Chapter 4
Liquid Fuels

4.1 Introduction

Liquid fuels are a major energy factor which determines the course of transportation, and the automobile is one of the most important consumers of such fuel. These liquid fuels include diesel oil, gasoline, liquid propane, alcohol (both methyl and ethyl), as well as the less common liquids such as ammonia and hydrazine. Though the boiling point of propane ($-42°C$) and ammonia ($-33°C$) are below ambient temperature (in most places), these substances are still classed as liquids because they can be stored as liquids at room temperature (25°C) at the modest pressure of about 10 atm.

Whale oil was used for lighting and heating long before the extensive use of petroleum oil. Similarly, vegetable oils (or biomass liquids and saps) are also potential fuels (see Chap. 1), but their modest production at present precludes their wide spread use. Perhaps when the energy farm has developed, it will be possible to consider biomass fuels as an alternative to fossil-based fuels.

Of the various liquid fuels, diesel oil requires the minimum of preparation from petroleum crude oil and therefore is usually the cheapest of the fuels.

4.2 Diesel Engine

The diesel engine was described in a patent in 1892 by Dr. Rudolf Diesel who originally designed it to operate using coal dust as the fuel. However, the characteristics of such fuel were not very reproducible, and it was quickly replaced by oil.

In the diesel engine, air is pulled into the cylinder and compressed to approx. 35 atm. This compression is effectively adiabatic and causes the temperature of the air to increase to about 550°C. At the end of the compression stroke, when the piston is at the top of the cylinder [top dead center (TDC)], an oil spray is injected into the hot air where it ignites on vaporization. The heat of combustion raises the temperature of the gas mixture which now expands at constant pressure as the piston moves down, increasing the volume of the gases. The heat generated and the larger volume of product gases thus further increase the volume as the pressure drops.

An ideal PV diagram for a diesel engine is shown in Fig. 4.1 where the four strokes are:

1. Compression $1 \rightarrow 2$
2. Expansion/combustion $2 \rightarrow 3 \rightarrow 4$
3. Exhaust $4 \rightarrow 1 \rightarrow 5$
4. Air intake $5 \rightarrow 1$

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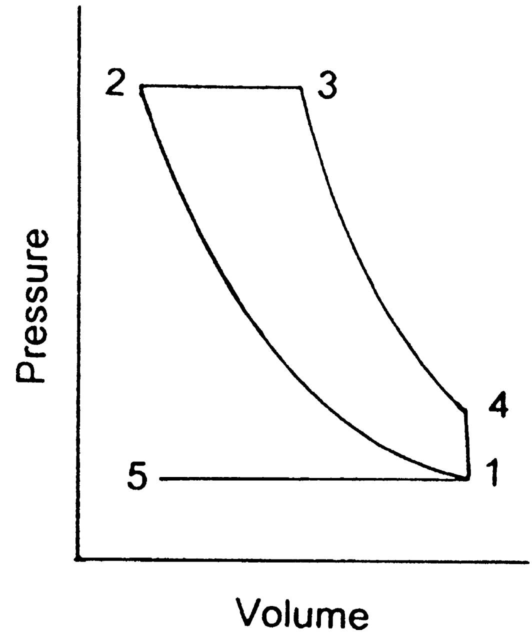


Fig. 4.1 Ideal PV diagram of a four-stroke diesel engine. (1) Compression 1 → 2. (2) Expansion/combustion 2 → 3 → 4. (3) Exhaust 4 → 1 → 5. (4) Air intake 5 → 1

In the compression stage, air is compressed to about 1/20 of its initial volume, i.e., the engine has a compression ratio (CR) of at least 20, and this high ratio accounts for the high efficiency of the engine.

Diesel engines are classified into indirect and direct injection engines. The former have a precombustion chamber where the fuel is initially injected and where combustion starts after an induction delay. The fuel-rich flame then expands into the main chamber. Such engines are common in high-speed diesel passenger cars.

Direct injection engines are normally used in larger engines with lower speed and with cylinder bores greater than 12 cm in diameter. They are more efficient and easier to start than indirect injection engines of comparable size.

Diesel engines are also classified according to their speed (rpm). Low-speed engines run at 100–500 rpm and are usually large stationary installations or marine engines. Medium-speed engines operate from 500 to 1,200 rpm and are usually installed in power generators, power shovels, tractors, and locomotives. The diesel-electric locomotive runs at about 20–28% efficiency, compared to the coal-fired steam engine which was only 5–8% efficient, or the electric powered engine which is about 23% efficient. The high-speed diesel engines run at 1,200–2,000 rpm and are found in the automobile, light trucks and buses, and aircraft. The type of fuel used in a diesel engine is determined, to a great extent, by the speed of the engine.

4.3 Diesel Fuel

The diesel fuel injected into the hot compressed air ignites only after a short delay. This ignition delay depends on the composition of the fuel. It is longer for aromatic hydrocarbons and cycloparaffins than for olefinic and paraffinic fuels. Thus, the best grade of diesel fuel consists of long straight chain hydrocarbons which can spontaneously ignite in the hot compressed air. The absence of an induction period is important since it results in a loss of efficiency. Long ignition delay times result in rapid combustion and sharp pressure rise, causing the engine to run roughly. The grade of diesel fuel is determined by an empirical scale and is based on the ignition characteristics of the fuel, which is compared with a blend of hexadecane (cetane) rated as 100 and 1-methylnaphthalene

Table 4.1 Comparison of components in diesel fuel and performance characteristics

	Conventional diesel fuel (Wt. %)	Cracked gas oil (Wt. %)	Synthetic diesel fuel (Wt. %)	Ignition quality	Cold flow character	ΔH comb by volume	Density	Smoking tendency
n-Paraffins	39	19	17	Good	Poor	Low	Low	Low
iso-Paraffins				Low	Good	Low	Low	Low
Naphthenes	34	16	37	Moderate	Good	Moderate	Moderate	Moderate
Olefins				Low	Good	Low	Low	Moderate
Alkyl benzenes	18	34	36	Poor	Moderate	High	High	High
2-Ring aromatics	8	28	8	Poor	Moderate	High	High	High
3-Ring aromatics	1	3	2	Poor	Moderate	High	High	High

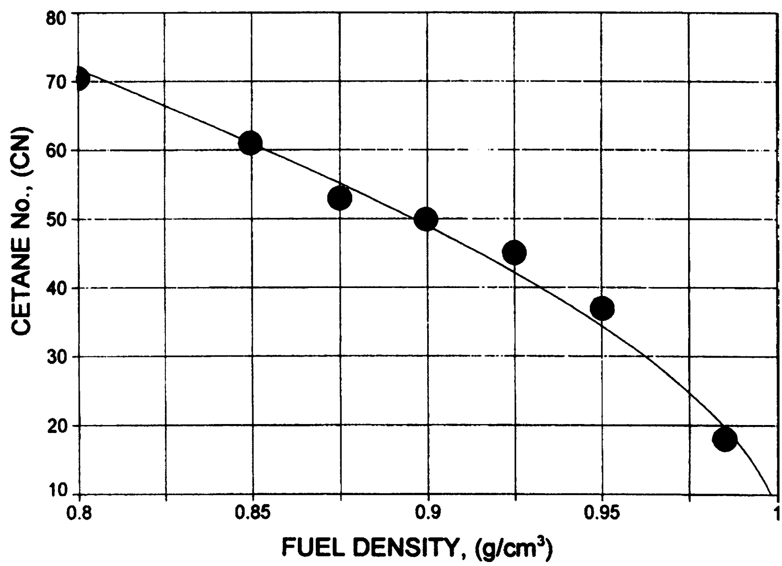


Fig. 4.2 General relationship between cetane number (CN) and density of the fuel

(α-methylnaphthalene) which is rated at 0. The recent use of 2,2,4,4,6,8,8-heptamethylnonane (HMN), CN = 15, has been introduced as a low cetane standard because it can be obtained easily in high purity. Low-grade fuels have a cetane number (CN) equal to about 20 which is suitable for low-speed engines, whereas a high-grade fuel will have CN = 70. High-speed engines require a fuel with CN = 50 or more. Table 4.1 shows some of the performance characteristics of diesel fuel.

A crude indication of the CN of a fuel can be obtained from its density. A plot of CN against density for various grades of fuel is shown in Fig. 4.2. In general, the CN is reduced by the presence of aromatics in the fuel.

Corrosion inhibitors and gum reducers are other additives designed to improve the quality of a fuel. In cold weather, it is customary to add ethanol to the fuel (not more than 1.24 mL/L) to prevent ice from clogging fuel lines.

The addition of barium compounds to diesel fuel has been shown to reduce the emission of black smoke. However, its use is limited, and proper engine maintenance can do much to reduce smoke in the exhaust.

Table 4.2 North American specification for diesel fuel (average of US and Canadian)

				ASTM		
	Type AA	Type A	Type B	1-D	2-D	4-D
Flash point °C min.	40	40	40	38	52	54
Cloud point °C max.	−48	−34	–	–	–	–
Pour point °C max.	−51	−39	–	–	–	–
Kinematic viscosity 40 °C cSt	min. 1.2 to	1.3	1.4	1.3	1.9	5.8
	max.–	4.1	4.1	2.4	4.1	26.4
Distillation						
90 % recovered °C max.	290	315	360	288	282″ min. to 338 max.	
Water and sediment, % vol. max.	0.05	0.05	0.05	0.05	0.05	0.5
Total acid number, max.	0.10	0.10	0.10	–	–	–
Sulfur, % mass max.	0.2	0.5	0.7	0.5″	0.5°	2
Corrosion, 3 h @ 100°C max.	No. 1	No. 1	No. 1	No. 3	No. 3	–
Carbon residue (Ramsbottom)	0.15	0.15	0.20	0.15	0.35	–
On 10 %″ bottoms, % mass max.						
Ash, % wt., max.	0.01	0.01	0.01	0.01	0.01	0.1
Ignition quality, CN, min.	40	40	40	40°	40″	30

Additives can be incorporated to improve the quality of diesel fuel. For example, ethyl nitrite, ethyl nitrate, and isoamyl nitrite when added to an oil will increase its CN value. The addition of 2.5% by volume of amyl nitrite to a diesel oil (CN = 26) increased the CN to 44. Additives such as amyl nitrate ($C_5H_{11}ONO_2$) when added at about 0.1% by volume will increase the CN by 4, and 0.25% will add 7 to the CN of the fuel. Other nitrates such as heptyl and octyl nitrates are also ignition improvers. A similar effect is obtained when ammonium nitrate is added to oil. A 2% by weight addition of a solution of 5 M NH_4NO_3 in water can increase the CN of a diesel fuel from 39 to 42. Other additives will prevent gum formation, decrease surface tension permitting a finer spray, or reduce the change in fuel properties due to changes in temperature.

Diesel fuel is a complex mixture of hydrocarbons which includes paraffins, naphthenes, and aromatics, and at low temperatures, phase separation can occur causing engine failure. The temperature, Tps, at which phase separation occurs is called the *cloud point* and is determined under standard conditions of cooling, e.g., 1°C/min. Long chain polymer additives at as low as 0.1% can lower the cloud point, Tps, by several degrees.

The recommended cloud point of a fuel is 6°C above the pour point, which is the temperature at which the fuel ceases to flow readily. A fuel is normally blended so as to make the pour point at least 6°C below normal driving temperatures. The ASTM (D-975-78) specification of diesel fuel oils is given in Table 4.2.

Vegetable oils are composed primarily of glycol esters of fatty acids with the general formula where R′, R″, and R are the same or different alkane or alkene radicals with carbon chains from 16 to about 20. The triglycerides are too viscous and of too high a molecular mass and too low a vapor pressure to be a useful diesel fuel. However, it is possible to convert the triglycerides to monomethyl esters by a transesterification process which can be represented by the equation

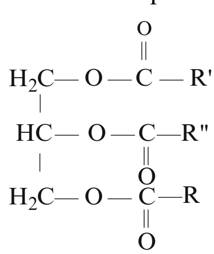
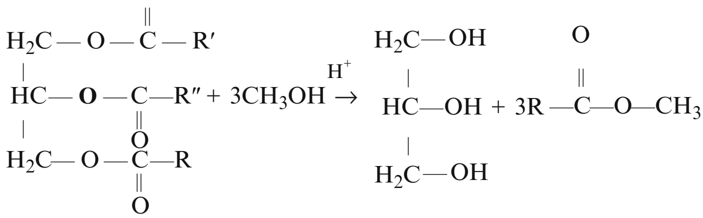


Table 4.3 Experimental CNs for selected transesterified vegetable oils (methyl esters)

Oil	CN
Babassu	63
Palm	62
Peanut	54
Soybean	45
Sunflower	49

The methyl esters are usually straight chain hydrocarbons and have relatively high cetane values shown in Table 4.3. The ethyl esters are between 2 and 5 units higher than the corresponding methyl esters. Such diesel fuel, though effective, is still too expensive and not competitive with petroleum-based fuels.



(4.1)

4.4 Ignition Temperature, Flash Point, Fire Point, and Smoke Point

Four important tests which are used to characterize an engine fuel are the spontaneous ignition temperature (SIT), flash point, fire point, and smoke point. These tests are standardized, and specialized fuels have specific requirements as defined by these tests. The SIT is dependent on the composition of the fuel and the conditions of the walls of the cylinder. Diesel fuels require low SIT with short delay times of the order of 1–2 ms. The SIT of heptane ($CN = 60$) is 330°C, whereas benzene with $CN = -10$ has a SIT of 420°C.

The flash point of a fuel is obtained by slowly increasing the temperature (5.6°C/min) of the liquid fuel in a standard container (flash cup) until sufficient vapor is given off to produce a flash as a flame is passed over the mouth of the cup every 30 s. The temperature of the oil at which this occurs is the flash point. This is an index of the volatility of the oil or liquid. It is used as an indication of the fire hazard of combustible liquids. For example, the Canadian specification for heating fuel oil stipulates a minimum flash point of 43°C, whereas the flash point of diesel fuel varies from 38°C to 52°C. The flash point and boiling point of various substances are compared in Table 4.4.

The fire point is the temperature to which the oil must be heated so that the vapor pressure is sufficient to maintain the flame after the flame source is removed.

The smoke point of a fuel is an arbitrary scale related to the height of a flame of the fuel burning in a standard lamp without smoking. Some values are given in Table 4.4 and show that aromatic hydrocarbons have low smoke point values, whereas saturated normal alkanes have the highest smoke points. Additives such as ferrocene [$Fe(C_5H_5)_2$] increase the smoke point. Fuels that have low smoke points tend to deposit carbon during the combustion process.

Water emulsified in diesel fuel can reduce smoke in the exhaust and carbon deposits in the engine. It was shown that, while 5% or less water increased the fuel consumption, more water showed an increase in the thermal efficiency, the maximum increase being 9.7% when the fuel contained 22.5% water.

Table 4.4 Boiling point (BP), flash point (FP), spontaneous ignition temperature (SIT), and smoke point (SP) of selected substances

Substance	BP (°C)	FP (°C)	SIT (°C)	SP (mm)
Acetone	56.5	−18		
Benzene	80	−11	560	8
n-Pentane	36	−49	308	150
n-Hexane	69	−23	247	149
n-Heptane	98	−4	447	147
Isopentane	28	−51	420	−135
Neopentane	9.5	–	440	−140
1-Pentane	30	−28	298	84
Toluene	110	4	536	6
p-Xylene	138	27	464	5
PCB	380 + 10	222	–	–
Kerosene	260 ± 10	54	–	27
Diesel 2-D	–	52	–	–
10-W-30	–	226	–	–

"In air." Specifications provide for modification of these requirements appropriate for individual situations

The internal combustion engine is a notorious polluter, but the diesel engine has the additional emission of particulate matter (10–25 μg/m^3) which is rich in polynuclear aromatic hydrocarbons such as phenanthrene, fluoranthene, benzo(a)pyrene, and benzoperylene—all of which are carcinogenic.

4.5 The Spark Ignition Internal Combustion Engine

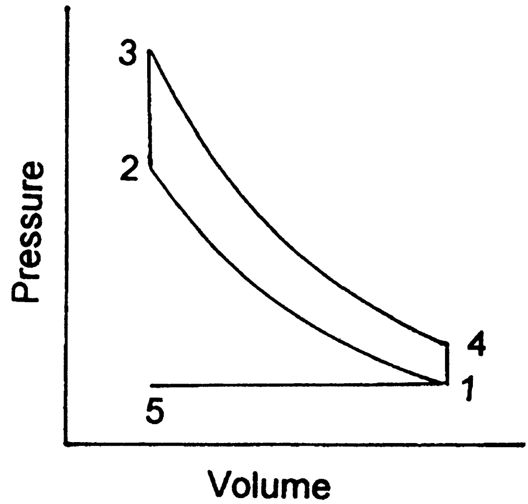
The four-stroke cycle spark ignition (SI) internal combustion engine (ICE) was initially proposed by Beau de Rockas in 1862 and first built by N. A. Otto in 1876. This engine has become the major piston engine in use today. The PV cycle of the engine is shown in Fig. 4.3 where the four strokes are indicated.

1a Compression of the air/fuel mixture 1 → 2
1b Spark ignitions, constant volume combustion 2 → 3
2a Expansion of product gases 3 → 4
2b Exhaust at constant volume 4 → 1
3 Exhaust of cylinder 1 → 5
4 Induction stroke air/fuel intake 5 → 1

The efficiency of the engine is a maximum of about 25% at a CR of about 15. Fuel injection, as in the diesel engine, means better control of the air/fuel ratio under variable temperature conditions.

The use of fuel injection with the two-stroke SI engine has added a new dimension to small and efficient engines. The major advantages over the four-stroke engine are lower cost and low weight/power ratio. These engines have been primarily used in motorcycles, outboard motors, lawn mowers, chain saws, and similar lightweight engines. Similarly the rotary two-stroke Wankel engine has reached the production stage in the Mazda car, but further extension of its use has not materialized. Two-cycle diesel engines have also been produced.

Fig. 4.3 Ideal PV diagram of the four-stroke spark ignition ICE. (**1a**) Compression 1 → 2. (**1b**) Spark ignition, constant volume combustion 2 → 3. (**2a**) Expansion of product gases 3 → 4. (**2b**) Exhaust at constant value 4 → 1. (**3**) Exhaust of cylinder 1 → 5. (**4**) Induction stroke air/fuel intake 5 → 1



4.6 Gasoline Fuel

The fuel for the SI–ICE was in the early years centered on alcohol. In 1895, Nikolaus Otto recommended that alcohol be used in his engine. One of Henry Ford's first models, the quadricycle, was meant to run on alcohol. His later model "T" was designed to run on either alcohol or gasoline requiring only a simple adjustment of the carburetor. Efforts in 1906 to extend the use of alcohol in the USA as a fuel for the automobile by rescinding the 40 cent/gal liquor tax failed. A 50/50 mixture of alcohol gasoline was used in France after World War I due to the oil shortage. The Great Depression of the 1930s made farm-produced alcohol a cheap fuel which was available in 2000 midwestern service stations.

However, the cheaper oil eventually predominated, and gasoline has become the common fuel for the automobile. The quest for greater power and efficiency has resulted in an increase in the CR from about 5 in 1928 to over 13 in 1995. This has resulted in the need to reformulate the fuel to meet the stringent demands of the newer engines.

The problem in the pre-1920 years was the tendency of the engine to "knock"—a violent explosion in the cylinder which, at times, cracked the cylinder head and pistons. This knock was shown to occur after ignition by the spark, and it was believed that the delayed vaporization of the fuel droplets caused the post-ignition explosion. Thomas Midgley Jr., a mechanical engineer working for Dayton Engineering Laboratory Co. (Delco), decided to add a colored component to the fuel and selected iodine. This had a beneficial effect and eliminated the engine knock. When several red dyes were tested, they showed no improvement, whereas ethyl iodide reduced the knock, proving that the iodine was the effective element. However, iodine and its compounds were too expensive and corroded the engine, and so a search was on for a simple alternative. By 1919, the research team found that 2 mL/L of aniline was better than 1 g of iodine. On December 9, 1921, after testing about 33,000 compounds, they found that 0.025% tetraethyl lead was a superior antiknock substance when compared to the 1.3% aniline which was the comparison standard. Thus, a smooth running fuel became a reality.

One difficulty caused by the added lead was the buildup of the yellow lead oxide (PbO) in the engine which coated the spark plugs and valves. This problem was solved by adding ethylene dibromide to the fuel, which converted the lead to the more volatile lead bromide ($PbBr_2$). The first sale of "ethyl" gas was on February 1, 1923. A list of antiknock additives is shown in Table 4.5. The present interpretation of knock has recently been reached by photographing the combustion process through a glass-top cylinder and observing the smooth propagation of the flame front from the spark to the farthest part of the combustion chamber. The gas to be burned last is called the end gas and is

Table 4.5 Relative effectiveness of antiknock compounds and some antiknock fuels (based on aniline = 1)

Benzene	0.085
Isooctane (2,2,4-trimethylpentane)	0.085
Triphenylamine	0.090
Ethyl alcohol	0.101
Xylene	0.142
Dimethyl aniline	0.21
Diethylamine	0.495
Aniline	1.00
Ethyl iodide	1.09
Toluidine	1.22
Cadmium dimethyl	1.24
m-Xylidine	1.40
Triphenylarsine	1.60
Titanium tetrachloride	3.2
Tin tetraethyl	4.0
Stannic chloride	4.1
Diethyl selenide	6.9
Bismuth triethyl	23.8
Diethyl telluride	26.6
Nickel carbonyl	35
Iron carbonyl	50
Lead tetraethyl	118

usually located in the combustion chamber furthest from the spark plug. This end gas is heated by compression, by the combustion taking place, and by the approaching flame front. The spontaneous ignition of this end gas results in an explosion and knock unless the normal flame reacts and consumes the end gas before it ignites. This is shown in Fig. 4.4.

Thus, antiknock additives are inhibitors of autoignition. The lead oxide aerosol which forms in the combustion is a free radical trap and prevents the chain reaction from branching and progressing to explosive rates.

4.7 Grading Gasoline

As the automobile engine developed, it became necessary to grade the gasoline on a realistic scale. This was established by determining the behavior of various organic substances as a fuel in a standard engine and observing the onset of knock as the CR is increased. The effect of structure on the critical CR was discovered for the various isomers of heptane.

The best isomer—trimethylbutane (called *triptane*)—proved to be too difficult to make in the large quantities required for testing, though it is superior to isooctane. The octane was selected as the rating of 100 on the octane scale. The compound *n*-heptane was selected as the 0 rating.

Other octane enhancers such as methyl tertiary butyl ether (MTBE) can act in a different manner by suppressing cool-flame reactions by consuming OH free radicals. MTBE is sufficiently soluble in water to contaminate the aquifer when MTBE/fuels have been spilled. As a result, efforts are under way to ban MTBE as a fuel additive. Ethanol is considered to replace it.

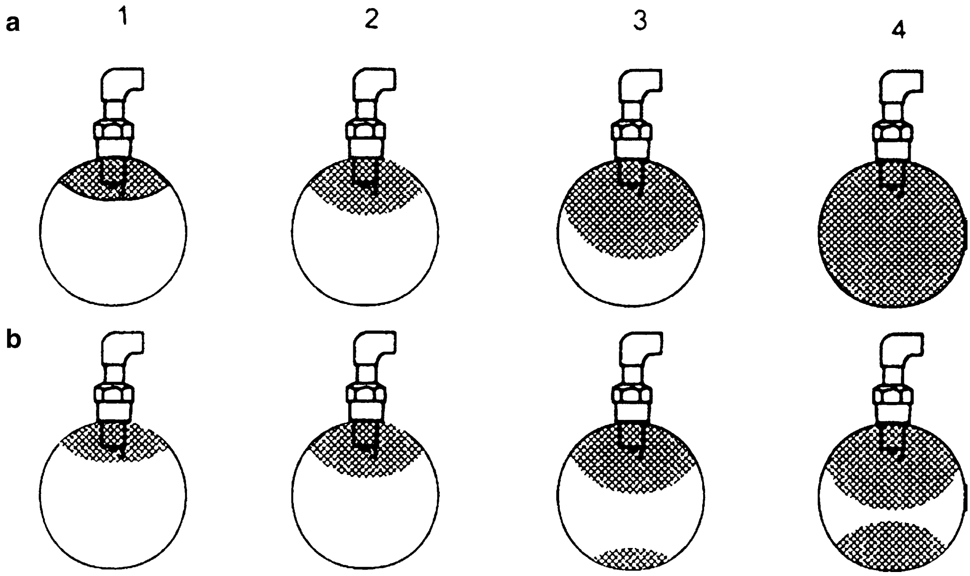


Fig. 4.4 Flame propagation from a spark in a SI–ICE. (Time increases from left to right.) (**a**) Normal process—the flame moves uniformly from the spark to the end gas. (**b**) Knock condition where the end gas ignites at B3 before the flame reaches the end gas

Table 4.6 Mercury and lead concentrations in the glacial samples[a]

Time of deposition	Mercury content[b]	Lead content[b]
800 BC	62	1
1724	75	10
1815	75	30
1881	30	–
1892	66	–
1946	53	–
1952	153	200
1960	89	–
1964 (fall)	87	–
1964 (winter)	125	–
1965 (winter)	94	–
1964 (spring)	230 ± 18	
1965 (summer)	98	–

[a]The sample deposited in 1724 was recovered from Antarctica, the others from Greenland
[b]Nanogram (Hg/Pb) content (per kilogram of water)

A good illustration of the global contamination by lead is a comparison of the lead and mercury content of the Greenland ice field at various depths. This is shown in Table 4.6 where the level of Hg in the ice has not changed significantly in 3000 years, whereas the level of Pb has increased 200-fold, showing the direct effect of the automobile. This implies that the contamination by mercury is of regional interest and not of global importance.

Because of the poisonous properties of lead and its compounds, some countries have replaced lead by other octane enhancers. One such additive is methylcyclopentadiene manganese (III) tricarbonyl (MMT).[1] This substance is probably as toxic as the lead compounds, but since much smaller quantities are used (1/20 of lead), it is argued that it is safer than lead. Actually, manganese will be contaminating the environment just as lead has done if its use is continued. Aromatic hydrocarbons such as benzene and toluene also act as octane enhancers even though they are known carcinogens.

The addition of water to gasoline is reported to improve the quality of the fuel. The water is sucked up into the carburetor and vaporized as it passes around the hot exhaust manifold and enters the intake manifold. As with diesel fuel, the mechanism by which the water acts is not fully understood.

The mechanism of oxidation of hydrocarbon (which can be represented by RH and $RCH_2CH_2CH_3$) involves the formation of peroxides (ROO) and hydroperoxides (ROOH) by the following series of reactions:

1. Initiation by spark

$$RCH_2 - CH_2 - CH_3 \rightarrow RCH_2 - CH_2 \rightarrow RCH_2 - CH_2 + CH_3$$
$$O_2 \rightarrow 2O$$

2. Chain branching

$$RCH_2 - CH_2 - CH_3 + O \rightarrow RCH_2 - CH - CH_3 + OH$$

3. Peroxide formation

$$RCH_2 - CH_2 + O_2 \rightarrow RCH_2CH_2O_2$$
$$RCH_2CH - CH_3 + O_2 \rightarrow RCH_2\underset{\substack{|\\O_2}}{CH}CH_3$$
$$CH_3 + O_2 \rightarrow CH_3O_2$$

4. Hydroperoxide formation

$$RCH_2 - CH_2O_2^{\cdot} + RH \rightarrow RCH_2CH_2O_2H + R^{\cdot}$$
$$RCH_2 - \underset{\substack{|\\O-O^{\cdot}}}{CH} - CH_3 + RH \rightarrow RCH_2 - \underset{\substack{|\\O-O-H}}{CH} - CH_3 + R^{\cdot}$$
$$CH_3O_2^{\cdot} + RH \rightarrow CH_3OOH + R^{\cdot}$$

[1] MMT, as well as lead, is no longer used as fuel additives in Canada.

5. Hydroperoxide decomposition

$$RCH_2CH_2O_2H \rightarrow RCH_2CH_2O^{\cdot} + OH$$

$$RCH_2{-}\underset{\displaystyle O_2H}{\underset{|}{CH}}{-}CH_3 \rightarrow RCH_2{-}\underset{\displaystyle O^{\cdot}}{\underset{|}{CH}}{-}CH_3 + OH$$

$$CH_2OOH \rightarrow CH_3O^{\cdot} + OH$$

$$RCH_2CH_2O \rightarrow RCH_2^{\cdot} + CH_2O$$

$$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$$

Recent kinetic modeling of the combustion mechanism involving about 2000 reactions has made it possible to calculate RON values. A list of comparable values is given in Table 4.7.

The price of gasoline in various parts of the world is given in Table 4.8. The major single component of the cost to the motorist is a government tax which varies from about 33% to 75%. The cost of gasoline should be compared to other liquid products such as bottled spring water which can sell for \$0.50 – \$0.75 per liter or distilled water at about \$2.00 per gallon (4.5 L) in Canada. Considering the processing involved in marketing gasoline compared to water, one must conclude that gasoline is still a bargain in most countries.

The problem of environmental contamination by vehicle exhaust is further illustrated by the presence of lead compounds in French wines from a vineyard at the intersection of two major autoroutes. It was recently shown that triethyl lead and trimethyl lead were present in older wines.

Table 4.7 Comparison of calculated and measured research octane number for various hydrocarbons

				Ignition time (ms)
Fuel	Formula	Measured RON	Predicted RON	After TDC
n-Heptane(PRFO)	C_7H_{16}	0	0	55.0
n-Hexane	C « H_{14}	25	20	55.2
PRF25	25 % C_8H_{18} + 75 % C_7H_{16}	25	25	55.3
2-Methylhexane	C_7H_{16}	42	40	55.5
PRF50	50 % C_8H_{18} + 50 % C_7H_{16}	50	50	55.8
n-Pentane	C_5H_{12}	62	55	55.9
3-Ethylpentane	C_7H_{16}	65	80	57.4
2-Methylpentane	C_6H_{14}	73	80	57.3
3-Methylpentane	C_6H_{14}	74	80	57.2
PRF75	75 % C_8H_{18} + 25 % C_7H_{16}	75	75	56.7
3,3-Dimethylpentane	C_7H_{16}	81	50	55.7
2,4-Dimethylpentane	C_5H_{12}	86	75	56.4
2,2-Dimethylpropane	C_7H_{15}	83	70	56.2
PRF90	90 % C_8H_8 + 10 % C_7H_{16}	90	90	58.0
2-Methylbutane	C_5H_{12}	92	100	59.1
2,2-Dimethylbutane	C_6H_{14}	92	100	59.9
2,2-Dimethylpentane	C_7H_{16}	93	>90	No ignition
n-Butane	C_4H_{10}	94	85	57.6
2,3-Dimethylbutane	C_6H_{14}	100	90	58.0
Isooctane (PRF 100)	C_8H_{18}	100	100	59.5
Isobutane	C_4H_{10}	102	>90	No ignition
Propane	C_3H_8	112	>90	No ignition
2,2,3-Trimethylbutane	C_7H_{16}	112	>90	No ignition
Ethane	C_2H_6	115	>90	No ignition

Table 4.8 Gasoline prices and tax component in the OECD, 1992 and 2000[a]

Country	Gasoline prices (SUS/L)	Tax component (% of total)
Australia	0.499	46.2
Austria	0.970	64.8
Belgium	0.987	70.0
Canada	0.455 (0.48)	46.2
Denmark	0.961	67.2
Finland	1.013	68.0
France	0.992 (1.04)	77.2
Germany	0.981 (0.97)	72.4
Greece	0.820	69.1
Ireland	1.001	66.6
Italy	1.236(1.00)	75.8
Japan	0.977 (0.94)	46.1
Luxembourg	0.746	62.0
Netherlands	1.141	72.4
New Zealand	0.5411	46.6
Norway	1.284	71.4
Portugal	1.083	75.4
Spain	0.943 (0.76)	69.8
Sweden	1.137	69.2
Switzerland	0.759	62.5
Turkey	0.745	63.7
United Kingdom	0.882(1.00)	69.5
United States	0.298 (0.36)	33.9

OECD = Organization for Economic Cooperation and Development Values in ( ) refer to year 2000.

The trimethyl lead and triethyl lead originate from the tetramethyl lead (TML) and tetraethyl lead (TEL) which were added to gasoline as antiknock agents. The levels of lead in the wines are still at least 10–100 times less than the 0.5/*.tg*/*L* limit of lead in drinking water.

Some general properties of gasoline and diesel fuel compared to some alternate fuels are given in Table 4.9. A major parameter which is missing from the table is the unit cost, which, to a great extent, determines the choice to be made.

Exercises

1. Smoke emission from a diesel engine is environmentally undesirable. Explain why and discuss methods which can eliminate this aspect of diesel fuel use.
2. How can the ignition temperature (SIT) of a fuel be altered?
3. Calculate the air/fuel ratio for gasoline. (Note: Assume gasoline can be represented by nonane [C_9H_{20}].)
4. The TLV (threshold limit value) of mercury in Canada and USA is 0.1 mg/m^3. If a droplet of mercury (density = 13.6 g/mL) 3 mm in diameter is spilled and allowed to evaporate completely in a room 3 m × 3 m × 2.5 m. What will its concentration be, relative to the TLV?
5. Show how dimethyl ether can be prepared from methanol.
6. Compare the energy density of dimethyl ether with diesel fuel.
7. What advantages are there in using dimethyl ether in a diesel engine?
8. Discuss the special characteristics and requirements of aviation fuel in comparison to automotive fuels.

Table 4.9 Fuel comparison chart

	Gasoline $(CH_2)_X$	Methanol CH_3OH	Ethanol C_2H_5OH	Methane CH_4	Propane C_3H_8	Hydrogen H_2	Ammonia NH_3	Gasohol 10 % C_2H_5OH	Diesel $(CH_2)_X$
RON/MON	90–96	106	132	105	101			128	CN
	82–87	92	103		95			99	45
Heat of combustion MJ/kg	43.9	21.0	26.8	50.1	46.5	120.0	18.6	43.1	42.5
Density (gm/mL)	0.73	0.791	0.789	0.466	0.50	0.071 @	0.771		0.85
Temp. (°C)	25°	25°	25°	−161°	20°	−252°	−33°		25°
Heat of Combustion MJ/L	32.3	16.6	21.1	23.3 liq	23.3 liq	8.5 liq	14.3		35.3
Latent Heat of Vaporization MJ/kg	0.35	1.18	0.92	0.51	0.34	0.45	1.37		
VP @ 20 °C (Torr) (atm)	450–680	99	38	45 atm @ −82 °C[a]	8 (atm)	12.8 atm @[a] −239 °C[a]	8 atm		1.1 @ 100 °C
F.P. °C	−80	−94	−117	−182	−187	−259	−77	−80	−50
B.P. °C	30–150	65	78	−161	−42	−253	−33	30–150	150–300
Ignition temp. °C	371	446	422	540	432	500	650	300	250
		385	370						
Flash point °C	−43	11	13					−40	>40
Explosion limits % vol. in air	1.4–7.5	6.0–36	3.3–19	5.0–1.5	2.1–9.5	4.0–75	16–25	1.4–7.5	
Stoichiometric air/fuel ratio (kg air/kg fuel)	14.7	6.4	9.0						

[a]Critical Temp. and Critical Pressure

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