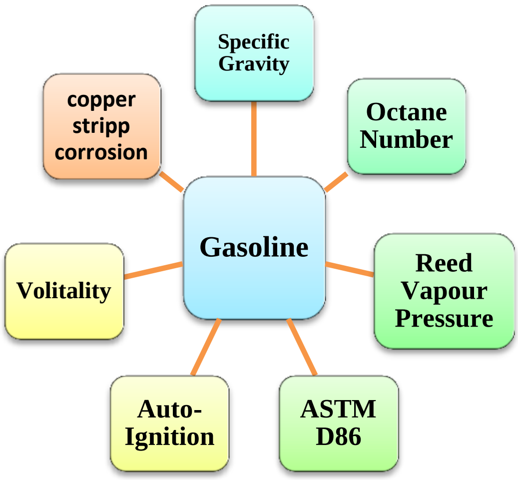
Quality Control Tests for Finished Petroleum Products

1- Gasoline

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

- Density: 0.660 to 0.750
- Average boiling range: 36-200°C & C5-C10

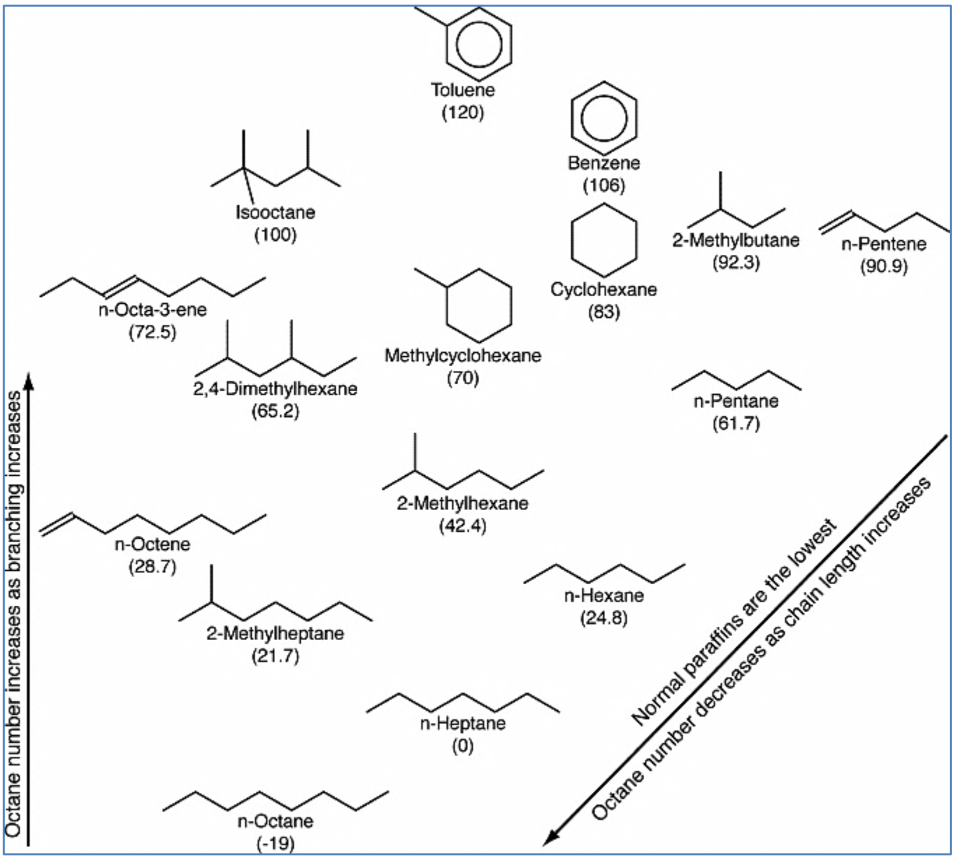


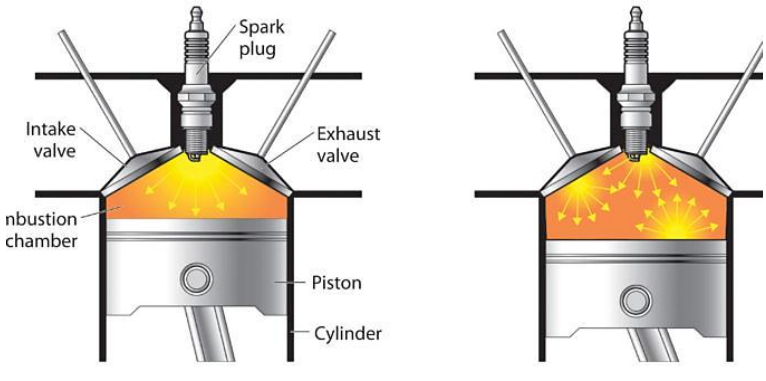
Octane Number

- **Octane number** is the percentage of **isooctane** (**ON: 100**) in a blend of isooctane and **normal heptane** (ON: 0) that exactly matches the knock behavior of the gasoline.
- **90-octane gasoline** matches the knock characteristic of a blend containing 90 % isooctane and 10 % n-heptane.
- The octane number is a **measure of the knocking tendency** of gasoline fuels in spark ignition engines.
- The ability of gasoline to **resist auto-ignition during compression** and prior to the spark ignition gives it a **high octane number.**
- **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).

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

- The **knock characteristics** are determined by using a standard **single-cylinder** test engine equipped with a super **sensitive knock meter**.
- The knock intensity of gasoline is determined by comparing with that of reference fuel (iC8 and nC7 blend).



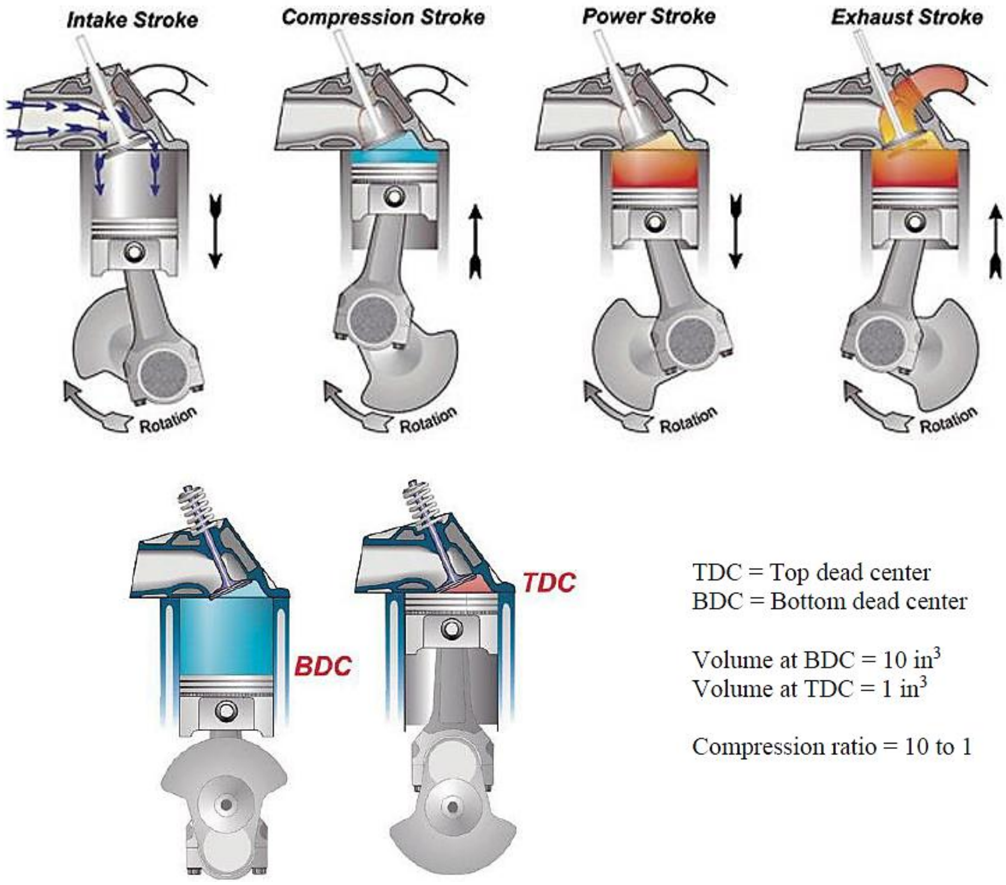


(a) Normal combustion (b) Premature combustion

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

Compression Ratio

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



Stroke cycles and compression ratios in internal combustion engines

- **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].**
- RON is **higher than** MON; the difference between them is the "**sensitivity**" or PON: is the ability of gasoline to **withstands the sever operating conditions** in the engine.

Calculations of Octane Number

RON of a fuel may be estimated from the **pseudo-component techniques** in the following form:

$$T\ RON = X_{NP}\,(RON)_{NP} + X_{iP}\,(RON)_{iP} + X_{o}\,(RON)_{o} + X_{N}\,(RON)_{N} + X_{A}\,(RON)_{A} \quad ..20$$

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.

$$RON = a + bT + cT^2 + dT^3 + eT^4 \quad ...21$$

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 as given in the table below. 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 $X_{ip} = X_P/2$

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

$$MON = 22.5 + 0.83\,RON - 20.0\,SG - 0.12\,(\%\,O) + 0.5\,(TML) + 0.2\,(TEL) \quad ....22$$

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).

Exercise: 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 and MON from the pseudocomponent method using experimental composition.

Solution:

For this fraction:

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

$$\boldsymbol{SG} = \mathbf{0.6501},\ \boldsymbol{xnp} = \mathbf{0.4933},\ \boldsymbol{xip} = \mathbf{0.4145},\ \boldsymbol{xN} = \mathbf{0.0914},\ \boldsymbol{xA} = \mathbf{0.008}$$

$$\text{RON (NP)} = 92{,}8 + \text{b}\,(0.428) + \text{c}\,(0.428)^2 + \text{d}(\text{o}.428)^3 + \text{e}(0.428)^4 = 54.628$$

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

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

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

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

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

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

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

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

MON $= 22.5 + 0.83 * (\text{RON} = 71.4566) - 20.0\,(\text{SG} = 0.6501) - 0.12\,(\%\,\text{O}) +$
$0.5\,(\text{TML}) + 0.2\,(\text{TEL}) = \mathbf{68.8}$

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:

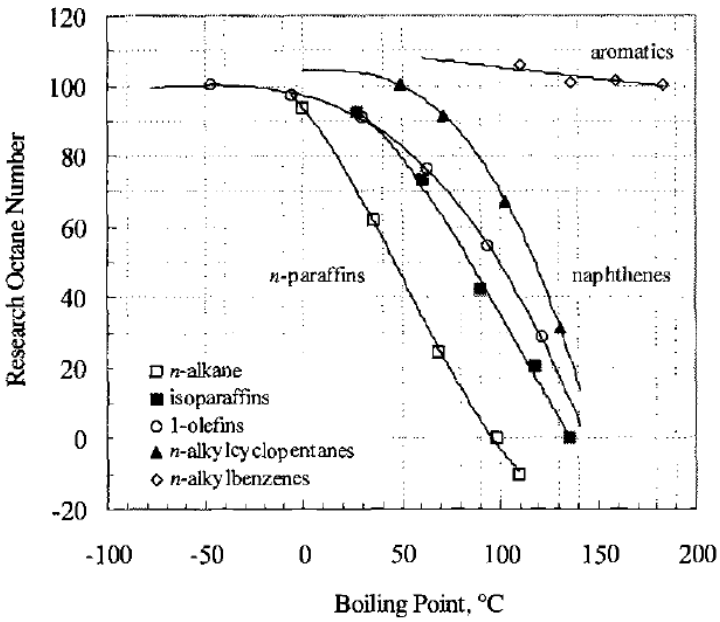


Figure 12: Research octane number for different families of hydrocarbons.

Estimation RON for naphtha in terms of Kw or paraffin content (wt%) and mid boiling point.

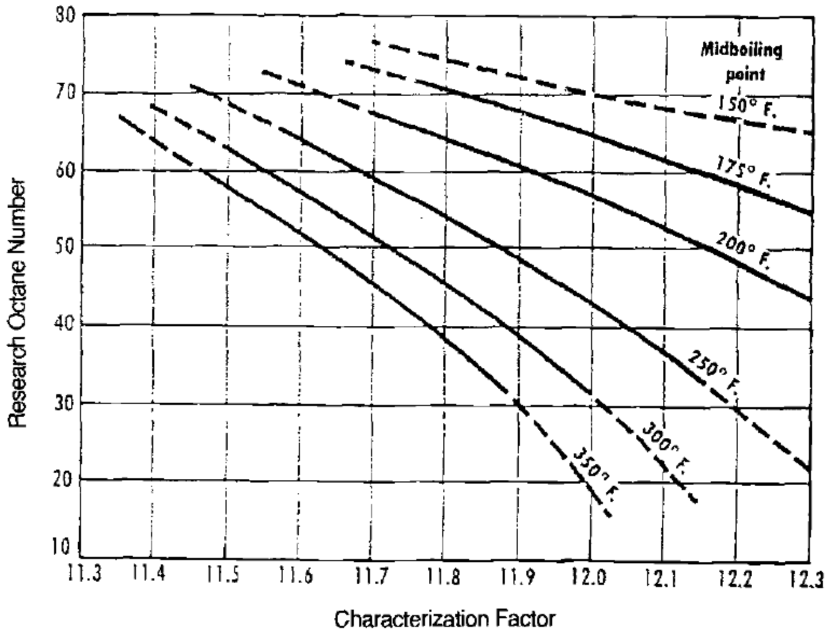


Figure 13: Research octane number from Kw at different mid-boiling points.

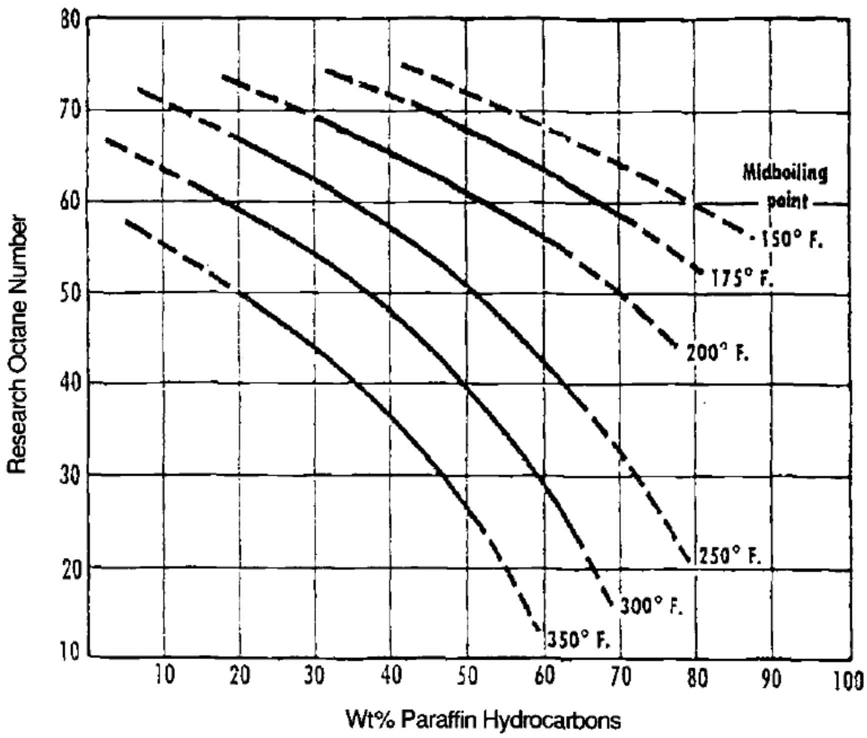


Figure 14: Research octane number from PF wt% at different mid-boiling points.

Calculations of octane number for blends

- There are a number of octane boosters that can improve octane number of gasoline fuel.
- These 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)**.

The following correlations are developed based on the data provided by Speight:

$$\mathbf{RON_a = RON_b + 11.06(TEL) - 3.406(TEL)^2 + 0.577(TEL)^3 - 0.038(TEL)^4 \ldots 23}$$

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

$$\boldsymbol{ON_{blend} = X_{ox}(ON)_{ox} + (1 - X_{ox})(ON)_{clear} \ldots 24}$$

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.
- This relation is valid for addition of additives in small quantities (low values of X_{ox}, i.e., < 0.15).

Exercise: 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 to **75**?

Answer:

(1) For this fraction:

$$Tb = \frac{68 + 170}{2} = 119°C \ where \ T = \frac{119}{100} = 1.19$$

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

$$RON\ (NP) = a + b\,(1.19) + c\,(1.19)^2 + dT^3 + eT^4 = -12.942$$

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

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

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

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

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

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

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

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

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

(2) 1.5 mL of TEL added

$$RON_a = (60.75) + 11.06(1.5) - 3.406(1.5)^2 + 0.577(1.5)^3 - 0.038(1.5)^4 = 71.43$$

(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.