUOYANCY CORRECTIONS

$\frac{W_2 - W_1}{W}$	Correction	$\frac{W_2 - W_1}{W}$	Correction
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Petrochemistry laboratory
Exp.8: Determination Aniline point and Diesel index

Petroleum and petroleum products are mixed with several organic solvents like benzene and toluene in normal temperature but in some solvents like aniline, mixing done in a specified temperature and it depend on the aniline percent.

Aniline point

The minimum temperature for a complete mixing of aniline and materials such as gasoline; it is also called the point temperature," which is the lowest temperature (°F or °C) at which equal volumes of aniline ($C_6H_5NH_2$) and the oil form a single phase.

The aniline point (AP) correlates roughly with the type of aromatic hydrocarbons in an oil sample. A product of high aniline point will be low in aromatics and naphthenes and, therefore, high in paraffins, A low AP is indicative of higher aromatics, Diesel oil with AP below 120°F [49°C] is probably risky oil-base mud.

The aniline point may be used to calculate the diesel index and heat of combustion for aviation fuels.

Diesel index

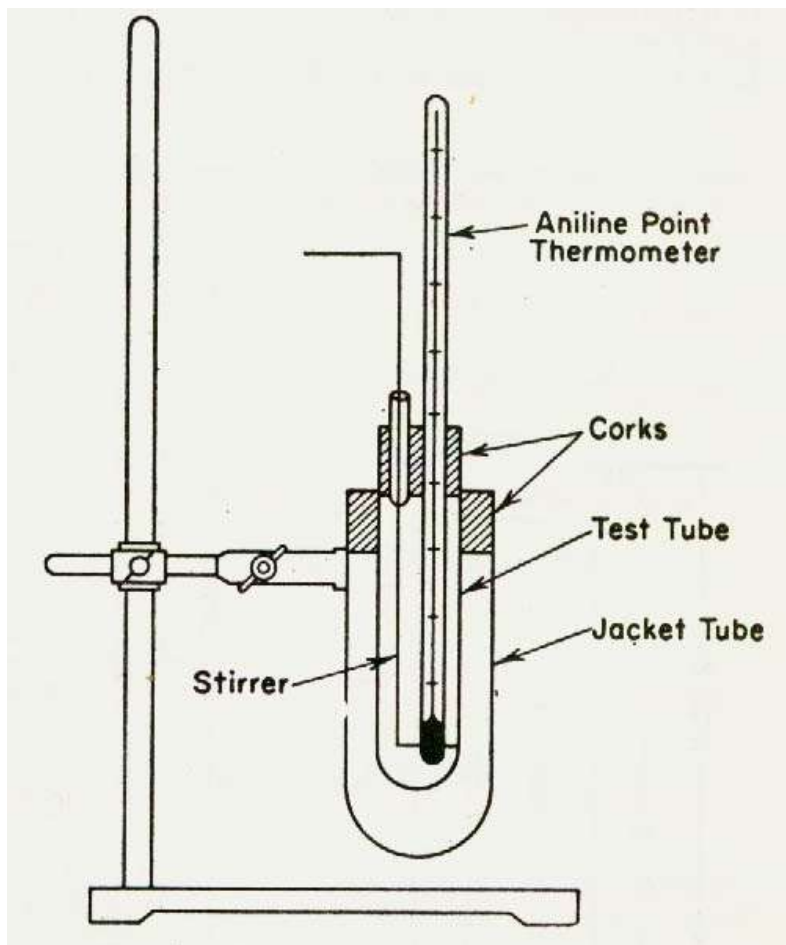
A measure of the ignition quality of diesel calculated from a formula involving its gravity and its aniline point.

Procedure

- 1- Prepare the apparatus as in the figure
- 2- Take 5ml of sample (crud oil, kerosene, gasoil) and 5ml of aniline in the test tube.

- 3- Heat the mixture by water bath with stirring until complete miscibility is obtained.
- 4- Remove the apparatus and let the solution to cool.
- 5- Record the temperature when the mixture is separated in two layers, which is the aniline point.
- 6- Determine the diesel index for the sample using the relation:

$$\text{Diesel index} = (\text{aniline point} * \text{API}) / 100$$



Petrochemistry laboratory
Exp.9: Flash Point by Cleveland Open Cup

The flash point of a flammable liquid is the lowest temperature at which it can form an ignitable mixture in air, or the lowest temperature at which application of an ignition source causes the vapors of a specimen of the sample to ignite under specified conditions of test.

The fire point is defined as the temperature at which the vapour continues to burn for at least 5 seconds after being ignited.

Measuring flash points

There are two basic types of flash point measurement: open cup and closed cup. In open cup devices the sample is contained in an open cup which is heated, and at intervals a flame is brought over the surface. The measured flash point will actually vary with the height of the flame above the liquid surface.

Closed cup testers, are sealed with a lid through which the ignition source can be introduced periodically. The vapour above the liquid is assumed to be in reasonable equilibrium with the liquid. Closed cup testers give lower values for the flash point (typically 5-10 °C) and are a better approximation to the temperature at which the vapour pressure reaches the lower flammable limit (LFL).

This experiment is a flash point and fire point test method is a dynamic method and depends on definite rates of temperature increases to control the precision of the test method. Its primary use is for viscous materials having flash point of 79°C (175°F) and above. It is also used to determine fire point, which is a temperature above the flash point, at which the test specimen will support combustion for a minimum of 5 s.

Significance and Use

- 1- The flash point is one measure of the tendency of the test specimen to form a flammable mixture with air under controlled laboratory conditions.

- 2- Flash point is used in shipping and safety regulations to define flammable and combustible materials.
- 3- Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively nonvolatile or nonflammable material.

Procedure:

- 1- Fill the test cup with the sample so that the top of the meniscus of the test specimen is exactly at the filling mark, and place the test cup on the center of the heater.
- 2- Light the test flame and adjust it to a diameter of 3.2 to 4.8 mm (1/8 to 3/16 in.) or to the size of the comparison bead.
- 3- Apply heat initially at such a rate that the temperature as indicated by the temperature measuring device increases 14 to 17°C/min. When the test specimen temperature is approximately 56°C (100°F) below the expected flash point, decrease the heat so that the rate of temperature rise during the last 28°C before the flash point is 5 to 6°C/min.
- 4- Apply the test flame when the temperature of the test specimen is approximately 28°C below the expected flash point and each time thereafter at a temperature reading that is a multiple of 2°C. Pass the test flame across the center of the test cup at right angles to the diameter, which passes through the temperature measuring device.
- 5- Record, as the observed flash point, the reading on the temperature measuring device at the time the test flame causes a distinct flash in the interior of the test cup.

Petrochemistry laboratory
Exp.10: Pour point test of petroleum products

The pour point of a liquid is the lowest temperature at which it will pour or flow under prescribed conditions. It is a rough indication of the lowest temperature at which

oil is readily pumpable. Also, the pour point can be defined as the minimum temperature of a liquid, particularly a lubricant, after which, on decreasing the temperature, the liquid ceases to flow.

Measuring the pour point of petroleum products

The specimen is cooled inside a cooling bath to allow the formation of paraffin wax crystals. At about 9 °C above the expected pour point, and for every subsequent 3 °C, the test jar is removed and tilted to check for surface movement. When the specimen does not flow when tilted, the jar is held horizontally for 5 secs. If it does not flow, 3 °C is added to the corresponding temperature and the result is the pour point temperature.

Significance and Use

The pour point of a petroleum specimen is an index of the lowest temperature of its utility for certain applications.

Procedure:

- 1- Pour the specimen into the test jar to the level mark.
- 2- Close the test jar with the cork carrying the high-pour thermometer.
- 3- See that the disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium.
- 4- Pour points are expressed in integers that are positive or negative multiples of 3°C. Begin to examine the appearance of the specimen when the temperature of the specimen is 9°C above the expected pour point (estimated as a multiple of 3°C).
- 5- Continue in this manner until a point is reached at which the specimen shows no movement when the test jar is held in a horizontal position for 5 s. Record the observed reading of the test thermometer.

6- Add 3°C to the temperature recorded in previous step and report the result as the Pour Point.

Petrochemistry laboratory
Exp.11: Octane number measurement

The Octane Number, is a measure of the antiknock quality of petrol - the ability of a petrol to resist knocking upon combustion in an engine. Knocking is a description of the

sound that an engine makes when it runs on a too low octane fuel, and it causes a drop in fuel efficiency.

Or it is the Measure of the ignition quality of gasoline or petrol. Higher this number, the less susceptible is the gas to 'knocking' when burnt in a standard internal combustion engine. Octane number denotes the percentage (by volume) of iso-octane in a combustible mixture (containing iso- octane and normal-heptane) whose 'anti-knocking' characteristics match those of the gasoline being tested.

In 1927, Graham Edgar suggested a test method to quantify the knocking behavior of a fuel. Edgar proposed the use of two fuels: n- heptane and 2,2,4-trimethyl pentane (iso-octane); fuels with a low and a high antiknocking value respectively.

Any commercial fuel that was available on the market at that time could be compared in knocking behavior to blends of these two compounds. The introduction of reference fuels lead to the design of various test engines and test conditions. Nowadays, the most commonly used test methods are the Research Octane Number (RON), and the Motor Octane Number (MON). The Research Octane Number settings represent typical mild driving, without consistent heavy loads on the engine. While The conditions of the Motor Octane Number method represent severe, sustained high speed, high load driving. For most hydrocarbon fuels, including those with either lead or oxygenates, the Motor Octane Number will be lower than the Research Octane Number.

Research Octane Number (RON)

RON is determined in a single cylinder variable compression ratio engine that operates at 600 RPM with a 125o F inlet air temperature at standard barometric pressure. The procedures and hardware for the RON test were originally developed in 1931. The hardware was revised in 1948 with procedural changes made until the late 1960s.

Motor Octane Number (MON)

MON is determined in a single cylinder engine similar to the RON engine with a few changes that make operating conditions more severe and therefore the octane numbers are lower. The MON engine runs at 900 RPM with a 300o F mixture temperature.

In most countries (including all of Europe and Australia) the "headline" octane rating, shown on the pump, is the RON, but in the United States, Canada and some other countries the headline number is the average of the RON and the MON, sometimes called the Anti-Knock Index (AKI), Road Octane Number (RdON), Pump Octane Number (PON), or $(R+M)/2$. Because of the 8 to 10 point difference noted above, the octane shown in the United States is 4 to 5 points lower than the same fuel elsewhere: 87 octane fuel, the "regular" gasoline in the US and Canada, is 91-92 in Europe. However most European pumps deliver 95 (RON) as "regular", equivalent to 90-91 US $(R+M)/2$, and some even deliver 98 (RON) or 100 (RON).

In this experiment the device used is a very advanced octane analyzer portable device depends on the infrared technology to analyze different types of gasoline and diesel as in the following procedure:

Procedure:

- 1) Switch power to **ON**. The display will show the version number followed by a 15-second countdown, after which "Clear Chamber and Press Measure" will appear.
- 2) Make sure there is no sample holder in the sample chamber. Cover the chamber with the light shield.

- 3) Press the **MEASURE** key to standardize the instrument. "Put in sample" will appear on the display. This indicates the instrument has been standardized: it is now ready to measure octane.
- 4) Remove the light shield from the sample chamber.
- 5) Place the sample holder containing gasoline in the sample chamber, being careful to align the alignment stripe on the jar with the **left** alignment stripe on the instrument.
- 6) Carefully replace the light shield over the jar. This shield must **always** be used when measuring a gasoline sample or a standard; otherwise, the results will be incorrect.
- 7) Press **MEASURE**. "Remove & Replace" will be displayed.
- 8) Remove the jar and rotate it to align the stripe on the jar with the **right** alignment stripe on the instrument.
- 9) Carefully replace the light shield over the jar.
- 10) Press **MEASURE**. "Remove & Press M" will be displayed.
- 11) Remove the jar and cover empty chamber with light shield. Press **MEASURE**. The results will appear in the display while they are printed.

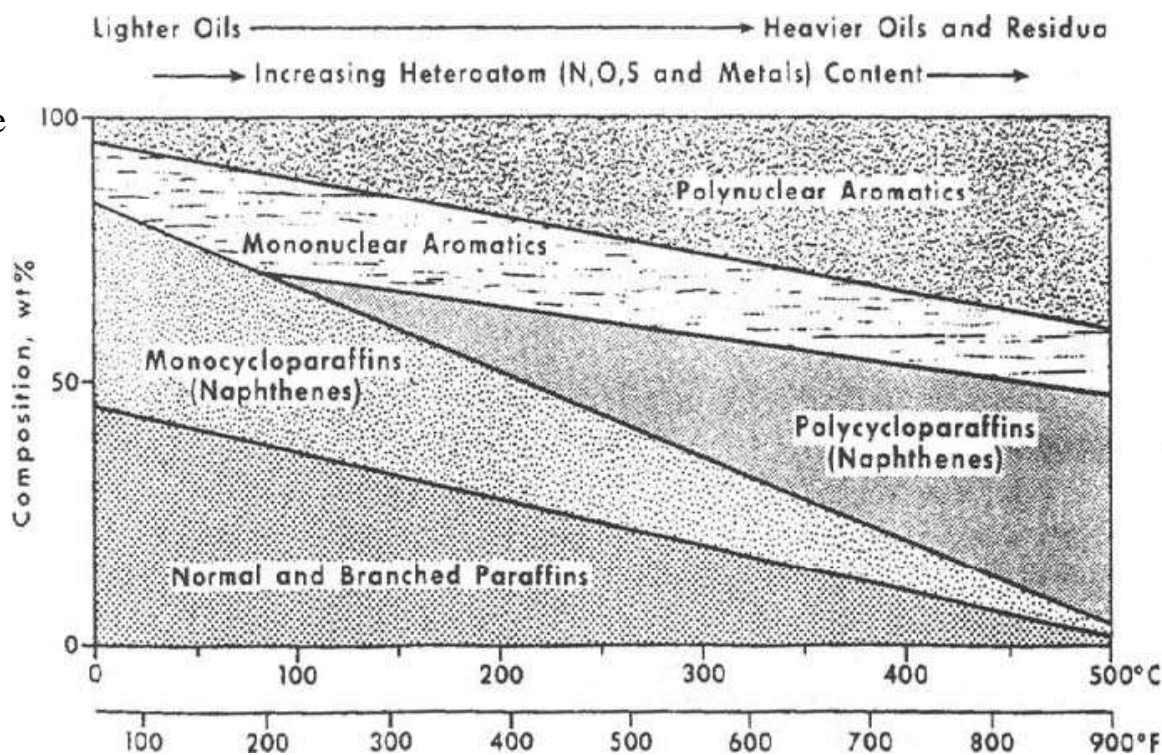
Petrochemistry laboratory

Exp.12: Carbon Residue and Ash Content Determination

Carbon Residue:

Carbon residue is a measure of the amount of material left after evaporation and pyrolysis of crude oil and provides some indication of the relative coke-forming propensity. The residue formed is not composed entirely of carbon but is a coke, the composition of which can be changed by further pyrolysis. which is designated by CR. Therefore, heavier fractions with more aromatic contents have higher carbon residues while volatile and light fractions such as naphthas and gasolines have no carbon residues. CR is particularly an important characteristic of crude oils and petroleum residues. Higher CR values indicate low-quality fuel and less hydrogen content.

While
ash



results from non-combustible extraneous solids such as dirt and rust present in a crude oil. Normally there is a close correlation between a crude oil's ash content and its sediment content. In use of crude oil as a fuel, it is important to know its ash content, as this can be related directly to particulate emissions.

Oils that have ash forming compounds have erroneously high carbon residues by both Carbon Residue methods. For such oils ash should be removed before the measurement. In most cases carbon residues are reported in wt% by Conradson method, which is designated by %CCR.

Carbon residue can be correlated to a number of other properties. It increases with an increase in carbon-to-hydrogen ratio (CH), sulfur content, nitrogen content, asphaltenes content, or viscosity of the oil. The most precise relation is between CR and hydrogen content in which as hydrogen content increases the carbon residues decreases. The hydrogen content is expressed in terms of H/C atomic ratio and the following relation may be used to estimate CCR from H/C

$$\%CCR = 148.7 - 86.96 \text{ H/C}$$

if $\text{H/C} \geq 1.71$ ($\%CCR < 0$), set $\%CCR = 0.0$ and if $\text{H/C} < 0.5$ ($\%CCR > 100$), set $\%CCR = 100$. H/C.

The carbon residue is nearly a direct function of high boiling asphaltic materials. One of the main characteristic of residuum is its asphaltene content. Asphaltenes are insoluble in low molecular weight nalkanes including n-pentane. Knowledge of n-pentane insolubles in residual oils is quite important in determining yields and products qualities for deasphalting, thermal visbreaking, and hydrodesulfurization processing. The relation between the normal pentane insolubles and carbon residue is as follows

$$\%NCs = 0.74195 (\%CCR) + 0.01272 (\%CCR)^2$$

Where %NC5 is the wt% of n-pentane insolubles and %CCR is the wt% of Conradson carbon residue.

Once %NCs is known, the asphaltene content (asphaltene wt%) of a residue can be determined from the following empirical relation:

$$\%Asphaltene = a(\%NCs)$$

Where a is 0.385 for atmospheric residue and 0.455 for vacuum residues.

A weighed quantity of sample is placed in a crucible and subjected to destructive distillation. The residue undergoes cracking and coking reactions during a fixed period

of severe heating. At the end of the specified heating period, the test crucible containing the carbonaceous residue is cooled in a desiccators and weighed. The residue remaining is calculated as a percentage of the original sample, and reported as Conradson carbon residue.

Procedure:

- 1- Weigh to the nearest 5 mg a 10-g sample of the oil to be tested, free of moisture and other suspended matter, into a tared porcelain or silica crucible containing two glass beads about 2.5 mm in diameter. Place this crucible in the exact center of the larger iron crucible. Apply covers to the iron crucible, and allow free exit to the vapors as formed.
- 2- On a suitable stand or ring, place the bare Nichrome wire triangle and on it the insulator. Next center the sheet-iron crucible in the insulator with its bottom resting on top of the triangle, in a hood in order to distribute the heat uniformly during the process.
- 3- Apply heat with a high, strong flame from the gas burner, so that the pre-ignition period will be 10 to 15 min. When smoke appears above the chimney, immediately move or tilt the burner so that the gas flame plays on the sides of the crucible for the purpose of igniting the vapors. Then remove the heat temporarily. When the vapors cease to burn and no further blue smoke can be observed, readjust the burner and hold the heat as at the beginning so as to make the bottom and lower part of the sheet-iron crucible a cherry red. The time periods shall be observed with whatever burner and gas is used.
- 4- Remove the burner and allow the apparatus to cool until no smoke appears, and then remove the cover of the crucible (about 15 min). Remove the porcelain or silica crucible with heated tongs, place in the desiccators, cool, and weigh. Calculate the percentage of carbon residue on the original sample.