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DIESEL FUELS

Diesel fuel is a mixture of a few hundred hydrocarbons derived from refining of crude petroleum. When petroleum prices were low, the diesel fuels were produced mostly by blending various refinery streams from the atmospheric distillation unit of petroleum refineries. To meet the increasing demand of the diesel fuels, products of secondary refinery processes like thermal and catalytic cracking, hydro-cracking, vis-breaking etc., also are used as blending components of the current diesel fuels. The diesel fuel streams evaporate generally in the temperature range of 150- 390º C. The key properties of the diesel fuel have already been given in Table 8.1. Besides these, other significant properties include cold flow characteristics at low ambient temperatures, water and sediment content etc. The important diesel fuel quality parameters are discussed below.

Ignition Quality

Ignition quality is a measure of ease of self-ignition of diesel fuel when the fuel is injected in hot compressed air in the engine cylinder. Cetane number (CN) is the most widely accepted measure of ignition quality as it is measured by a test on the engine. The cetane number scale is defined in terms of blends of two pure hydrocarbons used as reference fuels;

- A high ignition quality hydrocarbon: n- Hexadecane or Cetane (n-$C_{16}H_{34}$) given CN =100
- Another hydrocarbon with poor ignition quality: Hepta-methyl nonane (HMN) assigned CN =15.

The cetane number scale is given by:

$$CN = \%\ \text{n-cetane} + 0.15 \times \%\ HMN \qquad \textbf{(8.3)}$$

Cetane number is measured in a standard single cylinder, variable compression ratio CFR engine according to ASTM D613 method. The test engine is a prechamber diesel engine. The test conditions are:

(i) Intake air temperature = 65.6° C,

(ii) Coolant temperature = 100° C,

(iii) Engine speed = 900 rpm,

(iv) Injection advance = 13° btdc.

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Engine compression ratio is varied to obtain start of combustion at top dead centre i.e. ignition delay is maintained equal to 13° CA for the test fuel and two blends of reference fuels that bracket the compression ratio obtained with the test fuel. The reference fuel blends should not be more than 5 CN units apart. The cetane number of the test fuel is determined by interpolation from the compression ratio values and the corresponding cetane numbers of the reference fuel blends.

Correlations of ignition quality with the physical properties of the diesel fuels have also been developed for ease of quality control during refining. These correlations are applicable only to the neat petroleum derived diesel fuels when no additives are used to improve ignition quality. The Calculated Cetane Index (CCI) determined by ASTM D 976 or ASTM D 4737 methods are more commonly used as an alternative to CN for the neat diesel fuels. The calculated cetane index is not a substitute for ASTM cetane number. It is only a supplementary parameter for predicting cetane number when used keeping in view its limitations. The CCI calculation methods are not suitable for pure hydrocarbons, or non-petroleum based fuels derived from coal.
ASTM D 976 uses a two variable equation to determine CCI from the mid-boiling point and density of the diesel fuel as below,

$$CCI976 = 454.74 - 1641.416\ D + 774.74\ D^2 - 0.554\ B + 97.803\ (\log B)^2 \qquad \textbf{(8.5)}$$

where:
D = density at 15°C (g/ml) determined by Test Method ASTM D 1298.
B = 50% evaporation (mid-boiling) temperature (°C) determined by Test Method ASTM D 86 and corrected to standard barometric pressure.

ASTM D 4737 is a newer more exhaustive method in which CCI is correlated to four variables; the density and temperatures for evaporation of 10% (T_{10}), 50% (T_{50}) and 90% (T_{90}). Details are available in the relevant standards and other texts.
CCI values are quite close to the cetane number. Several national fuel standards also specify cetane index values in addition to cetane number.
Cetane or ignition improvers are used to improve ignition quality of the diesel fuels. Nitrates like isopropyl nitrate, cyclo-hexyl nitrates, ethyl-hexyl nitrate (EHN) and peroxides like di-tertiary-butyl peroxide are used as cetane improvers. These compounds readily decompose at the engine compression temperatures and produce free radicals that accelerate precombustion reactions and thereby reduce ignition delay. The cetane improvers are used typically in dosages of around 500 to 2000 ppm by volume.

With high cetane fuels cold starting is easier and engine warm up is faster. Therefore, use of high CN fuels results in lower HC emissions during engine warm-up phase and the reduction in HC is more significant at low ambient temperatures. High cetane number fuels give shorter ignition delay and thus, reduce the amount of fuel burned in premixed phase which results in lower peak combustion pressures and temperatures. Therefore, high CN fuels are expected to give lower NOx emissions. Typical effect of CN on NO_x emissions is shown on Fig. 8.5. Ratio of NO_x emissions obtained for 58 CN fuels relative to that obtained with 50 CN fuel are shown at different engine loads. Depending upon the engine load, up to 6 - 8% lower NO_x may result with increase of CN from 50 to 58. At full engine load however, a slight increase in NO_x with increase in CN was seen.

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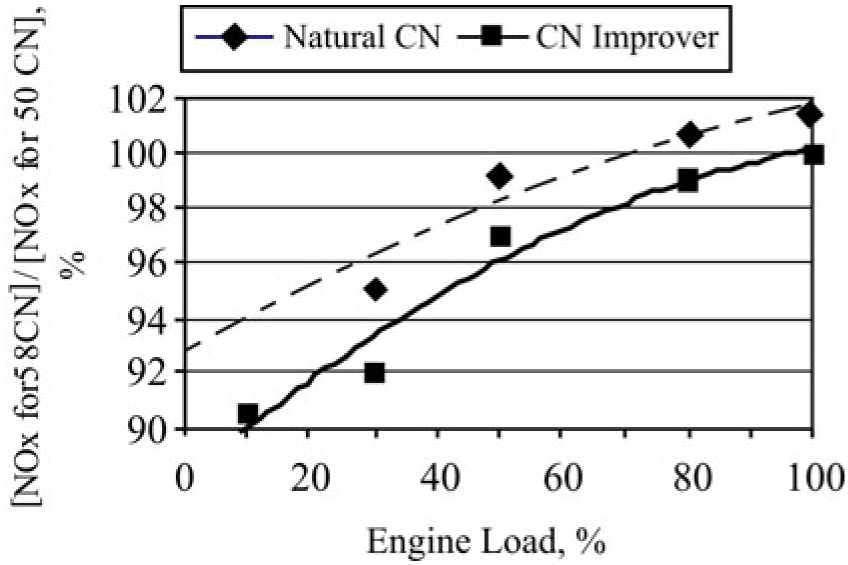

Figure 8.5	Effect of cetane number increase from 50 CN to 58 CN on NO_x emissions; natural and additive improved cetane number fuels have slightly different effects..

Effect of CN on PM emissions depends on the engine design. For high speed, light duty engines a small reduction in PM emissions with high CN has been observed while low speed, heavy duty engines showed no significant change. With high cetane fuels the ignition delay is shorter and more fuel burns in diffusion combustion phase, which may increase soot emissions depending upon the engine operating conditions and design. Current fuel specifications are setting minimum limits of more than 50 units for the CN and minimum cetane index is also being specified as the natural high cetane fuels generally give overall better engine performance with respect to PM and HC emissions.

Distillation Range

A typical distillation curve for diesel fuel is shown in Fig. 8.6. The temperature for 50 percent distillation temperature or mid-boiling point, 90 percent point and the final boiling point are the important distillation parameters.

Lower the boiling point of the fuel, more readily it vaporizes and mixes with air giving more complete combustion. The mid boiling volatility is also correlated to the other physico-chemical properties like, density, viscosity and ignition quality. A higher mid boiling point fuel has higher density and viscosity, and usually a lower CN. Low mid boiling point fuels give faster cold starting and hence lower HC emissions. The fuel components boiling above 350º C may not burn completely, forming high soot concentrations and combustion chamber deposits. Fuels with high T90 and final boiling point are seen to result in an increased injector coking leading to poor combustion and higher smoke emission.

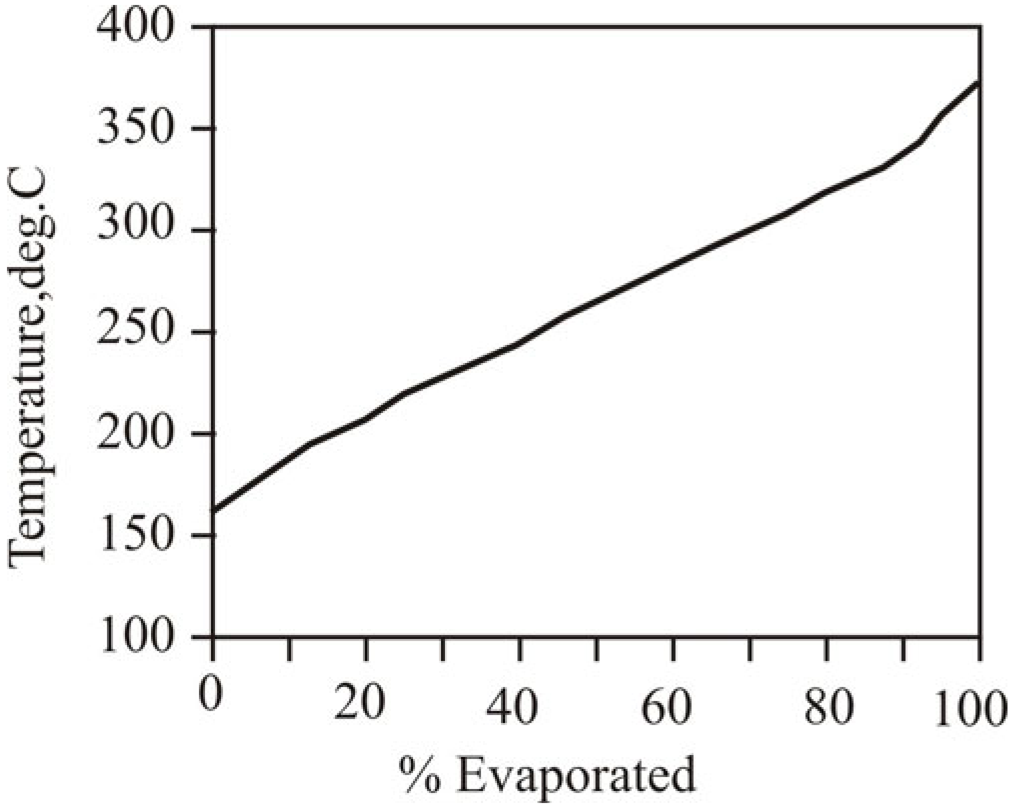

Figure 8.6	Typical distillation characteristics of diesel fuel.

For the modern diesel fuels low maximum permissible limits for T_{90} or T_{95} around 350 to 360º C are being stipulated due to their negative long-term effects on emissions

Density

The density of diesel fuel varies generally in the range 810 to 880 kg/m^3. The density, volatility, cetane number, viscosity and heat of combustion of petroleum fuels are interrelated. An increase of 10 percent in density increases the volumetric energy density (MJ/ m^3) of the fuel approximately by 6 percent. The balance 4 percent is accounted for by the decrease in heat of combustion (MJ/kg) for the 10% heavier (higher molecular weight) fuels is metered volumetrically by injection pumps. The fuel density affects engine calibration and power as the fuel mass injected/stroke varies with fuel density. High-density fuels also have a higher viscosity thus, influence injection characteristics. Increase in the fuel density advances the dynamic injection timing by up to 1 ºCA. Thus, the fuel density affects engine combustion and emissions.

PM emissions generally increase with increase in fuel density. As the fuel injection system is calibrated for a particular fuel density, the current fuel specifications set narrow limits acceptable fuel specific gravity e.g. from 0.82 to 0.85.

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Viscosity

- The viscosity of diesel has a strong influence on fuel atomization, a high viscosity fuel resulting in larger fuel droplets.
- An increase in viscosity reduces spray cone angle and increases spray penetration.
- Low viscosity on the other hand, results in an increase in leakage of fuel past the pumping elements and loss of fuel system calibration.
- High viscosity of fuel is necessary for lubrication and protection of the injection equipment from wear.

Most fuel specifications limit kinematic viscosity of diesel fuel in the range 2.0 to 5.0 centistokes.

Chemical Composition

- Olefins adversely affect oxidation and storage stability of diesel fuels. Poor fuel oxidation stability results in formation of gummy substances which cause plugging of fine fuel filters and sticking of injector needles.
- As the aromatic content of fuel increases, the particulate and PAH emissions increase.
- Fuels with high aromatic content have a lower natural cetane number and its consequent effect on combustion and emissions.
- Aromatics have higher flame temperatures and hence increase in aromatic content of fuel is expected to result in higher NO_x emissions.
- An increase in polycyclic aromatic content generally results in higher PM emissions. .

The diesel fuel specifications in the USA, Europe and several other countries now limit aromatic content to 10 percent maximum. Also, limits on the poly-aromatic hydrocarbons are being specified. One side effect of reduction in aromatic content is reduction in lubricity characteristics of the diesel fuels causing durability problems of injection pump and injectors.

Sulphur Content

- Sulphur on combustion produces sulphur dioxide (SO_2), of which about 1 to 3% is oxidized to sulphur trioxide (SO_3) and forms sulphates found in particulate emissions. The balance of SO_2 is exhausted as gas.
- Typically, increase of 500 ppm in sulphur content contributes to about 0.01 g/kWh increase in diesel PM emissions.
- The sulphur trioxide on combining with water forms sulphuric acid that causes wear of engine cylinder liner and piston rings.
- Sulphur increases deposit formation in the combustion chamber and the deposits become harder in presence of sulphur.
- Fuel sulphur has deleterious effect on functioning of advanced after-treatment devices such as NO_x storage- reduction (NSR) catalysts, continuously regenerating diesel particulate traps (CRT) and catalyzed diesel particulate filters (CDPF). The sulphur dioxide and trioxide poison the catalyst. NSR catalysts require practically sulphur free (< 5 ppm) fuel.
- In CRT, conversion of NO to NO_2 ahead of CRT is reduced by sulphur as it poisons the catalyst. Sulphur lower than 30 ppm is necessary for functioning of CRT

In most countries during early 1990s, sulphur content of diesel fuel was in the range from 0.2 to 0.5%

(2000 to 5000 ppm) by mass. After the year 2000, a number of European countries made available the diesel fuels with less than 0.005% (50 ppm) sulphur. A large number of countries around the world have diesel fuels with sulphur below 0.05% for road vehicle application. Trends in diesel fuel sulphur content in some countries are given in Table 8.10.

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Table 8.10

Trends in Diesel Fuel Sulphur in Some Countries

Country/Region	Effective date/Fuel Grade	Maximum allowable sulphur content, % m/m
European Union	1994 1996 2000	0.2 0.05 0.035
Sweden	1990 1993 EC1 EC2 EC3	0.20 0.001 0.005 As per the EN 590 standards
UK	1996 1998 (Ultra low sulphur grade, ULSD)	0.05 0.005
Japan	1997	0.05
India	1995 2000 2005 2010	0.5 0.2 0.05 0.005

Lubricity

The injection pump and injectors are lubricated by the diesel fuel itself. The heavier, high viscosity hydrocarbons and polar compounds provide natural lubricity to the diesel fuel. Hydro-treating of diesel fuel to remove sulphur also converts and removes polar compounds. Consequently, as the sulphur content of diesel fuel decreases, the lubricity of diesel fuel goes down resulting in excessive injection pump wear. A high frequency reciprocating rig (HFRR) test in which wear scar size on a standard test piece with the test fuel is measured, provides good correlation to the injection pump wear in real life. The HFRR test limit of 460µm wear scar diameter has been accepted in European diesel fuel specifications to provide adequate protection against injection pump wear.

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Summary of Effect of Diesel Fuel Quality on Emissions

Effect of changes in important diesel fuel properties on CO, HC, NO_X and PM emissions has been investigated in several programmes in Europe and the USA and also by other investigators. The overall effects of fuel properties on emissions are qualitatively summarized in Table 8.11.

Table 8.11

Summary of Overall Effects of Diesel Fuel Property Changes on Emissions

Vehicle type	Fuel Property	Property Change	CO	HC	NO_x	PM
Light-duty vehicles	Increase CN	50 → 55	↓↓	↓↓	±0	↓
	Reduce density	850 → 820 kg/m3	↓	↓	0	↓↓↓
	Reduce T95	370 → 330 C	-0	-0	-0	-0
	Reduce PAH	6 → 3 % v/v	?	?	?	?
	Reduce sulphur	2000 →500 ppm	0	0	0	↓
Heavy-duty vehicles	Increase CN	50 → 55	↓	↓	↓	↓
	Reduce density	850 → 820 kg/m3	0	0	↓	↓
	Reduce T95	370 → 330 C	-0	-0	-0	-0
	Reduce PAH	6 → 3 % v/v	?	?	?	?
	Reduce sulphur	2000 →500 ppm	0	0	0	↓↓

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

Diesel Fuel Specifications

Engine technology is being continuously modified and upgraded to meet the newer and more stringent emission regulations. Accordingly, the diesel fuel quality also has undergone significant improvements particularly related to CN, sulphur content, tail end volatility and wear protection of injection system. In some countries, bio-diesel is also being blended with diesel fuel. To keep injection pump calibration at acceptable level with diesel-fuel and biodiesel blends, a maximum oxygen content limit has been specified in the Indian fuel specifications. The key diesel fuel properties in Europe and India are given in Table 8.12.

Table 8.12

Diesel Fuel Specifications in Some Countries

Property	Europe (EN590: 1999)	India (IS 1460) (BS IV - 2010)
Cetane number, min.	51	51
Cetane index, min	46	46
Density @ 15º C, kg/m3	820-845	820-845

Viscosity @40º C, mm2/s	2.0 -4.5	2.0-5.0
Sulphur, %m/m, max.	0.035	BS III: 0.035 BS IV: 0.005
Total aromatics, % m/m, max.		-
Polyaromatics, (di+tri++), max.	11	11
Distillation:		
% recovered at 250º C, max.	65	
T 85, ºC, max.	350	
T90, ºC, max./range		-
T95, ºC, max.	360	360
FBP, ºC /range	-	-
Flash Point, ºC, min.	55	35
Carbon residue, % m/m, max.	0.30	0.30
Water content, mg/kg, max.	200	200
Oxidation stability g/m3, max.	25	25
Particulates, mg/l	24	-
Lubricity(HFRR scar dia. @ 60º C), µm	460	460
Oxygen content, % by mass max.	-	0.6

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