New octane booster molecules for modern gasoline composition

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Abstract

In the framework of reducing GHG emissions and accelerating the decarbonization of the road transport sector, vehicle efficiency is a key factor for competitiveness. In this sense, refining industry can make its contribution by reformulating high-octane petrol fuel. The impact of this type of gasoline from CO_2 emission balance, technical feasibility and economics standpoints has recently been assessed by the petroleum industry with promising results and new potential boosters that could improve the octane number of standard gasoline are more needed than ever.

The present work summarizes a comprehensive review aimed at collecting available data regarding chemical molecules that can be used in advanced gasoline formulations for modern spark-ignited car engines focusing on ash-free technologies. Potential boosters are divided into two categories: high octane gasoline components and octane enhancer additives, being 2 %vol. the considered frontier concentration between them. Targeted chemical compounds examined in the screening for high-octane components include isoparaffins, olefins, aromatics, alcohols, ethers, esters, ketones, furans, and carbonates. Chemical families assessed as additives were anilines, hydrazines, amines, pyridines, quinolines, indoles, N-nitrosamines, iodine compounds, selenium compounds, phenols, formates, oxalates, and, in lesser extension, other families. The scope of the analysis includes not only antiknock effectiveness, but also associated side effects for the engine, possible effects on both human health and environment, current applications, and compatibility with existing infrastructure, among others.

Promising opportunities in medium and long term for every family of chemical compounds that can potentially improve the anti-knock character of modern gasolines well beyond current specifications worldwide are presented. Furthermore, a few chemical families are identified as the most promising ones to be used in future gasoline formulations, either as high-octane components (such as ethers, ketones, and esters) or as octane booster additives (such as anilines, N-nitrosamines, and phenols).

1. Introduction

As it is known, vehicle efficiency is a key factor for competitiveness that can contribute to greenhouse gas (GHG) emissions reduction and acceleration of the decarbonization of the road transport sector. The refining industry could help achieving this goal by the formulation of high-octane petrol (HOP). The impact of this type of gasoline from CO_2 emission balance, the technical feasibility of its production in the EU refining system, and economic standpoints have been theoretically assessed by Concawe (Environmental Science for European Refining, an association of companies that operate petroleum refineries in the EU) with promising results. For instance, when compared to standard 95 and 98 grade gasoline, one can observe that an optimized engine operating with a high compression ratio presents a 1 % engine efficiency increase per 1 point of RON increase, with a reduction in CO_2 emissions [1,2]. A recent engine modelling and vehicle study also carried out by Concawe, has confirmed that the thermal efficiency and tailpipe pollutant emissions benefits previously predicted could be attributed to the use of HOPs in spark-ignited (SI) engines [3]. A newly designed high-octane rating fuel (Efitec 100 Neotech, an additivated gasoline) has been already launched successfully to the market [4]. This fuel not only reduces fuel consumption and gaseous and particle emissions but also does not produce any detrimental effects on commercial three-way catalytic converter (TWC) performance over the short catalyst aging acceleration test in comparison to a current commercial gasoline fuel used as baseline [5,6].

Accordingly, fuel and engine technologies interact synergistically, with HOPs enabling the engine to work in more efficient conditions leading to an effective GHG emissions reduction. Molecules that could improve the octane number of standard gasoline are more needed than ever, and their availability to the refining industry needs to be forwarded. For this reason, works reflecting on the state of the art in this field are essential at this point. Notwithstanding, there are many works and patents to be quoted, many of which are set out in recent reviews. Boot et al. (2017) studied the chemistry behind octane boosters and deduce generic design rules to guarantee good anti-knock performance, considering recent advances in engine technology [7]. They concluded that highly unsaturated cyclic compounds are the preferred octane boosters for modern SI engines. Multi-branched paraffins come in distance in second place and depending on the type and location of the functional oxygen group, oxygenates can have a beneficial, neutral, or detrimental impact on anti-knock quality. The review of Dunn et al. (2018) focuses on biomass-derived blendstocks that could be blended with gasoline and used in SI engines, regardless of the possibility that they could also be produced from petroleum or gas natural feedstocks [8]. Those promising bio-blendstocks, with Research Octane Number (RON) exceeding 98, were previously identified by the Co-Optimization of Fuels & Engines (Co-Optima) research initiative [9]. They were evaluated by means of 17 metrics, developed for economic viability, scalability, and energy and environmental impact. For each metric, three categories were established, into which each blendstock fell: favorable, neutral, or unfavorable. They sowed key knowledge gaps including the degree of purity needed for use as a bio-blendstock and the uncertainty about their blending level.

Together with the mentioned works, references can be found in the literature dealing with several aspects related to vehicle efficiency which are of paramount relevance, such as technical progress in internal combustion engine technologies (e.g., [10–12]), emission control (e.g., [13–15]), and, in significantly superior number, advanced fuel formulations (e.g., [16–20]). However, to date, scarce relevant references can be found focusing on identifying potential molecules able to boost HOPs. Recent relevant review papers covering different aspects related to gasoline boosters and/or topics directly linked to efficiency in car transportation engines are listed in Table 1.

Table 1. Previous relevant review papers related to vehicle efficiency.

Author(s)	Topic reviewed	Date until literature was covered
F. Zhao, M.C. Lai, D.L. Harrington [10]	Spark-ignited direct-injection gasoline engines	1999
B.L. Salvi, K.A. Subramanian, N.L. Panwar [16]	Alternative fuels	2013
A. Alagumalai [11]	Internal combustion engines	2014
W. Trindade, R. Santos [17]	Butanol as fuel in internal combustion engines	2016
M.D. Boot et al. [7]	Relationship between molecular structure and auto-ignition behavior	2016

O.I. Awad et al. [18]	Alcohol and ether as alternative fuels in spark ignition engine	2017
J. Farrel, J.Holladay, R. Wagner [9]	Potential fuel blendstocks to optimize gasoline engine performance	2017
J.B. Dunn et al. [8]	Evaluation of bio-.blendstocks for economic viability, scalability, and energy and environmental impact.	2017
T. Johnson, A. Joshi [13]	Vehicle engine efficiency and emissions	2018
S. Zhu et al. [12]	Water injection in internal combustion engine for combustion improvement	2018
S.M. Safieddin Ardebili et al. [19]	Fuel oil as a renewable fuel for internal combustion engines	2020
H. Stančin et al. [20]	Alternative fuels	2020

Thus, the goal of the present paper is to carry out a review aimed at collecting available data regarding chemical molecules that can be used in advanced gasoline formulations for modern SI car engines focusing on ash-free technologies. By this, more than 22 chemical compound families are assessed concerning their potential improvement on the anti-knock character of modern gasoline, well beyond current specifications worldwide. However, not only anti-knock effectiveness is considered when analyzing potential boosters but also associated side effects, distribution system compatibility, technology readiness and applications, including production viability, the sustainability of use, and associated toxicology according to Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

A brief introduction is conducted in Section 1, which is devoted to reviewing trends in engine and octane booster technology by presenting various indicators to assess the potential blendstocks (Section 1.2), to offering a historical perspective on anti-knock additives (Section 1.3), and to presenting and defining a set of metrics that allow proper comparison among candidate molecules (Section 1.4). Section 2 and Section 3 present the main properties of the assessed chemical families, which have been divided into two main categories, that is high-octane components (Section 2), which include potential molecules to be added to gasoline formulations in concentrations higher than 2 %vol., and octane enhancer additives, which deal with potential molecules to be included in lower concentrations (Section 3). Both sections include information regarding physical and thermochemical data, as well as associated hazard information, together with available information on associated side effects, distribution system compatibility, and current technology readiness, among other aspects. In Section 4, concluding remarks leading to preferred chemical compounds to be used in modern gasoline formulations are presented, according to the previously defined metrics. Finally, future scope and trends in the field are presented in Section 5.

1.1. Modern Spark-Ignited engines

During several decades, different strategies aimed at improving engine efficiency have been developed and adopted by car manufacturers. The main targets have been to reduce specific fuel consumption and to prevent knocking, as well as to comply with the increasingly more restrictive legislation requirements on pollutants emissions. Concerning the knocking phenomenon, the most widely adopted strategy is based on the fact that by modifying the engine operation conditions, the octane requirements for a given fuel are lower. As will be further discussed in Section 1.2.6, octane requirement (or octane appetite) is referred to the minimum fuel quality needed to prevent knocking for a given engine or engine operating conditions [7].

Among the different strategies adopted to improve efficiency, direct injection, turbocharging coupled with engine downsizing, and higher compression ratios with new valve timing to shorten the compression stroke, have been successful in lowering unburnt gas temperatures relative to pressure, which in turn have resulted in reducing actual octane appetite of modern cars and thus effectively reducing knocking [7,21,22].

With gasoline direct injection (GDI), the air-fuel mixture is injected in the form of a spray into the cylinder. As a consequence, the mixture vaporization is mainly driven by the absorption of heat by the charge, rather than by heat absorption from the surfaces of elements in the engine (such as the walls or the intake valve), as is the case with port fuel injection, which results in a reduction of the air-fuel mixture temperature before the compression stroke. Besides, when compared with carburetors (an earlier technology), GDI avoids freezing of less volatile, more knock-resistant, fuels [7,10].

Initially, turbocharging was meant to boost the engine power output but, with time, it became evident that fuel economy highly benefitted by downsizing, which involves displacing smaller volumes, and consumer's demand grew considerably due in part to legislation requirements. In principle, turbocharging an engine involves a slight increase of the air-fuel mixture temperature because of the higher compression, but the associated presence of an intercooler overcompensates such raise due to heat losses and, globally, the mixture temperature drops [7,23].

Concenrning compression ratios, the higher the ratio the greater the temperature drop relative to pressure. Even though generally, higher ratios involve both higher temperatures and pressures, at high ratios, the end gas volume is reduced in size and, as a consequence, hot combustion gases are expelled to a greater extent during the exhaust stroke. Thus, there is less hot gas to be cooled down during the intake stroke. Therefore, temperature relative to pressure is reduced at higher compression ratios [7].

On the other hand, application of the Miller cycle (i.e., shortening compression stroke in relation to expansion stroke) has proven to reduce both temperature and pressure at the end of the compression stroke. Such a cycle can be implemented by altering the closing timing of the intake valve. Either late or early intake valve closing has the potential to suppress knocking and to enhance fuel consumption economy [22].

Future trends also include Spark Controlled Compression Ignition (SPCCI) engines, which operate at a high compression ratio (at about 16:1) and with an extremely lean air-to-fuel ratio to achieve more complete combustion of the gasoline throughout the cylinder. In SPCCI engines, compression ratios are just below those in Homogeneous Charge Compression Ignition (HCCI), typical of diesel engines. This is achieved by using controlled auto-ignition of gasoline to take advantage of the consequential pressure rise. HCCI technology offers a wide range of fuel flexibility, a higher thermal efficiency, and low emissions (NO_X and soot emissions are suppressed from the engine) [24].

1.2. Fuel quality testing

1.2.1. Research and Motor Octane Number

Among gasoline quality testing, octane number (ON) is the most known measure of the auto-ignition character of a fuel. As early as 1932, two tests were defined to assess ON: Research Octane Number (RON) and Motor Octane Number (MON). Nowadays, both tests are run in Cooperative Fuel Research (CFR) engines worldwide according to EN ISO 25164 (or the equivalent ASTM D 2699) and EN ISO 25163 (or ASTM D 2700), respectively. CFR engines are standard single-cylinder, four-stroke engines, specially developed for this purpose. RON is used to assess ON in normal road performance, i.e., at mild conditions of air inlet temperature (52 ºC) and revolutions per minute (600 rpm), while MON corresponds to high-speed performance at more severe conditions (i.e., 149 ºC of air-fuel mixture and 900 rpm) [7,21,25].

RON and MON values of pure hydrocarbons decrease in the order: aromatics > isoalkanes (isoparaffins) > alkenes (olefins) > cycloalkanes (naphthenes) > n-alkanes (n-paraffins). Increasing molecular complexity (branching), decreasing molecular weight, and presence of unsaturation each tend to increase octane number [26,27].

ON is established by comparison of the auto-ignition performance of a given fuel in a CFR engine to that of standard binary mixtures, according to an arbitrarily established scale. These mixtures present different concentrations of n-heptane (for which ON = 0 was defined since it auto-ignites easily) and 2,4,4-trimethyl-pentane (or isooctane, which, by definition, has ON = 100, because it exhibits high knocking resistance). According to its knocking performance, the ON of a given fuel is presented as the volumetric percentage of isooctane of the standard binary mixture that produces the same knock intensity as the tested fuel [21,28]. However, some chemicals present higher antiknock resistance than isooctane, giving rise to fuels with ON greater than 100. In such cases, the tested gasoline is compared to reference fuels composed of isooctane and different amounts of tetraethyllead, an antiknock additive, using empirical relationships defined by either RON or MON tests [26].

ON of pure compounds are often noted as $\mathrm{ON_C}$, whereas ON of mixtures are $\mathrm{ON_M}$. On the other hand, the ON of a component in a gasoline mixture is part of what is often referred to as Blending Octane Number (BON). BON is useful because $\mathrm{ON_M}$ cannot be calculated directly from $\mathrm{ON_C}$. After all, either synergistic or antagonistic effects can arise when blending fuel components that result in nonlinear ON responses for real fuels. BON is related to $\mathrm{ON_M}$ according to: [27]

$$\mathrm{BON} = \frac{\mathrm{ON_M} - \mathrm{ON_{BG}}\left(1-x\right)}{x} \tag{1}$$

where $\mathrm{ON_{BG}}$ is the ON of the base gasoline and x the volume fraction of the component. Here, base gasoline refers to the gasoline mixture to which the component is added. Equation 1 is based on attributing all the differences between $\mathrm{ON_M}$ and $\mathrm{ON_{BG}}$ to the blended component and it provides a fictitious BON value obtained by linear extrapolation. Two possibilities can take place when the $\mathrm{ON_C}$ of the blended component is measured: either the obtained value is higher than BON or it is lower. If BON is larger than $\mathrm{ON_C}$ a synergistic effect further improves the gasoline antiknocking quality by the addition of the component and, conversely if BON is smaller than $\mathrm{ON_C}$ the addition of that component poses an antagonistic effect [27,28].

1.2.2. Road octane number

During the second half of the 20th century, the Coordinating Research Center (CRC) conducted studies aimed at assessing the octane requirements of US cars, and new tests were developed. CRC carried out tests on chassis dynamometers, with the cars being run at part or wide-open throttle that provided a more informative insight on the actual octane requirements of more realistic engines, and the Road Octane Number (RoadON) was defined thereof. RoadON is determined by the knocking performance of the tested engines under the specified operating conditions when fueled with a standard fuel with known RON and MON, which was designed to emulate commercial gasolines. RoadON can be expressed as a function of RON and MON, as follows:

$$\mathrm{RoadON} = a + b \cdot \mathrm{RON} + c \cdot \mathrm{MON} \tag{2}$$

where *a*, *b*, and *c* are parameters obtained by least-square regression. CRC data allowed observing that, over the years, RON became more important than MON, probably due to the generalization of newer technologies. As a consequence, RoadON is now considered almost an equivalent of RON [7].

1.2.3. Octane index

As commented, the knock resistance defined by RON and MON is based on CFR engine tests, representative of 1930s car engines. Therefore, in such testing, the engine operating conditions are far more severe than in modern car engines. This is particularly evident for temperatures, which nowadays are way lower (in the range of 30–50 ºC on average) since current technology is no longer run by heated carburetors and includes more adequate cooling systems. Consequently, a newer measure of the antiknock quality of fuel was defined to take this fact into account: Octane Index (OI). OI can be formulated as follows:

$$\mathrm{OI} = \left(1 - K\right) \cdot \mathrm{RON} + K \cdot \mathrm{MON} \tag{3}$$

where the parameter *K* depends not on the fuel but on the engine conditions, that is, on the end gas temperature-pressure history before the auto-ignition takes place. By definition, *K* equals zero for RON conditions and 1 for MON. Tested values of *K* using real engines rose from 0.5 in 1930 to 1 during the 1940s. The historical *K* value of 0.5 led to the definition of the Anti-Knock Index (AKI), still used nowadays, as can be deduced from Equation 3:

$$\mathrm{AKI} = \frac{\mathrm{RON} + \mathrm{MON}}{2} \tag{4}$$

From CRC data, it has been determined that, on average, *K* equaled zero by 2000 and is negative for current engines. Negative values of *K* imply that, for a given RON, gasolines with a high octane sensitivity (S) have better antiknock performance and, consequently, they do not necessarily improve when RON or MON are increased. Sensitivity is defined as the difference between RON and MON (S = RON – MON), which gives rise to the following reformulation of OI [7,29].

$$\mathrm{OI} = \mathrm{RON} - K \cdot \mathrm{S} \tag{5}$$

S is a measure of “octane depreciation” at increasing engine speed and temperature, which is the tendency of hydrocarbon fuels to exhibit antiknock behavior that becomes increasingly worse as conditions are more severe (i.e., high engine speed and temperature) [7,30]. Typically, aromatics, olefins, and oxygenates have S values that are greatly larger than those of paraffins [7], which encourages their usage in fuel formulation meant for modern engines. Currently, 10 points sensitivity is generally prescribed for every gasoline [31].

Interestingly, an empirical correlation has been reported between gasoline’s sensitivity and the blending ON that it will exhibit [27,32], according to which an increase in S would entail a decrease in BRON or BMON (that is, Blending Research or Motor Octane Number, respectively).

1.2.4. Front end octane number

The Front end Octane Number (FON, or R100) is the RON determined for the fuel fraction that boils at temperatures below 100 ºC. This measure is useful for fuels presenting a non-homogeneous concentration distribution (hence octane distribution). Light fractions tend to vaporize swiftly once in the intake system and to be well distributed among all cylinders, but heavier fractions usually condensate on the intake system walls and, therefore, their distribution in the engine cylinders can be non-uniform [33,34].

Historically, FON was particularly important during the era when lead-based compounds were used as octane enhancers (until the 2000s, approximately). Among lead-based compounds, tetraethyllead (TEL) tended to concentrate in the heavier fuel fraction whereas tetramethyllead (TML) improved FON greatly due to its lower boiling point [27]. Thus, to cover a broad range of gasoline fractions, mixed alkyl lead compounds were used.

Today, FON is still useful to ensure enough knocking resistance during the cold start warming up period since, at low ambient temperatures, vaporization of the different gasoline fractions might result in non-uniform octane distribution among the engine cylinders, especially when port fuel injectors are used [35].

1.2.5. Distribution octane number

The Distribution Octane Number (DON) is related to the octane requirement increase due to specific engine conditions. When operating at low speed and with a wide-open throttle, the fuel vaporization in the intake system is poor and, therefore, fractionation of the fuel is observed. DON is meant to evaluate antiknock performance under these conditions because the octane quality of the fuel injected into the cylinder might be substantially different than that of the fuel in the tank [36].

DON tests measure the knocking performance of the different gasoline fractions, which are obtained either by distillation or condensation, in single-cylinder laboratory engines designed for RON determinations [36].

DON and FON are related to one another by delta-RON, which is defined as the difference in RON values between the heavier and the lighter gasoline fractions, the lighter fraction being the one that boils below 100 ºC. The determination is carried out in three stages: 1) conventional determination of RON; 2) ASTM distillation up to 100 ºC and recovery of the distillate; and 3) measurement of RON of this volatile fraction. Values of delta-RON for most commercial gasolines are between 5 and 15. A value below 10 is considered satisfactory (Germany requires a minimum delta-RON = 8) [37].

1.2.6. Octane Requirement Increase

Firstly, it is convenient to define the Octane Requirement (OR) as the lowest octane number reference fuel that will allow an engine to run without knocking under standard conditions of service. This is a characteristic of each individual vehicle [38].

The accumulation of carbon deposits in the combustion chamber increases octane requirements for a given engine and fuel. The difference between the new OR and the original one is the Octane Requirement Increase (ORI). The formation of deposits increases with car mileage and depends on several aspects, such as driving conditions, engine design, gasoline composition, lubricant oils, and weather. Deposits are piled up on the piston top, on the intake and exhaust valves, on the end gas region, and on spark plugs. The effect of deposits on ORI is based on three possible mechanisms: i) as deposits accumulate, the available cylinder volume decreases, ii) presence of deposits may alter the normal combustion process chemistry, and iii) deposits store heat through the different cycles, what gives rise to the formation of hot spots [21,39].

High molecular weight additives usually increase the level of combustion chamber deposits, particularly those with higher ratios of mineral oil carriers. Detergents with optimized synthetic carrier fluids and compounds like polyether amines (PEA) minimize combustion chamber deposits build-up [40].

ORI tests are performed with CRC chassis dynamometers (see Section 1.3.2) after the car has been driven for a specified number of kilometers [39].

Since the phase-out of leaded gasoline, and with the newer car engine designs, the problem posed by ORI due to the formation of deposits has notably been reduced [21].

1.2.7. Supercharged

The term 'supercharged' refers to a modification of the basic engine design (naturally aspirated) that includes a mechanical compressor connected to the crankshaft to increase the pressure of the air supplied to the engine. The basic concept is similar to that of turbocharged engines, that is, to increase the engine efficiency and power output by forcing extra air into the combustion chamber. The main difference between these two options is that in turbocharged engines the extra pressure is given by a turbine powered by the exhaust flow of the engine [41].

In car engines, turbocharging has been the preferred option because turbochargers tend to be more efficient. However, in aviation engines, supercharging provides better results because, at high altitudes, temperature and pressure are lower.

This said a specific octane quality protocol was developed to assess the knocking performance of fuels for supercharged aviation engines. This protocol consists of assessing the fuel behavior under two different conditions: those at takeoff, when maximum power is required, and therefore a rich mixture is fed to the engine, and those at cruising speed when a weak mixture is more efficient. The ASTM D909 test allows quantifying the fuel knock resistance when rich mixtures are used, and ASTM D2700 (MON) is the test of choice for the weak mixture performance [42].

1.2.8. Pre-ignition measurement

In nowadays cars the occurrence of pre-ignition has gained importance due to the general trend of downsizing and turbocharging. Some tests have been developed to induce pre-ignition in modern engines. In these tests, the engine is run at relatively high speeds (i.e., 1750 rpm) and the pressure charge is increased until pre-ignition occurs for a given air-fuel mixture. Optical measurements can be employed to observe the formation and development of hot spots that trigger pre-ignition. [43,44]

1.3. Historical perspective on metallic anti-knock additives

1.3.1. Lead alkyls, MMT and Ferrocene

The antiknock effect of lead alkyl compounds was discovered in 1921 by Thomas Midgley, and the use of these compounds as additives to boost octane was finally patented in 1926 [45,46]. Since then, their use as antiknock additives was massively adopted worldwide until their phase-out, which ended by the turn of the century. General characteristics of lead alkyl compounds are listed in Table 2.

Table 2. General properties of alkylleads [47].

	TEL	TML	MTEL	TMEL	DEDML
Formula	$(C_2H_5)_4Pb$	$(CH_3)_4Pb$	$CH_3(C_2H_5)_3Pb$	$(CH_3)_3(C_2H_5)Pb$	$(CH_3)_2(C_2H_5)_2Pb$
Molecular weight (kg/kmol)	323.4	267.3	309.4	281.4	295.4
Boiling point (ºC)	200	109	70	27	51
Melting point (ºC)	-133	-30.2	-30	n.a.	n.a.
Vapor pressure at 20 ºC (Pa)	35	3000	100	973	293
Density at 20 ºC (kg/m^3)	1660	2000	1710	1880	1790
Solubility in water (mg/L)	0.25	15	1.9	7.65	4.6
Flash point (ºC)	85	38	n.a.	n.a.	n.a.
Odor	Fruity	Odorless	n.a.	n.a.	n.a.

TEL, tetraethyl lead; TML, tetramethyl lead; TMEL, trimethylethyl lead; MTEL, methyltriethyl lead; DEDML, diethyldimethyl lead. n.a.: not available.

Lead alkyl compounds were the most predominantly used metallic antiknock additives because they met most of the technical and economical requirements, also thanks to the joint introduction of other additives (antioxidants and scavengers) that improved their properties [27]. As seen in Table 3 tetraethyllead possesses relative antiknock effectiveness which, on a molar basis, is far superior to that of many other compounds.

Table 3. Relative antiknock effectiveness of different compounds on a mole basis, with aniline=1 [48].

tetraethyllead	118	tetraethyltin	4.0
tetraphenyllead	73	triphenylarsine	1.6
iron pentacarbonyl	50	xylidine	1.6
nickel carbonyl	35	diphenylamine	1.5
diethyl telluride	27	n-methylaniline	1.4
triethylbismuth	24	dimethylcadmium	1.2
diethyl selenide	7.0	aniline	1.0
stannic chloride	4.1	ethanol	0.1

With regards to other lead alkyl compounds different from TEL, the most important one in terms of their degree of implementation was tetramethyllead (TML). TML was introduced in the 1950s due to the predominance in the car market of engines with higher compression ratios, which increased the octane number demand [47]. Nevertheless, no alkyl-scavenger combination provides better results than TEL, and nowadays it is the only compound used for the niche markets where lead is allowed.

Lead-based additives formed solid combustion products that caused accumulation of deposits on valves, spark plugs, and combustion chambers, shortening the life of the engine. As other octane enhancers, they were prone to oxidation over long storage periods, leading to the separation of solid residues that could lead to blockages in the fuel system. To solve these problems, coaditives are used and they are discussed later in this work. Another unwanted side effect of using tetraethyllead was related to its antagonism with sulfur. Gasolines containing significant amounts of sulfur gave significantly smaller increases in octane number on the addition of tetraethyllead than sulfur-free gasolines with similar hydrocarbon composition and base octane number [49].

On the other hand, a positive side effect of using lead alkyl compounds is that they protected unhardened valve seats, present in older engines. In this sense, lead compounds formed in the combustion chamber inhibited erosion and wear of the valve seats because they avoided high-temperature corrosion and they acted as solid lubricants [27].

By the late 1970s, the once-massive use of lead-based additives began a steep decrease, especially in more developed countries, due to the population’s growing environmental awareness that ended up translating to more restrictive legislation, like the US’s Clean Air Act in 1970. Actually, it had been proved from the start that tetraethyllead was highly toxic (e.g., fatal poisoning of several workers already occurred in the mid-1920s) and, in addition, inorganic lead compounds resulting from its combustion were also highly toxic and environmentally hazardous—and about ¾ths of lead burned in the engine is emitted as inorganic lead [48].

However, it was not until General Motors announced that they were planning to install catalytic converters in all new cars in order to meet the air quality requirements of the engine exhaust, that leaded compounds stopped being so massively used due to their incompatibility with the noble metal oxidation catalysts in the converters. In particular, 1,2-dibromethane (one of the lead scavengers) was proven to be responsible for decreasing the catalyst activity, especially of catalysts containing palladium [48].

Another set of historically relevant octane-booster additives were manganese compounds. Particularly, methylcyclopentadienylmanganese tricarbonyl (MMT) has been commonly used as octane booster additives in some countries such as Russia until 2013 (see Table 4 for general properties of MMT), when the Worldwide Fuel Charter forced oil companies to stop using it for unleaded gasoline in the main developed countries (i.e., US, Canada, Europe, India, Japan) [27].

Table 4. General properties of MMT [47].

	MMT
Formula	$C_9H_7MnO_3$
Molecular weight (kg/kmol)	218.1
Boiling point (ºC)	231.67
Melting point (ºC)	2.22
Vapor pressure at 20 ºC (Pa)	933
Density at 20 ºC (kg/m^3)	1390
Solubility in water (mg/L)	29
Flash point (ºC)	96
Odor	Herbaceous

In this regard, a typical manganese concentration of 0.0165 g/L of gasoline enhanced the antiknock index by 0.5 to 1.0 units, depending on the gasoline composition. In Russia, 0.050 g Mn/L was established as the maximum allowed concentration [50]. Initially, MMT was meant to be used as a supplement to lead alkyl compounds, especially in paraffinic fuels [51]. It had been hoped that the use of MMT would not collide with the implementation of the noble-metal catalyst technology in exhaust systems following the 1970’s Clean Air Act, because manganese oxides only caused mild damage to the catalysts. However, manganese is responsible for wear and fouling, which pose detrimental effects on engine deposits and it is suspected to be a strong neurotoxin and respiratory toxin [38]. For all these reasons MMT ended up being either prohibited or strongly limited for standard motor gasoline in most territories worldwide [21,50,51]. Concerning aviation gasoline, ASTM working group 69284 is discussing the specification of an unleaded test fuel containing MMT with appropriate scavenger coadditive but balloting is not yet concluded.

Ferrocenes (see Table 5 for general characteristics) emerged as cheaper alternatives to MMT to boost octane numbers. Among the ferrocene compounds in antiknock compositions, alkylferrocenes and dimethylferrocenylcarbinol have been the most widely used [50].

Table 5. General properties of ferrocenes.

	Dicyclopentadienyl iron (ferrocene)	Iron pentacarbonyl
Formula	$C_{10}H_{10}Fe$	C_5FeO_5
Molecular weight (kg/kmol)	186.0	195.9
Boiling point (ºC)	245.9	102.9
Melting point (ºC)	175.0	-21
Vapor pressure (Pa)	6.6 (40 ºC), 340 (100 ºC)	5333 (30.6 ºC)
Density at 20 ºC (kg/m^3)	1107	1453
Solubility in water (mg/L)	insoluble	insoluble
Flash point (ºC)	n.a.	n.a.
Odor	camphor-like	musty

n.a.: not available.

Iron compounds were widely used as antiknock compounds in Russia in 1960-1970, but they were considered unfit due to ferrocene main drawback: the iron-containing deposits formed from ferrocene can lead to the formation of a conductive coating on the spark plug surfaces [25,50]. No effective iron evacuators could be found and, consequently, the only measure that could be applied was to limit the maximum concentration at 0.038 g Fe/L, at which high fouling is not observed [50]. Moreover, ferrocene oxides are abrasive, which entails rapid engine wear [51]. Furthermore, iron oxide was reported to act as a physical barrier between the catalyst/oxygen sensor and exhaust gases and led to erosion and plugging of the catalyst, resulting in poor functioning thereof [52].

1.3.2. Co-antiknock additives

The historical role of scavengers as co-antiknock additives in the era of leaded gasoline was to reduce the deposits formed by lead upon combustion. Such deposits accumulated on valves, spark plugs, and combustion chambers, which entailed shorter lifespans for engines. The most widely used scavengers were halogenated compounds, such as 1,2-dichloroethane and 1,2-dibromoethane. These halogens reacted with lead, forming lead bromide and lead chloride, which had great volatility at high temperatures and therefore helped to evacuate lead from the engine. As a result, the amount of lead deposits could be reduced by about 70–80% [27]. Numerous patents claiming huge lead deposit reductions with several scavenger compositions, including halides, sulfides, arsenides, and/or phosphines (e.g., US patents 2,398,281, 2,479,901, 2,479,902, 2,557,019, 2,750,267, 2,797,153, 2,999,739, 3,126,261, among others [53–60]) can be found. Similarly, scavengers for manganese antiknock additives were also designed with the same purpose. For instance, some references indicate that phosphates were useful in this regard (e.g., US patent 2018/0119037-A1 [61]).

On the other hand, the term ‘antiknock extender’ refers to co-antiknock additives different than scavengers that, without being able to increase the octane quality of fuel by themselves, were capable of increasing the efficiency of an octane booster additive. To avoid confusion, this concept should be well differentiated from that of the so-called ‘fuel extenders’, which refer to high-octane components such as oxygenates. Originally, antiknock extenders were meant to increase TEL antiknock efficiency in raising the octane quality of fuels. Two reasons explain the use of extenders in gasoline: on the one hand, adding a chemical that could improve the effectiveness of TEL was economically more attractive than adding larger doses of the more expensive TEL; on the other, along the years that followed the introduction of leaded gasolines, major changes occurred in both gasoline composition and engine design which, for obvious reasons, had not been considered in the early development of lead-based additives. Therefore, a reevaluation of the antiknock needs of more modern cars had to be undertaken [62].

Among antiknock extenders, carboxylic acids (such as acetic and ethylhexanoic acids) were singled out because they could improve the antiknock quality of high-octane gasoline in about 2.5 RON units [63]. A synergistic effect between the acid and TEL was clearly observed experimentally in their work. The mechanism to explain the action of TEL extenders is related to their interaction with the actual antiknock species resulting from TEL addition, that is lead oxides. Assuming that TEL antiknock effectiveness would diminish as lead oxides agglomerate forming deposits, it seems reasonable to anticipate that the octane enhancing action of the extender can be explained by its interference with lead oxides, which would prevent (or at least retard) their accumulation and would prolong the oxide particles action from effectively anchoring free radicals in the combustion chamber. It hence follows that excessive extender concentration would pose a negative effect on the antiknock ability of TEL for it would consume TEL before suppressing free radicals [62].

Besides scavengers and extenders, other co-antiknock additives that were highly relevant, such as antioxidants to prevent TEL oxidation during storage and transportation, were used. As TEL antioxidants, the most quoted ones are phosphine sulfides, hydroperoxides, alkylated phenols, or hydrogenated quinolines, among others [64,65].

1.4. Definition of general metrics to select candidate molecules

To establish proper comparison among molecules of different chemical families, a rather straightforward approach has been adopted. It mainly consists of comparing their general behavior according to selected key features that must be evaluated when considering new gasoline formulations. These features have been selected based not only on anti-knock effectiveness of compounds included in a chemical family—which for obvious reasons is a pivotal metric in the present work—but also on more collateral aspects that, thanks to the aforementioned historical perspective, are known to have an impact on the field. For instance, the side effects of a potential candidate on current engines need to be known so that potential co-additives are designed to be coupled with the anti-knock booster. Likewise, the compatibility of the candidate molecule with the existing gasoline distribution system or its sustainability of use is also of the utmost importance. Specifically, the metrics that have been used in the present work to assess chemical families are the following:

1. Anti-knock effectiveness: this category relates directly to octane boosters. In this sense, chemical families with compounds that have been quoted to provide blending octane numbers higher than 100 are considered attractive octane boosters. Depending on the available data, relative antiknock effectiveness has also been taken into account.
2. Side effects: this metric relates to the available data on potential additional effects that can arise when using compounds of the considered chemical family on the engine combustion chamber, injection system, or post-treatment exhaust gases.
3. Distribution system compatibility: it has to do with a global overview of some key features for the blending of compounds of the considered chemical family with gasoline (similar boiling point range, 35-205ºC; low water solubility, high log P value).
4. Technology readiness: it provides a global overview regarding the existence of already implemented industrial processes to obtain compounds of the considered chemical family.
5. Sustainability of use: this category relates to the existence of bio-based routes to produce compounds of the considered chemical family.
6. Associated toxicology: health and environmental hazards to be taken into consideration when dealing with a chemical family are included in this category. Due to the different nature of the hazards typically included in this category it has been deemed appropriate to treat human health hazards and risk towards the environment separately. Both aspects have been categorized based on the CLP Regulation (Regulation (EC) No 1272/2008). For more information on the toxicology of every compound, see Table S1 Table S2 in the Supporting Information section.

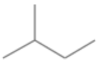
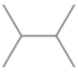
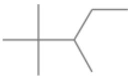
2. High-octane gasoline components (>2 vol%)

2.1. Isoparaffins

Isoparaffins are acyclic saturated hydrocarbons having the general formula C_nH_{2n+2}. A typical distribution of classes of compounds in crude oils can be found in the work of Barker et al. 2005 [66].

The main distinguishing feature of isoalkanes is their relatively low reactivity due to lack of unsaturation. Some general characteristics are shown in Table 6.

Table 6. General characteristic of relevant isoparaffins.

	iso-butane	iso-pentane	2,3-di-methyl butane	2,2,3-tri-methyl pentane	2,2,3,3-tetramethyl pentane	2,2,3,3-tetramethyl hexane
CAS Reg. No.	75-28-5	78-78-4	79-29-8	564-02-3	7154-79-2	13475-81-5
Empirical formula	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$
Chemical structure						
Molecular weight (kg/kmol)	58.1	72.1	86.2	114.2	128.3	142.3
Density at 20 °C (kg/m^3)	557	620.1	661.6	720.0	713[a]	718[a]
Boiling point (°C)	-11.2	28.0	58.1	110.0	140.3	159.4
Melting point (°C)	-133	-160.15	-130.15	-112.7	-10.15	-54
Self-ignition point (°C)	460	420	405			
Flash point (°C)	-82.8	-56.7	-29	8	27.8[a]	37.6[a]
Viscosity at 20 °C (cP)	0.238 (-10°C)	0.214	4.57×10^{-4} (0°C)	0.451[a]	0.522[a]	0.596[a]
Net (lower) calorific value						
MJ/kg	45.61	45.24	44.66	44.6[a]	44.5[a]	44.4[a]
MJ/L (at 20 °C)	25.0	27.8	29.7	32.1	31.7	31.9
Heat of vaporization at 25 °C (kJ/kg)	344	350	340	324	321	318
Vapor pressure at 25 °C (Pa)	348000	91800	31300	4880[a]	1260 (at 60 °C)	519
Solubility in water (g/L)	0.049	0.048	0.023	0.007[a]	0.006[a]	0.002[a]
Distribution ratio in octanol/water system (log P)	2.76	2.30	3.42	4.21[a]	4.50[a]	4.93[a]
GHS label codes[b]	2, 4	2, 7, 8, 9	2, 7, 8, 9	2, 7, 8, 9	None found	None found

Sources: [67–69]. [a] Estimated by means of the Garvin formula: $\Delta H_{net,Garvin} = \sum_i a_i w_i \sum_j b_j \left(n_j / M\right)$ [70].

[b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

Since the 1970s, low-octane straight-run gasoline has been increasingly converted into the higher octane isomerate (consisting mainly of isoparaffins) to boost the gasoline antiknock performance and, since isomerate is free from aromatics, it is gaining importance [21]. Isoparaffins use and production have been, therefore, studied extensively [71,72].

RON and MON values for several paraffins and isoparaffins are presented in Table 7, together with blending RON values (BRON). As can be seen in the table, more branched molecules present higher octane values.

Table 7. RON, MON, BRON and BMON values of several paraffins and isoparaffins.

Group	Compound	RON	MON	BRON[a]	BMON[b]
C_4 isomers	isobutane	102[c]	97.6[c]	122	
C_5 isomers	pentane	62[b]	62[b]	62[b]	67
	isopentane	92[c]	90.3[c]	99	104
	2,2-dimethyl propane			100	90
C_6 isomers	hexane	25[b]	26[b]	19[b]	22

	2-methyl pentane			83	
	3-methyl pentane			86	
	2,2-dimethyl butane	91.8[b]	93.4[b]	89	97
C_7 isomers	heptane	0	0	0	0
	2,2-dimethyl pentane	98.2[d]		89	93
	2,3-dimethyl pentane	91.1[d]		87	
	2,4-dimethyl pentane	83.1[d]		77	
	2,2,3-trimethyl butane	112[d]-112.8[b]	101.32[c]	113	113
C_8 isomers	2,2,4-trimethyl pentane	100	100	100	100
	2,2,3-trimethyl pentane	100[b]	100[b]	105	112
	C_8 trimethyls	105[c]	98.8[c]		
C_9 isomers	2,2,5-trimethyl hexane			91	
	C_9 trimethyls	100[c]	93[c]		
	2,2-dimethyl-3-ethyl pentane			108	
	2,2,3,3-tetramethyl pentane			123	
C_{10} isomers	C_{10} trimethyls	95[c]	87[c]		
	2,2,3,3-tetramethyl hexane			126	
C_{11} isomers	C_{11} trimethyls	90[c]	82[c]		
C_{12} isomers	C_{12} trimethyls	85[c]	80[c]		

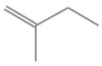
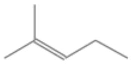
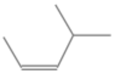
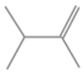
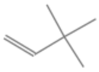
[a] BRON calculated for a reference fuel with RON_{BG} = 60 with 20 %vol. of the target hydrocarbon from [73] unless otherwise indicated. [b] [74]. [c] [28]. [d] [72].

Isoparaffins are obtained in the petrochemical industry from natural gas and crude oil. Catalytic reforming allows the transformation of normal paraffin and cycloparaffins into isoparaffins and aromatics [75]. The buildup of long-chain *n*-paraffins using the Fischer-Tropsch synthesis and isomerization of such paraffin into isoparaffins constitutes a viable biomass-derived route when syngas is of renewable origin [21].

2.2. Olefins

Olefins or alkenes are unsaturated hydrocarbons with at least one carbon-carbon double bond. Acyclic alkenes with only one double bond and no other functional group present the general formula C_nH_{2n} [76]. Some general characteristics are shown in Table 8.

Table 8. General characteristic of relevant olefins.

	2-Methyl-1-butene	2-Methyl-2-pentene	*cis*-4-Methyl-2-pentene	2,3-Dimethyl-1-butene	3,3-Dimethyl-1-butene
CAS Reg. No.	563-46-2	625-27-4	691-38-3	563-78-0	558-37-2
Empirical formula	C_5H_{10}	C_6H_{12}	C_6H_{12}	C_6H_{12}	C_6H_{12}
Chemical structure					
Molecular Weight (kg/kmol)	70.1	84.2	84.2	84.2	84.2
Density at 20 ºC (kg/m^3)	650	695	692	685	685
Boiling point (ºC)	31.2	67.1	55.9	55.9	41.3
Melting point (ºC)	-137	-135	-132[a]	-153	-115
Flashpoint (ºC)	<-7 (closed cup)	-27		-18	-28
Viscosity at 20 ºC (cP)[a]	0.239	0.27		0.29	
Net (lower) calorific value					
MJ/kg[b]	44.80	44.63	44.63	44.63	44.63
MJ/L (at 20 ºC)	29.1	31.0	30.9	30.6	30.6
Heat of vaporization at 25 ºC (kJ/kg)	371	375	351	347	318
Vapor pressure at 25 ºC (Pa)	81358	21332	28664	33197	57020
Solubility in water (g/L)	0.13	0.12[a]	0.07[a]	<0.1	0.15[a]

Distribution ratio in octanol/water system (log P)[a]	2.72	3.29	3.03	3.01	2.87
GHS label codes[c]	2, 7	2, 7, 8	2	2, 7, 8	2, 7, 8

Sources: [67–69]. [a] Predicted value [69]. [b] Estimated using the Garvin formula [70]. [c] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Olefins are the main contributors to octane in cracked gasoline. Olefin content in FCC gasoline generally varies between 40–60 %vol. As seen in Table 9, olefins present high RON values and very large sensitivity. As a general trend, the more branched the olefin the higher its RON value.

Table 9. RON, MON, and S values of several olefins [77].

Group	Compound	RON	MON	S
C_5 isomers	1-pentene	91	77	14
	2-methyl-1-butene	103	82	21
	2-methyl-2-butene	97.5	85	12.5
C_6 isomers	1-hexene	76.5	63.5	13
	2-methyl-1-pentene	94	81	13
	3-methyl-1-pentene	96	81	15
	trans-3-methyl-2-pentene	97	81	16
	4-methyl-2-pentene	99.5	84.5	15
	2-ethyl-1-butene	98.5	79.5	19
	2,3-dimethyl-1-butene	101.5	83.3	18.2
	3,3-dimethyl-1-butene	112.5	94	18.5
	2,3-dimethyl-2-butene	97.5	80.5	17
C_7 isomers	1-heptene	54.5		
C_8 isomers	1-octene	28.5		

Through comparison of the values listed in Table 7 and those in Table 9, it can be checked that branched olefins present far superior RON values than isoparaffins with the same number of carbon atoms, particularly more so as the branched character increases. Furthermore, this trend is self-evident when linear olefins are compared to their paraffinic counterparts (note, for instance, that RON of 1-heptene is 54.5 whereas heptane RON is, by definition, zero). More evidences in this regard can be retrieved from Magyar and coworkers [78], where differences between RON or MON values between olefins and their paraffin derivatives as high as 72.6 are stated. The fact that olefinic C bonds provide a site for addition reactions is what explains such divergence [7].

Gasoline with high olefin content presents some drawbacks, such as higher olefin content in the exhaust emissions, which have a higher tropospheric ozone formation potential, and an increased tendency to form deposits in engine injectors and intake valves [79].

On the other hand, increasing the olefin content of gasoline tends to reduce exhaust VOC emissions because olefins burn more easily and more completely than other hydrocarbons in gasoline. However, increasing olefin content also tends to increase NO_X formation and increases the concentration of olefin in evaporative emissions. As a consequence, measures to reducing the total olefin content in gasoline have been undertaken.

Olefins are typically obtained by thermal cracking of long-chain paraffins. Products distribution in this process is highly dependent on the conditions; i.e., the higher the temperature and pressure applied, the more severe the cracking [76]. A large number of patents can be found related to the production of olefins; e.g., US 5,171,921-A [80], US 2,426,829-A [81], or US 4,849,575-A [82].

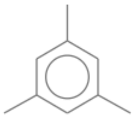
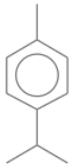
On the other hand, the Fischer-Tropsch process has been targeted as a cost-effective biomass-based synthesis route to obtain olefins [83]. Steam cracking of naphtha by the Bio-Synfining$^{\text{TM}}$ is another interesting process since it provides high yields for light olefins without traces of oxygenates [84].

Other possible biotechnological pathways to obtain olefins include, for example, the dehydration of biomass-derived isobutanol [85], which can be obtained in a commercially viable process through metabolically-engineered *Escherichia coli* at high yields without significant byproducts [86].

2.3. Aromatics

Aromatics are organic compounds consisting of carbon and hydrogen atoms with carbons arranged in a ring (Table 10). Aromatic compounds are characterized by having large resonance energies and by reacting through substitution rather than addition [87]. Petroleum contains between 3 %wt. and 30 %wt. of aromatics depending on its origin [25]. Straight-run gasoline, obtained by simple distillation of crude oil, contains 5 %vol. on average [21].

Table 10. General characteristic of some aromatics.

	benzene	ethylbenzene	1,3,5-trimethylbenzene	toluene	*p*-xylene	*p*-cymene
CAS Reg. No.	71-43-2	100-41-4	108-67-8	108-88-3	106-42-3	99-87-6
Empirical formula	C_6H_6	C_8H_{10}	C_9H_{12}	C_7H_8	C_8H_{10}	$C_{10}H_{14}$
Chemical structure						
Molecular weight (kg/kmol)	78.1	106.2	120.2	92.1	106.2	134.2
Density at 20 °C (kg/m^3)	876	867	864	862	861	857
Boiling point (°C)	80.2	136.2	164.7	110.7	138.3	176.9
Melting point (°C)	5	-94	-48	-95	13	-69
Self-ignition point (°C)	498	432	550	480	529	436
Flashpoint (°C)	-11 (closed cup)	18 (closed cup)	50 (closed cup)	4.4 (closed cup)	25 (closed cup)	47 (closed cup)
Viscosity at 20 °C (cP)	0.604	0.64	1.0[a]	0.560 (25 °C)	0.603 (25 °C)	1.47[a]
Net (lower) calorific value						
MJ/kg	40.170	40.938	41.4[b]	40.589	40.798	41.6[b]
MJ/L (at 20 °C)	35.2	35.5	35.7	35.0	35.1	35.7
Heat of vaporization at 25 °C (kJ/kg)	434	386	383	395	402	396
Vapor pressure at 25 °C (Pa)	12160	1264	322	3792	1181	200
Solubility in water (g/L)	1.79	0.169	0.048	0.526	0.165	0.0234
Distribution ratio in octanol/water system (log P)	2.13	3.15	3.42	2.73	3.15	4.10
GHS label codes[c]	2, 7, 8	2, 7, 8	2, 7, 9	2, 7, 8	2, 7, 8	2, 8, 9

Sources: [67–69]. [a] Predicted value [69]. [b] Estimated using the Garvin formula [70]. [c] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

The knock suppression ability of aromatic hydrocarbons is higher than that of paraffins, olefins, and naphthenes [88]. Both RON and MON of gasoline are increased by the addition of aromatic compounds. RON and MON values for some aromatic compounds are listed in Table 11. Alkyl-benzenes have a stronger impact on increasing MON than RON. Mesitilene (1,3,5-trimethylbenzene) has a very high potential for unleaded high octane aviation gasoline: fuel test specified on ASTM D7719 supported a blend composed by mesitylene (79-84 %wt.) and isopentane for volatility control.

Table 11. RON and MON values for pure aromatic hydrocarbons.

Compound	**RON**	**MON**
Benzene	90[a]-101[b]-102.7[c]	92 [a]-93[b]-105[c]
Ethylbenzene	107[a]	124[a]
Propylbenzene	129[a]	127[a]
1,3,5-Trimethylbenzene	137[a]	124[a]
Toluene	112[a]-120[b]-118[c]	124[a]-109[b]-103.5[c]
o-Xylene	103[a]	120[a]
m-Xylene	124[a]	145[a]
p-Xylene	127[a]-124[b]	146[a]-97[b]
p-Cymene	124[b]	101[b]
C_8 aromatics	112[c]	105[c]
C_9 aromatics	110[c]	101[c]
C_{10} aromatics	109[c]	98[c]
C_{11} aromatics	105[c]	94[c]

[a] [25], [b] [7], [c] [28].

Increasing aromatics content significantly increases carbon monoxide, nonmethane hydrocarbon, particulate matter mass, particle number, and black carbon emissions.

Traditional approaches for obtaining aromatic compounds are based on coal and oil extraction and further processing of the obtained benzene [89]. For economic reasons, toluene is extracted from reformates, from pyrolysis of hydrocarbons (steam cracking), or from liquid products from the gasification or coking (pyrolysis) of coal, lignite, etc. [25].

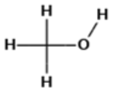
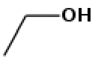
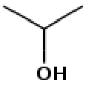
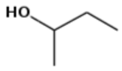
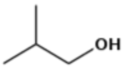
Using catalytic cracking a product with 30% aromatics can be obtained. As for catalytic reforming, about 60% of aromatics are obtained after partial dehydrogenation [19]. Recent studies show the potential production of aromatic compounds through bacterial fermentation of lignocellulosic biomass [20,21]. Production of aromatic compounds through pyrolysis of biomass has also been reported using zeolites as catalysts [22,23,24]. It is also worth mentioning that a non-commercial synthetic process exists, named the Cyclar process, consisting of the cyclization of propane and butane over zeolite catalysts [26].

2.4. Alcohols

Alcohols (Table 12) are hydrocarbons that have at least one hydroxyl group (—OH) bonded to a saturated carbon atom [87]. Methanol and ethanol are the simplest monoalcohols, which present the general formula $C_nH_{2n+1}OH$. Since the early 21st century, its use in the energy sector has gained importance [27].

Table 12. General characteristic of alcohols.

	Methanol	Ethanol	2-Propanol	1-Butanol	*sec*-Butanol	Isobutanol
CAS Reg. No.	67-56-1	64-17-5	67-63-0	71-36-3	78-92-2	78-83-1
Empirical formula	CH_4O	C_2H_6O	C_3H_8O	$C_4H_{10}O$	$C_4H_{10}O$	$C_4H_{10}O$

Chemical structure						
Molecular Weight (kg/kmol)	32.0	46.1	60.1	74.1	74.1	74.1
Density at 20 ºC (kg/m^3)	792	789	785	810	806	802
Boiling point (ºC)	64.7	78.4	82.4	117.5	98.9	107.7
Melting point (ºC)	-97	-114	-88	-85	-115	-107
Self-ignition point (ºC)	464	363	399	345	406	415
Flashpoint (ºC)	9.7 (closed cup); 15.6 (open cup)	12.8 (closed cup)	11.7 (closed cup)	29 (closed cup)	24 (closed cup); 31 (open cup)	28 (close cup); 37.7 (open cup)
Viscosity at 20 ºC (cP)	0.544 (25 ºC)	1.074	2.038 (25 ºC)	2.544 (25 ºC)	4.21 (15 ºC)	4.0
Weight fraction of Oxygen (%wt.)	50	35	27	22	22	22
Net (lower) calorific value						
MJ/kg	19.930	26.70	30.447	33.075	33.6[b]	32.959
MJ/L (at 20 ºC)	15.8	21.1	23.9	26.8	27.1	26.4
Heat of vaporization at 25 ºC (kJ/kg)	1173	918	749	702	648	688
Vapor pressure at 25 ºC (Pa)	16938	7869	5698	885	2190	1381
Solubility in water (g/L)	miscible	miscible	miscible	68 (25 ºC)	181 (25 ºC)	85 (25 ºC)
Distribution ratio in octanol/water system (log P)	-0.77	-0.31	0.05	0.88	0.61	0.76
GHS label codes[a]	2, 6, 8	2	2, 7	2, 5, 7	2, 7	2, 5, 7

Sources: [67–69]. [a] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Alcohol compounds heavier than methanol and ethanol, such as 1-propanol, 1-butanol, etc. have also been considered as potential octane enhancers due to their higher energy content and because they present more similarities with gasoline properties compared to methanol and ethanol.

It has been reported that the addition of amounts of alcohol less than 10%vol. provides a disproportionately large and nonlinear increase of the ON in the resulting gasoline. This fact indicates that BON values for alcohol-blended gasolines are much higher than measured ON$_C$ of pure alcohols [26]. Individual RON and MON values for some alcohols are provided in Table 13.

Table 13. RON and MON values for pure alcohols.

Compound	RON	MON
Methanol[a]	109.5	86
Ethanol[b]	109	90
1-Propanol[b]	104	89

2-Propanol[b]	106	99
1-Butanol	96[c]-98[b]	78[c]-85[b]
tert-Butyl alcohol[c]	105	89
Isobutanol	105[b]-113[c]	90[b]-94[c]

[a] [26], [b] [90], [c] [91].

Blending ON values for methanol have been reported to reach 133 and 99 for RON and MON, respectively [27]. Ethanol presents BON values of 130 and 96 for RON and MON, respectively [27]. Some blending values for ethanol blends up to 50 %vol. (E50) can be found in Table 14 as reproduced from a study that also investigated the suitability of isobutanol blends [92]. BON values for isopropyl alcohol (IPA) are 121 for the RON test and 96 for MON [27].

Table 14. Blending octane numbers for ethanol and isobutanol blends [92].

	Dose (%vol. / %wt.)	Oxygen (%wt.)	RON	MON	BRON[a]	BMON[a]
Base fuel			87.9	81.9		
Ethanol	9.3 / 9.9	3.5	93.0	84.1	143	106
	26 / 27.6	9.6	99.1	87.4	131	103
	47.1 / 49.2	17.1	102.6	88.7	119	96
Isobutanol	15.5 / 16.7	3.6	92.3	82.8	116	88

[a] Blending values calculated according to Eq. 1–1.

Some vehicles can be run with methanol-gasoline mixtures of up to 85% methanol (M85) [93]. Adding low amounts of methanol in commercial gasoline does not require any further modifications on SI engines, it improves engine cold start performance, and lower emissions of carbon monoxide, nitrogen oxides, unburned hydrocarbons, and particulate matter are achieved [94,95]. The main drawbacks of blending methanol are related to its high hygroscopicity and solubility in water, which entails the potential separation of phases in the engine with subsequent engine damage [96,97].

Blends containing up to 10 %vol. of anhydrous ethanol (E10) can be used in most modern engines without further modifications. E20 to E25 blends are mandatory in Brazil, E85 blends can be found in the US and Europe for flexible-fuel vehicles, and E100 blends are used in Brazilian neat ethanol vehicles [98]. Ethanol-blended gasoline allows higher compression ratios, shorter burn time, and weaker air-to-fuel ratios, which theoretically entails efficiency gains [25]. The main disadvantages of a direct blending of ethanol are quite similar to those cited for methanol. Besides, major biomass-derived ethanol production today competes with food supplies and promotes invasive plantations [99].

Technically, using 1-butanol instead of ethanol is favored because it can be processed in the existing refinery units, it is less corrosive than ethanol, it does not dissolve in or absorb water, and it does not increase fuel vapor pressure [100].

Industrial production of methanol is mainly derived from synthesis gas [45]. Natural gas is the most common feedstock, but also coal-based synthesis gas is used to produce methanol [101]. Methanol can also be recovered from raw glycerin, a waste product from biodiesel production [102]. From an environmental and economic perspective, the most promising strategy to produce methanol is via integrating carbon dioxide recovery units in power plants, which are among the major contributors to CO_2 emissions [103].

Ethanol is produced both in the petrochemical industry, by hydrolysis of ethylene, and through fermentation of biomass, mainly from edible feedstock like sugar cane, corn, or wheat. To overcome issues raised by the use of edible biomass, the production of biomass-based ethanol from cellulosic resources is a promising alternative [104].

Isopropyl alcohol (IPA) is obtained from acetone, but advances in biotechnology make it possible to synthesize IPA from biomass-derived sugars [105,106]. In a closer horizon, refiners with an excess of propylene can opt to produce IPA, since propylene is an immediate precursor to obtaining IPA [96].

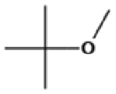
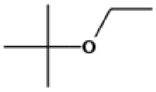
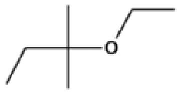
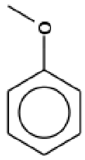
Alcohols like 1-propanol, 1-butanol, *sec*-butanol, and isobutanol are interesting because they can be obtained through the Fischer-Tropsch process of any carbon source, for instance, municipal and agricultural waste. Isobutanol can be also prepared from biomass [107].

Alternatively, some higher alcohols can be produced from biomass through the Guerbet catalysis process (condensation of ethanol and/or methanol), and through the ABE fermentation, which produces acetone, 1-butanol, and ethanol [108]. Biomass-based butanol production at an industrial scale has been accomplished early in the 20th century [100].

2.5. Ethers

Ethers are hydrocarbons with the general formula R—O—R’, where R and R’ are alkyl (or aryl; that is, aromatic) groups. General characteristics of some ether compounds are provided in Table 15.

Table 15. General characteristic of ethers.

	MTBE	ETBE	TAEE	Methylal	Anisole
CAS Reg. No.	1634-04-4	637-92-3	919-94-8	109-87-5	100-66-3
Empirical formula	$C_5H_{12}O$	$C_6H_{14}O$	$C_7H_{16}O$	$C_3H_8O_2$	C_7H_8O
Chemical structure					
Molecular Weight (kg/kmol)	88.1	102.2	116.2	76.1	108.1
Density at 20 ºC (kg/m^3)	741	752	760	859	996
Boiling point (ºC)	55.1	72.8	102.1	42.2	153.9
Melting point (ºC)	-109	-94	-84.1[a]	-105	-23
Self-ignition point (ºC)	435	375		235	475
Flash point (ºC)	-28 (closed cup)	-19 (closed cup)		-31 (closed cup)	52 (open cup)
Viscosity at 20 ºC (cP)	0.644[a]	0.682[a]	0.989[a]	0.330[a]	1.52 (15 ºC) 0.778 (30 ºC)
Weight fraction of Oxygen (%wt.)	18	16	14	21	15
Net (lower) calorific value					
MJ/kg[b]	35.5	36.7	37.5	23.4	33.5
MJ/L (at 20 ºC)	26.3	27.6	28.5	20.1	33.4
Heat of vaporization at 25 ºC (kJ/kg)	340	323	333	384	407
Vapor pressure at 25 ºC (Pa)	33330	16532	6666	53013	472
Solubility in water (g/L)	51	12	0.4	285	1.52

Distribution ratio in octanol/water system (log P)	0.94	1.28	2.24[a]	0.18	2.11
GHS label codes[c]	2, 7	2, 7	2, 7, 8	2, 7	2

Sources: [67–69]. [a] Predicted value [69]. [b] Estimated using the Garvin formula [70]. [c] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Together with alcohols, ethers are commonly employed in significant extents as octane improvers due to their high ON (Table 16), low toxicity, good distillation behavior, and better material compatibility than alcohols [27].

Table 16. RON and MON values for some ethers.

Compound	**RON**	**MON**	**(RON+MON)/2**
Methyl *tert*-butyl ether, MTBE[a]	118	100	
Ethyl *tert*-butyl ether, ETBE[a]	118	102	
Propyl *tert*-butyl ether, PTBE[b]		103	
Butyl *tert*-butyl ether, BTBE[b]		81	
tert-Amyl methyl ether, TAME[a]	111	98	
tert-Amyl ethyl ether, TAEE	(105)[c]	(95)[c]	111[d]
Isopropyl *tert*-butyl ether, IPTBE	(109)[e]	(101)[e]	113[d]
Diisopropyl ether, DIPE	(105)[c]	(98)[c]	105[d]

[a] Leppard 1991. [b] Egloff and Van Arsdell 1941. [c] instead of pure compound values, blending ON is given instead (International Energy Agency 2012). [d] Piel 1992. [e] Instead of pure compound values, blending ON is given instead [113].

Aromatic-containing ethers also provide good ON. Among this group, anisole derivatives have received some attention. An anisoles mixture is claimed to successfully improve the antiknock behavior of unleaded gasoline [114]. For instance, Table 17 lists results from a recent study that analyzes the effect on RON of anisole, MTBE, and three glycol ethers [115].

Table 17. Effect on RON of different ether compounds at several concentrations and calculated blending values thereof [115].

Concentration (%vol.)	**RON**				
	anisole	2-ethoxyetanol	2-butoxyethanol	2-(2-butoxyethoxy)-ethanol	MTBE
0	82.1	82.1	82.1	82.1	82.1
0.50	82.4	84.5	84.3	85.8	83.2
1.00	82.7	88.0	87.7	90.0	85.2
2.00	83.1	89.5	89.1	91.7	86.4
4.00	84.8	91.3	90.7	93.9	89.0
7.00	87.4	93.4	92.9	96.5	94.5
	BRON[a]				
	anisole	2-ethoxyetanol	2-butoxyethanol	2-(2-butoxyethoxy)-ethanol	MTBE
0.25	122.1	482.1	482.1	802.1	282.1
0.50	142.1	562.1	522.1	822.1	302.1
1.00	142.1	672.1	642.1	872.1	392.1
2.00	132.1	452.1	432.1	562.1	297.1
4.00	149.6	312.1	297.1	377.1	254.6
7.00	157.8	243.5	236.4	287.8	259.2

[a] BRON calculated according to Eq. 1–1.

Due to ethers lower oxygen relative content, they can be blended in greater amounts and still meet fuel regulations relative to maximum oxygen content (e.g., 3.7 %wt. in EU).

Furthermore, the specific fuel consumption associated with the blending of ethers is far lower than that of the corresponding alcohols (e.g., blending of ethanol leads to 40% higher fuel consumption than a blending of ETBE or TAEE) [99,116]. Ethers present low vapor pressure values compared to alcohols and they do not have azeotropic behavior with gasoline, which accounts for their compatibility with the already existing petroleum refining and distribution systems [117].

Well-known processes have been operational for decades now to obtain MTBE, ETBE, or TAME [99,116]. Provided that the designated alcohol is obtained from biomass, the produced ether is considered a ‘bioether’ and, consequently, it is a good candidate to accomplishing the biofuel target. Industrial-scale processes aimed at obtaining ‘bioolefins’ are not still implemented, even though recent advances have demonstrated the viability of obtaining biomass-derived olefins [84,118]. For instance, isobutene, the immediate precursor for MTBE, ETBE, TAME, or TAEE, can be obtained from 2-methyl-1-propanol (isobutanol) which in turn is obtained from the fermentation of biomass-derived sugars at high yields [85].

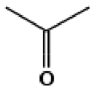
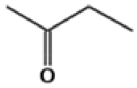
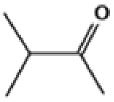
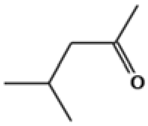
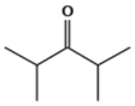
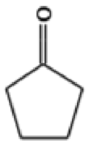
On the other hand, as it is well known, MTBE was either limited or banned in several regions, particularly in US states due to the risk of contamination of groundwater reservoirs [119,120].

With regards to mentioned glycol ethers, 2-ethoxyethanol can be synthesized by the reaction of ethylene oxide with ethanol. 2-Butoxyethanol is commonly obtained through two processes: the catalytic ethoxylation reaction of butanol and ethylene oxide or the etherification of butanol with 2-chloroethanol. On the other hand, 2-(2-butoxyethoxy)-ethanol is produced by the reaction of ethylene oxide and n-butanol with an alkaline catalyst.

2.6. Ketones

Ketones (Table 18) include a carbonyl group (C=O) bonded by its carbon to two other carbons on each side, that is, R—(C=O)—R’, with R and R’ being either the same or different alkyl groups [87].

Table 18. General characteristic of ketones.

	Acetone	2-Butanone	3-Methyl-2-butanone	4-Methyl-2-pentanone	2,4-dimethyl-3-pentanone	Cyclo-pentanone
CAS Reg. No.	67-64-1	78-93-3	563-80-4	108-10-1	565-80-0	120-92-3
Empirical formula	C_3H_6O	C_4H_8O	$C_5H_{10}O$	$C_6H_{12}O$	$C_7H_{14}O$	C_5H_8O
Chemical structure						
Molecular Weight (kg/kmol)	58.1	72.1	86.1	100.2	114.2	84.1
Density at 20 ºC (kg/m^3)	785	805	805	804	803	949
Boiling point (ºC)	56.2	79.9	93.9	115.9	124.9	129.9
Melting point (ºC)	-94	-105	-93.2	-84.0	-74.6	-51.5
Self-ignition point (ºC)	465	505	475	460		
Flash point (ºC)	-18 (closed cup)	-9 (closed cup)	52	23 (closed cup)	15	30 (closed cup)
Viscosity at 20 ºC (cP)	0.320	0.40 (25 ºC)	0.439[a]	0.551[a]	0.582[a]	0.897[a]
Weight fraction of Oxygen (%wt.)	28	22	19	19	19	16
Net (lower) calorific value MJ/kg	28.548	31.5[b]	33.5[b]	35.0[b]	36.0[b]	32.4[b]

MJ/L (at 20 ºC)	22.4	25.4	27.0	28.1	28.9	30.7
Heat of vaporization at 25 ºC (kJ/kg)	538	472	446	448	428	419
Vapor pressure at 25 ºC (Pa)	30600	11999	4067	2624	1937	1513
Solubility in water (g/L)	miscible	223	52.4	19	5.7	9.2
Distribution ratio in octanol/water system (log P)	-0.24	0.29	0.84	1.31	1.86	0.38
GHS label codes[c]	2, 7	2, 7	2	2, 7	2, 7	2, 7

Sources: [67–69]. [a] Predicted value [69]. [b] Estimated using the Garvin formula [70]. [c] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Ketones have been reported to provide high ON when mixed with commercial gasolines (see Table 19 for individual ON values of some ketone compounds, and Table 20 for the effect of acetone addition to RON of commercial unleaded gasoline).

Table 19. RON and MON values for some ketones.

Compound	**RON**	**MON**
Acetone (dimethyl ketone)[a]	115	
2-Butanone (methyl ethyl ketone)[b]	117	107
2-Pentanone[c]	105.7	103
3-Pentanone[c]	106.8	
3-Methyl-2-butanone[c]	108.9	102.2
3-Hexanone[c]	101.9	93.5
4-Methyl-2-pentanone (methyl isobutyl ketone)[c]	105.7	105.5
2,4-dimethyl-3-pentanone[c]	99	92.5
Cyclopentanone[c]	101	89.4

[a] [121], [b] [122], [c] [123]

Table 20. Effect on RON of the addition of acetone at different doses [115].

Acetone dose (%vol.)	**RON**	**BRON**[a]
0*	82.1	
0.25	82.3	162
0.50	82.5	162
0.75	82.7	162
1.00	82.9	162
2.00	83.7	162
3.00	84.6	165
4.00	85.6	170
5.00	87.0	180
6.00	87.6	174
7.00	88.0	166

* Base gasoline specifications are shown in Table 2.5–7. [b] Calculated according to Eq. 1–1.

In particular, 2-butanone (methyl ethyl ketone) has raised the most interest [123–125]. It has been found that by adding 10 %vol. of 2-butanone to conventional E10 gasoline (i.e., a gasoline with 10%vol. ethanol), RON over 98 is achieved, and increasing the amount of 2-butanone to 20 %vol. ensures S > 8, which is considered a favorable threshold for modern SI engines [123]. In terms of engine efficiency compared to standard RON95 gasoline, gains of 20% at full load have been quoted when blending 2-butanone, due to the higher effective compression ratio enabled by its high antiknock resistance.

Another example of the antiknock capability of ketone compounds can be appreciated in the ON results listed in Table 21, extracted from US patent 2,210,942.

Table 21. Effect on MON of the addition of ketone compounds at different doses [126].

Antiknock agent	Dose (%vol.)	MON[a]	ΔMON	BMON[b]
Methyl isobutyl ketone	10	49	8	121
	25	59	18	113
Methyl isopropyl ketone	10	48	7	111
Methyl *tert*-butyl ketone	25	59	18	113

[a] Base fuel is a Pennsylvania straight-run gasoline with MON = 41. [b] Calculated according to Eq. 1–1.

Ketones usually present high boiling points, high acidity, low material compatibility with other gasoline components, and high toxicity [27]. Also, ketones tend to be unstable, which makes them unsuitable fuels [7].

2-Butanone has a low boiling point (79.9 ºC) and a gasoline-like enthalpy of vaporization, which entails better performance at low engine speed and cold conditions compared to ethanol [125].

Although most acetone is made by the chemical industry, acetone can be produced utilizing renewable-based synthesis routes. A well-established biotechnological route that yields coproduction of acetone, ethanol, and 1-butanol is the ABE fermentation process. This technology is being revived by genetic engineering methods to ferment sugars to biobutanol [127].

2-Butanone can be obtained by fermentation of glucose with either *Escherichia coli* or *Saccharomyces cerevisiae* to obtain, firstly, 2,3-butanediol and, then, 2-butanone [128,129], but low yields have been reported so far. Industrially, 2-butanone is obtained mainly by catalytic dehydrogenation of 2-butanol (some process licensors are ABB Lummus Global-Petroquisa, IFP, and Tessag Edeleanu), which in turn can be obtained from biomass through Fischer-Tropsch or by fermentation [130]. 2-Butanone can also be obtained through direct oxidation of n-butene, as a byproduct in the manufacture of acetic acid from butane, or in a process developed by Shell that yields controllable amounts of phenol, 2-butanone, and acetone by co-oxidation of cumene and *sec*-butylbenzene [131].

Dunn and coworkers propose the synthesis of 2-butanone by using as feedstock a synthesis gas obtained from biomass gasification [8]. After conditioning, the synthesis gas is fermented to obtain 2,3-butanediol and small amounts of ethanol. Then, 2,3-butanediol is catalytically dehydrated to 2-butanone.

2.7. Esters

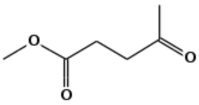
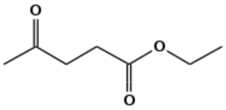
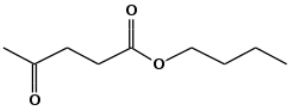
Organic esters are compounds with the general formula RCOOR’ where R and R’ are the same or different aliphatic, aromatic, or heterocyclic groups.

Esters have attracted some attention lately regarding their potential use as fuel antiknock components. In particular, small esters are considered interesting candidates among the biofuels pool [125]. In this regard, some references can be found targeting acetates as possible antiknock promoters—e.g., *tert*-butyl acetate is mentioned in US patent 4,191,536 [132], and a RON of 116 has been reported for ethyl acetate [125]—, or butyrates as suitable to be blended in aviation kerosene [133].

However, it seems clear that, among esters, alkyl levulinates, which traditionally have been used in fragrances and food flavors, are the group of interest. For instance, they have been proposed as additives to conventional diesel [90,134–139], as additives to gasoline fuels [134–136,140], to oil-based fuels [141] and even to biodiesels [134,135,142–144].

Among possible candidates, long alkyl chain levulinates (4-10 carbons) are currently in the spotlight due to greater solubility in the hydrocarbonated fraction concomitant to lower water solubility. However, a compromise between the above properties and other requirements, like density, viscosity, boiling, flash, and cloud points of the final mixture, has to be found (Table 22). For that, ethyl to butyl levulinates seem to be the main studied esters, and the addition ratio (alkyl levulinate/fuel) falls in the range of 0.5–20 %vol. [145].

Table 22. General properties of some alkyl levulinates.

	Methyl levulinate (ML)	Ethyl levulinate (EL)	Butyl levulinate (BL)
CAS Reg. No.	624-45-3	539-88-8	2052-15-5
Empirical formula	$C_6H_{10}O_3$	$C_7H_{12}O_3$	$C_9H_{16}O_3$
Chemical structure			
Molecular Weight (kg/kmol)	130.1	144.2	172.2
Density at 20 ºC (kg/m^3)	1050	1016	974
Boiling point (ºC)	196.1	205.9	237.6
Melting point (ºC)	-28[a]	25	-21[a]
Flash point (ºC)	72	94	92
Viscosity at 20 ºC (cP)	0.99[a]	1.19[a]	1.33[a]
Weight fraction of Oxygen (%wt.)	37	33	28
Net (lower) calorific value			
MJ/kg	23.4[b]	24.4	27.8
MJ/L (at 20 ºC)	24.6	24.8	27.1
Heat of vaporization at 25 ºC (kJ/kg)	332.5	306.7	277.5
Vapor pressure at 25 ºC (Pa)	47	27	14[a]
Solubility in water (g/L)	miscible	15.2	1.3
Distribution ratio in octanol/water system (log P)	-0.13	0.40	1.44[a]
GHS label codes[c]	7	None found	7

Sources: [67–69]. [a] Predicted value [69]. [b] Estimated using the Garvin formula [70]. [c] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Several examples were reported by Jungbluth and coworkers testing quantities of levulinate esters in four Eurosuper gasolines (ES), one Eurosuper plus gasoline (ESP), and one normal gasoline (N), with improved octane numbers (both RON and MON) [136]. Examples 1 to 13 of that work are listed in Table 23. Resulting BRON and BMON values for the addition of 10 %vol. levulinates to the tested base gasolines are shown in that table. In the case of examples 8 and 9, a 10 %vol. of mixtures of methyl levulinate and methyl formate (MF) are employed in 1:1 and 2:1 ratios, respectively. In example 14 (Table 24) a range of proportions from 5 %vol. to 90 %vol. of methyl levulinate in unleaded ESP gasoline was used. Similar increments of blending octane numbers have been reported by other researchers, such as [90,134,146].

Table 23. Comparison of the antiknock effect of some alkyl levulinates [136].

Example	Fuel	RON	MON	BRON	BMON
	ES 1	96.6	85.0	-	-
	ES 2	97.3	85.0	-	-
	ES 3	97.2	86.4	-	-
	ES 4	97.0	85.3	-	-
	ESP	99.3	88.0	-	-
	N	91.3	83.0	-	-
1	ES 3 + 10 %vol. ML	98.8	87.8	113	100
2	ES 1 + 10 %vol. EL	97.9	87.0	110	105
3	ES 2 + 10 %vol. PL	98.4	86.9	108	99
4	ES 4 + 10 %vol. iPL	98.3	86.8	110	100
5	ES 4 + 10 %vol. iBL	98.0	86.6	107	98
6	ES 4 + 10 %vol. sBL	98.0	86.5	107	98
7	N + 10 %vol. ML	92.9	84.6	107	99
8	ES 2 + 10 %vol. ML/MF 1:1	98.3	86.4	107	99
9	ES 2 + 10 %vol. ML/MF 2:1	98.3	86.5	107	100
10	ESP + 10 %vol. ML	100.2	89.0	108	98
11	ES 2 +10 %vol. EF	98.3	86.3	107	98
12	ES 1 +10 %vol. MTBE	98.4	86.4	115	96
13	ES 1 + 10 %vol. MF	97.6	86.1	107	96

Table 24. Effect of the amount of ML added to an unleaded fuel (Example 14) [136].

ML (%vol.)	RON	MON	BRON	BMON
0	97.1	85.5		
5	97.7	85.8	110.0	92.0
10	98.2	86.3	109.0	98.0
20	99.2	88.7	108.0	101.0
30	101.2		110.6	
40	102.5	93.1	110.6	105.6
60	105.6	100.7	111.2	111.2
80	113.0		117.0	
90		109.0		111.6

It has been stated that gasoline blends containing up to 5% ethyl levulinate, 1% water, and 2% non-ionic surfactant have similar Reid Vapor Pressures to those of the used base gasolines, and little or no effect has been observed on the blended gasoline flash point [137].

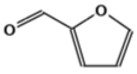
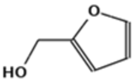
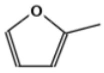
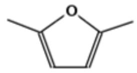
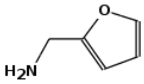
It has been shown that gasoline compositions containing ethyl levulinate together with particular nitrogen-containing detergents can give surprisingly enhanced engine cleanliness performance and that gasoline compositions containing ethyl levulinate are surprisingly more compatible with certain elastomeric seal materials than gasoline compositions containing similar concentrations of methyl levulinate [147].

There are several synthesis routes to obtain levulinic esters. Probably, the two most interesting ways are: (1) reaction of levulinic acid with an alcohol, which constitutes a very clean reaction with high yields (see the work by Tejero et al. 2016 as an example [148]); and (2) reaction between furfuryl alcohol and an alcohol. In both cases, all reactants can be obtained from biomass.

2.8. Furans

Furan is a compound with a 5-membered heterocyclic and unsaturated ring that contains oxygen. The term ‘furans’ often refers to all chemicals containing the furan ring (or the tetrahydrofuran ring) [149]. General characteristics of alkyl furans are listed in Table 25.

Table 25. General properties of some alkyl furans.

	Furfural	Furfuryl alcohol (FA)	2-Methyl-furan (MF)	2,5-Dimethyl-furan (DMF)	2-Furfuryl-amine (FAM)
CAS Reg. No.	98-01-1	98-00-0	534-22-5	625-86-5	617-89-0
Empirical formula	$C_5H_4O_2$	$C_5H_6O_2$	C_5H_6O	C_6H_8O	C_5H_7NO
Chemical structure					
Molecular Weight (kg/kmol)	96.1	98.1	82.1	96.1	97.1
Density at 20 °C (kg/m^3)	1159	1130	913	888	1050
Boiling point (°C)	161.6	156.9	63.9	93.9	145.6
Melting point (°C)	-39	-15	-89	-63	-70
Self-ignition point (°C)	393	391	450	286	350
Flash point (°C)	60 (closed cup)	75	-30	-1	37
Kinematic viscosity at 40 °C (mm^2/s)	1.07	2.3	0.39 (100 °C)	0.48 (100 °C)	
Weight fraction of Oxygen (%wt.)	33	33	19	17	16
Weight fraction of Nitrogen (%wt.)					14
Net (lower) calorific value					
MJ/kg	24.4	26.0	31.2	32.9	25.1
MJ/L (at 20 °C)	28.3	29.4	28.5	29.2	26.4
Heat of vaporization at 25 °C (kJ/kg)	444	540	358	332	
Vapor pressure at 37.8 °C (Pa)	690	480	18900	13400	530
Solubility in water (g/L)	10-74.1	miscible	3	<1	miscible
Distribution ratio in octanol/water system (log P)	0.41-0.46	0.28	1.85	2.30	0.55
GHS label codes[a]	6, 7, 8	6, 7, 8	2, 6, 7, 9	2, 6	2, 5, 6, 7

Sources: [67–69]. [a] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

According to published data on physicochemical and operational properties, 2-methylfuran (2-MF), 2,5-dimethylfuran (DMF), and furfurylamine (FAM) are the most promising compounds within this family in enhancing the knock resistance of gasoline [150,151].

The introduction of 2-MF (RON = 102) and DMF have become particularly important due to the ban of the use of n-methylaniline. Both products have excellent antiknock characteristics and will probably over time be able to compete with MTBE, ETBE, and TAME (Table 26). In this regard, two studies related to fuel and engine co-optimization have been released recently, which count with the participation of nine departments of the US Department of Energy National Laboratories, thirteen universities, an external advisory board, and industry partners, by the name of Co-Optima Project [9]. The first study “Fuel blendstocks with the potential to optimize future gasoline engine performance” identified eight high-octane blendstocks from five families. One of the bio-blendstocks, belonging to the family of furans, is a 40:60 mixture (by weight) of 2-MF and DMF.

Table 26. Reported effect on RON of furans addition to base gasoline [150].

Additive	**RON**	
	low-octane base gasoline (RON$_{BG}$ = 60–80)	high-octane base gasoline (RON$_{BG}$ = 90-97)
Furfural		131
FA		115–150
2-MF	170–180	130–140
DMF	170–180	119–140
FAM	194	126

The octane numbers of blends of 2-MF and DMF with a reference fuel containing n-heptane, isooctane, and toluene in various concentrations show a maximum blending RON at an additive concentration of 10 %vol., representing a 13% increase relative to basic fuel. At the same conditions, a mixture of fuel with 10 %vol. MTBE gives an increase of only 6.9%. The sensitivity (S = RON - MON) of the fuel increases to a small degree when 2-MF is added [152].

Recently, 2-MF has been confirmed as an excellent octane booster [153]. A blend of fuel representative of refinery naphtha with 2-MF (80/20 v/v) exhibited longer ignition delay times compared to blends with the same percentage of ethanol or toluene as an octane booster. 2-MF shows blending octane number (BON) closer to 208, as opposed to 146 for ethanol. In contrast to ethanol, the BON of 2-MF continues to increase with increasing the blend ratio, a testament to the better utilization of the fuel as a blending agent.

It has been found that the addition of 2-MF and DMF deteriorates gasoline oxidation stability and increases gum content [154]. This fact may impose serious restrictions on their use. The induction period of gasoline as a parameter of its oxidative stability can be used for the assessment of the ability of gasoline components to form gum upon storage. The minimum permissible time of the induction period for gasoline is 360 min. The lower the induction period, the lower the chemical stability of gasoline. Table 27 shows the induction period of blends with a 10 %vol. of oxygenates. Thus, the presence of furans increases the potential gum formation and, therefore, decreases chemical stability. Gum levels for 10 %vol. blends were 10-100 times higher than seen on specification conventional gasolines [155]. Peroxides were observed to be present in gums formed under ambient conditions. It is undetermined whether these pose a shock hazard. Antioxidants additives can be effective at limiting the oxidation reaction in gasoline but require much higher concentrations in presence of 2-MF and DMF than are commonly used in commercial gasolines.

Table 27. Induction period of blends with a 10 %vol. of oxygenates.

Fuel	**Induction period (min)**
Base gasoline	>1500
+ MTBE	>1500
+ MF	335
+ DMF	108

On the other hand, 2-MF and DMF do not enhance the corrosion activity of the fuel towards metals, although they somewhat increase the extent of the effect of the fuel on the mechanical rubber goods. Anyway, the above effects do not suggest the appearance of major restrictions on the use of these fuel additives. However, for the unambiguous conclusion about the possibility of using gasolines with the 2-MF and DMF additives, their effect on gum formation (chemical stability) and polymer materials should be studied in more detail. Another factor restricting the growth of the global 2-MF market is its high flammability and lower flash point, which complicate its transportation.

The widest method used to produce DMF from lignocellulose biomass involved pretreatment and subsequent decomposition of the biomass with the formation of glucose and fructose, which are then dehydrated to produce 5-hydroxymethylfurfural. [152]. The intermediate product is then hydrogenated selectively to DMF. Many methods of reducing 5-hydroxymethylfurfural with the use of various catalysts have now been developed

2-Methylfuran is also produced from lignocellulosic feedstock but, unlike DMF, the starting material is xylose, which is present in lignocellulose in the form of the polysaccharide xylan. After decomposition of the feedstock, the xylose undergoes catalytic dehydration with the formation of furfural, which is then hydrogenated selectively to MF [154]. Both processes have been well studied, and catalysts and conditions that secure yields of about 96% were selected.

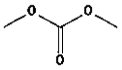
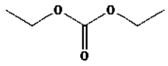
The bioethanol production from lignocellulose raw material is obtained after fermentation of C6 monosaccharides. C5 traditional fermentation does not give good results for bioethanol production, and its transformation in furfural by hydrolysis and dehydration could be a way to obtain a large tonnage of this building block.

2.9. Carbonates

Organic carbonates are known for their simple structure, high polarity, low viscosity, low toxicity, and easy degradability [156]. These remarkable properties make them an important group of chemicals as a potential substitute for toxics, flammable and harmful for the ecosystem [157]. Based on commercial value and their properties, organic carbonates are broadly distinguished as dimethyl carbonates (DMC), diethyl carbonate (DEC), cyclic carbonates (CC), diphenyl carbonate (DPC), etc. Among them, DMC has considered as most important due to its interesting physical-chemical properties and a wide range of applications.

DEC is considered a promising replacement from ethyl *tert*-butyl ether (ETBE) as an attractive oxygen-containing fuel additive due to its high oxygen content (40.6%). General properties of DMC and DEC are provided in Table 28.

Table 28. General properties of dimethyl and diethyl carbonate.

	DMC	DEC
CAS Reg. No.	616-38-6	105-58-8
Empirical formula	$C_3H_6O_3$	$C_5H_{10}O_3$
Chemical structure		
Molecular Weight (kg/kmol)	90.08	118.132
Density at 20 ºC (kg/m^3)	1069	975
Boiling point (ºC)	90.5	126-128
Melting point (ºC)	0.5	-43
Self-ignition point (ºC)	458	445
Flash point (ºC)	14 (closed cup)	25 (closed cup)
Viscosity at 20 ºC (cP)	0.664	
Weight fraction of Oxygen (%wt.)	53	41
Net (lower) calorific value		

MJ/kg[a]	14.5	21.2
MJ/L (at 20 ºC)	15.5	20.7
Heat of vaporization (kJ/kg)	426	
Vapor pressure at 25 ºC (Pa)	7381	1440
Solubility in water at 25 ºC (g/L)	138	21.5
Distribution ratio in octanol/water system (log P)	0.23	1.21
GHS label codes[b]	2	2, 7

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Carbonates are one of the chemical additives considered as oxygenates for fuel reformulation. There are indications that it might be possible to produce a completely smoke-free operation of a diesel engine by the incorporation of 38 %wt. oxygen into the fuel [158]. It has been demonstrated that the use of oxygenated compounds as fuel additive attributes considerably less soot than hydrocarbons [159]. Results from studies by Amoco researchers are shown in Table 29 which indicates DMC having Clean Air Act properties [160].

Table 29. A list of blending properties of alkyl carbonates measured at Amoco Research Center [160].

Parameter	**DMC**	**DEC**
ULR gasoline		
RON	111	114
MON	95	98
RVP	8.0	1.0
ULP gasoline		
RON	109	111
MON	102	101
RVP	5.4	-3.6

The use of dimethyl carbonate, and more generally alkyl carbonates, as fuel additive was put forward in numerous patents [160], the first occurrence being in a patent by Standard Oil Development Co. in 1943 which reported that adding 3 %wt. of diethyl carbonate and butyl carbonate to gasolines allowed both injection and vaporization of gasolines to be improved, by reducing their surface tension [161]. Although butyl carbonate was preferred, dimethyl carbonate was also mentioned.

European Patent EP0082688-A2 reported on high-octane fuels mixtures consisting of 90:10 (volume) gasoline: dimethyl carbonate or diethyl carbonate. The 90:10 aromatic gasoline-dimethyl carbonate had RON of 95.2, compared to 93.7 for the gasoline alone [162]. In another European patent (EP0098691-A2), specific data on RON for different blends of carbonates with gasoline can be found (Tables 30 through 32) [163]. As can be seen in the tables, DMC provides a much higher RON improvement than other di-alkyl carbonates, both in leaded and unleaded gasolines.

Table 30. RON and BRON for the addition of dimethyl carbonate to pure isooctane [163].

Additive	**Dose (%vol.)**	**RON**	**BRON**
dimethyl carbonate	0	100	
	3	100.9	130
	5	101.6	132

Table 31. RON, MON and calculated blending values for the addition of several carbonates to mixtures of isooctane and n-heptane (80:20 vol.) [163].

Additive	**Dose (%vol.)**	**RON**	**MON**	**BRON**[a]	**BMON**[a]
	0	80.0	80.0		
dimethyl carbonate	3	81.5	80.6	130	100
	5	82.6	81.0	132	100
diethyl carbonate	3	81.0	80.7	113	103
	5	81.4	81.1	108	102
di-n-propyl carbonate	3	80.8	80.3	107	90
	5	81.7	81.1	114	102
di-n-butyl carbonate	3	80.1	80.0	83	80
	5	80.2	80.1	84	82

[a] Calculated according to Eq. 1–1.

Table 32. RON, MON, and calculated blending values for the addition of several carbonates to leaded premium grade gasolines [163].

Additive	**Dose (%vol.)**	**RON**	**MON**	**BRON**[a]	**BMON**[a]
dimethyl carbonate	0	97.0	87.7		
	3	97.9	88.3	127	108
	5	98.3	88.8	123	110
diethyl carbonate	0	98.5	88.1		
	3	98.9	88.3	112	95
	5	99.2	88.5	113	96
di-n-propyl carbonate	0	97.4	88.6		
	3	97.8	89.0	111	102
	5	98.3	89.1	115	99
di-n-butyl carbonate	0	97.7	88.1		
	3	97.7	88.1	98	88
	5	97.7	88.2	98	90

[a] Calculated according to Eq. 1–1.

Wang and coworkers, who studied the effect that oxygen-containing compounds could have on the antiknock ability in the gasolines they were blended in, observed a clear synergistic effect with blends of dimethyl carbonate and cresol (a phenolic compound—see Section 3.10). An increase in RON of 2.9 units could be achieved by the addition of 3 %vol. of the combined additive.

Several other research studies and patents can be found reporting that significant gains in gasoline antiknock ability can be achieved by the addition of carbonates [164–167]. For instance, ΔRON = 3–6 were achieved by the addition of 4.7 %wt. dimethyl carbonate to gasoline [166].

It has been claimed that dimethyl carbonate helps mitigating CO, SO_X, and NO_X emissions [165,168]. Its low vapor pressure also helps in reducing evaporative emissions. The low freezing point of DMC (<1 ºC) is also counted among its characteristics of interest regarding its potential use as a gasoline additive or component.

The distribution of DMC in gasoline/water two-phase systems is another interesting physical characteristic. The values of DMC distribution calculated by Amoco Research Center are highly positive compared to C1-C3 light alcohols (Table 33).

Table 33. Comparative results of distribution coefficient properties in gasoline/water two-phase system (Basis: unleaded premium gasoline with 2 %wt. oxygen).

Oxygenate	**Distribution coefficient**

ETBE	>20
TAME	>20
DEC	≈ 20
MTBE	18
DMC	2.0
IPA	0.24
Ethanol	0.18
Methanol	<0.01

Carbonates toxicological effects and associated health and environmental hazards are remarkably low. On the other hand, carbonates emit acrid smoke and fumes when heated to decomposition [169].

Dimethyl carbonate (DMC) was historically formed by the reaction of methanol with phosgene or methyl chloroformate in the presence of a concentrated sodium hydroxide solution in a two-phase reaction in high yields and purity (see Eqs. 6 and 7, and the overall Equation 8). Other alcohols can also be phosgenated.

$$COCl_2 + CH_3OH \rightarrow CH_3OCOCl + HCl \quad (6)$$

$$CH_3OCOCl + CH_3OH \rightarrow CH_3OCO_2CH_3 + HCl \quad (7)$$

$$COCl_2 + 2\ CH_3OH \rightarrow CH_3OCO_2CH_3 + 2\ HCl \quad (8)$$

This process is nowadays undesirable because of phosgene toxicity and has been largely replaced by other synthesis routes. Therefore, DMC is now produced industrially by transesterification of ethylene carbonate or propylene carbonate with methanol, which also affords respectively ethylene glycol or propylene glycol. A second large-scale commercial synthesis route uses the Enichem process, where carbon monoxide, methanol, and oxygen react to form dimethyl carbonate at a temperature ranging from 120 to 140 ºC and under a total pressure of 20–40 bar [170].

Based on its large experience in the dimethyl oxalate (DMO) synthesis from nitrogen monoxide, a similar process was developed by the UBE society for synthesizing dimethyl carbonate in the gas phase through a catalytic redox process. The process is practiced commercially by Ube Industries in Japan using a palladium-supported catalyst [171].

Like DMC, since the conventional synthesis method of DEC involves the use of extremely poisonous phosgene, considerable effort has been devoted to the development of alternative technologies such as transesterification of methanol [172], oxidative carbonylation of ethanol [173], carbonylation of ethyl nitrite [174], the reaction of ethanol with urea [175], and decarbonylation of diethyl oxalate [176]. Nevertheless, the practical application of these non-phosgene routes is still restricted due to several disadvantages, such as the toxicity of carbon monoxide and ethyl nitrite, deactivation of the catalysts, and low product yields.

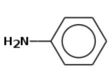
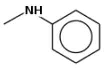
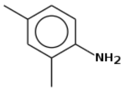
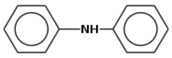
DEC is considered an important homolog in the family of dialkylcarbonates possessing eco-friendly features such as biodegradability to ethanol and carbon dioxide. Moreover, the fact that it can be prepared from bioethanol gives a “bio-derived” label to DEC and all the processes in which it is applied.

3. Ash-less octane enhancer additives (<2 vol%)

3.1. Anilines

Aniline ($C_6H_5NH_2$) is the prototypical aromatic amine, it presents a phenyl group attached to an amino group. In comparison to alkylamines, aromatic amines are much weaker bases due to the more electronegative carbon atoms in the phenyl group. In general, aromatic amines have low solubility in water (general properties of some aromatic amines are provided in Table 34).

Table 34. Main physicochemical properties of some aromatic amines.

	Aniline	N-methyl-aniline	2,4-Dimethylaniline (2,4-xylidine)	Diphenylamine
CAS Reg. No.	62-53-3	100-61-8	95-68-1	122-39-4
Empirical formula	C_6H_7N	C_7H_9N	$C_8H_{11}N$	$C_{12}H_{11}N$
Chemical structure				
Molecular weight (kg/kmol)	93.13	107.15	121.18	169.22
Density at 20 ºC, (kg/m^3)	1021.7	989	972.3	1068
Boiling point (°C)	184	196	218.05	302.05
Melting point (°C)	-6.15	-57	-15.9	52.85
Self-ignition point (°C)	615	500	520	634
Kinematic viscosity at 20 ºC (mm^2/s)	4.26	2.60	4.15	2.434
Nitrogen (%wt.)	15	13	12	8
Net (lower) calorific value				
MJ/kg	31.4	36.6[a]	37.4[a]	37[a]
MJ/L (at 20 ºC)	32.1	36.2	36.4	39.5
Heat of vaporization at 25 ºC (kJ/kg)	600 (25 ºC) 456 (184 ºC)	471.3	506 (44 ºC) 368 (203 ºC)	326
Vapor pressure at 25 ºC (Pa)	88.9	60.4	17.7	0.09
Solubility in water (g/L)	36 (25 ºC)	none	5 (20 ºC)	0.053 (20 ºC)
Distribution ratio in octanol/water system (log P)	0.9	1.66	1.68	3.5
GHS label codes[b]	5, 6, 7, 8, 9	6, 8, 9	6, 7, 8, 9	6, 8, 9

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Several aromatic amines have been identified as potential octane boosters because of the high octane numbers resulting from their blending with gasoline (see examples in Table 35). The antiknock ability of aromatic amines is explained by their tendency to form stable molecules during combustion that are unable to react to regenerate active radicals again which, as a consequence, reduces the overall combustion rate [177,178]. Within aromatic amines, n-methylaniline has drawn the most attention because it is responsible for an important octane boost and, at the same time, it presents the lowest gum formation, which is one of the aromatic amines main drawbacks [50].

Table 35. Effect of different doses of selected aromatic amines on several base gasolines [179–183].

Additive	**Base gasoline**	**Dose**	**RON (ΔRON[a])**	**BRON[b] (ΔMON[a])**	**Source**
aniline	RON 85.6	1 %vol.	88.5	376	[5]
		2 %vol.	91	356	[5]
2,4-dimethyl-aniline	RON 85.6	1 %vol.	89.5	476	[5]
		2 %vol.	92.7	441	[5]
		3 %vol.	93.4	346	[5]
n-methylaniline	RON 85.6	1 %vol.	90	526	[5]
		2 %vol.	95.3	571	[5]
		3 %vol.	96	432	[5]

	unspecified	5000 mg/L	(-0.8)	(0.4)	[6]
	RON 90	0.5 %vol.	91.8	450	[7]
		1.0 %vol.	91.9	280	[7]
		1.5 %vol.	93	290	[7]
		2.0 %vol.	94.7	325	[7]
		2.5 %vol.	96.8	362	[7]
	RON 91.6 (MON 80.8)	0.5 %wt.	92.5	272	[8]
		1.0 %wt.	93.5	282	[8]
		1.5 %wt.	94.4	278	[8]
		2.0 %wt.	95.2	272	[8]
		2.5 %wt.	95.8	260	[8]
	RON 93.8 (MON 84.7)	1.3 %wt.	96.8	325	[9]
		2.0 %wt.	97.2	264	[9]
		3.0 %wt.	98.4	247	[9]
	RON 95.6 (MON 86.0)	1.3 %wt.	98	280	[9]
		2.0 %wt.	99.2	276	[9]
		3.0 %wt.	100	242	[9]
n-methyl-o-toluidine	unspecified	5000 mg/L	(0.3)	(0.4)	[6]
n-methyl-p-toluidine	unspecified	5000 mg/L	(1.2)	(0.8)	[6]
n-methyl-p-methoxyaniline (p-anisidine)	unspecified	5000 mg/L	(1.8)	(0.2)	[6]
2,4,6-trimethyl-n-methylaniline	unspecified	5000 mg/L	(0)	(-0.8)	[6]
2-methylindoline	unspecified	5000 mg/L	(-0.2)	(-1.4)	[6]
Ethanox ® 4720 (n,n′-di-sec-butyl-p-phenylenediamine)	unspecified	5000 mg/L	(-0.4)	(-2.1)	[6]

[a] Calculated according to Eq. 1–1.

Furthermore, data is provided in US Patent 2012/0279112-A1 regarding the antiknock effect of several anilines, particularly of 2,4-dimethylaniline (2,4-xylidine), in different unleaded base gasolines, as listed in Table 36 [184].

Table 36. RON and MON values for the addition of anilines to different base gasolines [184].

Additive	**Base gasoline**	**Dose**	**RON/ MON**	**BRON[a]/ BMON[a]**
2,4-dimethyl-aniline	RON 98.8 (MON 88.7)	0.5 %wt.	99.6/89.1	259/169
		1.0 %wt.	100.9/89.8	309/199
		1.5 %wt.	101.6/90.2	285/189
	RON 91.0	0.26 %wt.	91.9	437
		0.8 %wt.	93.7	429
		1.3 %wt.	95.5	437
	RON 93.5	0.2 %wt.	94.4	544
		0.9 %wt.	96.0	371
	RON 69.4	1.0 %wt.	73.2	449
		3.0 %wt.	79.9	419
		6.0 %wt.	88.0	379
	RON 80.0	1.0 %wt.	82.8	360
		3.0 %wt.	87.6	333
		7.0 %wt.	97.3	327
	RON 63.0	1.0 %wt.	65.6	323
		3.0 %wt.	69.4	276
		5.0 %wt.	73.8	279
		7.0 %wt.	78.0	277
n-methyl-2,4-di-methyl-aniline	RON 98.8 (MON 88.7)	0.5 %wt.	99.3/88.95	199/139

2,3-dimethyl-aniline	RON 98.8 (MON 88.7)	0.5 %wt.	99.2/88.9	179/129
2,5-dimethyl-aniline	RON 98.8 (MON 88.7)	0.5 %wt.	99.12/88.85	163/119
o-toluidine	RON 98.8 (MON 88.7)	0.5 %wt.	98.95/88.78	129/105

[a] Calculated according to Eq. 1–1.

In addition to a blending of a single aromatic amine, several synergistic or antagonistic effects on the antiknock effect have been reported when a combination of an aromatic amine and other octane enhancing additives are blended with a given gasoline. For instance, Table 37 shows several RON values obtained for a gasoline after adding different compositions of both n-methylaniline and methylcyclopentadienyl manganese tricarbonyl (MMT), which are superior to RONs obtained after blending the same concentrations of each additive separately [182].

Table 37. Synergistic effect of blending n-methylaniline and MMT [182].

Base gasoline	Additive composition	RON	BRON[a]
RON 91.6 MON 80.8	1%wt. n-methylaniline–3 mg/kg Mn	93.9	322
	1%wt. n-methylaniline–6 mg/kg Mn	94.5	382
	1%wt. n-methylaniline–9 mg/kg Mn	94.9	422
	1%wt. n-methylaniline–12 mg/kg Mn	95.0	432
	1%wt. n-methylaniline–15 mg/kg Mn	94.8	412
	1%wt. n-methylaniline–21 mg/kg Mn	95.1	442
	2%wt. n-methylaniline–6 mg/kg Mn	95.5	287
	2%wt. n-methylaniline–9 mg/kg Mn	96.0	312
	2%wt. n-methylaniline–12 mg/kg Mn	96.5	337
	2%wt. n-methylaniline–18 mg/kg Mn	97.0	362
	2%wt. n-methylaniline–24 mg/kg Mn	96.8	352
	2%wt. n-methylaniline–30 mg/kg Mn	97.0	362
	2%wt. n-methylaniline–42 mg/kg Mn	97.1	367

[a] Calculated according to Eq. 1–1.

Contrarily, the combination of n-methylaniline (or aromatic amines, by extension) with other additives can give raise to certain antagonistic effects, as reflected in Table 38. Other antagonistic effects have been reported in RU 2235117, RU 2117691, FR 1255840, and RU 2129141 [185–188].

Table 38. Antagonistic effects in enhancing ON for combination of n-methylaniline, Fe, Mn, and K.

Base gasoline	Additive composition	ΔS_{RON}	ΔS_{MON}	Source
RON 95.0 (MON 83.9)	12 g/L Fe–4.5 ppm K	-0.7	-1.6	[189]
	12 g/L Fe–0.3 %vol. n-methylaniline	-0.3	1.0	
	12 g/L Fe–4,5 ppm K, 0.3 %vol. n-methylaniline	-0.2	-0.8	
	12-18 g/L Mn–0-4.5 ppm K–0-0.3 %vol. n-methylaniline	Unquantified antagonistic effects		

On the other hand, with higher aromatic amines doses (that is, up to 7 %vol.), higher RON values can be achieved, as listed in Table 39 [190].

Table 39. RON and MON of different fuel compositions [190].

Component	Fuel composition (%vol.)					
isooctane	45.5	45.5	45.5	40.5	-	-
toluene	23	23	23	15	15	34
m-xylene	21	21	21	14	14	15
isopentane	3.5	3.5	3.5	9.5	-	
aniline	7	-	-	-	7	7

m-toluidine	-	7	-	-	-	-
n-methylaniline	-	-	7	7	-	-
ETBE	-	-	-	14	14	-
alkylate	-	-	-	-	50[a]	44[b]
RON	116.33	116.0	115.0	117.67	118.0	114.0
MON	105.33	116.0	96.93	104.67	101.9	105.0

[a] alkylate composition: >30 %vol. naphtenes; <70 %vol. Isoparaffins; <1 %vol. normal paraffins; <1 %vol. Aromatics. [b] alkylate composition: <3 %vol. naphtenes; >90 %vol. Isoparaffins; <4 %vol. normal paraffins; 0 %vol. Aromatics.

Based on the works of both Boyd and Brown, Burns reported on liquid hydrocarbon fuel compositions containing antiknock quantities of ash-less antiknock agents comprising selected n-allylic aromatic amines and acetylenic amine compounds intended for use in internal combustion engines [191,192]. Specific antiknock agents included were n-methallylaniline, n-allyl-*o*-toluidine, n-crotyl-*p*-toluidine because these compounds have suitable solubility and volatility characteristics to permit their application as additives for hydrocarbon fuels. In general, those compounds were employed from 0.5 to 10 %wt. of the total fuel composition. The base fuel used was an unleaded Kansas Premium Pipeline Gasoline (FT-175) with a MON of 83.9 and RON of 91.5 (ASTM D 2599-47 method). Table 40 presents the increase in RON over the untreated fuel produced by the addition of the n-allylic aromatic amine compounds.

Table 40. Octane enhancement posed by N-allylic aromatic amines blended in FT-175 gasoline [191].

Compound	**Concentration (wt. %)**	**RON increase**
N-methallylaniline	2.0	1.7
N-allyl-*o*-toluidine	2.0	1.2
N-crotyl-*p*-toluidine	2.2	1.3

Further data on the influence of the atoms or radicals attached to nitrogen on its effect upon detonating combustion values of a number of derivatives of aniline were also studied. Replacing one of the hydrogen atoms of the amine group by organic radical increases the effectiveness in the cases of the methyl, ethyl, and phenyl radicals. Thus, methylaniline is 40 %mol. more effective than aniline, and diphenylamine is 10 %mol. more effective than methylaniline; but when an alkyl radical larger than ethyl is substituted in the amine group, the antiknock effect is lowered. Brown et al. correlated the change in antiknock effectiveness in automotive fuels with aromatic amines structure [178]. Taking a synthetic fuel mixture containing 6 %wt. n-methylaniline (NMA) for comparison purposes (RON: 94, MON: 86), they found that the most effective compounds tested were the nitrogen-substituted para-phenylenediamines, 4-*sec*-butyl-*o*-phenylenediamine, and n-nitroso-di-phenylamine (antiknock effectiveness as much as 2.3 times that of NMA). The most effective of the monoamines tested were the n-methyl-*p*-alkylanilines, n-methylaniline, *p*-ethylaniline, *p*-butylaniline, and the xylidines. All tests were based on the CFR knock-test engine (ASTM D 908-51 for RON and ASTM D 357-49 for MON).

While no detailed amine oxidation mechanism could be found in the literature, some clues are provided by Cullis et al., who linked amine anti-knock performance to the formation of stable intermediates. N-H bonds are relatively weak and therefore readily facilitate H atom abstraction. This process competes with H atom abstraction from fuel compounds by consuming active radicals. The aromatic amine radicals yielded as a result of the aforementioned H atom abstraction are resonance stable and thus tend to slow down the overall reaction rate [193].

In this regard, a list is provided in Table 41 containing blending RON and MON values for several aromatic amines. Also, from Brown et al. [178], a qualitative overview of the antiknock ability of amine derivatives allows to observe a general trend in relation to the antiknock effect of several aromatic amines—relative to aniline, small differences are observed in terms of octane enhancement when hydrogen atoms of the aromatic ring are substituted by methyl or ethyl groups, but if substituted by longer aliphatic chains the octane enhancement worsens. Primary (e.g., aniline) and secondary (e.g., diphenylamine) amines lead to much better antiknock performance than tertiary amines (e.g., n,n-dimethylaniline) [32]. Similar conclusions can be drawn from the observation of the values in Table 42, where the relative antiknock effect of several nitrogen-containing compounds is listed, using as a standard the effect of 3 %vol. aniline in kerosene as the fuel [194]

Table 41. Blending RON and MON values for several aromatic amines.

Aromatic amine	BRON	BMON
aniline[a]	310	290
n-methylaniline[a]	280	250
2,4-xylidine[b]	297	187
diphenylamine[a]	310	300
o-toluidine[b]	247	197
p-toluidine[a]	340	305
p-ethylaniline[a]	320	300
p-*tert*-butylaniline[a]	280	250
3,4-xylidine[a]	370	320
3,5-xylidine[a]	340	210
p-*tert*-butylaniline[a]	300	206
indoline[a]	300	150
n,n-dimethylaniline[a]	95	84

[a] 2.0 %wt. addition to premium base gasoline [32], [b] 1.0 %wt. addition to base fuel with RON 96.6 and MON 87 [195].

Table 42. Relative antiknock effect of nitrogen-containing compounds as compared to that of 3 %vol. aniline in kerosene [194].

Compound	Formula	Amount for given effect (g)	Relative effectiveness (%mol)
Aniline	$C_6H_5NH_2$	1.00	1.00
Cumidine	$(CH_3)_3C_6H_2NH_2$	0.96	1.51
Diphenylamine	$(C_6H_5)_2NH$	1.21	1.50
m-Xylidine	$(CH_3)_2C_6H_3NH_2$	0.92	1.40
Monomethylaniline	$C_6H_5NHCH_3$	0.83	1.40
Toluidine	$CH_3C_6H_4NH_2$	0.94[a]	1.22[a]
Amylaminobenzene	$C_5H_{11}C_6H_4NH_2$	1.53	1.15
Ethylaminobenzene	$C_2H_5C_6H_4NH_2$	1.14	1.14
Aminodiphenyl	$C_6H_5C_6H_4NH_2$	1.60	1.14
Methyl-*o*-toluidine	$CH_3C_6H_4NHCH_3$	1.15	1.13
n-Butylaminobenzene	$C_4H_9C_6H_4NH_2$	1.44	1.11
n-Propylaminobenzene	$C_3H_7C_6H_4NH_2$	1.32	1.10
Monoethylaniline	$C_6H_5NHC_2H_5$	1.27	1.02
Mono-n-propylaniline	$C_6H_5NHC_3H7$	1.95	0.75
Ethyldiphenylaniline	$C_2H_5N(C_6H_5)_2$	3.65	0.58
Mono-n-butylaniline	$C_5H_6NHC_4H_9$	3.10	0.52
Diethylamine	$(C_2H_5)_2NH$	1.59	0.495
Di-n-propylaniline	$C_6H_5NH(C_3H_7)_2$	7.15	0.27

Mono-isoamylaniline	$C_6H_5NHC_5H_{11}$	7.10	0.248
Diethylaniline	$C_6H_5N(C_2H_5)_2$	6.70	0.24
Dimethylaniline	$C_6H_5N(CH_3)_2$	6.20	0.21
Ethylamine	$C_2H_5NH_2$	2.40	0.20
Triethylamine	$(C_2H_6)_3N$	7.95	0.14
Triphenylamine	$(C_5H_6)_3N$	30.0	0.09
Ammonia	NH_3	–2.00[b]	–0.09[b]
Isopropyl nitrite	$C_3H_7NO_2$	–0.085[b] (aprox.)	–11.5[b] (aprox.)

[a] Average of *o*-, *m*- and *p*- values. [b] Negative values indicate proknock action.

The use of n-methylaniline, which is tagged as a non-traditional gasoline additive (NTGA), has been documented to form gum, drastically shorten the induction period, and sharply increase seal swell. Large levels of gum, caused by n-methylaniline oxidation, are responsible for higher carbon deposits in engine parts (e.g., pistons, fuel intake manifolds, and/or combustion chambers). Shorter induction times can cause gasoline stability to decline. Swelling of seal rings may cause oils to leak from engine pipes [32,50,196].

On the other hand, a study has been found that compares different aniline–gasoline blends [197]. Such a study concludes that blends with up to 20 % aniline can perform well in outdated car engines without further modifications. According to Usmani 2018, lower temperature in the exhaust gases is achieved by the aniline-blended fuel.

Aromatic amines show toxicity and a bad smell [27]. From the environmental point of view, it should be highlighted that all nitrogen-containing compounds increase nitrogen oxide emissions in the exhaust gases, due to nitrogen partial oxidation in the combustion [32]. Nevertheless, toxicity varies significantly depending on functional groups and structure. Some examples of different levels of toxicity are detailed in Table S1 of the Supporting Information section.

The most widely used method for preparing aromatic amines involves nitration of the ring and subsequent reduction of the nitro group to an amino group. To reduce the nitro group, multiple methods exist, the most frequent one involves catalytic hydrogenation with iron, zinc, tin, or a metal salt like $SnCl_2$ [87].

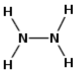
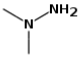
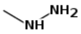
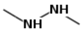
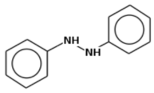
N-methylaniline was used as an octane enhancer for a short period after World War II in Germany [32]. Aromatic amines have been popular in countries lacking refining units producing high-octane gasoline (e.g., Russia, Kazakhstan, African countries, etc.), but Russia (and China) has already banned their use after the implementation of the Euro V standard. On the other hand, several events of vehicle fires, mainly motorbikes, in Vietnam, owing to the poor quality of gasoline have ended in a prohibition of n-methylaniline [27].

Since n-methylaniline is not an oxygenate, it is not mentioned in World Wide Fuel Charter and, therefore, its use is permitted in several jurisdictions (e.g., US, EU). However, due to its associated gum formation, when n-methylaniline is allowed, it needs to be mixed with detergents and fuel combustion modifiers to, allegedly, reduce such formation of gum [127].

3.2. Hydrazines

The term ‘hydrazines’ refers to a group of compounds that contain two nitrogen atoms joined by a single covalent bond. Included in this group are, among others, hydrazine, 1,1-dimethylhydrazine (known as unsymmetrical dimethylhydrazine, UDMH), monomethylhydrazine (MMH), 1,2-dimethylhydrazine (or symmetrical dimethylhydrazine, SDMH), and 1,2-diphenylhydrazine (DPH) (see Table 43 for general characteristics of hydrazines). The simplest compound, hydrazine, a simple pnictogen hydride, is an inorganic compound with the chemical formula $H_2N—NH_2$. It is a colorless flammable liquid with an ammonia-like odor.

Table 43. General characteristics of some hydrazines.

	Hydrazine	UDMH	MMH	SDMH	DPH
CAS Reg. No.	302-01-2	57-14-7	60-34-4	540-73-8	122-66-7
Empirical formula	N_2H_4	$C_2H_8N_2$	CH_6N_2	$C_2H_8N_2$	$C_{12}H_{12}N_2$
Chemical structure					
Molecular weight (kg/kmol)	32.05	60.1	46.07	60.1	184.2
Density at 20 ºC (kg/m^3)	1001	800	870	830	1160
Boiling point (ºC)	113.5	63.5	90.85	87.05	293
Melting point (ºC)	1.8	-57.2	-52.4	-9	131.3
Self-ignition point (ºC)	270	249	194		
Kinematic viscosity at 20 ºC (mm^2/s)	0.90	0.60	0.89		
Weight fraction of Nitrogen (%wt.)	87.4	46.6	60.8	46.6	15.2
Net (lower) calorific value					
MJ/kg	16.6	29.2[a]	24.7[a]	29.2[a]	35.0[a]
MJ/L (at 20 ºC)	16.7	23.3	21.5	24.2	40.7
Heat of vaporization at 25 ºC (kJ/kg)	1413	586	879	657	
Vapor pressure at 25 ºC (Pa)	1919.8	20973	6613	9321	0.06
Solubility in water (g/L)	miscible	miscible	miscible	1000	0.221
Distribution ratio in octanol/water system (log P)	-2.07	-1.19	-1.05	-0.54	2.94
GHS label codes[b]	2, 5, 6, 7, 8, 9	2, 5, 6, 8, 9	8	6, 8, 9	7, 8, 9

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Hydrazine has been reported to present a RON value of 110 [198]. This said, concerning the use of hydrazines in gasoline formulation, scarce literature has been found on their effect on the antiknock quality of the fuel. However, some patents have been found that either directly or indirectly deal with this topic. For instance, US Patent 1,883,593 mentions hydrazine as an additive to improve ON in gasolines, but no further details are provided on the subject [199]. Contrarily, US Patent 2,969,278 indicates that “the presence of minor amounts of unsubstituted hydrazine drastically reduces the octane rating of gasoline by 10 or more octane units” [200] and in a previous patent by the same author, US Patent 2,942,957, the following statement can be found: “the use of unsubstituted hydrazine as an additive is highly impractical as hydrazine is substantially insoluble in hydrocarbons” [201]. On the other hand, US Patent 4,695,292, which deals with gasoline-alcohol blends, provides data on RON and MON values of different base gasolines when hydrazines are used as additives (Table 44) [202].

Table 44. RON and MON values for base gasolines with hydrazines according to US Patent 4,695,292 [202].

Base fuel (Rel. Vols.)	**Hydrazine additive (%wt.)**	**RON**	**MON**
Gasohol[a] + MeOH[b] (70:30)	1,1-DPH (2)	95.1	81.1
Gasoline[c] + MeOH (60:40)	DPH (1)	97.3	83.7
Gasohol + MeOH (70:30)	DPH (1)	98.0	83.8

Gasoline + MeOH (60:40)	DPH (2)	95.4	81.4
Gasoline + MeOH (63:37)	phenylhydrazine (7)	72.8	66.0
Gasoline + MeOH (63:37)	UDHM (5)	67.7	58.2

[a] Gasohol: 90 %vol. unleaded regular gasoline + 10 %vol. ethanol (MON 92). [b] MeOH: 90 %vol. reagent grade methanol + 2.5 %vol. n-propanol + 2.5 %vol. n-butanol. [c] Gasoline: unleaded regular gasoline (MON 89).

According to this patent, the use of DPH entails significantly larger ON values than UDHM, which worsens gasoline antiknock performance to unacceptable levels. It should be highlighted, though, that the interest of hydrazines as gasoline additives in US Patent 4,695,292 is not as much focused on their effect on the octane quality as it is on the enhanced miscibility, low-temperature stability, and reduced corrosiveness towards engine parts when compared to the same gasoline-alcohol blends without such additives.

From Table 44, the low ON when phenylhydrazine is used seems to be confirmed by an earlier publication, which indicates that phenylhydrazine is a knocking promoter rather than an antiknock additive [203].

The main quoted uses of hydrazines in gasoline formulation are to help reducing deposit formation [204], as an anti-icing agent [205], and as a corrosion inhibitor [206].

Hydrazine and its derivatives are highly toxic and dangerously unstable in an anhydrous form. Hydrazine has a noxious effect on bacteria, algae, and aquatic wildlife. As a consequence, the emission of hydrazine-containing wastewater is not allowed [207]. Since this family of compounds potentially causes severe adverse effects on human health and the environment, numerous regulations have been established for hydrazines by various international and national agencies [208].

Among other applications, hydrazines are used in military, orbital, and deep space rocket fuels because they are storable liquids for long periods at reasonable temperatures and pressures and because they are excellent propellants. Hydrazines are also used within both nuclear and conventional electrical power plant steam cycles as oxygen scavengers to control concentrations of dissolved oxygen in an effort to reduce corrosion.

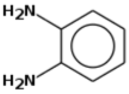
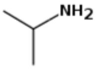
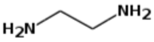
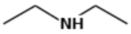
3.3. Amines

In organic chemistry, amines are compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines are formally derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group (these may respectively be called alkylamines and arylamines) [209]. In general, aromatic amines have low solubility in water. General properties of some amines are provided in Table 45. Important amines include amino acids, biogenic amines, trimethylamine, and aniline. Inorganic derivatives of ammonia are also called amines, such as chloramine ($NClH_2$) [210].

Anilines are an specific type of amines but, due to their relevant potential as octane boosters, they have been discussed previously in an specific section. They are also included in some discussions of this section for comparison purposes.

Table 45. Main physicochemical properties of some amines.

	4-*sec*-butyl-*o*-phenylene diamine	Isopropyl amine	Ethylene diamine	Diethyl amine
CAS Reg. No.	95-54-5	75-31-0	107-15-3	109-89-7
Empirical formula	$C_6H_8N_2$	C_3H_9N	$C_2H_8N_2$	$C_4H_{11}N$

Chemical structure				
Molecular weight (kg/kmol)	108.14	59.1	60.1	73.13
Density at 20 °C (kg/m^3)	1270	688	898	710
Boiling point (°C)	257.1	33.05	117.9	55.6
Melting point (°C)	100.8	-95.2	11	-50
Flash point (°C)		0.47	0.0154	0.319
Kinematic viscosity at 20 °C (mm^2/s)	270	194		
Weight fraction of Nitrogen (%wt.)	26	24	47	19
Net (lower) calorific value				
MJ/kg[a]	33.8	37.1	29.2	38.4
MJ/L (at 20 °C)	42.9	25.6	26.2	27.3
Heat of vaporization at 25 °C (kJ/mol)		480	732	428
Vapor pressure at 20 °C (Pa)	1.3	63500	1300	24200
Solubility in water (g/L)	39.3 (20°C)	soluble	soluble	soluble
Distribution ratio in octanol/water system (log P)	0.12 (25°C)	- 0.499	-2.04	0.58
GHS label codes[b]	6, 7, 8, 9	2, 7	2, 5, 7, 8	2, 5, 7

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Organic amines have been known to present certain antiknock properties since 1919. In 1924, Boyd described the relative effects of some nitrogen compounds upon detonation in engines (Table 46). The data presented in that published work show that in general the nitrogen compounds which are most effective for suppressing detonations are the primary and the secondary amines. Of these, the arylamines or those that contain at least one aryl group have a much larger influence for eliminating detonation from internal combustion engines [211].

Table 46. Influence of some groups attached to the atom on the antiknock effect of nitrogen [211].

Compound	Reciprocal of moles required to give antiknock effect equivalent to 1 mol of aniline[a]
Ammonia	0.09 (negative effect)
Ethylamine	0.20
Diethylamine	0.495
Triethylamine	0.14
Diethylaniline	0.24
Ethyldiphenylamine	0.58
Triphenylamine	0.09
Diphenylamine	1.5
Phenylamine (aniline)	1.0

[a] Based on concentrations of aniline of 3 %vol. in kerosene as fuel.

From these data, the best performances were achieved by diethylamine and diphenylamine, both secondary amines, and by ethyldiphenylamine, a tertiary amine. The superior effect of the phenyl radical for influencing the antiknock action of nitrogen explained the highest values for those compounds. Two compounds with intermediate performance were primary amines, ethylamine and aniline, and the other tertiary amine, phenyldiethylamine (diethylaniline). The greater effect of the aryl than the alkyl radicals for influencing the antiknock value of nitrogen is illustrated in the relative values for ethylamine and aniline, the latter of which is much more effective than the former.

US Patent 2,653,862 reported an invention based on the use of monoisopropylamine (MIPA) as an octane improver in lean and rich mixtures of gasoline for supercharged aviation spark ignition internal combustion engine [212]. A fuel of superior antiknock rating over a broad range of fuel, air, and compression ratios consisted essentially of 80-99 % gasoline, 1-20% monoisopropylamine, and from 0 to 7 mL of tetraethyllead (TEL) per gallon of fuel. The physical and chemical properties of automotive fuels upon which ASTM D357 tests were run are presented in Table 47.

Table 47. Physical and chemical properties of automotive fuels used along with the ASTM D357 tests results [212].

Fuel	**Base**	**MIPA percent**	**MON, mL TEL/gal**				**RON, mL TEL/gal**				**MON, 2.9 mL TEL/gal**	**RON, 2.9 mL TEL/gal**
			0	1	2	3	0	1	2	3		
A	100	0	58.8	67.1	71.0	73.8	62.6	70.9	75.6	78.4		
A	95	5	63.6				68.0				77.1	82.5
A	90	10	67.8				74.2				80.0	86.4

The addition of 5% MIPA to unleaded gasoline provided a substantial increase in both MON and RON. An additional improvement was obtained upon the addition of 10% MIPA to the unleaded gasoline. Considerable higher MON and RON ratings were obtained upon the addition of 2.9 mL per gallon to the fuels containing the MIPA than were obtained with the base fuel containing 3 mL TEL per gallon.

US Patent 3,197,292 reported that amine salts of selenious acid, having the formula $H_2SeO_3 \cdot (RNR'R'')_x$ improve the octane rating of motor fuels [213]. R is a C_{3-12} hydrocarbyl radical; R' and R'' are either a C_{3-12} hydrocarbyl radical, an alkoxy hydrocarbyl radical, or a C_{3-12} amino hydrocarbyl radical; and x is 1-2. The additives were prepared by mixing 1 mole H_2SeO_3 with 1 mole hydrocarbylamine, e.g. tert-$BuNH_2$, or Primene 81-R, a mixture of tertiary C_{11} to C_{14} primary aliphatic amines. The addition of 0.33 %vol. of such an additive to regular-grade gasoline and premium-grade gasoline increased their corresponding RON by 2.1 and 2.4, respectively.

In the case of acetylenic amine compounds, n-methylpropargylamine, n-benzyl-propargylamine, n-phenylpropargylamine, dipropargylamine, and n,n'-diethyl-2-butyne-1,4-diamine were used. Table 48 shows the efficacy of the ash-less antiknock compounds added.

Table 48. Octane enhancement posed by acetylenic amine compounds blended in FT-175 gasoline [192].

Compound	**Concentration (wt. %)**	**RON increase**
N-methylpropargylamine	1.0	0.7
N-benzyl-propargylamine	2.0	0.6
N-phenylpropargylamine	1.8	1.2
dipropargylamine	1.3	0.3
N,N'-diethyl-2-butyne-1,4-diamine	1.9	0.5

US Patent 5,468,264 claims to have used a non-metallic anti-knock fuel additive based on polyaryl amines [214]. A gasoline fuel composition comprising a major portion of gasoline and a minor portion of one or more polyaryl amines (particularly, between about 0.5 and about 2.0 %wt.), effectively increased the octane number of the fuel.

The preferred mixture of polyaryl amines which can be employed as the anti-knock agent in that patent is commercially available under the name Naugalube-680™, available from Uniroyal, Inc. of Naugatuck, Connecticut. A six-component reference gasoline blend (isopentane 30 %wt., n-heptane 10 %wt., i-octane 5 %wt., n-dodecane 7 %wt., toluene 25 %wt., and, i-butylbenzene 10 %wt.) was used to test the additive (2.0 %wt.). Table 49 lists reported results regarding RON and MON repeatability for samples of the base fuel and the base fuel plus the additive, using ASTM D2700 and ASTM D2699 for RON and MON, respectively.

Table 49. Gasoline final RON and MON with the addition of 2.0 wt.% of polyaryl amine [214].

Sample	**Experimental Base Fuel RON**	**Experimental Base Fuel plus 2.0 %wt. polyaryl amine RON**
1	81.5 / 72.7	84.0 / 75.4
2	81.8 / 73.1	83.0 / 75.0
3	81.5 / 73.3	82.7 / 75.5
4	81.5 / 73.5	83.0 / 75.3
5	81.5 / 73.3	83.3 / 75.3
Average	81.6 / 73.2	83.2 / 75.3

Thus, at a concentration of 2.0 %wt., the additive of the invention provides a significant average RON increase of 1.6 units and a significant average MON increase of 2.14 units. It provides this octane increase without recourse to metallic anti-knock additive agents.

US Patent 5,962,738 describes an improved method for the formation of a polymeric-amine fuel and lubricant additive with an increased nitrogen content [215]. Generally, polyamines are produced by reacting a polyolefinic halide with a substantial stoichiometric excess of amine to reduce, though not totally eliminate, the formation of dimers and trimers. It is known that oil-soluble polyamines containing at least one olefinic polymer chain or oil-soluble polyether can be employed to improve the detergent properties of fuel and lubricant compositions. The use of such compositions, their utility in providing a fuel with significantly reduced Octane Requirement Increase (ORI) characteristics—removal and/or beneficial modification of deposits in the combustion chamber, intake valves, and the like—, as well as potential improvement in fuel efficiency is already described by several prior US patents, such as 3,275,554, 3,565,804, 3,574,576, 3,898,056, 3,960,515, 4,022,589, and 4,039,300. Such polyamines have been used both alone and in combination with other additives, particularly polymeric additives. The polyamines used to form the polyamine compounds include primary, secondary, and tertiary low molecular weight aliphatic polyamines—ethylene diamine and tetraethylenepentamine being the preferred ones—and polymeric agents used as starting materials include polyolefins, polyoxyalkylenes, and polyethers. The invention also encompasses the fuel additive product produced by the foregoing process, and the novel motor fuel composition containing an amount of this additive of 0.5-5.0 ppm, expressed as basic nitrogen, which inhibits ORI and cleans up the induction system.

Japanese patent JP2002-110,093 describes an environmentally friendly gasoline composition for combustion engines with improved exhaust gas [216]. Claimed improvement regarding the exhaust gas is related to the suppression of engine chamber deposits with polyetheramines, which would act as a detergent. The fuel described in the patent would contain ≤1.5 %wt. of aromatic hydrocarbon and 100-300 ppm polyisobutene amine. Claimed content of actual gum would be ≤1 mg/100 mL and 11-20 mg/100 mL after and before washing, respectively, and the fuel is expected to have RON ≥ 98, sulfur content ≤ 10 ppm, Reid vapor pressure ≤ 65 kPa, and 70 % distribution temperature ≤ 128^{o}C.

Skobelev and coworkers made a phenomenological approach to the antiknock effect of amines [217]. For enhancing octane number and improving ecological characteristics of internal combustion engines nitrogen-containing compounds of amine class were applied. Although these additives are inferior to the additives based on iron and manganese (e.g., dicyclopentadienyl iron and methylcyclopentadienyl manganese tricarbonyl), are superior to oxygen-containing additives (e.g., low alkanes, MTBE alone, or mixed with *tert*-butanol). The influence of primary and secondary amines on the estimated octane numbers of a fuel with an octane number 86-90 was considered. All data on additives were recalculated and assigned to a 2 %vol. concentration and normalized per mole (See Table 50).

Table 50. Estimated octane number gain with the addition of primary and secondary amines [217].

	Additive	**ΔON (2 %vol. additive)**	**BON**[a,b]
Primary amines	aniline	4.6	321.5
	toluidines (mixed)	5.1	346.5
	p-toluidine		
	m-toluidine		
	o-toluidine	5.1	346.5
	1,3-diaminopropane	2.8	231.5
	m-xylidine	3.6	271.5
	p-xylidine	3.4	261.5
	ethylenediamine	1.6	171.5
	1,4-diaminobutane	2.0	191.5
	t-butylamine	2.4	211.5
	o-xylidine	1.04	143.5
	methylamine		
	ethylamine		
	n-butylamine		
	isopropylamine		
	benzylamine	0.56	119.5
	isobutylamine		
	cyclohexylamine		
	t-octylamine	0.33	108
	2-ethylhexylamine		
Secondary amines	*N*-methylaniline	6.2	401.5
	N-methyl-*p*-toluidine		
	N-methyl-*o*-toluidine		
	Pyrrolidine		
	N,*N*,-dimethylamine		
	N,*N*,-disopropylamine		
	N,*N*,-dipropyllamine		
	N,*N*,-diethylamine		
	t-butylfurfurylamine	3.2	251.5
	piperidine	1.26	154.5
	N,*N*,-dimethyl-*t*-butylamine	1.26	154.5
	N-ethylbenzylamine	0.74	128.5
	dibenzylamine	1.0	141.5
	diisobutylamine	1.2	151.5

[a] Calculated according to Eq. 1–1. [b] Base fuel with ON = 91.5.

An increase in octane number for fuels with various amines as additives was attempted to correlate with the molecular weight of amine, with the value proportional to the rate of heat motion of molecules and with the value proportional to the relative rate of molecular motion of trapping molecule (amine) and rate of motion of active radicals (hydroperoxides with molecular weight 40). Those correlations showed that the most active amines are those with the highest negative charge on the nitrogen atom, or, respectively, the highest positive charge on the amine proton.

Despite N-methylaniline (NMA) has been known as an effective knock suppressant since the 1920s, recent research shows a renewed interest in this compound for its knock suppressant effectivity, e.g., [124,218,219].

Chinese patent CN 105296027 describes a preparation method of an octane value enhancer for gasoline [220]. The enhancer composition was as follows: 50–55 %wt. of an active component, 1.5–4 %wt. antioxidant (4,6- dinitro-2-*sec*-butyl-phenol and/or *n,n'*-disalicylidene-1,3-diaminopropane), 1–3 %wt. dispersant (polyisobutylene amine and/or polyisobutylene-bis-succinimide), 4–7 %wt. co-stabilizer (any two of tetra-methyl piperidine, di- methyl malonate, di-ethyl malonate, and methyl 2-ethylhexanoate or a mixture of any two and xylene), 5–10 %wt. cosolvent (ethyl acetate, butyl propionate, etc.), and 30-35 %wt. solvent (mixed aromatic hydrocarbons, mixed xylenes, etc.). The active component was dissolved in the solvent, then a catalyst was added, and reaction at 120–130 ºC during 2–3 h took place. Then, after separation of the catalyst and cooling, antioxidant, dispersant, and co-stabilizer were added while stirring. The active component is selected from one of the following aromatic ester compounds: phenethyl 2-ethylhexanoate, cresyl 2-ethylhexanoate, di-phenil oxalate, phenylmethyl oxalate, bis(2,6-di-*tert*-butyl-4-methylphenyl)phthalate, bis(*p*-ethylphenyl)phthalate, bis(*o*-methylphenyl) 4-methylphthalate, bis(*p*-ethylphenyl) 3,5-dimethylphthalate, bis(2,6-di-*tert*-butyl-4-methylphenyl) 5-methylphthalate, and bis(2,6-di-*tert*-butyl-4-methylphenyl) 3, 5- dimethylphthalate; or the active component is dibutyl carbonate or diamyl carbonate. This improver of a gasoline octane number is claimed to be environmentally friendly and to have good compatibility with gasoline.

In another Chinese patent, CN 107523366-A, a gasoline additive is disclosed which has the advantages of improving the octane value, saving energy, and being environmentally friendly [221]. The gasoline additive includes the following raw materials (in weight parts): 0.2-0.25 parts methylcyclopentadienyl manganese tricarbonyl, 10–60 parts *tert*-butyl methyl ether, 5–40 parts anhydrous ethanol, 5–30 parts anhydrous methanol, 5–15 parts monomethyl aniline, 5–15 parts xylene, 5–40 parts naphtha, and 5–20 parts polyether amine.

In the Chinese patent, CN 108251167, a highly-efficient antiknock compound for gasoline is reported which includes the following components (in weight parts): 0.15–1.5 parts of lithium metal compounds, 40–70 parts of ester compounds, 10–45 parts of amines compounds, and 0.5–2 parts of phenolic compounds. This mixture shows many advantages, such as a high octane value, low vapor pressure, high heat of combustion, and good oil solubility, which makes gasoline combustion more complete and reduces noxious gas emission [222].

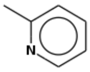
Finally, according to the website of the Canadian company Ole Bardahl, the use of a knockout octane booster as a fuel additive for gasoline engines based on Poly Ether Amine (PEA) is highly recommended [223]. They claim that this product increases octane number up to 7 units, in all 2 and 4-cycle gasoline engines. It also reduces dramatically knocking and pinging and ensures more complete combustion. In addition, PEA cleans power and intake valves, improves throttle response, cools the combustion chamber for better ignition, and maximizes engine performance.

Aromatic amines have been signaled to show toxicity and bad smell [27]. From the environmental point of view, it should be highlighted that all nitrogen-containing compounds increase nitrogen oxide emissions in the exhaust gases, due to nitrogen partial oxidation during combustion [32].

3.4. Pyridines

Pyridine is a basic heterocyclic organic compound with the chemical formula C_5H_5N. It is structurally related to benzene, with one methine group (=CH−) replaced by a nitrogen atom (Table 51). In organic reactions, pyridine behaves both as a tertiary amine, undergoing protonation, alkylation, acylation, and N-oxidation at the nitrogen atom, and as an aromatic compound, undergoing nucleophilic substitutions. Pyridine derivatives are part of the basic nitrogen compounds in crude oils [224,225].

Table 51. 2-Methylpyridine general properties.

	2-methylpyridine
CAS Reg. No.	109-06-8
Empirical formula	C_6H_7N
Chemical structure	
Molecular weight (kg/kmol)	93.1
Density at 20 ºC (kg/m^3)	944
Boiling point (ºC)	129
Melting point (ºC)	-67
Self-ignition point (ºC)	538
Kinematic viscosity at 20 ºC (mm^2/s)	1.20
Weight fraction of Nitrogen (%wt.)	15.0
Net (lower) calorific value	
MJ/kg	35.5[a]
MJ/L (at 20 ºC)	33.5
Heat of vaporization at 25 ºC (kJ/kg)	701
Vapor pressure at 25 ºC (Pa)	1483
Solubility in water (g/L)	miscible
Distribution ratio in octanol/water system (log P)	1.11
GHS label codes[b]	2, 7

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

With respect to pyridine derivatives anti-knock ability, some publications deal with the use of methylpyridines, also known as picolines, (mono-, di-, tri-, tetra-, and pentamethylpyridine) as RON enhancers [226]. Schulze and Mahan recommended the use of mixtures of methyl-substituted pyridines together with tetraethyl lead (TEL). They also recommended using mixtures of isopentane-pyridines due to the relatively high boiling points of pyridine derivatives. The quantity of methyl-substituted pyridines in their work varies from 1 to 20 %vol. of the blend, with a narrower range of between 1 to 10 %vol. preferred.

Hydroxypyridines (2-, 3- and 4-hydroxypyridine), which are solid at ambient temperature, are also quoted as octane boosters [227]. Their main handicap is their relatively poor solubility in gasoline which entails a need for a solubility promoter. Good solubility promoters are alcohols corresponding to the formula ROH in which R is an aliphatic or cycloaliphatic hydrocarbyl radical having 1 to 24 carbon atoms. The hydroxypyridine is employed in amounts ranging from 0.01 to 5 %vol. However, the presence of TEL seems to be necessary to observe improvements in fuel antiknock behavior.

3-Hydroxypyridines derivatives can also be employed as RON enhancers [191]. Specific examples of these derivatives are 2-(dimethylaminomethyl)-3-hydroxypyridine, 2-(diethylaminomethyl)-3-hydroxypyridine, 2-(pyrolidinomethyl)-3-hydroxypyridine, 2-(piperidinomethyl)-3-hydroxypyridine, and 2-(morpholinomethy)-3-hydroxypyridine. These compounds have limited solubility but suitable volatility characteristics to permit their application as additives for hydrocarbon fuels. Tested amounts of 3-hydroxypyridines range from about 0.5 to 10 %wt. of the total fuel composition. In all mentioned cases, other conventional fuel additives can be added to the formulated fuels.

With regards to alkylpyridines, some examples are presented to show the performance improvement of some alkylpyridines (or picolines) in aviation fuels. A 100-octane number aviation fuel was prepared according to blending formula A (see Table 52) [226]. The alkylate used was a cut from the product of a commercial hydrogen fluoride alkylation unit in which isobutene had been alkylated with butylenes to produce a mixture comprising largely isooctanes. The formula A was modified with the additives shown in Table 52 and 4.6 mL TEL per gallon was added to reach a 100-octane number.

Table 52. Performance improvement of some alkylpyridines in aviation fuels [226].

Formula	Alkylate	Isoheptane	Isohexane	Isopentane	Additive 10%vol.
A	21.3	41.0	22.6	15.1	None
B	21.3	41.0	22.6	15.1	Benzene
C	21.3	41.0	22.6	15.1	2-picoline
D	21.3	41.0	22.6	15.1	3-picoline
E	21.3	41.0	22.6	15.1	4-picoline

Blends in Table 52 were rated with Army-Navy test method AN-VV-F-746 (used for lean mixtures) and also according to the supercharged engine method AN-VV-F-748a, in both cases with 4.6 mL TEL per gallon (Table 53).

Table 53. Results of Army-Navy test method AN-VV-F-746 [226].

Formula	Antiknock Rating			Calculated Rich Mixture Blending Index of Additive[a]
	AN-VV-F-746	AN-VV-F-748a		
		Rating mL TEL	Index No.	
A	100	0.54	115.2	–
B	100	1.01	125.2	215.0
C	100	1.17	128.4	247.2
D	100	1.12	127.4	237.2
E	100	1.14	127.8	241.2

[a] The rich mixture blending index is adopted to reconcile the non-linearity of the concentration-performance relationship of the two methods used to rate octane numbers when this value is above or under 100. Rich mixture blending index numbers are so assigned and tabulated that they may be used directly with the volumetric percentage of the constituents to give the performance rating of the blend. Thus, a fuel with very poor performance, which is equivalent to a blend of 83.0 percent fuel S in fuel M has a blending index of 4. Pure isooctane has a blending index number of 100, while a superior fuel whose performance is equal to that of isooctane with 6.0 mL of TEL has a blending index number of 162.

Results in Table 52 indicate that picolines provided a significant improvement, compared to both fuel A alone and fuel B, which contained benzene. The effect of monomethylpyridine additives is very slight in the conventional (F-746) rating, which is also a measure of the lean mixture performance. The three picolines, when rated in blends with reference fuel A without the addition of lead by the ordinary engine test (AN-VV-F-746) gave blending octane numbers of 93.0, 89.0, and 91.0 for 2,3 and 4-picoline, respectively. Ratings in motor fuel base blends by the usual motor fuel test method (ASTM-D357-43T) gave octane numbers of only about 72 to 83 [226].

For the case of hydroxypyridines, a reference has been found reporting tests performed on premium gasoline with a RON of 101 and containing 3 cm^3 of tetraethyl lead mix per gallon [227]. The base fuel consisted of 35.5 percent aromatics, 9.5 percent olefins, and 55 percent aliphatic hydrocarbons as determined by FIA analysis and had an initial boiling point of 34 ºC and an endpoint of 188 ºC. Different formulations were tested adding 0.5 %vol. of alternatively 2- and 3-hydroxypyridine and different alcohols (typically 2 %vol.). As shown in Table 54, RON increased in all cases.

Table 54. Increased RON for the addition of 2-hydroxypyridine or 3-hydroxypyridine [227].

Hydroxypyridine (%vol.)	Alcohol (%vol.)	ΔRON[a]
2-Hydroxypyridine (0.5)	methanol (2.0)	+1.0
	isopropyl alcohol (2.0)	+0.5
	tert-butyl alcohol (2.0)	+0.8
	n-amyl alcohol (2.0)	+0.7
	iso-amyl alcohol (2.0)	+0.3
	n-hexyl alcohol (2.0)	+0.5
	cyclohexanol (2.0)	+0.5
	2,2-dimethyl-1-hexanol (0.5)	+0.5
	oleyl alcohol (2.0)	+0.2
3-Hydroxypyridine (0.5)	methanol (5.0)	+0.5

[a] The ΔRON is the difference between the octane number of the fuel containing hydroxypyridine and alcohol and that of the fuel containing only the alcohol.

The effect of 2-hydrodypyridine was compared to both leaded and unleaded gasolines. RON increased on increasing the amount of alkylpyridine in the leaded gasoline, while no significant effect was observed for the unleaded gasoline (Table 55).

Table 55. Effect of 2-hydrodypyridine was compared both in leaded and unleaded gasolines [227].

2-Hydroxypyridine (%vol.)	Methanol (%vol.)	Δ RON with 3 cm^3 TEL	Δ RON unleaded gasoline
0.10	1.0	+0.1	-0.2
0.20	1.0	+0.3	-0.2
0.30	1.0	+0.4	-0.0
0.40	1.0	+0.5	-0.0
0.50	1.0	+0.7	-0.0
0.60	1.0	+0.7	-0.0
0.70	1.0	+0.7	-0.0

The effect of the concentration of 2-hydroxypyridine on RON was tested using methanol as solubility promoter at a concentration of 2 %vol. The maximum increase in RON was achieved when 0.5 %vol. of 2-hydroxypyridine was added (Table 56).

Table 56. Effect of 2-hydroxypyridine on RON using methanol as solubility promoter [227].

2-hydroxypyridine (%vol.)	Δ RON
0.1	+0.1
0.3	+0.3
0.4	+0.5
0.5	+1.0
0.6	+0.6
0.7	+0.4
0.8	+0.3
0.9	+0.2
1.0	+0.3

On the other hand, the amines 2-(dimethylaminomethyl)-3-hydroxypyridine (tagged as compound I), 2-(diethylaminomethyl)-3-hydroxypyridine (compound II), 2-(pyrolidinomethyl)-3-hydroxypyridine (compound III), 2-(piperidinomethyl)-3-hydroxypyridine (compound IV), and 2-(morpholinomethy)-3-hydroxypyridine (compound V) were dissolved in gasoline [191]. A concentration of 0.1 molar was sought. Only compounds I and III were completely soluble with gasolines. Other compounds formed saturated solutions, and the actual concentration dissolved in gasoline was not determined. RON tests according to ASTM D 2599-47 were carried out on test gasoline with the following composition: 69.03 %vol. paraffins, 15.01 %vol. olefins, 6.63 %vol. naphtenes, 9.33 %vol. aromatics. Base gasoline had RON of 91.5, MON of 83.9, lead content 0.005 g/gal, and sulfur content 0.04 %wt. Test results showed the significant RON increases listed in Table 57.

Table 57. Gasoline tests [191].

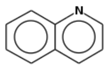
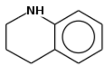
Compounds	Conc. (%wt.)	RON increase
I	2.1	2.3
II	Saturated <2.4	1.0
III	2.4	1.0
IV	Saturated <2.6	0.8
V	Saturated <2.6	0.3

As indicated previously, pyridine derivatives present high boiling points, hydroxypyridines are solid at ambient temperatures and present low solubility in gasoline, and 3-hydroxypyridines derivatives have limited solubility but suitable volatility characteristics to permit their application as additives for hydrocarbon fuels.

3.5. Quinolines

Quinoline (or 1-aza-naphthalene or benzo[*b*]pyridine) is a nitrogen-containing heterocyclic aromatic organic compound. Its structure is basically that of naphthalene except for the replacement of one carbon atom with nitrogen. Quinoline is a weak tertiary base; it can form a salt with acids and displays reactions similar to those of pyridine and benzene (see Table 58 for some general properties of quinolines). Together with indoles and pyridine derivatives, quinolines are part of the basic nitrogen compounds in crude oils [224,225].

Table 58. General properties of quinoline.

	quinoline	1,2,3,4-tetrahydroquinoline
CAS Reg. No.	91-22-5	635-46-1
Empirical formula	C_9H_7N	$C_9H_{11}N$
Chemical structure		
Molecular weight (kg/kmol)	129.2	133.2
Density at 20 ºC (kg/m^3)	1090	1020
Boiling point (ºC)	238	251
Melting point (ºC)	-17	20
Self-ignition point (ºC)	480	
Kinematic viscosity at 20 ºC (mm^2/s)	2.75	4.91
Weight fraction of Nitrogen (%wt.)	10.8	10.5
Net (lower) calorific value		
MJ/kg[a]	35.6	37.3
MJ/L (at 20 ºC)	38.7	38.0
Heat of vaporization at 25 ºC (kJ/kg)	434	506

Vapor pressure at 25 ºC (Pa)	8	
Solubility in water (g/L)	6.11	< 1
Distribution ratio in octanol/water system (log P)	2.10	2.29
GHS label codes[b]	7, 8, 9	7, 8

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

One publication was found concerning the use of quinolines as antiknock agents, US Patent 2,881,061 [228]. The authors found that if the n-alkyl group is made to form a ring attached to the benzene ring ortho to the amine function, the resulting substance is an anti-knock agent. Such a compound, for example, is tetrahydroquinoline, which its antiknock effectiveness is equal to n-methyl aniline. Furthermore, replacement of the nuclear hydrogens of the aromatic ring with lower alkyl or alkoxy groups in positions meta (position 5 or 7) or para (6) to the amine function does not lower the anti-knock effectiveness of the compound. However, the substitution in position ortho (8) or in the non-aromatic ring, as well as the length of the alkyl group, does decrease its performance. In the cited patent, the authors give 12 examples of tetrahydroquinoline derivatives compounds that could be considered, but for only 7 compounds they show data of their knock suppression ability: tetrahydroquinoline, 2,2,4-trimethyltetrahydroquiniline, 2,4-dimethyltetra-hydroquinoline, 2-methyltetrahydroquinoline, 8-methyltetrahydroquinoline, 6-methyl-tetrahydroquinoline, 6-metoxytetrahydroquinoline.

RON was determined for some mixtures of an ASTM primary reference fuel (60/40 isooctane/n-heptane; named Base fuel in Table 59), and 3 %wt. of some tetra-hydroquinoline derivative. Furthermore, results were also compared when adding 3 cm^3 of tetraethyl lead (TEL) per gallon of fuel.

Table 59. Obtained RON values for tetrahydroquinoline derivatives [228].

Compound	**Dose**		**RON**		**BRON[a] (%wt.)**		**BRON[a] (%mol)**	
	(%wt.)	**(%mol)**	**clear**	**with TEL**	**clear**	**with TEL**	**clear**	**with TEL**
Base fuel	–	–	60	84.3				
n-methylaniline	3	3.3	78	93.4	660	388	605	360
tetrahydroquinoline	3	2.7	77.3	94.4	637	421	701	458
2,2,4-trimethyl tetrahydroquinoline	3	2	64.6	86.3	213	151	290	184
2,4-dimethyl tetrahydroquinoline	3	2.3	70.7	88.3	417	218	525	258
2-methyl tetrahydroquinoline	3	2.5	72.2	90.5	467	291	548	332
8-methyl tetrahydroquinoline	3	2.5	74.6		547		644	
6-methyl tetrahydroquinoline	3	2.5	77.5	93.1	643	378	760	436
6-methoxy tetrahydroquinoline	3	2.2	78	92.5	660	358	878	457

[a] Calculated according to Eq. 1–1.

As can be observed in Table 59, all tetrahydroquinoline derivatives are octane improvers for both the leaded and unleaded-based fuels. Tetrahydroquinoline, 6-methyltetrahydroquinoline, and 6-methoxytetrahydroquinoline present similar RON improvement as n-methylamine on a weight basis. If the molar basis is considered, tetrahydroquinoline was 10% better, while 6-methyltetrahydroquinoline and 6-methoxytetrahydroquinoline were 30% better than n-methylamine [228].

In the same publication [228], the performance of tetrahydroquinoline was checked on two types of base fuels, namely, Fuel A—a blend of 70 % of catalytically-cracked gasoline and 30 % of thermally-reformed gasoline, having an initial boiling point of 40 ºC, a 50 % point of 108 ºC, and a 90 % point of 177 ºC—and Fuel B—100% catalytically-reformed gasoline (44 % paraffin, 3 % olefin, and naphthalene, and 53 % aromatics), having an initial boiling point of 43 ºC, a 50 % point of 121 ºC and a 90 % point of 160 ºC— (Table 60).

Table 60. Performance of tetrahydroquinoline on two types of base fuels [228].

Fuel blend	**RON (BRON[a])**	
	clear	**with 3 cm^3 TEL/gal**
Base Fuel A	83.3	93.2
Fuel A + 1.5% tetrahydroquinoline	87.6 (370)	95.9 (273)
Base Fuel B	89	97.7
Fuel B + 3% tetrahydroquinoline	95.2 (296)	iso + 0.13[b]

[a] Calculated according to Eq. 1–1. [b] Indicates fuel of same values as isooctane plus 0.13 mLTEL.

Authors conclude that the anti-knock action of quinolines derivatives is independent of other anti-knock agents of either the metallic or non-metallic type, and they may be used with other additives used to improve other properties of the fuel. In general, they propose an amount of additive ranging 0.1–10 %wt., depending on the fuel.

Quinolines adversely affect the stability of gasoline and there is research showing that nitrogen compounds are among the main factors promoting gum formation [229,230]. Actually, quinolines have been signaled as gum formation promoters in both jet fuels and diesel [231,232].

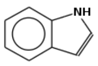
From an environmental standpoint, quinoline is not persistent in surface waters and it is biodegradable in soil when conditions favor microorganism's growth. However, there is evidence suggesting that quinoline is less biodegradable by microorganisms present in deep soil and groundwater, due to low oxygen levels, low temperatures, and few carbon sources. Quinoline is considered a persistent chemical when released to the atmosphere (in wintertime, it has an atmospheric half-life exceeding 99 hours) but it has a low potential to bioaccumulate [233].

Quinoline itself has few applications, but many of its derivatives are used as dyes, pesticides, and pharmacological drugs [234], e.g. the quinolones antibiotics. There is very scarce open literature concerning the use of quinoline derivatives as fuel additives, e.g., as anti-knock agents [228] or as oxidation inhibitors for gasolines or lubricants [235–238].

3.6. Indoles

Indoles are characterized by having a bicyclic structure in which a benzene ring is fused to a five-membered pyrrole ring. Its simplest compound, indole, presents the formula C_8H_7N (general properties are listed in Table 61). Indole is produced naturally by several bacteria and can be found in coal tar.

Table 61. General properties of indole.

	Indole
CAS Reg. No.	120-72-9
Empirical formula	C_8H_7N
Chemical structure	
Molecular weight (kg/kmol)	117.1
Density at 20 ºC (kg/m^3)	1220
Boiling point (ºC)	254
Melting point (ºC)	52
Self-ignition point (ºC)	
Kinematic viscosity at 20 ºC (mm^2/s)	
Weight fraction of Nitrogen (%wt.)	12.0

Net (lower) calorific value	
MJ/kg[a]	36.2
MJ/L (at 20 ºC)	44.2
Heat of vaporization at 25 ºC (kJ/kg)	
Vapor pressure at 25 ºC (Pa)	1.63
Solubility in water (g/L)	3.56
Distribution ratio in octanol/water system (log P)	2.14
GHS label codes[b]	6, 7

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Concerning the antiknock activity of this family of compounds, only one publication was found, US Patent 2,881,061, that recommends the use of indoles as knock suppressing additives [228] but, unfortunately, no data is provided in this regard. The following indoles are mentioned in that patent: 2-methyldihydroindole, 3-ethyldihydroindole, 5-methoxydihydroindole, 6-methyldihydroindole, 3-ethyldihydroindole, 5-propyldihydroindole, 5-butyl-dihydroindole, 5-butoxydihydroindole, and 2-methyl-6-butyldihydroindole.

On the other hand, US Patent 2,844,520 identifies indoles as part of the non-basic organic nitrogen compounds present in the feedstock of catalytic cracking operations [239]. According to this patent, non-basic nitrogen compounds do not need to be removed before cracking because they do not pose any detrimental effect on yields and product distribution in hydrocarbon cracking operations. On the contrary, the author proposes adding controlled amounts of pyrroles, indoles, and carbazoles to crude oil before starting the cracking process because the obtained gasoline thereof would present enhanced antiknock ability (Table 62).

Table 62. RON of catalytic-cracking gasoline with indole.

	RON after catalytic cracking		
	–	with 2.7 %wt. indole	with 5.2 %wt. indole
Crude oil distillate (b.p. range: 260–566 ºC)	93.5	94.8	95.1
Crude oil distillate (b.p. range: 260–566 ºC) + 3 mL TEL	98.3	99.6	99.7

Another patent has been found that, among other aromatic amines, indoles are proposed as antiknock additives, included in a lubricating composition which the authors claim that can be used to advance the spark timing and therefore tune ignition in spark-ignited engines [240]. Some references can be found indicating the use of indoles in the preparation of metal salts to be used as additives for gasoline engines, e.g., US Patent 3,321,485 [241].

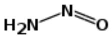
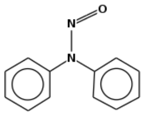
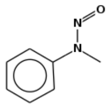
No records have been found on the effects of indoles in gasoline composition. In the case of diesel fuels, indoles and n-alkyl indoles are important constituents of deposits from ambient temperature storage [242].

Indoles' main uses are in the fields of dyes, synthetic flavors, and pharmaceutics (many alkaloids are derived from indoles). There are several mature routes of production of indol depending on raw material: *o*-nitrotoluene (reaction with formaldehye, N,N-dimethyl formamide, dimethyl acetal, or dimethyl oxalate), aniline (reaction with chloroacetonitrile), or phenyl hydrazine (with acetaldehyde). Plants and microorganisms can produce indole by tryptophanase or its analogs in the presence of indole-3-glycerol phosphate and tryptophan, thus indole is present in plants and bacteria-rich niches, such as soil, rhizosphere, sludge, and intestinal tracts [243].

3.7. N-nitrosamines

N-nitrosamines are chemical compounds with the chemical structure $R_1N(–R_2)–N=O$. General characteristics are shown in Table 63.

Table 63. General properties of n-nitrosamines.

	nitrosamine	n-nitroso-diphenylamine	n-nitroso-n-methylaniline
CAS Reg. No.	35576-91-1	86-30-6	614-00-6
Empirical formula	H_2N_2O	$C_{12}H_{10}N_2O$	$C_7H_8N_2O$
Chemical structure			
Molecular weight (kg/kmol)	46.0	198.2	136.15
Density at 20 °C (kg/m³)	1500	1230	1124
Boiling point (°C)	211	101	225
Melting point (°C)	-76	65.5	14.7
Self-ignition point (°C)			
Kinematic viscosity at 20 °C (mm²/s)			
Weight fraction of Oxygen (%wt.)	34.8	8.0	11.8
Weight fraction of Nitrogen (%wt.)	60.9	14.0	20.6
Net (lower) calorific value			
MJ/kg[a]	8.8	31.8	29.2
MJ/L (at 20 °C)	13.2	39.1	32.8
Heat of vaporization at 25 °C (kJ/kg)	768	293	328
Vapor pressure at 25 °C (Pa)			
Solubility in water (g/L)		0.0351	insoluble
Distribution ratio in octanol/water system (log P)	-0.37	3.13	1.804
GHS label codes[b]	None found	7, 8, 9	6, 7, 8

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

In Brown et al. 1955, N-nitrosodiphenylamine is tagged as a highly effective antiknock additive, and n-nitroso-n-methylaniline is slightly as effective compared to n-methylaniline [178]. The authors consider that the nitroso group in n-nitrosodiphenylamine could act as a hydrogen atom, neutralizing a free radical, and the remaining amine portion of the molecule as a non-propagating free radical.

Few other references have been found regarding the antiknock effect of n-nitrosamines [7,179]. US Patent 2012/0279112-A1 (and, subsequently, 8,894,727-B2) proposes using n-nitrosodiphenylamine as an octane enhancer additive for several unleaded base gasoline compositions, with RON ranging from 95 to 102.4 to reach levels as high as 104.7 for a small addition of the additive, as listed in Table 64 [31,184].

Table 64. Additive (n-nitrosodiphenylamine) response in terms of RON.

Amount (%wt.)	RON			BRON[a]		
	base gasoline 1	base gasoline 2	base gasoline 3	base gasoline 1	base gasoline 2	base gasoline 3
0	95.9	102.4	95			
0.175	96.9			667		

0.185		103.4			643	
0.25			97			895
0.35	97.5			553		
0.375		103.7			449	
0.5625		104.0			387	
0.75		104.4			369	
1.125		104.7			307	

[a] Calculated according to Eq. 1–1.

N-nitrosodiphenylamine has been reported not to cause any damage to the anti-emission devices of recent internal combustion engines [179]. Nitrosamines have also been proposed as lubricants for fuel compositions to reduce the combustion chamber deposits [244] and as oxidation inhibitors [245].

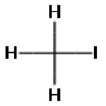
N-nitrosamines can be formed through the reaction of several nitrosating agents with primary, secondary, and tertiary amines, as well as from amides, in the gas phase. Synthesis can be accomplished in both acid and basic media and in organic solvents [246]. However, the nitrosation of secondary amines with sodium nitrite in the presence of acids is the most widely used method for the preparation of n-nitrosamines [247].

More recently, alternative synthesis methods have been reported, such as the iodide-catalyzed process to obtain n-nitrosamines from amines and nitromethane using *tert*-butylhydroperoxide (TBHP) as the oxidant, which is operated under mild conditions and counts with operational simplicity. Commercially available and inexpensive catalysts and oxidants are used in this method [248].

3.8. Iodine compounds

Elemental iodine was the first antiknock discovered by Midgley and Boyd [249] but it was soon discarded because it was found to be too expensive to use as an antiknock additive on a wide scale [250]. Table 65 shows the general properties of these compounds.

Table 65. General properties of iodine and some of its derivatives.

	iodine	methyl iodide	ethyl iodide	cyanogen iodide
CAS Reg. No.	7553-56-2	74-88-4	75-03-6	506-78-5
Empirical formula	I_2	CH_3I	C_2H_5I	CIN
Chemical structure				
Molecular weight (kg/kmol)	253.8	141.939	155.97	152.9
Density at 20 ºC (kg/m^3)	4933	2280	1936	2840
Boiling point (ºC)	184.4	42.55	72.35	sublimation at T > 45 ºC
Melting point (ºC)	113.7	-66.45	-111.1	146.7
Self-ignition point (ºC)		355		
Viscosity (cP)	2.27 (116ºC)	0.606 (0ºC)		
Heat of vaporization at 25 ºC (kJ/kg)	135	192		262
Vapor pressure at 25 ºC (Pa)	40	54000	18132	133.3
Solubility in water (g/L)	0.3	14	4	35.6
Distribution ratio in octanol/water system (log P)	2.49	1.51	2	1.52
GHS label codes[a]	7, 9	6, 7, 8	2, 7, 8	6, 7

Sources: [67–69]. [a] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Iodine, methyl iodide, ethyl iodide, and cyanogen iodide have been quoted as effective antiknock additives but, unfortunately, no quantitative data has been found in such regard [249,251–253]. As a qualitative reference, 1.6 %vol. ethyl iodide was needed to appreciate knocking suppression whereas only 0.04 %vol. TEL was required [249]. Also, as shown in Table 66, the relative effectiveness of ethyl iodide is slightly superior to that of aniline.

Table 66. Relative effectiveness of antiknock compounds and some antiknock fuels (based on aniline = 1.00) [254].

Benzene	0.085
Isooctane (2,2,4-trimethylpentane)	0.085
Triphenylamine	0.090
Ethanol	0.101
Xylene	0.142
Dimethyl aniline	0.210
Diethylamine	0.495
Aniline	**1.00**
Ethyl iodide	**1.09**
Toluidine	1.22
Cadmium dimethyl	1.24
m-Xylidine	1.40
Triphenylarsine	1.60
Titanium tetrachloride	3.20
Tin tetraethyl	4.00
Stannic chloride	4.10
Diethyl selenide	6.90
Bismuth triethyl	23.8
Diethyl telluride	26.6
Nickel carbonyl	35
Iron carbonyl	50
Lead tetraethyl	118
MMT	2000

Iodine and its derivative have been signaled to be corrosive for some car engine constituents [254]. On the other hand, iodine derivatives can be useful in inhibiting smog formation due to car exhaust emissions [255].

Iodine is obtained from brine containing iodide ions in Oklahoma and in Japan, and from nitrate ores in Chile. In China, almost all iodine is produced as a byproduct of seaweed processing.

When it is obtained from brines, iodine is purified and acidified with sulfuric acid. It is then chlorinated to liberate the iodine. Three methods are employed to purify iodine: blowing out, carbon adsorption, and ion-exchange.

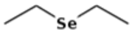
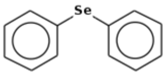
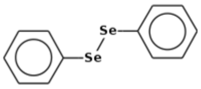
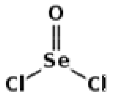
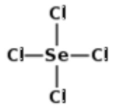
In Chile, iodine occurs as iodate ions in nitrate deposits. The ore typically contains 95% sodium nitrate and 5% sodium iodate. After removing the sodium nitrate by crystallization, iodate solutions are extracted from the caliche ore and the iodate is then reduced to iodine.

Methyl iodide is prepared by reaction of methanol with phosphorous and iodine; from potassium iodide and methyl sulfate or methyl p-toluenesulfonate; by reaction of dimethyl sulfate with an aqueous iodine slurry containing a reducing agent such as iron or sodium bisulfite; by reaction of methanol and hydrogen iodide; and by reaction of methanol, iodine, and diborane [256]. Methyl iodide can also be obtained from seawater [257–261] and from biomass with engineered microorganisms [262]. Ethyl iodide is prepared by reactions similar to those used for methyl iodide production.

3.9. Selenium compounds

Selenium is a member of group 16 of the periodic table; it belongs to the chalcogen family. Since it is placed between the nonmetal sulfur and the metalloid tellurium, it has mainly nonmetallic properties as shown in Table 67.

Table 67. General properties of selenium and selenium compounds.

	diethyl selenide	diphenyl selenide	diphenyl diselenide	selenium oxychloride	selenium tetrachloride
CAS Reg. No.	627-53-2	1132-39-4	1666-13-3	7791-23-3	10026-03-6
Empirical formula	$C_4H_{10}Se$	$C_{12}H_{10}Se$	$C_{12}H_{10}Se_2$	Cl_2OSe	Cl_4Se
Chemical structure					
Molecular weight (kg/kmol)	137.08	233.17	312.13	165.87	220.77
Density at 20 °C (kg/m³)	1232	1338	1557	2420	2600
Boiling point (°C)	106	116	202	180	288
Crystallization point (°C)	-70.1	2.5	58–61	8.5	200–210
Heat of vaporization (kJ/kg)	284	269		320	
Vapor pressure (Pa)	25731	1.17	0.97	132	
Solubility in water (g/L)		insoluble	insoluble	decomposes in water	decomposes in water
Distribution ratio in octanol/water system (log P)	1.567	1.342	4.36		0.47
GHS label codes[a]	2, 6, 8, 9	6, 8, 9	6, 8, 9	5, 6, 8, 9	6, 8, 9

Sources: [67–69]. [a] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Numerous references can be found quoting selenium compounds as being effective antiknock agents [263–265]. In particular, diethyl selenide and selenium oxychloride appear to be very effective anti-knockers but also are of interest dipropyl selenide, diphenyl selenide, and selenium tetrachloride [266]. Likewise, selenium cyanide is mentioned as a potential antiknock additive [253]. Phosphorus sesquiselenide, PSe_3, [267], and trialkyl lead selenides [268,269] are effective at improving the antiknock character of lead compounds.

Diethyl selenide antiknock action is similar to that of TEL; it reduces the concentration of free radicals and, as a result, combustion reaction rates are slowed down. In this regard, selenium seems to act as an antioxidant or free-radical trap [270].

US Patent 1,575,436-A ensures that diethyl selenide, dipropyl selenide, diphenyl selenide, selenium oxychloride, and selenium tetrachloride can be successfully employed as antiknock additives [266]. In the more recent US Patent 3,240,577, several RON values are provided concerning the effect of diisobutyl selenide addition to gasoline, as shown in Table 68 [271].

Table 68. RON values for unleaded and leaded fuels after addition of different amounts of diisobutyl selenide [271].

		Unleaded fuel[b]					**Leaded fuel**[b] **(3 cm^3/gallon TEL)**		
	diisobutyl selenide (%vol.)	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
RON	0.00	100.0	97.5	52.0	91.2	94.7	94.0	99.4	106.0
	0.50	103.2	99.2	53.6	94.0	99.4	95.4		
	0.75						96.4	100.5	108.3
	1.00	105.4	101.7	58.0	96.4	100.7	97.4	101.3	109.6
	1.50						99.5	104.3	110.5
	2.00	107.4	106.0	66.0		102.6		105.4	111.1
	2.50							106.4	
BRON[a]	0.50	740.0	437.5	372.0	651.2	1034.7	374.0		
	0.75						414.0	246.1	412.7
	1.00	640.0	517.5	652.0	611.2	694.7	434.0	289.4	466.0
	1.50						460.7	426.1	406.0
	2.00	470.0	522.5	752.0		489.7		399.4	361.0
	2.50							379.4	

[a] Calculated according to Eq. 1–1. [b] Tested fuels: I. pure isooctane; II. alkylate fuel, boiling range: 52-187 ºC; III. heavy straight run naphtha; IV. platformate fuel, boiling range: 54-201 ºC; V. motor fuel, boiling range: 36-190 ºC; VI. regular grade gasoline, boiling range: 40-214 ºC; VII. premium grade gasoline, boiling range: 33-188 ºC; VIII. super premium grade gasoline, boiling range: 31-188 ºC.

US Patent 1,906,724 indicates that diselenide compounds are suitable for use as anti-knock agents. Rosenstein & Hund 1933 claim to have used satisfactorily selenocyanates ($N{\equiv}C{-}Se^-$), diethyl diselenide, and diphenyl diselenide, among others. To quantify the antiknock effect of diselenide compounds, a comparison is provided using benzol as the reference compound. Benzol consists primarily of benzene, toluene, and xylene, as well as some sulfur (depending on the source, it can be assumed that benzol has a RON of approximately 110). As shown in Table 69, diphenyl diselenide is up to 5 times more effective than diphenyl selenide.

Table 69. Comparison of the antiknock effect of mono- and di-selenide compounds (adapted from Rosenstein and Hund 1933).

	benzol equivalent (%)	
Additive amount (g/L)	diphenyl diselenide	diphenyl selenide
5.0	31	10
2.5	16	6
1.2	8	2
0.6	5	1

The relative effectiveness of selenium compounds regarding their antiknock action can also be checked by observation of Table 66 in the previous section, where diethyl selenide was found to be 6.9 times more effective than aniline [254]. Also, as shown in Table 70, another reference has been found that provides a relative measure of the antiknock effectiveness of diethyl selenide, using benzol as a reference [273].

Table 70. Relative effectiveness of antiknock compounds [273].

Benzol	**1**
Toluene	1.1

Xylene	1.2
Ethanol	1.8
Aniline	11.5
Toluidine	11.9
Xylidine	12.0
Ethyl iodide	13.9
Tetraethyl tin	20.4
Diethyl selenide	**62.5**
Diethyl telluride	250
Iron carbonyl	250
Nickel carbonyl	277
Tetraethyl lead	528

US Patent 2,151,432 states that residual deposits can be left by selenium compounds in the combustion chamber when the containing fuel is burned in the operation of the engine [274].

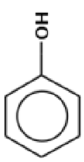
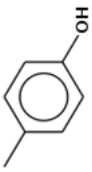
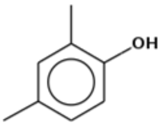
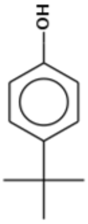
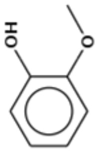
Selenium occurs in low concentrations (i.e., 1–5 g/t) in some types of coal and mineral oil. Selenium production is closely linked to copper production because most copper concentrates from ore flotation contain about 100–400 g/t selenium and are therefore the most important sources of selenium [270]. Selenium is commercially produced by either soda ash roasting or sulfuric acid roasting of the copper slimes [275]. Also, recycling of the selenium contained in photocopying drums and rectifiers is becoming an important source of selenium [270].

Organic selenium compounds are often synthesized from dialkyl selenides (R_2Se) or dialkyl diselenides (R_2Se_2), which are formed from the corresponding alkyl halide and sodium selenide. Sodium selenide is prepared through the reaction of selenous acid with the corresponding hydroxides or oxides, followed by crystallization, and is an important additive in glass manufacture [270].

3.10. Phenols

The term ‘phenol’ refers to both hydroxybenzene and any other molecule comprising at least one hydroxyl group attached to an aromatic ring. Table 71 shows the general properties of these compounds.

Table 71. General properties of some phenol derivatives.

	Phenol	*p*-Cresol	2,4-Xylenol	4-*tert*-Butyl-phenol	Guaiacol
CAS Reg. No.	108-95-2	106-44-5	105-67-9	98-54-4	90-05-1
Empirical formula	C_6H_5OH	C_7H_7OH	C_8H_9OH	$C_{10}H_{13}OH$	$C_7H_8O_2$
Chemical structure					
Molecular weight (kg/kmol)	94.1	108.1	122.2	150.2	124.1
Density at 20 ºC (kg/m^3)	1071	1034	965	908	1128.7
Boiling point (ºC)	181.9	201.9	210.9	233.9	205
Melting point (ºC)	40.9	33.9	24.9	98.9	28
Self-ignition point (ºC)	715	558	599	475	335

Flash point (ºC)	79 (closed cup); 85 (open cup)	86 (closed cup)	>112 (closed cup)	115 (open cup)	>66 (closed cup) - 82 (open cup)
Viscosity at 20 ºC (cP)	3.437 (50 ºC)	4.48 (50 ºC)	5.38[a]	8.11[a]	6.37[a]
Weight fraction of Oxygen (%)	17	15	13	11	26
Net (lower) calorific value					
MJ/kg[b]	31.7	33.3	34.5	36.2	28.0
MJ/L (at 20 ºC)	33.6	34.4	33.3	32.9	31.6
Heat of vaporization (kJ/kg)	625	431	535	452	504
Vapor pressure at 25 ºC (Pa)	46.66	15	13.6	30 (50 ºC)	13.7
Solubility in water at 25 ºC (g/L)	82.8	21.5	7.87	0.58	18.7
Distribution ratio in octanol/water system (log P)	1.46	1.94	2.3	3.31	1.32
GHS label codes[c]	5, 6, 8	5, 6	5, 6, 7, 9	5, 7, 8, 9	7

Sources: [67–69]. [a] Predicted value [69]. [b] Estimated using the Garvin formula [70]. [c] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

The antiknock ability of aromatic compounds was traditionally explained by the electronic properties of the ring. It has also been reported that phenols would present an antiknock mechanism similar to that of aromatic amines, being their ability to destroy chain-propagating radicals the reason for their knock suppressing effect [276]. As seen in Table 72, blend octane numbers of some phenol derivatives are between 140 and 190 [32].

Table 72. Blending RON and MON values for selected phenols [32].

Component	BRON	BMON
3,4-Dimethylphenol	180	180
Phenol	190	160
m-Cresol	160	150
o-Cresol	160	140

Phenol derivatives, particularly *p*-cresol, have been tagged as potential antiknock additives in several research papers and patents [277–279]. For instance, US patents 3,836,342 and 3,976,437 include gasoline compositions containing methyl-substituted phenols and ethers to obtain motor fuel of improved octane rating [277,280]. The methyl-substituted phenols mentioned in these patents include cresols (e.g., *p*-cresol, which is preferred over the *o*- and *m*- isomers), xylenols (e.g., 2,3-dimethyl phenol) and trimethyl-substituted phenols (e.g., hydroxy pseudocumene, hydroxy mesitylene, and hemimelitol), and they are to be blended in amounts ranging 0.5–10 %wt., preferably. They report synergistic effects in the antiknock ability of the fuel when *p*-cresol and methyl methoxy propane are blended into gasoline. In patent 3,836,342, data are given on some examples, for instance 5 %wt. *p*-cresol is added to a low-RON gasoline (base stock I in Table 73) and 5 %wt. methyl methoxy propane to a high-RON gasoline (base stock II), and the RON values of several mixtures of these two gasolines with and without the additives are presented.

Table 73. RON values of several mixtures of two gasolines with and without 5 %wt. *p*-cresol and methyl methoxy propane [277].

Mixture	Base composition (%vol.)		RON (Clear[a])	RON (Additivated[b])	BRON
	Base stock I	Base stock II			

A	100	-	83.7	89.05	191
B	-	100	96.25	97.8	127
C	85.7	14.3	85.3	90.5	189
D	71.4	28.6	87.0	91.7	171
E	57.1	42.9	88.85	93.0	172
F	42.9	57.1	90.35	94.6	175
G	28.6	71.4	92.0	95.6	164
H	14.3	85.7	93.6	96.9	160

[a] 'Clear' refers to RON of mixture without additives. [b] 'Additivated' refers to RON of mixture containing 5 %wt. *p*-cresol included in base stock I and 5 %wt. methyl methoxy propane included in base stock II.

Gouli and coworkers concluded that substituted phenols constituted a very effective class of compounds in terms of their knock suppressing ability [278]. According to their findings, increasing the number of carbon atoms in the substitute group of *para*-phenols leads to a decrease in their BRON value and their antiknock efficiency relative to that of MTBE, which they used as the reference compound (see Table 74). They also tested Mannich base phenols, which are substituted phenols that include one amino group, and found that these compounds show superior antiknock performance. Similar to substituted *para*-phenols, the antiknock effectiveness of Mannich base phenols is dependent on the size of the substitute groups containing the nitrogen atom—increasing the number of carbon atoms of those groups leads to lower BRON values (Table 74). Another reference to the antiknock effect of Mannich base phenols can be found in GB patent 2,308,849-A [281].

Table 74. RON and BRON values for the addition of several phenol derivatives on three base fuels, and relative effectiveness of their antiknock performance on a molar basis as compared to the reference compound MTBE [278].

Additive	Dose	Base fuel			BRON	Relative effectiveness
	(%w/v)	UN-1	UN-3	UN-4		
MTBE	2.0	92.1			117	1.0
	4.0			95.5	126	1.0
	7.0		95.4		128	1.0
2-(α-Dimethylamino)-methylene-4-methyl-phenol	2.0	93.8			202	8.3
2-(α-Diethylamino)-methylene-4-methyl-phenol	2.0	92.7			147	4.8
2-(α-Diisopropylamino)-methylene-4-methyl-phenol	1.0	91.5			82	-
2-(α-Dimethylamino)-methylene-4-*t*-butyl-phenol	1.0	92.4			172	7.5
2-(α-Diethylamino)-methylene-4-ethyl-phenol	2.0	92.8			152	5.7
6-(α-Diethylamino)-methylene-2,4-dimethyl-phenol	2.0	93.0			162	6.6
p-Cresol	2.5		95.4		176	2.9
	1.0			95.2	161	2.5
4-*tert*-Butyl-phenol	0.7		93.6		163	3.3
	1.4			95.6	141	2.5
4-Ethyl-phenol	1.3			95.5	159	2.8

In another study, the antiknock ability of different phenolic additives was arranged as follows: 2,4-xylenol > *p*-cresol = *o*-cresol > *m*-cresol > 2-ethylphenol > guaiacol [279]. Interestingly, engine-like simulations were performed to predict the anti-knock performance of phenols, which fairly agrees with the RON change promoted by the additives (Table 75).

Table 75. Experimental and computed RON values for different blends of phenol derivatives [279].

Compound	Experimental RON Dose (g/L)		Computed RON[a] Dose (%mol)		ΔRON relative error (%)
	0	20	0	2	
2,4-Xylenol	95.6	97.3	97	98.5	12
p-Cresol	95.6	97.2	97	97.8	50
o-Cresol	95.6	96.9	97	97.8	38
m-Cresol	95.7	96.6	97	97.3	67
2-Ethylphenol	95.7	96.2	97	97.5	0
Guaiacol	95.7	95.5	97	96.1	350

[a] RON simulations are referred to blending of additives with pure butane (experimental RON = 94).

On the other hand, US patents 3,976,437 and 4,133,648 mention the synergistic effects on octane enhancement of using cerium and phenols. In particular, US patent 4,133,648 discloses the use of an additive consisting of *p*-cresol (or an alkanediol) in combination with an organo-cerium (IV) chelate [282]. According to the authors, observed octane changes can be attributed to the synergistic effect of the added compounds (Table 76).

Table 76. ΔRON and ΔMON when blending *p*-cresol and organo-cerium chelates with regular unleaded gasolines [282].

Cerium[a] (g/gal)	Rare earth metals[b] (g/gal)	*p*-Cresol (g/gal)	ΔRON	ΔRON due to *p*-cresol	ΔRON due to synergistic effect	ΔMON	ΔMON due to *p*-cresol	ΔMON due to synergistic effect
1.0		11.6	0.9	0.3	0.6	0.4	0.1	0.3
1.0		23.2	0.9	0.7	0.2	0.7	0.3	0.4
1.0		30.9	1.1	1.0	0.1	0.7	0.4	0.3
1.0		46.3	0.7	1.4	-0.7	0.4	0.6	-0.2
	1.5	5.8	0.5	0.0	0.5	-0.1	0.0	-0.1
	1.5	11.6	0.2	0.1	0.1	0.0	0.1	-0.1
	1.5	23.2	0.3	0.4	-0.1	0.0	0.4	-0.4

[a] Added as ceric 2,2,6,6-tetramethyl-3,5-heptanedionate. [b] A mixture of rare earth metals containing 50% cerium, added as the 2,2,6,6-tetramethyl-3,5-heptanedionate chelate.

US patent 4,280,458 claims that the incorporation of *ortho*-azidophenol to unleaded gasoline stocks results in octane quality improvements of about 0.29 RON units per gram per gallon of gasoline [283]. As listed in Table 77, different amounts of *o*-azidophenol to both leaded and unleaded gasolines enhance RON. In Table 78, the effect on RON of several related compounds is shown.

Table 77. RON of leaded and unleaded gasolines with *o*-azidophenol [283].

Base gasoline	*o*-azidophenol (g/gal | %wt.)	RON
unleaded	0	91.2
	5.0 | 0.17	92.6
	15.1 | 0.52	94.6
leaded (2.4 g Pb/gal as lead alkyls)	0	92.9
	5.7 | 0.20	93.6
	11.4 | 0.40	94.0

Table 78. ΔRON after addition of azidophenols and similar compounds. Negative signs note proknock action [283].

Additive	Dose (g/gal)	ΔRON
o-azidoaniline	4	+0.29
p-azidoaniline	4	-0.10
o-azidophenol	4	+0.29
p-azidophenol	4	-0.51
o-azidoanisole	9	-0.10
o-azidobronobenzene	9	-0.40
o-azidobenzoic acid	2	0.0
trans-2-azidocyclohexanol	8	0.0
o-azidothiophenol	4	0.0

On the other hand, substituted dimethylaminomethyl phenols are the ash-less antiknock agents proposed in US patent 4,378,231, to be added in amounts of preferably 1–5 %wt. to unleaded gasolines [284]. When blended with an unleaded base gasoline (RON = 91.5, MON = 83.9, lead content = 0.005 g/gal), addition of 2.4 %wt. of 2-dimethyl-aminomethyl-4-methoxyphenol provides a RON gain (ΔRON) of 2.6, and 2.3 %wt. 2-dimethyl-aminomethyl-4-fluorophenol gives ΔRON = 2.7. This octane raise contrasts with the worse antiknock enhancement provided by other compounds, given for comparative purposes, such as *p*-hydroxyanisole (ΔRON = 0.4), anisole (ΔRON = 0.3), phenol (ΔRON = 0.7), n,n-dimethyl-benzylamine (ΔRON = –0.6), and *p*-fluoro-phenol (ΔRON = 0.9).

Several records can be found regarding the use of phenolic derivatives as antioxidants or as lubricants in internal combustion engines with both gasoline and diesel fuels (e.g., [267,285–292]).

Together with ester and ketone derivatives, phenolic compounds are stand out for their high BON values but, due to other inappropriate properties (such as high boiling points, high acidity, low material compatibility, and high toxicity), their usage in gasoline composition at high concentrations is not possible [27,32].

Phenol is commercially obtained by oxidation of cumene. The process is divided into four stages, namely oxidation, concentration, cleavage, and distillation. Oxidation is carried out under over-pressure at temperatures between 90 and 120 ºC or at atmospheric pressure below 100 ºC.

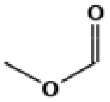
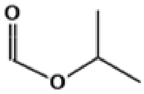
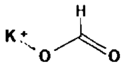
Provided that the world demand for phenol rises, alternative processes able to obtain coproduct-free phenol will become economically more viable, such as benzene oxidation or toluene oxidation with benzoic acid, developed by the California Research Corp. and Dow Chemical [293].

Alkylation of phenols is industrially achieved mainly by catalytic alkylation of phenol, cresols, or xylenols with olefins which are readily available petrochemicals [294]. On the other hand, four well-established synthetic routes exist for the industrial production of cresols: 1) alkali fusion of toluenesulfonates, 2) alkaline chlorotoluene hydrolysis, 3) splitting of cymene hydroperoxide, and 4) methylation of phenol in the vapor phase. Processes 1 to 3 were developed from the corresponding benzene–phenol syntheses and are mainly carried out in converted phenol plants, whereas process 4 was specifically developed to produce cresols and xylenols [295].

3.11. Formates

The term ‘formate’ (or methanoate) refers to the anion derived from formic acid ($CHOO^-$) and, by extension, it is used to describe any salt or ester of formic acid. Some general characteristics are shown in Table 79.

Table 79. General properties of formates.

	Methyl formate	Butyl formate	Isopropyl formate	Potassium formate
CAS Reg. No.	107-31-3	592-84-7	625-55-8	590-29-4
Empirical formula	$C_2H_4O_2$	$C_5H_{10}O_2$	$C_4H_8O_2$	$KHCO_2$
Chemical structure				
Molecular weight (kg/kmol)	60.1	102.1	88.1	84.1
Density at 20 °C (kg/m^3)	977	920	872.8	1560
Boiling point (°C)	31.9	106.6	68.3	
Melting point (°C)	-99.9	-90.0	-87.8	167
Self-ignition point (°C)	449	265	510	
Flash point (°C)	-2 (closed cup)	18 (closed cup)	-5.56 (closed cup)	
Viscosity at 20 °C (cP)	0.325			
Weight fraction of Oxygen (%wt.)	53	31	36	38
Net (lower) calorific value				
MJ/kg[a]	14.3	26.5	23.7	
MJ/L (at 20 °C)	14.0	24.3	20.7	
Heat of vaporization (kJ/kg)	483	393		
Vapor pressure at 25 °C (Pa)	78000	3850	18500	
Solubility in water at 25 °C (g/L)	230	7.56	20.7	soluble
Distribution ratio in octanol/water system (log P)	0.03	1.32	0.75[b]	
GHS label codes[c]	2, 7	2, 7	2, 7	7

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] Predicted value [69]. [c] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Scarce references have been found regarding the potential use of formate esters as antiknock additives, and available information relates, mostly, to relatively high concentrations (>2%). In US patent 5,232,464, RON and MON values are provided for several fuel compositions including methyl formate both as a sole additive and in combination with MTBE and methanol (see Table 80). As described in the patent, pure compound RON and MON values of methyl formate are 115 and 114.8, respectively, which are superior to the calculated blending values (also included in Table 80 as BRON and BMON, respectively) [296].

Table 80. RON and MON values for gasoline compositions with methyl formate and/or MTBE and methanol and calculated BRON and BMON values thereof [296].

Base gasoline	**Additive**			**RON**	**MON**	**BRON**[a]	**BMON**[a]
	Methyl formate (%vol.)	**MTBE (%vol.)**	**Methanol (%vol.)**				
Regular gasoline[b]	0	0	0	90.3	81.6		
	5	0	0	91.1	82.3	106.3	95.6
	10	0	0	91.8	83.0	105.3	95.6
	20	0	0	93.1	84.2	104.3	94.6

	30	0	0	94.2	85.1	103.3	93.3
	40	0	0	95.2	86.1	102.6	92.9
	50	0	0	96.1	87.0	101.9	92.4
	0	10	0	91.9	82.4		
	0	20	0	93.1	84.0		
	0	30	0	94.3	84.8		
	5	5	0	82.0	83.3		
	10	10	0	94.5	84.9		
	5	5	5	92.1	83.6		
	10	10	10	94.4	85.0		
Eurosuper gasoline[c]	0	0	0	96.0	84.5		
	5	0	0	96.6	85.1	108.0	96.5
	10	0	0	97.1	85.6	107.0	95.5
	20	0	0	98.1	86.9	106.5	96.5
	30	0	0	99.0	88.1	106.0	96.5
	40	0	0	99.9	89.0	105.8	95.8
	50	0	0	101.0	89.9	106.0	95.3
	0	10	0	97.0	85.9		
	0	20	0	98.2	86.2		
	0	30	0	99.1	87.7		
	5	5	0	98.0	86.2		
	10	10	0	98.7	86.7		
	5	5	5	98.0	86.6		
	10	10	10	99.3	87.9		

[a] Calculated according to Eq. 1–1. [b] Boiling fraction of 30 ºC to 180 ºC of a petroleum base stock with density 0.740 g/cm^3. [c] Boiling fraction of 30 ºC to 185 ºC of a petroleum base stock with density 0.745 g/cm^3.

US patents 2,228,662 and 2,334,006 both relate to the addition of esters to motor fuels consisting essentially of branched paraffin hydrocarbons, such esters being either acetates or formates to be added in 25–50 %vol. [297,298]. Values of MON and BMON of ethyl formate and isopropyl formate provided in these patents are listed in Table 81.

Table 81. MON and BMON values for the addition of ethyl or isopropyl formate to a motor fuel with MON = 90 [297,298].

Additive	Dose (%vol.)	MON	BMON	Base fuel
Ethyl formate	25	92.9	101.6	MON 90
Isopropyl formate	25	93.9	105.6	
	50	100.0	110.0	

On the other hand, US patent 3,009,793 indicates that tertiary alkyl esters are useful octane improvers, particularly for leaded gasolines. *tert*-Butyl formate is included among the tertiary alkyl esters cited in the patent but, unfortunately, no data is provided in this regard [299]. Likewise, methyl formate, ethyl formate, n-propyl formate, and n-butyl formate are included in US patent 6,076,487 as potential constituents of a secondary fuel stream aimed at increasing the octane number of a dual fuel system, whose primary stream would be constituted by acetylene [300].

Formates can be used as anti-icing agents. For instance, US patent 5,232,464 claims the addition of 2 %vol. methyl formate avoids turbidity due to low-temperature storage and sedimentation of the gasoline mixture at room temperature for several days [296].

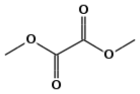
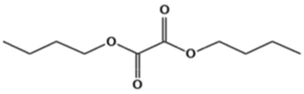
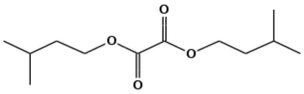
Carbonylation of alcohols at a pressure up to 700 bar in the absence of olefins gives formates. For instance, methyl formate is obtained by carbonylation of methanol at 70–80 ºC and 20–200 bar [301].

Also, in the absence of strong acids, like sulfuric or hydrofluoric acid, formic acid reacts readily with olefins to give formate esters [302], which gives raise to potential biological routes to obtain formate esters, since formic acid can be obtained by aqueous catalytic partial oxidation of wet biomass (OxFA process) [303].

3.12. Oxalates

Oxalate (IUPAC: ethanedioate) is the dianion with the formula $C_2O_4^{2-}$, also written $(COO)_2^{-2}$. Either name is often used for derivatives, such as salts of oxalic acid. General properties of some oxalates are provided in Table 82.

Table 82. Main physicochemical properties of oxalates used as octane/cetane number improvers.

	Dimethyl oxalate	Dibutyl oxalate	Diisopentyl oxalate
CAS Reg. No.	553-90-2	2050-60-4	2051-00-5
Empirical formula	$C_4H_6O_4$	$C_{10}H_{18}O_4$	$C_{12}H_{22}O_4$
Chemical structure			
Molecular weight (kg/kmol)	118.1	202.2	230.3
Density at 20 ºC (kg/m^3)	1148	986	982
Boiling point (ºC)	164.3	239.5	267.5
Melting point (ºC)	54.8	-29.0	-9.00
Flash point (ºC)	75	228	114.3
Weight fraction of Oxygen (%wt.)	54	32	28
Net (lower) calorific value			
MJ/kg[a]	13.0	26.1	28.3
MJ/L (at 20 ºC)	15.0	25.8	27.8
Heat of vaporization (kJ/mol)	463		254
Vapor pressure (Pa)	152	5.3	1.1
Solubility in water (g/L)	60 (25 ºC)		
Distribution ratio in octanol/water system (log P)	-0.170	2.957	2.165
GHS label codes[b]	5, 7	5, 7	None found

Sources: [67–69]. [a] Estimated using the Garvin formula [70]. [b] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Diisopentyl oxalate is mentioned as an octane number improver, which can be synthesized with oxalic acid and isopentyl alcohol as raw materials using titanium sulfate doped with lanthanum oxide as the catalyst [304].

Chinese patent CN 103254949 reported on an efficient gasoline octane number accelerant [305]. Its formulation comprises the following components: 10–18 %wt. active ingredient (benzyl iso-octoate or phenyl iso-octoate or dimethyl oxalate), 1-3 %wt. detergent, 0–3 %wt. antioxidant, 15–26 %wt. synergist, and 50–70 %wt. cosolvent. The gasoline octane number accelerant has easily accessible raw materials, good antiknocking performance, no heavy metals, strong dispersion, good miscibility with naphtha and nonhydrocarbons, large octane number amplification, and is environmentally friendly.

Chinese patent CN 107118814 disclosed the application of a novel oxygenated fuel or fuel additive of oxalate [306]. The invention also reported on a process for screening compounds or components for fuel oil or fuel additives. Among them, dimethyl oxalate, ethyl methyl oxalate, dibutyl oxalate, and isopropyl methyl oxalate were included. The invention also disclosed a preparation method of the oxalate compounds for fuel oil. The oxalate fuel oil has the advantages of environmental friendliness and good combustion property.

The use of oxalates as octane enhancers has attracted some attention because they present excellent blending capabilities, since they are miscible with gasoline in any proportion at a temperature above -10 ºC, and due to positive environmental effects, such as reduction of soot emissions and easy degradation in the natural environment in the event of fuel leakage [307]. As main drawbacks, since the traditional catalyst for their production was sulfuric acid, oxalates are often considered to be unavoidably corrosive and highly susceptible to water [181].

Dimethyl oxalate can be obtained by esterification of oxalic acid with methanol using sulfuric acid as a catalyst. There is also an oxidative carbonylation route that has attracted much interest since it requires only C1 precursors [308].

Alternatively, the oxidative carbonylation of methanol can be carried out with high yield and selectivity with 1,4-benzoquinone (BQ) as an oxidant in the system $Pd(OAc)_2/PPh_3$/benzoquinone with mass ratio 1/3/100 at 65 ºC and 70 atm CO [309].

Ube Industries has used a liquid phase Pd-catalyzed process for the manufacture of dibutyl oxalates since 1978 at a capacity of several thousand tons per year [310].

3.13. Other ash-less octane improvers

Several antiknock compounds are listed in Table 83 by ascending order of antiknock ability on a molar basis, being aniline the reference compound.

Table 83. Relative effect of the antiknock action of several compounds as compared to that of 2 %vol. aniline on a molar basis [194,254,311].

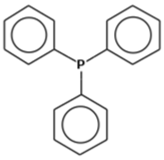
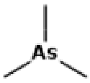
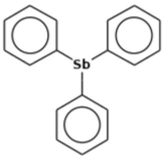
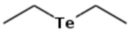
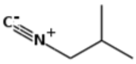
Compound	Relative antiknock effect (%mol)
Benzene^{a}	0.085
Isooctane (2,2,4-trimethylpentane)^{b}	0.085
Triphenylamine^{c}	0.090
Triphenylphosphine^{a}	0.91
Ethanol	0.101^{c}–0.104^{a}
Toluene^{a}	0.112
Xylene^{a}	0.142
Dimethyl aniline^{c}	0.210
Diethylamine^{c}	0.495
Aniline	1.00
Ethyl iodide^{a}	1.09
Toluidine^{c}	1.22
Cadmium dimethyl	1.24^{c}-1.25^{a}
Triphenylarsine	1.35^{a}-1.60^{c}
m-Xylidine^{c}	1.40
Triphenylstibine^{a}	2.42
Titanium tetrachloride^{a}	3.20
Tin tetraethyl	3.80^{a}–4.00^{c}
Stannic chloride^{c}	4.10
Diphenylselenide^{a}	5.2
Diethylselenide^{a}	6.9
Triphenylbismuthine^{a}	21.5
Diphenyl telluride^{a}	22.0

Bismuth triethyl[a]	23.8
Diethyl telluride[a]	26.6
Nickel carbonyl[a]	35.0
Iron carbonyl[b]	50.0
Lead tetraphenyl[a]	69.5
Lead diphenyl diethyl[a]	110
Lead tetraethyl[a]	118
MMT[c]	2000

[a] [194]; [b] [311]; [c] [254].

Among the compounds listed in Table 83, those of interest for the present section are the non-metallic organic compound triphenylphosphine, and the metalloid-containing compounds triphenylarsine, triphenylstibine, diphenyltelluride, and diethyltelluride. General properties for some of these compounds are listed in Table 84.

Table 84. General properties of some compounds.

	Triphenyl-phosphine	Trimethyl-arsine	Triphenyl-stibine	Diethyl-telluride	*p*-Fluoro-toluene	Isobutyl isocyanide
CAS Reg. No.	603-35-0	593-88-4	603-36-1	627-54-3	352-32-9	590-94-3
Empirical formula	$C_{18}H_{15}P$	C_3H_9As	$C_{18}H_{15}Sb$	$C_4H_{10}Te$	C_7H_7F	C_5H_9N
Chemical structure						
Molecular weight (kg/kmol)	262.3	120.0	353.1	185.7	110.1	83.1
Density at 20 ºC (kg/m^3)	1200	1124	1530		1001	
Boiling point (ºC)	368.5	53.8	377.0	113.0	115.9	105.0
Melting point (ºC)	79.7	-87.3	55.0	-42.9	-57.6	-82.5
Self-ignition point (ºC)	425					
Flash point (ºC)			109		11.9	
Heat of vaporization (kJ/kg)	347 (105 ºC)	231	236 (245 ºC)	224	358	
Vapor pressure at 25 ºC (Pa)	0.017 (50ºC)	35000		2800	2800	40500
Solubility in water at 25 ºC (g/L)	0.00009		insoluble	550	immiscible	3.1
Distribution ratio in octanol/water system (log P)	5.69			2.31	2.58	0.397
GHS label codes[a]	7, 8	2, 6, 7, 9	6, 7, 9	2, 6	2, 7	None found

Sources: [67–69]. [a] According to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

With regards to the use of phosphines as antiknock compounds, scarce references can be found except for that of Boyd 1927, where triphenylphosphine is found to be slightly less effective than aniline on a molar basis (Table 83), and US Patent 2,953,596, which states that secondary alkylphosphine oxides containing more than three carbon atoms in each alkyl radical, such as di-n-butyl phosphine oxide, di-n-octylphosphine oxide, and didodecylphosphine oxide are useful as antiknock agents in gasolines and as antifriction additives for lubricating oils [312].

In US Patent 1,575,438 several arsines, such as diethylarsine, triethylarsine, trimethylarsine, and triphenylarsine, are signaled to be effective as knock suppressors [313]. Also, in US Patent 2,151,432 and Charch et al. 1926, the authors indicate that organic compounds of arsenic, among others, present antiknock properties [251,274]. No literature references have been found providing quantitative data in this regard. Trimethylarsine ($(CH_3)_3As$) can be prepared by treatment of arsenic oxide with trimethylaluminum. Triphenyl arsine ($As(C_6H_5)_3$) is prepared by reaction of arsenic trichloride with chlorobenzene using sodium as the reducing agent. Trialkylarsines can also be prepared from arsenic trioxide through reaction with trialkylaluminums at 60 ^oC [314]. Dimethylarsine can also be synthesized by methanobacterium through reduction and methylation of arsenate under anaerobic conditions [315].

As for stibines, triphenylstibine ($C_{18}H_{15}Sb$), triisobutylstibine ($C_{12}H_{27}Sb$), tricyclopentadienylstibine ($C_{15}H_{15}Sb$), and trioctylstibine ($C_{24}H_{51}Sb$) are mentioned in at least one literature reference as useful antiknocking compounds for gasoline [314]. US Patent 2,151,432 and Charch et al. 1926 mention antimony compounds as being anti-knockers [251,274]. Trialkylstibines can be synthesized by the conversion of antimony trihalides with organometallic compounds in ether tetrahydrofuran or benzene. Triarylstibines are also formed by treating antimony trihalides with aryl halides and sodium or magnesium in benzene or ether [314].

On the other hand, many references can be found in the literature indicating the suitability of the metalloid tellurium as an effective knock suppressor (e.g., [249,251,274,316]). The use of 0.2 % diethyl telluride increases the octane rating of gasolines and is said to eliminate carbon deposits [317]. Midgley and Boyd stated that just one molecule of diethyl telluride in about 50,000 molecules of the total mixture was sufficient to exert a noticeable antiknock action [249]. The authors claim that 1 volume of diethyl telluride is equivalent in effect to 250 volumes of benzene (Table 85). In US patent 1,575,437, Midgley claimed to successfully have used diethyltelluride, dipropyltelluride, dimethyltelluride, and diphenyltelluride to suppress knocking [318].

Table 85. Relative effect of the antiknock action of several compounds as compared to benzene (adapted from Midgley and Boyd 1922 [249]).

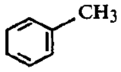
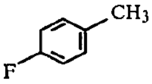
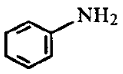
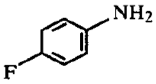
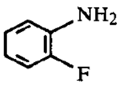
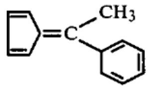
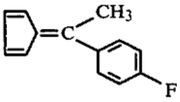
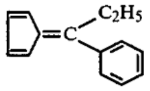
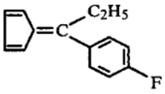
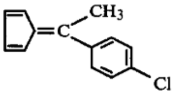
Element	Compound	Amount required to suppress knock in kerosene (%vol.)
	Benzene	25.00
Iodine	C_2H_5I	1.60
Nitrogen	Xylidine	2.00
Tin	$(C_2H_5)_4Sn$	1.20
Selenium	$(C_2H_5)_2Se$	0.40
Tellurium	$(C_2H_5)_2Te$	0.10
Lead	$(C_2H_5)_4Pb$	0.04

Three main routes exist to obtain symmetrical alkyl or aryl tellurides: *i*) direct reaction of nucleophilic telluride dianions (usually as Na_2Te) with alkylating or arylating reagents, *ii*) oxidation of tellurolate anions, and *iii*) reduction of the corresponding organyltellurium trichlorides [319]. Also, the production of dimethyl telluride by facultative anaerobe bacteria *Pseudomonas fluorescens* K27 has been quoted [320].

Halogen compounds, like ethylene dibromide ($C_2H_4Br_2$) and ethylene dichloride ($C_2H_4Cl_2$), have been extensively added as anti-knock agents in leaded gasoline [321]. According to Brown et al. 1955, *p*-fluoroaniline and n-methyl-*p*-fluoroaniline are very effective antiknock additives, while *m*-trifluoromethylaniline presents slight antiknock activity [178].

US patent 4,264,336 quotes *p*-fluorotoluene, *p*- and o-fluoroaniline and the halofulvenes 6-methyl-6-(*p*-fluorophenyl)fulvene, 6-ethyl-6-(*p*-fluorophenyl)-fulvene, and 6-methyl-6-(*p*-chlorophenyl)fulvene as antiknock additives for unleaded gasolines [322]. As seen in Table 86, when a fluorine atom is added to toluene or aniline RON decreases but when a fluorine atom is added to a substituted fulvene RON increases. The chlorine atom also increases RON. However, as seen in the table, none of these halogenated additives exerts a better antiknock effect than the reference compound aniline. Halogenated Fulvenes can be prepared from cyclopentadiene and the corresponding halogenated aceto- or propiophenone, as described in the same patent.

Table 86. Antiknock effect of halogenated additive compared to reference compounds. Additive dose was 0.1 M in 1 L base gasoline [322].

Additive[a]	**Chemical structure**	**ΔRON**
Toluene		0.2
p-Fluorotoluene		-0.6
Aniline		2.8
p-Fluoroaniline		2.5
o-Fluoroaniline		2.4
6-Methyl-6-phenyl-fulvene		0.5
6-Methyl-6-(*p*-fluoro-phenyl)fulvene		0.9
6-Ethyl-6-phenyl-fulvene		0.3
6-Ethyl-6-(*p*-fluoro-phenyl)fulvene		0.6
6-Methyl-6-(*p*-chloro-phenyl)fulvene		0.8

[a] 0.1 M of the additive in 1 L gasoline. Base gasolines were unleaded Kansas City premium pipeline gasoline from Phillips Petroleum; RON 91.5-92, MON 84.9-83.9.

The use of cyanides has been historically linked to metallic antiknockers (e.g., [323–326]), but US patent 1,948,449, which also deals with the antiknock action of organometallic-cyanides, quotes the nonmetallic isobutyl isocyanide (C_5H_9N) as an effective antiknock agent [253]. No quantitative data is provided in this regard.

In the case of C-nitroso compounds, US Patent 3,647,777 describes a method for producing nitrosoalkanes and nitroso aromatic compounds and states that such compounds are useful as antiknock agents [327].

4. Future scope and trends in the field

High-octane petrol for half of EU market could save more than 3 Mt/year of CO_2 emissions on a Well to Wheel basis. An effort to increase RON from 95 to 102 supports fuel consumption benefits in advanced engines of 4 %; this improvement can be higher when a transition from less advanced engines is considered [3]. Although higher octane is not the only solution to cut CO_2 from road transport, it is one of the most cost-effective and technology-neutral strategies available to reach climate and energy goals by 2030.

From the energy industry standpoint, the production of high-octane gasoline is regarded as an opportunity to contribute to CO_2 reduction goals. CONCAWE has investigated the feasibility of high-octane gasoline production and its cost for EU refining [4]. Considering current specifications of gasoline (EN-228), hydrocarbon, and oxygenates components, including ETBE and bioethanol, it is possible to supply high-octane products (RON 102) to 50 % of European demand, with a RON 95 price differential of 33 $/t. Nevertheless, if demand rose over 70 % of gasoline market, the production would be strongly constrained. Therefore, the energy industry needs alternative solutions.

In this regard, high efficiency octane boosters could solve the two critical barriers of the enhanced anti-knocking product, for they reduce significantly the cost and increase the volume capacity of supply. Octane enhancer research is not new but the systemic approach of this work adds very high value to the current state of the art and it is the cornerstone for any further research. Effectiveness is the most important factor but other considerations are the key to success: side effects, distribution compatibility, technology readiness and sustainability of use and, just as importantly, the health and environmental hazards.

Although the first octane boosters used on a large scale were metallic, their use is limited or forbidden due to their toxicity and impact on vehicle exhaust catalysts. Ash-less octane improvers are preferred to metallic ones. N-nitrosamines show high efficiency and bibliographic results are very favorable to them, including technology readiness. Phenols are also efficient additives but their handling is worse because of their limited distribution system compatibility. The conclusions of this work support deeper research on both families. With respect to the aniline family, this study demonstrates the very different properties depending on the specific molecule; therefore, some further research on this type of chemical products could pave the way to some molecules with acceptable side effects and toxicology.

High-octane components, which are efficient at concentrations higher than 2 %vol, are also very valuable. They do not have the advantages of cost and potential to high volume production of octane boosters; nevertheless, they could add value to fuels in some specific cases, associated with local low costs or renewable origin opportunities. Furthermore, they could be used as co-additives for ash-less octane improvers. The high solvent capacity of glycol ethers is a very valuable property for this purpose. The renewable production potential of some high-octane components such as aromatics, alcohols, and ethers is well known, and sustainability could be the deciding factor in some scenarios.

The recommended next steps in high octane research are to work, both “in silico” and experimentally, on the most promising octane boosters in combination with high octane components, in order to identify the best combination to help the industry obtaining high octane gasoline that is technically, economically, and environmentally viable.

5. Concluding remarks

A schematic qualitative comparison of the chemical compounds presented in Section 2 and Section 3 is presented familywise in Table 87 (for high-octane components) and Table 88 (for ash-less octane-enhancer additives). For the sake of simplicity, information on each chemical family accounting for the different metrics defined in Section 1.4 is presented on the basis of favorable, neutral, or unfavorable categorization. Thus, green, amber and red circles in the table represent favorable, neutral, and unfavorable categorization, respectively. Gray circles reflect a lack of information to categorize the substance for the established metric.

Table 87. Qualitative comparison of the chemical families in Section 2 (high-octane components).

High-octane component	Anti-knock effectiveness	Side effects	Distribution system compatibility	Technology readiness	Sustainability of use	Toxicology	
						Health hazards	Environmental hazards
Isoparaffins	🟡	🟢	🟢	🟢	🔴	🟡	🔴
Olefins	🟢	🔴	🟡	🟢	🔴	⚪	🔴
Aromatics	🟢	🔴	🟢	🟢	🔴	🟡	🔴
Alcohols	🟢	🟡	🔴	🟢	🟢	🟡	🟡
Ethers	🟢	🟢	🟢	🟢	🟡	🟢	🟡
Ketones	🟢	🔴	🟢	🟢	🟢	🟡	🟡
Esters	🟡	🟢	🟡	🟢	🟢	🟢	🟢
Furans	🟢	🔴	🟡	🟢	🟢	🟡	⚪
Carbonates	🟢	🟢	🟡	🟢	🟢	🟡	⚪

Green, amber, and red circles represent favorable, neutral, and unfavorable categorization, respectively. Gray circles reflect a lack of information to categorize the substance for the established metric.

As seen in Table 87, regarding the global outcome of the different considered metrics, it can be identified that most of the selected families present positive effects on the anti-knock behavior of gasoline, and that all of them are technologically available nowadays. Stronger differences among families can be appreciated regarding the rest of the defined metrics.

About the suitability of the compared chemical families, taking into account the defined metrics, ethers, ketones and esters are the considered families presenting a larger number of favorable categorizations (i.e., five out of seven). Among these, ethers seem to be the most favored compounds to be added to gasoline as high-octane components since no unfavorable categorizations have been identified for them. On the other hand, given that esters present a relatively more modest effect on the anti-knock behavior of gasolines, their suitability appears to be lower than that of ethers, provided that anti-knock effectiveness is regarded as the most important feature for high-octane components. Regarding ketones, reported negative side effects would make them less eligible compounds compared to ethers and esters, unless co-additives were designed to palliate such effects.

Table 88. Qualitative comparison of the chemical families in Section 3 (ash-less octane improvers).

Ash-less octane improver	Anti-knock effectiveness	Side effects	Distribution system compatibility	Technology readiness	Sustainability of use	Toxicology	
						Health hazards	Environmental hazards
Anilines	🟢	🔴	🟢	🟢	🟢	🟡	🔴
Hydrazines	🔴	🟢	🟡	🟢	🔴	🔴	🔴
Amines[a]	🔴	🔴	🔴	🟢	🟢	🟡	🔴
Pyridines	🟡	⚪	🔴	🟢	🟢	🟢	⚪
Quinolines	🟢	🔴	🟡	🟢	🟡	🟡	🟡
Indoles	⚪	⚪	🟡	🟢	🟢	🟡	🔴
N-nitrosamines	🟢	🟢	🟢	🟢	🟢	🟡	🟡
Iodine compounds	🟢	🟡	🟢	🟢	🟢	🟡	🔴
Selenium compounds	🟢	🔴	🟢	🟢	🟡	🟡	🔴
Phenols	🟢	🟢	🟡	🟢	🟢	🟡	🟡
Formates	🟡	🟢	🟡	🟢	🟢	🟡	⚪
Oxalates	⚪	🟡	🟢	🟢	🟢	🔴	⚪
Other ash-less octane improvers:							
Phosphines	⚪	⚪	🟡	🟢	🟢	🟡	⚪
Arsines	⚪	⚪	⚪	🟢	🟢	🟢	🔴
Stibines	⚪	⚪	🟡	🟢	🟢	🟢	🟡
Tellurides	🟢	🔴	🟡	🟢	⚪	⚪	⚪
Halogenated compounds (halogenated fulvenes)	🟡	⚪	🟢	🟢	🟢	🟡	🟡
Cyanides	⚪	⚪	🟡	⚪	⚪	⚪	⚪
C-nitroso compounds	⚪	⚪	⚪	⚪	⚪	⚪	⚪

Green, amber, and red circles represent favorable, neutral, and unfavorable categorization, respectively. Gray circles reflect a lack of information to categorize the substance for the established metric. [a] Anilines, nitrosamines, or any other type of chemical that is already included in a separate category is excluded from the category 'Amines'.

According to results depicted in Table 88, strong differences can be appreciated when comparing the available information on ash-less additives for the different metrics. As in the previous case, technological readiness does not appear to be an issue but environmental hazards can be, as a general rule, more severe for considered additives than for high-octane components (see Table 87). Regarding compounds eligibility as octane-enhancer additives, anilines, iodine compounds, N-nitrosamines, and phenols are the most favored ones, since they present between four and five favorable categorizations out of the seven defined metrics. Among these compounds, iodine compounds could be discarded due to their high cost. For some of the presented compounds within families of anilines, N-nitrosamines, and phenols, the promising results reproduced in this work should motivate further research.

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Acknowledgments

Present work is included in the Project “Desarrollo de gasolina para motores eficientes”, partially funded by Spanish CDTI (Centro de Desarrollo Tecnológico Industrial), identified as IDI-20180217.

Supporting Information

Information regarding toxicology associated to high-octane components and to ash-less octane enhancer additives are supplied as Supporting Information.

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