Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering Department

Properties of Petroleum & Natural Gas
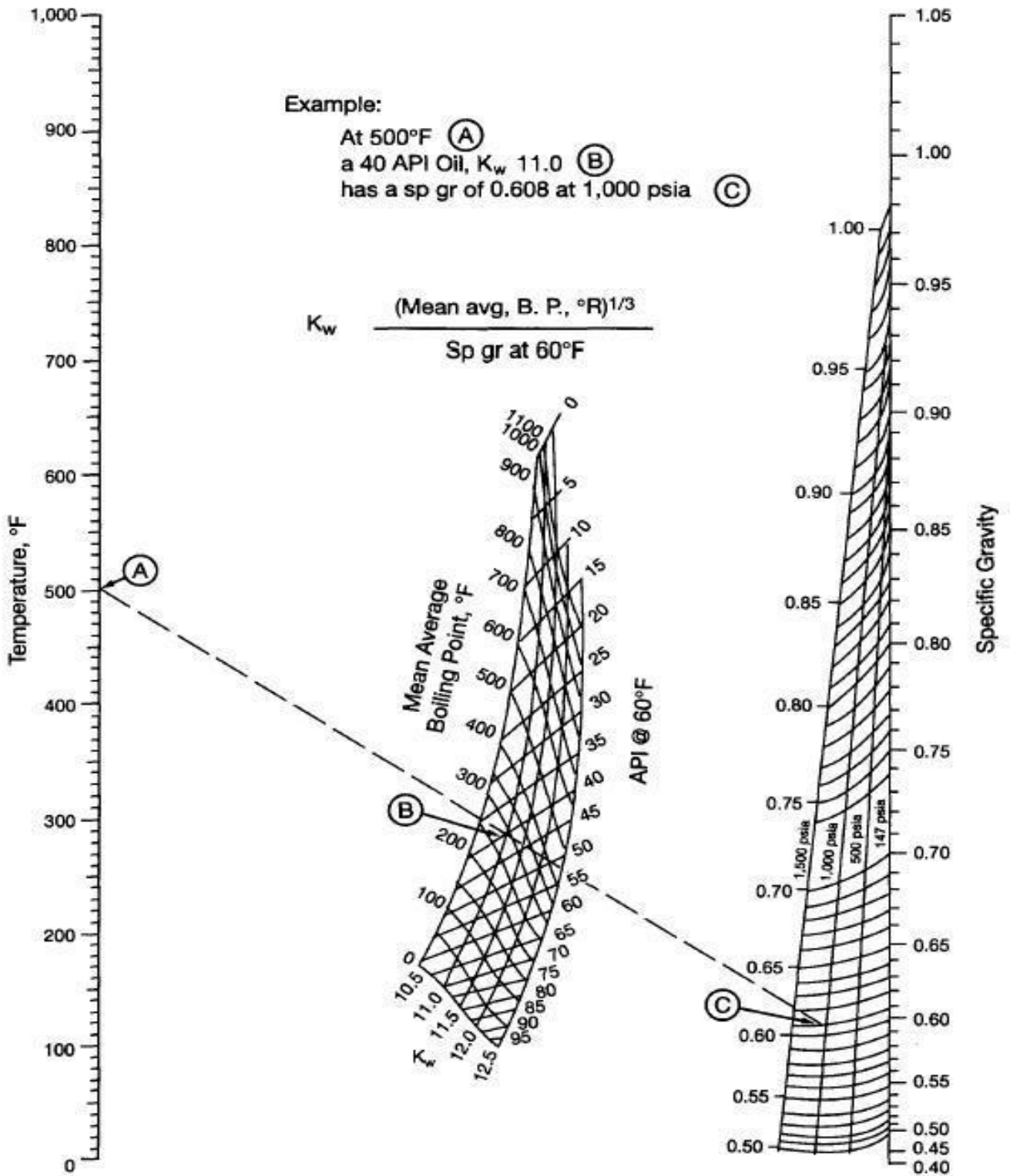
Third Class

Lecture 9

By

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Specific gravity of petroleum fractions as a function to Kw, API, MeABP and temperature

Example:
At 500°F Ⓐ
a 40 API Oil, Kw 11.0 Ⓑ
has a sp gr of 0.608 at 1,000 psia Ⓒ

$$K_w \quad \frac{(\text{Mean avg, B. P., °R})^{1/3}}{\text{Sp gr at 60°F}}$$

Methods for Prediction of Specific Gravity/API Gravity and Molecular weight

Estimation of specific gravity using boiling point, molecular weight, or kinematic viscosity as the input parameters.

❖ Riazi-Daubert Methods

✛ These correlations for the estimation of specific gravity require **Tb and I** or **viscosity** and **C/H** weight ratio as the input parameters.

✛ Parameter (**I**) dimensionless parameter: represents the fraction of total volume occupied by molecules.

✛ Parameter I is proportional to the volume occupied by the molecules and it is close to unity for gases (Ig =0), while for liquids it is greater than zero but less than 1 (0 < Iiq < 1).

$$SG = 2.4381x10^7 \left[\exp(-4.194x10^{-4} T_b - 23.5535I + 3.9874x10^{-3}T_bI)\right]T_b^{-0.3481}I^{6.9195}$$

Where Tb is in kelvin.

✛ For heavy hydrocarbons (**T$_b$ is not available**) with molecular weight in the range 300-700, the following equation in terms of **M and I** can be used.

$$SG = 3.3131x10^4 \left[\exp(-8.77x10^{-4} M - 15.0496I + 3.247x10^{-3}MI)\right]M^{-0.01153}I^{4.9557}$$

✛ For heavier fractions (molecular weight from 200 to 800) the following relation in terms of kinematic viscosities developed by Riazi and Daubert may be used.

$$SG = 0.7717\left[v_{38}^{0.1157}\right]\left[v_{99}^{-0.1616}\right]$$

v_{38} **and** v_{99} are kinematic viscosities in cSt at 100 and 210°F (37.8 and 98.9°C), respectively.

❖ Predication of Molecular Weight (Riazi-Daubert Methods)

➕ Any material or energy balance calculations would certainly require the estimation of molecular weight of a petroleum fraction.

➕ Most oil fractions have molecular weights in the range of **100-700**.

$$M = 42.965[\exp(2.097 \times 10^{-4} T_b - 7.7812SG + 2.08476 \times 10^{-3} T_bSG)]T_b^{1.26007}SG^{4.98308}$$

Where M is the molecular weight of the petroleum fraction, T_b is the mean average boiling point of the petroleum fraction in K, and SG is the specific gravity at 60°F.

➕ This equation can be applied to hydrocarbons with molecular weight ranging from 70 to 700, which is nearly equivalent to boiling point range of 300-850 K (90-1050°F) and theAPI gravity range of 14.4-93.

➕ For heavy petroleum fractions, Riazi and Daubert developed a three-parameter correlation in terms of kinematic viscosity based on the molecular weight of heavy fractions in the range of 200-800: the equation below is only recommended when the boiling point is not available.

$$M = 223.56\left[v_{38}^{-1.2435+1.228SG} \; v_{99}^{3.4758-3.038SG}\right]SG^{-0.6665}$$

✚ It should be noted that viscosities at two different temperatures represent two independent parameters: one the value of viscosity and the other the effect of temperature on viscosity. A graphical presentation of Equation above is shown in Figure below:
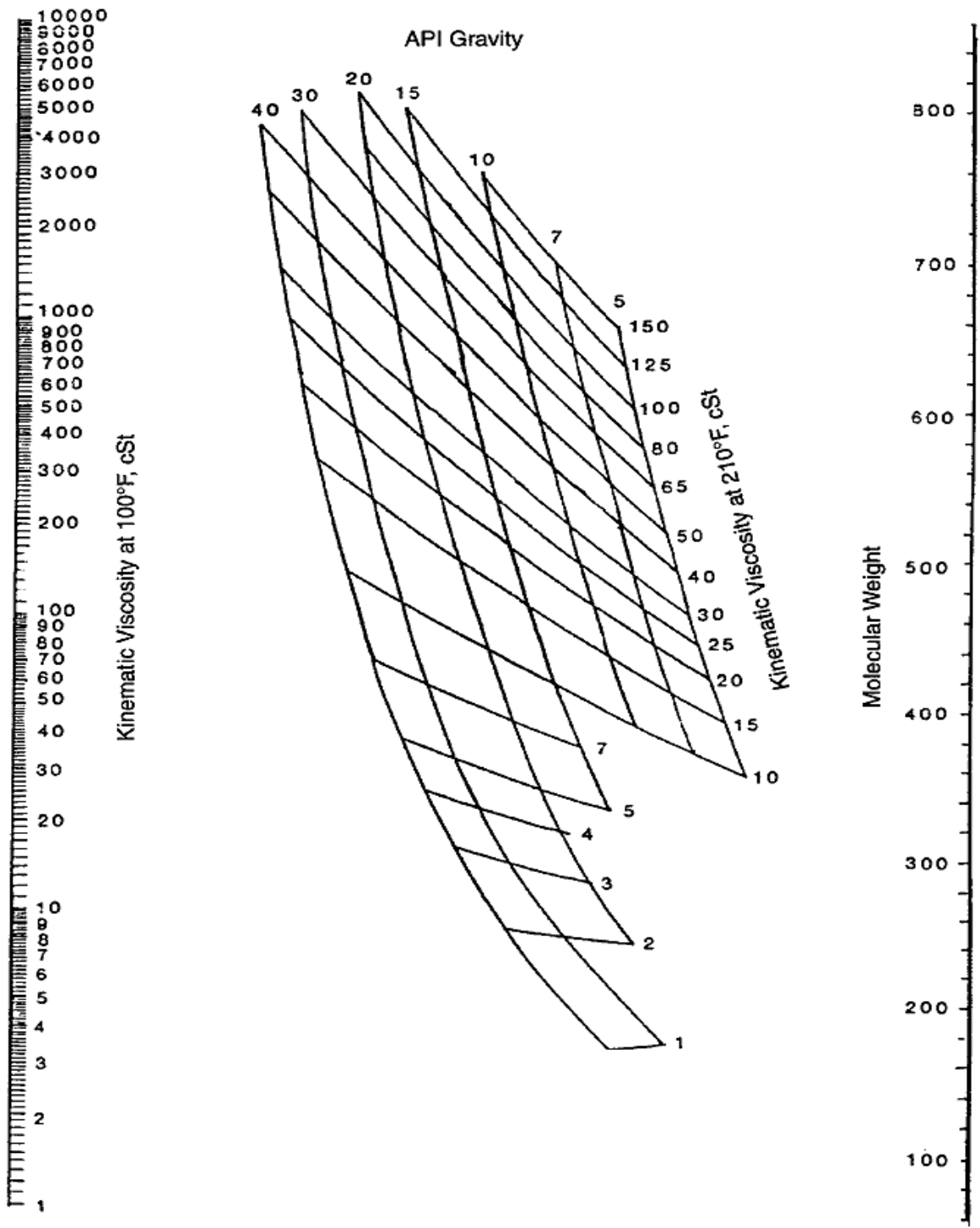
To use this figure, based on the value of v_{38} a point is determined on the vertical line, then from v_{99} and SG, another point on the chart is specified. A line that connects these two points intersects with the line of molecular weight where it may be read as the estimated value.

❖ Prediction of Normal Boiling Point Riazi-Daubert Correlations

✚ The best input parameter to predict boiling point are (M and SG). For hydrocarbons or petroleum fractions with molecular weight in the range of 70-300, equation below can be used.

$$T_b = 3.76587[\exp(3.7741x10^{-3} M + 2.98404SG - 4.25288x10^{-3}MSG)] M^{0.40167} SG^{-1.58262}$$

✚ For hydrocarbons or petroleum fractions with molecular weight in the range of 300-700 but with less accuracy, equation below can be used.

$$T_b = 9.3369 [\exp(1.6514x10^{-4} M - 1.4103SG + 7.5152x10^{-4}MSG)]M^{0.5369} SG^{-0.7276}$$

❖ Average Boiling Points

✚ Boiling points of petroleum fractions are presented by distillation curves such as ASTM D86 or TBP.

✚ In prediction of physical properties and characterization of hydrocarbon mixtures a single characteristic boiling point is required.

✚ Average boiling point for a fraction is defined to determine the single characterizing boiling point.

- There are five average boiling points defined by the following equations. Three of these average boiling points are VABP (volume average boiling point), MABP (molal average boiling point) and WABP (weight average boiling point), defined for a mixture of n components as

$$ABP = \sum_{i=1}^{n} x_i T_{bi}$$

- Where **ABP** is the VABP, MABP, or WABP and xi is the corresponding volume, mole, or weight fraction of component i. $\mathbf{T_{bi}}$ is the normal boiling point of component **i in kelvin**.

- Two other average boiling points are CABP (cubic average boiling point) and MeABP (mean average boiling point) defined as

$$MeABP = \frac{MABP + CABP}{2}$$

- For petroleum fractions in which volume, weight, or mole fractions of components are not known, the average boiling points are calculated through ASTM D 86 distillation curve as

$$VABP = \frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5}$$

Where T_{10}, T_{30}, T_{50}, T_{70}, and T_{90} are ASTM temperatures at 10, 30, 50, 70, and 90 vol% distilled.

❖ Slope of the ASTM distillation curves

➕ A parameter that approximately characterizes slope of a distillation curve is the slope of a linear line between 10 and 90% points. This slope shown by SL is defined as

$$SL = \frac{T_{90} - T_{10}}{90 - 10}$$

➕ When the boiling points of compounds are near each other the value **of SL and the boiling range of the fraction are low.**

➕ **For heavy fractions and vacuum distillates in which distillation data by ASTM D1160 are available, they should first be converted to ASTM D 86 and then average boiling points are calculated.**

➕ Analytical correlations for estimation of average boiling points are given by the following equations in terms of VABP and SL.

$$ABP = VABP - \Delta T$$

$$WABP = VABP - \Delta T_W$$

$$MABP = VABP - \Delta T_M$$

$$CABP = VABP - \Delta T_C$$

$$MeABP = VABP - \Delta T_{Me}$$

Where ABP is an average boiling point such as WABP, MABP, CABP, or MeABP and ΔT is the corresponding correction temperature for each ABP. **All temperatures are in kelvin**.

$$\ln(-\Delta T_w) = -3.64991 - 0.02706(VABP - 273.15)^{0.6667} + 5.163875\ SL^{0.25}$$

$$\ln(\Delta T_M) = -1.15158 - 0.01181(VABP - 273.15)^{0.6667} + 3.70612\ SL^{0.333}$$

$$\ln(\Delta T_C) = -0.82368 - 0.08997(VABP - 273.15)^{0.45} + 2.456791\ SL^{0.45}$$

$$\ln(\Delta T_{Me}) = -1.53181 - 0.0128(VABP - 273.15)^{0.6667} + 3.646064\ SL^{0.33}$$

➕ The most useful type of ABP is MeABP, which is recommended for correlation of most physical properties as well as calculation of Watson K.

➕ For calculation of specific heat, VABP is recommended.

Q1: For the straight run SR Naphtha fraction, the experimental ASTM D86 data with 98.8% recovery vol% are given below. Calculate VABP, WABP, CABP, MABP, and MeABP. Find the base of the fraction by Kw method.

Vol% Distilled	IBP	5	10	30	50	70	90	95	FBP
ASTM D86 °F	92	118	128	164	198	230	262	272	300

$$VABP = \frac{128 + 164 + 198 + 230 + 262}{5} = 196.4\,°F = 91.33°C = 364.48\ kelvin$$

$$SL = \frac{127.77 - 53.33}{90 - 10} = 0.9305°C$$

$$\ln(-\Delta T_w) = -3.64991 - 0.02706(364.48 - 273.15)^{0.6667} + 5.163875 * 0.9305^{0.25}$$

$$\ln(\Delta T_M) = -1.15158 - 0.01181(364.48 - 273.15)^{0.6667} + 3.70612 * 0.9305^{0.333}$$

$$\ln(\Delta T_C) = -0.82368 - 0.08997(364.48 - 273.15)^{0.45} + 2.456791 * 0.9305^{0.45}$$

$$\ln(\Delta T_{Me}) = -1.53181 - 0.0128(364.48 - 273.15)^{0.6667} + 3.646064 * 0.9305^{0.33}$$

$\Delta T_W = -2.39393$ $WABP = 91.33 - (-2.39393) = 93.923°C$

$\Delta T_M = 9.273415$ $MABP = 91.33 - 9.273415 = 82.05658°C$

$\Delta T_C = 2.38374$ $CABP = 91.33 - 2.38374 = 88.94626°C$

$\Delta T_{Me} = 5.86485$ $MeABP = 91.33 - 5.86485 = 85.46514°C$

If specific gravity of a fraction is not available, it may be estimated from available distillation curves at 10 and 50% points as given by the following equation:

$$SG = a[(T_{10})^b (T_{50})^c]$$

where constants *a, b,* and c for the three types of distillation data, namely, ASTM D 86, TBP, and EFV, are given in the Table below. Temperatures at **10 and 50% are both in kelvin**.

Distillation type	T_{10} range,^{a}°C	T_{50} range,^{a}°C	SG range	a	b	c
ASTM D 86	35–295	60–365	0.70–1.00	0.08342	0.10731	0.26288
TBP	10–295	55–320	0.67–0.97	0.10431	0.12550	0.20862
EFV	79–350	105–365	0.74–0.91	0.09138	−0.0153	0.36844

$$SG = 0.08342[(326.37)^{0.10731}(365.37)^{0.26288}] = 0.7323$$

$$K_w = \frac{\sqrt[3]{645.828\ R}}{0.7323\ @\ 60°F} = 11.80$$

❖ Mean average boiling point of petroleum fractions

- Based on our experience, for narrow boiling range fractions **with SL < 0.8 °C the MeABP is very close to T_{50} temperature in ASTM D86.**
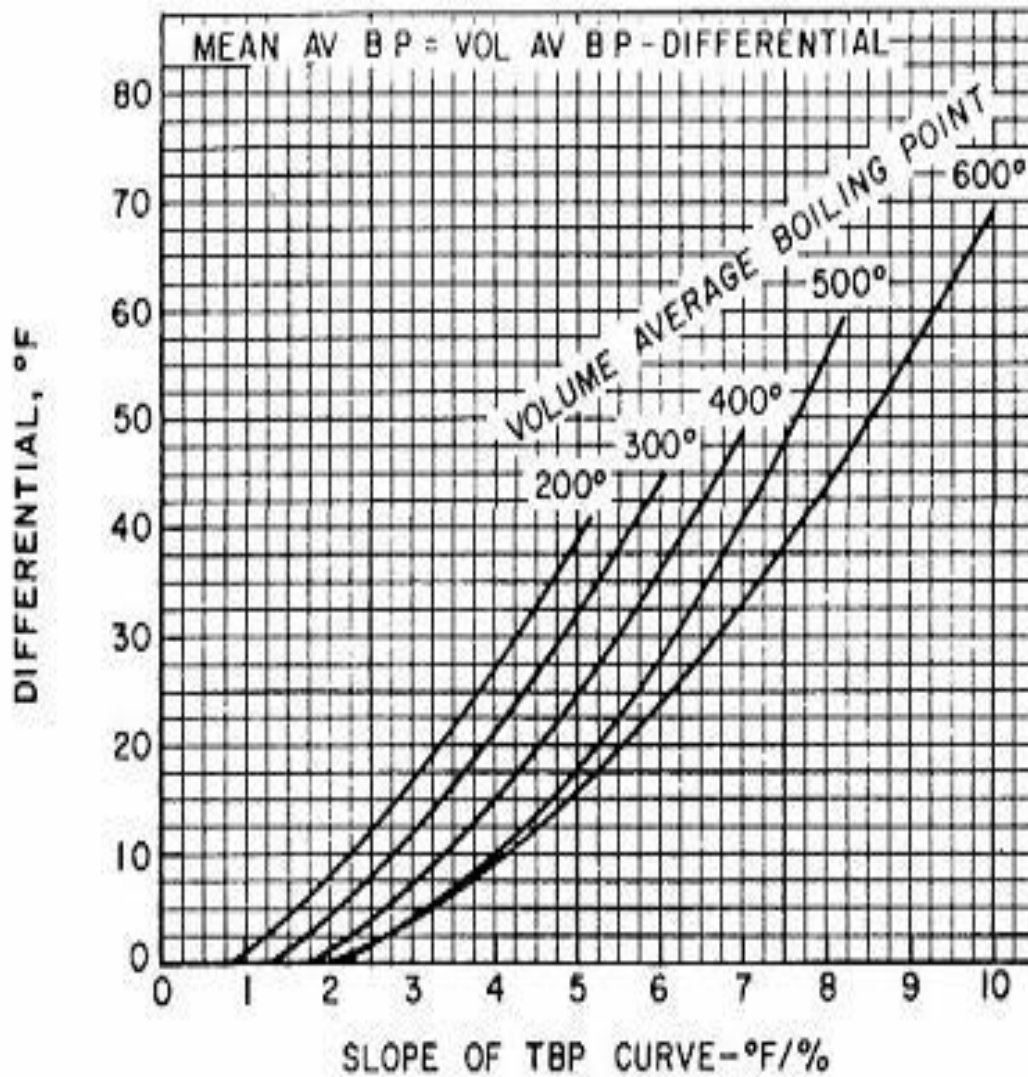
Types of Distillation Curve

1- True Boiling point(TBP) Distillation

2- ASTM Distillation

3- Semi-fractionating Distillation

4- Equilibrium Flash Vaporization(EFV)

1) TBP: This type of distillation is commonly used due to the accuracy of the results obtained by this method which is very close to that obtained via real distillation or industrial distillation. In this distillation, there is a fractionation column located between the condenser and the flask. In general, this type of distillation is carried out by two steps: firstly, under atmospheric pressure until 300°C (1% distilled very 2 min), secondly under vacuum pressure (to prevent cracking process and to reduce the boiling point) at 40mmHg (1% distilled every 3-5 min). In this process, the vapor press. temp. is plotted vs. distilled(%) to get TBP curve.

2) ASTM: In this type of distillation there is on fractionation column located between the condenser and the flask. On the other hand, the raised vapor will not be fractionated in this process. This distillation is used with fractions having short range of the boiling point.

3) Semi-fractionating distillation: In this type of distillation, their will be some fractionating process on the raised vapor via package located between the condenser and the flask.

4) Equilibrium Flash Vaporization (EFV): Is a single stage separation technique. A liquid mixture feed is pumped through a heater to raise the temperature and enthalpy of the mixture. It then flows through a valve and the pressure is reduced, causing the liquid to partially vaporize. Because the vapor and liquid are in such close contact up until the "flash" occurs, the product liquid and vapor phases approach equilibrium.