4. Analysis of Petroleum

The composition of crude oil and its fractions are not expressed in terms of pure components, but as 'cuts' expressed between a range of boiling points because it is not possible to separate the components of crude oil into individual chemical compounds. These 'cuts' are further defined by splitting them into smaller sections and treating those sections as though they were pure components. As such, each of these components will have precise properties such as specific gravity, viscosity, mole weight, pour point, etc. These components are referred to as pseudo components and are defined in terms of their mid boiling point.

To establish a basis for the comparison between different types of crude oil, it is necessary to produce experimental data in the form of what is known as an ''assay''. The crude oil assay is a complete and definitive analysis. This is more detailed than a crude TBP curve. A complete crude assay contains some of the following data:

1. Whole crude salt, gravity, viscosity, sulfur, light-end carbons, and the pour point.
2. A TBP curve and a mid-volume plot of gravity, viscosity, sulfur, and the like.
3. Light-end carbons analysis up to C8 or C9.
4. Properties of fractions (naphtha, kerosene, diesels, heavy diesels, vacuum gas oils, and resides). The properties required include yield as volume percent, gravity, sulfur, viscosity, octane number, diesel index, flash point, fire point, freeze point, smoke point, and pour point.
5. Properties of the lube distillates if the crude is suitable for manufacture of lubes.
6. Detailed studies of fractions for various properties and suitability for various end uses.

Crude assay are of two types:

1. Inspection data: gives primary information about the source and type of crude oil as well as some important properties such as viscosity, density, and boiling point.
2. Full assay: involves the determination the properties of crude oil, the properties of fractions obtained and their percentage yield.

The **boiling point** of a substance is the temperature at which the vapor pressure of the liquid equals the pressure surrounding the liquid and the liquid changes into a vapor, and for mixture of more than one component (like petroleum) it has boiling point range depend on number of components and boiling point temperature for each one as well as on applied pressure and the apparatus used for distillation .

The true boiling point curve is basically a plot of the boiling point of each component of the mixture as a function of the cumulative volumetric fraction distilled. The composition of any crude oil sample is approximated by a true boiling point (TBP) curve. The method used is basically a batch distillation operation, using a large number of stages, usually greater than 60, and high reflux to distillate ratio (greater than 5). The temperature at any point on the temperature-volumetric yield curve represents the true boiling point of the hydrocarbon material present at the given volume percent point distilled. TBP distillation curves are generally run only on the crude and not on petroleum products.

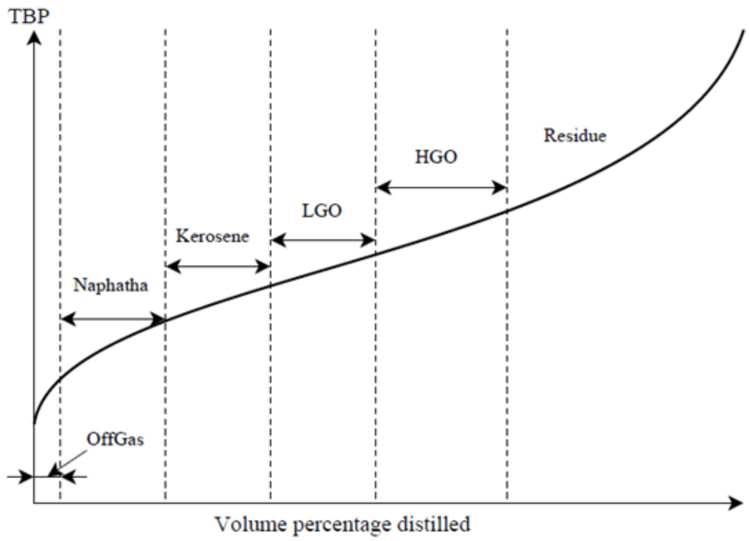
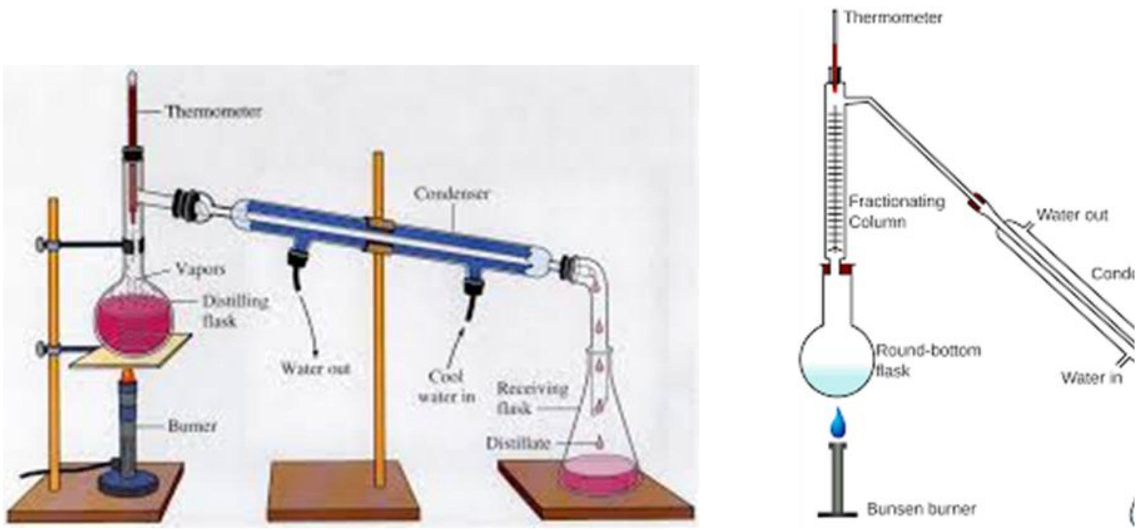


Figure 1 True boiling point curve for crude oil

Distillation is a process of separating the component substances from a liquid mixture by selective vaporization and condensation. The first step in refinery is distillation in which the crude oil separated into fractions according to its boiling point. There are at least four types of distillation curves or ways of relating vapor temperature and percentage vaporized.

The ASTM distillation curve

Standard method of ASTM distillation curves are conducted on the whole crude oil. This type of distillation curve is used however on a routine basis for plant and product quality control. This test is carried out on crude oil using a simple apparatus designed to know the boiling range by boiling the test liquid and condense the vapors as they are produced. Vapor temperatures are noted as the distillation proceeds and are plotted against the distillate volumes. Because only one equilibrium stage is used and no reflux is returned, the separation of components is poor. Thus, the initial boiling point (IBP) for ASTM is higher than the corresponding TBP point and the final boiling point (FBP) for ASTM is lower than that for the TBP curve.

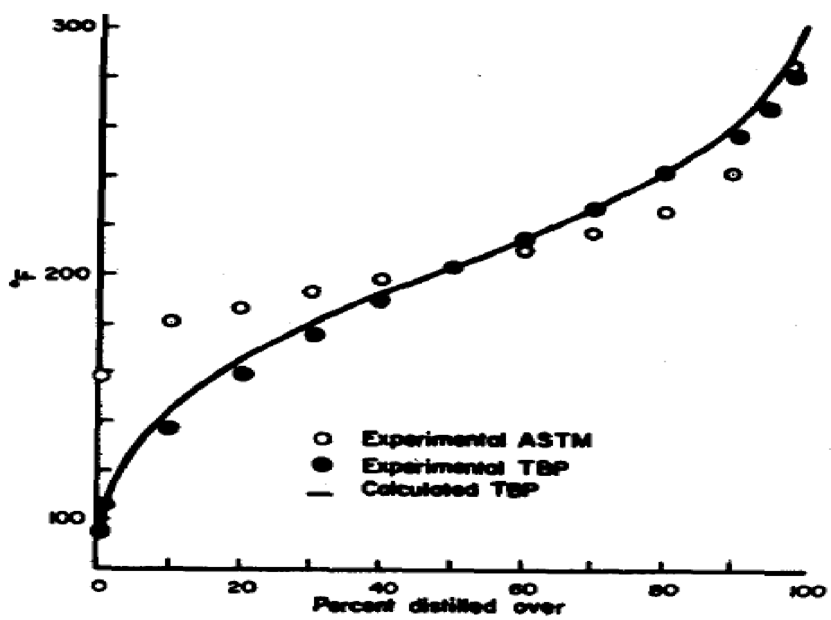


a b

Figure 2 (a) Standard distillation Apparatus, (b) fractionation distillation aperture

Both TBP, ASTM distillation curves are measured at 1 atm pressure. In both these cases, the boiling points of various volume fractions are being measured.

The basic difference between TBP curve and ASTM distillation curve is that while TBP curve is measured using batch distillation apparatus consisting of no less than 100 trays and very high reflux ratio, the ASTM distillation is measured in a single stage apparatus without any reflux. Therefore, the ASTM does not indicate a good separation of various components.



Cut point: A cut point is defined as that temperature on the whole crude TBP curve that represents the limits (upper and lower) of a fraction to be produced. Consider the curve shown in below figure for a typical crude oil TBP curve.

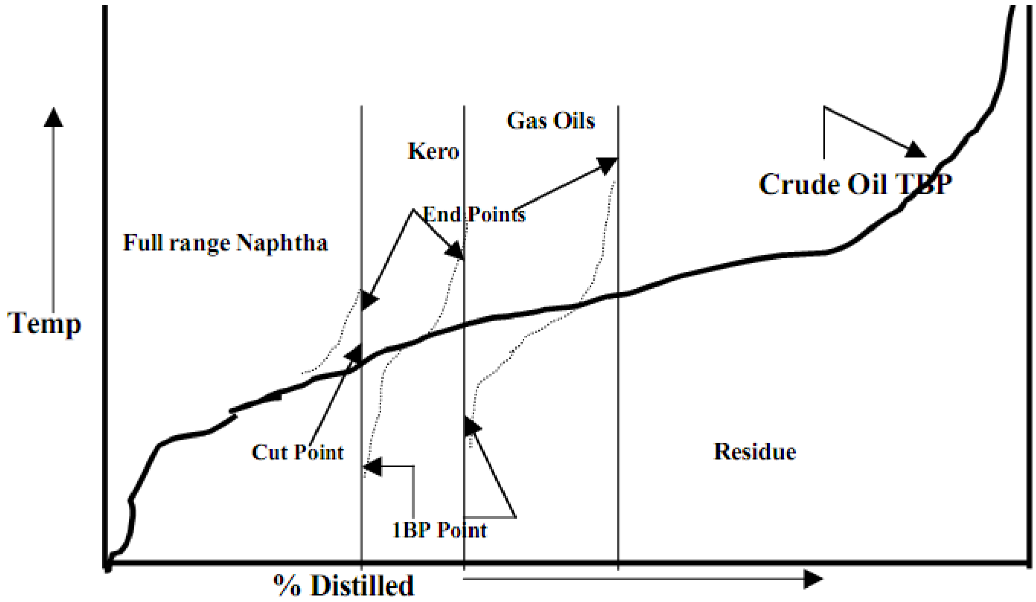


Figure 3 cut point and end point

A fraction with an upper cut point of 100◦F produces a yield of 20% volume of the whole crude as that fraction. The next adjacent fraction has a lower cut point of 100◦F and an upper one of 200◦F this represents a yield of 30−20%=10% volume on crude.

Initial boiling point: The temperature at which the first drop of distillate collected from the condenser is called initial boiling point.

Middle boiling point: The temperature at which the 50% of distillate collected from the condenser is called middle boiling point.

Final boiling point: The maximum temperature at which the distillate cannot be collected is called final boiling point.

End points: While the cut point is an ideal temperature used to define the yield of a fraction, the end points are the actual terminal temperatures of a fraction produced commercially.

Mid boiling point components:

The physical properties of an oil found to vary gradually throughout the range of compounds that constitute the oil. The properties such as color, specific gravity, and viscosity are found to be different for each drop or fraction of the material distilled. The rate at which these properties change from drop to drop may plot as mid per cent curves. For the first component take an arbitrary temperature point A. Draw a horizontal line through this from the 0% volume. Extend the line until the area between the line and the curve on both sides of the temperature point A are equal. The length of the horizontal line measures the yield of component A having a mid-boiling point A ◦F. Repeat for the next adjacent component and continue until the whole curve is divided into these mid boiling point components.

Volume of Residue =Volume of sample - Volume of distillate collected

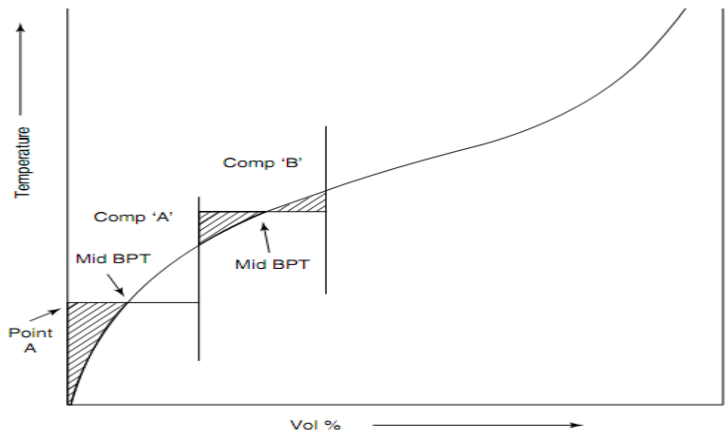


Figure 4 example of mid boiling point

Mid volume percentage point components:

Sometimes the assay has been so constructed as to correlate the crude oil properties against components on a mid-volume percentage basis. In using such data as this the TBP curve is divided into mid volume point components. This is easier than the mid boiling point concept and requires only that the curve be divided into a number of volumetric sections. The mid volume figure for each of these sections is merely the arithmetic mean of the volume range of each component.

Calculations of TBP

Vol %	°F
0	406
10	447
30	469
50	487
70	507
90	538
100	578

Average boiling point calculated by

$$ABP = \frac{T^0F@10\% + (2 \times T^0F@50\%) + T^0F@90\%}{4}$$

= (447 + 974 + 538)/4 = 490 ° F

Important Product-Properties and Test Methods

Distillation of crude yields number of cuts or fractions having varying boiling ranges, these are

1- Light products
   a. Natural gas.
   b. Aviation gasoline.
   c. Motor gasoline.
   d. Kerosene.
2- Mid products
   a. Gas oil.
   b. Diesel oil
   c. Lubricants.
3- Heavy product
   a. Bunker / Fuel oil.
   b. Bitumen.
   c. Wax.

General Summary of Product Types and Distillation Range

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
Refinery gas	C_1	C_4	−161	−1	−259	31
Liquefied petroleum gas	C_3	C_4	−42	−1	−44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	−1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$>C_{20}$		>343		>649	
Wax	C_{17}	$>C_{20}$	302	>343	575	>649
Asphalt	$>C_{20}$		>343		>649	
Coke	$>C_{50}$*		>1000*		>1832*	