CHAPTER 16

Fuel Effects on Emissions

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16.1 BACKGROUND

To date, the absolute majority of fuels consumed by internal combustion engines (ICE) are fossil fuels, mainly gasoline and diesel fuel. For big size, stationary or naval engines various fuel oils are generally used. Automotive fuels are the most important products manufactured and marketed by oil companies, because large amounts (between 30 and 70%) of the crude oil run in a refinery is converted into gasoline and diesel fuel, [1].

Through the fuels history their properties have kept changing because of various reasons, such as crude oil prices, progress in refinery technology, changes in vehicle technology, environmental legislation and political considerations.

Modern automotive fuels, both gasoline and diesel fuel, must satisfy various requirements, such as: to enable fast refueling; fluently pass from the tank to the engine cylinders; effectively mix with the air; efficiently burn in the cylinders to produce adequate power and minimal amounts of pollutants in a wide range of ambient conditions. The main features required from automotive fuels, following from these demands, are summarized in Table 16.1.

The environmental legislation has become the most important factor affecting requirements of automotive fuels, due to: (a) Additional limitations caused by changes in vehicle technology (such as the need of unleaded gasoline for catalyst-equipped vehicles); (b) The growing importance of direct fuel effects (their weighting factor rising sharply as a result of very low emission levels mandated in ecological regulations).

Numerous research works have been performed in order to investigate the fuel composition effects on engine exhaust emissions. Recent comprehensive works are the American Auto/Oil Air Quality Improvement Research Program (AQIRP), [2, 3, 4] and the European Programme on Emissions, Fuels and Engine Technologies (EPEFE), [5, 6]. The former was initiated by three US automakers (GM, Ford and Chrysler) and fourteen petroleum companies, mainly for SI engines. The objective of this cooperative study was to develop data on potential improvements in vehicle emissions and air quality from reformulated gasoline, various other alternative fuels and developments in vehicle technology. The latter program was aimed at extending benefits achieved from the former to the European conditions (fuels, vehicles and test procedures are quite

Table 16.1: Main features required from automotive fuels

Feature	Relationship with engine and vehicle performance
Good combustion quality	Better ignition and combustion qualities, lead to better vehicle fuel economy and less emission of pollutants. High octane or cetane numbers are critically important for good combustion quality in SI or CI engines
Minimized deposit formation	Assists in maintaining engines close to their designed optimal efficiency and relieve the deterioration of performance, fuel economy and emissions. Deposit control additives are low-cost, widely recognized means for suppressing deposit formation
High heat of combustion	A smaller fuel quantity needs to be carried in the vehicle tank when its chemical energy content is high
Suitable latent heat of vaporization	High latent heat of vaporization causes the charge to be cooled and therefore become denser. However, there is danger of freezing ambient moisture in the carburettor
Good performance at high and low temperatures	A fractional composition of fuel must enable easy cold start, good driveability, fuel economy, low exhaust and evaporative emissions, and reliable hot re-starting without lubricant dilution in a wide range of ambient conditions. Usually, fuels are blended appropriately for both seasonal and geographical variations in temperature
Materials compatibility	Materials compatibility is essential for the preventing corrosion of fuel system components
Stability	Better fuel stability enables to minimize deposit formation and to store fuel without deterioration longer periods of time
Low foaming tendency	Low foaming tendency is relevant for diesel fuels, enabling faster vehicle refueling with lower evaporative emissions

different in Europe from those in the US), to study the remaining gaps in the knowledge about fuel/emissions relationships and, finally, to provide the European Commission with the necessary information enabling a strategy to be proposed for vehicles and automotive fuels for the 21st century. The EPEFE study involved active participation of fourteen vehicle manufacturers, represented by the Association des Constructeurs Europeens d'Automobiles (ACEA), and eleven petroleum companies, represented by the European Petroleum Industry Association (EUROPIA). The scope of EPEFE was restricted to gasoline and diesel fuel with emphasis and priority given to the latter, [5].

Effects of different fuel variables on regulated (CO, HC, NO_x, PM) and unregulated (benzene, 1,3-butadiene, aldehydes, PAH, etc.) engine exhaust emissions were investigated in the above mentioned and many other research programs, e.g. [7, 8, 9, 10]. The accumulated knowledge allows main fuel parameters to be defined affecting pollutants emission and fuel/engine/emissions relationships to be revealed with good agreement between different studies.

Table 16.2 summarizes the main gasoline and diesel fuel properties found to have essential effects on engine exhaust emissions, e.g. [5].

Table 16.2: Main fuel properties affecting engine exhaust emissions

Gasoline	Diesel fuel
Lead content Sulphur content Oxygenates content Aromatics content Benzene content Olefins content RVP Distillation characteristics	Sulphur content Density Aromatics content Cetane number Distillation characteristics

Since it is sometimes difficult to separate the effects of some fuel parameters (for example, density and aromatics, [5]), there are still some unresolved issues and additional studies are needed in this field. Moreover, even relationships which have already been established must be further investigated, in order to validate them for different vehicle technologies, test procedures and refining processes.

Increasing severity of environmental legislation, together with considerations of long-term security of supply, have led to the rise of activities aimed at developing alternatives to conventional automotive fuels. Some of them, such as hydrogen, natural gas, etc., may provide sharp reductions of engine pollutants emission.

This chapter includes a discussion of the above mentioned relationships between automotive fuels composition and engine emissions, and of main trends in fuel specifications developments, initiated by severe environmental legislation. Possibilities of exhaust emission reduction by using some alternative fuels are also discussed.

16.2 GASOLINES (SI ENGINES)

16.2.1 Origin, composition and properties

16.2.1.1 Gasoline origin

As mentioned above, gasoline is one of the two conventional liquid hydrocarbon fuels widely used today in motor vehicles. Gasoline (other terms sometimes used are petrol or motor spirit) is a fossil fuel produced from the crude oil (Technical term - petroleum) by a refining process.

The yield of gasoline products from crude oil is greatly dependent on its source. Table 16.3 includes estimates of proportions of distillation products from various crude oil sources. As can be seen from the Table the yield of gasoline fractions (light gasoline and naphtha) can widely range from 25% for the North African crude to under 2% for the South American. Therefore, refineries generally need to be much more complex than simple distillation plants in order to accommodate processing of any available crude oil.

Table 16.3: Yield (%wt) of main products from crude oil by distillation, [11]

	N. Africa	N. Sea	Mid. East	N. America	S. America
Sulphur	0.1	0.3	2.5	1.0	5.5
Wax	3	9	6	7	2
Light gasoline					
0-70°C	8.9	5.8	4.7	2.4	0.1
Octane No.	73	76	72	75	70
Naphtha					
70-180°C	16.0	11.0	7.9	6.5	1.1
Kerosine					
180-250°C	26.3	18.6	16.4	15.6	4.4
Diesel oil					
250-350°C	18.2	19.1	15.3	19.6	9.6
Cetane No.	55	53	58	45	30
Residue					
350°C+	27.5	36.2	47.2	47.9	76.9

16.2.1.2 Gasoline Composition

Generally, gasoline is a complex mixture of a great number (up to about 400, [1]) of different hydrocarbons. The name implies that these compounds contain carbon and hydrogen only, but many thousands of different combinations are possible depending on how the individual atoms in molecule are arranged. Carbon is a quadrivalent element and can combine with itself by single, double or triple bonds. The stability of hydrocarbon molecule depends on the strength of chemical bonds and this, in turn, depends on the nature and structure of the various groupings present, [1]. Hydrocarbons contained in gasoline belong mainly to the classes of paraffins, cycloparaffins (to a lesser degree), olefins and aromatics.

Paraffins, or alkalines, (chemical formula C_nH_{2n+2}) is a class of saturated hydrocarbons with only single bonds. There are two types of paraffins in gasoline: normal and isomers (with carbon atoms arranged as a straight chain and branched chain, respectively). The more carbon atoms there are in a hydrocarbon molecula, the more isomers are possible. Generally normal paraffins and isomers are essentially different substances which differ in many properties. For example, the boiling points of normal octane (n-octane) and isooctane are 126 ^{o}C and 99 ^{o}C, respectively [1]. The normal, or n-paraffins, usually have low octane quality compared to iso-paraffins with relatively high antiknock performance, [12].

Cycloparaffins, or naphthenes, (chemical formula C_nH_{2n}) is a class of hydrocarbons having a cyclic structure. In their simplest form they consist of CH_2 groups arranged in a cycle. Hydrogens attached to carbon atoms can be substituted by methyl or other groups, [1]. These products are generally of low octane quality and require secondary processing in order to enhance their knock resistance, [12].

Olefins, or alkenes, (chemical formula C_nH_{2n}) is a class of unsaturated hydrocarbons, containing one or more double bonds. Although olefins have the same general formula as naphthenes, their behavior and characteristics are entirely different, [1]. The double bond is a very reactive group, so the oxidation stability of olefins is much lower than that of saturated or aromatic hydrocarbons. Olefins in gasoline affects the emission of 1,3 - butadiene, known as a dangerous air toxin. Therefore, olefins content in gasoline have been limited in some national specifications (see Appendix 1: US Federal and Californian Specifications).

Aromatics (chemical formula C_nH_{2n-6}) is a class of hydrocarbons based on the benzenoid ring having three double bonds. The simplest member of this class is benzene (C_6H_6). The benzenoid (aromatic) rings can be fused together in different combinations. These compounds are called polycyclic aromatic hydrocarbons (PAH) or polynuclear aromatics (PNA). Benzene is known as a dangerous product and air toxin. Its content in gasoline is controlled by legislation. Other aromatics are of concern too, because they too affect engine exhaust emissions. On the other hand, the aromatics generally have high antiknock performance, thus they are needed for achieving target values of octane quality.

In addition to hydrocarbons of various classes, which form, as mentioned above, a motor gasoline, it usually contains small amounts of non-hydrocarbon compounds, such as: oxygenates, lead, phosphorus, sulphur, water, etc.

Oxygenates are usually added to unleaded gasoline in order to boost its octane quality. The types of oxygenates which are used, their effects on emissions and restrictions on the use of oxygenates in gasoline are discussed in the following sections.

Lead content in both leaded and unleaded gasoline is highly controlled by legislation, because of its high toxicity and poison effect on vehicle catalytic converters.

Phosphorus is an additional material which reduces the effectiveness of catalytic converter, therefore its content in unleaded gasoline is strongly restricted.

Sulphur content in gasoline is limited because of its negative effects on engine exhaust emissions by catalyst deactivation.

Water can be present in a gasoline both in dissolved and free form, because of contact with aqueous solutions during gasoline manufacture in the refinery and also due to the usual presence of free water at the bottom of storage tanks. Water may lead to a number of negative effects, such as: line blockage, icing of intake system, promotion of corrosion, etc., therefore its content in gasoline is usually restricted.

A detailed description of gasoline chemistry can be found in special literature, e.g. [1].

16.2.1.3 Gasoline properties

Octane Quality. In spark ignition engines the knocking phenomenon is a problem of great concern and gasoline with good octane quality is needed. The use of gasolines of low knock resistance in high compression ratio engines causes efficiency losses, an increase in pollutants emission and may lead to catastrophic engine damage under high load conditions.

Octane number (ON) of a gasoline is defined as the volume percentage of iso-octane in a blend with n-heptane (with ON taken to be 100 and 0, respectively), that shows the same antiknock performance as this gasoline when tested in a standard engine under standard conditions. There are two main methods of octane quality rating. These are Research Octane Number (RON) obtained according to ASTM standard D2699 and Motor Octane Number (MON) obtained according to ASTM standard D2700. Both tests are similar and are based on the same laboratory equipment. The main difference between them is the engine operation regimes relating to different driving conditions: RON – mainly urban driving, with engine speed and load relatively low; MON – severe driving conditions with higher engine speed and load.

In real driving, the engine operates most of the time at speeds and loads located between those corresponding to MON and RON. Therefore, the additional parameter of octane quality, known as antiknock index, has gained wide acceptance in the USA and some other countries. The antiknock index of gasoline is defined as an average of its RON and MON:

Antiknock index = (RON + MON)/2

Sometimes, so called Road Octane Number is used in order to evaluate octane requirements of vehicles on roads. A detailed description of this fuel rating is given in [1].

An additional important measure of gasoline octane quality is its "sensitivity", defined as the difference between the RON and MON ratings:

Sensitivity = RON - MON,

which represents the sensitivity of the fuel to changes in the severity of engine operating conditions in terms of knock resistance.

Volatility. Gasoline volatility is a measure of its evaporating characteristics. Gasolines with higher volatility evaporate more readily and at lower temperatures; in general, they contain more light and volatile hydrocarbons. The volatility of a gasoline is usually evaluated by the following parameters: distillation performance, Reid Vapor Pressure (RVP) and Vapor Lock Index (VLI) or Vapor - Liquid Ratio (VLR). The distillation performance, usually evaluated by a test according to ASTM standard D86, [13], is defined in terms of the following parameters:

- percentage of gasoline which is evaporated at certain temperature, or temperature at which a certain percentage of gasoline is evaporated, see Figure 16.1;

- distillation residue, i.e. the volume of residue left in a cold flask after the distillation is complete;

- distillation loss, which represents mainly those very light hydrocarbons that are not condensed during the distillation process.

Reid Vapor Pressure is an important parameter of gasoline volatility and is determined according to ASTM D323 procedure. Higher values of RVP indicate more volatile gasoline.

Vapor Lock Index values are calculated according to the formula:

$$VLI = RVP + n \times E70$$

where n is a constant. The value of $n = 7$ is widespread, especially in European countries.

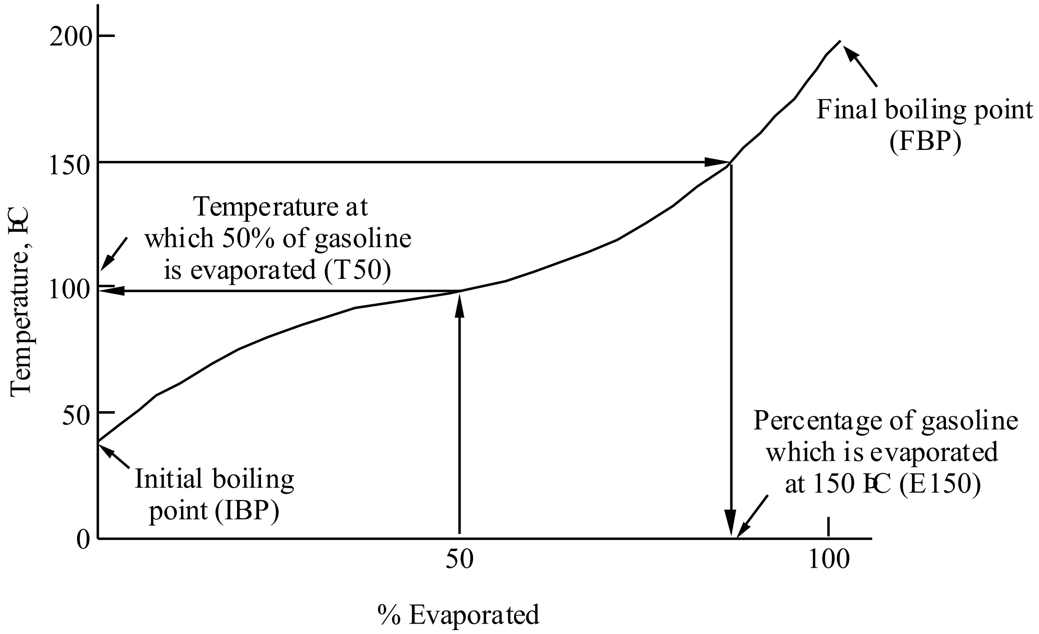

Figure 16.1: Typical distillation curve of gasoline

VLI is a measure of the likelihood of a gasoline to cause fuel flow irregularities in vehicles on the road, due to the formation of vapor plugs in the engine fuel system (vapor lock). This parameter is very important for derivability and hot startability evaluation of a vehicle at hot ambient conditions. In the USA and some other countries, the term Vapor - Liquid Ratio is used instead of VLI. The VLR values are usually evaluated according to ASTM D2533 procedure, [13], indicating the volume of vapor formed at atmospheric pressure from a given amount of gasoline at a specified test temperature, [1]. The VLR parameter, as also the VLI, is used to define the tendency of gasoline to vaporize in the fuel system of a vehicle.

Oxidation stability. Oxidation stability of a gasoline indicates its suitability for long-term storage and in part at least, its tendency to form deposits in the engine. Several test methods are used in order to evaluate it. The most commonly used are: Induction Period Method, performed according to ASTM D525 procedure, and Existent Gum test, according to ASTM D381 standard. In the former, the stability is evaluated by oxidation of the gasoline in a closed vessel with oxygen at certain pressure and temperature, by measuring the duration of the induction period. This test is mainly intended for evaluation of gasoline suitability for long-term storage.

The existent gum value is the n-heptane insoluble part of a distillation residue, and it indicates, in part at least, the tendency of a gasoline to cause deposits formation in the engine, fuel filters blockage, and as a result - to cause severe driveability problems, and, of course, rise of fuel consumption and pollutants emission.

Some other gasoline properties. Corrosivity of gasoline is a problem of great concern because it can lead to damage of fuel system elements, cause filters blockage by corrosion products and increase wear rates. In addition, dissolved metals such as copper can catalyze oxidation reactions and lead to excessive deposit formation, [1].

The corrosivity of gasoline is usually evaluated by the Copper Strip Corrosion test, according to ASTM D130 procedure. There are also some steel corrosion tests outlined in [1].

Density of gasoline is its mass per unit volume. Usually, gasolines have a density between 0.72 and 0.78 kg/l and it is a function of the composition.

Conductivity of gasoline is a parameter indicating the tendency of gasoline to static electricity build-up, mainly during pumping operations. The higher the fuel conductivity, more rapid is the dissipation of static electricity charge and hence, there is the less risk of an electrical discharge fire. Usually, conductivity values are specified for aviation gasoline and jet fuels, [14]. Other gasoline properties, such as heat of combustion, viscosity, appearance, etc. are discussed in [1].

National requirements of gasoline quality in different countries worldwide are summarized in Appendix 1. This information is mainly based on the CONCAWE data, [15]. Average values of some gasoline parameters (typical for Europe and USA) affecting pollutants emission and mentioned earlier in Table 16.2 are given in Table 16.4, based on [6, 7].

Table 16.4: Typical values of gasoline parameters

Property	European market average gasoline	1990 US industry average gasoline
Sulphur (ppm wt)	300	295
RVP (kPa)	68	57.9
Aromatics (% vol.)	40	34
Benzene (% vol.)	2.3	1.7
Olefins (% vol.)	11	7.7
Oxygenates	0.6% vol. O_2	0.1% vol. ethanol 0.2% vol. MTBE 0.1% vol. TBA
Distillation	E100 = 53% E150 = 84%	T50 = 102°C T80 = 144°C T90 = 163°C

Abbreviations used in this Table: RVP - Reid Vapor Pressure;
MTBE - Methyl Tertiary Butyl Ether; TBA - t - Butyl Alcohol.

16.2.2 Requirements of engine technologies on fuel quality

General requirements to automotive fuels, outlined earlier and summarized in Table 16.1, are discussed here in more detail for the case of gasoline use in SI engines.

Pressures to reduce air pollution from motor vehicles have led to a wide range of modifications and innovations in modern engine and vehicle design, such as catalytic converters sharply reducing the tailpipe emissions, evaporative emission control systems preventing discharge of light hydrocarbons into the atmosphere, exhaust gas recirculation (EGR) providing effective means of NO_x emission reduction, etc. Complex electronic engine management systems, providing precise fuel metering, together with advanced design of combustion chambers, inlet/outlet ports, etc., enable highly efficient combustion and optimal engine operation to be provided with minimum emissions under a wide range of vehicle operation conditions. The proper engine functioning and maintenance of its performance on the designed level are strongly dependent on fuel quality.

The attempt to further fuel economy improvement (particularly aimed at lowering the emissions of the "greenhouse" gas CO_2) has led to the development of engines with high compression ratios. The proper operation of such an engine is only possible by using gasoline with high knock resistance in a wide range of engine operation conditions, i.e. gasoline with high octane quality and low sensitivity is needed.

Motor gasoline must minimize deposit formation in engine systems, such as formed in the engine intake system, on intake and exhaust valves, inlet ports, combustion chamber, in carburetor or in injectors, etc. Deposits lead to a multitude of various engine problems and malfunctions, such as octane requirement increase (ORI), abnormal combustion phenomena (surface ignition, preignition), derivability problems, reduction of engine power, increase of fuel consumption and pollutants emission, etc. One of the least expensive and most effective ways to reduce deposits formation is the use of fuel additives (see section 16.2.3). The use of additives is also an important marketing factor for the modern, highly competitive fuel market. Obviously, the fuel composition significantly affects the tendency of gasoline to form deposits. The use of EGR systems may lead to increased levels of deposits formation in engine intake system, therefore the relevant gasoline properties, discussed above, are of great importance also here.

The gasoline volatility is an important fuel parameter, with contradictory influence on many engine characteristics, such as: cold and hot starting, derivability in a wide range of ambient conditions, engine warm-up time, deposits formation, exhaust and evaporative emissions, etc. A typical example of volatility effects on SI engine characteristics is illustrated in Figure 16.2, based on [1].

As can be deduced from the Figure 16.2 and the above discussion, the optimal gasoline volatility will always be a compromise between different contradictory requirements.

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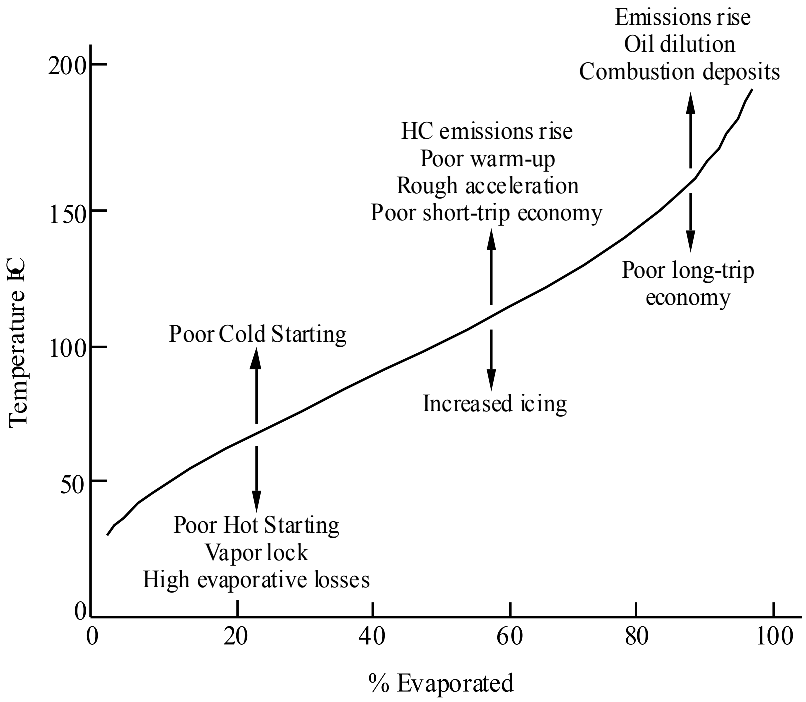


Figue 16.2: Gasoline volatility effects on vehicle characteristics, based on [1]

Vehicles equipped with catalytic converters may use only unleaded gasolines, free from phosphorus contaminants, because such materials, as mentioned above in section 16.2.1, are catalyst poisons, i.e. sharply reduce its effectiveness. It is important to note here, that using unleaded gasoline in old vehicles with "soft" valve seats may lead to severe recession problems of these seats, [16]. To overcome them, the use of special fuel additives is needed. At present such additives are already in use in some countries, for example Austria and Sweden, [15, 17]. Recent research programs clearly demonstrate that sulphur also reduces the catalytic converter effectiveness, hence its content in gasoline must be further restricted.

The environmental legislation is continuously becoming more severe, which has led to additional requirements on gasoline quality, such as: reduction of benzene, total aromatics and olefins content, use of oxygenates, etc. These requirements are discussed in detail in section 16.2.4.

16.2.3 Additives to gasoline

As pointed out in the previous sections, additives to gasoline play an essential role in treatment of fuels aimed at improving their properties in order to meet required specifications and to give them additional competitive benefits. The use of additives enable, in many cases, substantial reduction of engine exhaust emissions.

Gasoline additives can be classified, according to their functional objectives, to some main groups such as, [1, 18]:

- additives influencing combustion;
- additives protecting fuel system;
- additives improving lubrication;
- additives improving oxidation stability;
- additives used in gasoline distribution.

Evidently, this classification is quite arbitrary, and other classification approaches are possible too. For example, deposits control additives (for cleaning both the combustion chamber and the fuel system) may be selected as a separate and important group of additives.

Antiknock additives, anti-ORI additives, anti-preignition, anti-misfire and spark-aid additives together with additives which improve fuel distribution between cylinders, may be related to the group of additives influencing combustion. Most of the additives, of all groups, have generally positive influence on emissions.

The Antiknock additives, which have been widely used worldwide are the lead alkyls tetraethyl lead (TEL) and tetramethyl lead (TML). Over the past two decades, a general reduction in the use of lead compounds has occurred, because of two main factors:

- general concern over health effects of the lead;

- the increasing severity of vehicle emissions legislation which has required the use of catalyst technologies and resulted in a need for unleaded gasoline to prevent catalyst poisoning.

Extensive research works have been performed over the years for suitable alternatives to lead alkyls as gasoline antiknocks, [1, 12]. Organometallic compounds have typically been associated with greatest antiknock activity, [12], especially MMT – methyl cyclopentadienyl manganese tricarbonyl, which even was commercialized. However, there are some factors which significantly restrict the development of organometallic compounds and particularly MMT as antiknocks: their high cost, adverse effects on fuel stability and deposits build-up in engines, increased hydrocarbons emissions from catalyst controlled vehicles, toxicity of manganese emissions, etc.

Another group of relatively effective antiknock compounds is organic ashless antiknocks, such as: N - methylaniline (NMA), amines, N - nitrosamines, iodine, selenium compounds, etc. [18]. None of these compounds were found to be as cost-effective as further crude processing, [1].

As mentioned above, various oxygenates, mainly ethers and alcohols are widely used at present in unleaded gasolines to ensure required gasoline octane quality. However, their needed quantities are much larger than it is common for antiknock additives, thus it is more convenient to refer to them as gasoline blending compounds rather than as additives. The main types of ethers, which are used for this purpose are:

- Methyl tertiary butyl ether (MTBE);
- Tertiary amyl methyl ether (TAME);
- Ethyl tertiary butyl ether (ETBE).

The most important alcohol compounds used in gasoline blending, for improving octane quality, and reducing pollutants emission, are:

- Methanol;
- Ethanol;
- Tertiary butyl alcohol or t-Butanol (TBA);
- Isopropyl alcohol or isopropanol;
- Isobutyl alcohol or isobutanol.

There are two major problems limiting the amount of oxygenate which can be added to gasoline intended for use in vehicles designed for conventional hydrocarbon fuel, [1]: chemical leaning effect because of the oxygen content, and the adverse effect on vehicle fuel system materials. The effects of oxygenates on engine exhaust emissions is discussed in the next section.

Anti-ORI additives usually operate by removing and/or preventing deposits in the engine combustion chamber and in the ports. Polyetheramines are used for this purpose; they are added to the fuel intermittently and at high treat rates. Detergents in thermally stable carrier oil are used to reduce port deposits, but care must be taken to prevent the adverse effect of such a carrier oil on the formation of deposits in the combustion chamber.

In the case of leaded gasoline, the lead deposits in the combustion chamber may be prevented by using boron compounds such as glycol borates, [1]. Halogen-based additives are also effective, but there is great concern about their environmental impact. Indeed, most of the additives marketed now are halogen-free, [19].

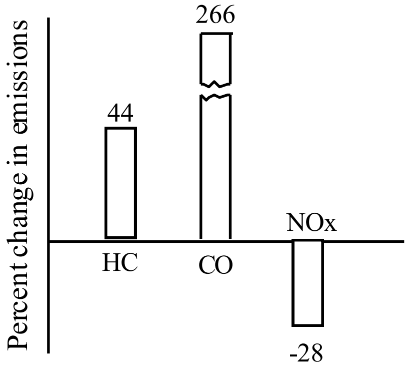
Anti-preignition and anti-misfire additives, based on phosphorus containing compounds, have been used in leaded gasoline. As the use of the latter has declined, so has that of the formers.

Spark-aid additives are intended to yield higher spark energy by controlled deposit formation on the plug electrodes. Such additives are usually based on an organic gasoline-soluble potassium or other Group I or II metal compounds.

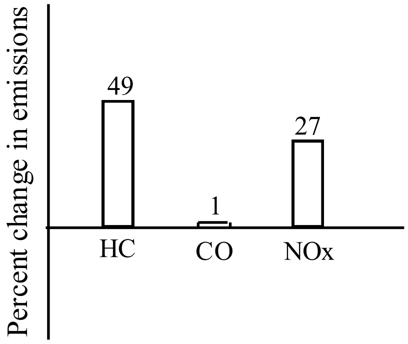
Additives which improve fuel distribution between cylinders and operate by forming a low surface energy coating inside of the intake manifold. Such additives are based on a mixture of tallow amines.

The group of additives intended to protect vehicle fuel systems, generally includes deposit-control additives, corrosion inhibitors and anti-icing additives.

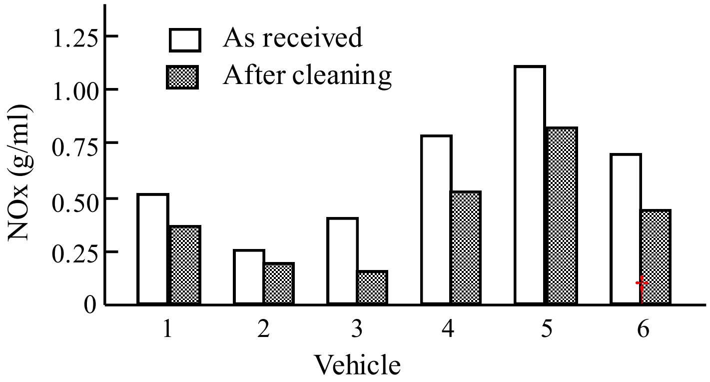
The use of deposit-control additives is recently becoming more abundant, mainly due to ecological concerns. The results of many investigations clearly show that deposit formation in carburettors or fuel injectors (especially port fuel injectors), intake manifolds, ports and on the valves, adversely affect engine performance and in particular, pollutants emission (see Figure 16.3).



a) injector deposits (injector restriction 23%), [19]



b) intake valve deposits - IVD (IVD rating change from 9-10 to 6), [20]



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c) intake manifold deposits,reproduced from [20]

Figure 16.3: Influence of deposits on engine exhaust emissions

The use of deposits control additives to gasoline allows engine systems to be kept clean and, therefore, in-service vehicle emissions to be brought as close as possible to the designed levels. In order to ensure fuel system cleanliness, detergent/dispersant additives to gasoline are usually used. These additives are based, as a rule, on polyetheramine, succinimide or polybuteneamine technologies, [1, 18, 21]. From 1995 all gasolines in the US must contain additives to prevent deposits accumulation in engines and fuel supply systems, [15]. In Israel, deposit-control additives in gasoline were mandated from 1994. Some national European specifications (for example, in Sweden, France) also provide for the use of such additives in certain types of gasoline, see Appendix 1.

Corrosion inhibitors are used to prevent deterioration of fuel storage and distribution systems and also to protect vehicle fuel systems from corrosion damage. Another benefit is the reduction of the quantity of corrosion products, which can block filters, nozzles and cause fuel pump wear. A wide range of various compounds are used as corrosion inhibitors, including amine salts of alkenyl succinic acids, alkyl orthophosphoric acids, aryl sulfonic acids, Manich amines, etc., [1, 18].

Anti-icing additives, generally surface-active agents, prevent ice adhering to the critical parts of the carburetor. Addition of alcohols to the gasoline, which reduces the freezing point of water, is also reliably used to control icing.

Additives for improving lubrication are of limited use with today's highly sophisticated lubricants, although there is some renewed interest in antisludge additives, because of a "black sludge" problem in certain vehicles, [1].

Additives against a valve seat recession are sometimes needed for protecting "soft" valve-seats of some old vehicles operating on unleaded (or low-leaded) gasoline. As mentioned above, in the absence of lead, having a lubrication function, severe problems of valve-seat recession may occur. Such problems lead to performance losses, emissions increase and finally – to engine damage. Sodium- and potassium-based compounds are found to be effective as suitable additives against valve-seat recession, [17].

Additives improving gasoline oxidation stability may be classified into subgroups: antioxidants and metal deactivators.

Antioxidants, operate by inhibiting the free radical chain reactions involved in hydrocarbons oxidation, [1]. The type and amount of antioxidants needed depend on the gasoline composition and storage demands. The majority of these additives are based on the aromatic diamine and alkylphenol compounds.

Metal deactivators are used to prevent metals present in gasoline (such as copper, for example) to function as oxidation reaction catalysts. The most commonly used metal deactivator is N,N - disalicylidene - 1,2 - propanediamine.

Additives used in gasoline distribution generally include various dyes and markers, drag reducing agents and the above mentioned corrosion inhibitors. Demulsifiers, dehazers, antistatic additives and sometimes even biocides are occasionally added to a gasoline, depending on storage, handling and distribution conditions.

16.2.4 Influence of gasoline quality on emissions

As noted above in this chapter, there is a strong correlation between gasoline performance and vehicle exhaust emissions. The overall fuel effects on emissions will be discussed henceforth. These are listed in Tables 16.5, 16.6, which summarize a large amount of present data, including the comprehensive results of the EPEFE and AQIRP

Table 16.5: Summary of gasoline parameters effects on non-catalyst cars emissions, [5]

Property	Change	Lead	CO	HC-EXH	HC-EVAP	NO_x	Benzene	Butadiene	Aldehydes
Reduce Lead	0.15∅0.08 g/l	¬¬¬	0	0	0	0	0	0	0
Add Oxygenate	0∅2.7%O2	0	¬¬¬	¬	0 - ‾	±0	0	0	—
Reduce Aromatics	40 ∅ 25% v/v	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
Reduce Sulphur	300 ∅ 100 ppm	0	0	0	0	0	0	0	0
Reduce RVP	70 ∅□60 kPa	0	0	±0	¬¬¬	0	0	0	0
Increase E 100	50 ∅ 60%	0	+0?	¬ ?	±0	0	0	0	0
Increase E 150	85 ∅ 90%	0	0	¬¬?	0	$\overline{?}$	0	¬?	¬ ?

* Some decrease in reactivity.

Note(1): Europia expressed the opinion that the effect of E 100 and Aromatics content had not been effectively decoupled. In addition, the Effect of olefins on exhaust HC and NOx were smaller than represented here Reducing aromatics increases butadiene (replace 0 by ‾).

Note (2): ACEA broadly agreed with the effects as written.

Table 16.6: Summary of gasoline parameters effects on catalyst cars emissions, [5, 22, 23, 24]

Property	Change	Lead	CO	HC-EXH	HC-EVAP	NO_X	Benzene	Butadiene	Aldehydes
Reduce Lead	0.013∅0.005	¬	¬	¬	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 E 100	35∅ 65%	0	¬	¬¬¬	0	– — –	0-¬¬¬	- 0?	0-¬¬
Increase E 150	85 ∅ 90%	0	0- –	¬¬	0	?	0	¬?	¬ ?

* Some decrease in reactivity

** Reduction from a very low level of emission

*** Contradictory results were obtained in EPEFE and AQIRP

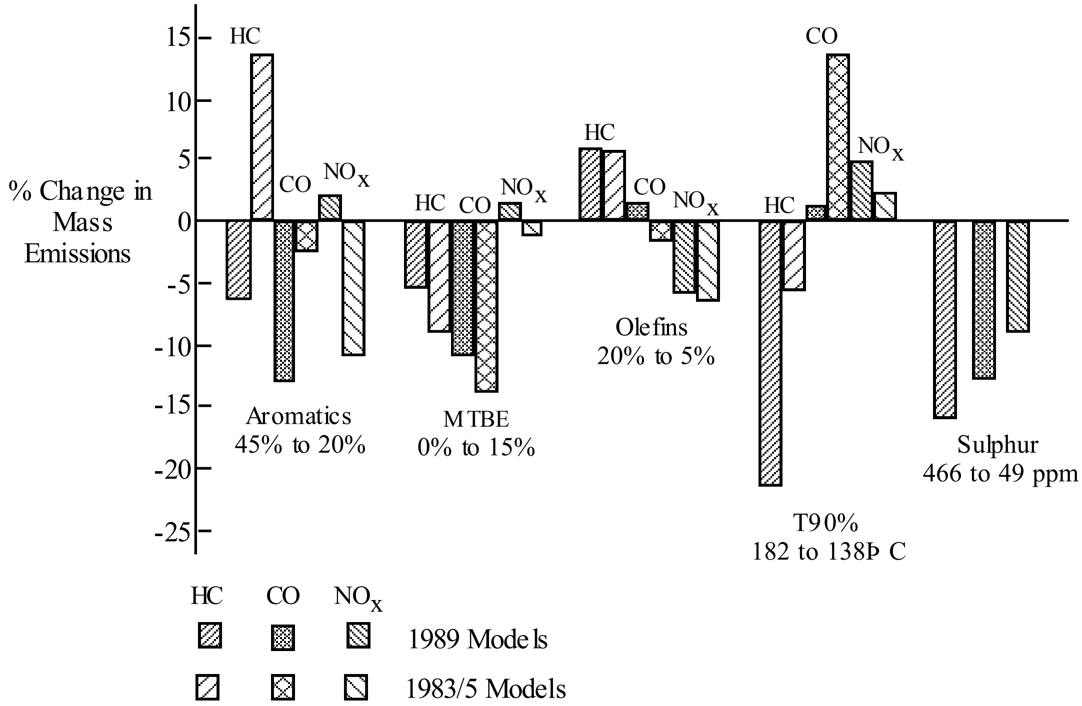
Key

— 0 - no effect — or ¬¬¬ ±0 = -2 to 2% > 20% effect – or ¬ = 2–10% effect ? = Insufficient information — or ¬¬ = 10 – 20% effect

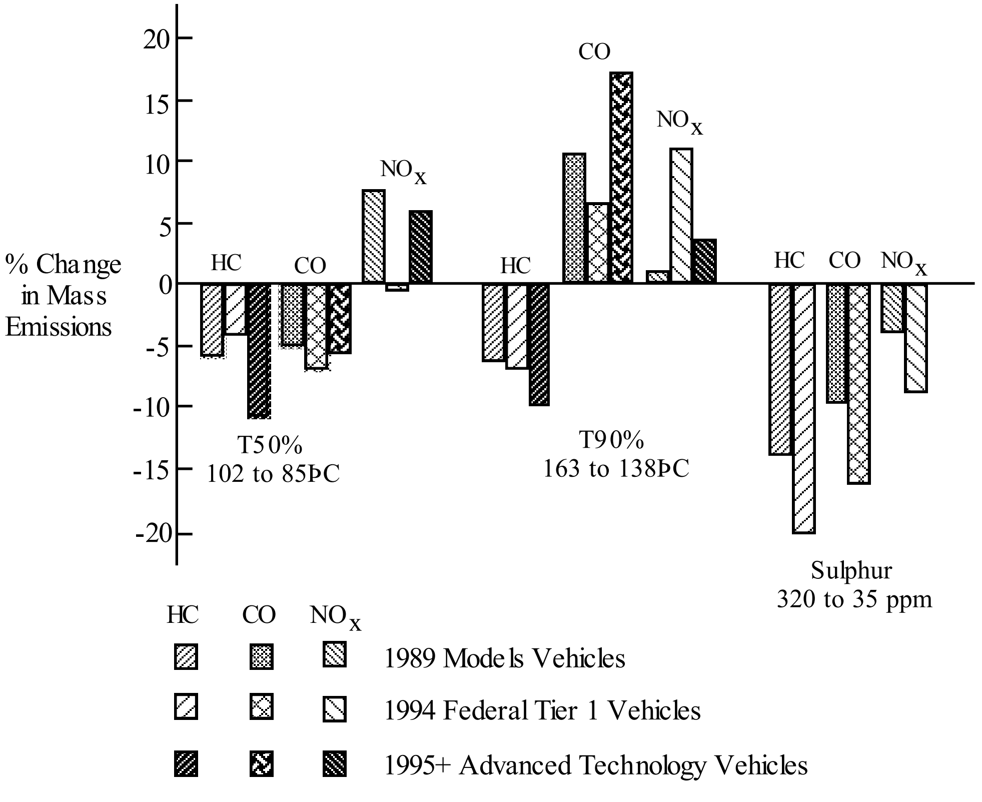
—

programs. These Tables are mainly based on those published in [5], with the addition of results concerning the sulphur, aromatics and volatility effects, which were obtained in the EPEFE and AQIRP programs, [22, 23, 24].

Evidently, fuel effects on emissions are dependent on vehicle technology. For example, vehicles equipped with catalytic converters containing palladium (Pd) are generally more sensitive to sulphur content in the gasoline than those with Pt/Rh catalysts, [22]. There is an opposite correlation between aromatics reduction and NO_X emissions for catalyst and non-catalyst vehicles, etc.



a) Phase 1 results, based on [3,4].



b) Phase 2 results, based on [24].

Figure 16.4: Fuel effects on emissions for various vehicle technologies (AQIRP results

A comparison of emissions response to fuel quality for various vehicle technologies was performed in the AQIRP program, [3, 4, 24]. The main results of this comparison are summarized in Figure 16.4.

As can be seen from this Figure, some differences were found in the magnitude of the fuel effects between the 1989 vehicle technology and that of 1983/5 (Phase 1 results), for example in their response to changing aromatics content or T90%. On the other hand, the fuel effects on fleets having newer technologies (since 1989) were more uniform, especially for HC and CO emissions. Fuel effects on NO_x emissions were found to be less consistent among the fleets and often less significant, [24]. The comparison of fuel effects on emissions for normal emitting vehicles and high emitters was performed in the framework of the AQIRP program, [64]. The results show that most fuel effects (on a relative basis) on exhaust emissions of HC, CO and NO_x were not distinguishably different in the normal and high emitters tested. Relative fuel effects on toxic emissions and specific reactivity were also found to be similar in the normal and high emitting vehicles, [64].

It is observed that the AQIRP results indicate for all fleets tested (see Figure 16.4) a negative effect of T90 reduction on carbon monoxide emissions. This fact is not noted in the EPEFE analysis, [5]. The data summarized in Tables 16.5, 16.6 and Figure 16.4 are discussed in the following.

Lead content. Lowering of lead content obviously yields a reduction of air pollution by lead, and in case of unleaded gasoline – allows to keep higher catalyst's effectiveness and thus to diminish emissions of pollutants.

Oxygenates content. Oxygenates addition leads, both for catalyst and non-catalyst vehicles, to reduction of CO and HC emissions, but also cause a rise of aldehydes emission, mainly formaldehyde, [8, 25], well known as a carcinogenic air toxic with high photochemical activity.

Aromatics content. Aromatics reduction allows to reduce CO, HC and benzene emissions both for catalyst and non-catalyst vehicles, but it exercises an opposite influence on the NO_X emissions: a reduction of NO_X in non-catalyst vehicles and an increase in NO_X in catalyst cars. The reason for this is the reduced efficiency of NO_x catalyst conversion with low aromatic fuels, [23]. Some trend of increase of aldehydes emissions with reduction of aromatics content is noted, because partial oxidation of aromatics is not a significant source of aldehydes compared to oxidation of paraffins.

There is a direct correlation between aromatics content in gasoline and emission of polynuclear aromatic hydrocarbons (PAH), some of which are known as possible carcinogens and others to have mutagenic activity. Evidently, control of these species may contribute to the health of the community. An example of a correlation between fuel aromatics content and PAH emissions for non-catalyst vehicles is given in Table 16.7. As can be seen from the Table, the PAH amount in the exhaust is dependent on the aromatics content, but not necessarily on the PAH concentration in the fuel.

Table 16.7: Benz-α-pyrene (BαP) emissions, based on [8]

Fuel Composition		Emissions of BαP, μg/l
Aromatics, % v/v	BαP, μg/l	
44	0.8	56.8
15	64.7	23.5

Benzene content. Reduction of benzene content relates directly to benzene emissions in the exhaust gases: the lower is its level in fuel, the lower are its emissions.

Olefins content. Olefins reduction leads to a decrease in the emissions of air-toxic 1,3 - butadiene for both catalyst and non-catalyst vehicles. The reduction of light, volatile and very reactive olefins, (such as butenes and pentenes), leads to improvement of gasoline oxidation stability and reduction of ozone formation from evaporative emissions, [1, 28].

Sulphur content. The AQIRP and EPEFE studies confirmed the role of fuel sulphur as a deactivator of vehicle's catalytic converter. Fuel sulphur has the greatest effect on a warmed up catalyst. Lowering the sulphur content in gasoline leads to reduced emissions of CO, HC, NO_X and benzene. The emissions response to fuel sulphur content is strongly affected by vehicle technology. As mentioned above, vehicles equipped with Pd-based catalytic converters have been found to be more sensitive to fuel sulphur than vehicles with Pt/Rh-based catalysts, [22]. Sulphur content is more critical for vehicles with a close-coupled catalytic converter, due to its much lower light-off time and hence longer operation during a test with fully warmed-up catalyst. In the European test program, no increase of 1,3-butadiene and aldehydes emissions was found when reducing sulphur content in gasoline, in contrast to the AQIRP results where formaldehyde increase was indicated. Additional research work is needed in order to clarify these results; some possible explanations are: difference in vehicles' catalyst technologies and inhibition of formaldehyde formation by increasing sulphur in the fuel, which could occur before the catalyst reaches its operating temperature (in the US FTP, the catalyst operates a greater proportion of the test sequence at fully warmed-up condition than in the European test), [22].

Vapor pressure. Lowering of the RVP leads to the reduction of evaporative emissions in both non-controlled and evaporative emission controlled vehicles. When RVP of gasoline is lower, fewer light hydrocarbons (such as butane) are contained in it, which leads to reduction of refueling, evaporative and running losses of hydrocarbons, [26].

Distillation performance. Increase of mid-range volatility (characterized by E100 or T50 distillation points) leads to the reduction of HC emissions for both catalyst and non-catalyst vehicles and CO emissions – mainly for catalyst equipped cars. From the EPEFE program results it follows that CO emissions have their lowest value, 50%, at E100, [23]. Increase of gasoline mid-range volatility leads to a rise of NO_X emissions. Benzene emissions generally decrease with increasing the mid-range volatility, but the effect becomes weaker at low aromatics content.

The increase of back-end volatility (characterized by E150 or T90 distillation points) contributes towards reduction of HC emissions, both for non-catalyst and catalyst equipped vehicles, but leads to some rise in CO and NO_X emissions, [24, 27].

Different attempts were made in order to quantify, by equations, the complex relationships between gasoline properties and vehicle exhaust emissions. Such equations have been developed, for example, in the AQIRP program. General principles used in equation development were described in [100]. Regression coefficients and equations for various specific cases can be found in the relevant AQIRP publications, e.g. [3, 101, 102].

The US EPA has developed empirical "simple" and "complex" models which correlate a gasoline's properties to its emissions characteristics. Refiners are required to use these models in order to certify their reformulated gasolines. Until late 1997 use of a "simple model" is allowable, but from January 1998 refiners will be required to use only a "complex model" for certification. This "complex" model uses regression equations to calculate changes in emissions of NO_x, total VOCs (volatile organic compounds) and air toxics as a result of fuel properties variations. The equations are based on the RVP, distillation parameters and sulphur, oxygen, aromatics and olefins content, together with weighting factors defined for old and new technology vehicles, [15]. The above mentioned equations of the "simple" and "complex" models together with the allowable ranges of fuel properties, weighting factors and baseline data, as reproduced from the CONCAWE report [15], are given in Appendix 3.

An attempt was made also in EPEFE to quantify the relationships between gasoline properties and emissions by equations based on data generated up-to-date. Such equations, [6], are reproduced in Table 16.8. The relationships are not simple and it is not possible to use individual fuel properties alone in order to derive emission factors. However, these equations open new possibilities of predicting the fuel performance effects on the emission responses of given emission control technologies used in motor vehicles. As mentioned by EPEFE, [6], the developed equations are valid within a wide range of test procedures, vehicle/engine technologies and fuel parameters, used in their study, but great care must be taken in extrapolating from these results. The model developed should be validated for fuels and vehicles in production and according to technology evolution processes.

As can be seen from Table 16.8, the oxygenates content are expressed in such formulae as weight percentage of oxygen in the fuel. However, it is sometimes more convenient to use the volumetric content in the fuel of a specific oxygenate (MTBE, ETOH, TBA, etc.). The coefficients for converting from the latter to the former values are summarized, for convenience, in Table 16.9. An example of comparison between experimental data generated in the EPEFE program, [22], and the results of calculations according to the formulae in Table 16.8 are shown in Table 16.10 and Figure 16.5.

As can be seen from the Figure and Tables, the calculated and measured effects are in quite good agreement. However, a similar comparison with the AQIRP results, performed for studying the effects of back-end volatility on emissions does not give such a good correlation between the experimental and calculated data. These results are summarized in Table 16.11. As can be seen from this Table, the EPEFE formulae do not predict the CO emissions rise as a result of back-end volatility increase (see also Tables 16.5, 16.6 and Figure 16.4). Therefore, as mentioned above, great care must be taken in using them.

Table 16.8: AUTO/OIL PROGRAMME - Equations of the Fuel/Engine Technologies Responses (sources: SAE Paper No. 961076; private communication by M. Hublin, 1997)

FORMULAE FOR GASOLINE

CO (g/km)

[2.459 - 0.05513 E100 + 0.0005343 $E100^2$ + 0.009226 Aro - 0.0003101 (97 – Sulphur(]
x [1 - 0.037)% O_2 - 1.75([]1 - 0.008)E150 - 90.2(]

HC (g/km)

[0.1347 + 0.0005489 Aro + 25.7 Aro exp(- 0.2642 E100) - 0.0000406)97 – Sulphur(]
x [1 - 0.004)Olef - 4.97)] [1 - 0.022 (%O_2 - 1.75([ ]1 - 0.01)E150 - 90.2(]

NO_x (g/km)

[0.1884 - 0.001438 Aro + 0.00001959 E100 Aro - 0.00005302 (97 – Sulphur(] x
x [1 + 0.004)Olef - 4.97)] [1 + 0.001 (% O_2 - 1.75([ ]1 + 0.008)E150 - 90.2(]

Benzene (mg/km)

[-0.454 + 5.374 Fuelbenz + 0.913 x)Aro – Fuelbenz(] x HC

E100	% vol. evaporated at 100 ^oC (%vol)	**Sulphur**	fuel sulphur content (ppm)
E150	% vol. evaporated at 150 ^oC (%vol)	**Fuelbenz**	fuel benzene content (% vol)
Aro	fuel aromatic content (%vol)	**% O_2**	fuel oxygen content (%wt)
Olef	fuel olefins content (%vol)		

Table 16.9: Conversion factors for oxygenates content

To convert from	To	Multiply by
% vol. MTBE	% wt O_2	0.18
% vol. Methanol	% wt O_2	0.528
% vol. Ethanol	% wt O_2	0.366
% vol. TBA	%wt O_2	0.227
% vol. TAME	% wt O_2	0.161

Table 16.10: Change in exhaust emissions due to sulphur content reduction – comparison of experimental (EPEFE [22]) and calculated data (sulphur reduction from 382 to 18 ppm)

Pollutant	Change in emissions, %	
	Experiment	Calculation
HC	-8.1	-9.1
CO	-9.4	-8.7
NO_x	-11.2	-10.1

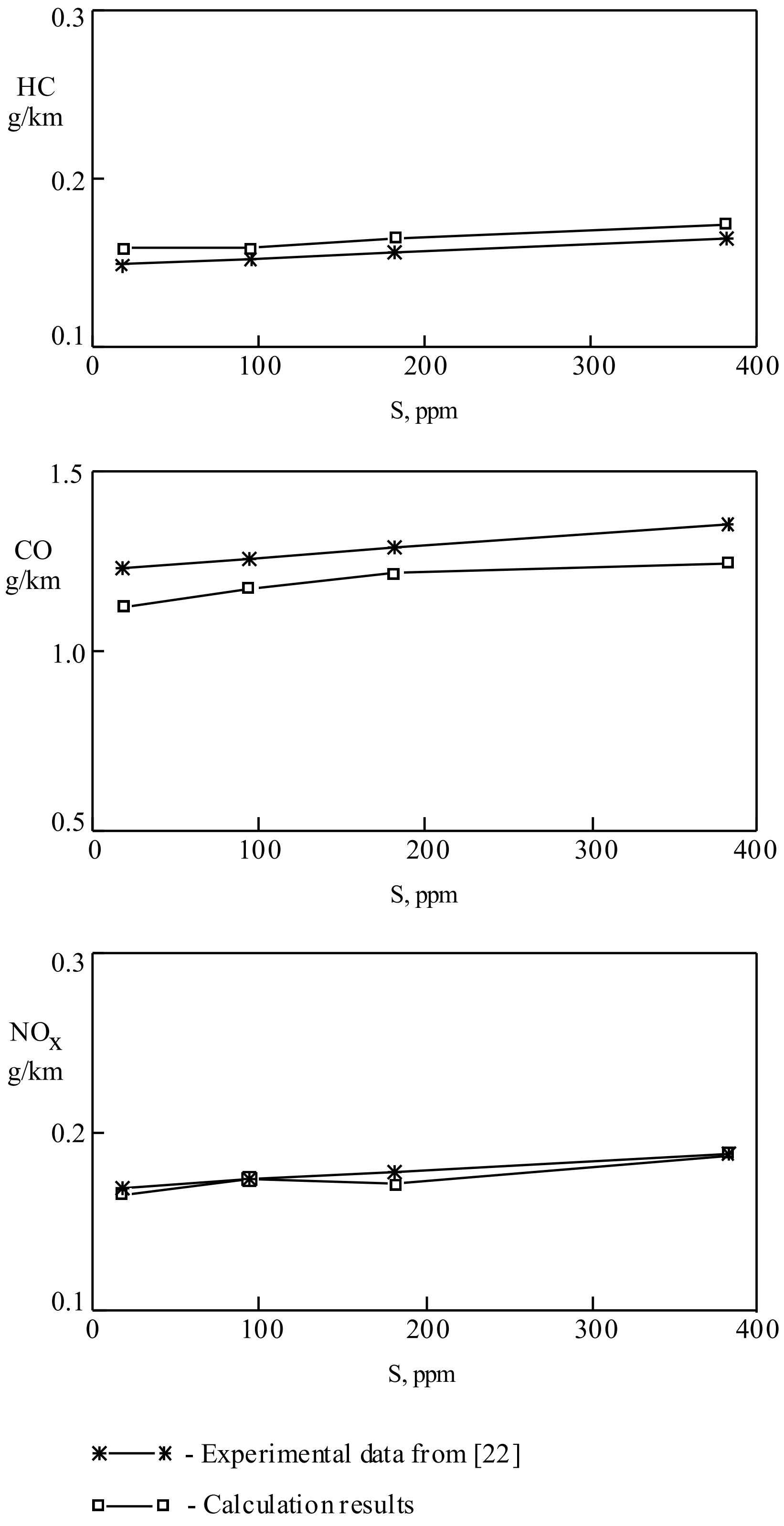


Figure 16.5: Sulphur effects on exhaust emmissions - comparison of experimental and calculation results.

Table 16.11: Change in exhaust emissions due to back-end volatility increase – comparison of experimental (AQIRP [24]) and calculated data (T90 reduction from 162 to 137°C)*

Pollutant	Change in emissions, %	
	Experiment (Federal Tier 1 fleet)	Calculation
HC	-6.9	-5.7
CO	6.6	-5.1
NO_x	11.0	3.9

* distillation parameters, E100 and E150, used in the calculation were approximately estimated based on T50 and T90 data.

16.2.5 Main trends in gasoline specifications developments

The main trends of the development in gasoline properties and composition are in accordance with environmental legislation trends and with fuel/emissions responses, as described in the previous section. The ecology - related changes in gasoline specifications in the USA over the last few decades are summarized in the Table 16.12, reproduced from [28].

As can be seen from the Table, the term "reformulated gasoline" (RFG) is used. It was introduced for the first time in the USA in order to distinguish the gasoline formulated for reducing vehicle's emissions from other conventional gasolines. Reformulated gasolines are also called, sometimes, Clean Gasolines or Environmental gasolines. The US Clean Air Act Amendments of 1990 include the requirement for RFG to be sold in major metropolitan areas, which fail to meet ambient ozone and carbon-monoxide standards. In general, reformulated gasoline specifications reflect the main trends in gasoline formulations development as outlined in the following.

- Lead phase-out. At present, sales of leaded gasoline are totally banned in the USA, Japan, Austria, Sweden, Canada, Brazil, South Korea, Thailand and others [15], and this trend is growing rapidly all over the world. In 1994, over 64% of the gasoline sold in Europe was unleaded. Furthermore, the lead content in unleaded gasolines is the subject of continuous restriction, for example – the change from the common value of 0.013 g/l to 0.005 g/l or even lower (see Appendix 1). The reduction of lead content in the unleaded gasolines allows, as mentioned above, not only to reduce lead emissions, but also to lower catalyst deactivation, and hence – to reduce emission levels.

- Addition of oxygenates to gasoline is recently becoming widespread as a tool for ensuring high octane and for reducing exhaust emissions. However, because of some restrictions (discussed above), the use of oxygenates in gasoline is limited, depends on the oxygenate type (as in Europe) or by weight content of the oxygen in the gasoline (as in the USA). Oxygenates limits set out in the European Directive 85/536/EEC are summarized in Table 16.13, reproduced from [15]. The federal requirements in the USA are 2.7% O_2 maximum. According to some forecasts, e.g. [29], this value may grow to 3% in 2010.

- Aromatics content reduction. Because of the need to boost octane, unleaded gasolines typically contain higher concentrations of aromatics, [26, 30]. For example, according to [31], in France premium unleaded gasoline contains an average of about 41% vol. aromatics compared to 33.5% vol. for leaded grades; similarly, in Great Britain unleaded and leaded gasolines contain, respectively, about 31 and 26% vol. aromatics. As discussed above, however, aromatics lead to increased vehicle exhaust emissions, therefore there are "environmental pressures" to limit and reduce their content in gasoline.

To date, there are no limits on aromatics content in most of the modern gasoline specifications (see Appendix 1). Nonetheless, in California Phase 2 reformulated gasoline requirements for 1996, the aromatics content is already restricted to 25% vol. maximum, [15]. Also, the Swedish specifications for Class 2 Environmental gasoline put the so called "empirical limit" (EL) on aromatics content in this gasoline:
(EL = % Vol Aromatics/13 + % Vol Benzene), [15]. Because the amount of benzene in gasoline is also limited, such a requirement actually limits the aromatics content, but it also allows more flexibility to the refineries. It is possible to forecast, with high degree of probability, that the aromatics content will be limited and consequently reduced in most of the future gasoline formulations; one of the predicted aromatics limits for the year 2010 is 20% vol, [29].

Table 16.12: Summary of ecology related changes in gasoline specifications, [28]

Year	Agency	Regulation	Purpose
1959	CA	Bromine Number - 30 Max. for Southern CA	To limit formation of eye irritants, ozone, and aerosols
1971	CA	Vapor Pressure-9.0 psi Max. summer months	To reduce evaporative hydrocarbon emissions and ozone
1974	US	Unleaded Gasoline Required in Service Stations	To assure proper fuel for exhaust catalyst-equipped vehicles
1976	CA	Sulfur Limit-500 ppm Max.	Reduce sulfur dioxide and sulfur trioxide (sulfate emissions)
1977	CA	Lead Phasedown	To protect public health
1977	US	Manganese Banned Until Walver Obtained	To prevent increase in hydrocarbon emissions
1977	CA	Manganese Banned	To prevent increase in hydrocarbon emissions
1978	CA	Sulfur Limit-400 ppm Max.	Reduce sulfur dioxide and sulfur trioxide (sulfate emissions)
1980	US	Lead Phasedown	To protect public health
1980	CA	Sulfur Limit - 300 ppm Max.	Reduce sulfur dioxide and sulfur trioxide (sulfate emissions)
1981	US	Substantially Similar Rule	To control additive and oxygenate use
1989	US	Vapor Pressure Phase I 10.5 /9.5/9.0 psi Max. Summertime	To reduce evaporative hydrocarbon emissions and ozone
1992	US	Vapor Pressure Phase II 9.0/7.8 psi Max. Summertime	To reduce evaporative hydrocarbon emissions and ozone
1992	US	Oxygen Content - 2.7 wt % Min. Wintertime administered by states	To reduce wintertime carbon monoxide emissions in carbon monoxide nonattainment areas
1992	CA	Vapor Pressure Phase 1 7.8 psi Max. Summertime	To reduce evaporative hydrocarbon emissions and ozone
1992	CA	Deposit Control Additive Requirement	To minimize exhaust emissions caused by carburetor, injector, and intake valve deposits
1992	CA	Lead Banned	To protect public health
1992	CA	Oxygen Content - 1.8- 2.2 wt % Wintertime	To reduce carbon monoxide wintertime emissions without increasing oxides of nitrogen emissions
1994	CA	Required All Gasoline to be Unleaded	To protect public health and catalysts
1995	US	Deposit Control Additive Requirement	To minimize exhaust emissions caused by carburetor, injector, and intake valve deposits
1995	US	Reformulated Gasoline Simple Model	To reduce ozone in specified and opt in ozone non-attainment areas
		Benzene Limit-1.3 vol % Max. per gallon cap	To reduce toxics
		Oxygen Content - 1.5 Wt % Min. per gallon cap	Required by CAAA 1990
		Vapor Pressure-7.4/8.3 psi Max. per gallon cap	To reduce evaporative hydrocarbon emissions and ozone
		No Heavy Metals	To protect public health
		Indirect Aromatics Max. of -27 vol %	To reduce toxics
		Sulfur, olefins, and 90% evaporated point < 1990 average levels	To prevent increased emissions caused by changes in other fuel properties
1996	US	Lead Banned for Highway Fuel	To protect public health
1996	CA	California Phase 2 Reformulated Gasoline	To achieve maximum cost-effective reductions in criteria and toxic pollutants
		Vapor Pressure - 7.00 psi Max.	To reduce evaporative hydrocarbon emissions and ozone
		Sulfur Limit - 80 ppm Max. per gallon cap	Reduce sulfur dioxide and sulfur trioxide (sulfate emissions) and minimize temporary deactivation of exhaust catalysts thereby reducing hydrocarbon, carbon monoxide, and oxides of nitrogen emissions
		Benzene Limit - 1.2 vol % Max. per gallon cap.	To reduce toxics
		Aromatics Limit-30 vol % Max. per gallon cap	To reduce toxics and hydrocarbon emissions
		Olefins Limit-10.0 vol % Max. per gallon cap	To reduce oxides of nitrogen exhaust emissions and ozone formation from evaporative emissions
		90% Evaporated Point-330 ^{o}F Max. per gallon cap.	To reduce hydrocarbon exhaust emissions
		50% Evaporated Point - 220 ^{o}F Max. per gallon cap.	To reduce hydrocarbon and carbon monoxide emissions
		Oxygen Content - 0.-2.7 Wt % Summertime	To reduce carbon monoxide and hydrocarbon emissions without increasing oxides of nitrogen emissions

Table 16.13: Oxygenates limits in gasoline (European Directive 85/536/EEC), [15]

	A (% vol)	B (% vol)
Methanol, suitable stabilizing agents must be added(a)	3%	3%
Ethanol, stabilizing agents may be necessary(a)	5%	5%
Isopropyl alcohol	5%	10%
TBA	7%	7%
Isobutyl alcohol	7%	10%
Ethers containing 5 or more carbon atoms per molecule(a)	10%	15%
Other organic oxygenates defined in Annex section I	7%	10%
Mixture of any organic oxygenates defined(b) in Annex section I	2.5% oxygen weight, not exceeding the individual limits fixed above for each component	3.7% oxygen weight, not exceeding the individual limits fixed above for each component

Notes: Member States must permit fuel blends containing levels of oxygenates not exceeding the level set out in Column A. If they so desire, they may authorize proportions of oxygenates above these levels. However, if the levels so permitted exceed the limits set out in column B, the dispensing pump must be clearly marked accordingly, in particular to take into account the calorific value of such fuels.

(a) In accordance with national specifications or, where these do not exist, industry specifications

(b) Acetone is authorized up to 0.8% by volume when it is present as a by-product of the manufacture of certain organic oxygenate compounds

(c) Not all countries permit levels exceeding those in column (A) even if the pump is labeled.

- Benzene content reduction. Benzene is the lightest of the aromatics, known as air toxic, and is present in air environment mainly due to vehicle emissions, [8]. The strong correlation between benzene content in fuel and its emissions has been discussed in the previous section. Most of today's unleaded gasoline specifications limit the maximal permissible amount of benzene is gasoline. For example, in Europe (according to CEN standard EN 228, the limit of benzene content is 5% vol. However, for reformulated gasolines marketed now in the USA, it has already been reduced to 1% vol (see Appendix 1). The same trends of the benzene content reduction in RFG are observed also in the European countries: in Finland - 1% vol, in Sweden - 3% vol. In Italy, according to local agreements between major city authorities and oil companies, the benzene content is limited to 1.8% vol maximum, with a further move to 0.8% vol proposed in Rome, [31]. Predictions of future trends indicate the possibility of restricting the benzene content up to 0.6% vol maximum in 2010, [29].

- Olefins content reduction. As discussed in the previous sections, the olefins contained in gasoline mainly contribute to 1,3 - butadiene emissions and adversely affect the gasoline oxidation stability. Today, the olefins content is not limited in the European gasoline specifications, but for reformulated gasolines marketed now in California, according to Phase 2 RFG requirements, the amount of total olefins in a gasoline has been restricted to 6% vol maximum (see Appendix 1).

There are considerations for future limits of 5% vol maximum for total olefins and 1% vol maximum for the most volatile and photochemically active olefins (C_4/C_5), [32].

- Sulphur content reduction is essential, as has been established, to prevent the deterioration of catalyst effectiveness during the vehicle service life. In Europe, today, (according to EN 228), the maximal permissible sulphur content in unleaded gasoline is 0.05% wt. Allowed sulphur amounts for leaded grades, intended for non-catalyst cars, are generally higher: 0.1 to 0.2% wt maximum (see Appendix 1). However, in some countries the limits for sulphur content in reformulated grades of gasoline has been restricted more severely: to values of 0.01% wt or even lower (see Appendix 1). For example, the Phase 2 reformulated gasoline in California may contain only 0.004% wt maximum of sulphur.

The most severe restrictions on sulphur content in Europe are in Finland (reformulated gasoline) and Sweden (Class 2 - cat.) - 0.01% wt.

Vapor pressure reduction. Since 1989, there is a continuous trend of lowering the maximal RVP values of US gasolines permitted by federal regulations on vapor pressure, [28]. Such a trend is common for both winter and summer gasolines. Today's RVP limit for reformulated gasoline marketed in California is only 48.3 KPa. Some reformulated grades in Europe must also have reduced vapor pressure values (see Appendix 1). For example, the RVP of the Finnish reformulated gasoline must not exceed 70 kPa, while the common value today in European countries with similar climatic conditions is 95 kPa.

- Tailoring the gasoline distillation. The trend in vapor pressure reduction generally corresponds with the reduction of gasoline front-end volatility. At the same time, as can be seen from Tables 16.5 and 16.6, some increase of gasoline mid-range and back-end volatility leads to the reduction of CO and HC emissions. It reflects in the California Phase 2 reformulated gasoline specification, where the T50% and T90% distillation points have been reduced to 99^{o}C and 149^{o}C max, respectively, compared to 121^{o}C and 190^{o}C max for conventional gasolines. There are forecasts which predict further rise of mid-range and, to some extent, also back-end volatility of future gasolines: T50% = 88^{o}C and T90% = 143^{o}C in the year 2010, [29].

- The use of deposit control additives is becoming widespread in modern gasolines. Most gasolines marketed in Europe, both leaded and unleaded, now contain detergent additives, [31]. All gasoline sold in the US from 1995 contains deposit control additives. It may be assumed, with high degree of probability, that all future gasolines will contain multi-functional additive packages.

16.3 DIESEL FUELS (CI ENGINES)

16.3.1 Origin, composition and properties

16.3.1.1 Diesel fuel origin and composition

Diesel fuels are complex compounds of hydrocarbon molecules which generally boil within the temperature range of 150 to 380^{o}C, [1, 33]. They are normally blended from several refinery streams, mostly coming from the primary distillation unit. However, in a conversion refinery, components from other units, like cracking processes, are often used to increase diesel fuel production. In the primary refining unit, distillation takes place at atmospheric pressure, the furnace temperature being set to give maximum distillation without cracking. The quality and quantity of the streams drawn off will be determined both by their boiling range and by the crude boiling used. Tables 16.14 and 16.15 give general indications of how the type of crude oil can influence diesel fuel characteristics and properties, [1, 34].

16.3.1.2 Diesel fuel properties

Cetane number. The most universally accepted measure of the ignition quality of diesel fuel is the cetane number (CN), [1, 33]: the higher the number, the easier it is to ignite. The method used to determine the ignition quality in terms of the CN is similar to that used for determining the antiknock quality of gasoline in terms of octane number. The CN scale is defined by blends of two pure hydrocarbon reference fuels. Cetane (n -

Table 16.14: Influence of crude oil type and origin on diesel fuel characteristics, [1]

Crude oil source	Hydro-carbon type	Cetane number	Sulphur content	Cloud point	Calorific value
UK/Norway	Paraffinic	High	Low/Medium	High	Low
Denmark	Naphtenic	Moderate	Low	Low	Moderate
Mid. East	Paraffinic	High	High	High	Low
Nigeria	Naphtenic	Low	Low	Low	Moderate
Venezuela / Mexico	Naphtenic/ Aromatic	Very Low	Low/ Medium	Low	High
Australia	Paraffinic	High	Low	High	Low
Mexico	Paraffinic	High	Low	High	Low

Table 16.15: Influence of crude oil source on diesel fuel properties, [34]

Property	Crude source		
	Kuwait crude	Forties crude	Nigerian crude
Density (kg/l at 15 °C)	0.8517	0.8558	0.8785
Viscosity (cSt at 40°C)	4.5	4.6	4.5
Cloud point (°C)	4	6	-8
Cold filer plugging point (°C)	-4	1	-11
ATM distillation			
50% distilled at °C	304	294	283
Sulphur (% wt)	1.40	0.19	0.13
Cetane number (ASTM D6130	54.1	52.2	40.9

hexadecane), a compound with high ignition quality, represents the top of the scale with a cetane number of 100. An isocetane, heptamethyl nonane, a highly branched paraffin which has a very low ignition quality, represents the bottom of the scale with a cetane number of 15. A fuel with the same ignition quality as a mixture of the two reference fuels has a cetane number derived from the equation:

CN = percent n-cetane + percent heptamethyl nonane

The engine used in CN determination is a standardized single cylinder, variable compression ratio. The engine, the operating conditions and the test procedure are specified by ASTM method D613, [1].

The importance of higher cetane numbers is attached to the performance benefits provided in terms of: Improved cold starting; Reduced smoke emission during warm-up; Reduced noise; Reduced fuel consumption and exhaust emission. Therefore, there is a general tendency in some countries to increase the cetane number of diesel fuel.

Since the cost of the cetane number determination is quite high, many correlations which predict ignition quality based on the physical properties of diesel fuels have been developed, [34 - 36]. A calculated cetane index, CCI, is often used to estimate it, based on API gravity and the mid boiling temperature (of 50% evaporated), cf. ASTM D976, [34]. It is applicable to straight-run fuels, catalytically cracked stocks, and blends of the two, [34]. The use of this index (CCI) is suitable for most diesel fuels and yields values that correspond quite closely to the cetane number. A Diesel Index is also used, based on the fact that ignition quality is linked to hydrocarbon composition: n-paraffins have high ignition quality and aromatic and naphtenic compounds have low ignition quality, [34]. The aniline point (the lowest temperature at which equal volumes of the fuel and aniline become just miscible) is used together with the API gravity, to give the Diesel Index, [1, 35, 36]:

Diesel Index = Aniline Point (^{o}F) x API Gravity/100

where the API gravity is based on the specific gravity and is calculated by:

API Gravity, deg = (141.5 / specific gravity at 60^{o}F - 131.5).

The Diesel Index usually gives values slightly above the cetane number. It provides a satisfactory indication of ignition quality in many (but not all) cases.

As indicated by [35,36], the formulae known as cetane indices or cetane correlations lead to significant errors in the prediction of the cetane number of a diesel fuel which is very different from the fuels used to derive the index. This stems from the following reasons:

- Relationships between physical properties and chemical structure of the fuel have not yet been developed.

- The physical properties measured commonly, i.e. density, boiling range, aniline point and viscosity, do not fully describe the fuel chemistry (lack of representation).

- In most predictive equations, commonly measured physical properties have been used randomly without relying on generally accepted physical and/or chemical models.

- The correlations have usually been based on the assumption that aromatic hydrocarbons are low in cetane number, paraffins have high cetane numbers, and naphtenes fall somewhere in between. No attempt has been made to represent the degree of branching. This is important since different isomers react differently in regard to cetane numbers just as they do in octane numbers.

Volatility. The volatility characteristics of a diesel fuel can be expressed in terms of the temperature at which successive portions are distilled from a sample of the fuel under controlled heating in a standardized apparatus. The distillation method recommended by the standard ASTMD 86 is one of the more widely used versions of distillation, [1]. Information obtained during the distillation includes: Initial boiling point (IBP); End point (EP) or final boiling point (FBP); Percent of condensate recovered; Percent residue of non-volatile matter. A typical diesel fuel distillation curve is shown in Figure 16.6.

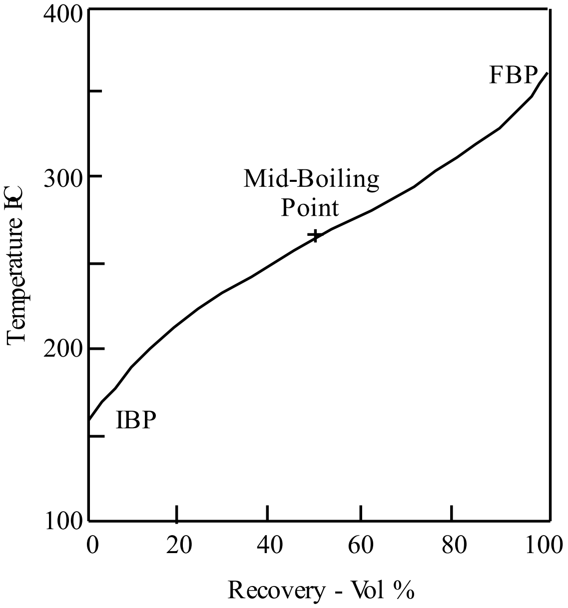


Figure 16.6: Typical diesel fuel distillation curve, [1]

The volatility (the distillation or boiling range of the fuel) influences many other properties, including density, flash point, autoignition temperature, viscosity and cetane number. High volatility could cause vapor lock and lower the flash point. The vapor lock can cause engine misfiring or failure to restart after a brief shutdown in hot conditions. However, the higher the volatility – the more easily does complete vaporization of the fuel take place in the combustion chamber. Consequently, high boiling components may not burn completely, forming engine deposits and increasing smoke levels, [1,33]. Within the range 350 to 400^{o}C, however, the effects of low volatility on exhaust emissions is relatively small [33]. The mid-volatility of a diesel fuel has a marked effect on the tendency to smoke, possibly through influence on the injection and mixing of the fuel. However, there is also interest in the 50% distillate recovery temperature for the calculation of Cetane Index by ASTMD 976, [1].

It is emphasized that in practice, it is the mix of volatilities that is most important: high volatility components at the lower end of the curve (Figure 16.6) improve cold starting and warm-up, while low volatility components at the upper end tend to increase deposits, smoke and wear, [33].

Density. The density of diesel fuel can provide useful indications about its composition and performance-related characteristics, such as ignition quality, power, economy, low-temperature properties and smoking tendency. The density may sometimes be expressed as specific gravity or as API Gravity. In units of kg/m^3, the densities of fuels obtained by the different refining processes are approximately as follows, [33]:

Straight-run distilled	805 to 870
Hydrocracked gasoil	815 to 840
Thermally cracked gas oil	835 to 875
Catalytically cracked gas oil	930 to 965

Viscosity of a fluid indicates its resistance to flow. It is an important property of the diesel fuels because of its influence on the performance of the fuel injection equipment, especially at low temperature, when the increase in viscosity affects the fluidity of the fuel. Increasing viscosity reduces the injector spray cone angle, fuel distribution and penetration, while increasing the droplet size. It will therefore affect optimum injection timing, [33]. For a given injector nozzle configuration and a fuel pressure, the viscosity will certainly influence the quantity of fuel injected.

Diesel specifications usually impose an upper limit on viscosity to ensure adequate fuel flow for cold starting and an additional minimum limit is often also specified to guard against loss of power at high temperatures.

Figure 16.7 shows temperature/viscosity characteristics for typical automotive diesel fuel. The figure includes marks of the viscosity range allowed in the British specification for automotive diesel fuel (BS2869), together with the upper and lower limits (cold and hot risk points) for the UK climate, as defined by Lucas Diesel Systems.

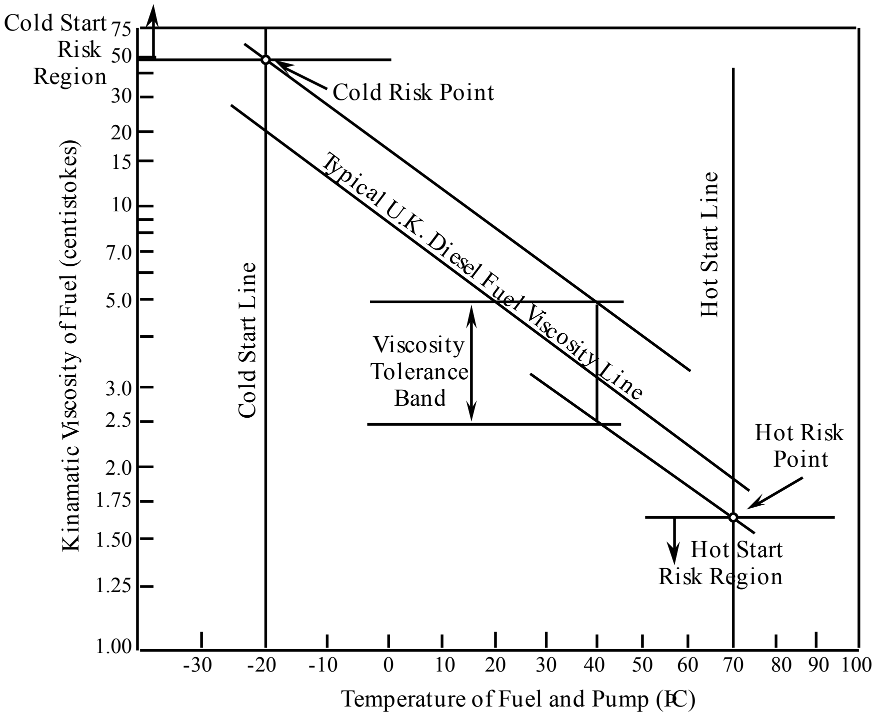


Figure 16.7: Diesel fuel viscosity limits for the UK. The upper and lower limits on the 40°C line are those of BS2869, while those at -20°C and 70°C are recommendations by Lucas Diesel Systems, [1]

Diesel Fuel Low Temperature Characteristics. As much as 20% of the diesel fuel may consist of relatively heavy paraffinic hydrocarbons, which have limited solubility in the fuels, [1]. Paraffins are most likely to deposit out as wax if cooled sufficiently. This is unfortunate because they have high cetane numbers. Wax in a vehicle fuel system is a potential source of problems of operation. The low temperature properties of the fuel are defined by wax related tests as follows:

- The Cloud Point test measures the temperature at which wax becomes visible when the fuel is cooled, according to the method described in ASTM D2500. It has the disadvantage of relying on the tester's judgment.

- The Wax Appearance Point is the temperature at which wax starts to come out of the solution, (ASTM D 3117).

- The Pour Point test is used to measure the temperature at which the amount of wax out of solution is sufficient to gel the fuel, (ASTM D 97).

- Other tests, like Cold Filter Plugging test and the Low Temperature Flow tests, are described in [1].

- Another way to estimate operational performance of a fuel is to combine the cloud point (CP) and the pour point (PP) in an empirical equation to obtain a Wax Precipitation Index (WPI):

$$WPI = CP - 1.3\,(CP - PP - 1.1)^{0.5}$$

<u>Stability of diesel fuel.</u> The ability of a diesel fuel to remain unchanged during the period between its manufacture and its eventual use in an engine is obviously a very important quality. The formation of sediment during the long term storage of diesel fuels, particularly those containing catalitically cracked stocks, has been recognized for many years, [37, 38]. Nitrogen and sulphur-containing compounds have always been strongly implicated in the fuel degradation process since these elements tend to become concentrated into fuel sediments. The mechanism by which the oxidation of hydrocarbons progresses occurs in several stages, starting with the chain initiation involving the generation of free radicals. Once a hydrocarbon free radical has been formed, it can combine with oxygen to form a peroxide radical which, in turn, can react with another hydrocarbon molecule, thereby generating other hydrocarbon free radicals and a hydroperoxide. The oxidation process is therefore self-perpetuating. The free radicals can also give rise to polymerization as well as oxidation reactions, to form high molecular-weight materials. These can deposit in the fuel system. The final stage (chain termination), in the absence of an antioxidant, is a reaction which leads to no free radical products.

More cracked gas oil is being diverted nowdays into diesel fuel. Distillates from cracking operations are more olefinic than those from atmospheric distillation and contain more nitrogen compounds, such as pyrolles and indoles. As a result, they are less stable being prone to oxidation by free radicals, as explained above. This is the reason why oxidation stability limits are being introduced into more diesel fuel specifications.

The ability of a fuel to maintain satisfactory storage stability is dependent upon a series of parameters which control its rate of autoxidation. With diesel and distillate fuels, the end products of these complex autoxidation reactions manifest themselves in two general types, namely a "soluble gum" which is essentially nonvolatile, and an "insoluble gum" which precipitates out in the fuel, [38]. It has been postulated that the insoluble gum, usually referred to as sediment, is the most harmful product of fuel deterioration in storage.

References [39, 40] show that although no significant degradation of diesel fuel quality has been observed in conventional storage of locally produced straight-run stocks, formation of degradation products in bus engine fuel systems has been observed by filter clogging and deposit formation. The main cause of these operational problems in the field may be attributed to the fact that diesel fuel, which serves also as an injector coolant, most probably deteriorates at the relatively high temperatures prevailing in part of the fuel tank, cooled and then heated again. The succession of heating and cooling cycles may cause deterioration of thermally unstable diesel fuel.

If oxidation take place, engine operation could be affected due to filter blocking or gummy deposits in the ignition system and on injector nozzles.

There does not yet exist a universally accepted test to predict the stability characteristics of a diesel fuel kept in normal storage facilities for prolonged periods, [1]. One accelerated method to test oxidation stability is described in ASTM D2274. The color of the fuel before and after aging can be determined by ASTM D1500. One of the alternative methods for predicting long term storage stability is ASTM D4625. Another test to evaluate gas oil stability during long term storage was proposed by [40], with a procedure designed to simulate diesel engine operation under field conditions. The test was successfully applied, especially after some improvements, [41].

Other alternative fuel oxidation stability test methods, like Esso Test, Du Pont F-21 Test, etc. are descried in [1].

Sulphur Content. One known method for reducing the total emission levels of particulate matter (TPM) from diesel engines is to use low sulphur (< 0.05 wt%) diesel fuel, [6, 42]. During the combustion process, the majority of the sulphur in the fuel is converted to sulphur dioxide (SO_2) which is mostly emitted into the environment where additional chemical reactions may occur, leading to atmospheric pollution. The rest of the SO_2 is oxidized in the oxygen-rich diesel exhaust and forms sulphur trioxide (SO_3). The high diesel exhaust temperature maintains the SO_3 emission in the vapor phase, which has a high affinity towards water. An exothermic reaction leads to formation of sulphuric acid aerosols, which, together with the chemically bonded water, is emitted as particulate matter, [42].

Another benefit of decreasing the sulphur level in diesel fuel is the wear reduction. It is known that high sulphur levels in the fuel cause wear in piston rings and cylinder liners. The contribution of sulphur to wear is due to two mechanisms: corrosive wear and deposit formation, which are directly dependent on fuel sulphur levels and engine operating conditions. Most legislation worldwide with respect to diesel fuel quality has focused, until now, on sulphur content.

In the US, a sulphur limit of 0.05% has been adopted for on-highway diesel fuel, and at the same time in Europe for automotive Diesel fuel, [15]. In 1991 Sweden enacted legislation that resulted in very stringent regulations: the maximum level of sulphur, revised in 1992 for the two classes 1 and 2 diesel fuels, are respectively 0.001% and 0.005%, [15]. To produce fuels with a sulphur content of less than 50 ppm and an aromatics content of 5 vol% or less (according to the specifications for the diesel fuel class 1), it is necessary to apply more severe hydro-processing conditions or invoke unconventional hydro-processing technology. Such processing technology will remove polar species from the fuel which adsorb onto the mating surfaces to form a protective low-friction layer. In fact, there is strong evidence that by severe hydro-treating, the manufactured automotive diesel fuel may increase the risk of premature mechanical failure of certain classes of fuel injection pumps. The events observed for the first time in Sweden, where strict, environmentally driven fuel specifications have been introduced, have confirmed the existence of this risk, [43]. The test method to determine the sulphur content is published in ASTM D 2622-82.

<u>Aromatic components</u> in diesel fuel is a problem of great concern because they tend to contribute to particulate emissions. A maximum content of 10% has been imposed by the California Air Resources Board (CARB) and there are suggestions by the Association of European Automobile Constructors (ACEA) for the aromatics content to be included in diesel fuel specifications. This association recommended in 1994 the limitation of the three-ring aromatics content to maximum 1.0% wt, [1]. It is emphasized that

aromatics make a major contribution to the lubricity of the fuel, so their removal can give rise to abnormally high rates of wear of the injection pump, a problem which was mentioned above, [33].

Water and Sediment Content. Water can not be completely eliminated from diesel fuel. The earliest stage at which water can get in is during the manufacturing processes. The main risks of water contamination are during transportation and storage in tanks. The presence of water in storage tanks may encourage growth of fungi or bacteria. Microbial contamination can cause significant problems with the working parts of engines, particularly the fuel system (for example filter blockage).

Sediments likely to be found in diesel fuel are mainly inorganic in origin: rust, metal particles and dirt. A certain part can also be organic, from degradation of unstable fuel components, bacterial action at the oil-water interface or wax from the fuel.

Water and sediments can contribute to filter plugging in the vehicle or in the distribution network and cause problems due to corrosion and wear in the engine and fuel injection systems. A standard test for water and sediment content is by a centrifuge method, ASTM D1796, which is in the ASTM D975 specifications for diesel fuel, [1].

Other diesel fuel properties, such as carbon residue, ash content, corrosivity, heating value, etc. are discussed in [1].

National requirements to diesel fuel quality in different countries worldwide are summarized in Appendix 2. This information is based on standards and CONCAWE data, [15]. Average values of some diesel fuel parameters (typical for Europe and USA), affecting pollutant emissions, are given in Table 16.16.

16.3.2 Requirements of engine technologies on diesel fuel quality

Pressure to reduce air pollution from motor vehicles has led to a wide range of modifications and innovations in modern diesel engines. For example, research and development work is devoted worldwide to: high pressure injection systems, with peak pressure at the injection nozzle varying between 1200 and 1800 bar with electronic control; injection timing control as a function of load and speed; using three, four and five valves per cylinder in light duty diesels; using of variable-resonance intake system and common rail systems. Turbochargers with variable geometry, as well as the continuous improvement of EGR use via electronic management systems, will also contribute to easier control of future emission limits, [45,46].

Table 16.16: Typical values of average-market diesel fuel parameters, [6, 44]

Property	Europe	USA, Winter 1996		
		East Coast	Mid West	West Coast
Cetane number	51	51	44	49
Density (g/l)	843	846	847	845
Poly - Aro (%)	9			
T95 (^{o}C)	355			
T90 (^{o}C)		314	310	320
Sulphur (ppm)	450	300	400	300

Oxidation catalysts will be used to lower CO, HC and particulate emissions, and also to improve the odor of diesel exhaust.

In order to decrease the fuel consumption and the emitted quantity of CO_2, the tendency now is to move from indirect (IDI) to direct injection (DI) diesels. It is claimed that they are showing 15 to 20% fuel economy advantages over the comparable IDI.

Even after engines have been optimized as regards emissions and fuel economy, increasingly stringent regulations are unlikely to be met unless fuel quality is maintained. The motor industry around the world has been active in promoting its ideas of appropriate fuel quality. In Europe, ACEA issued its Fuels Charter in late 1994. Based on the results obtained in the European Programme on Emissions, Fuels and Engine Technologies (EPEFE), a jointly funded project of the European Oil and Automobile Industries, represented respectively by Europia and ACEA this Fuels Charter will be changed. From these results it is concluded that the diesel fuel parameters which have the greatest influence on engine emissions are: cetane number, sulphur content, density, T_{95} (temperature at which 95% fuel is evaporated) and fuel polyaromatic content, [6, 47].

US diesel fuel has come under the spotlight from the Engine Manufacturers Association which is asking for improved quality for 1998. It proposes a huge change in cetane number to a 56 minimum as well as a minimum viscosity of 2.5 cs at 40° C, a big reduction in aromatics and a lubricity requirement, [47].

The quality of diesel fuel can also be improved by the use of additives, whose positive role has led the European motor industry to advocate their use or approve specific high quality fuels which have been upgraded accordingly. This is documented in the European Standard EN590 and was presented at the 1992 EC Symposium "Auto Emissions", [48]. Additives to improve the quality of diesel fuels are therefore beneficial for refineries, customers and the environment. Like gasoline additives, the use of diesel fuel additives is also an important marketing factor for the modern competitive fuel market.

16.3.3 Diesel fuel additives

Additives can enhance various diesel fuel properties. For example, ignition improver additives are used to increase the cetane number of the fuel. Detergent additives are considered to be of growing importance in controlling the formation of fuel deposits which can have detrimental effects on combustion. The build-up of lacquer and carbonaceous deposits on injector tips can affect the amount of fuel injected and the spray pattern, causing problems of reduced power and higher smoke emission. The cold flow performance of diesel fuel can be adjusted to prevailing climatic conditions by base component selection, but at the expense of cetane quality and an availability penalty. However, by using cold flow additives, the required low temperature filterability can be obtained at nearly constant cetane number and with less availability constraints.

Diesel fuel additives have the potential to improve the quality of diesel fuels with regard to emissions, noise, engine performance and customers perception, whilst offering flexibility in the optimization of refinery production costs.

There are several possible ways to classify diesel fuel additives. In the following, they are divided into two classes:

1. Additives influencing diesel fuel combustion: ignition improvers, combustion improvers, catalysts for regeneration of after-treatment devices and detergents.

2. Additives influencing storage and flow (antioxidants, antirust, anticorrosion, antifoam, dehazers, biocides, additives for low temperature operability, etc.).

16.3.3.1 Additives influencing diesel fuel combustion

Cetane (ignition) improvers are used to improve the cetane quality of marketed fuel components by reducing the delay between injection and ignition when fuel is sprayed into the combustion chamber. These additives are used in two different ways:

- To increase the cetane number of diesel fuel which would otherwise fail the specification limits.

- To increase the cetane number of diesel fuel above the specified minimum standard, to yield premium grade products now being marketed by many oil companies in certain locations throughout the world.

The chemicals most commonly used as ignition improvers are nitrates and specifically Ethyl-Hexyl Nitrate (EHN). Certain peroxides have been identified as effective cetane improvers, but there is less experience with the handling of these products in concentrated form in refineries and fuel depots. They are all materials that decompose readily, and at elevated temperatures generate free-radicals that accelerate oxidation of the fuel and initiate combustion.

The response to cetane improvers is dependent on individual fuel characteristics and on the cetane level, [49]. Results presented in Figure 16.8. were obtained from a large sample of fuels and show that, on the average, an improvement of about 3 numbers was obtained with a treat level of 500 ppm, and with 1000 ppm the gain was 5 numbers. The results show considerable variation about the average line and it was also found that the lower-cetane fuels had the poorest response. Another important result, seen from the figure, is that the same cetane number produces the same ignition delay, irrespective of whether the former is that of base fuel or treated one.

Figure 16.9. shows a very clear monotonic relation between the concentration of the ignition improver EHN and the cetane number for various chemical compositions of the fuel, [48]. Unfortunately, parrafins which have a comparatively high cetane number

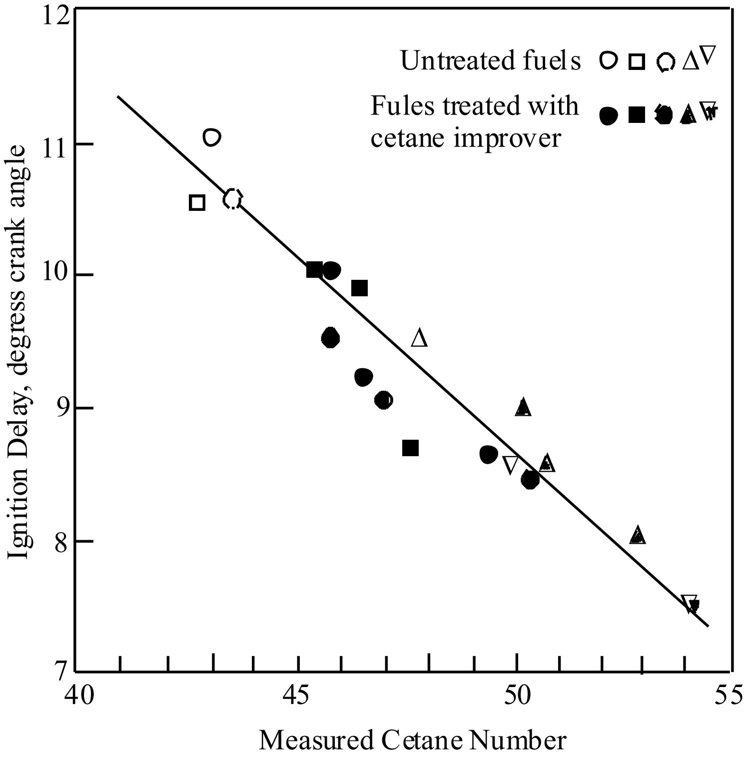


Figure 16.8: Influence of cetane number on ignition delay, [49]

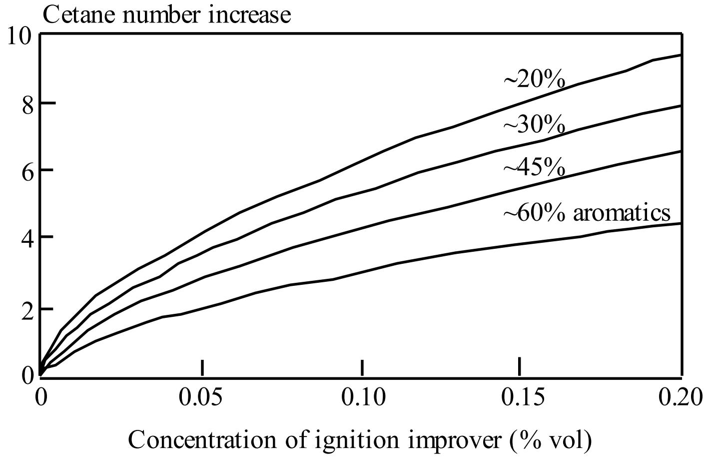


Figure 16.9: Response of different base fuels to ignition improvers, [48]

respond best, and aromatics, with their lower intrinsic cetane quality, have a poorer additive response. The graphs in Figure 16.9 show also that increasing the amounts of EHN produce smaller improvements. In practice, for example, the cetane quality of typical European market diesel fuels can be increased by about 2 - 4 units using 500 ppm of EHN as shown in Figure 16.10 [48].

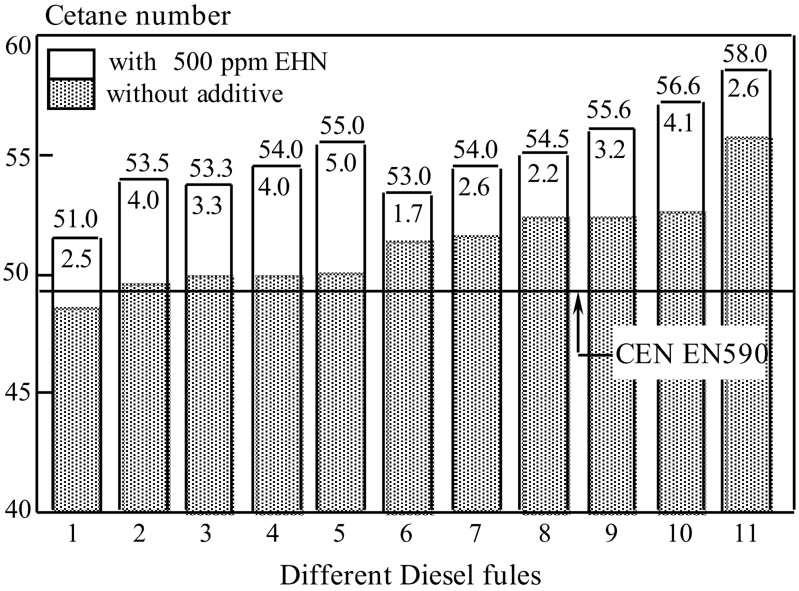


Figure 16.10: Increasing cetane number by adding ignition improver for different European diesel fuels, [48]

A very comprehensive study of cetane response of post 1993 US no. 2 diesel fuels, following the introduction in 1993 of the federally mandated 0.05% sulphur on-highway diesel fuel, is presented in [50]. Seven fuels, obtained from the East Coast, Gulf Coast and Midwest refineries, an emissions certification fuel and a low aromatic California fuel were evaluated. EHN was used as cetane improver in concentration of up to 1% vol. The test results demonstrated relatively low cetane response of non-California fuels and an exceptionally high response of the low aromatic California fuel. In the conclusions of this study, an inter-industry program was proposed to gain a detailed understanding of diesel fuel composition and property effects on cetane response, and proved cetane response equation applicable to the range of diesel fuels, [50].

Cetane improved fuels, whether achieved by component blending or by additives, improve cold starting, and reduce idle noise, white smoke and regulated emissions.

Figure 16.11 shows the influence of ignition improver on the decrease of particulates for a heavy duty engine.

The positive effect of adding ignition improvers to fuels, with different cetane numbers on HC and CO emitted from heavy duty and passenger engines, are shown in Figure 16.12.

Combustion Improvers additives for diesel fuels are additives which have a catalytic effect on the combustion process in the engine. The majority of these are organo-metallic compounds in nature, containing manganese, iron, barium or calcium. These additives are effective in reducing smoke emissions. During the 1960s and 1970s a range of products containing barium (sometimes together with calcium or iron) were commercialized as smoke-suppressant additives. Despite their obvious effectiveness in reducing smoke from diesel engines, widespread use of smoke suppressant additives did not develop. Additive cost, together with concern over deposit build-up within engines, the negative effect of additives on particulates emissions and the high toxicity of barium compounds, are all contributory factors, [1, 34, 51, 52].

Different studies, carried out recently, have had the objective of using additives for particulate traps regeneration. Diesel soot ignites at 550 - 650^{o}C. If the diesel engine exhaust gases reach these temperatures during operation, the heat of the exhaust is sufficient to ignite the soot and regenerate the filter. However, diesel exhaust is fairly cool, and typical exhaust gas temperatures in diesel engines are in the range of just 150 - 350^{o}C. Regeneration temperatures in the low 400-s ^{o}C have been achieved with catalytic coatings on the particulates trap substrate, while it has been shown that organo-metallic additive compounds are effective in promoting carbon oxidation by lowering its ignition temperature, [34, 53].

Table 16.17 summarizes the organo-metallic compounds used as fuel additives for catalytic regeneration of particulate traps (after-treatment devices) in diesel engine exhaust systems.

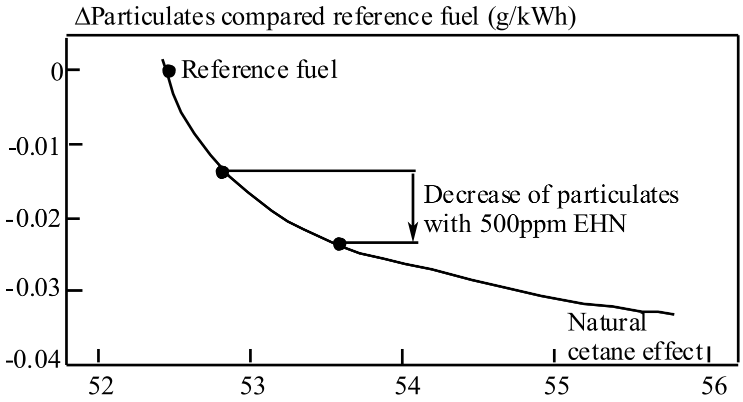


Figure 16.11: Influence of cetane improvers and of natural cetane effect on particulates reduction of a 6.9 DI engine, [48]

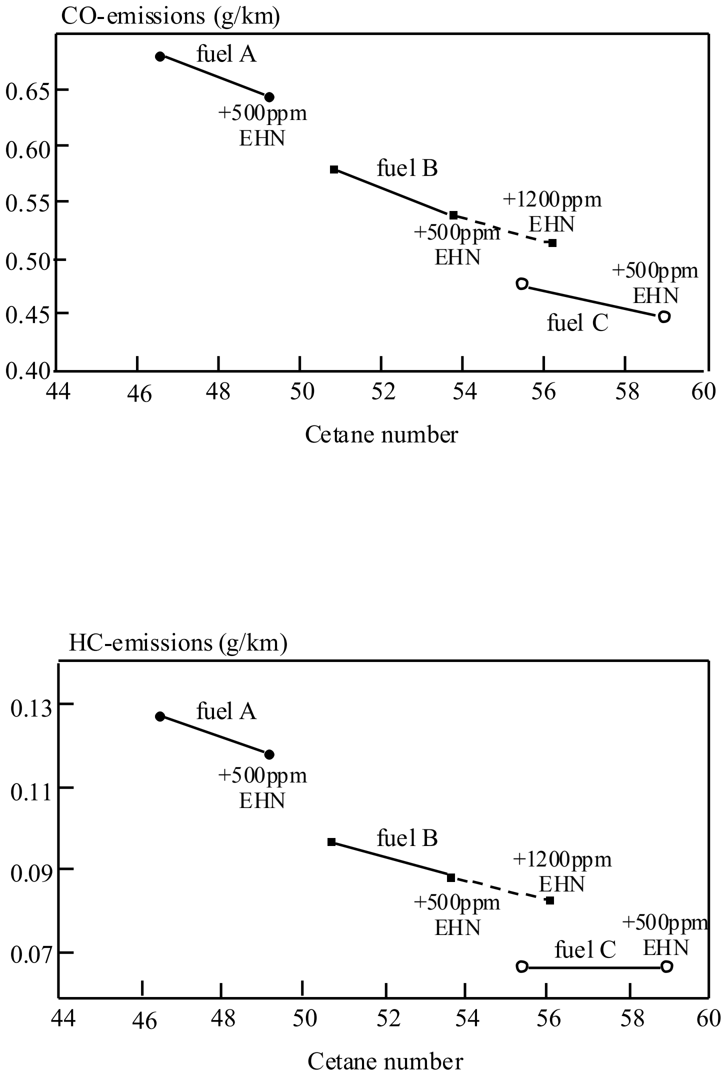


Figure 16.12: Influence of cetane improvers on HC and CO emissions of 3 IDI diesel , [48]

Table 16.17: Organo-metallic compounds used as catalytic additives for particulate traps regeneration, [53]

Metal	Organometallic compounds
Ba	carbonate, sulphonate
Ca	carboxylate, naphtente, sulphonate
Ce	carboxylate, carbonate
Ce+Mn	?
Cu	naphtenate, carboxylate, octoate, pivaloylpinacolonate
Cu + others	cetate, naphthenate, octoate + (Ce, Mn, Ni, Pb) organometallic compounds
Fe	acetylacetonate, carboxylate, ferrocene, naphtenate
Li	*t*-butoxy
Mn	corboxylate, methylcyclopentadienyl-Mn-tricarbonyl, oxide, sulphonate
Na	*t*-butoxy
Ni	naphtenate
Pb	naphthenate, tetra-ethyl
Zn	carboxylate

The exact nature of the organic part of the fuel additive is of limited importance, since after combustion metal oxide or metal sulphate particles remain, which are well distributed within the diesel particulates. The organic part of the additive determines its fuel solubility, and for some metals this solubility is found to be a problem. Several metals have been used in fuel additives, as can be seen in Table 16.17. The concentration of the additives can influence both the activity and the lifetime of the filter which becomes clogged by ash. As underlined by [53], data in the literature are ambiguous regarding the relative activity of such additives: some authors have found copper to be the most active fuel additives, others claim that manganese or its combination with copper are more active.

Many problems still remain to be solved before organo-metalic additives can be introduced into the market for general application: too high temperature or thermal stresses during filter regeneration; fuel deposits in combustion chambers or fuel injector nozzles; accumulated ash in the traps, etc. However, in spite of these problems, it seems that the concept of fuel additives for regeneration of after-treatment devices provides an interesting and promising route for catalytic removal of soot from diesel exhaust gases.

Detergent additives. An important property of the reformulated diesel fuel (called also premium or low-emission) is its detergency, which is essential for maintaining good performance of the engine between periodic servicing. The use of detergent additives, which has become widespread in Europe during the last decade, was evoked by problems of injector nozzle fouling (or coking). Nozzle coking is induced by thermal degradation of fuel and crankcase lubricant components, and worsened by hot combustion gases. This results in slower initial combustion and pressure rise delay in the cylinder, with subsequent increased rate and higher peak pressure, [54]. These effects cause increased engine noise, emission of pollutants and fuel consumption. Detergent/dispersant additives containing surfactants can prevent deposit formation ("keep-clean"), and remove detrimental deposits already formed ("clean-up") in fuel injectors. Thus they yield and ensure good spray pattern characteristics, and maintain engine performance and pollutants emission at best levels possible for in-use engines, [54-56]. A range of substances is now suitable as detergent additives for diesel fuels: amines, imidazolines, amides, fatty acid succinimides, polyalkylene succinimides, polyalkyl amines, polyether amines, etc., [48, 58]. Evaluating the performance of detergent/dispersant additives is an important aspect in the development of good quality product for use. Care must be taken when selecting additives in order to avoid any problems created by adverse side effects resulting from their addition to the base fuel, [55]. Two recognized test methods are mainly employed now for performance evaluation of detergent additives: in Europe, the test is based on the widely used Peugeot XUD 9 1.9l light duty IDI diesel engine, and in the US on the Cummins L-10 engine, [54]. The latter is increasingly becoming accepted as test standard for performance evaluation of detergent additives for controlling nozzle fouling in DI engines. A screening test for evaluating available detergent/dispersant additives to diesel fuel is described in [58].

The detergent influence on emission performance is illustrated by a test vehicle which was operated under part load city type driving conditions with and without a detergent in the fuel (Figure 16.13). While the base fuel shows a clear increase of particulates emissions over the test periods, the fuel containing maintains nearly constant emission level.

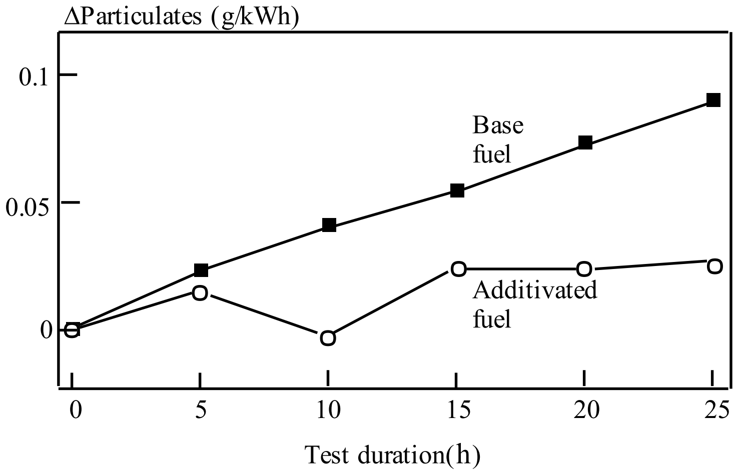


Figure 16.13: Effect of diesel fuel detergent additive on particulates emissions, [48]

16.3.3.2 Additives influencing storage and flow

Stability additives exert a favorable effect on diesel fuel in the course of prolonged storage; on the other hand, relatively little is known on the resistance of various stabilized diesel fuel to thermal stresses, [40]. Antioxidants, stabilizers and metal deactivators are types of additives which are sometimes used in diesel fuels, considered to be prone to oxidative or thermal instability due to the components used in their preparation. The additives work by terminating free-radical chain reactions that would result in color degradation and the formation of sediment and insoluble gums. In some countries a fuel might be unacceptable for marketing as automotive diesel fuel if the maximum color specification is exceeded, [34]. Additive treatment does not only mean that the refiner has to control the oxidation reactions that occur in uninhibited cracked gas-oils. As explained above, diesel fuels have to conform to a sulphur specification, and this is achieved by a hydrodesulphurization process. The process also improves fuel stability by removing nitrogen- and oxygen-containing compounds and saturating the more reactive olefinic compounds, which are typically present in catalytically cracked gas-oil. When only a mild degree of hydrogen treating is required to meet the sulphur specification, an antioxidant may be added to ensure that the fuel is adequately stabilized, [34].

Antioxidants used in diesel fuels are usually hindered phenols that prevent high temperature gum-forming reactions.

Stabilizers are amines or other nitrogen-containing basic compounds that prevent sediment formation at ambient temperatures by interfering with acid-base reactions. The effectiveness of additive treatment strongly depends on the dominant fuel characteristics that determine the degradation reactions.

Metal deactivators are sometimes used in conjunction with stability improvers to prevent oxidation reactions from being catalyzed by heavy metal ions, particularly copper, which may be present in trace amounts in the fuel. One of the most commonly used metal dactivator additives is N,N' - disalicylidene - 1,2 - propanediamine, which works by chelating the dissolved metal to form a non-catalytically active compound, [34].

Corrosion inhibitors are often used to prevent corrosion or rusting because it is almost impossible to avoid the presence of water in diesel fuel systems. These additives include esters or amine salts of alkenyl succinic acids, alkyl orthophosphoric acids, alkyl phosphoric acid and aryl sulfonic acids. Selection of the suitable additive and treat rate is usually determined by using the rusting test ASTM D665, [1].

Biocides are used sometimes for diesel fuel treatment to prevent the growth of bacteria and fungi in the bottom of fuel tanks. The commercial biocides are based on a wide range of chemical types including boron compounds, amines, imines, imidazolines, etc., which need to be soluble in both the fuel and water or in the water phase only, [1, 34, 57]. A problem with biocidal treatments is that the bacteria can develop resistance, so the additive type must be changed from time to time, [57].

Dehazers and demulsifiers may be used occasionally if the fuel becomes hazy due to the presence of finely dispersed droplets of water. If the haze persists after the normal one or two days settling time, additive treatment may be necessary to accelerate clearance. Effective dehazer additives include quaternary ammonium salts.

Antifoam additives must reduce the amount of foam build-up in the vehicle tank during filling and must destroy quickly the foam produced. Antifoamants are sometimes added to diesel fuel, often as a component in a multifunctional additive package. Using them enables avoiding the nuisance of stains and unpleasant odor, and reducing the risk of spills polluting the ground and the atmosphere. Typical antifoam additives are silicones having, a molecular weight suited to the fuel charactristics [34].

Odor Masks and Odorants. Because diesel fuel is less volatile than gasoline, the stain and smell of spills will persist, which can be very unpleasant, particularly if clothing is contaminated. Elimination of the smell is undesirable because it facilitates the detections of leaks, so the aim is at modifying it by partial masking with a more acceptble odor. Various products, with a choice of fragrances, are commerically available to satisfy the consumer's preference.

Antistatic Additives are added to diesel fuel to avoid the risk of an explosion due to a charge of static electricity building up during fast rates of pumping, as may occur during the filling or the discharge of road tankers. These additives lead to increase of the fuel conductivity, allowing an electrostatic charge generated during pumping to be dissipated. The treatment is usually with a chromium-based additive, [1].

Drag reducers are sometimes used to increase pipelines capacity. They are high molecular-weight, oil soluble polymers which shear very rapidly and reduce drag. In a pipline, effectiveness of a flow improver can be expressed in terms of percent drag reduction, defined as:

$$Percent\ DR = \frac{p - p_{DR}}{p} \cdot 100$$

where p is the frictional pressure drop associated with the untreated fluid and p_{DR} is the frictional pressure drop of the fluid containing the drag reducing polymer, [59].

Additives to improve cold weather performance. Cold flow improvers or wax anti-settling additives (WASA) were among the first additives used in diesel fuels. However, they are difficult to distribute uniformly throughout the fuel in quantities adequate for them to be efficient. This was the reason for developing new additives for modifying the shape of the wax crystals to enable them to pass the Cold Filter Plugging Point test (CFPP), [59]. A number of different materials were found to be effective as CFPP improvers, but all the products in current commercial use are ashless co-polymers of ethylene and vinylacetate or other olefin ester co-polymers. These additives have no influence on the fuel other than on its low temperature properties and are compatible with the other types of additives used in automotive diesel fuel. They modify the shapes of the wax crystals, which otherwise are flat platelets, tending to gel together. There are three types of wax crystals modifiers: pour point depressants (PPD), flow improvers and cloud point depressants (CPD), [1, 33, 34]. Close studies into the effect of wax modifiers have shown that some olefin-ester co-polymers appear capable of suppressing wax crystallization by a few degrees, [60]. The small compact wax crystals formed in a flow-improved fuel, have a greaer tendency to settle to the bottom of the fuel tank. This is more of a problem in storage tanks than vehicle fuel tanks, but wax anti-settlilng additive can nevertheless play a useful part in the avoidance of wax enrichment, as vehicle fuel tanks become empty, especially in very cold climates, [34].

Anti icers additives are used in some countries to prevent ice plugging of fuel lines by lowering the freezing point of small amounts of free water which may be separated from the fuel. These additives are relatively low molecular-weight alcohols or glycols with a strong affinity to water, [1].

Lubricity additives is a new class of diesel fuel additives, which have to be used when the diesel fuels lose their own lubricity proprieties. As explained above, the reduction in sulphur content can reduce the lubricating properties of the fuel, [1, 47].

16.3.4 Influence of diesel fuel quality on emissions

Many independent studies have been carried out to assess the effect of fuel properties on diesel engines emissions [42, 53, 61, 62, 63]. A general conclusion from these studies is the clear correlation between certain fuel characteristics and vehicle exhaust emissions. This fact is confirmed by the recent results obtained in the EPEFE research programme, which was a very comprehensive investigation of the effects of vehicle/fuel technologies on exhaust emissions, [5, 6, 65, 66]. It involved a set of light duty (LD) vehicles, including engines with indirect injection combustion chambers (IDI) and engines with direct injection (DI); part of them turbo-charged and the majority intercooled. The heavy duty (HD) engines were all DI designs, and were all turbochargd and intercooled. All of the light duty vehicles were equipped with exhaust catalysts and all except two with exhaust gas recirculation (EGR), [65].

The test vehicles and engines were all designed to meet the least 1996 European emissions standards, as shown in Table 16.18. A matrix for 11 diesel fuels, shown in Figure 16.14, was created in this programme to cover the selected variables of density, poly-aromatics, cetane number and T95. The fuel properties were changed in this study over the range of the EPEFE fuel matrix, i.e.: density – 855 to 828 kg/m^3; poly-aromatics – 8% to 1% wt; cetane number – 50 to 58; T95 – 370^{o}C to 325^{o}C.

The emissions measured in this study included toal hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO$_x$) and particulates (PM) as well as hydrocarbon speciation and compositional analysis of particulates, tested to the European driving cycle for the year 2000, [66]. The overall fuel effects on emissions, obtained from the results of

Table 16.18: European emission limits for diesel engines, [65]

LD limit, g/km		HD limit, g/kWh	
		NO$_x$	7.0
PM	0.08	PM	0.15
HC + NO$_x$	0.7	HC	1.1
CO	1.0	CO	4.0

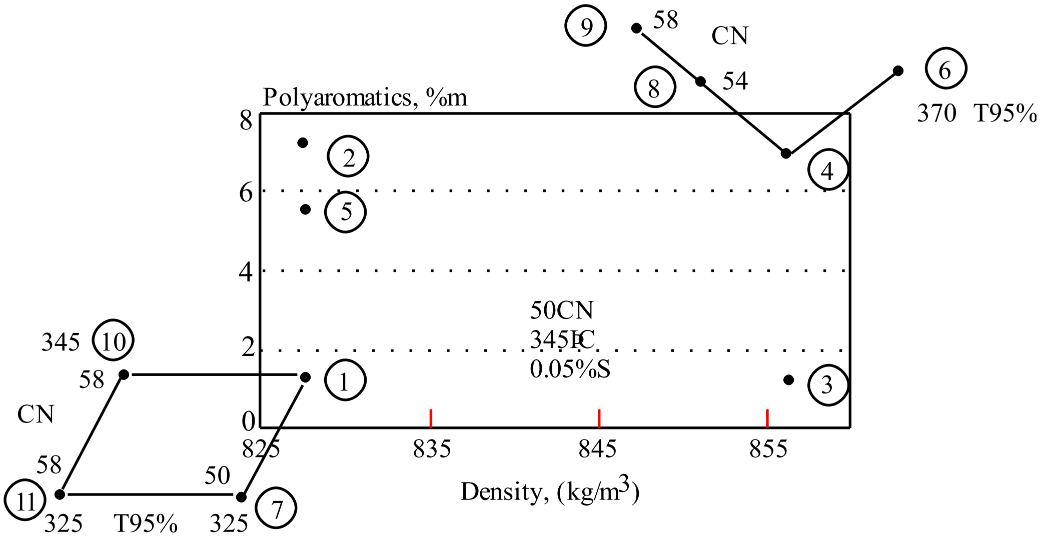


Figure 16.14: EPEFE diesel fuel matrix for 11 fuels, [67]

a large amount of data, are summarized in Table 16.19. The overall effects on emissions of changing simultaneously all four fuel properties are shown in Figure 16.15 for LD and HD engines.

Table 16.19: Summary of estimated effects of fuel property changes on diesel engine/vehicle emissions, [5]

	Property	**Change**	CO	HC	NOx	PM
Light Duty Vehicles**	Reduce Sulphur	2000 to 500 ppm	0	0	0	↓
	Reduce Density*	850 to 820 kg/m^3	↓	↓	0	↓↓↓
	Reduce Poly-Aromatics*	6 to 3% v/v				
	Increase Cetane No.	50 to 55	↓↓	↓↓	±0	↓
	Reduce T95	370 to 330 ÞC	-0	-0	-0	-0

	Property	**Change**	CO	HC	NOx	PM
Heavy Duty Engines**	Reduce Sulphur	2000 to 500 ppm	0	0	0	↓↓
	Reduce Density*	850 to 820 kg/m^3	0	0	↓	↓
	Reduce Poly-Aromatics*	6 to 3% v/v				
	Increase Cetane No.	50 to 55	↓	↓	↓	↓
	Reduce T95	370 to 330 ÞC	-0	-0	-0	-0

Note (1) : *Insufficient data is available to reliable separate the influence of these parameters, which will be subject of further study.
**Above effects are not necessary additive.

Note (2) : Europia also requested the following uncertainties to be expressed
- Light duty replace↓ by↓? for HC and CO
- Heavy duty replace↓ by↓? for NOx
- For T95 all zeros should be plus/minus zero

Note (3) : ACEA broadly agreed with the effects as written

Key

0=no effect	±0=-2to+2%	↑ or ↓= 2-10%effect	↑↑ or ↓↓= 10-20%effect
↑↑↑ or ↓↓↓= >20%effect	?=Insufficient information		

Density: 855 > 828g/l, Poly-aromatics: 8 > 1%, CN: 50 > 58, T95 : 370 > 325ÞC

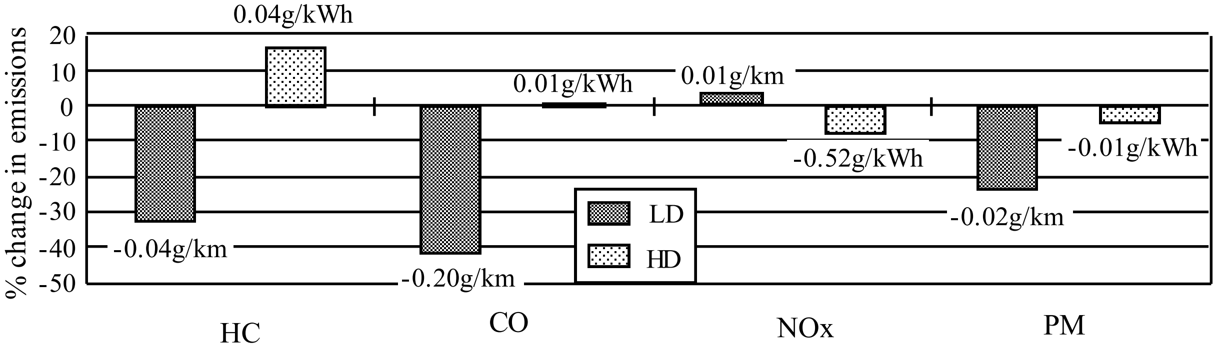


Figure 16.15: Overall effects on emissions of changing simultaneoulsy fuel properties (two sets of data: LD and HD engines), [65]

From results in Table 16.19 and Figure 16.15, the following important conclusions can be drawn:

- Fuel effects are greater for light duty vehicles than for heavy duty engines.

- The variation of diesel fuel quality can lead to considerable spread in the emissions of CO, HC and particulates.

- For LD vehicles, the change in fuel properties with regard to the reference point (a hypothetical fuel with density 855 kg/m^3, poly-aromatics 8%, CN 50 and T95 370^{o}C) caused decrease of CO, HC and PM emissions with a slight increase of NO$_x$, whereas for HD engines NO$_x$ and PM were decreased with an increase of HC emissions.

- When fuel properties were changed in this way, only PM changed in the same direction for LD and HD engines, but HC and NO$_x$ changed in opposite directions.

- The principal fuel parameters affecting vehicle emissions (both light and heavy duty) are sulphur content, cetane number, density and poly-aromatic content. Distillation characteristics can be considered an additional factor but their effects appear to be small.

Other conclusions from this research programme, [5], are:

- Sulphur has little effect on emissions from light duty vehicles without catalysts but has a larger effect on heavy duty emissions, especially when an oxidation catalyst is used.

- Emissions from cetane improved fuels are equivalent to fuels of the same cetane number without additives.

Figure 16.16 shows separately the effects of vehicle and fuel on emissions. In this Figure, two marks are shown for each emissions parameter for the two data sets (LD and HD vehicles). The left mark shows the mean and the range of variation for the different test of vehicles/engines, calculated as the average of the results for all tested fuels. The right mark shows the same data for all the tested fuels, based on the average for all vehicles or engines. It is clear from this Figure that fuel effects on emissions is strongly dependent on the engine technology.

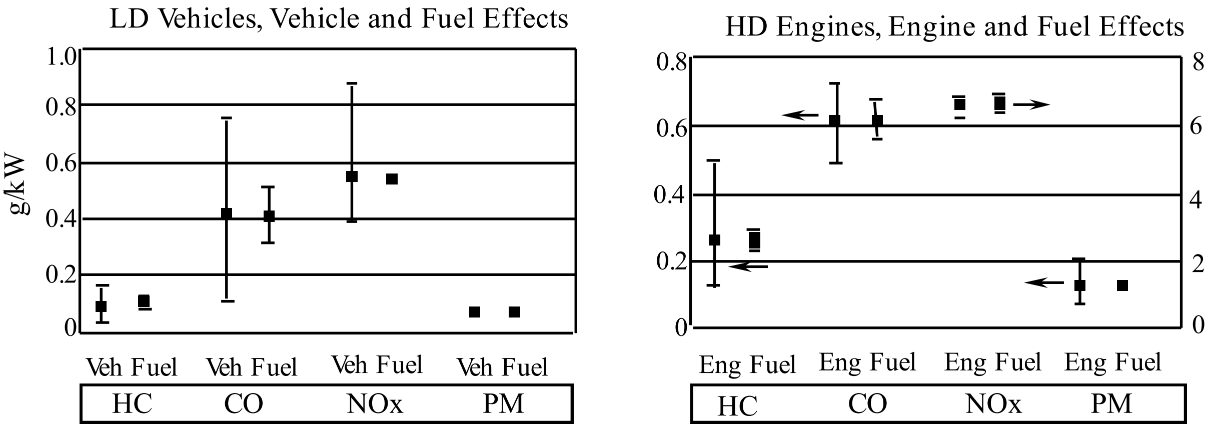


Figure 16.16: Vehicle and fuel effects on emissions, [65]

Figure 16.17 shows the effects of separate fuel changes on HC, CO, PM and NO_x emissions.

For a better understanding of the relationship between fuel/engine technology, two generations of development, 1992, 1996 and also one heavy duty engine from the same model line were tested on the EPEFE diesel fuel matrix by a CONCAWE research group. A set of test results concerning, for example, the effects of fuel density change on emissions is shown in Figure 16.18 for the two HD engines. One conclusion of this comparative study is that advanced engine technology has reduced the sensitivity to fuel property changes, [67]. The variations observed in Table 16.19 and in Figures 16.15 - 16.18 suggest that more remains to be learned about the interaction of vehicle/engine technology and fuels, [65].

Based on the experimental data obtained in the EPEFE study and on recent data from the literature which involve parameters not considered in the former, like the effect of sulphur on emissions, quantifying equations were established. These equations, [6], are reproduced in Table 16.20. They represent complex relationships between diesel fuel properties and vehicle emissions. These equations are not simple and it is not possible to use individual parameters alone to derive emission factors. However, they open new possibilities of predicting the fuel performance effects on the emission responses of given emission control technologies used in vehicles diesel engines. As underlined in [6], these equations were essential for the Auto-Oil proceedings, since they provided the required

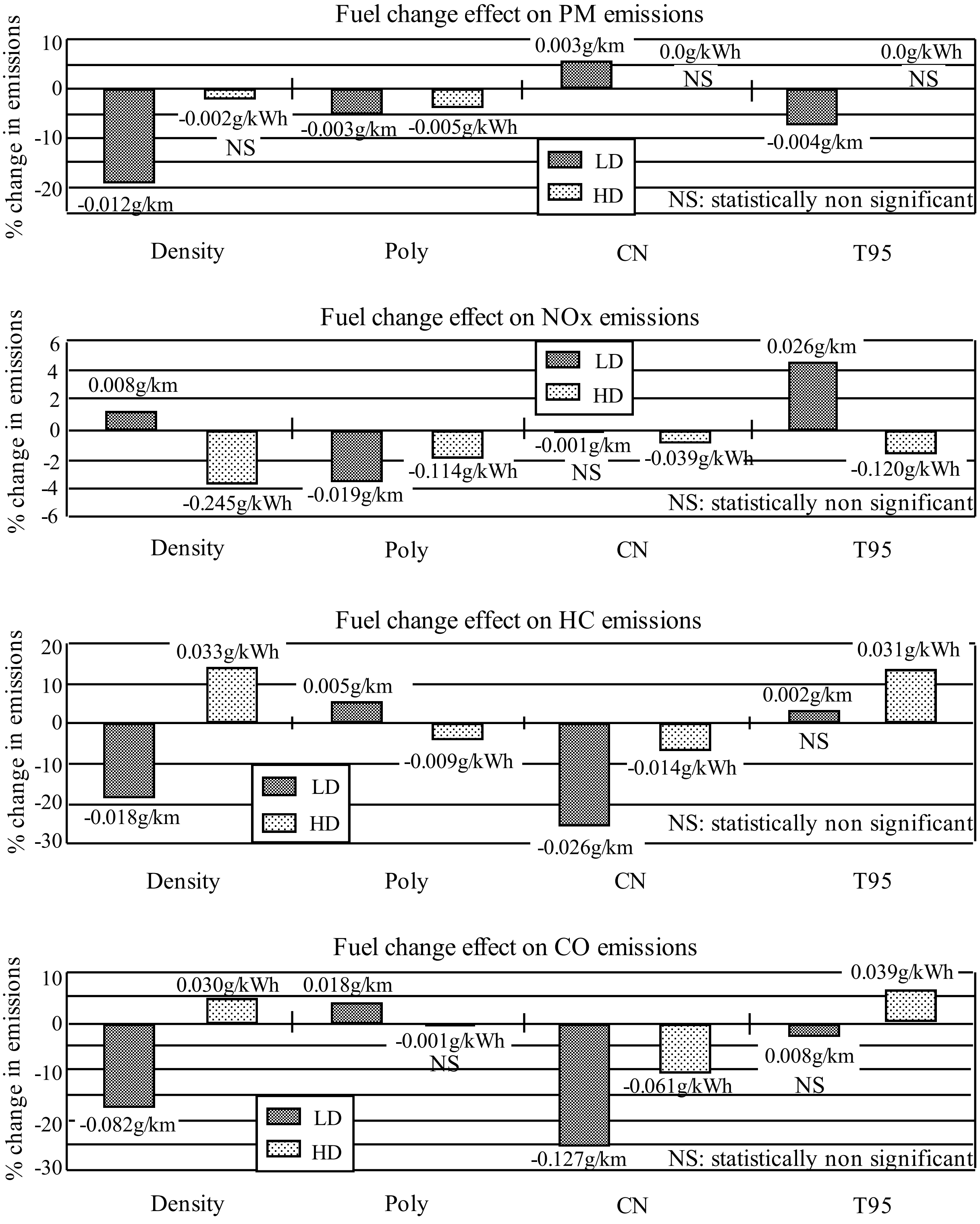


Figure 16.17: Effects of separate fuel changes on emissions, [65]

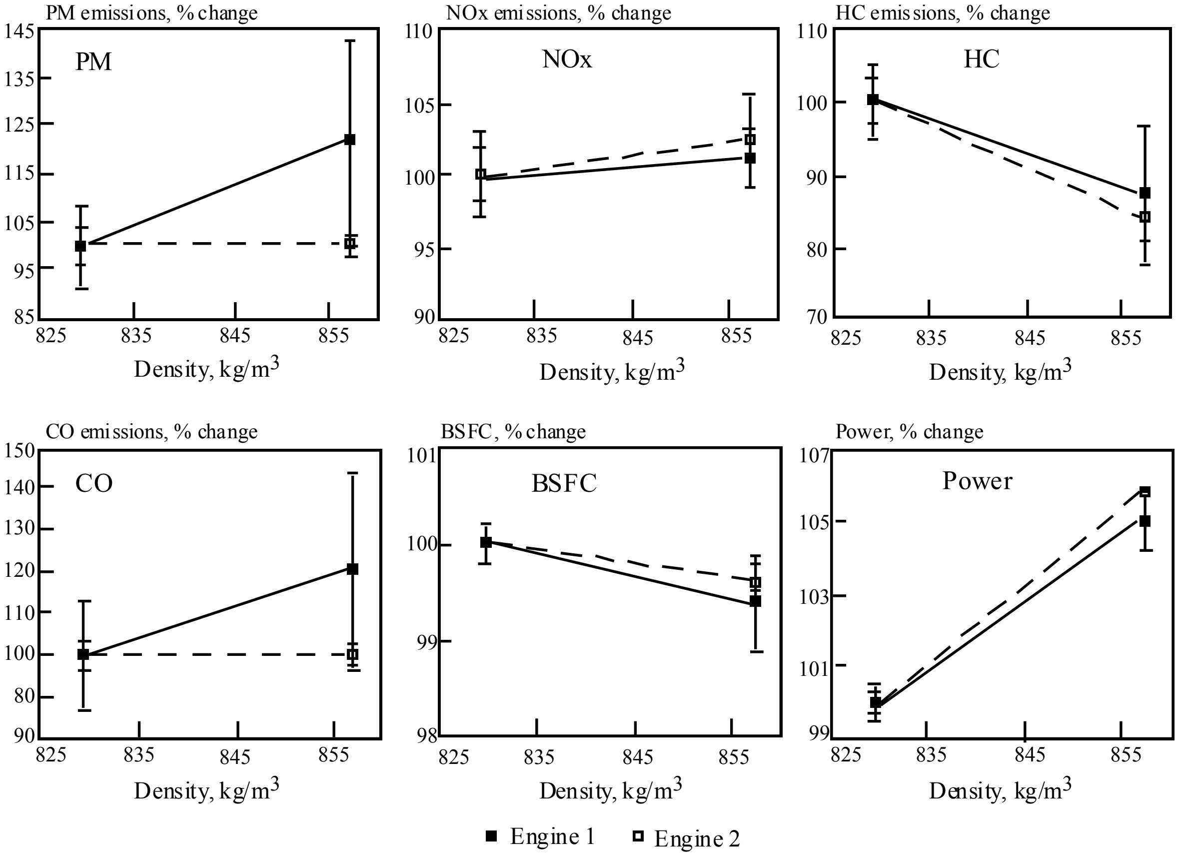


Figure 16.18: Comparison of engine technology response to fuel density, [67]

input (for both the air quality models and the processes whereby these models were used) for searching the optimum combination to achieve the air quality objectives for Europe for the period 2000 - 2010. As mentioned by EPEFE, [6], the developed equations are valid within a wide range of test procedures, vehicle/engine technologies and fuel parameters, used in their study, but great care must be taken in extrapolating from these results. According to the developments of vehicle technologies, test procedures and refining process, it will be necessary to further investigate and validate the conclusions reached.

16.3.5 Main trends in diesel fuel specification developments

Environmental legislation pressure will continue to be the major factor in influencing fuel quality. Thus the main trends of the development in diesel fuel properties and composition are in accordance with environmental legislation trends, and with fuel-emission responses related to the change in engines/vehicle technologies as described in the previous section. The various research programmes which were carried out, especially

Table 16.20: AUTO/OIL PROGRAMME - Equations of the Fuel/Engine Technologies Responses (source: SAE Paper No. 961076)

A. Light Duty Diesel

CO (g/km)

-1.3250726 + 0.003037 **DEN** - 0.0025643 **POLY** - 0.015856 **CN** + 0.0001706 $\mathbf{T}_{95}$

HC (g/km)

-0.293192 + 0.0006759 **DEN** - 0.0007306 **POLY** - 0.0032733 **CN** - 0.000038 $\mathbf{T}_{95}$

$\mathbf{NO}_x$ (g/km)

1.0039726 - 0.0003113 **DEN** + 0.0027263 **POLY** - 0.0000883 **CN** - 0.0005805 $\mathbf{T}_{95}$

PM (g/km)

[-0.3879873 + 0.0004677 **DEN** + 0.0004488 **POLY** + 0.0004098 **CN** + 0.0000788 $\mathbf{T}_{95}$[x
x]1 - 0.00016)450 – **Sulphur**([

B. Heavy Duty Diesel

CO (g/kW.h)

2.24407 - 0.0011 **DEN** + 0.00007 **POLY** - 0.00768 **CN** - 0.00087 $\mathbf{T}_{95}$

HC (g/kW.h)

1.61466 - 0.00123 **DEN** + 0.00133 **POLY** - 0.00181 **CN** - 0.00068 $\mathbf{T}_{95}$

$\mathbf{NO}_x$ (g/kW.h)

-1.75444 + 0.00906 **DEN** + 0.0163 **POLY** - 0.00493 **CN** + 0.00266 $\mathbf{T}_{95}$

PM (g/kW.h(

)0.06959 + 0.00006 DEN + 0.00065 **POLY** - 0.00001 **CN**( ]1 - 0.000086 x
x)450 – **sulphur([**

DEN density (g/l) **CN** Cetane Number **Sulphur** fuel sulphur content (ppm)
POLY fuel polyaromatic content (%wt)
$\mathbf{T}_{95}$ Temperature at which 95% fuel is evaporated

in USA: California Air Resource Board (CARB), Coordinating Research Council (CRC), Air Pollution Research Commission (APRAC), etc., and Europe: European Programme on Emissions and Engine Technologies (EPEFE), etc., have had the objective to investigate the effects of fuel properties on emissions. These include cetane number, sulphur content, aromatic (or only poly-aromatic) content, density, distillation (volatility upper limits), etc. Based on these studies, new fuel specifications were recommended for the future or have already been implemented, [1, 15, 62, 68, 69]. These reformualted products have been given many other names, such as clean diesel, premium diesel, high purity fuel or low emission diesel fuel (LEDF). Some of these products are currently available in different countries.

The new specifications would include higher values for cetane numbers, lower sulphur content, a maximum aromatic content (especially polycycle aromatics), lower density value, lower T95 or distillation end point, use of additives to control injector deposits, etc. In general, reformulated diesel fuel specifications reflect the main trend in the formulation developments of diesel fuels as follows:

Increase of cetane number. The performance of diesel engines has traditionally been strongly related with cetane quality of diesel fuel as principal parameters. Table 16.21 shows the cetane number specifications for different countries together with samples test results. The engine manufacturers from the USA and Europe continue to request fuels with higher cetane number, so there exist further opportunities for fuel reformulation and for the utilization of cetane number improver. Thus, the European Association of Automobile Constructors (ACEA) and the US Association of Engine Manufacturers are pressing for higher cetane number specifications to enable more stringent emissions targets to be attained. As mentioned in section 16.3.4, the ACEA Fuel Charter recommends a minimum cetane number of 53 and the Engine Manufacturers Association proposes a huge change in cetane number to a 56 minimum.

Decrease of sulphur content. In order to reduce emissions from diesel engines, especially particulate, legislation is being implemented around the world to lower the level of sulphur present in diesel fuels. Table 16.22 shows the allowed maximum sulphur content, for different countries, in comparison to the limits before these new implementations In the proposal of the Auto Oil European Commission for diesel fuel specification which is intended to be implemented by the year 2000, that the sulphur content be limited to 350 ppm (see Table 16.23).

Table 16.21: Cetane number specifications for different countries and sampling test results (winter 1996), [13, 15, 43]

Country	Standard	Grade	Cetane number	Winter 1996 - Quality survey		
				Typical Ranges		Average
				Min.	max.	
Austria	0-Norm EN 590 1.2.94	Winter Fuel Intermediate Summer	49	48.7	50.4	49.7
Belgium & Luxemburg	NBM EN 590	Winter Intermediate Summer	49	47.2	54.4	50.5
Denmark	CEN Diesel	CEN Diesel	49	49.3	53.7	50.8
Finland	Reformulated Diesel	Summer Winter	49 47	48.2	50.8	49.6
France	EN 590: 1993	Summer Winter Grand Froid	49	46.5	50.7	49.2
Germany	DIN EN590: 1993	Summer Intermediate Winter	49	47.7	54.7	50.9
Italy	EN 590-93	Summer Winter	49	46.3	54.8	49.3
Japan	JIS K2204 (1992)	Grade 2 Grade 3	45 45	46.9 48.3	59.8 54.0	53.2 50.3
Spain	EN 590 (1993)	Summer Winter	49	46.7	58.0	51.2
Sweden			50	51.6	53.6	52.6
U.K.	BS EN 590:1993		49	47.9	55.2	50.9
U.S.A.	ASTM D975 (1994)	Low Sulphur	40	40.8* 39.6** 43.3***	49.0* 49.5** 56.8***	44* 43.9** 48.6***

* US East Coast; ** US Mid-West; *** US West Coast

Table 16.22: Maximum allowable sulphur content of automotive diesel fuel for different countries, [14, 15]

Country	Effective date	Maximum Sulphur Content % m/m (max)	
		present values	previous values
Europen Union	from 01.10.1996	0.05	0.2 (1994)
Austria	from 01.10.1995	0.05	0.15 (from 1986)
Germany	by agreement	0.05	0.2 (1994)
Switzerland	from 01.01.1994	0.05	0.2 (1993)
United States	from 01.10.1993	0.05	0.5 (1992)
Japan	from 01.05.1997	0.05	0.2 (1996)
Israel	from 01.07.1997	0.05	0.2 (1996)
Sweden(1	from 1993	grade EC_1 0.001 grade EC_2 0.005 grade EC_3 0.20	0.2 (1990)
Denmark(1	from 01.06.1992	grade $A_{\text{quality}}^{\text{CEN}}$ 0.2 grade $B_{\text{qualaity}}^{\text{CEN 0.05\%}}$ 0.05 grade $C_{\text{UltraLightDiesel}}^{\text{PublicBusService}}$ 0.05	
Finland(1)	from 01.06.1993	Reformulated Diesel 0.005 Standard Diesel 0.2	0.2 from 01.01.89

(1) A special tax policy for diesel fuels was introduced.

It is possible that further reduction of sulphur content in diesel fuel will be needed by catalysts. As of now, oxidation catalysts are being developed for reducing the SOF (soluble organic fractions) of the total particulates matter (TPM), the vapor phase HC and CO emissions from diesel engines. The content of sulphur is related to quantities of the SO_4 adsorbed on the catalyst surface and the emitted sulphur compounds. The suppression of SO_4 emissions is important since sulphates have bound water to them and this effect can tend to negate the SOF reduction relative to TPM reduction. This problem can be eliminated if fuel sulphur contents were reduced further from 0.05% to 0.01% or lower levels, [61].

Table 16.23: Vehicle diesel fuel specifictions for the year 2000, [69]

parameter	units	current specification	proposed year 2000 specification	predicted market average without proposal	predicted market average with proposal
cetane number	number, min.	49	51	51	53
poly-aromatics	% mass, max.	-	11	9	6
density	kg/m^3, max.	86-	845	843	835
T95	C^o , max.	370	360	355	350
sulphur	ppm, max.	500	350	450	300

Aromatics content limitations. Tests on fuels with 0 up to about 35% total aromatics, typical for currently marketed fuels, show no influence of total aromatics content on particulates emissions, but there were indications of an upturn at higher levels, [1]. It is important to note that engines differ in their sensitivity to the influence of aromatic content on particulates emission, [1]. Other recent evaluations suggest that while total aromatics may have no influence on particulates emissions, a more significant role may be played by polycyclic aromatics, [5, 65].

Limits on aromatics have already been imposed in some countries, [1, 15, 62]. For example, the diesel fuel specifications introduced in Sweden in 1991 have limited the maximum aromatics content to 5 and 20% vol. for Urban Diesel 1 and Urban Diesel 2 respectively, [1], and in California limits were introduced by CARB of 10% vol. aromatics content and of 1.4% wt (max.) for polycyclic aromatics from 1993, [15].

In the USA, the Engine Manufacturers Association which is asking for improved quality for 1998, proposes for the new diesel fuel specifictions a big reduction in aromatics, [47]. The maximum poly-aromatics content is limited to 11% mass in the proposed year 2000 specifications for the European Community, [69].

Density and T95. The results presented in [66] indicate that the density and cetane number have the largest effect (in percentage terms) on emissions. Poly-aromatics and T95 have smaller effects. From the specifications for the reformulated and new clean diesel fuel in Sweden, Finland and Switzerland it is possible to observe a very slight tendency of reducing the density value. A similar trend is seen from the data in Table 16.23. It can also be observed from this Table that there is a tendency to decrease the distillation values (T95) for the new, or future, diesel fuels.

Extended use of diesel fuel additive in the future can be useful for the oil refineries for extra processing and blending as a means to improve the fuel properties (adddditives to restore the cold properties in case of cutting deeper into the crude oil, ignition improvers for low cetane material which is being diverted into automotive diesel fuel, etc.) or for improving the aftermarket properties like detergency, lubricity, etc.

16.4 ALTERNATIVE FUELS

Continuous increase in the severity of environmental legislation together with considerations of security of energy supply have recently led to significantly increasing interest in alternative fuels. The US Clean Air Act Amendments (CAAA) of 1990 point out the importance of using the "clean alternative fuels" such as: "methanol and ethanol (and mixtures thereof), reformulated gasoline, natural gas, LPG, electricity and any other fuels which permit vehicles to attain legislated emission standards", [15]. Biogas, vegetable oils, ethers and hydrogen also have been considered as potential fuel alternatives. Reformulated gasoline and its effects on vehicle exhaust emissions have been discussed already in section 16.2 of this Chapter.

Gasoline and diesel fuel may also be produced from synthetic hydrocarbon liquids. The catalytic synthesis of hydrocarbons is performed, generally, from carbon monoxide and hydrogen by the so called Fischer - Tropsch Process, [1]. Generally, the sources of CO and H_2, needed for synthesis reactions, are coal, natural gas or methanol. In South Africa, for example, synthetic gasoline has been produced commercially from coal (the SASOL method), see Appendix 1. The process has a low efficiency and is only used where supplies of crude oil are limited, [1]. Because of their similar composition, synthetic hydrocarbon fuels have similar effects on vehicle emissions as conventional ones.

In the following, the above mentioned alternative fuels and their effects on vehicle exhaust emissions are briefly reviewed.

16.4.1 Alcohols

Two alcohols, methanol and ethanol, are generally considered as alternative motor fuels. Ethanol containing 5% water (E95) has been used successfully in the vehicle parc of Brazil. In the USA (California in particular), Germany, Japan, Australia and New Zealand, increasing attention in alcohol fuels is primarily focused on methanol, mainly due to manufacturing cost and supply considerations, [1]. As mentioned above, in section 16.2, both methanol and ethanol are used together with other oxygenates for blending reformulated gasolines.

Methanol is mainly produced from natural gas, coal and sometimes – from heavy residual oils. Technologies for methanol production from lignite, peat and biomass are also available. Methanol production from natural gas takes place, generally, near the gas source and not in the consumer's area, in order to avoid the high costs for transport of gas compared to that of easy-to-handle liquid methanol, [70]. Ethanol is generally produced by fermentation of biomass feedstocks, mainly sugar cane, wheat and wood.

The main advantages of using alcohols as alternative motor fuels are:

- Both methanol and ethanol, as mentioned above, can be derived from non-crude, sometimes renewable resources that are much more evenly distributed over the glove, compared to crude oil, of which over 50% are located in the Middle East, [1]. This fact significantly contributes to the solution of the "security of supply" problem.

- Both methanol and ethanol have excellent antiknock performance, which enables higher compression ratios to be used than are possible with gasoline-fueled engines, so improved engine thermal efficiency can be achieved. Some properties of methanol and ethanol are summarized together with other alternative fuels and compared with gasoline and diesel fuel in Table 16.24.

- Alcohols burn with lower flame temperatures and luminosity, so that the heat losses are lower, [1].

- Both methanol and ethanol have very high latent heat of vaporization (see Table 16.24), which allows the achievement of higher volumetric efficiency compared to gasoline-fueled engines due to the increased charge density.

- By using alcohol fuels it is possible to reduce hydrocarbons emissions and to lower the photochemical reactivity of emitted pollutants. An example of alcohol fuel effects on exhaust emissions is shown in Figure 16.19, based on results from the US AQIRP program for methanol and ethanol, [74 - 76]. These were obtained with flexible/variable fuel vehicles (FFV/VFV) for the near-neat methanol (M85) and ethanol (E85) blends with gasoline. Each blend contained 85% of alcohol fuel and 15% of gasoline. As can be seen from the Figure, using methanol or ethanol as alternative fuel leads to reduction of OMHCE, benzene and 1,3 Butadiene emissions, together with lowering photo-chemical reactivity of the exhaust gases. At the same time, use of alcohol fuels resulted in rising of NMOG and aldehydes emissions (the latters – quite sharply).

Table 16.24: Properties of various fuels (based on [71-73])

Property	Diesel Fuel(1)	Gasoline(1)	Methanol	Ethanol	Methane	Propane	Dimethyl Ether (DME)	Vegetable Oil (RME)(6)	Hydrogen
Density at 15°C, kg/l	0.82-0.86	0.72-0.78	0.79	0.79	0.72(2)	0.51 (liquefied)	0.66	0.88	0.090(2)
Lower Heating Value (LHV), MJ/kg(MJ/l)	42.5 (35.7(3))	44.0 (33.0(4))	19.7 (15.6)	26.8 (21.2)	50.0 (36.0(2))	46.3 (23.6)	27.6 (18.2)	37.2 (32.7)	120 (10.8(2))
Heat of Vaporization(5), KJ/kg	250	305	1110	904	509	426	460 (410at 20°C)		
Boiling Point, °C	180-360	25-215	65	78	-162	-43	-20	330-340	-253
Flammability Limits (%vol gas in air)	0.6 - 7.5	0.6 - 8	5.5 - 26	3.5 - 15	5- 15	9 - 9.5	3.4 - 18		4 - 77
Octane Rating (RON)		91-98	111	108	130	112			
Cetane Number	40-55		5	8			>>55	51-52	

(1) - Typical values
(2) - Per nm^3
(3) - For density 0.84kg/l
(4) - For density 0.75kg/l
(5) - At 1 atm. and 25°C for liquid fuels; at 1 atm and boiling temperature for gaseous fuels.
(6) - RME - rapeseed oil methyl ester.

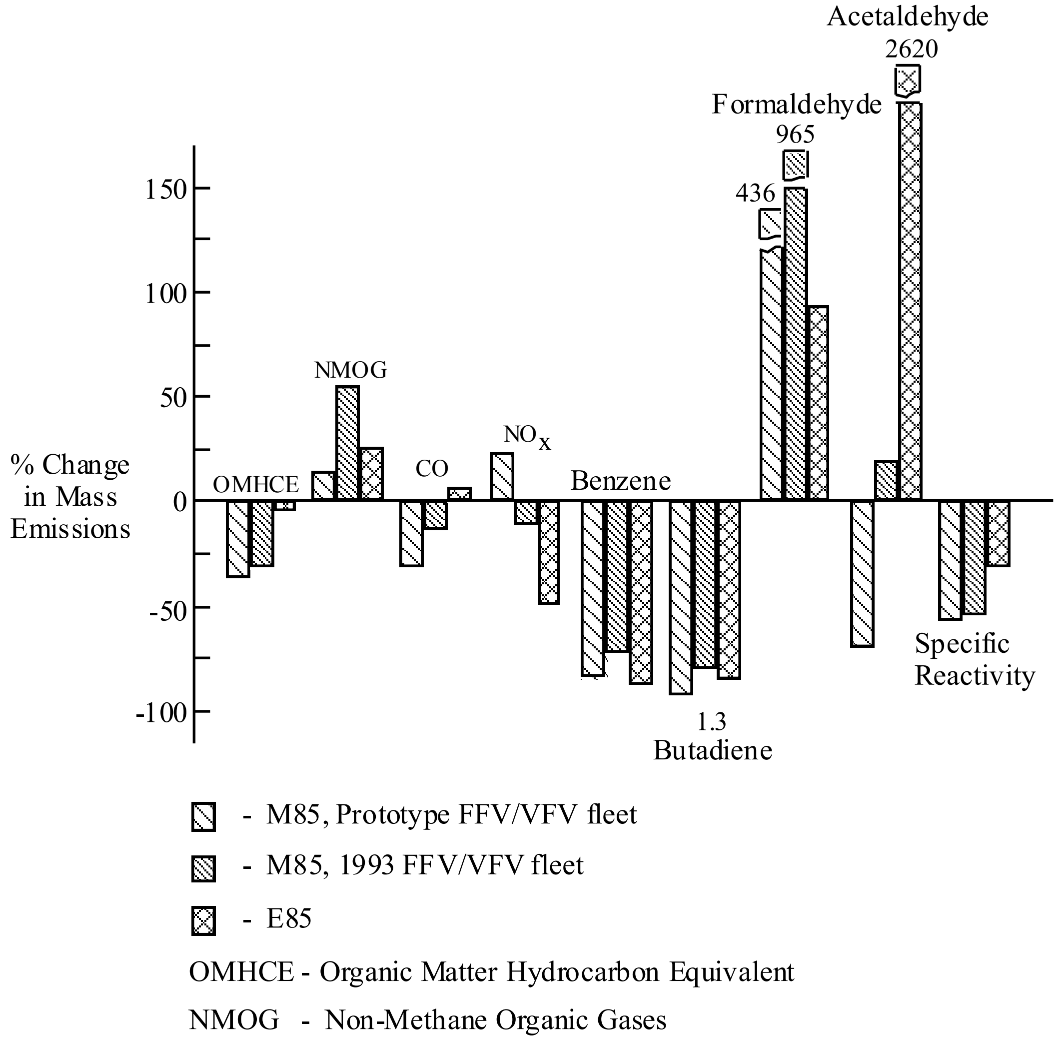


Figure 16.19: Alcohol fuels effects on emissions (compared to Industry Average Gasoline), AQIRP results [74-76]

There is no clear picture about CO and NO_X emissions, although lower flame temperature may contribute to reduction of NO_X formation.

The physical and chemical characteristics of alcohols do not make them particularly suitable for compression ignition engines as a direct replacement of diesel fuel. As can be seen from Table 16.24, the cetane number of methanol and ethanol is 5 and 8, respectively. Use of alcohol as an alternative fuel for diesel engine is generally possible by one of the following ways, [77]: in blended fuels, in engines with forced ignition and in dual-fuel engines. Blending alcohol with high cetane number fuels is one of the simplest ways of using alcohol fuels, but large amounts of ignition improver and also additives preventing phase separation are generally required. One of the commonly used ignition improvers is the so called Avocet, containing a nitrate ester dissolved in methanol, [78]. Use of neat alcohols is only possible in engines with forced ignition by glow or spark plugs. The forced ignition method possesses also a good flexibility for a variety of fuels. Dual-fuel engines may be operated with pilot injection or with alcohol carburation (fumigation) into the engine's intake manifold. The pilot injection method allows the ignition of a large amount of alcohol injected into the cylinder by a small ignition dose of diesel fuel. Double injection nozzles are generally used here. The method of fumigation is beneficial due to its relative simplicity and the potential for application to gaseous as well as liquid fuels. However, knocking or misfiring may occur with this method and it is generally used for relatively low percentages of alcohol in total fuel energy, [77, 79]. As follows from various published research works, [1, 77, 79], use of alcohols in diesel engines generally contributes toward reduction of particulates and NO_X emissions.

The main shortcomings of alcohols as alternative motor fuels, in addition to the above mentioned increase in emission of some kinds of pollutants (NMOG, aldehydes etc.), are:

- Alcohols have a much lower energy content (heating value) than gasoline or diesel fuel (see Table 16.24), therefore more fuel is needed in order to supply to the engine the same amounts of energy or, in other terms - the volumetric fuel economy will always be lower.

- Alcohols have low vapor pressures and high latent heats of vaporization, and therefore show poor cold starting and warm-up performance. Near-neat alcohols, containing small amounts of gasoline or other fuels (for example, M85 and E85 fuels) are frequently used in order to overcome this problem.

- Methanol, and in less degree also ethanol, are corrosive to many of the metals, elastomers and plastic components that are used in conventional fuel systems. The correct choice of suitable materials for the fuel system of alcohol fueled vehicle is very important and several test programs have been carried out for this aim, [1, 80].

- Accelerated cylinder and piston ring wear have been found to occur in neat alcohol fueled engine, [1]. The possible reasons are: washing away of lubricant film during cold starting and/or corrosion due to formic or performic acids formation during combustion.

- Alcohols have lower viscosity relative to diesel fuel and poor lubricity, which would cause increased wear of conventional fuel injection equipment.

- Methanol burns with an almost invisible flame (low luminosity) and so presents a somewhat safety hazard. Use of near-neat alcohol fuel with the addition of gasoline or other materials allows this problem to be overcome by increasing flame luminosity, [1].

16.4.2 Natural gas

Natural gas is frequently considered as the most promising near term alternative fuel because of its long term availability, well-balanced geographic distribution and clear ecological benefits.

Using natural gas in mobil and stationary engines is not a new concept – several companies for many decades have manufactured gas engines for stationary uses such as gas compression and electric power generation, [81]. Also, over one million natural gas vehicles (NGVs) are operating now on the world's roads. Between the leading users of NGVs are countries of the former Soviet Union, Italy, Argentina, Australia, New Zealand, USA and Canada. Table 16.25 includes data about the NGVs numbers in different regions worldwide, based on the estimate performed for the European THERMIE programme, [82].

Table 16.25: Regions with greatest NGV populations (based on data from [82])

Area	Number of Vehicles
Former Soviet Union	350,000
Italy	300,000
South America	200,000
Australia	150,000
North America	130,000

Natural gas, as it is found in the earth, is basically composed of between 88% and 96% methane with small and varying amounts of non-methane hydrocarbons, CO_2, water, N_2, H_2S, He, Ar and other trace gases, [1, 81, 82]. In most cases, natural gas from the gas field undergoes an upgrading process. This is necessary for removal of water, H_2S and excess amounts of higher hydrocarbons and inert gases, to prevent corrosion damage and condensing problems in pipeline networks, to achieve the required heating value and to obtain valuable by-products. In order to minimize the negative effect of variations in natural gas composition on vehicle performance and pollutants emission, the California Air Resources Board (CARB) has established special requirements for natural gas sold commercially as vehicle fuel, see Table 16.26.

Table 16.26. CARB specification of natural gas used as automotive fuel (based on data from [15])

Constituent, mole %	Specified value
Methane	88.0 (min)
Ethane	6.0 (max)
C_3 and higher	3.0 (max)
C_6 and higher	0.2 (max)
Hydrogen	0.1 (max)
Carbon Monoxide	0.1 (max)
Oxygen	1.0 (max)
Inert Gases	1.5 - 4.5

Natural gas may be stored on-board a vehicle either as a compressed natural gas (CNG) in high-pressure cylinders or as a cryogenic liquid. In order to provide vehicles with acceptable independent range, CNG has to be compressed and stored in tanks on vehicle at pressure of about 200 bar. To liquefy natural gas at atmospheric pressure, its temperature needs to be brought down to about -162^{o}C (see boiling point of methane in Table 16.24). Use of liquified natural gas (LNG) as an automotive fuel is the subject of some serious safety problems, such as the possibility of excess vapor entering into an enclosed area, that may lead to explosion. There are additional technical challenges, for example: need to ensure that the liquid phase does not become significantly enriched with non-methane hydrocarbons compared to initial tank levels, [81]. Therefore, almost all NGVs used today are fueled by CNG. Natural gas vehicles operating on CNG may be refueled either in fast-fill mode (refueling times are comparable with those of conventional vehicles) or in slow-fill mode. The latter allows vehicles to be refueled over a period of several hours overnight.

As can be seen from Table 16.24, natural gas has a superior octane quality which makes it a beneficial fuel for spark-ignition engines. Vehicles using natural gas may be:

- bi-fuel, converted from conventional ones and operating on gas or gasoline at the driver's choice;

- dedicated to the gaseous fuel with forced ignition of fuel-air mixture;

- dual-fuel, in which the gaseous fuel is ignited by injecting a small amount of diesel fuel. Frequently, these vehicles are also bi-fuel, because of the possibility to run them on diesel fuel only, [83].

The main advantages of natural gas use for fueling vehicles, as partially mentioned above, are:

- Natural gas is a primary fossil fuel, widely available worldwide and with well-balanced geographic distribution. Using it as an alternative motor fuel will contribute to the improvement of "security of supply" of energy resources.

- Very high antiknock resistance of natural gas (RON of methane is 130) allows it to be used in dedicated engine concepts with much higher compression ratios as compared to gasoline engine. It is especially beneficial, because it opens the possibility of converting heavy-duty diesel engines to high-compression, lean-burn, spark-ignition ones operating on CNG without changing basic engine design.

- Unlike their gasoline counterparts, natural gas vehicles do not require mixture enrichment for cold starting, so that pollutants emission from NGVs are unaffected by low temperatures.

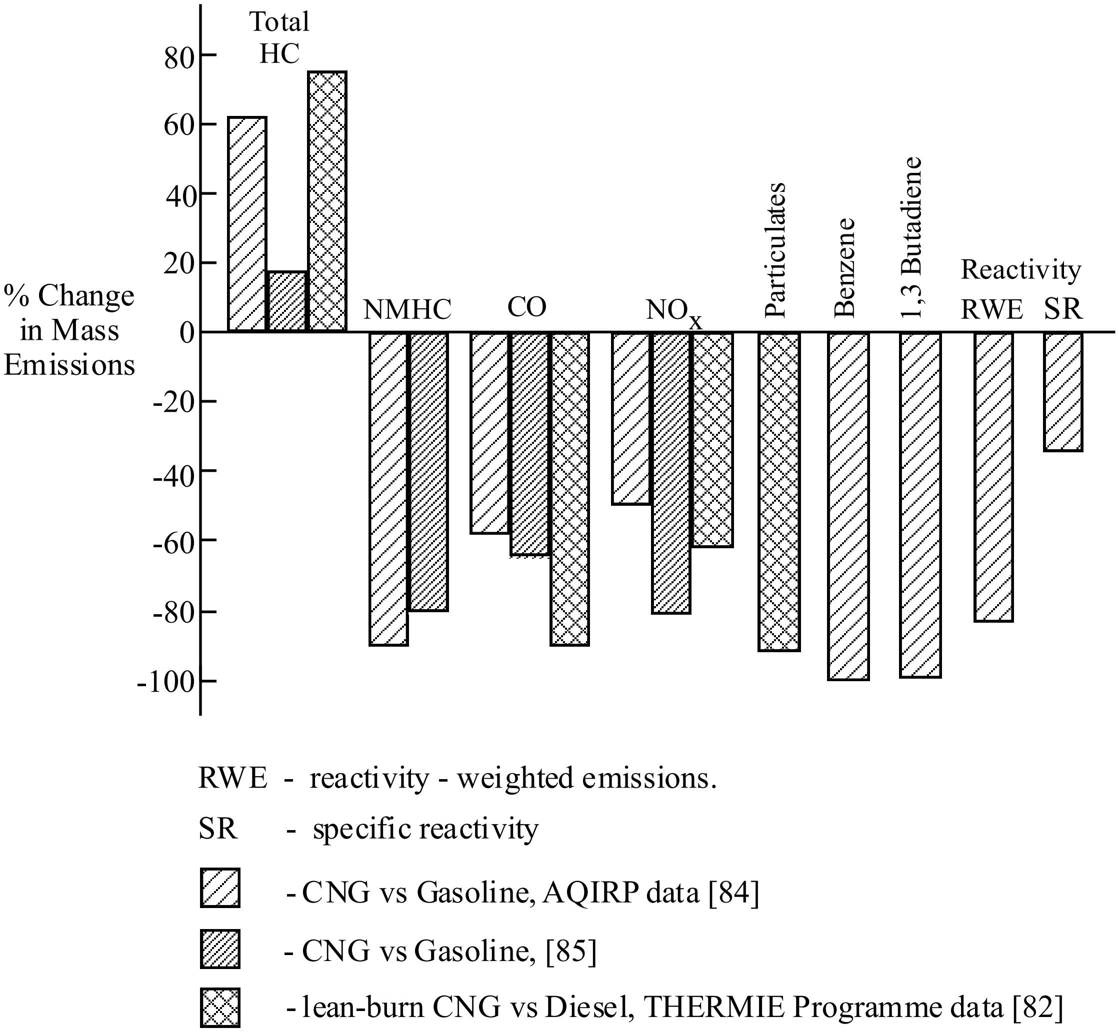


Figure 16.20: Natural gas effects on emissions

- Use of natural gas allows drastic reductions to be achieved in pollutants emission compared to either gasoline or diesel fueled vehicles. Emissions data from a number of NGVs using modern electronic emission control systems, clearly show the ability to meet ULEV emissions standards of CARB, [1]. The examples in Figure 16.20 illustrate the changes in emission levels of vehicles operating on natural gas, compared to gasoline or diesel fuel. As can be seen from the Figure, there are some superior ecological benefits of NGVs:

  - Low emissions of non-methane hydrocarbons;
  - Reduction of CO and NO_x emissions, especially substantial for lean-burn heavy-duty natural gas engines as compared to their diesel counterparts;

- Extremely low emissions of particulates;
- Low emissions of air toxics such as benzene and 1,3 butadiene;
- Low photochemical activity of exhaust gases.
- Another environmental benefit of natural gas compared to conventional fuels is zero evaporative emissions, due to the sealed fuel system. Also, some reductions in CO_2 emissions have generally been achieved compared to gasoline engines, due to lower carbon/hydrogen ratios in the natural gas.

- An important advantage of heavy-duty NGVs compared to diesel counterparts is a reported noise reduction (by 3-8 dB(A)), [83, 86].

The <u>main and principal disadvantage</u> of natural gas as an automotive fuel lies in the fact that it is a gas. Therefore, special approaches, as mentioned above, are needed in order to store it on-board a vehicle. Extra weight, needed for fuel tanks in buses with CNG compressed to 200 bar, for example, may reach or even exceed 1,000 kg, in order to provide a reasonable operational range of the vehicle, [82].

- Special infrastructure of filling stations etc., must be developed for refueling purposes.

- As can be understood from Figure 16.20, NGVs emit generally much more unburned methane than its gasoline or diesel counterparts. Effective methane oxidation in catalytic converters is a problem, because of its high chemical stability. Methane is known as an active greenhouse gas, but NGVs' contribution to global warming, even in the scenario of their wide penetration into the market, is considered quite negligible, because the great majority of global methane emissions to the atmosphere originate from natural uncontrolled sources, [1, 81].

- Like all otto-cycle engines, natural gas ones have generally fuel economy about 20% lower than that of diesel engines.

From the safety point of view, CNG vehicles are generally not a subject of increased concern and even expected to be safer than gasoline vehicles, [1].

16.4.3 Biogas

Biogas can be produced from a large diversity of various sources as long as they contain organic material. Examples of such sources are municipal sewage, agricultural waste, waste dumps, manure, etc., [70]. Depending on the source, the composition of the gas may vary, but the dominant component will always be methane. The conversion of organic mass with biogas formation is generally carried out by a fermentation process. The main and most significant advantage of biogas as an alternative fuel is that it may be produced from renewable energy sources. Because biogas is mainly methane, its effects on exhaust emissions will be much similar to those of natural gas.

16.4.4 Liquefied petroleum gas

Liquefied petroleum gas (LPG) broadly refers to commercial propane, commercial butane and mixtures of the two. LPG is generally derived from two sources: natural gas processing and petroleum refining. Produced by either one of them, LPG is essentially a by-product. The name "LPG" is explained by the fact that the gas assumes a liquid state at pressures of 2 to 20 bar; the actual value depends upon the propane/butane ratio, [71].

The composition of commercial LPG varies greatly from one country to another. In the USA, automotive LPG generally contains more than 85% propane, [15, 87]. In Europe, on the other hand, LPG contains nearly equal parts of propane and butane, [1, 87]. Table 16.27 illustrates US specifications for automotive LPG.

Over 3 million vehicles are operating on LPG worldwide. Between the leading users of LPG are Italy, Netherlands and North America area. Some data about the numbers of LPG vehicles in different countries are shown in Table 16.28, [82].

Table 16.27: US Specifications for automotive LPG, [15]

Property	US ASTM D1835
Propane, % vol	85 min
Propylene, % vol	5.0 max
Vapor pressure at 37.8°C, kPa	1430 max
Volatile residue evap. temperature 95%, °C	-38.3 max
or	
Butane and heavier, % vol	2.5 max
Sulphur, ppm	120 max

Table 16.28: Countries with greatest LPG vehicles populations
(based on data from [82])

Country or area	Number of vehicles
Italy	1,300,000
Netherlands	610,000
North America	610,000
Japan	300,000
Australia	250,000

LPG, as also natural gas, is a fuel intended for use in engines with forced ignition (otto-cycle). Generally, any vehicle equipped with an IC engine can be converted for operation on LPG, and in most cases spark-ignition gasoline engines will then run in bi-fuel mode (the system can be switched between gasoline and LPG). However, engine optimization for operation on LPG is only possible in dedicated gas engines. A possible problem here is variations in octane quality of LPG as a function of propane/butane ratio (RON of butane is 94 and it is much lower than that of propane – 112).

The main advantages of LPG as automotive fuel, compared to gasoline are:

- Higher octane quality for potential performance gain.

- Good cold starting and driveability because of its gaseous state.

- Emissions from an LPG engine are substantially lower than those achieved with the gasoline or diesel counterparts. The ecological benefits are mainly similar to those pointed out above for NGVs with the exception of higher emissions of NMHC, relative to natural gas, [1], and exhaust gases photo-chemical reactivity. The latter is mainly due to higher contents in LPG of very reactive olefins compounds. An example of a comparison between different fuels effects on photochemical reactivity (summersmog potential) of exhaust gases is given in Figure16.21 (reproduced from [88]).

- Compared to the diesel counterpart, an LPG engine (similar to NGVs) has a lower noise level, [82].

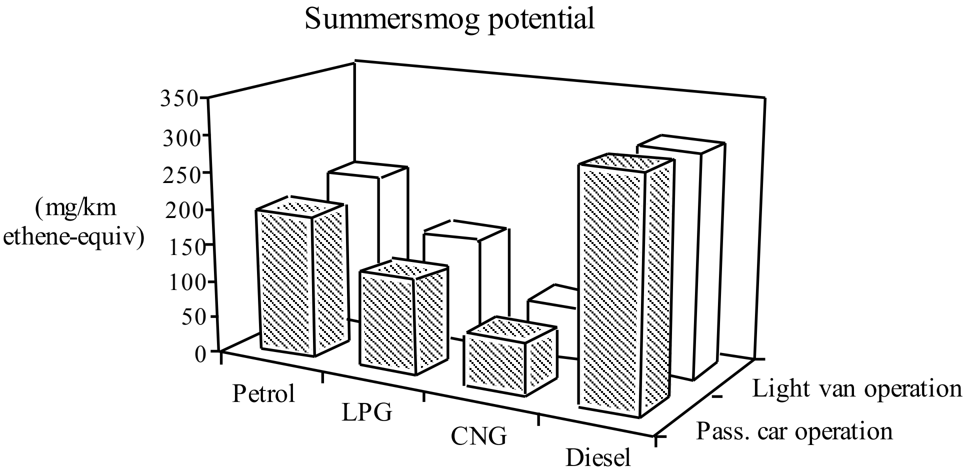


Figure 16.21: Summersmog potential of the different fuels, [88]

<u>The main disadvantages of LPG</u> are:

- Lower fuel energy content (see Table 16.24), which leads to higher volumetric fuel consumption.

- Supplementary safety regulations must be considered, as LPG is stored on-board a vehicle under pressure.

- LPG is heavier than air, therefore use of LPG vehicles is currently the subject of considerable restrictions in some countries, such as prohibition of parking in confined spaces, [82].

16.4.5 Vegetable oils and ethers

Vegetable oil is an interesting alternative fuel for compression ignition engines, mainly because it is produced from renewable energy sources – various sorts of oil-yielding plants. The most common oil-plant for vehicle use in Western Europe is rape and the final product produced from it as an automoive fuel is the methyl ester of rapeseed oil (RME). One thousand and three hundred square kilometers of land in France have been cultivated in 1994 to produce about 130,000 tons of this fuel, frequently named biodiesel, [89]. A European Council Directive draft proposal for a specification of vegetable oil methyl esters has been developed, along with the objective of securing a 5% market share of total motor fuel consumption for biofuels, of which, as expected, the bio-diesel would form the major part, [15]. This draft specification, which has been reproduced from [15], is shown in Table 16.29.

Rapeseed oil (or vegetable oil in general), that has been processed to methyl ester, has many characteristics close to those of diesel fuel; for instance – density, viscosity, energy content and high cetane number, see Table 16.24. From the results of the three year large-scale research program, carried out in France, [89], and some other publications, for example [90], it follows that the use of vegetable oil methyl ester (and particularly, RME) leads to some reduction of hydrocarbons, particulates and slight increase of NO_X emissions.

Reduction of volatile aromatics together with benzene and aldehydes emission rise was also reported by [89]. Worsening the volumetric fuel economy is generally proportional to the change in LHV (lower heating value) – see Table 16.24.

Results of limited fleet tests, with 30% - 100% blends of RME and diesel fuel, show no serious side effects and no significant differences in wear rates have been found. However, according to [89], original elastomers are unsuitable for pure RME use. Deposits formation on certain surfaces has also been reported, [89].

Table 16.29: EU draft specification for vegetable oil methyl ester diesel fuel (CONCAWE data, [15])

Properties		**Limit**	**Analytical Method**
A. Fuel Specific Properties	**Units**		
Density at 15 °C	g/cm^3	0.86 - 0.90	ISO 3675
Kinematic viscosity at 40 °C	mm^2/s	3.5-5.0	ISO 3104
Flash point	°C	min. 100	ISO 2719
Cold filter plugging point CFPP	°C	summer max. 0 winter max. < -15	DIN EN 116
Sulphur content	% m/m	max. 0.01	ISO 8754/DIN EN 41
Distillation:			
5% vol. evaporated at	°C	to be indicated	ASTM-1160/ISO 3405
95% vol. evaporated at	°C	to be indicated	
Carbon residue Conradson (10% by vol. residue on distillation at reduced pressure)	%m/m	max. 0.30	ISO 10370
Cetane number	-	min. 49	ISO 5165/DIN 51773
Ash content		max. 0.01	EN 26245
Water content (Karl Fischer)	mg/kg	max. 500	ISO 6296/ASTM D 1744
Particulate Matter	g/m^3	max. 20	DIN 51419
Copper corrosion (3h/50 °C)	corrosion -rating	max. 1	ISO 2160
Oxidation stability	g/m^3	max. 25	ASTM D 2274
B. Methyl Ester Specific Properties	**Units**		
Acid value	mg KOH/g	max. 0.5	ISO 660
Methanol content	%m/m	max. 0.3	DIN 51413.1
Monoglycerides	%m/m	max. 0.8	GLC
Diglycerides	%m/m		GLC
Triglycerides	%m/m		GLC
Bound glycerine	%m/m	max. 0.2	calculate
Free glycerine	%m/m	max. 0.03	GLC
Total glycerine	%m/m	max. 0.25	calculate
Iodine number	-	max. 115	DIN 53241/IP 84-81
Phosphorous content	mg/kg	max. 10	DGF C-VI 4

Note: Many of the test methods have yet to be finalized.

Increasing interest has recently been focused on the possibility of using Dimethyl Ether (DME) as a very promising alternative fuel for compression ignition engines, [72, 91, 92]. DME is manufactured today from methanol in relatively low amounts (about 100,000 ton/year worldwide, [91]) mainly for the aerosol industry, as a replacement for CFC materials. Haldor Topsoe has developed the process for direct production of DME from synthesis gas, [93]. This gas, which is a mixture of H_2, CO and CO_2, can be generated from various sources, including natural gas, coal and biomass. The latter allows to qualify DME as a renewable fuel.

Dimethyl ether (chemical formula CH_3-O-CH_3) is the simplest ether known as environmentally benign. Some relevant properties of DME are listed in Table 16.24. Due to its excellent autoignition quality (cetane number over 55), it is used sometimes as fuel additive for methanol operating engines, [94, 95]. However, its combustion is possible also as a primary engine fuel.

The main advantages of DME as an alternative automotive fuel are:

- The chemical structure of DME, with its high oxygen content, promises an almost smokeless combustion when burned in a proper manner, [72].

- The very high cetane number allows reduction of NO_X emission and noise.

Figure 16.22 shows emissions results which have been obtained by [91], with the Navistar T 444E diesel engine, operted on pure DME without any exhaust aftertreatment. It must be noted that the optimization for DME of a fuel injection system, combustion chamber, inlet port geometry and compression ratio, may further lower NO_x and CO emissions rates without deterioration of fuel economy.

- Unlike methanol, DME is noncorrosive to metals.

- DME flame luminosity is quite good. It burns with a visible blue flame, similar to natural gas. As mentioned above, this is an important safety aspect.

- DME provides good engine cold starting.

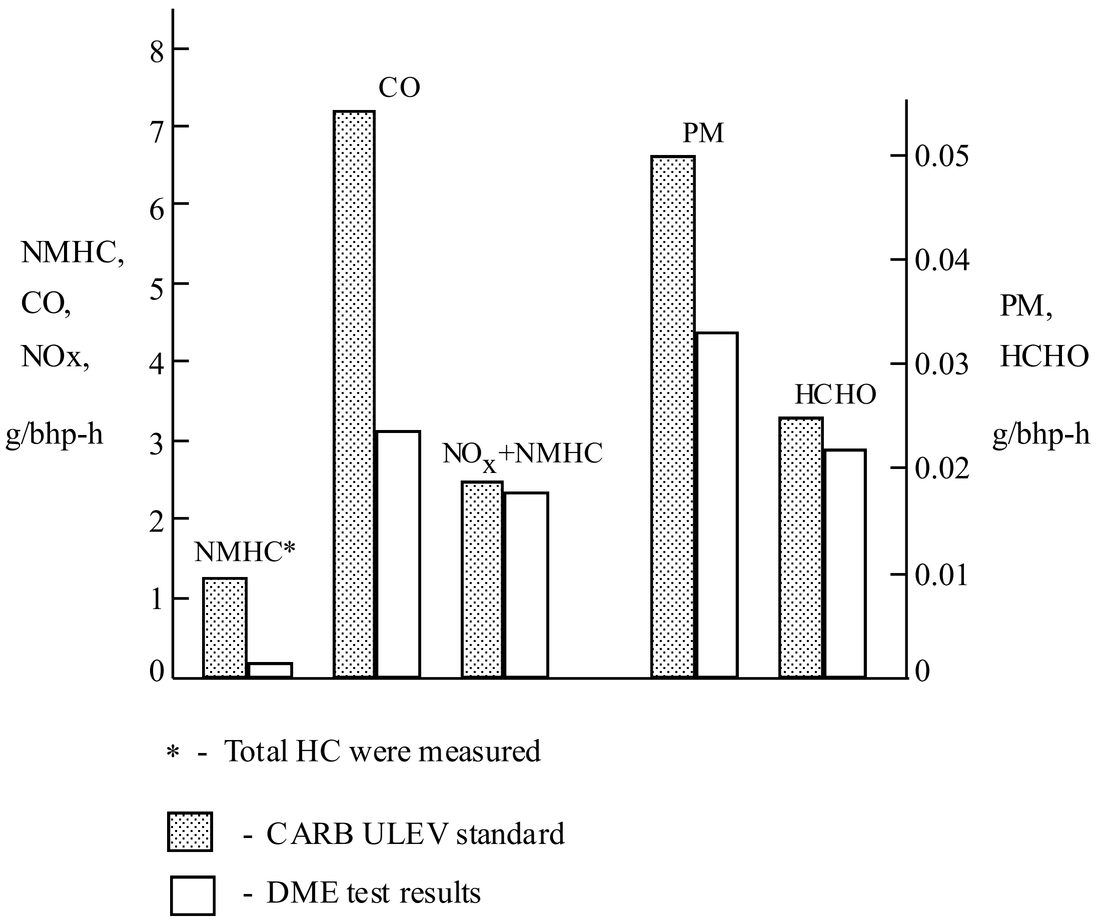


Figure 16.22: Test results of Navistar diesel engine fuelled with DME in comparison with CARB ULEV standards, based on [91] data

<u>The main shortcomings of dimethyl ether</u> as an automotive fuel are:

- On-board a vehicle, storage and handling of DME need some precautions similar to LPG, because the boiling point of DME is too low (- 20°C) and it is a gas under normal atmospheric conditions. Special care must be taken to avoid leakage of DME, because it could form an explosive mixture with air.

- The energy content and density of DME are significantly lower than those of diesel fuel (see Table 16.24), which cause a proportional increase of volumetric fuel consumption and requires changes in fuel injection apparatus, providing an increase of injected fuel volume per stroke.

- Some elastomers are not compatible with this fuel, therefore careful selection of seal materials is necessary.

- The lubrication performance of DME has not yet been sufficiently investigated, but using a lubricity additive is probably necessary.

16.4.6 Hydrogen

The limited availability of fossil energy sources stimulates the increasing interest in hydrogen (H_2) as a potential alternative automotive fuel. Although the problems of hydrogen production, infrastructure development, refueling and on-board storage are quite difficult, their solutions seem to be technically feasible in long term perspective.

Among the many methods of hydrogen production, stripping it from hydrocarbons (such as natural gas or heavy petroleum oils) is the least expensive large scale process, [70]. The cost of hydrogen produced this way is 3 - 15 times higher than that of natural gas and 1.5 - 9 times of gasoline, [96]. Hydrogen can also be produced by gasification of coal. Production of H_2 by electrolysis of water is used today in some industrial plants, [70], but this method is extremely expensive, [96]. Production of hydrogen by photoelectrolysis with the use of solar energy is also considered as a potential option.

Storage of hydrogen on-board a vehicle remains a major technical challenge. The problem is directly related to the physical properties of hydrogen (see Table 16.24): very low volumetric energy content and extremely low boiling point (-253°C). The methods of on-board H_2 storage considered today are as follows:

- Storage of compressed H_2 in pressurized tanks. High pressure (about 300 bar, [71]) is required for storage of hydrogen in gaseous state. This leads to high weight penalties and safety risks.

- Storage of liquefied H_2 in cryogenic tanks. The extremely low temperature of liquefaction (20 K) puts heavy demands on thermal insulation. The process itself is highly energy-demanding. According to [96], it takes almost as much energy to liquefy hydrogen as is contained in the resulting liquid. Environmental heat causes boil-off of the hydrogen from the safety valve, resulting in losses of about 2% per day when the vehicle is parked, [71]. This venting of hydrogen may also represent a serious safety concern.

- Hydrogen can also be stored in metal hydrides adsorbed on carbon or other materials. The main advantage of this method is that there are no storage losses. The main drawbacks are associated with low hydrogen storage capacity, sensitivity to contamination by impurities in the hydrogen gas and high cost of materials.

- Hydrogen can be stored as a constituent in a chemical compound (methylcyclohexanol storage is most widely considered). This method of on-board storage requires a catalyst to dehydrate the hydrogenous methylcyclohexane at high temperature of about 500^{o}C.

Regardless of the on-board storage type, in all current hydrogen fueled vehicles it is injected into the intake manifold in gaseous form, [71]. The second possibility – liquid H_2 injection directly into the cylinder, provides some advantages, such as: mixture cooling for low NO_x emissions and reduced heat losses, no danger of back-fires. However, the short injector life time means that this type of fuel system for H_2 cannot be a viable option for the near future, [71].

The nature of hydrogen, which does not contain carbon and oxidize during combustion into water, allows ultra-low tailpipe exhaust emissions to be obtained from hydrogen vehicles. Only trace amounts of CO, CO_2 and HC, originated from the lubricating oil, may be emitted. Very wide flammability limits of hydrogen in air (see Table 16.24) allow to realize the concept of very lean-burn engine and hence low NO_x emissions and higher thermal efficiency. An example of regulated pollutants emission from hydrogen fueled Mazda vehicle with rotary engine are shown in Figure 16.23, in comparison with the CARB ULEV standards, [96].

As can be seen from this Figure, levels of emissions which are lower by order of magnitude than ULEV standards can be achieved by use of hydrogen as an automotive fuel. As mentioned above, almost no CO_2 emissions are produced during hydrogen vehicle operation. However from the calculations performed by [96], it follows that in total account hydrogen fueled motor vehicles have no noticeable advantage and in many cases are worse, regarding greenhouse gas emissions, when hydrogen is produced from fossil sources.

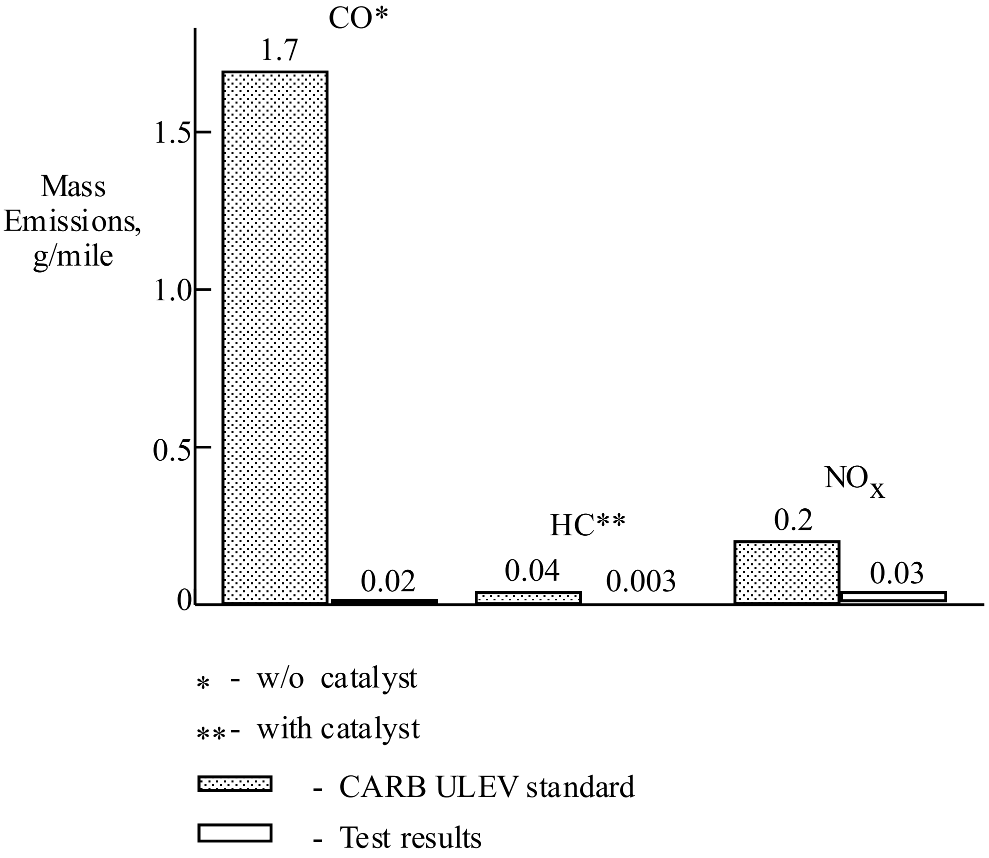


Figure 16.23: Tailpipe emissions of hydrogen fuelled Mazda vehicle with rotary engine, based on data from [96]

16.4.7 Electricity

In connection with the content of the previous sub-section, it is important to note that hydrogen can be used as a fuel not only for ICE, but also for fuel cell devices, in which the chemical energy of hydrogen is converted directly to electricity for propulsion of electric vehicles (EV).

The main benefit of fuel cells is their high theoretical efficiency (70 - 90%, [96]) together with zero tailpipe emissions. The main disadvantage – unsuitably high cost. Development of an effective and reliable on-board source of hydrogen is also a serious technical challenge. Using on-board methanol dissociation is considered, today, a promising method of supplying hydrogen to fuel cells, [97]. Because of the above mentioned shortcomings, automotive fuel cells, as they seem today, are only a long-term possibility. Nonetheless, experiments with EVs powered by fuel cells have recently intensified in the light of California' zero emission vehicles (ZEV) mandate. One of the latest examples of R&D in this area is the NECAR II vehicle of Daimler - Benz powered by fuel cells, [98].

A more realistic candidate for powering a zero emission vehicle (with today state of art technology) is an electric battery. Although battery-powered EV is not yet competitive with conventional fuel vehicles, (mainly because of the high cost and short driving range), due to California ZEV mandate almost all auto makers devote now much effort in order to bring the electric vehicle to the market. Several advanced battery technologies are now in various stages of research and development, the most promising being: Ni-Metal Hydrid, Lithium based, Na - $NiCl_2$ and Zn-Air chemistries. Comparison of the power and energy densities of some of the advanced technology batteries and gasoline appear in Table 5.4.7.

In order to advance the more promising battery technologies, three big US auto makers in cooperation with the US DOE, formed the US Advanced Battery Consortium (US ABC) in January of 1991, [92]. The prime objectives of the US ABC, as well as other involved organizations for both the mid-term and long-term goals, are to reduce cost, improve performance and increase time between charging of the batteries.

Table 16.30: Comparison of power and energy densities of some advanced batteries for EV (based on data from [92, 99])

Battery Chemistry	Energy Density, Wh/kg	Power Density, W/kg
Lead - Acid (conventional)	33 - 40	100
Nickel - Cadmium	48 - 60	165 - 210
Nickel - Metal Hydride	73 - 80	175
Nickel - Iron	48 - 50	100
Sodium - Sulphur	100 - 117	120 - 150
Nickel - Zinc	65	200
Lithium - Polymer	500*	N/A
Zinc - Air	215	98
Sodium - $NiCl_2$	88-94	75 - 135
Gasoline	12200	

* - only for test cells N/A - not available

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APPENDIX 1

National Gasoline Specifications

(based on the CONCAWE data, [15])

Country	Standard (date)	Gasoline type	RON min	MON min
Australia	AS 1876 (1994)	Leaded	96	
		Unleaded	P 95 R 91 - 93	82 82
Austria	O-Norm EN 228	Leaded	Not available From Oct. 1993	
		Unleaded	S 98.0 P 95.0 R 91.0	87.0 85.0 82.5
Belgium	NBN T52-705 1990	Leaded	P 97.5	-
		Unleaded	S 98.0 P 95.0 R 90.0	88.0 85.0 80.0
California (U.S.A.)	CARB requirements	Leaded	Not sold from 1.92	
		"Phase 2" reformulated gasolilne (1.3.1996)		
Canada	CAN/CGSB-3.5-M87	Leaded	Not sold from 12.90	
		Unleaded Type 1	87.0-90.0(1)	
		Unleaded Type 2	83.5 - 87.0(1)	(2)
Denmark	Danish Petroleum Institute 1/10/90	Leaded	P 98.0	P 88.0
	DS EN 228	Unleaded	S 98.0 P 95.0 R 92.0	88.0 85.0 83.0
Finland		Leaded(1)	P 99.0	P 87.4
	EN 228; 1993	Unleaded (standard)	S 98.0 P 95.0	88.0 85.0

	01/1993 03/1994	Unleaded (citygasoline) Unleaded (reformulated)	S 99.0 P 95.0	88.0 85.0
France	NFM 15-005 (1994)	Leaded	P 97.0 - 99.0	P 86.0
	NF EN 228: 1993	Unleaded	P 95.0	85.0
	Cahier des Charges	Leaded	97.0	86.5
	NFM 15-001 (1994)	Leaded	89-92	

National Gasoline Specifications (cont-ed)

Country	Standard (date)	Gasoline type	RON min	MON min
Germany	DIN 51600	Leaded	98.0	88.0
	EN 228: 1993	Unleaded	S 98.0 P 95.0 R 91.0	88.0 85.0 82.5
Greece	Greek Government Gazette (P) 556/93 (R) 581/91	Leaded	P 96 - 98 R 90	
	EN 228: 1993	Unleaded	P 95	85
Israel	Israeli Standard 90 (1995)	Leaded	S 98 P 96 R 91	86(2) 85(1) 81
		Unleaded	P 95 R 91	85(3) 81 4)
Italy	NC 623-01	Leaded	P 97.0	P 87.0
	UNI-CUNA EN 228: 1993 (1.10.93)	Unleaded	P 95.0	85.0
Japan	JIS K2202 (1991)	Unleaded No.1	96.0	
		Unleaded No.2	89.0	
The Netherlands	NEN-EN 228: 1993	Unleaded	P 95	85.0
Portugal	Ministerio da Economia Portaria Feb. '94	Leaded	P 98.0 R 90.0	P 87.0
	NPEN 228 1993	Unleaded	95.0	85.0
South Africa	SABC 299 (1988)	Leaded	97 93 87	
	SABC 1598 (1993)	Unleaded	95 91	85(1) 81(2)
Spain	Royal Decree 1485/1987	Leaded	P 97.0 R 92.0	P 87.0 R 82.0
	EN 228 (1994)(1)	Unleaded	95.0	85.0

National Gasoline Specifications (cont-ed)

Country	Standard (date)	Gasoline type	RON min	MON min
Sweden		Leaded	No longer available	
	(1993)	Unleaded (Class 4-SS EN 228)	P 95.0	85.0
		Unleaded (Class 3)		
	(12/1994)	Unleaded (Class 2 - Non- Cat.)		
		Unleaded (Class 2 - Catalyst)		
		Unleaded (Class 1)	will be developed	will be developed
Switzerland	SN 181 161/1 (Jan. '86)	Leaded	P 98.0	88.0
	SN EN 228: 1993	Unleaded	P 95.0	85.0
United Kingdom	BS 4040 (Amended 1.10.94)	Leaded 4 star	97.0	86.0
		Leaded 3 star	93.0	82.0
		Leaded 2 star	90.0	80.0
	BS EN 228: 1993	Unleaded	S 98.0	87.0
			P 95.0	85.0
U.S.A.	ASTM D4814-94d with	Leaded	No longer available	
	EPA requirements (40 CFR Part 80)	Unleaded	87(2)	82
	EPA regulation based on CAAA	Reformulated gasoline (1.1.95) (3) Phase I (1/1/2000)(4) Phase II		

National Gasoline Specifications (cont-ed)

Country	RVP kPa	VLI	Distillation						
			E70 %vol	E 100 %vol	E180 %vol min	10%,°C max	50%,°C max	90%°C max	FBP °C max
Australia									
Austria	not available								
	S 35-70	<950	15-45	40-65	>85	-	-	-	215
	I mixtures								
	W 55-90	<1150	15-47	43-70	>85	-	-	-	
Belgium	45-95	-	15-45	40-70	90	-	-	-	215
	S45-80	<1050	15-45	40-65	>85	-	-	-	-
	I mixtures								
	W60-95	<1200	15-47	43-70	>85	-	-	-	-
California (U.S.A.)	not available								
	48.3 max(1)						99/93 (1)	149/143 (1)	
Canada	not available								
	A 79 max B 86 max C 97 max D 69-107					35-65 60 55 50	70-120 70-117 70-113 70-110	190 190 185 185	
Denmark	S45-80	700-1100	15	44-68	90	-	-	-	210
	I 58-90	800-1200	20	45-70					
	W 70-95	900-1300	25	45-72					

	S 45-80	<1050	15-45	40-65	>85	-	-	-	215
	I 58-90	<1150	15-47	43-70	>85				
	W 70-95	<1200	15-47	43-70	>85				

National Gasoline Specifications (cont-ed)

Country	RVP kPa	VLI	Distillation						
			E70 %vol	E 100 %vol	E180 %vol min	10%,°C max	50%,°C max	90%°C max	FBP °C max
Finland	S 60-80	<1050	20-40	40-63	90	-	-	-	210
	I 70-90	<1150	23-43	43-66					
	W 85-100	<1250	25-45	45-68					
	S60-80	< 1050	-	40-63	-	-	-	-	215
	I 70-90	< 1150		43-66					
	W 85-100	< 1250	-	45-68					
	S 60-70	<1000	20-40	43-63	91				
	I 70-80	<1100	23-43	45-66					
	W80-90	<1200	25-45	48-70					
France	S45-79	≤900	10-47	40-70	>85	-	-	210	215
	I 50-86	≤1000							
	W 55-99	≤1150							
	S35-70	<900	15-45	40-65	>85	-	-	-	-
	I 45-80	<1000	15-45	40-65	>85				
	W 55-90	<1150	15-47	43-70	>85				
	S35-70	<850	S≤40						
	I 45-80(1)	<1000	I≤43						
	W 55-90	<1150	W≤45						
	S 45-79	≤ 900	10-47	40-70	>85	-	-	210	215
	I 50-86	≤ 1000							
	W 55-99	≤ 1150							
Germany	S45-70		15-40	42-65	≥90	-	-	-	215
	W60-90		20-45	45-70	≥90	-	-	-	215
	S35-70	<950	15-45	40-65	>85	-	-	-	215
	I mixtures								
	W55-90	<1150	15-47	43-70	>85				

National Gasoline Specifications (cont-ed)

Country	RVP kPa	VLI	Distillation						
			E70 %vol	E 100 %vol	E180 %vol min	10%,°C max	50%,°C max	90%°C max	FBP °C max
Greece	S 62 max		10min	30-65	85	-	-	-	215
	W 80 max								
	S 65 max								
	W 80 max								
	S35-70	900	15-45	40-65	85	-	-	-	215
	W45-80	1000	-	-	85	-	-	-	215
Israel	45-66	≤910				75	125	180	
						73	125	180	215
						70	125	180	
	45-66	≤910				73	125	180	215
Italy	S40-74		10-45	30-70	85	-	-	-	220
	S35-70	<900	15-45	40-65	>85	-	-	-	215
	I45-80	<1000	15-45	40-65	>85	-	-	-	215
	W 55-90	<1100	15-47	43-70	>85				
Japan	44-78					70	125	180	220
Netherlands	S40-80	< 1050	15-45	40-65	>85				215
	I mixtures								
	W60-95	<1200	15-47	43-70	>85				
Portugal	S35-70		15-45	40-65	>85				215
	I 45-80								
	W60-95		15-47	43-70					
	S35-70	<900	15-45	40-65					
	I 45-80	<1050	15-45	40-65	>85				215
	W 60-95	<1200	15-47	43-70					

National Gasoline Specifitions (cont-ed)

Country	RVP kPa	VLI	Distillation						
			E70, %vol	E 100 %vol	E 180 %vol min	10%, °C max	50%, °C max	90%, °C max	FBP, °C max
South Africa	≤75	20(1)				65	77-115	185	215
		S ≤950 W≤1000 S≤890 W≤940				65	77-115	185	215
Spain	S48-64 W55-78		10-45	30-70	80				210
			15-45	40-65	>85				215
Sweden			No longer available						
	S45-80 W60-95	<1050 <1200	15-45 15-47	40-65 43-70	85				215
	S45-75 W65-95			43min 45min					215
	S45-70 W65-95			47min 50min					200
	S45-70 W65-95			47min 50min					205
			will be developed						
Switzerland	S45-70 W60-90	<990 <1230	15-42 20-47	40min 42min	85 85				215 215
	S35-70 I mixtures W60-95	<950 <1200	15-45 15-47	40-65 43-70	>85 >85				215 215

National Gasoline Specifications (cont-ed)

Country	RVP kPa	VLI	Distillation						
			E70, % vol	E 100, % vol	E 180 % vol min	10%, °C max	50%, °C max	90% °C max	FBP, °C max
United Kingdom	S45-80 I 103max W60-115	<1050 <1240 <1360	15-45	40-65	90				220
	S45-80 W65-100	<1050 <1250	15-45 20-50	40-65 43-70	>85 >85				215 215
U.S.A.			no longer available						
	AA 54 max A 62max	20max(3)				70 70	77-121 77-121	190 190	225 225
	South 50 max North 56 max							167(2)	

National Gasoline Specifications (cont-ed)

Country	Residue %vol max.	Oxidation stability, minutes min	Existent gum, mg/100 ml max	Copper corrosion 3h at 50°C max	Density at 15° C, kg/m³	Sulphur, % wt max
Australia		240	4	1		0.2
		240	4	1		0.05
Austria	Not sold since Oct. 93					
	2	360	5	1	735-780 720-770	0.05
Belgium	2.0	-	5	1	720-770	0.10
	2.0				730-780 725-775 720-770	0.10
California (U.S.A.)	Not sold since Jan. 92					
						0.004/0.003(1)
Canada	Not sold since Dec. 90					
		240	5	1		0.15
Denmark	2	480	4	1	730-770	0.10
	2	360	5	1	730-780 730 - 770 710 - 750	0.05
Finland	2	530	5	1	725-770	0.10
	2	360	5	1	725-780	0.05
						0.04 0.01
France	2		10	1B	720-770	0.15
	2	360	5	1	730-780	0.05
	2		10	1B	700-750	0.20
Germany	2		5	≤1	730-780	0.10
	2	360	5	1	725-780	0.05
Greece	2	360	4	1	720-770 700-750	0.10 0.15
	2	360	5	1	725-780	0.05

National Gasoline Specifications (cont-ed)

Country	Residue %vol max.	Oxidation stability, minutes min	Existent gum, mg/100 ml max	Copper corrosion 3h at 50°C max	Density at 15° C, kg/m^3	Sulphur, % wt max
Israel	1.5	240	5	1	715-780	0.15
	1.5	360	5	1	715-780	0.05(5)
Italy	2		8	1	725-770	0.20
		360	5	1	725-780	0.05
Japan	2	240	5	1	≤ 783	
Netherlands	2	360	5	1	725-780	0.05
Portugal	2	360	5	1	P720-770 R710-760	0.10
	2	360	5	1	725-780	0.05
South Africa	2	240	4.0	1		0.15
	2	360	4	1	710-785	0.10
Spain	2	240	5	1B	P720-780 R710-760	0.13
	2	360	5	1	725-780	0.05
Sweden	Not available					
	2	360	5	1	725-775	0.05
						0.1
						0.03
						0.01
	Will be developed					
Switzerland	-	240	5	1	-	0.10
	2	360	5	1	725-780	0.05
United Kingdom	2	240	5	1	-	0.20
	2	360	5	1	725-780	0.05
U.S.A.	Not sold since Jan. 95					

	2	240	5	1		0.10
						0.0338(2)

National Gasolilne Specifications (cont-ed)

Country	Lead Content, g/l max	Benzene Content, % Vol max	Aromatics Content, % Vol max	Olefins Content, % Vol max	Phosphorus Content, g/l max	Silicon Content, g/l max
Australia		5				
	0.013	5			0.0013	
Austria	Not sold since Oct. 1993					
	0.013	3.0			See column "Fuel Additives"	
Belgium	0.15					
California	Not sold since Jan. 1992					
		1.0/0.0.8(1)	25/22(1)	6.0/4.0(1)		
Canada	Not sold since Dec. 1990					
	0.013				0.0013	
Denmark	0.15					
	0.013	5.0			See column "Fuel Additives"	
Finland	0.15					
	0.013	5.0			See column "Fuel Additives"	
		3.0 1.0				
France	0.15	5.0				
	0.013	5.0			See column "Fuel additives"	
	0.08-0.15					0.002
	0.15	5.0				
Germany	0.15					
	0.013	5.0			See column "Fuel additives"	
Greece	0.15					
	0.013	5.0			See column "Fuel additives"	
Israel	0.15	5				
	0.013	5	to be reported		0.0013	

National Gasoline Specifications (cont-ed)

Country	Lead Content, g/l max	Benzene Content, % Vol max	Aromatics Content, % Vol max	Olefins Content , % Vol max	Phosphorus Content, g/l max	Silicon Content, g/l max
Italy	0.15					
	0.013	3.0			See column "Fuel additives"	
Japan	0.001-0.02					
Netherlands	0.013	5.0			See column "Fuel additives"	
Portugal	0.40					
	0.013	5.0			See column "Fuel additives"	
South Africa	0.4					
	0.013					
Spain	0.15					
	0.013	5.0			See column "Fuel additives"	
Sweden	Not available					
	0.013	5.0			See column "Fuel additives"	
	0.013	5.0			nil(1)	
	0.005	3.0	6(4)		0.002	
	0.005	3.0	5.5(4)		nil(1)	
	Will be developed					
Switzerland	0.15					
	0.013	5.0			See column "Fuel additives"	
United Kingdom	0.15					
	0.013	5.0			See column "Fuel additives"	
U.S.A.	Not sold since Jan. 1995					
	0.013				0.0013	

	(1)	1.0-batch basis 0.95-average basis	28.6$^{(2)}$	10.8$^{(2)}$		

National Gasoline Specifications (cont-ed)

Country	Oxygenates Content	Deposits control	Use of Additives
Australia	Adding to gasoline is allowed		The use of additives is allowed
Austria	Not sold since Oct. 1993		
	According to the Directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
Belgium	According to the Directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
California (U.S.A.)	Not sold since Jan. 1992		
	Oxygen 1.8 - 2.2% mass	PFI Injector Cleanliness (Chrysler 2.2 l engine). Intake Valve Cleanliness (BMW 318i engine)	Deposits control additives must be used
Canada	MTBE ≤ 11% vol.		The use of additives intended to improve a gasoline performance is allowed.
Denmark			
	According to the Directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
Finland			
	According to the Directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
	2.0 - 2.7%wt O_2		The use of additives is allowed but no phosphorous containing compounds
France	Methanol ≤ 3% vol. Ethanol ≤ 5% vol Ethers ≤ 15% vol		
	According to the Directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
	No alcohols and no ketones Ethers ≤ 15% vol.	Carburettor Cleanliness(3) (CEC F-03-T-81): Merit > 8. Injector Cleanliness(4) (GFC-TAE-1-87): flow rate losses < 4%. Intake Valve Cleanliness (CEC F-04-A-87)(5): Merit ≥ 9 (CEC F-05-A-94)(6): Merit ≥ 9.	

	Methanol ≤ 3% vol Ethanol ≤ 5% vol Ethers ≤ 15% vol		

National Gasoline Specifications (cont-ed)

Country	Oxygenates Content	Deposits control	Use of Additives
Germany	Methanol ≤ 3% vol. Ethanol ≤ 5% vol. Ethers: ≤ 15% vol.		
	According to the Directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
Greece			
	According to the directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
Israel	MTBE ≤ 10% vol.		Deposits control additives must be used.
	Methanol ≤ 3% vol Ethanol ≤ 5% vol Ethers ≤ 15% vol Oxygen ≤ 2.8% wt	Carburettor cleanliness (CEC F-03-T-81): Merit > 8. Injector cleanliness (Peugeot 205 GTI test): Flow rate losses < 4%. Intake Valve Cleanliness (CEC F-04-A-87): Deposits reduction ≥ 50%	
Italy			
	According to the directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
Japan			
Netherlands	According to the directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
Portugal			
	According to the directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
South Africa	The 93 RON grade manufactured by the SASOl oil-from-coal process contains 8-12% alcohols (mainly ethanol)		
	Oxygen ≤ 2.8% mass(3) Oxygen ≤ 3.7% mass(3)		
Spain			
	According to the directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds

National Gasoline Specifications (cont-ed)

Country	Oxygenates content	Deposits control	Use of Additives
Sweden	Not available		
	According to the directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
	Oxygen ≤ 2% wt	Intake Valve cleanliness(2) (CEC F-05-T-92): Merit ≥ 9. Injector cleanliness (3) (GFC-TAE-1-87): flow rate losses ≤ 4%.	Additives must not contain ash-forming constituents
	Will be developed		
Switzerland			
	According to the directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
United Kingdom			
	According to the Directive 85/536/EEC		The use of additives is allowed but no phosphorous containing compounds
U.S.A.	Not sold since Jan. 1995		
	Oxygen ≤ 2% mass Oxygen ≤ 2.7% mass for fuels containing aliphatic ethers or/and alcohols (not methanol)		
	Oxygen 2 - 2.7% mass	PFI Injector cleanliness (Chrysler 2.2 l engine): flow rate losses < 5%. Intake Valve cleanliness (BMW 318i engine).	From January 1, 1995 all gasolines in the U.S. must contain deposits control additives.

National Gasoline Specifications (cont-ed)

Country	Remarks
Australia	
Austria	Not sold since October 1993
California (U.S.A.)	Not sold since January 1992 (1) - Batch basis/average basis
Canada	Not sold since December 1990 Manganese content ≤ 18 mg Mn/l (1) Antiknock Index = (RON+MON)/2 (2) MON must not be lower from Antiknock Index at more than 5 units.
Denmark	
Finland	(1) - According to [6], leaded gasoline is already not available
France	(1) - Equivalent vapor pressure at 37.8°C according to "Grabner method". (2) - MTBE ≤ 15% vol; ETBE ≤ 15% vol., with residual alcohols ≤ 1% vol. (3) - Renault R5 test. (4) - Peugeot 205 GTI test. (5) - Opel Kadett test. (6) - Mercedes M102E test.
Germany	
Greece	
Israel	(1) - Allowed 84 until 1/4/1997. (2) - Allowed 84 until 1/2/1996 and 85 - until 1/4/1997; (3) - Allowed 84 until 1/4/1997. (4) - Allowed 80 until 1/4/1997. (5) - Allowed 0.10 until 1/4/1996.
Italy	
Japan	
The Netherlands	
Portugal	

National Gasoline Specifications (cont-ed)

Country	Remarks
South Africa	(1) - Vapor/Liquid/Ratio at 325 K/Pa (max) calculated according to ASTM D2533 (1) - MON = 87 for blends with alcohol content > 0.2% vol. (2) - MON = 83 for blends with alcohol content > 0.2% vol. Every alcohol blended with gasoline must contain minimum 85% mass of ethanol with the balance, which is mainly iso- and n-propanol. (3) - It is possible to use ethers with 5 or more atoms of carbon in the molecula.
Spain	(1) Had to be put into force from winter 1994
Sweden	Not available
	(1) - negligible. (2) - Mercedes M-102E test. (3) - Peugeot 205GTI test. (4) - Empirical limit = $\frac{\text{Aromatics, \%vol.}}{13}$ + Benzene, %vol. (max).
	Will be developed
Switzerland	
United Kingdom	
U.S.A.	Not sold since January 1995
	(1) - This requirement is not official, excluding number of states, where it already put into force. (2) - Antiknock Index = (RON + MON)/2. (3) - Vapor/Liquid Ratio according to ASTM D2533.
	(1) - Heavy Metals - none without an EPA waiver. (2) - Statutory Baseline Parameters - 1990 average quality. Emissions reduction relative to 1990 baseline average quality: (3) NO_X - 1.5% min; Toxics - 16.5% min. (4) - NO_X =- 6.8% min; Toxics - 21.5% min.

APPENDIX 2

National Specifications for Automotive Diesel Fuel

(based on the CONCAWE data, [15])

Country	National Standard reference (date)	Grade	Cetane number min.	Cetane index min.	Flash Point PM °C min.	Sulphur Content % m/m (max.)
Australia	AS 3570 1989	Summer Winter	45	-	(1)	0.5
Austria	O Norm EN 590 (1.2.94)	Winter Intermediate Summer	49	46	55	(1)0.05
Belgium	NBN EN 590	Winter Intermediate Summer	49	46	55	0.2
California (U.S.A.	CARB Diesel 1.10.1993		48		54	0.05
Canada	CAN/CGSB 3.6-M90	A	40		40	0.30
		B	40		40	0.30
Denmark		CEN Diesel	49	46	55	0.2
		CEN Low sulphur	49	46	55	0.05
		Bus Diesel	50	47		0.05
Finland	SF-EN590	C	49	46	55	0.2
		1	47	46	55	
		3	45	43	55	
		4	45	43	55	
	Reformulated Diesel: 1.7.93	Summer	49	49	56	0.005
		Winter	47	47	56	0.005
France	EN590:1993	Summer	49	46	(3)55	0.2
		Winter				
		Grand Froid	50	49		0.15
Germany	DIN EN590:1993	Summer Intermediate Winter	49	46	55	0.2
Greece	EN 590:1993	Summer Winter	49	46	55	0.3
Ireland	IS EN:590 1993	Summer Winter	50	50	55	0.3
Israel	Israel Standard No. 107 1995	Winter Summer	50	48	66	0.20

Italy	UNI-CUNA EN 590:93 1.10.93	Summer Winter	49	46	55	0.2

National Specifications for Automotive Diesel Fuel (cont-ed)

Country	National Standard reference (date)	Grade	Cetane number min.	Cetane index min.	Flash Point PM°C min.	Sulphur Content %m/m (max.)
Japan	JIS K2204 1992	Special No. 1	(2)	50	50	(4)0.20
		No. 1	(2)	50	50	0.20
		No. 2	(2)	45	50	0.20
		No. 3	(2)	45	45	0.20
		Special No. 3	(2)	45	45	0.20
Netherlands		Winter Intermediate Summer				0.2
Portugal	EN 590 1993	Summer Winter	49	46	55	0.3
South Africa	SABS 342 1994		45		55	0.55
Spain	EN 590 1993	Summer Winter	49	46	55	0.3
Sweden	SS 155435 13.03.91	Urban Diesel 1 Summer	50	50	56	0.001
		(TD1 Grade) - Winter				
		Urban Diesel 2				
		Summer	47	47	56	0.005
		(TD2 Grade) - Winter				
		Normal Summer Diesel D 10				0.20
		Winter Diesel 1 D 26	49	46	56	0.20
			47	46	56	0.20
		Winter Diesel 2 D32				
		Winter Diesel 3 D36	46	46	56	0.20
			45	43	56	
Switzerland	SN EN 590	Summer (01.05-30.09)	49	46	55	0.05
		All year	47	46	55	0.05
United Kingdom	B S EN 590:1930		49	46	55	0.2
U.S.A.	ASTM D975 (1994)	Low Sulphur No. 1-D-A	40	40(4)	38	0.05
		Low Sulphur No. 2-D-A	40	40(4)	52	0.05
		No. 1-D-A	40	-	38	0.50
		No. 2-D-A	40	-	52	0.50

National Specifications for Automotive Diesel Fuel (cont-ed)

Country	CFPP °C Max.	Density at 15°C kg/m³	Kinematic Viscosity mm²/sec	
			at 20°C	at 40°C
Australia	+12; +3; +1; -7;	820 - 870		1.9 - 5.5
Austria	-20 -15 + 5	820 - 860		2.0 - 4.5
Belgium	-15 - 5 0	820 - 860		2.0 - 4.5
California		830 - 860		2.0 - 4.1
Canada				1.3 - 3.6 1.7 - 4.1
Denmark		820 - 860 820 - 860 820 - 855		2.0 - 4.5 2.0 - 4.5
Finland	-5 -26 -38 -44 -15 -34	820 - 860 800 - 845 800 - 840 800 - 840 820 - 850 800 - 830		2.0 - 4.5 1.5 - 4.0 1.4 - 4.0 1.2 - 4.0 2.0 - 3.5 1.4 - 2.6
France	0 -15 -20	820 - 860		2.0 - 4.5 2.0 - 4.5
Germany	0 -10 -20	820 - 860		2.0 - 4.5
Greece	+5 -5	820 - 860		2.0 - 4.5
Ireland	-	820 - 860		2.0 - 4.5
Israel	+9 -2	820 - 860		2.5 - 6.0
Italy	0 -10	820 - 860		2.0 - 4.5
Japan	- -1 -5 -12 -19			2.7 min(3) 2.7 min 2.5 min 2.0 min 1.7 min

National Specifications for Automotive Diesel Fuel (cont-ed)

Country	CFPP °C Max.	Density at 15°C kg/m³	Kinematic Viscosity mm²/sec	
			at 20°C	at 40°C
Netherlands	-15 -5 0			
Portugal	0 -6	820 - 860		2.0 - 4.5
South Africa	-4			2.2 - 5.3
Spain	0 -10	820 - 860		2.0 - 4.5
Sweden	-10(S)(1); -26(W) -10(S); -26(W) -10 -26 -32 -38	800 - 820 800 - 820 820 - 860 800 - 845 800 - 840 800 - 840		1.2 - 4.0 1.2 - 4.0 2.0 - 4.5 1.5 - 4.0 1.5 - 4.0 1.4 - 4.0
Switzerland	-10 -20	820 - 860 800 - 845		2.0 - 4.5 1.5 - 4.0
U.K.	-15	820 - 860		2.0 - 4.5
U.S.A.				1.3 - 2.4 1.9 - 4.1 1.3 - 2.4 1.9 - 4.1

National Specifications for Automotive Diesel Fuel (cont-ed)

Country	Distillation (°C)								Aromatics content % v.v max.
	IBP min.	10% min.	50% max.	65% min.	85% min.	90% max.	95% min.	FBP min.	
Australia						357			
Austria				250	350		370		
Belgium				250	350		370		
Californ. (U.S.A.)	170-215	205-255	245-295			290-320		-305 350	10(1)
Canada						290			
						360			
Denmark				250	350		370		
				250	350		370		
							325		
Finland				250	350		370		
		180					340		
		180					340		
		180					340		
							350		
							310		
France				250	350		370		
				250	350		370		
				250	350		370		30(4)
Germany				250	350		370		
Greece				250	350		370		
Ireland				250	350		370		
Israel						357			
Italy				250	350		370		
Japaan					360				
					360				
					350				
					330(1)				
					330				
Nether-lands					350		370		
				250					
Portugal				250	350		370		
South Africa						362			
Spain				250	350		370		

Sweden	180						285	300	5(2)
	180						295		20(3)
				250	350		370		
		180					340		
		180					340		
		180					340		
Switzerland		180		250	350		370		
		180(max)					340		

National Specifications for Automotive Diesel Fuel (cont-ed)

Country	Distillation (°C)	10% min.	50% max.	65% min.	85% min.	90% max.	95% min.	FBP min.	Aromatics content % v.v max.
U.K.				250	350		370		
U.S.A.						288 338(1) 288 338(1)			35((4) 35(4)

National Specifications for Automotive Diesel Fuel (cont-ed)

Country	Oxidation Stability mg/l max.	Copper corrosion 3h at 50°C max.	Ash % m/m	Water Content % m/m (max.)	Cloud Point °C max.	Pour Point	Fuel Additives
Australia	25	2(2)	0.01	0.05/vol.	+15;+6;+4; -4+7;0;-1; -4;		May include additives
Austria	25	1	0.01	0.02			Fuel additives using is allowed to improve the fuel quality
Belgium	25	1	0.01	0.02			Fuel additives using is allowed to improve the fuel quality
California (U.S.A.)							
Canada		1(1)	0.01	0.05(2)/vol			
Denmark	25 25	1 1	0.01 0.01	0.02 0.02			
Finland					- -16 -28 -34 - 5 -29		
France	25 15	1 5%(2)	0.01	0.02	- -8		Fuel Additives using is allowed to improve the fuel quality. (Detergents antifoams etc.)
Germany	25	1	0.01	0.02			Fuel additives using is allowed to improve the fuel quality.
Greece	25	1	0.01	0.02	- 0		Fuel additives using is allowed to improve the fuel quality.

National Specifications for Automotive Diesel Fuel (cont-ed)

Country	Oxidation Stability mg/l max.	Copper corrosion 3h at 50°C max.	Ash % m/m	Water Content % m/m (max.)	Cloud Point °C max.	Pour Point	Fuel Additives
Ireland	25	1	0.01	0.02			Fuel additives using is allowed to improve the fuel quality.
Israel	25	1(1)	0.01	0.05/vol		+5 -6	It is possible to use additives to decrease Pour Point temperature or to improve performance.
Italy	25	1	0.01	0.02			Fuel additives using is allowed to improve the fuel quality.
Japan						+5 -25 -7.5 -20 -30	
Netherlands							
Portugal	25	1	0.01	0.02			Fuel additives using is allowed to improve the fuel quality.
South Africa		1(1)	0.01	0,05/vol			
Spain	25	1	0.01	0.02			Fuel additives using is allowed to improve the fuel quality.

National Specifications for Automotive diesel fuels (cont-ed)

Sweden	25 25 25 25 25 25	1 1 1 1 1 1	0.01 0.01 0.01 0.01 0.01 0.01	0.01 0.01 0.02 0.02 0.02 0.02	(w)-16(s)0 (w)-16(1)(s) 0 -16 -22 -28		The fuel may include any additives that is chifly intended for high- speed diesel engines, i.e. engines running at not less than 16 r/s under full load.
Switzerland	25	1	0.01	0.02			Fuel additives using is allowed to improve the fuel quality.
U.K.	25	1	0.01	0.01	0.02		addditives is allowed to improve the fuel quality.
U.S.A.		3 3 3 3	0.01 0.01 0.01 0.01	(2)0.05/vol 0.05/vol. 0.05/vol. 0.05/vol.	(3)		Stability and biocide additives are allowed. On May 27, 1994 EPA finalised regulations which contains test requirements for fuel addities.

National Specifications for Automotive Fuels (cont-ed)

Country	Remarks
Australia	(1) In accordance with the law (2) 3 hours at 100°C
Austria	(1) From 10.01.1995 (Regulation No. 123 - Ministry of Environmental 03.01.1992
Belgium	
California (U.S.A.)	(1) PAH - 1.4% m/m (max.)
Canada	(1) 3 hours at 100°C (2) Water content and sediment
Denmark	
Finland	
France	(1) 820 - 855 with Cetane Index ≥ 50 and Cetane Number ≥ 51.; (2) ASTM D655-83 Instruction A; (3)AFNOR T60103 (this for > 52°C PM); (4) It is possible to limit the content of PAH (to be defined)
Germany	
Greece	Greek Government Gazette 336 /94
Ireland	
Israel	(1) 3 hours at 100°C
Italy	
Japan	(1) If fuel viscosity ≥ 4.7 cSt, T90 must be ≥ 350°C (2) Cetane number can replace Cetane Index (3) at 30°C (4) 0.05 from May 1997.
Netherlands	
Portugal	
South Africa	(1) 3 hours at 100°C
Spain	
Sweden	(1) (s) - summer; (w) winter (2) PAH - 0.02% v/v (max.) (3) PAH - 0.1% v/v (max.)
Switzerland	
United Kingdom	

USA	(1) 282°C min. (2) Water and sediment content (3) Winter fuel properties must be settled by agreement between refiners and customers. (4) It is necessary to fulfill one of these requirements.