8- Octane number

An octane number is a measure of the knocking tendency of gasoline fuels in spark ignition engines. The ability of a fuel to resist auto-ignition during compression and prior to the spark ignition gives it a high octane number. Two octane tests can be performed for gasoline. The motor octane number (MON) indicates engine performance at high way conditions with high speeds (900 rpm). On the other hand, the research octane number is indicative of low-speed city driving (600 rpm).

RON of a fuel may be estimated from the pseudocomponent techniques in the following form:

$$\mathrm{RON} = x_{\mathrm{NP}}(\mathrm{RON})_{\mathrm{NP}} + x_{\mathrm{IP}}(\mathrm{RON})_{\mathrm{IP}} + x_{\mathrm{O}}(\mathrm{RON})_{\mathrm{O}} + x_{\mathrm{N}}(\mathrm{RON})_{\mathrm{N}} + x_{\mathrm{A}}(\mathrm{RON})_{\mathrm{A}} \quad \text{.....(1)}$$

where x is the volume fraction of different hydrocarbon families i.e., n-paraffins (NP), isoparaffins (IP), olefins (O), naphthenes (N), and aromatics (A). RON_Np, RON_Ip, RON_o, RON_N, and RON_A are the values of RON of pseudocomponents from n-paraffin, isoparaffins, olefins, naphthenes, and aromatics families whose boiling points are the same as the mid boiling point or the ASTM D86 temperature at 50% point of the fraction and can be determined from Figure:

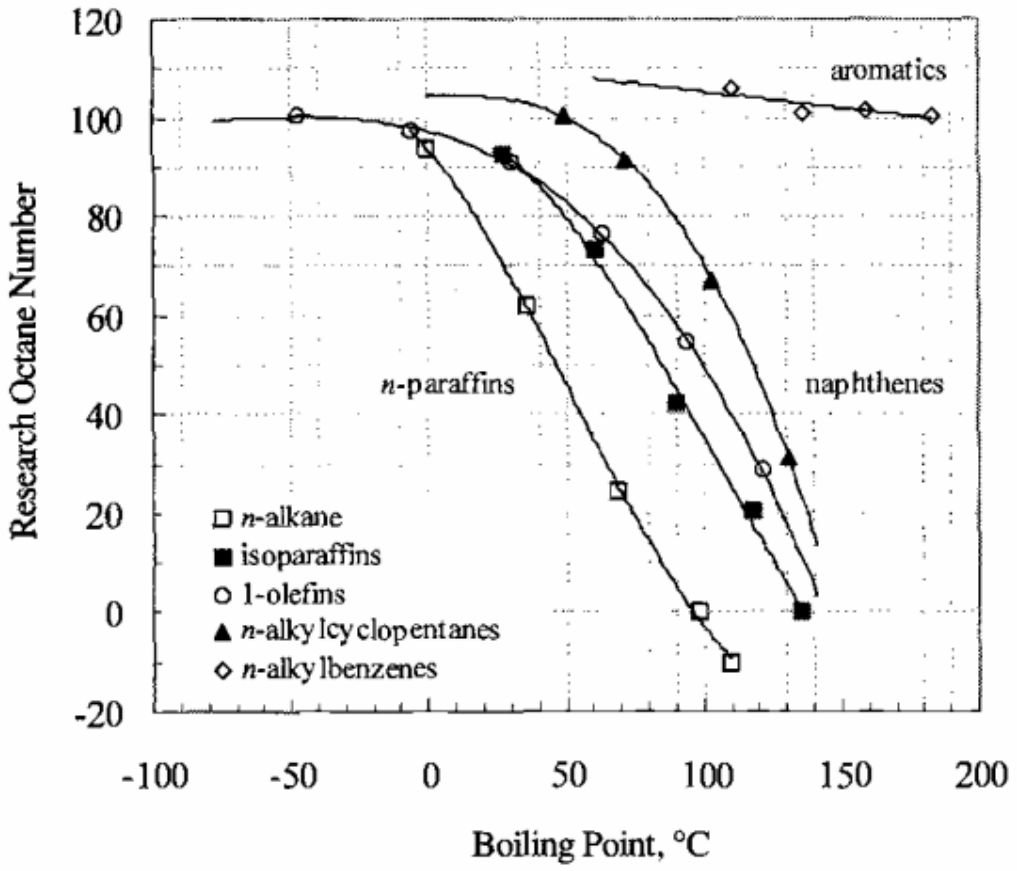

Figure 2: Research octane number of different families of hydrocarbons.

There is another graphical relation for estimation of RON of naphthas in terms of Kw characterization factor or paraffin content (wt%) and mid boiling point as given in Figures below

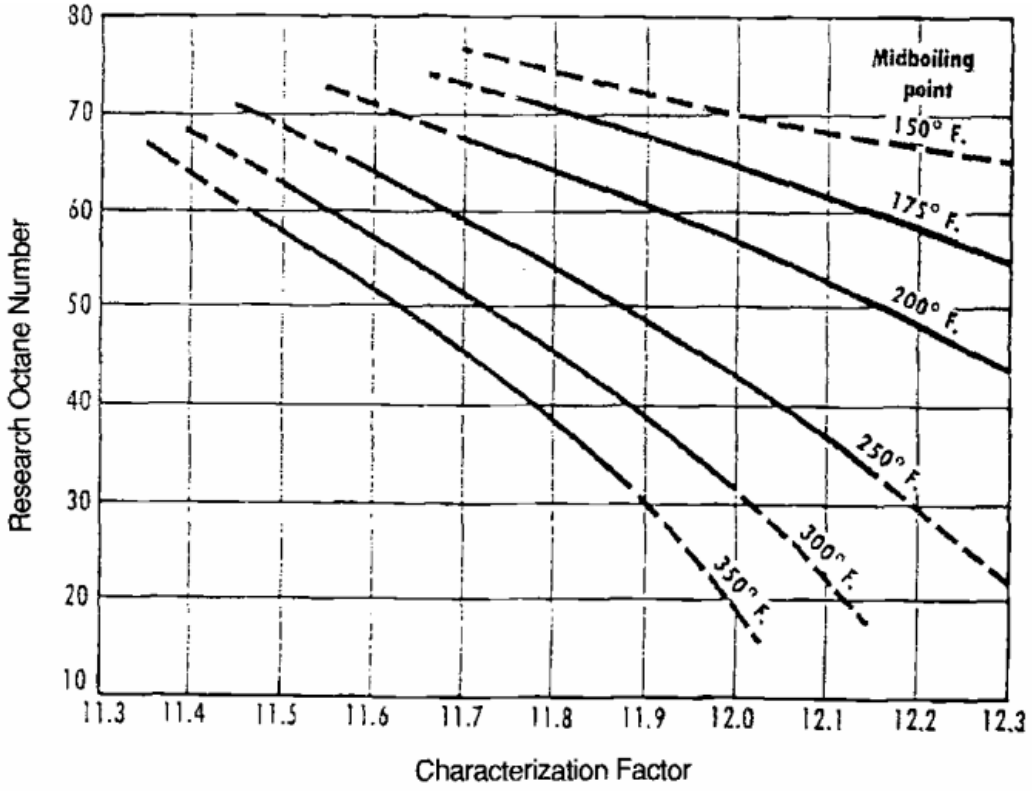

Figure 3: Research octane number of naphthas

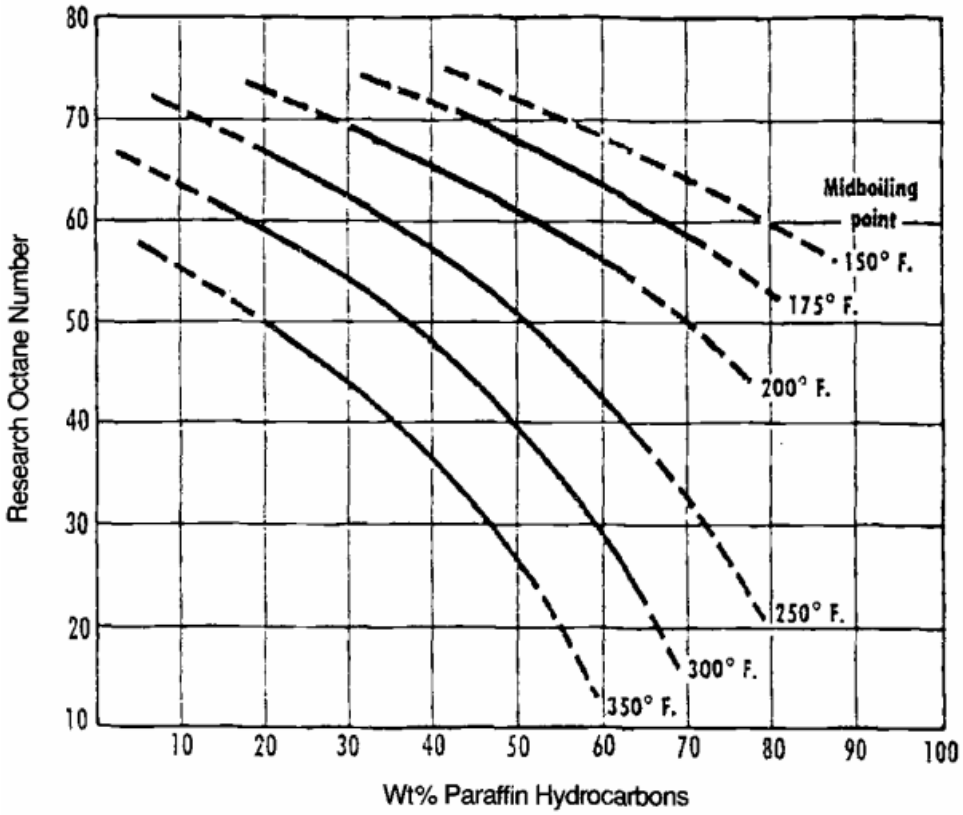

Figure 4: Research octane number versus paraffin content

RON for these various hydrocarbon groups have been correlated to normal boiling point, Tb in the following form:

$$RON = a + bT + cT^2 + dT^3 + eT^4 \quad \text{.....(2)}$$

Where RON is the clear research octane number and T = (Tb-273.15)/100 in which Tb is the boiling point in kelvin. Based on the data taken from the API-TDB, the coefficients a - e were determined and are given in Table below:

Coefficients of eq. 2 for estimation of RON

Hydrocarbon family	*a*	*b*	*c*	*d*	*e*
n-Paraffins	92.809	−70.97	−53	20	10
*iso*paraffins					
2-Methyl-pentanes	95.927	−157.53	561	−600	200
3-Methyl-pentanes	92.069	57.63	−65	0	0
2,2-Dimethyl-pentanes	109.38	−38.83	−26	0	0
2,3-Dimethyl-pentanes	97.652	−20.8	58	−200	100
Naphthenes	−77.536	471.59	−418	100	0
Aromatics	145.668	−54.336	16.276	0	0

Example: A naphtha sample from an Australian crude oil has the following characteristics: boiling point range 15.5 – 70°C specific gravity 0.6501, n-paraffins 49.33%, isoparaffins 41.45%, naphthenes 9.14%, aromatics 0.08%, clear RON 69.6, and MON 66.2. a) Estimate RON from the pseudocomponent method using experimental composition, b) Estimate RON from Fig.4, and c) Estimate RON from Fig.4.

Solution:

For this fraction: Tb = (15.5 + 70)/2 = 42.8°C, SG = 0.6501, xp = 0.4933, xw = 0.4145, x_N = 0.0914, x_A =0.008:

a) RON can be estimated from Eq.(1) through pseudocomponent method using RON values for pure hydrocarbons calculated from Eq. (2) and Table above with Tb= 315.9K. Results of calculation are $(RON)_{np}$ =54.63, $(RON)_{lp}$ = (90.94 + 104.83 + 88 + 87.05)/4 = 92.7, $(RON)_N$ = 55.57, and $(RON)_A$ =125.39. In calculation of (RON)w, an average value for RON of 4 families in Table above is calculated. From eq.2, clear RON can be calculated as:

$$RON = 0.4933 \times 54.63 + 0.4145 \times 92.7 + 0.0914 \times 55.57 + 0.0008 \times 125.39 = 70.55.$$

In comparison with the reported value of 69.6 the error is 70.55 - 69.6 = 0.95.

b) To use Fig.3 we need Tb = 42.8°C =109F and Kw, which is calculated as Kw = 12.75. Since the Kw is outside the range of values in Fig.3, accurate reading is not possible, but from value of the boiling point it is obvious that the RON from extrapolation of the curves is above 70.

c) To use Fig. 4 we need total paraffins which is % = 49.33 + 41.45 = 90.78 and Tb = 109F. In this case Tb is outside the range of values on the curves, but with extrapolation a value of about 66 can be read. The error is about = 3.6.

9- 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 Tb is the mid boiling point in kelvin and API is API gravity.

10- 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 naphtha-lene 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:

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

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

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

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

11- 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:

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

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.

Example: A Nigerian kerosene has an API gravity of 41.2, aniline point of 55.6°C. Estimate the smoke point of this fuel and compare with the experimental value of 20 mm.

Solution:
From API gravity, SG = 0.819, AP=55.6°C, the calculated SP is SP = 20 mm. The ASTM smoke point is then 19.3 mm which is in very good agreement with the experimental value of 20 with deviation of -0.7 mm.

12- 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.

13- 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:

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

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

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

$$T_r = 311/T_c$$

Where Tb is the mid boiling point and Tc is the pseudocritical temperature of the fraction in kelvin. Pc is the pseudocritical pressure and RVP is the Reid vapor pressure in bars.

Example: Estimate RVP of a gasoline sample has molecular weight of 86 and API gravity of 86 and Tb=388K, Tc=501.2K, Pc=28.82bar.

Solution:

Tr = 0.6205, X = 1.3364, and Y = -3.7235. Thus we calculate RVP = 0.696 bar or 10.1 psia. The experimental value is 11.1 psia

14- 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 pridicted by using the following equation:

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

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:

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

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

15- 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 Fig. and Table below)

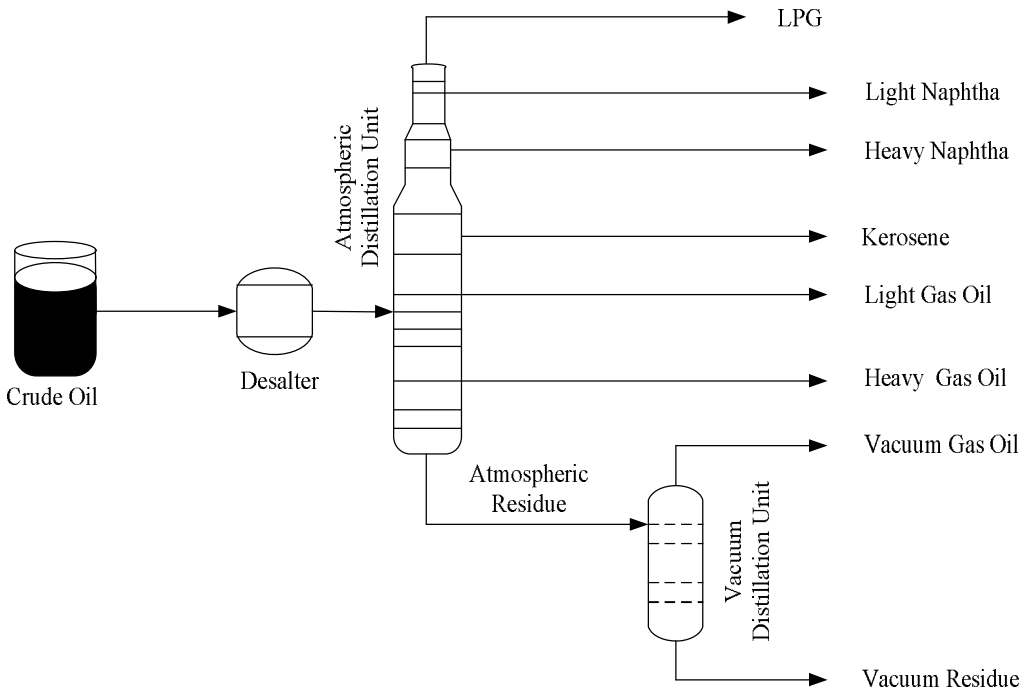

Table 1: Oil fractions destinations and ultimate products with their boiling ranges

Oil Fractions	**Approx. Boiling Ranges (^{0}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