Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering Department

Properties of Petroleum & Natural Gas

Third Class

Lecture 15

By

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Quality Control of Finished Products in Petroleum Refining

1- Gasoline

Physical description: Is a clear, volatile liquid used as a fuel in spark ignition internal combustion engines.

Chemical description: a complex mixture of hydrocarbons, **5-10 carbon atoms** per molecule.

Blended Gasoline: is a mixture of unfinished gasoline or SRG, catalytically cracked gasoline, cooker gasoline, alkylate, Isomerate and reformate.

Flash point: -45°F. (-43°C).

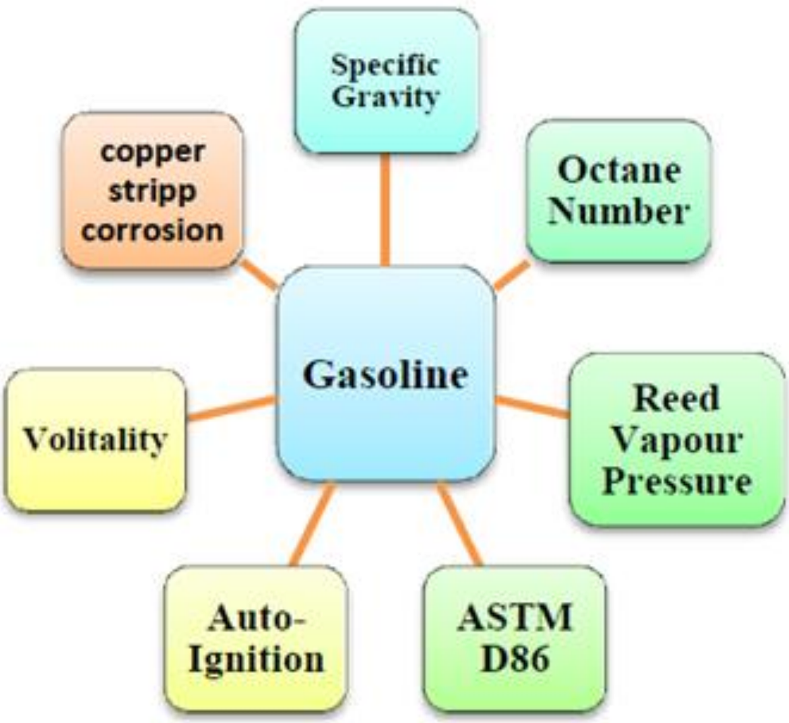
Density: 0.660 to 0.730

Auto-ignition temperature: (350°C).

Gasoline contains about 46.7 MJ/kg

Viscosity: Slightly less than water

Average boiling range: 32-184°C.

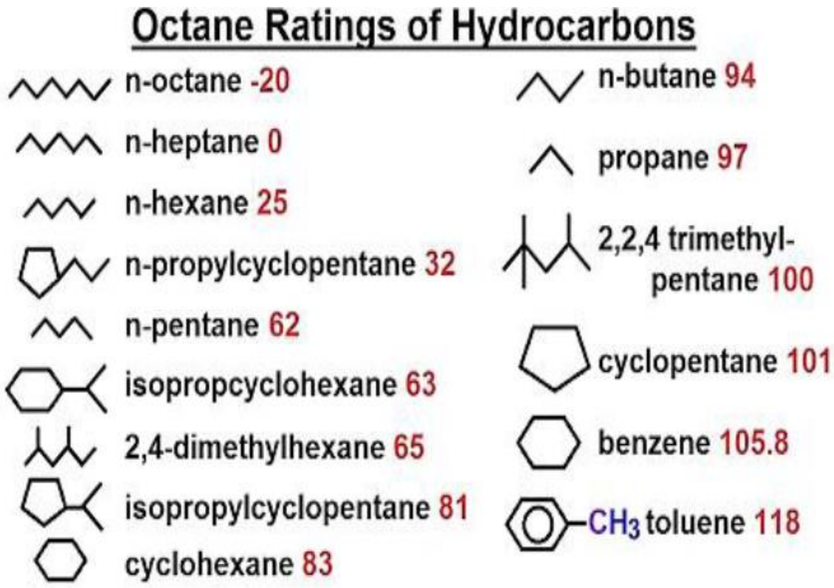


Octane Number

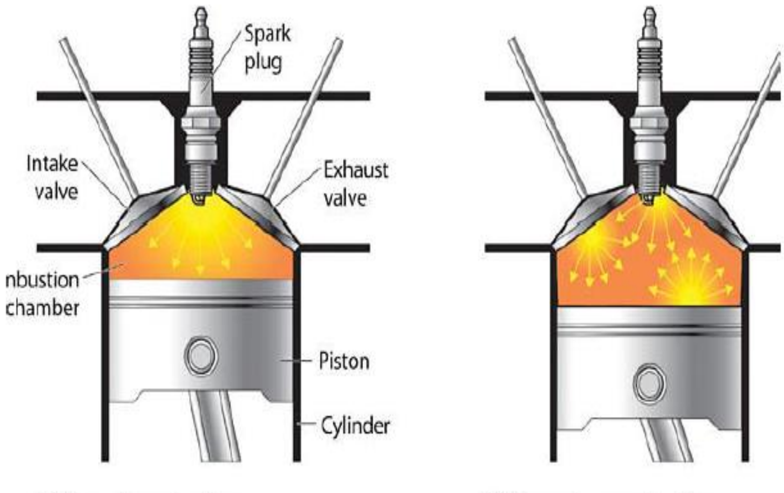
Standard Test Method: ASTM D357 (Motor Octane Number MON) and D908 (Research Octane Number RON)

- Octane number is that percentage of isooctane in a blend of isooctane and normal heptane that exactly matches the knock behavior of the gasoline. Thus, a 90-octane gasoline matches the knock characteristic of a blend containing 90 % isooctane and 10 % n-heptane.
- The **knock characteristics** are determined in the laboratory using a standard single-cylinder test engine equipped with a super sensitive knock meter.
- The reference fuel (isooctane and C7 blend) is run and compared with a second run using the gasoline sample.

- Two octane numbers are usually given: the first is the research octane number (RON) and the second is the motor octane number (MON).
- The significance of the two octane numbers is to evaluate the sensitivity of the gasoline to the severity of the operating conditions in the engine.
- The research octane number is higher than the motor octane number; the difference between them is the "sensitivity" of the gasoline.



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.



(a) Normal combustion (b) Premature combustion

Principle: Combustion in a variable compression ratio.

- It compares the degree of combustion of gasoline to that of a mixture of n-heptane (zero octane) and iso-octane (100 octane) expressed as V% iso-octane (2,2,4- trimethylpentane).

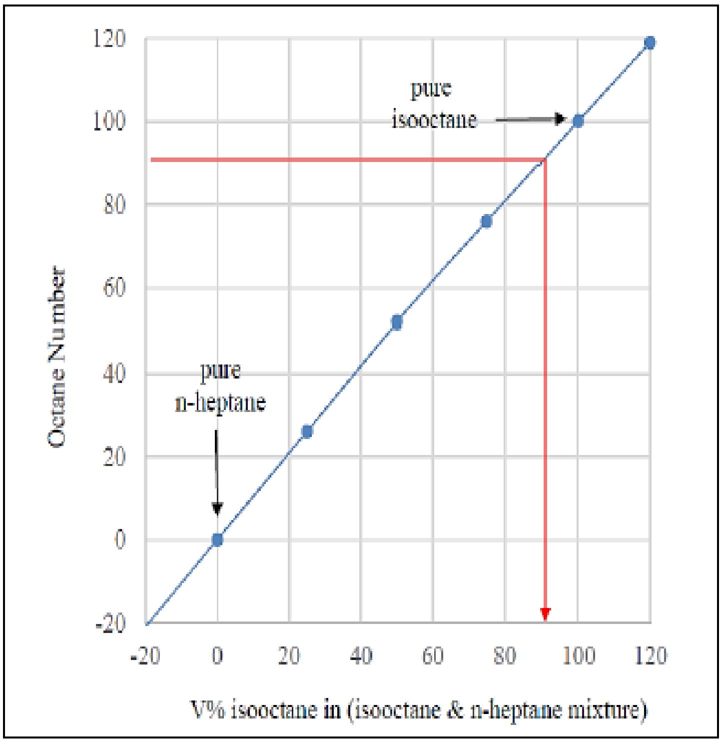
MON = - 17 (n-octane)

MON = 100 (iso-octane) 2,2,4-trimethylpentane

High-performance engines = higher compression ratios = prone to detonation = require higher octane fuel.

Compression Ratio

The ratio of the maximum to minimum volume in the cylinder of an spark ignition internal-combustion engine.



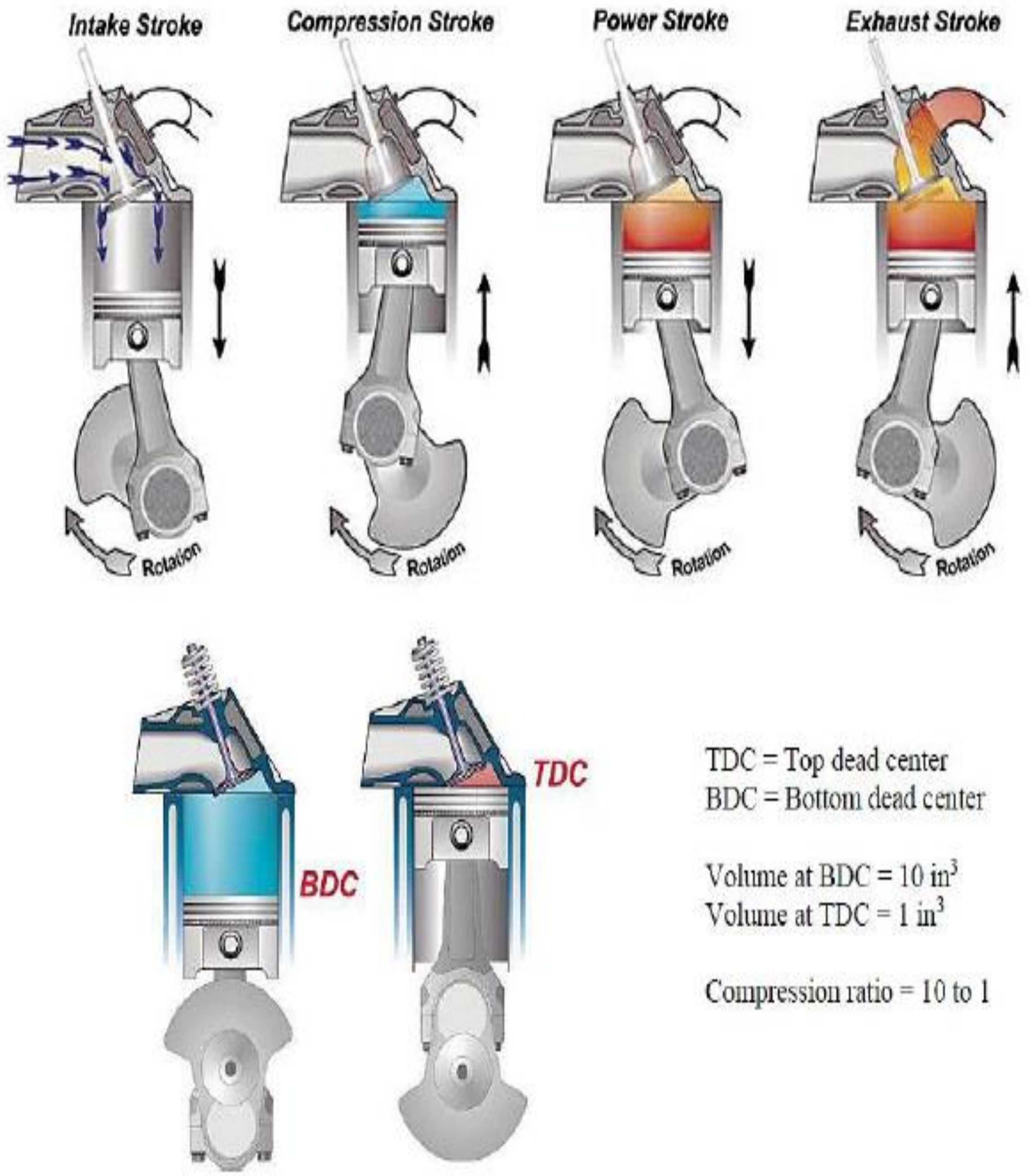


Figure. Stroke cycles and compression ratios in internal combustion engines

There are two methods for measuring octane number.

- *Motor Octane Number* (MON) is indicative of high-speed performance (900 rpm) and is measured under heavy road conditions.
- *Research Octane Number* (RON) is indicative of normal road performance under low engine speed (600 rpm) city driving conditions.
- The *Posted Octane Number* **(PON) or AKI (anti-nocking index)** is the average of the MON and RON [PON = (MON + RON)/2].

The octane number of a fuel can be improved by adding tetraethyl- lead (TEL) ($(CH_3CH_2)_4Pb$) or methyl-tertiary-butyl-ether (MTBE).

Auto-ignition Temperature

AIT is the minimum temperature at which hydrocarbon vapor when mixed with air can **spontaneously ignite without any external source**. The values of auto-ignition temperature for gasoline is about 351 °C (660 °F). With an increase in pressure the auto-ignition temperature decreases. This is particularly important from a safety point of view when hydrocarbons are compressed.

Surface tension or interfacial tension (IFT)

IFT is the measurement of a tensile force between molecules between two states (solid-liquid and liquid-gas).Volatility of petroleum fractions is expected to increase as the surface tension decrease. Therefore, gasoline is highly volatility because it has a low surface tension.

Calculations of Octane Number

Octane number is an important characteristic of spark engine fuels such as gasoline and jet fuel or fractions that are used to produce these fuels.

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

$$T\ RON = X_{NP}\,(RON)_{NP} + X_{iP}\,(RON)_{iP} + X_o\,(RON)_o + X_N\,(RON)_N + X_A\,(RON)_A$$

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 for n-paraffin, isoparaffins, olefins, naphthenes, and aromatics.

$$RON = a + bT + cT^2 + dT^3 + eT^4$$

Where RON is the clear research octane number and $T = (T_b)/100$ in which T_b is the boiling point in °C.

In the case of calculating RON_{Ip} the coefficients are given for four different groups of 2-methylpentanes, 3-methylpentanes, 2,2-dimethylpentanes, and 2,3-dimethylpentanes. Octane numbers of various isoparaffins vary significantly and for this reason an average value of RON_{Ip} for these four different iso-paraffinic groups is considered as the value of RON_{Ip}.

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

Normally when detailed PIONA composition is not available, PNA composition should be predicted. For such cases $X_o = 0$ *and* $X_{NP} = X_{ip} = X_P/2$

Once RON is determined, MON can be calculated from the following relation proposed by Jenkins

$$MON = 22.5 + 0.83\,RON - 20.0\,SG - 0.12\,(\%\,O) + 0.5\,(TML) + 0.2\,(TEL)$$

Where SG is the specific gravity, TML and TEL are the concentrations of tetra methyl lead and tetra ethyl lead in mL/UK gallon, and %O is the vol% of olefins in the gasoline. For olefin and lead-free fuels (% O = TML = TEL = 0).

Q: A naphtha sample 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%. Estimate RON from the pseudocomponent method using experimental composition.

Solution:

For this fraction:

$$Tb = \frac{15.5+70}{2} = 42.8°C \ where\ T = \frac{42.8}{100} = 0.428$$

$$SG = 0.6501,\ xnp = 0.4933,\ xip = 0.4145,\ xN = 0.0914,\ xA = 0.008$$

$$\text{RON (NP)} = a + b\,(0.42) + c\,(0.42)^2 + dT^3 + eT^4 = 54.628$$

$$\text{RON (2MP)} = a + bT + cT^2 + dT^3 + eT^4 = 90.9400$$

$$\text{RON (3MP)} = a + bT + cT^2 + dT^3 + eT^4 = 104.8277$$

$$\text{RON (2,2 DMP)} = a + bT + cT^2 + dT^3 + eT^4 = 87.997$$

$$\text{RON (2,3 DMP)} = a + bT + cT^2 + dT^3 + eT^4 = 87.049$$

$$\text{RON (IP)} = \frac{\text{RON 2MP} + \text{RON 3MP} + \text{RON 2,2DMP} + \text{RON 2,3DMP}}{4} = 92.703$$

$$\text{RON (N)} = a + bT + cT^2 + dT^3 + eT^4 = 55.573$$

$$\text{RON (A)} = a + bT + cT^2 + dT^3 + eT^4 = 125.393$$

$$T\,RON = X_{NP}\,(RON)_{NP} + X_{iP}\,(RON)_{iP} + X_o\,(RON)_o + X_N\,(RON)_N + X_A\,(RON)_A = 71.4566$$

$$\text{MON} = 22.5 + 0.83 * (\text{RON} = 71.4566) - 20.0\,\text{SG} - 0.12\,(\%\,O) + 0.5\,(\text{TML}) + 0.2\,(\text{TEL}) = 68.8$$

RON for PIONA families whose boiling points are the same as the mid boiling point or the ASTM D86 temperature at 50% point can be determined from figure below:

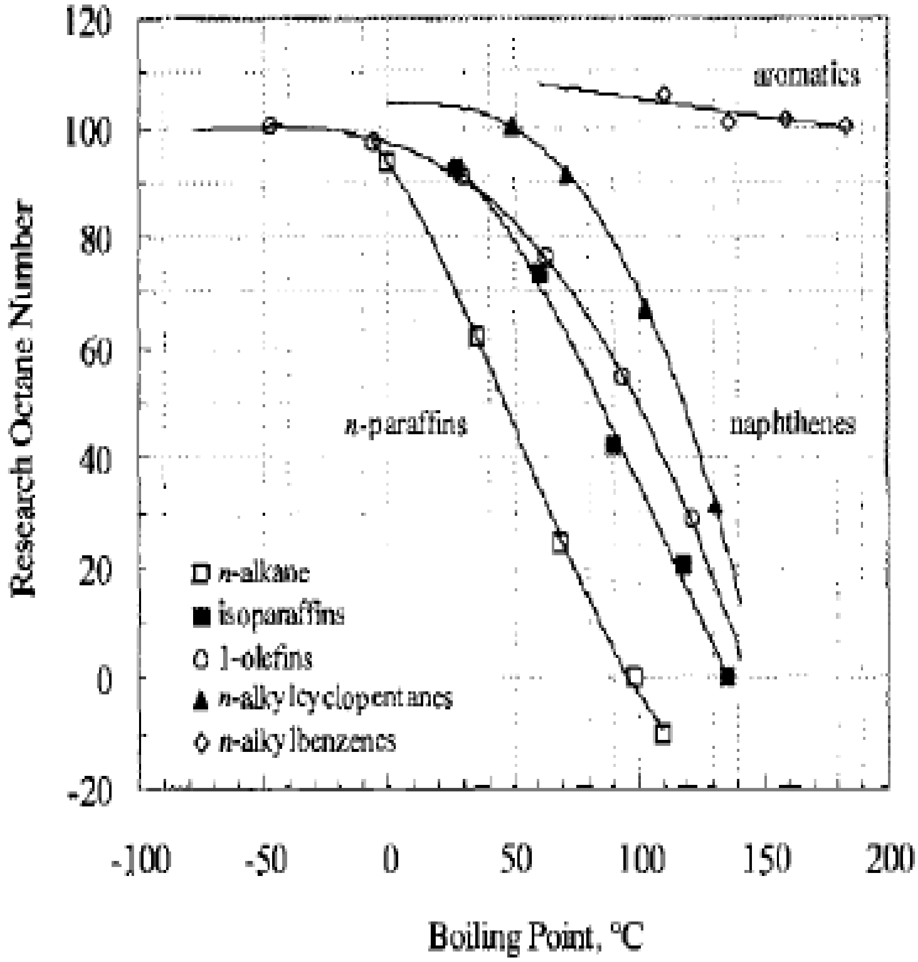
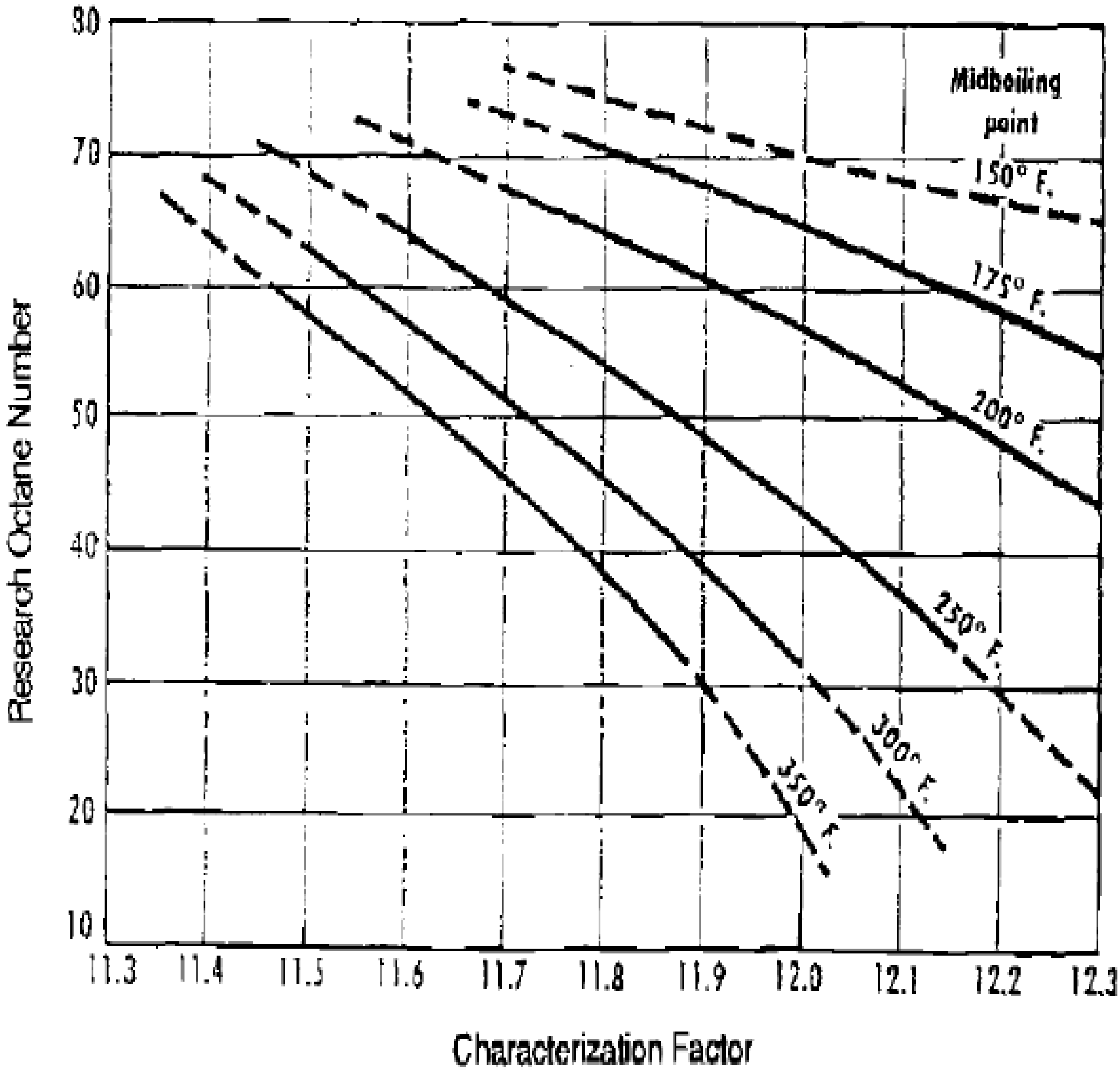


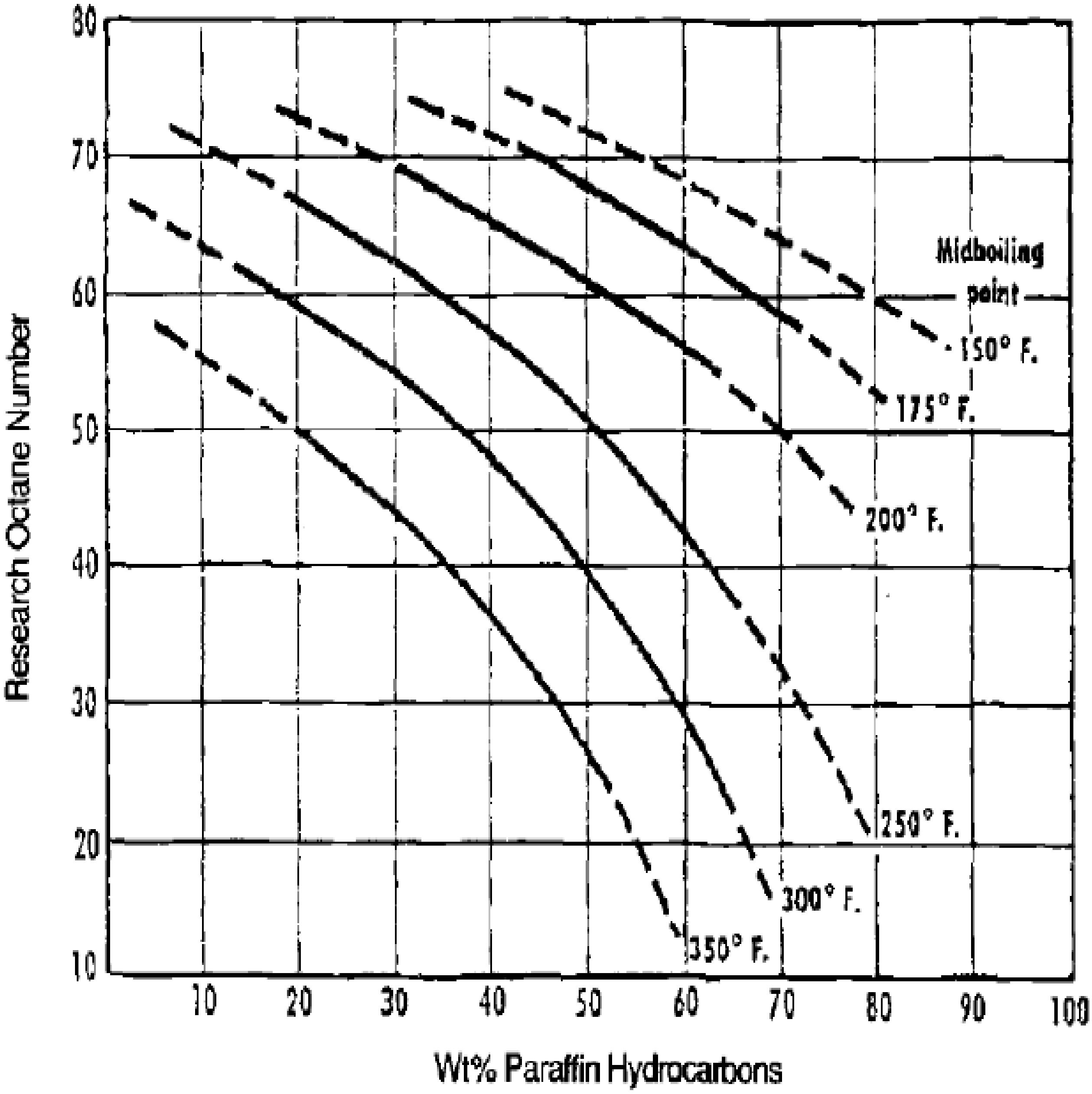
Figure: Research octane number for different families of hydrocarbons.

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

Figures below:



Midboiling point
150° F.
175° F.
200° F.
250° F.
300° F.
350° F.
80
70
60
50
40
30
20
10
11.3
11.4
11.5
11.6
11.7
11.8
11.9
12.0
12.1
12.2
12.3
Research Octane Number
Characterization Factor



The role of isoparaffins on octane number is significant as they have ON values greater than n-paraffins. In addition different types of isoparaffins have different octane numbers at the same boiling point. As the number of branches in an iso-paraffin compound increases the octane number also increases.

Calculations of octane number for blends

- There are a number of additives that can improve octane number of gasoline or jet fuels.
- These additives are tetra-ethyl lead **(TEL)**, **alcohols** such as ethanol, and ethers such as methyl-tertiary-butyl ether (MTBE), ethyl-tertiary-butyl ether (ETBE), or tertiary-amyl methyl ether (TAME).

For a fuel with octane number of 100, increase in the ON depends on the concentration of TEL added. The following correlations are developed based on the data provided by Speight:

$$RON_a = RON_b + 11.06(TEL) - 3.406(TEL)^2 + 0.577(TEL)^3 - 0.038(TEL)^4$$

This equation gives ON of fuel after a certain amount of TEL is added. For example, if 0.3 mL of TEL is added to each U.S. gallon of a gasoline with RON of 95, the equation above gives ON of 104.4, which indicates an increase of 9.0 in the ON.

Octane numbers of some oxygenates (alcohols and ethers) are given in Table below. Once these oxygenates are added to a fuel with volume fraction of X_{ox} the octane number of product blend is

$$ON_{blend} = X_{ox}\,(ON)_{ox} + (1 - X_{ox})(ON)_{clear}$$

Compound	RON	MON
Methanol	125–135	100–105
MTBE	113–117	95–101
Ethanol	120–130	98–103
ETBE	118–122	100–102
TBA	105–110	95–100
TAME	110–114	96–100

MTBE: methyl-tertiary-butyl ether; ETBE: ethyl-tertiary-butyl ether; TBA: tertiary-butyl alcohol; TAME: tertiary-amyl-methyl ether.

- ON_{clear} is the clear octane number (RON or MON) of a fuel.
- ON_{blend} is the octane number of blend after addition of an additive.
- ON_{ox} is the octane number of oxygenate, which can be taken as the average values for the ranges of RON and MON. For example for MTBE, the range of RON_{ox} is 113-117; therefore, for this oxygenates the value of RON_{ox} for use in equation above is 115. Similarly the value MON_{ox} for this oxygenates is 98.
- Equation above represents a simple linear relation for octane number blending without considering the interaction between the components.
- This relation is valid for addition of additives in small quantities (low values of X_{ox}, i.e., < 0.15).

Q: Naphtha produced from a modern refinery has the following PIONA composition 25%, 20%, 0.0%, 15% and 40%, respectively. The product has a boiling point range from C_6-170°C and specific gravity of 0.7700 at 60/60°F. For this product, calculate:

1. MON and RON
2. Calculate RON if 1.5 mL of TEL/US gallon has been added to this product.
3. How much MTBE should be added to this naphtha to increase the RON from 60 to 75?

Answer:

(1) For this fraction:

$$Tb = \frac{68+70}{2} = 119°C \ where\ T = \frac{119}{100} = 1.19$$

$$SG = 0.7700,\ xnp = 0.25,\ xip = 0.20,\ xN = 0.15,\ xA = 0.40$$

$$\text{RON (NP)} = a + b\,(0.42) + c\,(0.42)^2 + dT^3 + eT^4 = -12.942$$

$$\text{RON (2MP)} = a + bT + cT^2 + dT^3 + eT^4 = 92.87$$

$$\text{RON (3MP)} = a + bT + cT^2 + dT^3 + eT^4 = 68.602$$

$$\text{RON (2,2 DMP)} = a + bT + cT^2 + dT^3 + eT^4 = 26.353$$

$$\text{RON (2,3 DMP)} = a + bT + cT^2 + dT^3 + eT^4 = 18.535$$

$$\text{RON (IP)} = \frac{\text{RON 2MP} + \text{RON 3MP} + \text{RON 2,2DMP} + \text{RON 2,3DMP}}{4} = 51.60$$

$$\text{RON (N)} = a + bT + cT^2 + dT^3 + eT^4 = 60.244$$

$$\text{RON (A)} = a + bT + cT^2 + dT^3 + eT^4 = 104.05$$

$$T\ RON = X_{NP}\,(RON)_{NP} + X_{iP}\,(RON)_{iP} + X_o\,(RON)_o + X_N\,(RON)_N + X_A\,(RON)_A = 60.753$$

$$\text{MON} = 22.5 + 0.83 * (\text{RON} = 60.753) - 20.0\,\text{SG} - 0.12\,(\%\,\text{O}) + 0.5\,(\text{TML}) + 0.2\,(\text{TEL}) = 57.52$$

(2) 1.5 mL of TEL added

$$RON_a = RON_b + 11.06(TEL) - 3.406(TEL)^2 + 0.577(TEL)^3 - 0.038(TEL)^4 = 71.43$$

(3) How much MTBE

$$RON_{blend} = X_{ox}\,(RON)_{ox} + (1 - X_{ox})(RON)_{clear}$$

$$75 = X_{ox}\,(115)_{ox} + (1 - X_{ox})(60)_{clear} \rightarrow X_{ox} = 0.2727\ (27.27\ \%\ volume)$$

Required RON of gasoline vary with parameters such as:

- air temperature,
- altitude, humidity,
- engine speed,
- Coolant temperature.

- Generally for every **300 m altitude RON required decreases by 3** points and for every **11°C rise** in temperature **RON required increases by 1.5** points.
- Improving the octane number of fuel would result in reducing power loss of the engine, improving fuel economy, and a reduction in environmental pollutants and engine damage.
- For these reasons, octane number is one of the important properties related to the quality of gasoline.