

Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering

Department

Petroleum Refining Processes

Fourth Class

Lecture 4

By

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Physical and Chemical Properties of Crude Oil and Oil Products

11- Aniline Point

The lowest temperature at which an equal volume mixture of the petroleum oil and aniline are miscible is the aniline point. Since aniline is an aromatic compound, petroleum fractions with high aromatic content will be miscible in aniline at ambient conditions. Aniline point can be estimated using the following relation:

$$AP = -183.3 + 0.27(API)T_b^{1/3} + 0.317T_b$$

Where AP is in °C T_b is the mid boiling point in kelvin and API is API gravity.

12- Cetane number

The cetane number measures the ability for auto ignition and is essentially the opposite of the octane number. The cetane number is the percentage of pure cetane (n-hexadecane) in a blend of cetane and alpha methyl naphthalene which matches the ignition quality of a diesel fuel sample. This quality is specified for middle distillate fuels. Since determination of cetane number is difficult and costly, ASTM D976 (IP 218) proposed a method of calculation. Calculated number is called

calculated cetane index (CCI) and can be determined from the following relation:

$$\text{CCI} = 454.74 - 1641.416\text{SG} + 774.74\text{SG}^2 - 0.554T_{50} + 97.083(\log_{10} T_{50})^2$$

Where T_{50} is the ASTM D 86 temperature at 50% point in °C Another characteristic of diesel fuels is called diesel index (DI) defined as:

$$\text{DI} = \frac{(\text{API})(1.8\text{AP} + 32)}{100}$$

Which is a function of API gravity and aniline point in °C.

13- Smoke Point

The smoke point is a test measures the burning qualities of kerosene and jet fuel. It is defined as the maximum height in mm, of a smokeless flame of fuel. The smoke point (SP) can be calculated using the following equation:

$$\text{SP} = -255.26 + 2.04\text{AP} - 240.8 \ln(\text{SG}) + 7727(\text{SG}/\text{AP})$$

Where AP is the aniline point in °C and SG is the specific gravity at 15.5°C. Equation above estimates SP according to the IP test method. To estimate SP from the ASTM D1322 test method, 0.7 mm should be subtracted from the calculated IP smoke point.

14- Freezing Point

Petroleum fractions are mostly liquids at ambient conditions. However, heavy oils contain heavy compounds such as waxes or asphaltenes. These compounds tend to solidify at low temperatures, thus restricting flow. The freezing point is the temperature

at which the hydrocarbon liquid solidifies at atmospheric pressure. It is one of the important property specifications for kerosene and jet fuels due to the very low temperatures encountered at high altitudes in jet planes.

15- Reid Vapor Pressure (RVP)

Is a common measure of the volatility of gasoline. It is defined as the absolute vapor pressure exerted by a liquid at 100 °F (37.8 °C) as determined by the test method ASTM-D- 323. The matter of vapor pressure is important relating to the function and operation of gasoline powered, especially carbureted, vehicles. High levels of vaporization are desirable for winter starting and operation and lower levels are desirable in avoiding vapor lock during summer heat. Fuel cannot be pumped when there is vapor in the fuel line (summer) and winter starting will be more difficult when liquid gasoline in the combustion chambers has not vaporized. Thus, oil refineries manipulate the Reid Vapor Pressure seasonally specifically to maintain gasoline engine reliability. RVP data on 52 different petroleum products (light and heavy naphthas, gasolines, and kerosenes) from the Oil and Gas Journal data bank have been used to develop a simple relation for prediction of RVP in terms of boiling point and specific gravity in the following form:

$$\text{RVP} = P_c \exp(Y)$$

$$Y = -X \left(\frac{T_b \text{SG}}{T_r} \right) (1 - T_r)^5$$

$$X = -276.7445 + 0.06444T_b + 10.0245\text{SG} - 0.129T_b\text{SG} \\ + \frac{9968.8675}{T_b\text{SG}} + 44.6778 \ln T_b + 63.6683 \ln \text{SG}$$

$$T_r = 311/T_c$$

Where T_b is the mid boiling point and T_c is the pseudocritical temperature of the fraction in kelvin. P_c is the pseudocritical pressure and RVP is the Reid vapor pressure in bars.

16- Molecular Weight

Molecular weight (M) is perhaps the most important characterization parameter for petroleum fractions and many physical properties may be calculated from this parameter. M can be predicted by using the following equation:

$$M = 42.965[\exp(2.097 \times 10^{-4}T_b - 7.78712SG + 2.08476 \times 10^{-3}T_bSG)]T_b^{1.26007}SG^{4.98308}$$

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 (90-1050F) and the API gravity range of 14.4-93. For heavy petroleum fractions based on the molecular weight of heavy fractions in the range of 200-800:

$$M = 223.56 \left[v_{38(100)}^{(-1.2435+1.1228SG)} v_{99(210)}^{(3.4758-3.038SG)} \right] SG^{-0.6665}$$

The three input parameters are kinematic viscosities (in cSt) at 38 and 98.9°C (100 and 210F) shown by $v_{38(100)}$ and $v_{99(210)}$, respectively, and the specific gravity (SG) at 15.5°C.

17- Distillation Range

The boiling range of the crude gives an indication of the quantities of the various products present. The most useful type of distillation is known as a true boiling point (TBP) distillation and generally refers to a distillation performed in equipment that accomplishes a reasonable degree of fractionation. (See Figure and Table below)

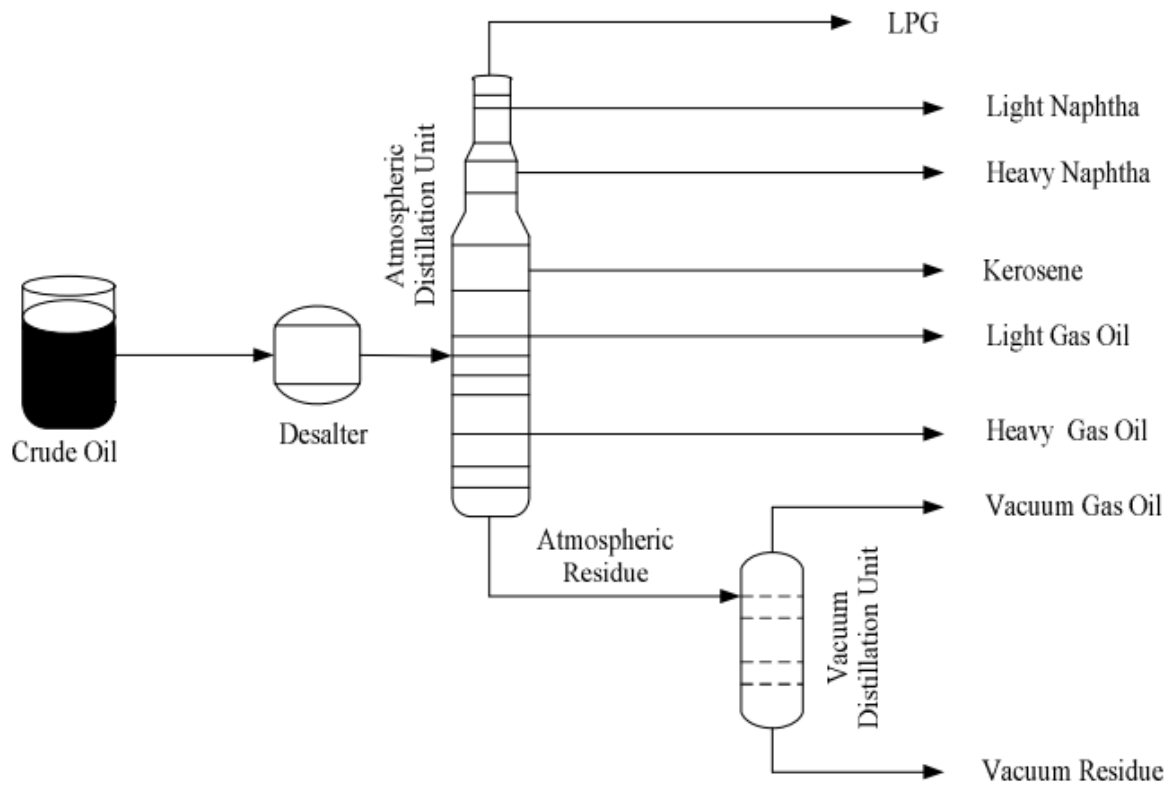


Table 1: Oil fractions destinations and ultimate products with their boiling ranges

Oil Fractions	Approx. Boiling Ranges ($^{\circ}\text{C}$)	Next Destination	Ultimate Products
LPG	-40 to 0	Sweetener	Propane fuel
Light Naphtha	IBP - 85	Hydrotreating	Gasoline
Heavy Naphtha	85 – 200	Cat. Reformer	Gasoline, aromatics
Kerosene	170 – 270	Hydrotreating	Jet fuel, diesel No.1
Gas Oil	180 – 240	Hydrotreating	Heating oil, diesel No.2
Vacuum Gas Oil	340 - 566	FCC	Gasoline, LGO, gases
		Hydrotreating	Fuel oil, FCC, feed
		Lube Plant	Lube basestock
		Hydrocracking	Gasoline, jet fuel, diesel, FCC feed, basestock
Vacuum Residue	> 540	Coker	Coke, coker gas oil,
		Visbreaking	Visbreaker gas oil, resid
		Asphalt Unit	Deasphalted oil, asphalt
		Hydrotreating	FCC feed

Types of Distillation Curve

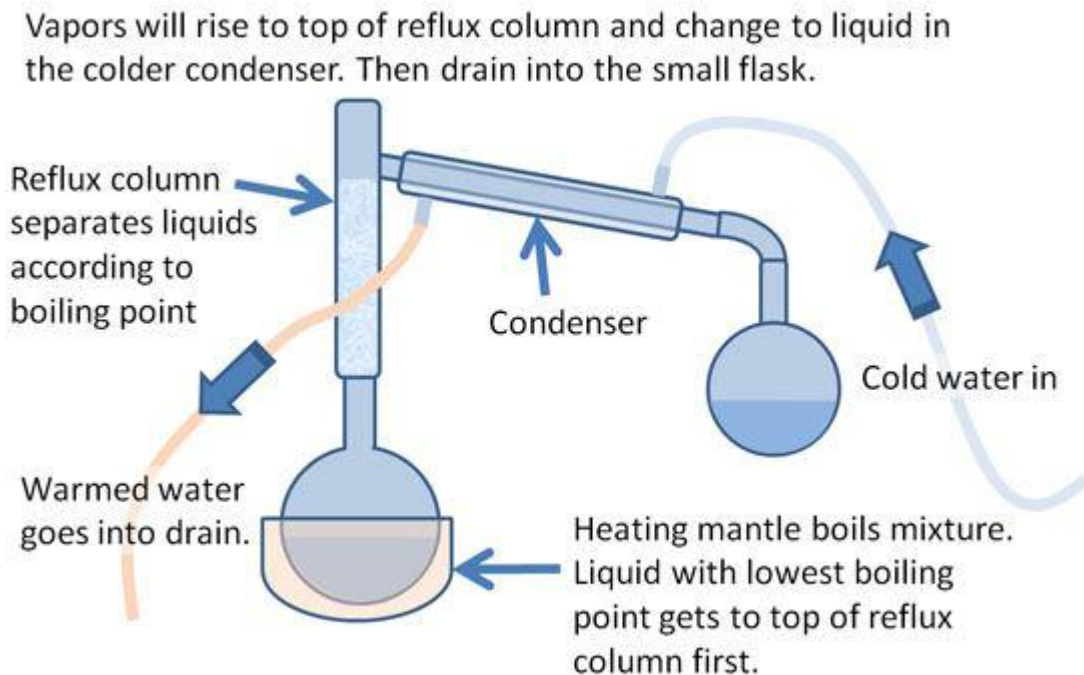
1- True Boiling point(TBP) Distillation

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 every 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.



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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, there 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.