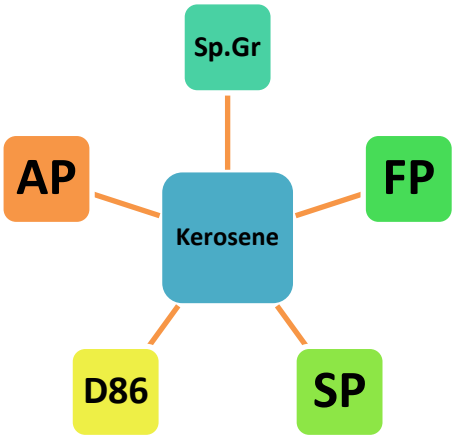
Quality Control Tests of Finished Petroleum Products

2- Kerosene



Typical kerosene cut **(C_{10} - C_{14})** obtained from fractional distillation of crude oil.

- Flash point: (**38°C**) minimum
- Density range: **0.740** minimum
- Average boiling range: (**174-260°C**)
- Smoke point **20 mm** (min)
- Sulfur content **100 ppm** max
- Copper strip corrosion **class 1** max
- Aromatic content **1 wt%** max

Flash Point test for middle and heavy petroleum distillates

- Flash point of petroleum fractions is the **minimum temperature** at which **vapour over** the **liquid fuel surface** **instantly flash**, when exposed to an ignition source (**spark or flame**).
- A liquid is considered to be **flammable** if its flash point is **less than 60°C**
- The flash point indicates the maximum temperature that the fuel can **be stored without serious fire hazard** in high temperature environment.
- Flash point is a measure for **safe storage** and **transportation.**
- Flash point decreases with increasing **volatility of fuel, i.e**. the higher vapour pressure the lower is the flash point.
- Crude oils with RVP **greater than 0.2 bar** the flash point is **less than 20°C**.
- **High flash** point fuel does not ignite easily and is **safe.**

There are several methods of determining flash points of petroleum fractions.

- **The Closed Tag method (Abel) (ASTM D56)** is used for petroleum stocks with flash points below **80°C** (175 °F).
- **The Pensky-Martens method (close cup) (ASTM D93)** is used for all petroleum products except waxes, solvents, and asphalts.
- **The Cleveland Open Cup method (ASTM D 92)** is used for petroleum fractions with flash points **above 80°C** (175°F) excluding fuel oil.
- This method usually gives flash points 3-6°C higher than the above two methods.

The main reason for the requirement of flash point test is to:

- Assess the **fire hazards** and to enable the correct precautions to be taken when using, storing or transporting the liquid.

Fuel	Flashpoint	Autoignition temperature
Ethanol (70%)	**16.6 °C**	**363 °C**
Gasoline (petrol)	**−43 °C**	**280 °C**
Diesel (2-D)	**>52 °C**	**210 °C**
Jet fuel (A/A-1)	**>38 °C**	**210 °C**
Kerosene	**>38–72 °C**	**220 °C**
Vegetable oil (canola)	**327 °C**	**424 °C**
Biodiesel	**>130 °C**	

Fire Point

Fire point of petroleum fractions is **the lowest temperature** at which vapour above the oil surface **instantly ignite, i.e. fired**, when exposed to a **spark or flame**. Therefore, the fire point of a fuel indicates the maximum temperature that **must not reach it to prevent the combustion** of the petroleum fractions.

Walsh and Mortimer estimated flash point of hydrocarbon mixtures from vapour pressure using equation below**.**

$$T_F = 231.2 - 40\, log P^{vap} \quad \ldots 31$$

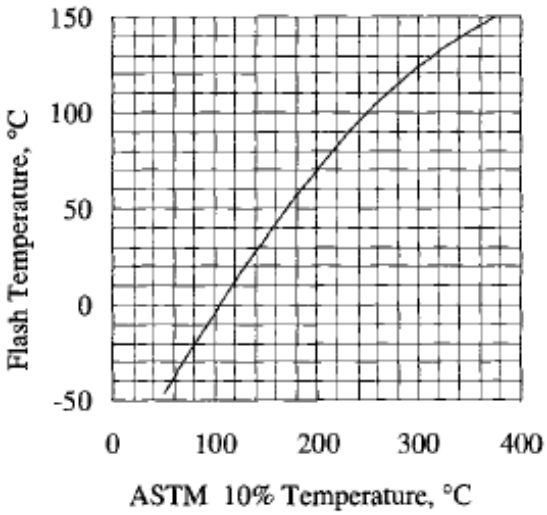
Where P^{vap} is the vapour pressure at 37.8°C (100°F) in bar and T_F is the flash point in **kelvin**. For simplicity RVP may be used for P^{vp}.

API method, which was developed by Riazi and Daubert.

$$T_F = \frac{1}{-0.024209 + \frac{2.84947}{T_{10}} + 3.4254\, x\, 10^{-3}\ \ln T_{10}} \quad \ldots 32$$

For pure hydrocarbons T_{10} is normal boiling point, while for petroleum fractions T_{10} is distillation temperature at **10 vol% vaporized** (ASTM D 86 at 10%) and **it is in kelvin**.

Equation 32 predicts flash points with **(PRD%) of 6.8°C.** Equation 32 should be applied to fractions with normal boiling points **from 65 to 590°C**.



Equation 32 can be simplified into the following linear form

$$T_F = 15.48 + 0.70704\,T_{10} \ldots . 33$$

Both **T_{10} and T_F are in kelvin**. **Equation 33** is applicable to fractions with normal boring points **(i.e., ASTM D 86 temperature at 50%) less than 260°C** (for light fractions is slightly more accurate than the equation 32).

Blending Products of Different Flash Points

If the flash point of a petroleum fraction does not meet the required specification, it can be adjusted by blending with other compounds having different flash points.

In **hot regions** where the **temperature is high**, heavy hydrocarbons may be added to a fraction to **increase its flash** point.

The flash point of the blend should be determined from the **flash point indexes** of the components as given below:

$$\log_{10} BI_F = -6.1188 + \frac{2414}{T_F - 42.6} \ldots . 34$$

BI_F is the **flash point blending index**, and **T_F is the flash point in kelvin**. Once BI_F is determined for all components of a blend, the blend flash point index (BI_B) is determined from the following relation:

$$BI_{FB} = (1 - X_{add})BI_{FK} + X_{add}\ BI_{Fadd} \ldots . . 35$$

Exercise: kerosene product with boiling range of 175-260°C, has the API gravity of 41.31 (a) Estimate its flash point and compare with the experimental value of 59°C (b) For safety reasons it is required to have a minimum flash point of 65°C to be able to store it in a hot summer. How much n-tetradecane n-C_{14} should be added to this kerosene for a safe storage?

Solution:

$T\ mid = \frac{175+260}{2} = \mathbf{217.5}℃ = \boldsymbol{T_{50}}$

(a) Use **Eq. (33)** $T_{50} < 260$ **,** which require ASTM 10% temperature T_{10}.

$API = 41.31 \rightarrow SG = 0.8188\ calculated\ from\ API$

$SG = a[(T_{10})^b (T_{50})^c] \quad \rightarrow \quad 0.8188 = 0.08343[T10]^{0.10731}\ [217.5 + 273.15]^{0.26288}$

$T_{10} = 449.9\ k$

$\boldsymbol{T_F = 15.48 + 0.70704\ T_{10} \rightarrow T_F = 60.4}℃$

(b) To increase the flash point from 59 to 65°C, n-C_{14} with flash point of 100°C is used. If the volume fraction of n-C_{14} needed, is shown by $\mathbf{X_{add}}$, then using **Eq. 35**

Where $\boldsymbol{BI_{FB}, BI_{FK}\ and\ BI_{Fadd}}$ are the blending indexes for flash points of final blend, kerosene sample, and the additive (n-C_{14}), respectively.

The blending indexes can be estimated from Eq. (34)

$$\log_{10} BI_{FK} = -6.1188 + \frac{2414}{(59 + 273.15) - 42.6} = 165.3$$

$$\log_{10} BI_{F\,C14} = -6.1188 + \frac{2414}{(100+273.15)-42.6} = 15.3$$

$$\log_{10} BI_{FBlend} = -6.1188 + \frac{2414}{(65+273.15)-42.6} = 111.9$$

$$from\ eq.35$$

$$111.9 = (1 - X_{add})165.3 + X_{add}\ 15.3 \rightarrow X_{add}$$

$= \mathbf{0.356}$ **(35.6% in volume of C14** is required to increase flash point from 59 to 65℃

Exercise: 20% kerosene with a flash point of 120°F is to be blended with 80% fuel oil with a flash point of 250°F. Calculate the flash point of the blend.

Solution

for 20% Kerosene $BI_{Fk} = 310 * 0.2 = 62$

for 80% fuel oil $BI_{F\,oil} = 5.5 * 0.8 = 4.4$

$total\ BI_{FB} = 66.4$

The flash point corresponding to an index of **66.4** (from Figure 15) is **166°F**.

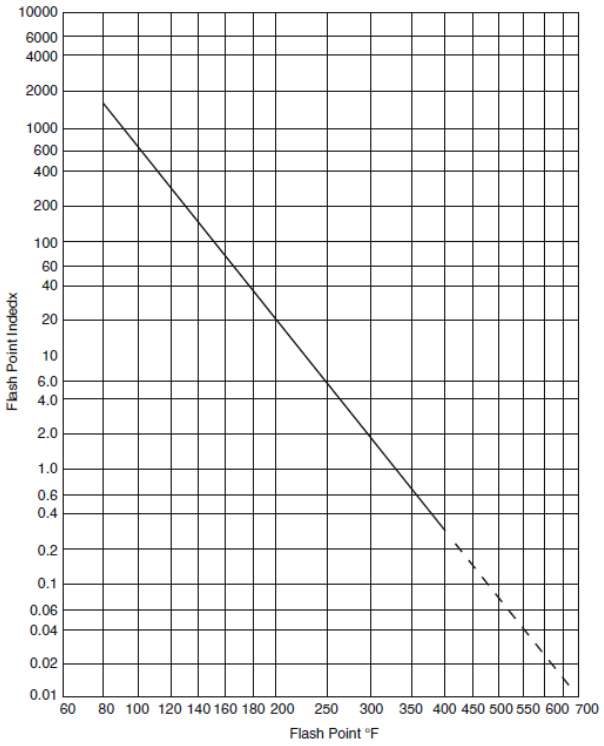
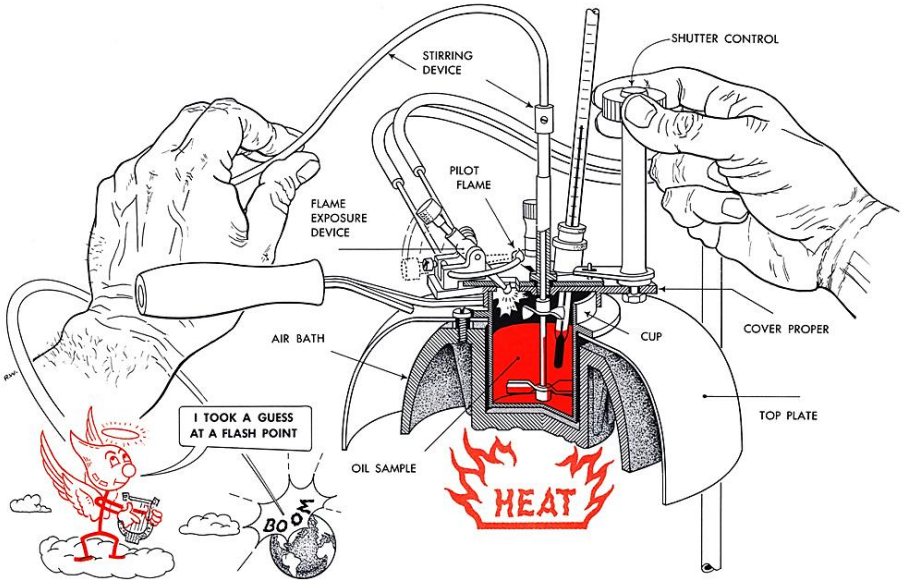


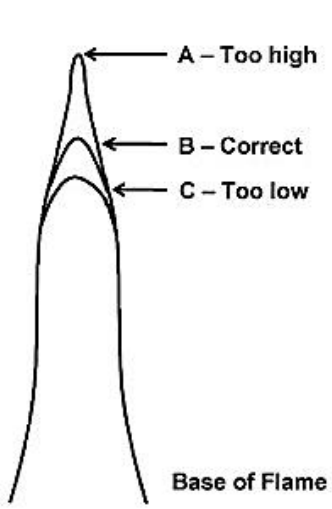
Figure 15. Flash point blending index

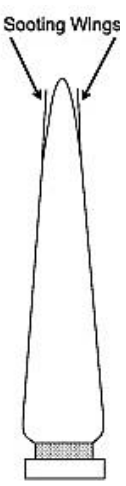


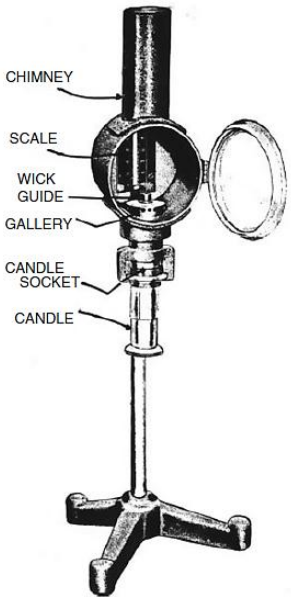
Flash point tester section view

Smoke Point ASTM D1322

- **The smoke point (SP) is a maximum flame height in mm at which a fuel can be burned in a standard wick-fed lamp without smoke**.
- Smoke point is a characteristic of **aviation turbine fuels and kerosene** and indicates the tendency of a **fuel to burn with a smoky flame**.
- Higher amount **of aromatics in a fuel causes a smoky characteristic** for the flame and energy loss due to thermal radiation.







Smoke point may be estimated by **PNA composition**.

$$\mathbf{SP = 1.65\,X - 0.0112\,X^2 - 8.7 \ldots 36}$$

$$\boldsymbol{X = \frac{100}{0.61\,x_P + 3.392\,x_N + 13.518\,x_A}}$$

The second method is proposed by Jenkins and Walsh using aniline point as follows:

$$\boldsymbol{SP = -255.26 + 2.04AP - 240.8\,ln(SG) + 7727\left(\frac{SG}{AP}\right) \ldots . 37}$$

Where AP is the aniline point in °C and SG is the specific gravity at 15.5°C.

Equations above are based on data with specific gravity in the range of **0.76-0.82**, and smoke points in the range of **17-39 mm**.

Albahri et al also proposed the following relation for prediction of smoke point using API gravity and boiling point:

$$\boldsymbol{SP = 0.839(API) + 0.0182634(T_b) - 22.97 \ldots . 38}$$

Where SP is in mm (ASTM method) and T_b is the **average boiling point in kelvin**. This equation when tested for 136 petroleum fractions gave an average **error of about 2 mm**.

Aniline Point ASTM D611(indication of fuel aromaticity)

- The **lowest temperature** at which **equal volume** of aniline and the oil are completely miscible.
- Petroleum fractions with high aromatic content will be miscible in aniline at ambient conditions.
- If the oil has more paraffin, it will require a higher temperature and thus higher aniline point.
- This property is important for the s**pecifications of kerosene and diesel fuels**.

- Fractions with 75% aromatic content, have aniline point between **32.2 and 48.9°C**.
- Naphthenic oil (40% aromatic structures), have aniline point between **65.6° and 76.7°C**.
- Paraffinic oil with 15% aromatic content, have aniline point between **93.3° and 126.7°C.**
- **Low aniline** point indicates a **low diesel** index (**ignition quality of fuel**).

The **aromatic content** in petroleum fraction may be calculated from aniline point by the following formula:

$$\%\mathbf{A} = \mathbf{692.4} + \mathbf{12.15}\,(\mathbf{SG})(\mathbf{AP}) - \mathbf{794}\,(\mathbf{SG}) - \mathbf{10.4}\,(\mathbf{AP}) \ldots \mathbf{39}$$

%A is the aromatic content, SG is the specific gravity, and AP is the aniline point **in °C**.

Linden Method

$$\boldsymbol{AP} = \mathbf{-183.3} + \mathbf{0.27}(\boldsymbol{API})\,\boldsymbol{T_b^{1/3}} + \mathbf{0.317}\,\boldsymbol{T_b} \ldots . \mathbf{40}$$

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

Albahri et al. Method

Based on the idea that aniline point is mainly related to the aromatic content of a fuel, the following relation was proposed:

$$\boldsymbol{AP} = \mathbf{-9805.269}(\boldsymbol{R_i}) + \mathbf{711.85761}(\boldsymbol{SG}) + \mathbf{9778.7069} \ldots \mathbf{41}$$

$$\boldsymbol{Ri} = \boldsymbol{n} - \frac{\boldsymbol{d_{20}}}{\mathbf{2}}$$

Ri is high for aromatics and low for naphthenic stocks.

where n = **refractive index at 20°C** and 1 atmosphere, d is the liquid density at 20°C and 1 atmosphere in grams per cubic centimetre.

Refractive Index

The refractive index is the ratio of the **velocity of light** in a vacuum to the **velocity of light** in the **oil.** This parameter is used as a characterization parameter for petroleum fraction composition.

$$\boldsymbol{n} = \frac{\boldsymbol{velocity\ of\ light\ in\ the\ vaccum}}{\boldsymbol{velocity\ of\ light\ in\ the\ substance}}$$

Refractive index is a state function and depends on the temperature and pressure of a fluid. Since the **velocity of light in a fluid is less than the velocity of light in a vacuum**, its value for a fluid is **greater than unity**. Liquids have higher values of refractive index than that of gases. For gases the values of refractive index are very close to unity.

Refractive index at 20°C and 1 atm is used as a characterization parameter for hydrocarbons and petroleum fractions. Values of n vary from about **1.3 for propane** to **1.6 for some aromatics**. **Aromatic hydrocarbons have generally higher n values than paraffinic compounds.**

Prediction of Refractive Index

The refractive index of liquid hydrocarbons at 20°C is correlated through **parameter I** defined previously. If parameter (I) is known, the refractive index, n, can be calculated as follows:

$$\mathbf{n} = [\frac{\mathbf{1 + 2I}}{\mathbf{1 - I}}]^{0.5}$$

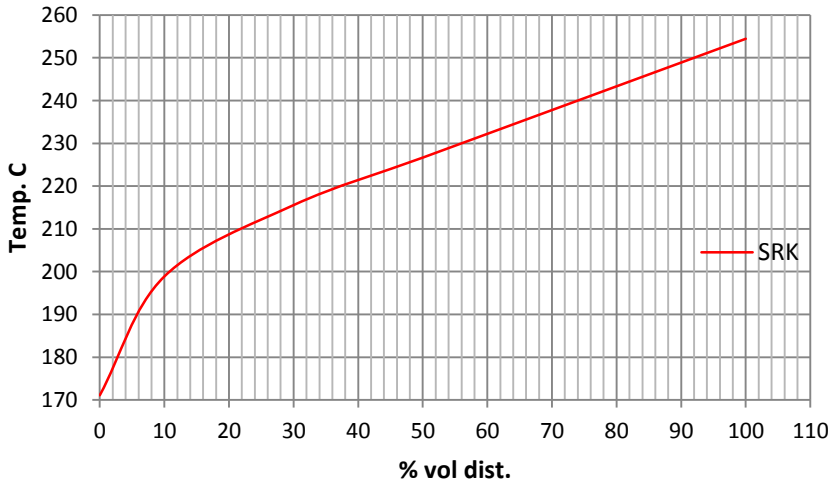
For all types of hydrocarbons and narrow-boiling range petroleum fractions the simplest method to estimate parameter (I) is given by Riazi and Daubert for the molecular weight range of 70-300 as follows:

$$\boldsymbol{I = 0.3773 T_b^{-0.02269} SG^{0.9182} \ldots..42}$$

Where T_b is in Kelvin, this equation predicts n with an average **error of about 1%** for pure hydrocarbons from C_5 to C_{20}. The following method developed by Riazi and Daubert have accuracy of about 0.5% on n in the molecular weight range of 70-300.

(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 zero for gases (**I_g =0**), while for liquids it is greater than zero but less than **1 (0 < I_{iq} < 1**).

Exercise: SRK straight run kerosene has the TBP distillation curve below with specific gravity (sp.gr.) of 0.790. How do you use the TBP curve to calculate the following: FP, AP, SP



Solution:

T10 = 198.88 and T0 = 170 EP = 255 and Sp.G = 0.790

Average boiling point **Tb = (170 + 255)/2 = 212.5 °C**.

$\boldsymbol{T_F = 15.48 + 0.70704\, T_{10}}$ **where T10 = 198.88 °C = 472k**

$\boldsymbol{T_F = 76°C}$

Flash point can also be calculated from the following equation

$$T_F = \frac{1}{-0.024209 + \frac{2.84947}{T_{10}} + 3.4254\,x\,10^{-3}\ \ln T_{10}} = 342.6 = 69.6℃$$

$$AP = -183.3 + 0.27(API)\,T_b^{1/3} + 0.317\,T_b$$ **where Tb must be in k**

API is equals to 47.6 this give AP = 71.65°C

$$SP = 0.839(API) + 0.0182634(T_b) - 22.97$$ **= 25.83 mm**

Problem: The ASTM D86 data for kerosene fraction produced by Baiji refinery is given in the Table below. The experimental value for Sp.gr is 0.7890 at **15.5 °C**, flash point **55°C**, smoke point **23 mm**, and **AP 60°C**. Use the suitable empirical equations to calculate the quality tests above then find PRD. What would be flash point of the kerosene fraction if **36.5%** of (C13, T_F=78.9) was added.

Vol % distilled	T0	T10	T30	T50	T70	T90	T100
ASTM D86 °C	165	177	183	188	195	209	242