Internal Combustion Engines – MAK 493E

IC-Engine Fuels

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IC Engine Fuels

- Introduction
- Classification of fuels
- Manufacture of engine fuels
- Fuel specifications in general
- Specifications of SI-engine and CI-engine fuels

IC Engine Fuels

In IC engines, the chemical energy contained in the fuel is converted into mechanical power by burning (oxidizing) the fuel inside the combustion chamber of the engine.

As a result of the chemical reactions which occur inside the cylinder, heat is released. The fuel-air mixture (the working fluid before combustion) must stay in the cylinder for a sufficient time so that the chemical reactions can be completed.

Fuels suitable for fast chemical reaction have to be used in IC engines.

Hydrocarbons in liquid form
Alcohols (methanol, ethanol)
LPG (propane and butane)
Natural gas (methane)
Hydrogen

Classification of Engine Fuels

Liquid hydrocarbons $C_n H_m$

Fuels are mainly mixtures of hydrocarbons, with bonds between carbon atoms and between hydrogen and carbon atoms.

During combustion these bonds are broken and new bonds are formed with oxygen atoms, accompanied by the release of chemical energy. Principal products are carbon dioxide and water vapour.

Fuels also contain small amounts of O_2 , N_2 , S , H_2O

Alkanes

Alkanes or Paraffins can in general be represented by $C_n H_{2n+2}$

- all the carbon bonds are single bonds – they are "saturated"
- high number of H atoms, high heat content and low density (620 – 770 kg/m^3)

The carbon atoms can be arranged as, a straight chain or as branched chain compounds.

Straight chain group (normal paraffins)

- shorter the chain, stronger the bond
- not suitable for SI engines – high tendancy for autoignition
- according to the value of "n" in the formula, they are in gaseous (1 to 4), liquid (5 to 15) or solid (>16) state.

Alkanes

Branched chain compounds (isoparaffins)

when four or more C atoms are in a chain molecule it is possible to form isomers – they have the same chemical formula but different structures, which often leads to very different chemical properties.

example : iso-octane $C_8 H_{18}$

2. 2 .4 trimethyl pentane

Naphthenes

Also called cycloparaffins $C_n H_{2n}$

saturated hydrocarbons which are arranged in a circle

have stable structure and low tendancy to autoignite compared to alkanes (normal paraffins)

can be used both in SI-engines and CI-engines

low heat content and high density (740 – 790 kg / m^3)

Alkenes

Also called olefins

mono-olefins $C_n H_{2n}$ or dio-olefins $C_n H_{2n-2}$

have the same C-to-H ratio and the same general formula as naphthenes, their behavior and characteristics are entirely different

they are straight or branch chain compounds with one or more double bond. The position of the double bond is indicated by the number of first C atom to which it is attached, ie,

CH2=CH.CH2.CH2.CH3	called pentene-1
CH3.CH=CH3	called butene-2

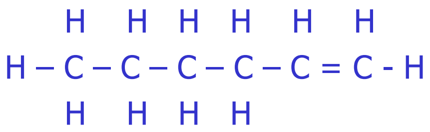
olefinic compounds are easily oxidized, have poor oxidation stability

can be used in SI-engines, obtained by cracking of large molecules

low heat content and density in the range 620 – 820 kg / m^3

Alkenes

Hexen (mono-olefin)



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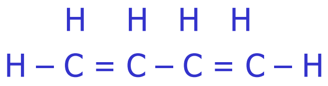
Butadien (dio-olefin)



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ H & - & C & = & C & - & C & = & C & - & H \end{array}$$

Aromatics

Aromatic hydrocarbons are so called because of their "aromatic" odor

$C_n H_{2n-6}$

they are based on a six-membered ring having three conjugated double bonds

aromatic rings can be fused together to give polynuclear aromatics, PAN, also called polycyclic aromatic hydrocarbons, PAH

simplest member is benzene $C_6 H_6$

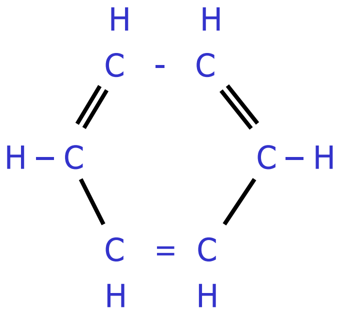
can be used in SI-engines, to increase the resistance to knock

not suitable for CI-engines due to low cetene number

low heat content and high density in the range 800 – 850 kg / m^3

Aromatics

Benzen C_6H_6



Alcohols (monohydric alcohols)

these include methanol (methyl alcohol), ethanol (ethyl alcohol), propanol (propyl alcohol), butanol (butyl alcohol) as compounds

the OH group which replaces one of the H atoms in an alkane, gives these compounds their characteristic properties.

specific heating value is lower than gasoline (42 – 43 MJ/kg)

methanol (19.7 MJ/kg) and ethanol (26.8 MJ/kg)

for air-fuel mixture s.h.v. is comperable with gasoline (MJ/kg-mixture at stoichiometric mixtures)

other alcohol groups such as dihydric and trihydric alcohols are not used as a fuel in IC engines

Alcohols

Methanol $CH_3\,OH$

- can be obtained from natural gas – has near and long-term potential
- has high octane quality (130 RON, 95 MON)
- can be used in low-concentration (5-15 %) in gasoline to increase octane number of the mixture

Problems;

- poor solubility in gasoline, toxicity, low energy content (about half of gasoline), high latent heat of vaporization and oxygen content contribute to poor driveability, incompatibility with some metals

Ethanol $C_2H_5\,OH$

- produced from biomass
- has high octane number – can be used in low–concentrations in gasoline

Gaseous Fuels

- due to storage and transportation problems they are not widely used
- reduce volumetric efficiency and power output of engine (5 – 10 %)
- have low tendancy to knock and low emissions

LPG (liquefied petroleum gas)

- consists of propane and butane
- provides good mixture with air – cleaner combustion
- has excellent cold weather performance
- low sulphur content
- high octane number (propane 111 RON and 100 MON)
- lower density and lower heat content of LPG versus gasoline (23.5 MJ/liter for propane and 32 MJ/liter for gasoline) results a loss in fuel economy – but better combustion efficiency can reduce this loss.

Manufacture of Engine Fuels

crude oil is the liquid part of the naturally occuring organic material composed mostly of HCs that is trapped geologically in underground reservoirs – it is not uniform and varies in density, chemical composition, boiling range etc. for different fields.

Four different crude oils are shown in Table for different boiling ranges :

Table - Main products from crude oil by distillation (%)

Crude type	Arabian light	Nigerian	Brent	Maya
LPG	0.7	0.6	2.1	1.0
Naphtha	17.8	12.9	17.8	11.7
Gas oil/Kerosene	33.1	47.2	35.5	23.1
Residue	48.4	39.3	44.6	64.2

Manufacture of Engine Fuels

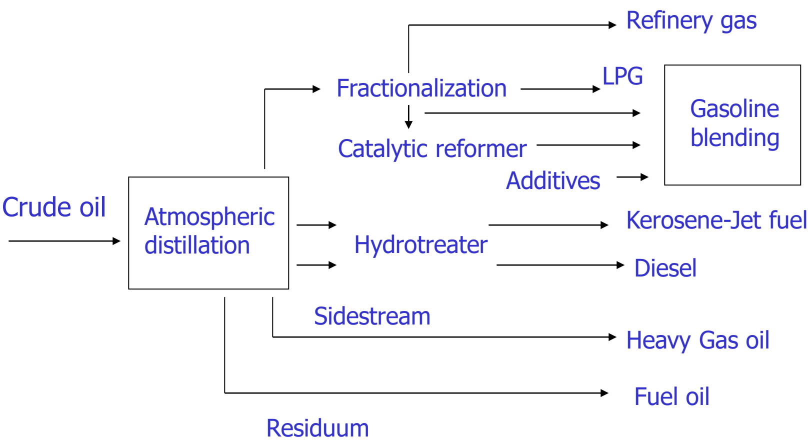
naphtha represents the persentage of HC boiling to gasoline range

gas oil-kerosene represents the persentage boiling to diesel fuel range, including jet fuel and kerosene

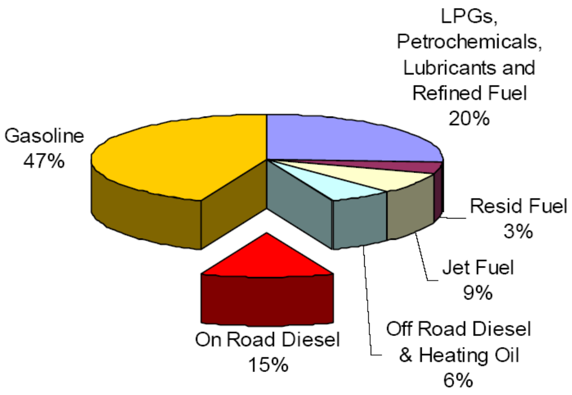
Refineries consist basically of distillation units with processes for upgrading the octane quality of naphtha and for removing sulfur compounds – these are called hydroskimming refineries

Refineries today have conversion processes – convert heavier streams to lighter streams by cracking

Refinery Process



Typical Refinery Production



Distillation

This is the initial process used in all refineries – aims to separate the crude oil into different boiling range fractions, each of which may be a product in its own right, a blend component or feed for further processing step

Crude oil contains many thousands of different HCs, each has its own boiling point – lightest are gases at ambient T but can remain dissolved in heavier liquid HCs unless T is raised, heaviest are solids at ambient T but stay in solution unless T is lowered.

Gasoline distillation temperature is	35 – 200 ^{O}C
Jet fuel	35 - 150
Diesel fuel	175 – 370
Heavy fuels, oil	370 – 550

Generally distillation of crude oil produces 30% gasoline, 20-40 % diesel fuel, 20 % heavy fuels, 10-20 % heavy oils.

Cracking Process

There are two types of cracking process for engine fuel production : thermal cracking and catalytic cracking

Visbreaking and coking are also cracking procedures for fuel oil etc.

Thermal cracking take place through the creation of HC free radicals by C-to-C bond scission

The feed is heated to around 500 - 600 ^{O}C and 70 - 100 bars and passed into a soaking chamber where cracking takes place. The cracked products are fractionated. The product is relatively unstable and requires the use of antioxidants and other treatments to prevent gum formation in use. It has relatively poor MON.

Catalytic Cracking

It is the most important aand widely used process for converting heavy refinery streams to lighter products – to increase the ratio of light to heavy products from crude oil.

Compared to thermal cracking, it has higher yiels, improved quality product for gasoline (not for diesel fuel) and superior economics.

A fluidized bed of catalyst is used – feed is intoduced into it. Catlyst flows from one vessel to another through a pipe (between reactor and regenerator). Cracked oil vapour pass to fractionating towers where smaller molecules are separated from heavier products (gas, catalytic naphthas, cycle oils and residue).

Aluminium silicate known as zeolite is used as a catalyst – has high activity and suppress the formation of light olefins.

Hydrocracking and steam cracking mechanisms are also used.

Other mechanisms

Alkylation is a process for producing a high-octane gasoline component (alkylate) by combining light olefins with isobutane in the presence of a strongly acidic catalyst (sulfuric or hydrofluoric acid).

Isomerization is a process for converting straight chain paraffins to branch chain – used to provide isobutane feed for the alkylation process or to convert relatively low-octane quality of straight paraffins to more valuable branch chain molecules.

eg. n-pentane with RON 62 can be converted to isopentane with RON 92

Process involves contacting HCs with a catalyst (platinum on a zeolite base) and separating any unchanged straight paraffins for recycle through the unit. The product is clean burning and has better RON quality.

Other mechanisms

Polymerization is a process where light olefins such as propene and butenes are reacted together to give heavier olefins whicch have good octane quality and low vapour pressure in gasoline.

Most commonly used catalyst is phosphoric acid on keiselguhr.

The product is almost 100 % olefinic and has relatively poor MON compared with RON.

eg.

$CH3CH2CH=CH2 + CH3CH=CH2 \rightarrow CH3(CH2)4CH=CH2$

butene propene heptene

Fuel Specifications

Relative density (specific gravity)

Fuel composition

Specific heating value

Flash point

Viscosity

Surface tension

Freezing point

Relative Density

Relative density (specific gravity) is related to the measurement of the ratio of the weight of a given volume of fuel to the weight of the same volume of water, both at 20 ^{O}C and 101.325 kPa

American Petrolium Institute, also defines degrees API as,

$$\text{Specific Gravity} = \frac{141.5}{131.5 + API}$$

For gasoline, the relative density is around 0.72 to 0.78 - which is equivalent to an API range of 65 to 50

$$\rho = 700 - 800 \ [\mathrm{kg/m^3}]$$

for unleaded gasoline this value is higher due to the aromatics

For diesel fuel, $\rho = 830 - 950 \ [\mathrm{kg/m^3}]$

Fuel Composition

C and H : carbon content of aromatics is around 89 %, and of paraffins and naphthenes is around 86 %

benzene - max allowable concentration is specified because it is highly toxic material, the level is 5 % (v)

sulphur content – HC fuels contain free sulphur, hydrogen sulphide and other sulphur compounds which are objectionable

it is a corrosive element that can corrode fuel lines, carburettor and injection pump. It will unite with oxygen to form sulphur dioxide, which in presence of water at low T, forms sulphurous acid.

It has low ignition T, promote knock in SI engines.

limited to approx 50 ppm

Fuel Composition

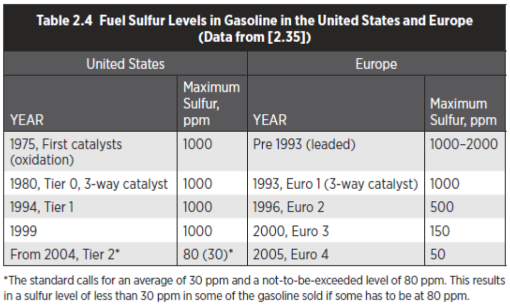


Table 2.4 Fuel Sulfur Levels in Gasoline in the United States and Europe (Data from [2.35])

United States		Europe	
YEAR	Maximum Sulfur, ppm	YEAR	Maximum Sulfur, ppm
1975, First catalysts (oxidation)	1000	Pre 1993 (leaded)	1000–2000
1980, Tier 0, 3-way catalyst	1000	1993, Euro 1 (3-way catalyst)	1000
1994, Tier 1	1000	1996, Euro 2	500
1999	1000	2000, Euro 3	150
From 2004, Tier 2*	80 (30)*	2005, Euro 4	50

*The standard calls for an average of 30 ppm and a not-to-be-exceeded level of 80 ppm. This results in a sulfur level of less than 30 ppm in some of the gasoline sold if some has to be at 80 ppm.

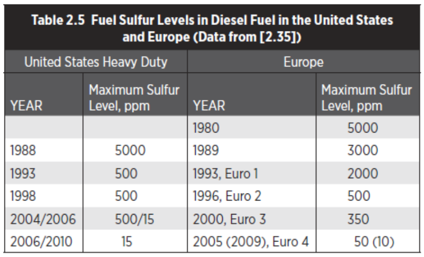


Table 2.5 Fuel Sulfur Levels in Diesel Fuel in the United States and Europe (Data from [2.35])

United States Heavy Duty		Europe	
YEAR	Maximum Sulfur Level, ppm	YEAR	Maximum Sulfur Level, ppm
		1980	5000
1988	5000	1989	3000
1993	500	1993, Euro 1	2000
1998	500	1996, Euro 2	500
2004/2006	500/15	2000, Euro 3	350
2006/2010	15	2005 (2009), Euro 4	50 (10)

Fuel Composition

Gum deposits – gasoline with unsaturated HCs forms gum in the engine, paraffin, naphthene and aromatic HCs also form some gum – it causes operating difficulties, sticking valves and piston rings, deposits in the manifold etc.

Water - both dissolved and free water can be present in gasoline, free water is undesirable because it can freeze and cause problems. Dissolved water is usually unavoidable during manufacture.

Lead - for leaded and unleaded gasoline max lead content is specified, lead causes pollution and destroys catalytic converters in the exhaust system.

Manganese - used for antiknock in gasoline (MMT), max amount is specified, 0.00025 to 0.03 gMn/L

Fuel Composition

Oxygenates - oxygenated compounds such as alcohols are used in gasoline to improve octane rating.

In USA gasohol (10% ethanol contains 3.5% oxygen), TBA and methanol up to 3.5% oxygenmethanol up to 5% volume, MTBE up to 15% are used.

In EC monoalcohols and ethers with atm boiling points lower than the final atm boiling point of gasoline in the standards can be used. Higher concentrations require modifications on the vehicles - carburator or fuel inj system must be modified to compensate for the oxygen content of the fuel.

Blends with 15% methanol can be used.

Specific Heating Value

Specific heating value, H_u is a measure of the energy content of the fuel per unit mass (kJ/kg or kcal/kg)

gaseous fuels sp heating value is given in terms of energy content per unit volume (kJ/liter or kJ/m^3 , kcal/m^3)

in IC engines lower heating value is given as the combustion products contain water in vapour form.

For gasoline and diesel fuel

$$H_u = 42000 - 44000 \ \text{[kJ/kg]}$$

$$H_u = 10200 - 10500 \ \text{[kcal/kg]}$$

heating value of the combustible air-fuel mixture is a decisive factor for engine performance.

Flash Point

Flash point is the lowest temperature of a sample at which the fuel vapour starts to ignite when in contact with a flame (ignition source).

Marcusson method – fuel container is slowly heated, while the fuel vapour is in contact with an open flame – T is measured

For gasoline it is 25 ^{O}C, diesel fuel 35 ^{O}C and heavy diesel 65 ^{O}C

Viscosity

Viscosity is an important parameter for CI engines, also influences fuel metering orifices since Re is an inverse function of fuel viscosity

lower the viscosity, smaller the diameter of the droplets in the spray.

Below certain limits, low viscosity increases the leaks in the fuel system. It is a strong function of T – must be given at certain T values

at 50 ^{O}C, 1.5 – 5.0 Engler

0.5 to 0.6 centistokes

Freezing Point

Freezing point

the precipitation of paraffin crystals in winter can lead to clogged filters. It can be prevented by either removing paraffins from the fuel or adding flow improvers (additives).

Antifreezing properties are determined by its filterability.

For gasoline freezing point is –65 ^{O}C and for diesel fuel –10 ^{O}C

Surface Tension

Surface tension is a parameter which effects the formation of fuel droplets in sprays

increasing the surface tension will reduce mass flow and air-fuel ratio in gasoline engines

lower the value, smaller the droplet diameter

diesel fuel	0.023 – 0.032 N/m
gasoline	0.019 – 0.023 N/m

Fuel Specifications for Gasoline

Volatility

Antiknock quality

Gasoline Volatility

Benzene, C_6H_6 for example has vapor pressure of 0.022 MPa at 38 °C

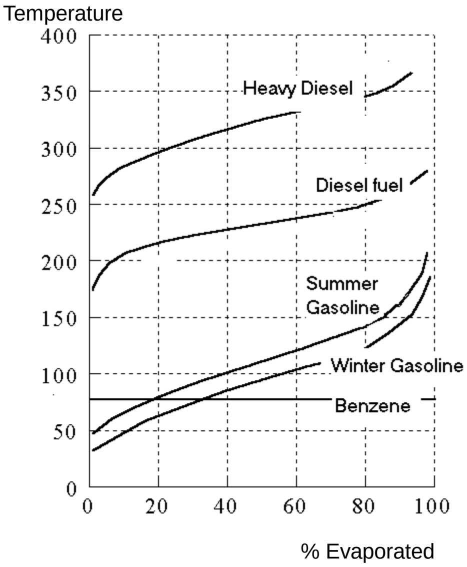
in a closed container of 38 °C, benzene evaporates until the partial p has a value of 0.022 MPa, If T is raised to 80.5 °C, then saturation p will be 0.1 MPa and will be constant during the boiling

For gasoline it is not possible to indicate a single value of evaporation T or vapor pressure.

Gasoline contains large number of compounds - up to about 400

It has a smooth distillation curve - with good fractionation efficiency

Gasoline Distillation Curve



Low fractionation efficiency effects engine performance at different operating conditions :

if distillation curve is displaced downward, gasoline becomes more volatile - poor hot start, vapor lock, high evaporative losses

Gasoline Distillation Curve

Gasoline having boiling point up to 70 ^{O}C controls ease of starting and hot weather problems such as vapor lock

Mid-range controls the driving in cold weathers, particularly at warm up period of engine. It also influences the ice forming in carburetor.

Back end of the curve contains all the heavier, high boiling point compounds and these have high heat content - they are important in improving fuel economy for fully warmed up engine.

Some of the heavier compounds may pass into the crankcase and dilute the crankcase oil. They are not readily combusted as the lighter compounds - cause combustion chamber deposits.

Gasoline Distillation Curve

%10 evaporation point should be at low T for start up at cold temperatures - at hot weathers this may cause problems - vapor lock.

50% evaporation should be slightly above 100 ^{O}C at summer and slightly below 100 ^{O}C at winter. For warmed up engine conditions this point is not important.

90% evaporation must not be high - produces fuel film on intake manifold walls and dilutes lubricating oil. Back end of the curve must not exceed 215 ^{O}C.

Gasoline volatility should be arranged according to weather conditions - particularly ambient T. Altitute has some minor effect due to pressure changes.

It is also effected by the characteristics of the vehicle itself (drivability, fuel system design etc).

Cold Starting

For SI engines to start, A/F ratio must be within the ignitable range, ie in general must be between 7:1 to 20:1 by weight.

When the engine is cold, it is difficult to ignite lean mixtures, because fuel may not vaporize sufficiently - under these conditions the mixture is richened to bring it to ignitable range.

This is done by inc the injection time or by the use of a choke with carburetted engines.

Measurement of Gasoline Volatility

Tests usually define Reid Vapor Pressure - ASTM Distillation test and Vapor/Liquid ratio.

Reid vapor pressure - obtained at air-to-liquid ratio of 4:1 and temperature 37.8 ^{O}C.

Fuel is filled into a metal chamber which is connected to an air chamber and that is connected to a pressure gauge. The apparatus is immersed in water bath at 37.8 ^{O}C and is shaken until constant p is obtained - Reid VP

For gasoline allowable RVP is 0.7 bar in summer and 0.9 bar in winter (at 37.8 ^{O}C)

ASTM Distillation procedure - distillation rate is controlled by the heat input - distillation curve is plotted (temperature vs % evaporated).

Antiknock Quality of Gasoline

Knock occurs when the unburnt gases ahead of flame front (the end gases) spontaneously ignite causing a sudden rise in pressure accompanied by a characteristic pinging sound - this results in a loss of power and can lead to damage the engine.

Combustion chamber shape, spark plug location, ignition timing, end gas temperatures, in cylinder gas motion, air-fuel ratio of the mixture, fuel specifications etc effects the occurance of knock.

Compression ratio of the engine also strongly effects knock. The higher the CR, the better the thermal efficiency - but the greater the tendancy for knock to occur.

Critical compression ratio - when knock starts

So higher fuel octane quality is required.

Antiknock Quality of Gasoline

Autoignition of the end gases causes a rapid inc of p, producing p waves which resonate in the combustion chamber at a frequency of between 5000 - 8000 Hz, depending on the geometry of the chamber

Knock results in an inc of T in the cylinder and causes a severe damage to engine components like cylinder head gasket, piston, spark plugs etc.

Measurement of Gasoline Antiknock Quality

Prior to 1929, fuels were rated using an engine in which CR could be varied between 2.7:1 to 8:1 - each fuel was run in this engine at various A/F ratios and ignition timing to obtain conditions for max power output.

Fuels were assigned values in terms of Highest Useful Compression Ratio, HUCR

in 1929 Octane scale was proposed by Graham Edgar. In this scale two paraffinic HCs have been selected as standards (PRF, primary reference fuels)- iso-octane (2-2-4 trimethyl pentane) with very high resistance to knock (arbitrary assigned a value of 100) and n-heptane with extremely low knock resistance (assigned a value of 0).

Octane number of the fuel is the volume percentage of iso-octane in a blend with n-heptane (PRF), that shows the same antiknock performance as test fuel tested in standard engine and standard conditions.

Octane Number

Test engine for determining Octane values, was developed by Cooperative Fuel Research Committee (CFR). It is a single cylinder, variable CR engine.

Two different test conditions specifies the Research Octane Number (RON) and the Motor Octane Number (MON)

RON correlates with low speed, mild driving conditions, MON relates to high speed, high severity conditions. Most gasolines have higher RON than MON. This difference is called fuel sensitivity (=RON-MON) - for fuels of same RON, high sensitivity gasoline has lower MON.

Antiknock Index = (RON + MON) / 2

For PRF, Octane Number changes linearly (for paraffinic fuels)

Test Conditions for RON and MON

Test	Research	Motor
ASTM method	D2699	D2700
Engine rpm	600	900
Intake air temp, ^{O}C	depends on p (~ 51.7 ^{O}C)	38
Mixture temp, ^{O}C	not specified	149
Humidity, kg/kg dry air	0.0036 - 0.0072	
Coolant temp, ^{O}C	100	100
Ignition advance, ^{O}CA	13 BTDC	varies with CR (14 - 26 BTDC)
A/F ratio	adjusted for max knock	

Test Conditions for RON and MON

Test engines -

CFR : D = 3.25”, H = 4.50”, CR = 4 - 12

BASF : D = 65 mm, H = 100 mm, CR = 4 - 12

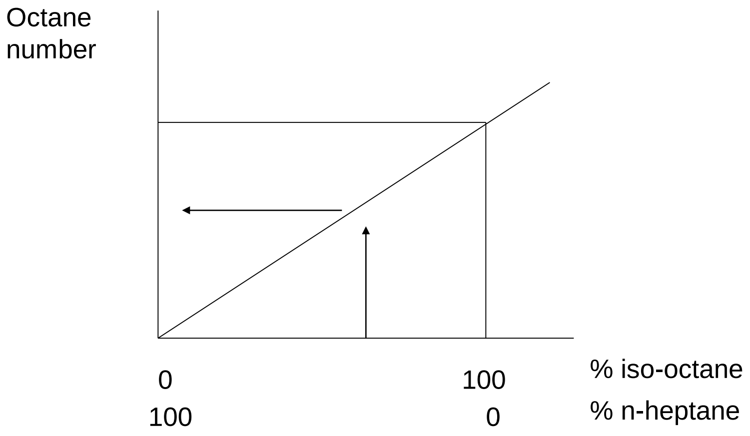
Critical compression ratio -

autoignition occuring at CRs for different fuel Octane numbers

CR	6	7	8	9	10	11	12
ON	78	85	91	96	100	103	106

CFR Test Engine with Variable Compression Ratio

Octane Number Measurement



for fuels with ON greater than 100, the sample is mixed with certain amount of n-heptane - a linear correction is done according to the percentage of n-hepthane added.

Octane Number Measurement

For non paraffinic fuels, ON relation is not linear

TEL is added to the PRF to increase the ON above 100

or n-heptane is added to the sample to reduce ON below 100, then nonlinear extrapolation is applied

Increasing Octane Number

Modern gasoline contains some chemical additives designed to improve fuel quality. These are used to raise ON, control surface ignition, reduce spark plug fouling, resist gum formation, prevent rust, reduce carburetor icing, remove carb or inj system deposits, minimize deposits in intake system, prevent valve sticking.

ON can be increased by antiknock agents - at less expense than modifying HC composition by refinery process.

Most effective agents are lead alkyls -

- TEL - tetraethyl lead, $(C_2H_5)_4$ Pb
- TML - tetramethyl lead,
- MMT

addition of about 0.8 g lead per liter, provides a gain of about 10 ON in gasoline

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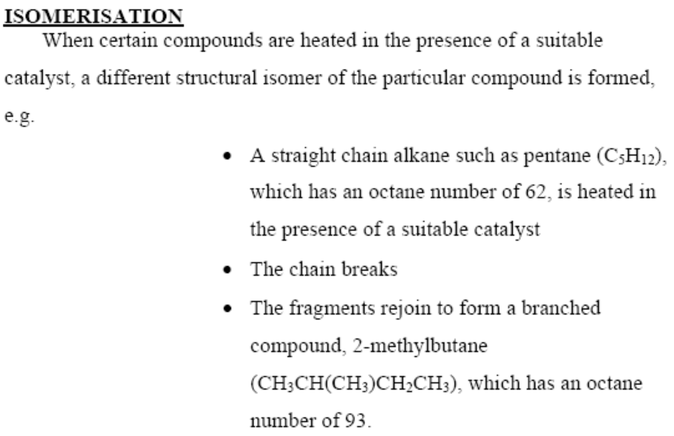
Increasing Octane Number

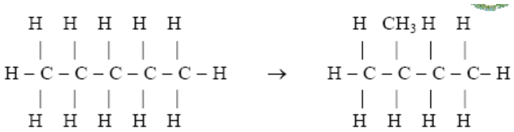


ISOMERISATION

When certain compounds are heated in the presence of a suitable catalyst, a different structural isomer of the particular compound is formed, e.g.

- A straight chain alkane such as pentane (C_5H_{12}), which has an octane number of 62, is heated in the presence of a suitable catalyst
- The chain breaks
- The fragments rejoin to form a branched compound, 2-methylbutane ($CH_3CH(CH_3)CH_2CH_3$), which has an octane number of 93.

Increasing Octane Number



pentane 2-methylbutane

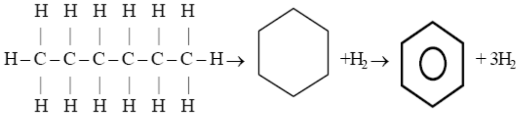
Clearly the product would be a much more suitable component of petrol than the original pentane.

Increasing Octane Number

DEHYDROCYCLISATION

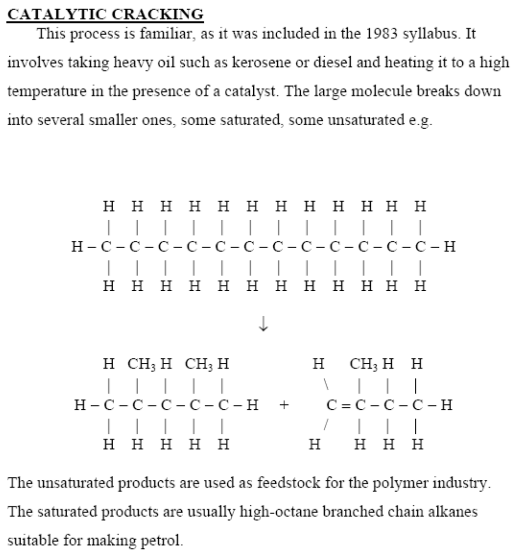
This process involves the formation of a ring compound, accompanied by the removal of a valuable by-product, hydrogen gas, e.g.

- A straight chain alkane such as hexane (C_6H_{14}), which has an octane number of 25, is heated in the presence of a suitable catalyst
- The catalyst causes the alkane to change to a cycloalkane e.g. cyclohexane, of octane number 83
  $C_6H_{14} \rightarrow (CH_2)_6 + H_2$
- The catalyst causes the cycloalkane to further change to an aromatic compound, e.g. benzene, of octane number greater than 100
  $(CH_2)_6 \rightarrow C_6H_6 + 3H_2$



hexane cyclohexane benzene

Increasing Octane Number



CATALYTIC CRACKING

This process is familiar, as it was included in the 1983 syllabus. It involves taking heavy oil such as kerosene or diesel and heating it to a high temperature in the presence of a catalyst. The large molecule breaks down into several smaller ones, some saturated, some unsaturated e.g.

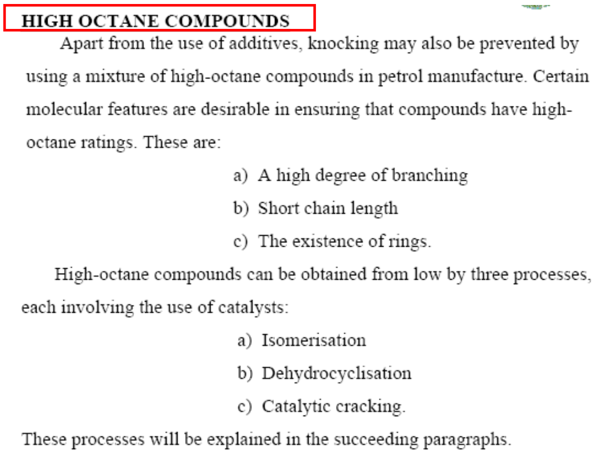
$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

$$\downarrow$$

$$H-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \quad + \quad {}^{H}_{H}\!\rangle C=\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

The unsaturated products are used as feedstock for the polymer industry. The saturated products are usually high-octane branched chain alkanes suitable for making petrol.

Increasing Octane Number



HIGH OCTANE COMPOUNDS

Apart from the use of additives, knocking may also be prevented by using a mixture of high-octane compounds in petrol manufacture. Certain molecular features are desirable in ensuring that compounds have high-octane ratings. These are:

a) A high degree of branching
b) Short chain length
c) The existence of rings.

High-octane compounds can be obtained from low by three processes, each involving the use of catalysts:

a) Isomerisation
b) Dehydrocyclisation
c) Catalytic cracking.

These processes will be explained in the succeeding paragraphs.

Octane Number

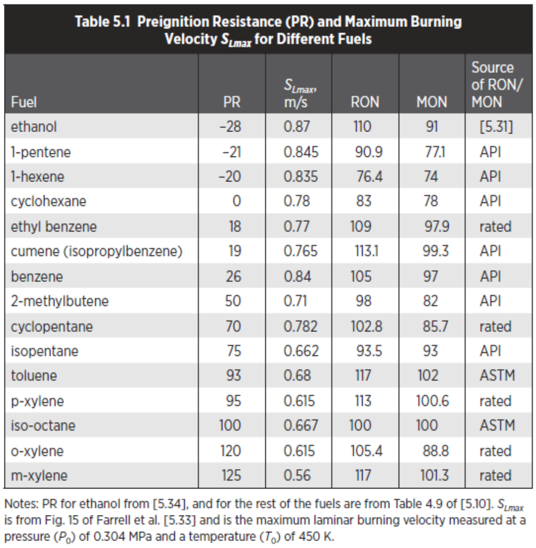


Table 5.1 Preignition Resistance (PR) and Maximum Burning Velocity S_{Lmax} for Different Fuels

Fuel	PR	S_{Lmax}, m/s	RON	MON	Source of RON/MON
ethanol	−28	0.87	110	91	[5.31]
1-pentene	−21	0.845	90.9	77.1	API
1-hexene	−20	0.835	76.4	74	API
cyclohexane	0	0.78	83	78	API
ethyl benzene	18	0.77	109	97.9	rated
cumene (isopropylbenzene)	19	0.765	113.1	99.3	API
benzene	26	0.84	105	97	API
2-methylbutene	50	0.71	98	82	API
cyclopentane	70	0.782	102.8	85.7	rated
isopentane	75	0.662	93.5	93	API
toluene	93	0.68	117	102	ASTM
p-xylene	95	0.615	113	100.6	rated
iso-octane	100	0.667	100	100	ASTM
o-xylene	120	0.615	105.4	88.8	rated
m-xylene	125	0.56	117	101.3	rated

Notes: PR for ethanol from [5.34], and for the rest of the fuels are from Table 4.9 of [5.10]. S_{Lmax} is from Fig. 15 of Farrell et al. [5.33] and is the maximum laminar burning velocity measured at a pressure (P_0) of 0.304 MPa and a temperature (T_0) of 450 K.

Diesel Fuel Specifications

Viscosity

Surface tension

Cetane number

Diesel Fuel Viscosity

Viscosity of a fluid indicates its resistance to flow - higher the viscosity, the greater the resistance to flow.

It may be expressed as absolute viscosity (Poise, P) or kinematic viscosity (stoke, St).

It varies inversely with temperature, usually given at 20 - 40 ^{O}C

Fuel atomization depends on viscosity
2 - 8 mm2/s (cSt) at 20 ^{O}C

Cetane Number

Cetane number is used to specify the **ignition quality of diesel fuel** Running on low cetane number will produce cold start problems. Peak cylinder p, combustion noise and HC emissions will increase - more fuel will be injected before ignition, less time for combustion.

Higher CN results in a sooner ignition - extremely high CN may ignite before adequate F-A mixing can take place - higher emissions. Power output can be reduced if burning starts too early.

Cetane Number Measurement

Cetane number is measured by comparing the "ignition delay time" of the sample fuel with a mixture of **cetane (C16H34)** and **alphamethyl naptane (C10H7 CH3).** The cetane percentage in the mixture gives the CN of the sample fuel.

CN of the reference fuel cetane is arbitraryly set at 100, and of alphamethyl naptane at 0.

CFR engine is used to measure the compression ratio at which ignition starts. CR is gradually increased while the engine id driven by an electric motor - a curve of CN vs critical CR is obtained.

Inlet air temp is 30 ^{O}C and cooling water temp is at 100 ^{O}C

Cetane Number Measurement

An easier and practical method to obtain Cetane Number is by calculating the Diesel Index.

Increasing the DI, increases the tendancy to ignite.

$$DI = \frac{\text{annilin point } [^{O}F] \text{ x API} [\text{at } 60\ ^{O}F]}{100}$$

AP is obtained by heating equal amounts of annilin and diesel fuel. While cooling down, the temp at which the annilin separates from the mixture is the AP

Cetane Number values

Cetane number is in the range of,

50 - 60	for high speed Diesel engines
25 - 45	for low speed Diesel engines

Normal Diesel fuel CN is 40 - 55

DI of 50 gives a CN of around 50

Fig. 3.1b. Deposits at a diesel injector tip. (Copyright by Afton Chemical Ltd. Reproduced with permission.)

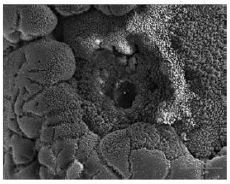
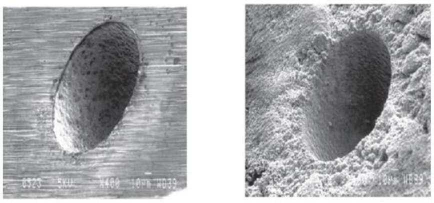


Fig. 3.1c. Micrograph of diesel injector deposits near the nozzle hole. (Copyright by Afton Chemical Ltd. Reproduced with permission.)

Cetane Number values

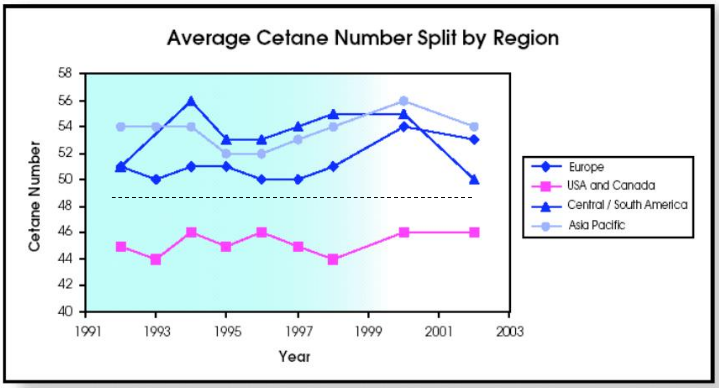


NEW INJECTOR FOULED INJECTOR

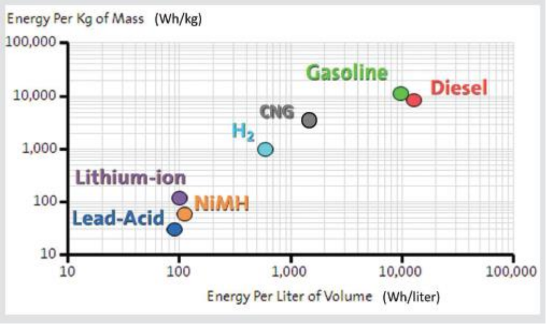
Fig. 3.3. Electron micrographs of the combustion chamber end of the nozzle hole of a diesel injector—with and without deposits: new injector, fouled injector. (Copyright by Shell Global Solutions. Reproduced with permission.)

Fig. 3.4. Effects of injector deposits on the spray pattern of a diesel injector spray. The clean injector is on the left. The injector with deposits on the right shows very uneven spray pattern. (Copyright by Shell Global Solutions. Reproduced with permission.)

Cetane Number values



Conventional Fuels



Conventional Fuels

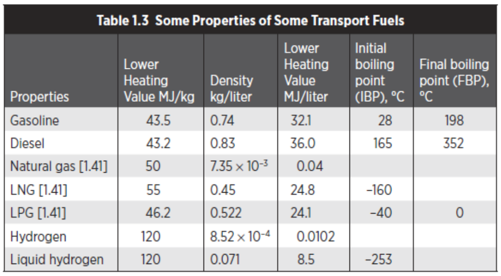


Table 1.3 Some Properties of Some Transport Fuels

Properties	Lower Heating Value MJ/kg	Density kg/liter	Lower Heating Value MJ/liter	Initial boiling point (IBP), °C	Final boiling point (FBP), °C
Gasoline	43.5	0.74	32.1	28	198
Diesel	43.2	0.83	36.0	165	352
Natural gas [1.41]	50	7.35×10^{-3}	0.04		
LNG [1.41]	55	0.45	24.8	−160	
LPG [1.41]	46.2	0.522	24.1	−40	0
Hydrogen	120	8.52×10^{-4}	0.0102		
Liquid hydrogen	120	0.071	8.5	−253	

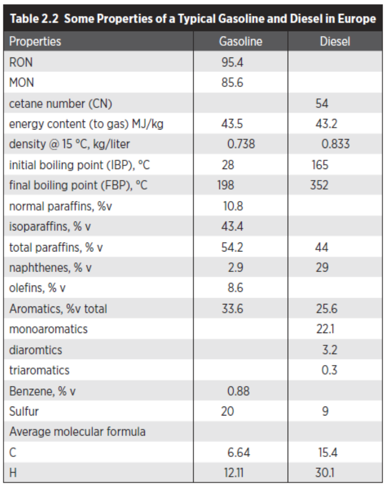


Table 2.2 Some Properties of a Typical Gasoline and Diesel in Europe

Properties	Gasoline	Diesel
RON	95.4	
MON	85.6	
cetane number (CN)		54
energy content (to gas) MJ/kg	43.5	43.2
density @ 15 °C, kg/liter	0.738	0.833
initial boiling point (IBP), °C	28	165
final boiling point (FBP), °C	198	352
normal paraffins, %v	10.8	
isoparaffins, % v	43.4	
total paraffins, % v	54.2	44
naphthenes, % v	2.9	29
olefins, % v	8.6	
Aromatics, %v total	33.6	25.6
monoaromatics		22.1
diaromtics		3.2
triaromatics		0.3
Benzene, % v	0.88	
Sulfur	20	9
Average molecular formula		
C	6.64	15.4
H	12.11	30.1

Conventional Fuels

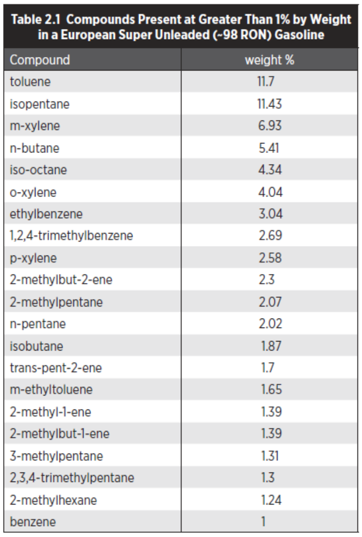


Table 2.1 Compounds Present at Greater Than 1% by Weight in a European Super Unleaded (~98 RON) Gasoline

Compound	weight %
toluene	11.7
isopentane	11.43
m-xylene	6.93
n-butane	5.41
iso-octane	4.34
o-xylene	4.04
ethylbenzene	3.04
1,2,4-trimethylbenzene	2.69
p-xylene	2.58
2-methylbut-2-ene	2.3
2-methylpentane	2.07
n-pentane	2.02
isobutane	1.87
trans-pent-2-ene	1.7
m-ethyltoluene	1.65
2-methyl-1-ene	1.39
2-methylbut-1-ene	1.39
3-methylpentane	1.31
2,3,4-trimethylpentane	1.3
2-methylhexane	1.24
benzene	1

Conventional Fuels

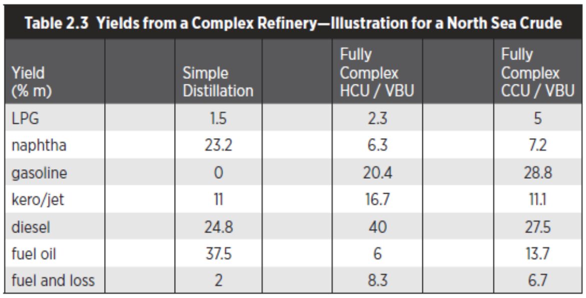


Table 2.3 Yields from a Complex Refinery—Illustration for a North Sea Crude

Yield (% m)		Simple Distillation		Fully Complex HCU / VBU		Fully Complex CCU / VBU
LPG		1.5		2.3		5
naphtha		23.2		6.3		7.2
gasoline		0		20.4		28.8
kero/jet		11		16.7		11.1
diesel		24.8		40		27.5
fuel oil		37.5		6		13.7
fuel and loss		2		8.3		6.7

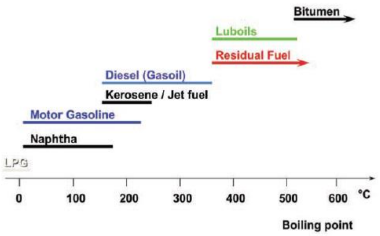
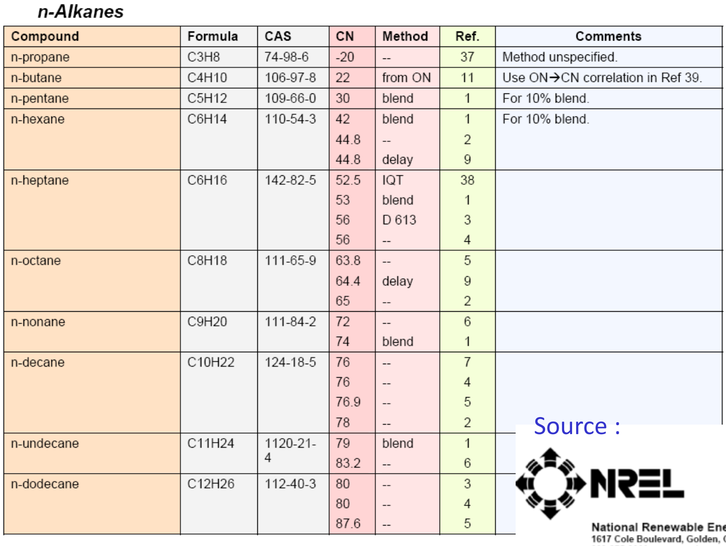


Fig. 2.3. Boiling ranges of different refinery components.

Cetane Number values



n-Alkanes

Compound	Formula	CAS	CN	Method	Ref.	Comments
n-propane	C3H8	74-98-6	-20	--	37	Method unspecified.
n-butane	C4H10	106-97-8	22	from ON	11	Use ON→CN correlation in Ref 39.
n-pentane	C5H12	109-66-0	30	blend	1	For 10% blend.
n-hexane	C6H14	110-54-3	42	blend	1	For 10% blend.
			44.8	--	2	
			44.8	delay	9	
n-heptane	C6H16	142-82-5	52.5	IQT	38	
			53	blend	1	
			56	D 613	3	
			56	--	4	
n-octane	C8H18	111-65-9	63.8	--	5	
			64.4	delay	9	
			65	--	2	
n-nonane	C9H20	111-84-2	72	--	6	
			74	blend	1	
n-decane	C10H22	124-18-5	76	--	7	
			76	--	4	
			76.9	--	5	
			78	--	2	
n-undecane	C11H24	1120-21-4	79	blend	1	
			83.2	--	6	
n-dodecane	C12H26	112-40-3	80	--	3	
			80	--	4	
			87.6	--	5	

Source :

NREL
National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
303-275-3000 • www.nrel.gov

Cetane Number values

iso-Alkanes

Compound	Formula	CAS	CN	Method	Ref.	Comments
2,2-dimethylbutane	C6H14	75-83-2	24.4	IQT	38	
2-methylpentane	C6H14	107-83-5	23 33 34	blend -- from ON	1 4 40	Use ON→CN correlation in Ref 39.
3-methylpentane	C6H14	96-14-0	30 30	blend --	3 4	
2,3-dimethylpentane	C7H16	565-59-3	21	IQT	38	
2,4-dimethylpentane	C7H16	108-08-7	29	--	1	
2,2,4-trimethylpentane	C8H18	540-84-1	12 12 14 17.5 17.5	blend -- -- -- delay	3 4 6 9 9	
2,2,5-trimethylhexane	C9H20	3522-94-9	24 24	-- --	1 8	
2,2-dimethyloctane	C10H22	15869-87-1	59	--	7	
3-ethyldecane	C12H26		46 48	-- --	3 10	Value is cetene number x 0.875.

Cetane Number values

Olefins

Compound	Formula	CAS	CN	Method	Ref.	Comments
1-hexene	C6H12	592-41-6	27 27.3	blend delay	1 9	
1-heptyne	C7H12	628-71-7	22	IQT	38	
1-heptene	C7H14	592-76-7	32	IQT	38	
cis-2-heptene	C7H14	14686-13-6	44	blend	1	Cis isomer surmised from boiling point and density data.
vinyl cyclohexane	C8H14	695-12-5	38	--	8	Use ON→CN correlation in Ref 39.
1-octene	C8H16	111-66-0	40.5 41	-- --	5 2	
2,4,4-trimethyl-1-pentene	C8H16	107-39-1	10 11	-- blend	4 1	
2-octene	C8H16	7642-04-8	43	blend	1	
1-nonene	C9H18	124-11-8	50.7 51	-- --	6 2	
2,6-dimethylheptene	C9H18		51	blend	1	
1,9-decadiene	C10H18	1647-16-1	39.8	IQT	38	
1-decene	C10H20	872-05-9	50.2 59 60.2	-- -- --	5 6 2	
1-undecene	C11H22	821-95-4	65 65.5	-- --	6 2	
1-dodecene	C12H24	112-14-4	71 71.3	-- --	2 5	

Cetane Number values

Aromatics

Compound	Formula	CAS	CN	Method	Ref.	Comments
benzene	C6H6	71-43-2	-10 0 14.3 23	-- blend delay blend	3 3 9 1	
toluene	C7H8	108-88-3	-5 9 18.3	blend from ON blend	3 11 1	Use ON→CN correlation in Ref 39. Value is extrapolation of 20, 10, and 5% blends to 0%.
ethyl benzene	C8H10	100-41-4	8	blend	1	
1,2-dimethylbenzene	C8H10	95-47-6	8.3	delay	9	
1,3-dimethylbenzene	C8H10	108-38-3	1	blend	1	
1,4-dimethylbenzene	C8H10	106-42-3	-13	blend	1	
isopropyl benzene	C9H12	98-98-8	15	blend	1	
1,3-diethylbenzene	C10H14	141-93-5	9	blend	1	
sec-butylbenzene	C10H14	135-98-8	6	blend	1	
tert-butyl benzene	C10H14	98-06-8	-1	blend	1	
1,2,3,4-tetramethylbenzene	C10H14	488-23-3	17	blend	1	
1-methyl-4-isopropylbenzene	C10H14	99-87-8	2	blend	1	
n-pentylbenzene	C11H16	538-68-1	8 9 18	-- -- blend	7 3 3	Value is cetene number x 0.875.
biphenyl	C12H10	92-52-4	21 21	-- --	3 7	Value is cetene number x 0.875.

Cetane Number values

Alcohols

Compound	Formula	CAS	CN	Method	Source	Comments
methanol	CH4O	67-56-1	2 3 3 5	-- -- -- --	37 13 14 15	
ethanol	C2H6O	64-17-5	2 8 11 12	-- -- -- delay	16 13 36 17	
1-propanol	C3H8O	71-23-8	12	--	36	
1-butanol	C4H10O	71-36-3	17	--	36	
1-pentanol	C5H12O	71-41-0	18.2 20	-- --	18 36	
1-hexanol	C6H14O	111-27-3	23.3	--	18	
1-heptanol	C7H16O	111-70-6	28 29.5	IQT --	38 18	
1-octanol	C8H18O	111-87-5	39.1	--	18	
2-ethyl-1-hexanol	C8H18O	104-76-7	23.4	IQT	38	
3-octanol	C8H18O	589-98-0	25.1	IQT	38	
1-nonanol	C9H20O	143-08-8	46.2	--	18	
1-decanol	C10H22O	112-30-1	50.3	--	18	
1-undecanol	C11H24O	112-42-5	53.2	--	18	
1-dodecanol	C12H26O	112-53-8	63.6	--	18	