Distillation of Thermal cracking residue

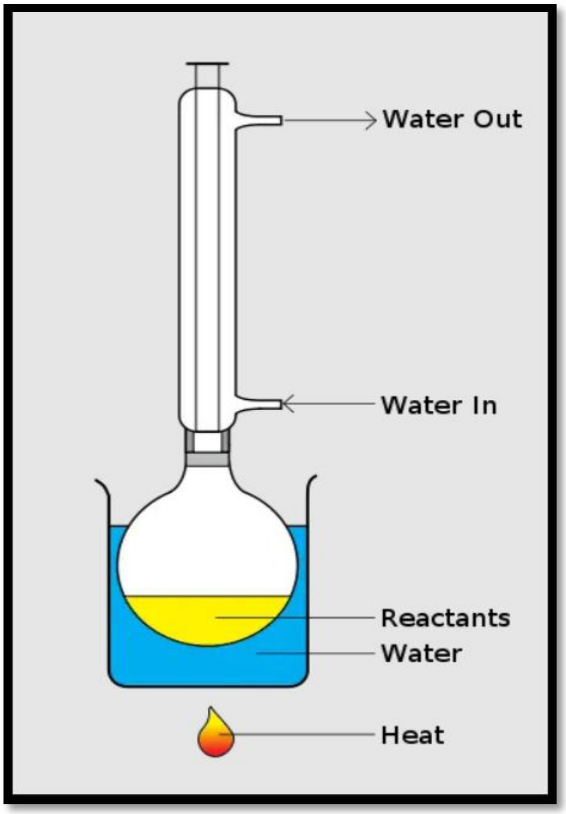
Thermal cracking:

Distillation which have distillation range up to (>350 °C) cannot be distillated through fractional distillation

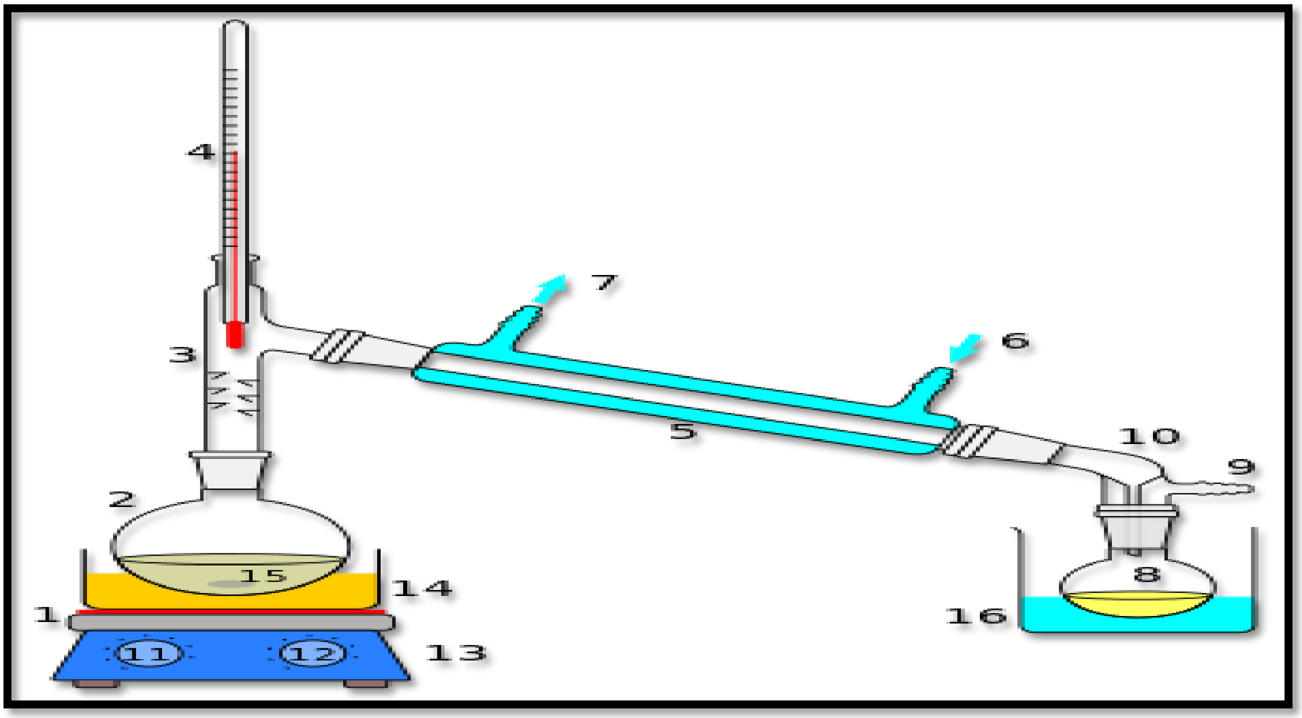
Because they may suffer from thermal cracking reactions. Therefore; high boiling range distillates are distillated under vacuum. Thermal cracking process is a very important process, because it used to convert high molecular weight distillates into smaller ones of higher economical value. There are two types of thermal cracking process, conventional and cataylatic .In the catalyatic thermal cracking, actalayst is used to accelerate the process, Zeolite (a mixture of silica and alumina) is widely used for the purpose. There are two types of zeolite that was used in the catalytic thermal cracking , high alumina(Al_2O_3/SiO=25/75%) and low alumina zeolite(Al_2O_3/SiO_2=12.5/87.5%).

The method of work:

1- After distillation residue being reached room temperature, its volume should be measured.
2- Transfer the distillation residue to a round bottom flask, 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 is occurred .
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- List your results as in Table 1 and 2.



The refulaxe apparatus



The simple distillation apparatus

Separation of straight paraffins from oil fractions

The most important hydrocarbons found in oil are: aromatic ,naphthenic and paraffinic .

Naphthenic compounds are cyclic paraffins. You have learnt in the organic chemistry that there are two types of paraffins ,straight and branched paraffins .straight paraffins decrease the octane number of gasoline ,while branched paraffins increase it .the octane number or octane rating is defined as is the volume percentage of iso-octane in mixture contains iso-octane and n-heptanes. It is used as ameasure of quality of gasoline, i.e. anti –knock property.

Paraffines have an acceptable smell whene its content of S and N compounds as less as possible. High content of S and N compounds in paraffins add to them un-acceptable smell (strong smell).

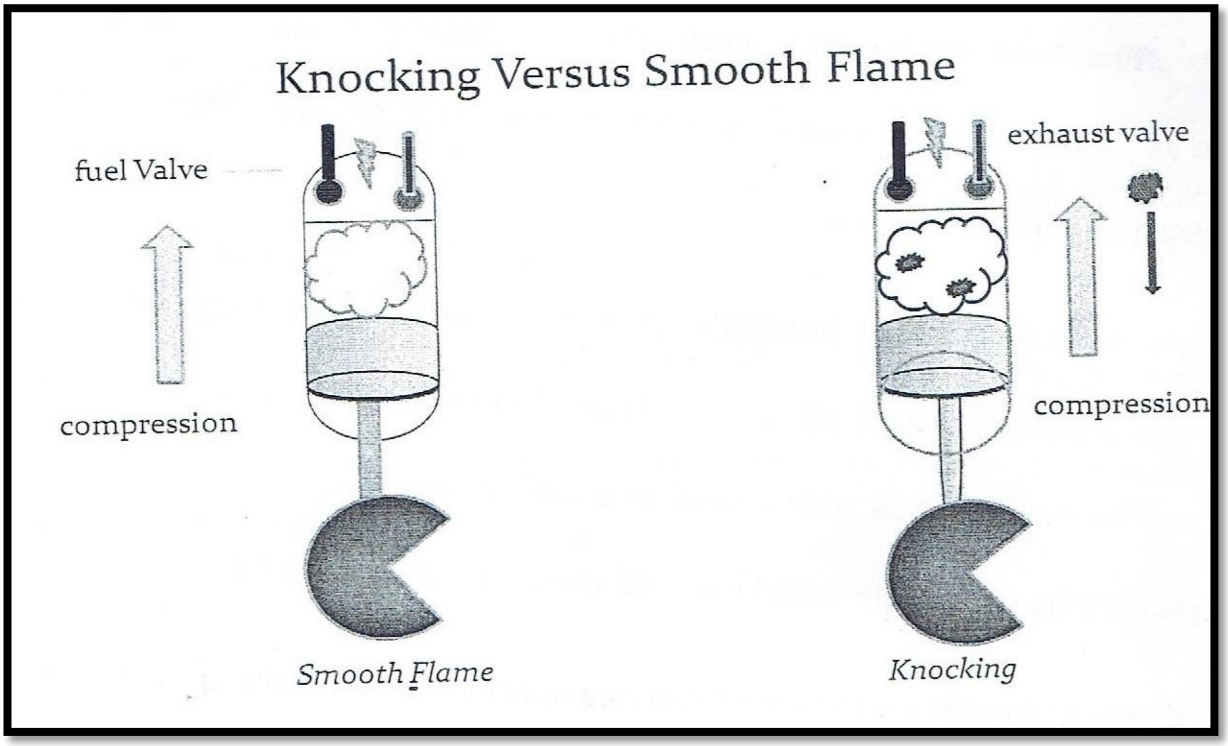
Low molecular weight paraffin s lie within gasoline range hydrocarbons, while middle molecular weight paraffin are found in the higher boiling range distillates like kerosene , which widely used as a fuel for heating . high moleculare weight paraffins are used in the manufacture of matches and isolating materials.

Straight paraffins have a potential role in petrochemical industry .it is used in the manufacture of detergents , because they are bio-degradable unlike the branched paraffins. The latter cause water Pollution by forming biological undegradabal foam.

The chemical fractionating methods of hydrocarbons are based on treatment of petroleum distillates with som chemicals. For exampale, separation of straight paraffins through formation of molecular complexes with urea is widely used . bases of separation depends greatly on the variation in molecular size of the paraffin, its shape and the type of molecule used in the information of the molecular complex (urea or thiourea) as well.

Urea adduct

Formation of the molecular complexes is based on formation of hydrogen bonds among urea molecules which results in the formation of a channel or cave (hexagonal shape). Certain molecules of paraffins can be trapped in the cave to form a molecular complex between urea and straight paraffins.



Procedure:

The main goal of the present experiment is to separate straight paraffins from a certain petroleum distillate and determination of its perecentage.

Chemicals used :

1- Isopropyl alcohol .
2- A petroleum distillate.
3- Urea .
4- Distillated water .

Experiment steps:

1. weight (10g) of urea , petroleum distillate and isopropyl alcohol.
2. mix well the petroleum distillate and isopropyl alcohol in a beaker . then add urea gradually with continues stirring.
3. add (3ml) of distillated water to mixture gradually from a burette.
4. stirr the mixture continuously for (45minutes).
5. Filtter the mixture through decantation.
6. Add(20 ml) of boiled distillated water to precipitate with stirring until the precipitate is completely dissolved.
7. Transfer the mixture to a separating funnel to obtain two layers , the upper is the (paraffins). And the lower is the (aqueous). Transfer the upper layer to a pre –dried and weighted a beaker. Percentage of straight paraffins can be calculated as follows:

$$\boldsymbol{Yiled}(\%) = \frac{\textbf{Wt of the obtained paraffins}}{\textbf{Wt of petroleum distillate used}} \times \mathbf{100}$$

Determination of water content in petroleum and its distillates by using dean –stark apparatus

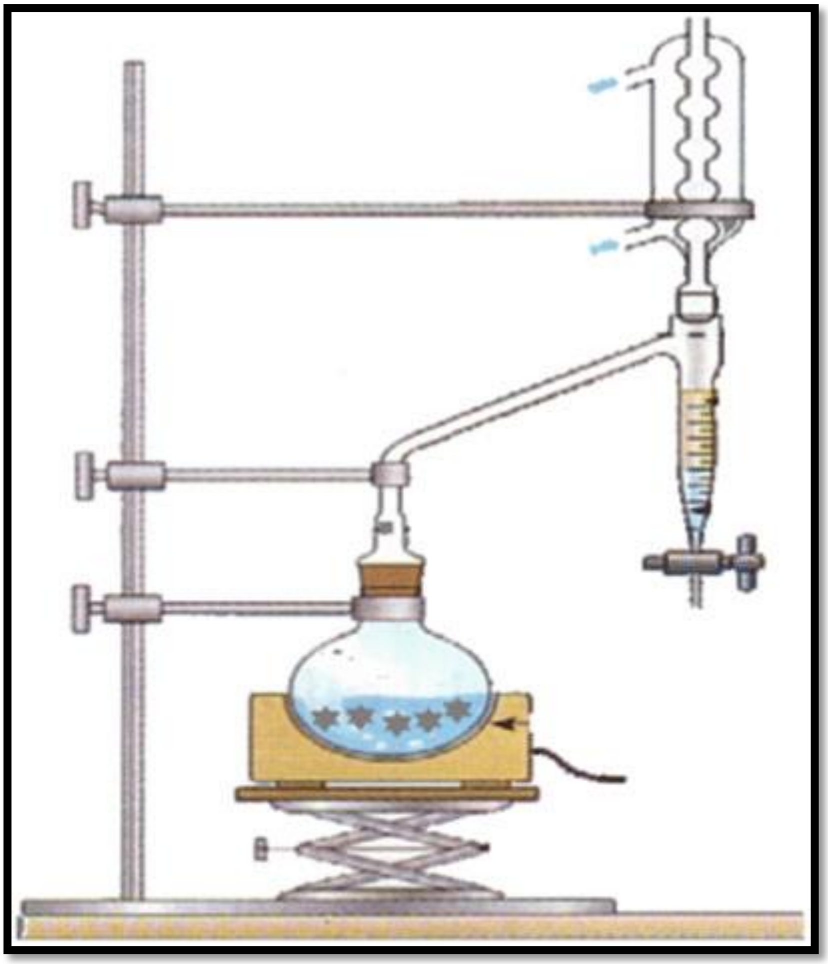
The presence of water in oil or oil products has a big impact on an oil refining process therefore the first steps that must be performed before oil fractionation by distillation is removal of water to an acceptale limits .crude oil coming from the well contains about 80%-90% water. a part of this water could be free, while other may be as emulsion . there is a limitation for water content in crude oil based on method used for transferring it . for example crud oil transferred through pipes should not contain more than (0.5-2 %) water as maximum. Thus , the presence of water in crude oil is unfavorable , because it causes many effects “what are they”?.

Procedure:

1- Transfer (25 ml) of the sample (contains a known content of water) to a(100ml) round bottom flask.
2- Add (25ml) of the solvent (pet.ether 80-100c) to the sample using a graduated cylinder . wash the cylinder at least twice with petroleum ether , and return it to the round bottom flask .
3- Mix the mixture well(add boiling stones).
4- Connect the dean _stark apparauts as you learnt previously .
5- Heat the mixture slowly (with a condensation rate of 2-5 drops/minutes) and collect the separating water and solvent .
6- After separation was over , transfer the collected water and solvent to a separating funnel to obtain two layers.
7- Separate each layer ,and calculate its percentage as follows :
8-

$$\mathbf{H_2O}(\%) = \frac{\text{vol.}\,\mathbf{of}\ \mathrm{H_2O\ separated}}{\text{Total vol. of sample}} \times \mathbf{100}$$

$$\textbf{Solvent recovered vol.}\ (\%) = \frac{\textit{volume of solvent recovered}}{\textit{Total volume of the solvent used}} \times \mathbf{100}$$



The dean –stark apparatus

Purification of raw sulfur

Iraq production of sulfur from al- mishraq filed exceeds million ton annually . sulfur industry is the second national industry in Iraq after petroleum . the raw sulfur is extracted (recovered) by frasch method all over the world . after extraction , it sent to a filtration unit to remove sands and gravel .then it become ready to export.

In Iraq , sulfur contains a bituminous impurity (^{o}C) that affected its color . this impurity is the result of the inetraction of qiayarah crude oil filed with al- mishraq sulfur filed . as a results , qiayrah crude oil contains the highest percentage of sulfur (8.55%) compared to other petroleum . on other hand , al- mishraq sulfur contains a hydrocarbon impurity (1%) .

Principle of the experiment :

The experiment based on extraction of sulfur from sulfur contains the HC impurity via a continuous extraction method using the soxhlet apparatus . the soxhlet principle can be conducted at the industrial scale such as extraction of sugar from sugar cane and beet, and extraction of vegetable oils from seeds.

Procedure:

1- Transfer(50 ml) of petroleum ether (80-100 ^{o}C) to a round bottom flask . add boiling chips .

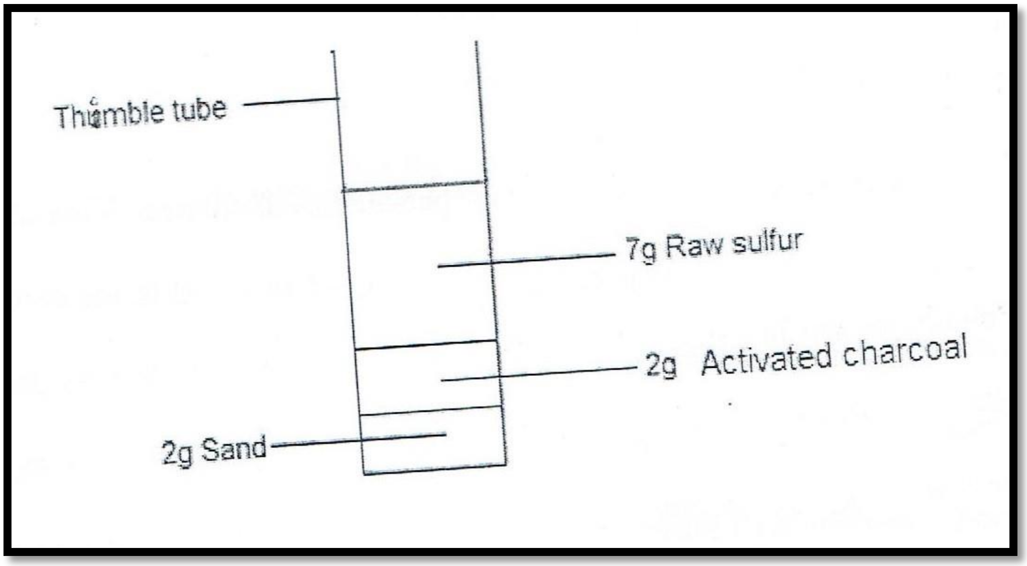
2- Weight (2gm) of the raw sulfur and place it into a thumble contains a layer of sand and another of activated charcoal.

3- Connect the soxhlet apparatus and start heating until the solvent starts boiling and continue heating for (15 minutes).

4- After the extraction was over (how?) ,let the apparatus to cool down to room temperature then transfer the solvent with extracted sulfur into a beaker (pre- weighted).

5- Cool the beaker using an ice bath . then decant the solvent and dry the obtained sulfur in an oven at low temperature .

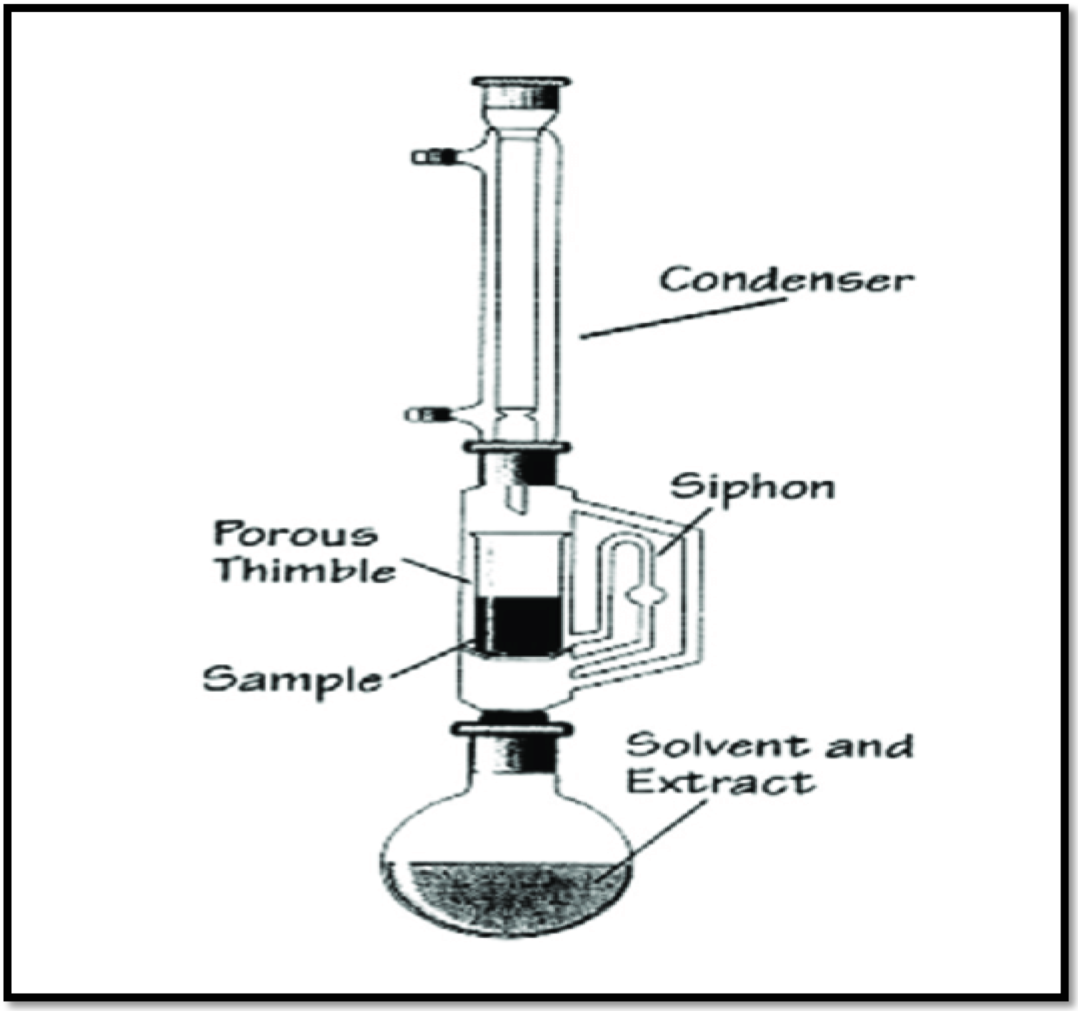
6- Calculated percentage of the recovered sulfur and solvent



Calculation :

$$\mathrm{S(\%)} = \frac{\text{wt. of sulfur recovered}}{\text{wt. of raw sulfur used}} \times \mathbf{100}$$

$$\text{Solvent recovered (\%)} = \frac{\text{vol. of solvent recovered}}{\text{vol. of solvent used}} \times 100$$



The soxhlet extraction apparatus

Extraction the oils from some seeds

Some of the seeds as (flax seeds ,sesame ,sun flower..etc.) contain feasible amount of oil materalies in various ratio which can be used for different purposes

To extract these oil materials applying laboratory method soxhlet extraction apparatus can be used depending on suitable solvent organic as (pet. Ether or chloroform and hexane) which dissolve the oil material and when the solvent evaporated or distillated is possible to get the oil material and its percentage could be found in the seeds .

The material and devices:

Flax seed , sesame or sunflower, pet-ether (60-80 ^{o}C) or hexane ,soxhlet, condenser ,round bottom flask .

Procedure :

1. Weight dry round bottom flask, record the weight , put (100ml) of pet-ether or hexane.
2. Weight (10gm) from the seeds and put it in the thimble tube then fix it in the soxhlet apparatus .
3. Heat the flask for one hour and quarter and notice the change of color of the solvent in the flask .
4. Distil the solvent and(keep it) , weight the flask containing the resulting oil in order to find its weight , then find the percentage of the oil in the applied seeds .

$$\textbf{the oils} = \frac{\textbf{wt. gm of oil}}{\textbf{wt . gm of seeds}} \times 100$$

Measuring volatility of some types of fuels

Volatility is the ability of liquid on evaporation . evaporation of any liquid depends on its vapor pressure (vp). Vp is the pressure applied by the liquid molecules on the walls of the container , which is in an equilibrium with atmospheric pressure . vp increase with the increase temperature . the liquid is boiled when its vp is equals the atmospheric pressure. Boiling point (bp). Is greatly associated with vp of the liquid .

As petroleum distillates such as gasoline or kerosene ,etc., are a mixture of hydrocarbons , they have no specific (bp). Therefore , we used range(bp) rather than the (bp).

Distillation is used to measured volatility of petroleum distillates . volatility of a distillate is a characteristic property , ex: gasoline is used as a fuel in the combustion engines that work through spark plug. As a result its volatility is very important property . therefore , volatility of gasoline is varied depending on climate. in winter, gasoline should contain high ratios of(high volatile hydrocarbons), and vice versa in summer (low volatile hydrocarbons) , in winter , the engine could be shut down due to a phenomenon called (carburetor icing) ,therefore , the icing factor should be higher to avoid this a phenomenon.

The gasoline used in winter is not suitable as fuel in summer , due to vapor lock phenomenon . the presence of high vapor . pressure hydrocarbons in gasoline increase of the evaporated fuel . consequently , the optimum (air/fuel ratio=15/1) will change , resulting in insufficient combustion

$$\mathbf{2C_8H_{18}+25O_2 \xrightarrow{\qquad\qquad} 16CO_2+18H_2O}$$

Two factors can be used in determination of the volatility properties of a fuel :

1. **1-** Warm up factor . it is the temperature at which a suitable amount of the fuel vapor and air are injected to a carburetor . this factor is responsible for preparing the suitable mixture of fuel and air for combustion .

$$\text{Warm up factor} = \frac{T90}{\mathbf{2}} + T50$$

Where , T90 is the temperature at which (90% vol.) of the sample is distillated and T50 is the temperature at which (50% vol.) of the sample is distillated .

2. **2-** Icing factor : it is the temperature at which water is unable to be condensed as well as sulfuric acid . this factor is important after the combustion

$$\textbf{Icing factor} = \frac{T90}{\mathbf{5}} + T50 + T10$$

Where , T10 is the temperature at which (10% vol.) of the sample is distillated.

Procedure :

1- Transfer (100ml) of the distillate to a (250ml) round bottom flask . add boiling stones .

2- Connect the distillation apparatus firmly so that no leakage could be observed .

3- Heat the sample, and collect the distillates in a (100ml) graduate cylindero . record the initial boiling point record temperature at which (5ml) of the distillate is collected successively until the distillation is stopped .

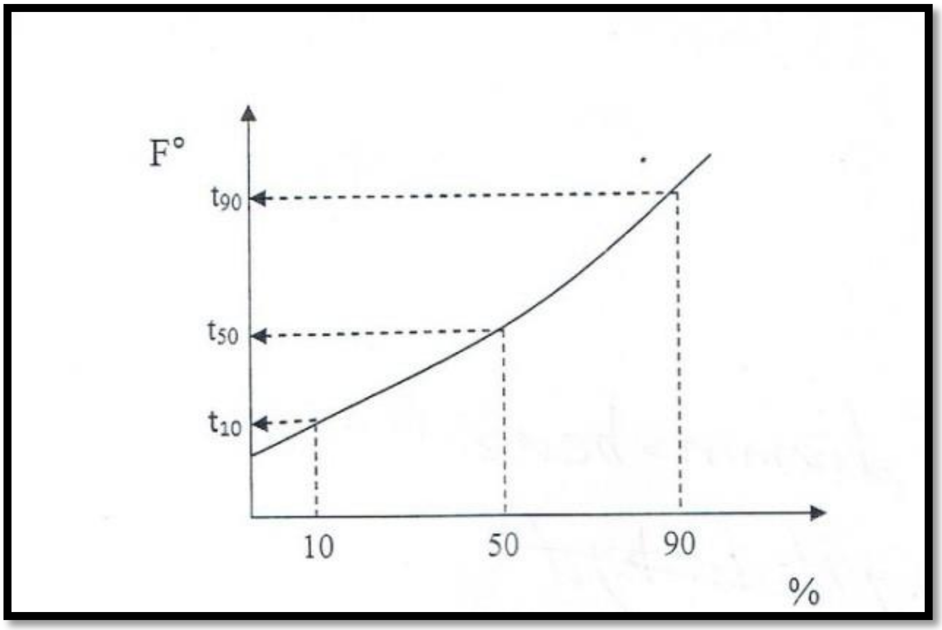
Calculation :

Draw a plot between percentage of the collected fraction and the distillation temperature (F).

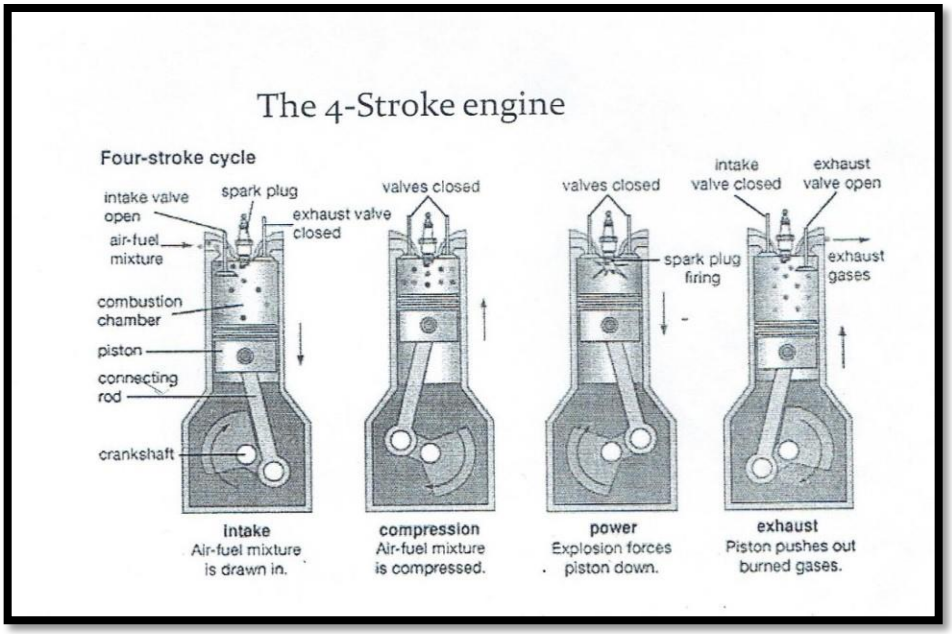
$$\textbf{Recovery}\ (\%) = \frac{\textbf{vol. of the distillate}}{\textbf{vol. of sample}} \times 100$$

The following formula is used to convert temperature from center grade (^{o}C) to Fahrenheit(F).

$$F = (\frac{9}{5} \times c) + 32$$



Calculated the warm up and icing factors values of T90, T50 and T10 can be obtained from the plot.



The 4-Stroke engine

Four-stroke cycle

intake Air-fuel mixture is drawn in.

compression Air-fuel mixture is compressed.

power Explosion forces piston down.

exhaust Piston pushes out burned gases.