Lecture 37:Motor Gasoline

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MOTOR GASOLINE

Motor gasoline is a mixture of nearly 400 different hydrocarbons consisting of n-paraffins, iso-paraffins, olefins, aromatics and some cycloparaffins. Typical gasoline has hydrogen to carbon atom ratio in the range 1.8 to 1.95 and it may be assigned a molecular formula, C_8H_{15}. It is liquid at room temperature and boils in the range from about 35 to 215º C. The principal characteristics of gasoline that are important for engine performance and emissions have been given in Table 8.1. Key fuel properties and their effects on engine performance and emissions are discussed below.

Antiknock Quality

In SI engines, use of a higher compression ratio results in higher thermal efficiency and higher engine power. With increase in compression ratio however, knocking combustion occurs. Persistent and high intensity combustion knock causes engine overheating, loss in efficiency and may lead to mechanical damage to the engine components particularly under high load operation. To prevent or minimize knocking combustion, gasoline of a high antiknock quality is needed.

Knock resistance of a fuel is measured by octane number (ON), which is determined by comparing knocking combustion characteristics of the sample fuel to that of standard reference fuels in a standardized CFR (Cooperative Fuel Research, USA) test engine. The two reference fuels that define the octane scale are:

- A fuel with high knock resistance: Isooctane (C_8H_{18}) or 2-2-4 trimethyl pentane given octane number equal to 100, and
- A fuel with low knock resistance: n-heptane (n-C_7H_{16}) given octane number equal to 0.

The blends of these two reference fuels define the intermediate octane number on a linear scale. For example, a blend of 90 % isooctane and 10% n-heptane has 90 ON.

The ASTM CFR knock test engine used worldwide is a single cylinder, variable compression ratio engine The engine compression ratio can be varied while the engine is running between 3 and 30 by moving cylinder and cylinder head assembly up or down with respect to the crankshaft. Thus the engine clearance volume is changed while the swept volume remains constant. A knock sensor is mounted on the combustion chamber and knock signal is a function of rate of pressure rise during combustion. Two test methods performed for automotive fuels on the standard CFR test engine are:

- Research method (ASTM D-2699) that measures *Research Octane Number* (RON), and
- *Motor method* (ASTM D-2700) measuring *Motor Octane Number* (MON).

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The engine operating conditions for the research and motor methods are given in Table 8.4. During the test, the air-fuel ratio of the engine with the sample fuel is adjusted for maximum knock intensity. Then on these settings, the engine compression ratio is varied and the knock intensity obtained with the test fuel is bracketed by two blends of the reference fuels that differ by not more than 2 ON units. The octane number of the sample fuel is obtained by interpolation between the knock intensity readings for the two blends of the reference fuels and their octane numbers. The octane number above 100 ON is determined by using isooctane and varying amounts of TEL (tetraethyl lead) in terms of ml TEL/ per litre. Tetraethyl lead is an antiknock additive. ASTM standards have specified octane numbers to the blends of isooctane and TEL.

Table 8.4

Engine Test Conditions for ASTM Research and Motor Methods

Operating Conditions	Research Method	Motor Method
Engine Speed, RPM	600	900
Inlet temperature, °C	52	149
Inlet Pressure	Atmospheric	Atmospheric
Humidity, kg/kg of dry air	0.0036-0.0072	0.0036-0.0072
Coolant Temperature, °C	100	100
Spark Advance, °CA btdc	13 (constant)	19-26 (varies with CR)
Air-fuel ratio	Adjusted for maximum knock	Adjusted for maximum knock

The test operating conditions used in Motor Method viz., higher intake mixture temperature and higher spark advance are likely to produce more knock and thus, the method is more severe. For the most fuels motor octane number is lower than the research octane number. The difference between RON and MON is known as ***fuel sensitivity***:

$$\text{Fuel Sensitivity} = \text{RON} - \text{MON} \qquad \textbf{(8.1)}$$

The fuel sensitivity for fuels is mostly in the range 0 to 12 octane units. The reference fuels being paraffins, the paraffinic hydrocarbons have low octane

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sensitivity while the olefins and aromatics have high octane sensitivity. The commercial gasoline have fuel sensitivity around 7 to 10 units. The test engine operates at low speeds and has an old design of combustion chamber. In the production high speed engines, under actual operation at varying load, speed and ambient conditions the antiknock performance of commercial motor gasoline may match neither to research method nor to motor method under all operating conditions. In Europe therefore, both the RON and MON for a gasoline are specified in the standards.. Many national gasoline specifications like those in the USA and India use average of the research and motor octane numbers to specify the antiknock quality of motor gasoline. The average of RON and MON is termed as *antiknock index* (AKI):

$$AKI = (RON+MON)/2 \qquad \textbf{(8.2)}$$

Earlier, tetra-ethyl lead (TEL), an anti-knock additive was used to produce high octane number fuels at a low cost. However, in 1975 when the gasoline vehicles for the first time employed catalytic converters for emission control, lead was required to be phased out of gasoline. Lead by itself is hazardous to human health. Now, gasoline is totally lead-free in most of the countries. The lead-free gasoline is blended with high-octane fuel components like aromatics, isoparaffins, alcohols and methyl tertiary butyl ether (MTBE) to improve its anti-knock quality.

Octane number has no direct effect on engine emissions. Severe knocking increases combustion temperatures and may result in higher NO formation. The fuel octane number may affect emissions through dependence of engine compression ratio on the octane number. For lead free gasoline, hydrocarbon composition depends on its octane number. High ON lead free gasoline may contain more of aromatics and olefins and hence unburned hydrocarbons also are likely to have higher concentration of aromatics and olefins, which are more photo-chemical reactive.

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Distillation

The distillation characteristics of gasoline are presented by a curve relating percent volume of fuel evaporated to temperature as shown in Fig 8.1. Temperatures for evaporation of 10 % (T10), 50% (T50), 90% (T90) and final boiling point (FBP) of fuel are important features of the distillation curve and their limits or equivalent are specified in the gasoline standard specifications.

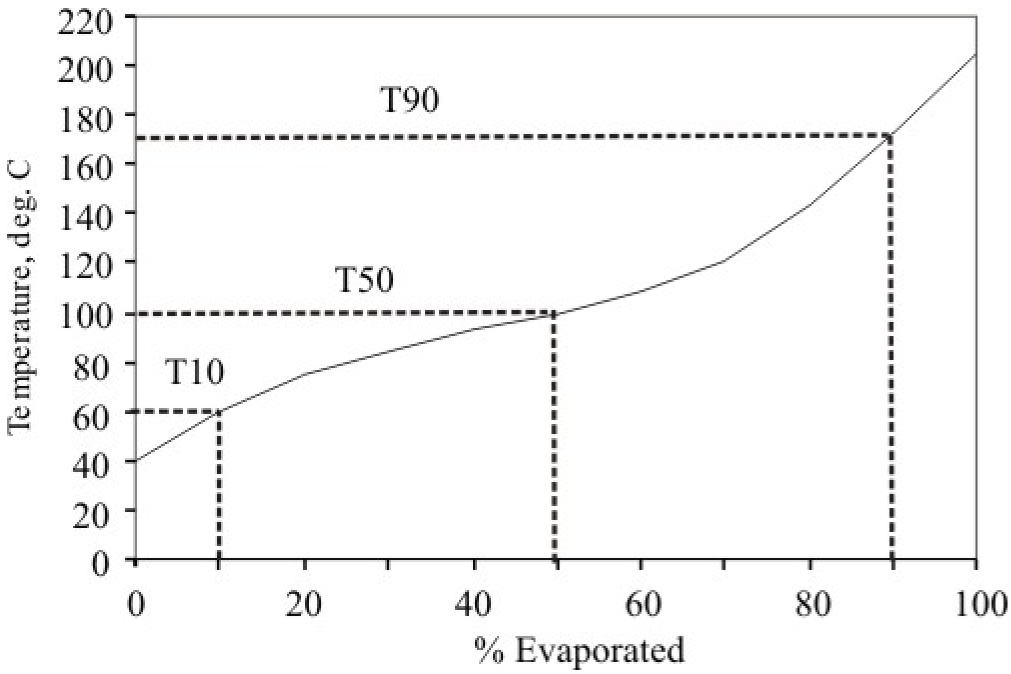

Figure 8.1	Typical disillation curve of motor gasoline

Distillation range influences engine exhaust emissions through its effect on fuel evaporation characteristics, mixture formation and hydrocarbon composition. HC emissions during cold start and warm-up may be influenced by the front-end volatility (T_{10}). An increase in T_{50} has been seen to decrease HC emissions. A lower T_{90} has been seen to increase CO and NO_x emissions in some engines but it reduces other air pollutants; butadiene and formaldehyde which are known as 'air toxics'.

Reid Vapour Pressure

Reid vapour pressure (RVP) is measured at 37.8º C in a closed bomb having 4 times the volume of liquid fuel.. At low ambient temperatures for good cold starting and faster engine warm-up a high vapour pressure is required. But, in warm and hot ambient conditions, a high Reid vapour pressure results in high evaporative emissions and may overload the carbon canisters of the evaporative control system with the hydrocarbon vapours. RVP has good correlation with the fuel evaporation losses during refuelling and from the fuel tank and carburettor. Evaporative hydrocarbon emissions as a function of RVP and ambient temperature are shown on Fig. 8.2. The evaporative emissions increase almost linearly with increase in RVP. For a given fuel RVP, the evaporative hydrocarbons increase as the ambient temperature increases.

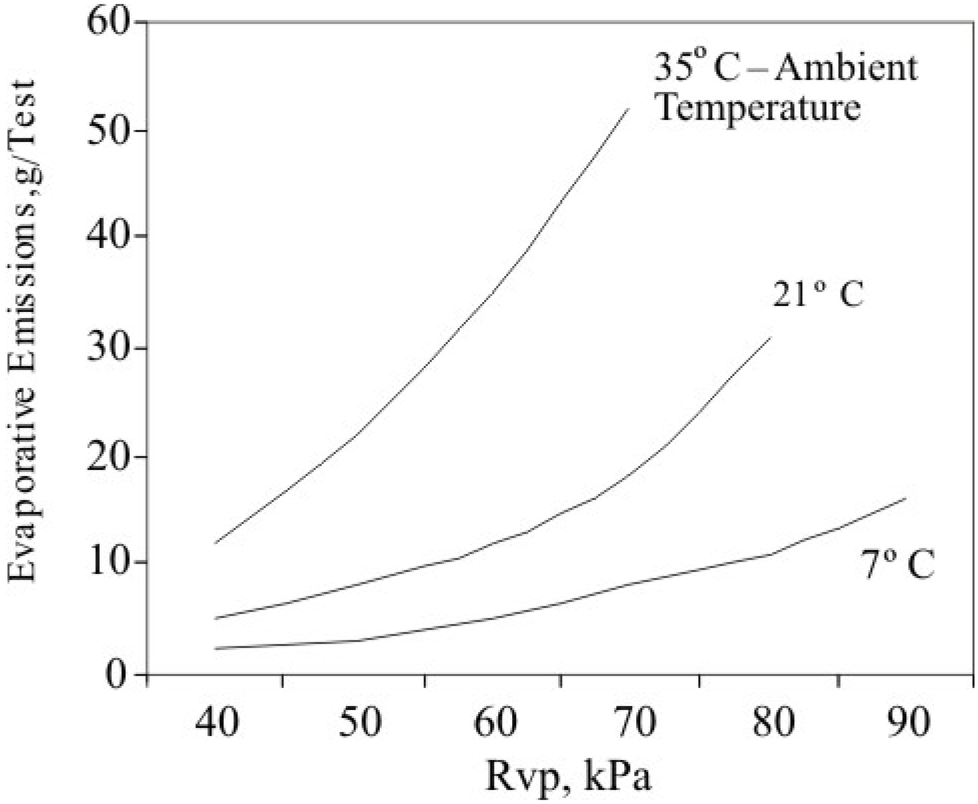

Figure 8.2	Dependence of evaporative hydrocorbon emissions on RVP and ambient temperature .

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Oxidation and Storage Stability

The fuel may remain in the storage and transportation systems for several weeks. During storage before it is consumed, fuel undergoes slow oxidation under the atmospheric conditions producing gummy substances. Low temperature oxidation stability of gasoline is measured in terms of induction period (ASTM D 525) and existent gum test (ASTM D381). Induction period measures oxidation characteristics at a specified temperature and pressure in presence of oxygen denoting the time period when sharp drop in oxygen pressure occurs, which indicates the beginning of oxidation. The existent gum is a resin like substance that is formed due to slow oxidation of gasoline during transportation, handling and storage which is present in the fuel sample. To improve oxidation stability of gasoline chemical additives known as antioxidants are used.

The gum formed in gasoline during storage, leads to formation of deposits in carburettor, fuel injectors, intake manifold, on intake ports and intake valves, and in the combustion chamber. The gums clog fuel metering orifices, result in sticking of intake valves and form carbon deposits in the combustion chamber. Deposit formation in fuel system and combustion chamber lead to loss in fuel efficiency and

increase in carbon monoxide and unburned hydrocarbon emissions. Plugging of the fuel injector holes reduces fuel flow rate that disturbs the calibration of feedback controlled engine fuel management system. A 30 percent flow reduction in port fuel injectors has been seen to increase HC emissions by 10 to 30 %.

The formation of deposits in the combustion chamber increases the effective engine compression ratio. These deposits being porous in nature act like small crevices adsorbing hydrocarbons during compression. The hydrocarbons released from the combustion chamber deposits during expansion stroke escape combustion resulting in higher HC emissions. The combustion chamber deposits can increase HC and NO_x emissions by up to 10 to 15%. To prevent deposit formation in the engine intake, fuel system and combustion chamber, detergent/ dispersant type additives are added to gasoline.

Hydrocarbon Composition

Olefins and aromatic hydrocarbons are high octane gasoline components but affect engine emissions in several ways;

- Olefins have poor oxidation and storage stability and their presence leads to formation of higher existent gum.
- Reduction in olefin content lowers emissions of the air toxic 1, 3-butadiene.
- Lowering the content of smaller molecular weight olefins in gasoline, reduces ozone forming potential of evaporative hydrocarbons.
- Aromatics have higher adiabatic flame temperatures and hence, a tendency for higher NO formation.
- Combustion of aromatics leads to higher deposit formation in the combustion chamber.
- Benzene is a natural constituent of gasoline and also is formed in the combustion chamber due to dealkylation of alkylbenzenes. Lower benzene and aromatic content of fuel results in lower exhaust and evaporative benzene emissions, Benzene being carcinogenic in nature its content in gasoline is now controlled to less than 1% by volume in many countries.

Sulphur

Sulphur has a significant deactivation effect on the catalytic converter reducing its efficiency. The conversion efficiency of modern 3-Way catalysts may reduce by 40 % with 900 ppm sulphur compared to 100 ppm sulphur in fuel. Most of the loss in 3-Way catalyst efficiency caused by sulphur is recovered once the engine is operated on low sulphur fuel. More advanced catalysts systems like de-NO_x catalysts and the closed-coupled catalysts operating at high temperatures suffer more serious and

poermanent loss of efficiency. NSR de-NO_x catalysts require practically sulphur-free (< 5 ppm by mass) fuel for their operation.

Sulphur also has an adverse effect on the working of heated exhaust oxygen sensor by deactivation of platinum electrodes.

Oxygenates

Oxygen containing compounds like alcohols and ethers which may be blended in gasoline are commonly termed as *oxygenates*. The alcohols and ethers that are permitted as blending components in gasoline are given in Table 8.5. The amount of oxygenates or oxygen content of fuel for use in engines designed to operate on the conventional petroleum fuels is limited mainly due to;

(i) Leaning effect of mixture caused by presence of oxygen in the fuel, which may increase NO_x emissions,

(ii) Effect on fuel Reid vapour pressure particularly when blending methanol

(iii) Adverse effect on the fuel system materials.

The oxygen in the fuel is limited to 2.7% mass of O_2 maximum in the USA and 2.5% O_2 maximum in Europe. Now in the USA, use of methanol as a blending component of gasoline is not permitted due to its toxic nature.

Table 8.5

Permissible Limits of Oxygenates in Gasoline in Europe

Oxygenate Type	% vol.
Methanol, suitable stabilizing agents must be added	3
Ethanol, stabilizing agents may be necessary	5
Isopropyl alcohol	7
Tertiary butyl alcohol	7
Iso-butyl alcohol	10
Ethers containing 5 or more carbon atoms per molecule	7
Other organic oxygenates or their mixtures	2.5% m/m oxygen, not exceeding the individual limits

defined in the regulations	fixed above for each component

Use of oxygenates in gasoline have the following features;

- Addition of oxygenates results in lower CO and HC emissions primarily due to mixture leaning effect more so in the carburettor vehicles.
- When oxygenates are added, oxygen is attached with some of the fuel molecules and hence an enhanced oxidation of fuel may be expected resulting in somewhat higher reduction in CO and HC emissions than the leaning effect alone.
- The magnitude of CO emission reduction for the closed loop feedback controlled vehicles using 3-Way catalysts is low as the mixture leaning effect occurs only during engine warm-up and acceleration phases. Under normal operating conditions, the feedback system controls air-fuel ratio close to stoichiometric.
- Excessive leaning caused by oxygenates can result in poor vehicle drivability and higher unburned hydrocarbons. Leaning effect may increase NO_x.
- Use of oxygenates particularly alcohols also increases emissions of formaldehyde, which is a known carcinogen and has high photochemical reactivity.

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Contaminants

Contaminants like silicon may get into gasoline fuel at fuel distribution outlets due to poor housekeeping or due to waste solvents being used as blending component at the market place. Silicon can cause failure of oxygen sensors even in very small concentrations. Water can be present in dissolved as well as in free form in gasoline. Water may lead to blockage of fuel lines, icing of intake system during severe winters in cold countries and corrosion of fuel system components. Water content limits for gasoline are specified in the fuel specifications.

Summary of Gasoline Properties on Emissions

Effects of gasoline quality on the engine emissions are summarized in Table 8.6. The effects of fuel quality on emissions are also dependent on vehicle technology. In this table the results for catalyst equipped vehicles are presented.

Table 8.6

Summary of Effects of Gasoline Properties on Emissions from Catalyst Cars

Property	Change	Lead	CO	HC-Exh	HC-Evap	NO_x	Benz-ene	Buta-diene	Alde-hydes
Reduce Lead	0.013→ 0.005 g/l	↓	↓	↓	0	↓	-0	-0	-0
Add Oxygenate	0→2.7% O2	0	↓↓	↓	0-↑	+0	0	0	↑↑
Reduce Aromatics	50→ 20% v/v	0	↓↓	↓	0	↑	↓↓↓	+0	+0
Reduce Benzene	3→ 2 % v/v	0	0	0	0	0	↓↓	0	0
Reduce Olefins	10→ 5% v/v	0	0	+0	-0	-0	0	↓↓	0
Reduce Sulphur	380→ 20 ppm	0	↓	↓	0	↓	↓	0	0 - ↑*
Reduce RVP	70→ 60 kPa	0	0	-0	↓↓	0	0	0	0
Increase E100	35→ 65%	0	↓	↓↓↓	0	↑-↑↑	0-↓↓↓	-0?	0 - ↓↓
Increase E150	85→ 90%	0	0-↑	↓↓	0	↑?	0	↓?	↓?

*Contradictory results obtained in different investigations.

Key: 0 = No effect; ± 0 = -2 to 2% effect; ↓ or ↑ = 2 to 10% effect; ↓↓ or ↑↑ = 10 to 20 % effect; ↓↓↓ or ↑↑↑ = > 20% effect; ? = Insufficient data

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Reformulated Gasoline

During late 1980s, in several large US cities the ambient air quality could not meet the prescribed limits for CO and ozone even after enforcement of the then stringent vehicle emission standards. The US Clean Air Act Amendments of 1990 therefore, legislated additional measures besides further tightening of the emission standards. Five organic compounds called 'Air Toxics' were identified for control through fuel quality modifications. These toxic substances emitted through exhaust and fuel evaporation are: benzene, formaldehyde, acetaldehyde, 1, 3 butadiene and 'polycyclic organic matter' (POM).

Gasoline quality was proposed to be modified for introduction in the big cities that did not meet the ambient air carbon monoxide and ozone standards. This modified gasoline was called 'reformulated gasoline (RFG)'. The RFG programme in the USA was implemented in two phases as given in Table 8.7.

Table 8.7

Performance Targets of US Reformulated Gasoline Programme

RFG Programme	Performance Target
Phase 1(Started on Jan 1, 1995)	15 to 17% reduction in both the exhaust and evaporative emissions of volatile organic compounds (VOC) and air toxics compared to 1990 industry average gasoline. NO_x however, must not increase above the 1990 gasoline.
Phase 2(Started on Jan 1, 2000)	25-29% reduction in VOC, 17-20% reduction in air toxic emissions and 5 to 7% reduction in NO_x

The RFG is basically a gasoline containing oxygenates for reduction in CO and through control of volatility and composition to reduce VOC and 'Air toxics'. All the reformulated gasolines were required to contain a minimum of 2 % by mass (m/m) oxygen and a maximum of 1% by volume (v/v) benzene. The RFG must not contain heavy metals. Further, their average T_{90}, sulphur, and olefins contents must not be higher than the 1990 average gasoline. Typical properties of Phase 1 and Phase 2 RFG are shown in Table 8.8

Table 8.8

Characteristics of Typical US Reformulated Gasoline

Properties	Phase 1- RFG	Phase 2- RFG
Aromatics, %v/v	23.4	25.4
Olefins, %v/v	8.2	4.1
Benzene, %v/v	1.3	0.93
RVP, kPa, Summer	50	46

Winter	79	-
T50, ºC	94	94
T90, ºC	158	145
Sulphur, mass ppm	305	31
MTBE, %v/v	11	11.2
Ethanol, % v/v	4	0
Oxygen , % mass	2.0 – 2.7	2.0 – 2.7
Heavy metals	Not permitted	Not permitted
Detergent Additives	Compulsory	Compulsory

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Average effects of reformulated gasoline on emissions from catalyst equipped cars are compared with those from a regular conventional unleaded gasoline on Fig. 8.3. These effects are primarily due to leaning effect caused by presence of oxygenates. The CO and HC emissions are reduced significantly while a small increase in NO_x emissions is observed.

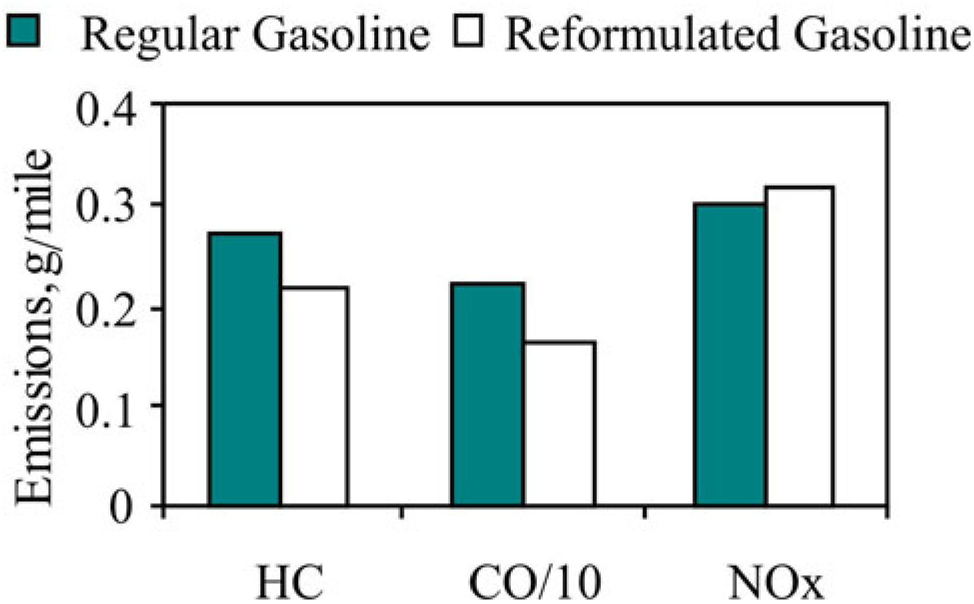

Figure 8.3	Comparison of effects of reformulated gasoline on emissions for catalyst equipped cars with those with regular grade unleaded gasoline

Trends in Gasoline Specifications

As the effect of gasoline properties on engine out emissions and on performance of catalytic converters is quite significant, fuel specifications all over the world have been progressively revised. Engine and vehicle manufacturers in Europe, America and Japan are making efforts to harmonize fuel quality through out the world. They have come out on fuel quality recommendations based on the level of emission control technology and customer satisfaction, which are referred as Worldwide Fuel Charter. As an example of current day gasoline properties, Indian Specifications of Euro IV emission compliant fuel are given in Table 8.9

Table 8.9

Indian Specifications for Euro IV/Bharat Stage IV Emmission Norms Compliant Motor Gasoline

	Characteristics	Limits	
		Gasoline 91 RON	Gasoline 95 RON
1	Density @ 15°C, kg/m3	720-775	720-775
2	Distillation:		
	a) % evaporated at 70°C (E-70), v/v	10-45	10-45

	b) % evaporated at 100°C (E-100), v/v	40-70	40-70
	c) % evaporated at 150°C (E-1500), v/v , min	75	75
	d) Final boiling point, ºC, max	210	210
	e) Residue, percent by volume, max	2	2
3	Research Octane Number (RON), min	91	95
4	Motor Octane Number (MON), min	81	85
5	Existent gum, g/m3, max	40	40
6	Sulphur, total, mg/kg, max	50	50
7	Lead content (as Pb), g/1, max	0.005	0.005
8	Reid vapour pressure (RVP) at 38ºC, kPa,	60 (67)	60 (67)
9	Benzene content, percent by volume, max	1	1
10	Olefin content, percent by volume, *Max*	21	18
11	Oxidation stability, minutes, *Min*	360	360
12	Aromatic content, percent by volume, *Max*	35	35
13	Oxygen content, percent by mass, *Max*	2.7	2.7
14	Oxygenates, percent by volume, *Max*		
	a) Methanol	Nil	Nil
	b) Ethanol	5	5
	c) Iso-Propyl alcohol	10	10
	d) Iso-butyl alcohol	10	10
	e) Tertiary-butyl alcohol	7	7
	f) Ethers containing 5 or more 'C' atoms per molecule	15	15
	g) Other Oxygenates	8	8

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