University of Mosul

Science of College

Department of Chemistry

Undergraduate Studies

The 4th Stage

EXPERIMENTS IN PETROLEUM CHEMISTRY

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EXP (1): Distillation of crude oil.

The crude oil is a complicated mixture of hydrocarbon compounds (paraffinic, naphthenic, and aromatics) of different molecular weights and various physical and chemical properties. It also contains some sulfur, nitrogen and oxygen compounds as well as traces of organo- metallic compounds.

Distillation is considered one of the early processes which had been used in oil industry, to simplify petroleum into various fractions such as gasoline, kerosene, gas oil, etc.

Distillation: is a physical separation method that is used for separation of a mixture of liquids into various fractions as well as for purification of organic liquids.

Fractionation of the crude oil in the refinery is conducted using various types of distillation as follows:

1. Simple distillation
2. Distillation under reduced pressure (vacuum distillation)
3. **Atmospheric distillation (fractional distillation)**
4. A zeotropic distillation.
5. Extraction distillation.
6. Steam distillation

Principle Distillation

Distillation of any liquid depends on its vapor pressure and boiling point. Each liquid has its own boiling point. Boiling point (BP) is a temperature at which vapor pressure (VP) of the liquid equals the atmospheric pressure.

Liquids of high vapor pressure have low boiling point and vice versa. This means that distillation depends on the volatility of the liquid. The more the volatile liquid, the lower the boiling point and vice versa.

1. **Fractional distillation of petroleum.**
   Is the most important refining process that is used for fractionation of the crude petroleum into various distillates according to their boiling point

Procedure:

1. Transfer (100 mL) of the crude oil to a round bottom flask. Add boiling stones.

2.Connect the distillation apparatus as shown in Figure 2. Avoid any leakage in the reactor by putting a little amount of silicon grease among the distillation parts.

3. Make sure that the reactor is connected firmly and in the right manner.

4. Heat the sample by using a hot plate or an electrical mantle, and collect the distillates according to their boiling range.

5. Record the initial boiling point (IBP), **IBP is the temperature observed when the first drop of liquid is condensed.**

6. Collect the samples as follows:

From IBP to 120 °C

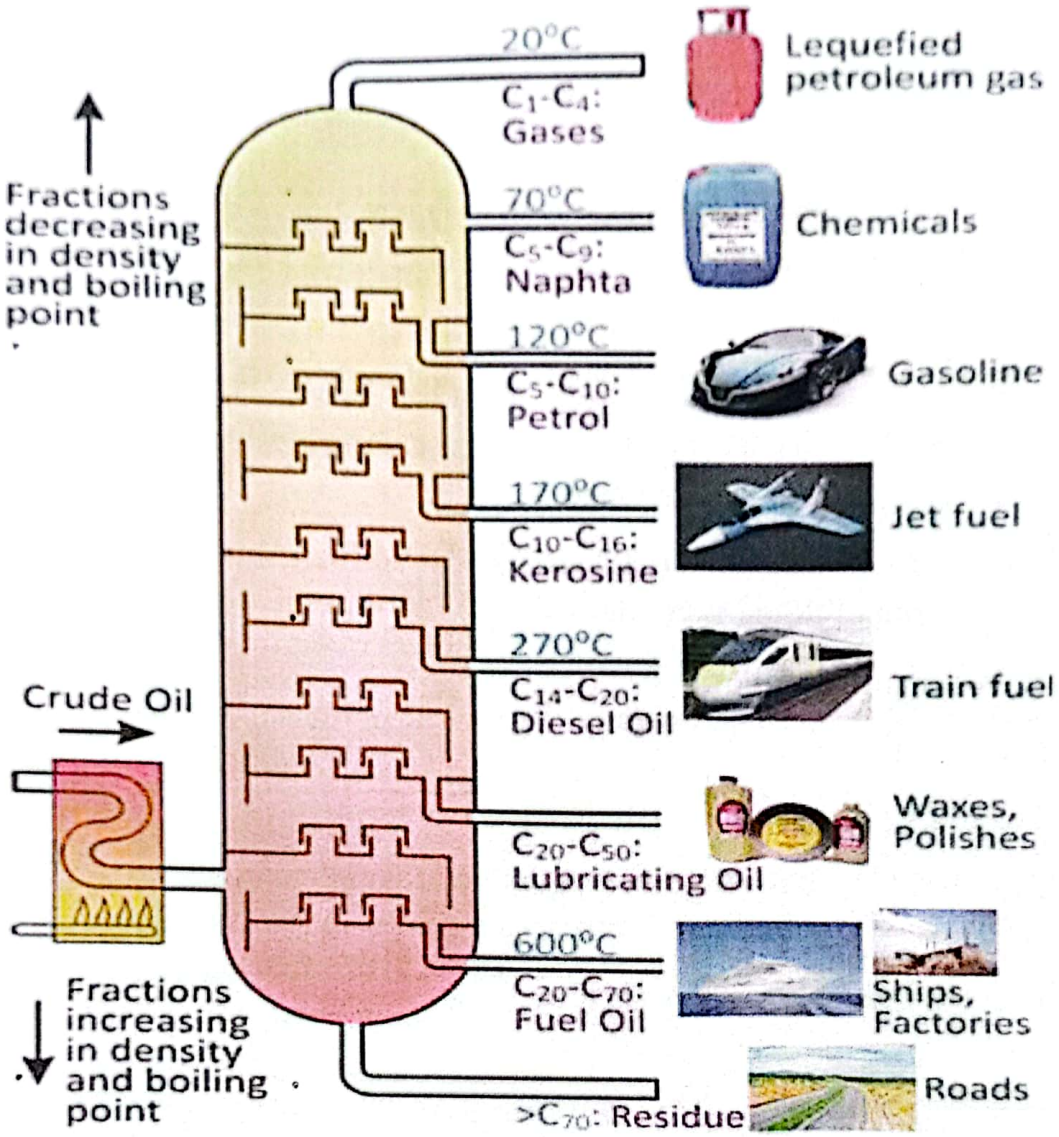
From 121 to 180°C

From 181 to FBP. **FBP is the final boiling point. It is the maximum temperature**

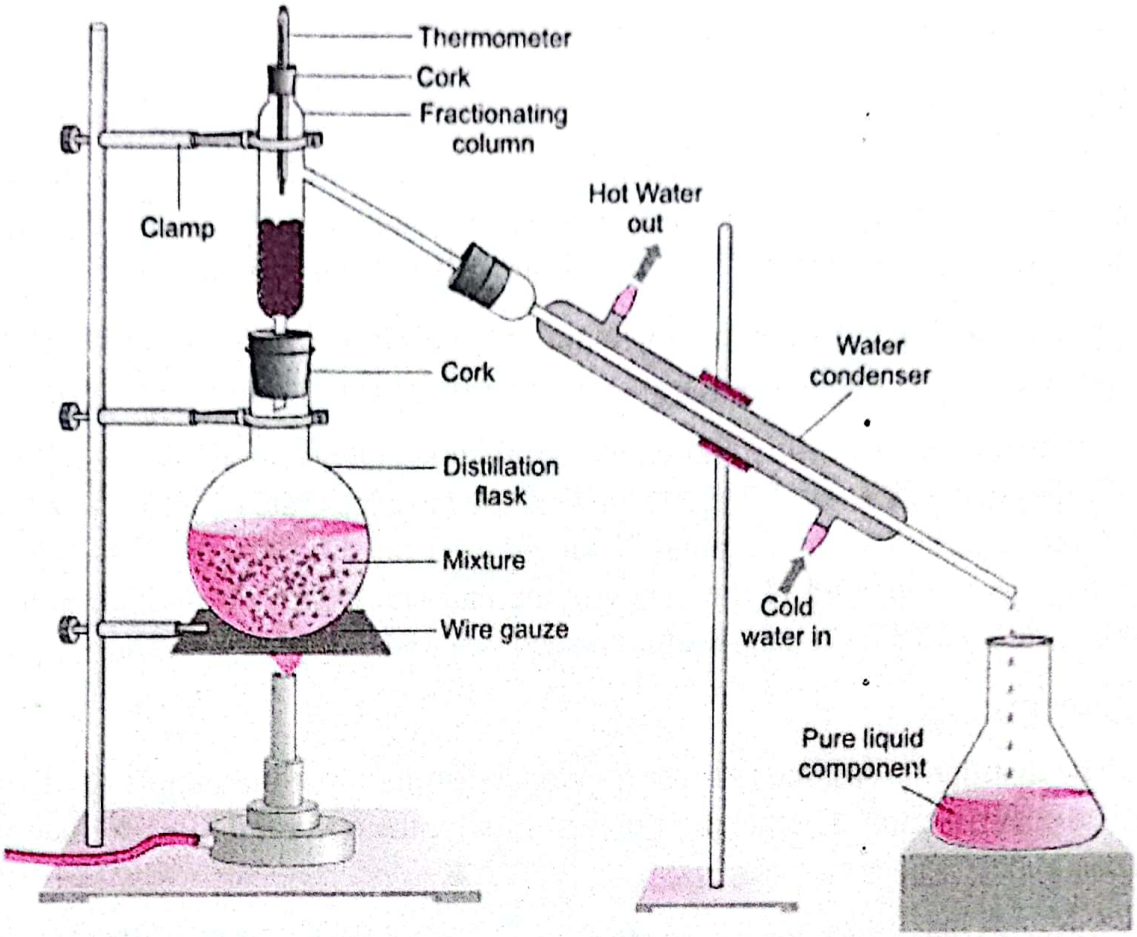
7. List the results in a table as shown below.

Table (1):

Distillate No.	Distillation Range °C	Volume of distillate (ml)	Accumulated volume of distillate (ml)	% of the accumulated volume
1	IBP to 120 °C			
2	121 to 180°C			
3	181 to FBP			



A Diagram Showing Fractional distillation of the crude oil at the refinery.



Fractional distillation apparatus

2. Thermal cracking of distillation residue

Thermal cracking:

Distillates whose distillation range >350 °C cannot be distillated through fractional distillation, because they may suffer from thermal cracking reactions. Therefore, high boiling ranges distillates are distillated under vacuum.

Thermal cracking process is a very important process. It was used to convert high molecular weight distillates into smaller ones of higher economical value.

There are two types of thermal cracking process, conventional and catalytic. In the catalytic thermal cracking, a catalyst is used to accelerate the process. Zeolite (a mixture of silica and alumina) is widely used for this purpose. Two types of zeolite were employed in the catalytic thermal cracking, namely high alumina (Al_2O_3/SiO_2-25/75%) and low alumina zeolite (Al-O/Si-O12.5:87.5%).

Procedure:

1. The distillation residue leftover fractional distillation of the sample of oil, was utilized in the thermal cracking process. Firstly, the volume of this residue was measured.

2. Transfer the distillation residue to a round bottom flask, and then add (3%w/w) of the catalyst (silica-alumina).

3. Reflux the mixture and observe the temperature (320-350°C for 1 hour) so as to observe the temperature at which the cracking occurres.

4. After the reaction is over, let the product to cool down to room temperature.

5.Measure volume of thermal cracking products, (observe the difference between the volume of the residue before and after thermal cracking process), why.?

6. Distillation of thermal cracking product should be conducted, so as to examine number of distillates that could be obtained after thermal cracking process.

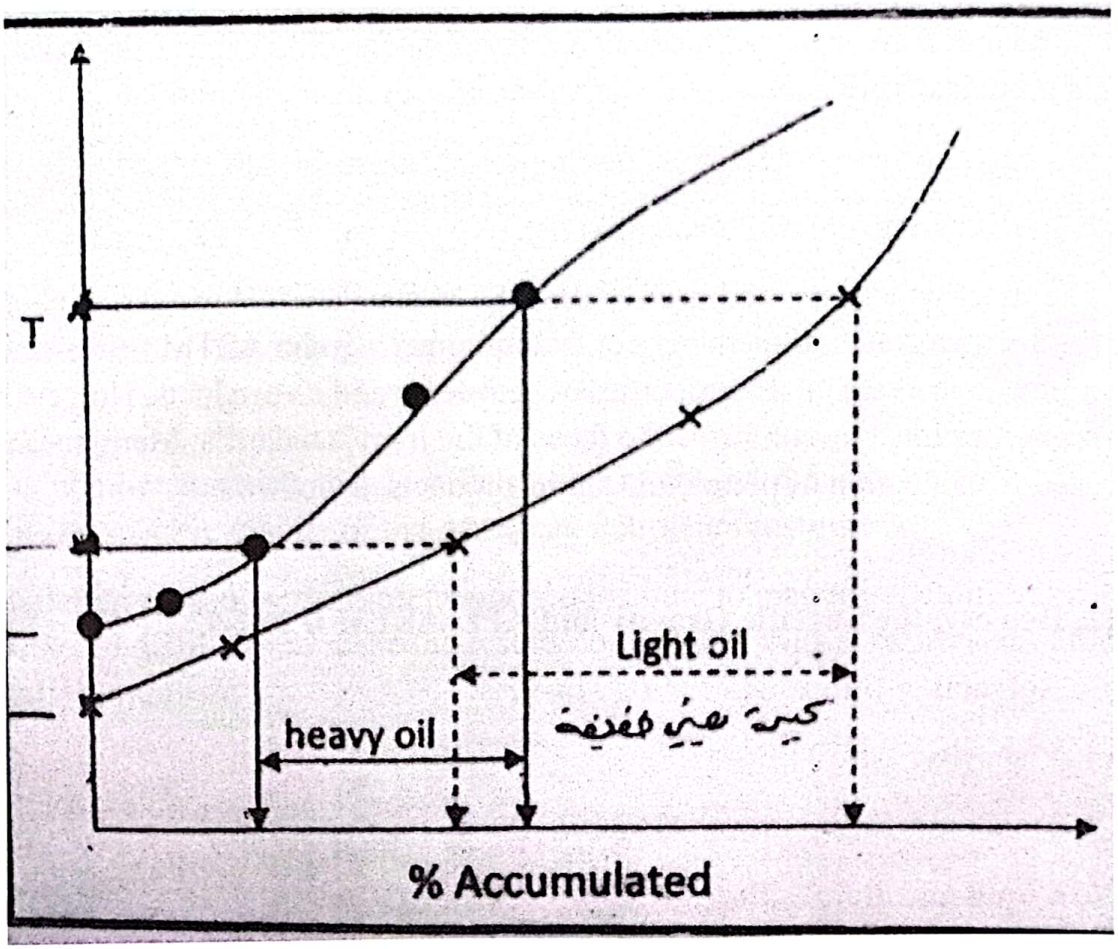
7. Tabulate your results as demonstrated in Table 1 and 2.

3. Distillation of unknown sample.

Now you have gained practical experience on petroleum distillation. Therefore, to examine your knowledge, you will be given an unknown sample, and you should conduct all steps you made previously on it.

After completing all the tests. Draw the distillation curves of both samples. This curve will help you to conclude the following information:

1. The relation between the volumetric accumulated percentages with temperature.
2. Predicting whether the quality of oils (heavy, medium, or light).
3. It can be used as a simple means to estimate percentage of oil fractions.



Distillation Curve

Test methods for petroleum products.

Evaluation of petroleum products aims to:

1 .To know whether the products properties are fulfilled to the standards limits.

2. Finding suitable conditions for transportation, storage and treatment.

3. Determination of impurities percentage (purity of the product).

There are many standard methods used to evaluate properties of petroleum and its products. The most widely methods used are:

1. The American Society for Testing and Materials (ASTM).

2. British Institute of Petroleum (IP).

The most widely method used is the ASTM standards. However, each country has its own standard methods, for example, in Iraq, the ASTM test methods are followed to evaluate the properties of petroleum and its products. However, these properties must be conformed to those of the Iraqi standard!s. Many methods are used in evaluation of petroleum and its products, as follows:

1. Distillation.

2. Density, the Specific Gravity and API. ASTM D 287-92

3. Refractive Index. ***ASTM D1218-92***

4. Viscosity. ASTM D 445

5. Flash and Fire points. ASTM D 93-99c

6. Cloud and Pour points. ASTM D 5853-95

7. Acid Number.

8. Surface Tension.

9. Carbon Residue. ASTM D 4530

10. Aniline Point. ASTM D 611-82

EXP (2)

Physical properties:

1. Density and specific gravity

Density is the ratio between the weight of the sample to its volume. It was first used as a principal measurement of petroleum quality. The specific gravity (SG) is used rather than density in petroleum industry.

The SG represents the weight of a certain volume of a liquid to a similar volume of water at 15.6 C° (60 F°).

Light oils is characterized by their lower SG values than heavier ones, because the former contain higher percentages of light distillates such as gasoline.

The density of petroleum is inversely proportional with its quality. Moreover, the density varies with the variation of its base, as follows.

The density **Aromatic/Naphthenic / Paraffinic**

There is another function that is widely used in the oil industry called (**API**), which is the specific gravity of the American Petroleum Institute API.

It is a function placed by the aforementioned institute to magnify the differences in densities of distillates to make the results comparable. API is expressed in the followed equation:

$$API\ gravity = \frac{141.5}{S.G@15.6\ °C} - 131.5$$

The higher the API, the better the petroleum quality and vice versa. Measuring density can be achieved using the following apparatus:

á. Volumetric flask.

b. Pycnometer.

c. Hydrometer.

Procedure:

The specific gravity is measured by using a pycnometer at 15.6 °C.

$$\text{Density} = \frac{\text{Wt}}{\text{V}}$$

$$\text{SG} = \frac{\textbf{Wt of sample}}{\textbf{Wt of the same vol. of } H_2O} \text{ @ } 15.6\ ^\circ C$$

Note: Pycnometer should not be dried in the oven. Use acetone only to dry Pycnometer.

According to the API gravity, crude oils were classified into:

Light crude oils (API >30)

Mid. crude oils (API 20-30)

Heavy crude oils (API 20-10)

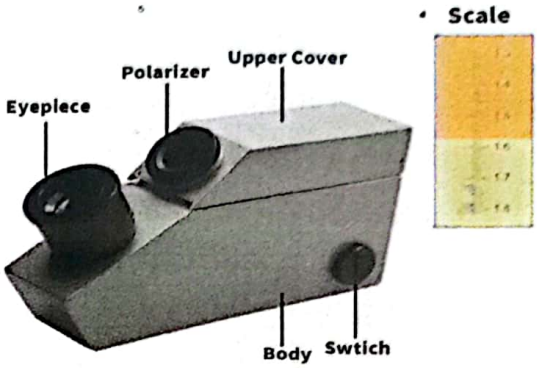
Extra heavy oil ((API < 10)

EXP (3)

Optical properties

Refractive index (RI)

It is the ratio between speed of light in the space to its speed within the medium. The RI is widely used in evaluating of petroleum distillates. It gives information on paraffinic, naphthenic, and the aromatic content of distillates. The RI increases with increasing the molecular weight of the hydrocarbon family. When number of carbon atoms are fixed, the RI increases with the change of the hydrocarbon type, as shown in the following diagram:



Benzene, Cyclohexane, Hexane

⟵

(+) RI and SG

A digital refractometer will be used for measuring the RI of the distillates. (*) Density, SG, API and RI of each distillate should be measured and listed in a table.

Table (2):

Sample No.	Boiling Range °C	D g/cm^3	SG	API	R.I
1					
2					
3					

EXP (4):

A) Viscosity

It is an important physical property of liquids. It is defined as the resistance of liquids on flow.

In general, viscosity determines the nature and type of the crude oil and its products. It is an important characteristic for lubricant oils.

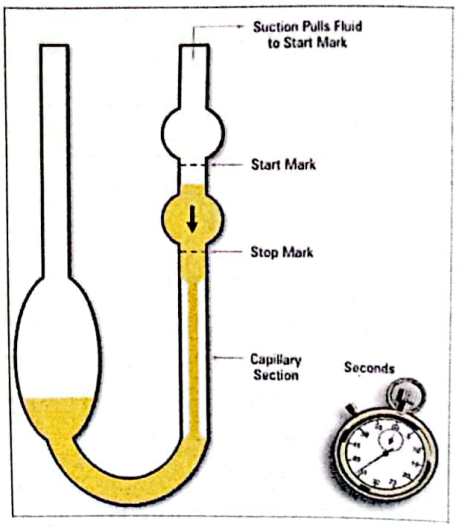
The average decrease in viscosity with temperature called the **viscosity index (VI).**

Liquids of high (VI) are slightly affected by variation of temperature. In petroleum industry, the kinematic viscosity which is a type of viscosity is widely used. It can be expressed by the following formula:

Kinematic viscosity = Dynamic viscosity /Density

The unit of kinematic viscosity (Stoke-dyne.cm. sec/gm)

The unit of dynamic viscosity (poise - dyne. sec/cm²)



Procedure :

1. Fill the viscometer (Ostwald) with suitable volume of liquid

2. Place the viscometer in a water both (to fix the required temperature

°38C).

3. Determine the time required for flow of the liquid from the upper bulb to the lower bulb (repeat it for at least three times and record the value as the average)

4. The viscosity can be determined using the following formula

$$\frac{d_1 t_1}{d_2 t_2} = \frac{\mu_1}{\mu_2}$$

Where, d_1,t_1, and μ_1 are density, time and viscosity of distilled water, while d_2 ,t_2 and μ_2 are density, time and viscosity of the sample.

EXP (5)

Flash and fire points

The flash point is the lowest temperature at which the liquid can vaporize to form a mixture with air that will ignite but not continue to burn by the aid of a flame source.

The fire point is the lowest temperature at which the mixture of the liquid vapor and air ignites and continues to burn by the aid of a flame.

How the combustion is occurred?

Every liquid has its own vapor pressure, which increases with the increment of temperature, so that the amount of vapor must be sufficient to sustain combustion (to make the combustion continues).

The importance of the flash point can be summarized as follows.

1. To estimate volatility of the product.
2. Selection of suitable conditions for storage, transportation and safety.
3. To assess contamination of the distillate.

Procedure:

1.Transfer (20 ml) of the sample to a beaker.

2. Cover the beaker with a cover with a thermometer through it.

3. Heat the beaker and monitor the temperature.

4. When the vapor starts to evolve, bring a flame close to the sample surface to detect the flash point.

5. If the sample ignited for a while (like the camera flash), record the temperature.

6. After you got the flash point, go on heating the sample until you get the fire point (the sample will ignite contentiously).

EXP (6)

Cloud point and pour point.

The **cloud point** is the temperature at which wax crystals begin to form in the sample when it was cooled under specific conditions, while the **pour point** is the lowest temperature at which the sample begin to flow when it was cooled under specific conditions.

Procedure:

1. Clean and dry the test tubes and fill it with heavy petroleum product to minimum required level.

2. Heat the test tube to get clear.

3. Seal the test tube with a cork having a thermometer of a required range which its bulb should be dipped in the sample.

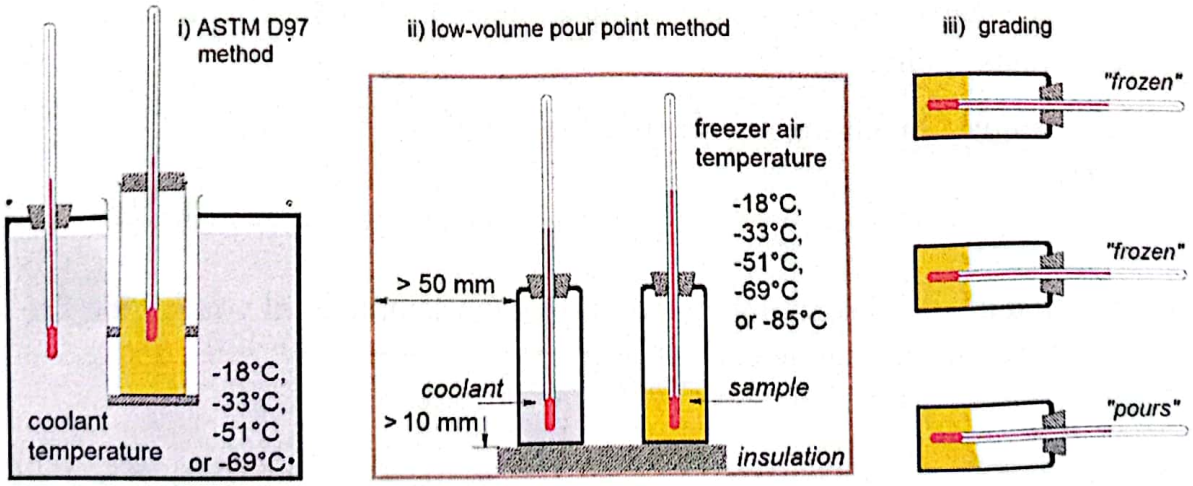
4. Place the test tube in the ice bath in a vertical position.

5. Observe the sample after a reduction of temperature (3°C minimum) to watch the cloud point.

6. Note down the temperature, at which cloud or crystals are observed, report it as cloud point of the sample.

7. Continue cooling the sample until the temperature at which the sample become unpourable is obtained.

8. Pour point is the temperature reported in (step 7) + 3°C.



The advantages of cloud and pour point:

1.It refers to the thermal limits suitable to pump distillates.

2. It can be used as a measure of wax content in oils.

3. It determines durability of petroleum or its distillates to the reduction in temperature.

EXP (7)

The acid numbers.

The acid number is defined as the number of milligrams of KOH required to neutralize acids found in a sample.

Fat or oil is hydrolyzed by different microorganisms, resulting in the formation of free fatty acids. The amount of free fatty acids present in the oil refers to the aging and the quality of the oil. Thus the high acid number indicates that the oil is old and rancid.

The presence of acids in petroleum and its distillates may be attributed to the presence of naphthenic acids and other organic acids as well as the inorganic acids. The presence of these acids results in corrosion of the pipes and equipment's.

Procedure:

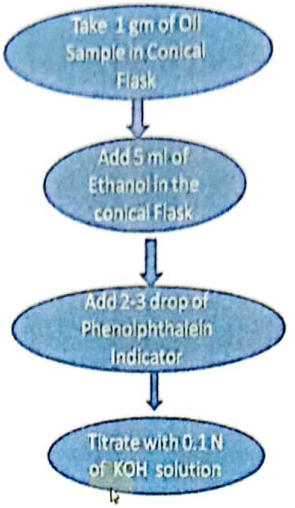
1. Prepare 0.1 N of KOH in isopropyl alcohol.

2. Weight 1.0 gm of the sample in a conical flask.

3. Add 25ml of petroleum ether to dissolve the sample, then add few drops of phenolphthalein (indicator).

4. Titrate against KOH solution until the solution tunes into a pink

5. Repeat the same steps without sample (Blank).



Calculation:

Acid number = $\frac{(A-B) \times N \times 56.1}{Wt \text{ of sample}}$

Where:

A= Volume of KOH required for the sample.

B= Volume of KOH required for the blank (0.10 mL)

N= Normality of KOH solution. 56.1 Equivalent weight of KOH.

56.1= Equivalent Weight of KOH

Wt =Weight of the sample.

EXP (8)

Surface tension

The surface tension is defined as the force which is found at the surface separates two different phases (liquid - solid), (liquid - vapor) or (gas - liquid), while the interfacial tension is defined as the force which is found at the surface separates two phases (liquid-liquid).

The surface tension of a liquid results from an imbalance of intermolecular attractive forces. The difference between the cohesive forces and the adhesive forces determine the behavior of a liquid in contact with a solid surface. The attraction forces between the liquid and the solid surface are called the adhesive forces, while the cohesive forces are the attraction forces among the molecules of the liquid itself.

E.g. Water/wax (cohesive forces > adhesive forces).

E.g. Water/glass (cohesive forces < adhesive forces).

The capillary is the ability of the liquid on raising through a capillary

Tube when it is immersed in the liquid.

The liquid creeps up the side of the tube (as a result of adhesive forces between the liquid and the inner walls of the tube) until the adhesive and cohesive forces of the liquid are balanced by the weight of the liquid. The smaller the diameter of the tube, the higher the liquid rises

Procedure:

1. Clean the capillary tube carefully with acetone or petroleum ether, and then connect it with a rubber tube to raise the sample.

2. Fix the capillary tube vertically in the sample.

3. With draw the sample by the rubber tube to rise the liquid through the capillary tube. Then the liquid will fall dawn until it occupies a certain height (b) of the tube.

4. Use a roller to measure the height of the liquid.

5. Repeat the measurement three time, and record the result as the mean.

Note: The surface tension is usually measured at room temperature.

Calculation:

Surface tension y can be estimated from the following relation:

$$\gamma = \frac{1}{2} h g d r$$

where, γ is the surface tension (dyn/cm), h is the height (cm), g is the gravity (dyn/g), d is the density (g/ml) and r is the radius (0.045 cm).

EXP (9)

Carbon residue

The carbon residue is the tendency-of a fuel to form-carbon-deposits under high temperature condition in an inert atmosphere. It may be expressed as a Ramsbottom Carbon Residue (RCR), Conradson Carbon Residue (CCR) or Micro Carbon Residue (MCR). Numerically, the CCR values the same as that of MCR. The carbon residue of a fuel depends on its chemical structure. For example, gasoline and kerosene have very low carbon residue compared to fuel oil and asphalt.

The carbon residue can be used as a function of quality of petroleum's. The lower the carbon residue, the higher the API. The carbon residue increases with the increment of the asphaltic components of petroleum. It can also be used as an indication of heaviness of crude oil and its tendency on the production of gasoline.

Procedure:

1. Clean the crucible and dry it in a furnace at 350 °C for 20 minutes, then place the crucible in a dissector to cool dawn to room temperature.

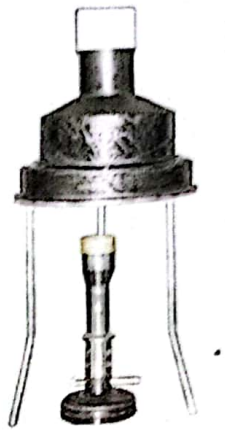
2. Weight the crucible to the nearest 4 digits.

3.Weight into the crucible one gram of oil sample (to the nearest 4 digits).

4.Place the crucible on a wiregause and cover it with Conrad son apparatus. Burn the crucible by benzene burner until all vapors stop evolving.

5. Leave the crucible to cool dawn to room temperature. Then re-weight the crucible and the difference between the weight of the crucible with carbon and its original weight represents the weight of the carbon residue.

$$\text{Carbon residue (\%)} = \frac{\text{Wt carbon produced}}{\text{Wt of sample}} \times 100$$



EXP (10)

Aniline point

The aniline point is the lowest temperature at which a sample is completely miscible with an equal volume of aniline, Aromatic hydrocarbons exhibit the lowest values of aniline point. Cyclo paraffin's and olefins exhibit values that lie between those for paraffin and aromatics. It increases with the increment of the molecular weight of the same hydrocarbon family.

Aromatic, olefins, Cyclo paraffin's, paraffin $\longrightarrow$

Increase aniline point

The aims of determining the aniline point are:

1.To evaluate aromaticity of a fuel.

2.Indicates whether the fuel ignited with a smoke or not (it determines Combustion characteristics of fuels).

Procedure:

1. Mix 5 ml. of the sample with an equal volume of pure aniline in a test tube.

2. Seal the test tube with a cork provided with a thermometer to measure temperature. Do not let bulb of the thermometer in contact with bottom of the test tube.

3. Place the tube in a water bath and mix the mixture.

4. Record the temperature at which the two samples is completely miscible with each another.

EXP (11)

Diesel index and cetane number

The diesel index is an indication of ignition quality of a diesel fuel, while the **Cetane number** is a measure of the ignition characteristic of a diesel fuel by comparison with a range of fuel, in which cetane is given a value 100, while methyl naphthalene is zero.

Procedure:

1. Determine the aniline point of diesel fuel.

2.Determine the density of diesel fuel by using a pycnometer.

Calculation:

$$\text{Density} = \frac{\text{Wt}}{\text{Vol.}}$$

$$\text{Specific gravity} = \frac{\text{Density of diesel}}{\text{Density of water}} \quad @\ 15.6\ C$$

$$\text{API} = \frac{141.5}{\text{Specific gravity @ 15.6 C}} - 135.5$$

$$\text{Cetane Index} = \frac{\text{API} \times \text{Aniline points}}{100}$$

Cetane number = 0.72 x Cetane Index x 10