

ABSTRACT

This paper reviews the fundamental requirements of liquid hydrocarbon fuels for spark-ignition engines, namely that the fuel should vaporize satisfactorily and burn in a controlled manner. The phenomenon of knock and the development of the octane scale are discussed. The variation in pressure time histories between engines is discussed, along with how this leads to different fuel requirements. The difference in the octane rating tests, and how engine down-sizing exacerbates these differences in the pressure time histories is discussed. The applicability of RON and MON to modern engines is reviewed, along with the phenomenon of low speed preignition and mega-knock. The effect of hydrocarbon fuel distillation characteristics on drivability and emissions is reviewed, and placed in a historical context and the current legislative requirements. Brief mention is made of other fuel requirements such as density, gum content and aromatic content.

1. INTRODUCTION

The fundamental requirements of gasoline are that it should vaporize and form a flammable mixture with air, and then for it to burn in a controlled way.

The volatility is expressed in terms of key points on distillation curves, the final boiling point and the vapour pressure at a reference temperature. These aspects are discussed further in Section 3. The requirements for normal combustion are more complex to define as they are dependent on both the engine and its operating point.

In a Spark Ignition (SI) engine fuel and air are premixed (except in some stratified charge engines at some operating conditions), and energy release occurs in a flame front initiated by a spark. Initially the flame is laminar, but as it grows beyond the characteristic turbulence length scales the flame front becomes wrinkled by the turbulence, and by the time about 5 or 10 per cent of the fuel has been burnt, the flame is fully turbulent. Modern SI engines operate with a stoichiometric mixture so that a three-way catalyst can reduce tail-pipe emissions of unburned hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) to extremely low levels; (even engines that can operate with stratified charge will be operating at stoichiometric for part of their operating envelope). Spark Ignition engines also have to guard against an abnormal form of combustion known as “knock” caused by the autoignition of the unburned gas, termed “end-gas”, ahead of the expanding flame front. As combustion progresses the cylinder pressure increases, and the adiabatic core of the unburned gas will be compressed isentropically. If the temperature in the unburned gas is high enough for long enough then self-ignition or auto-ignition can occur. If spontaneous ignition of the unburnt gas occurs, there is a rapid pressure rise which leads to pressure waves which can cause structural vibrations and a “knocking” sound. As a result of the pressure increase and oscillations the rate of heat release is increased significantly, and the thermal boundary layer at the combustion chamber walls can be destroyed. This causes increased heat transfer and higher surface temperatures. This can lead to both component failure and for certain surfaces to cause pre-ignition. In summary, knock can substantially increase the rate of heat release and heat transfer, thereby causing engine damage.

The primary development trend for SI engines is to improve efficiency. Practical engines have to operate over a wide range of speeds and loads. In fact passenger cars operate at low load most of the time, but engine size is determined by the maximum power that the car might need. In order to reduce load, the amount of fuel energy introduced in the engine has to be reduced. Since SI engines have to work at a fixed air/fuel ratio, the amount of air also has to be reduced by partly closing the throttle, and throttling is a major source of inefficiency in passenger cars which use SI engines. One solution is to choose a smaller engine size to match the requirement of the car in most of its operating regime, i.e. low load, rather than for the maximum load requirement. A smaller engine can operate near full throttle, and hence near its best efficiency over more of the vehicle operating regime, but its maximum load, (and hence power at a given speed) will be reduced because of its smaller size. When the vehicle needs more power e.g. during acceleration, more air is forced into the smaller engine by supercharging or turbocharging and more fuel is injected. Figure 1 illustrates how a boosted 1.6 L engine can have the same maximum output (130 kW) as a naturally aspirated 2.5 L engine, with the road load operating points moved to a more efficient part of the engine map. It should also be noted that the boosted engine has a higher maximum torque occurring at a lower speed, and this will improve the torque back-up and drivability of the vehicle.

The level of downsizing indicated in Fig. 1 will require a boost pressure ratio of about 2:1, and so as to maximize the charge density and specific output of the engine, then the air will be cooled prior to entering the engine. This cooling will also minimize the compression ratio reduction that is needed to avoid knock. The cooling will also mean that the temperature will be lower, for a given pressure during compression, compared with a naturally aspirated engine, and this has implications for the 'octane appetite' of the engine (see section 5.1).

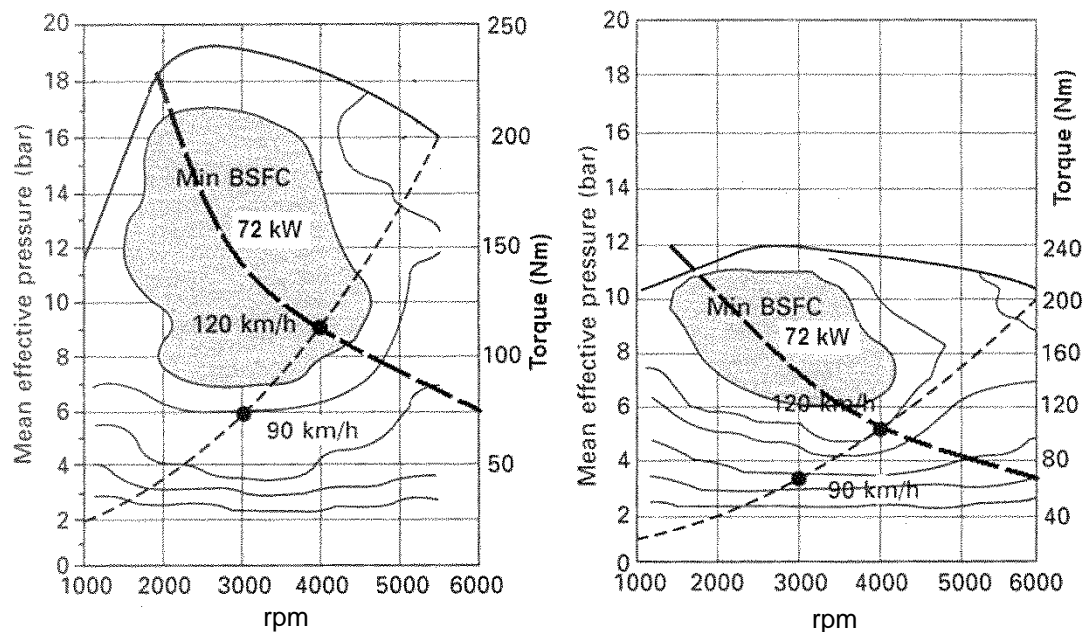


Fig. 1 Downsizing, in which a boosted 1.6 L engine can have the same maximum power output (130 kW) as a naturally aspirated 2.5 L engine, but with lower throttling losses and a higher mechanical efficiency, adapted from Zhao (1).

The lower weight of the engine also helps in improving vehicle efficiency. This approach, downsizing coupled with turbocharging, is being pursued by all engine manufacturers to improve the efficiency of SI engines. However this increases the maximum pressure and temperature in the engine and increases the probability of knock. It has also made other abnormal combustion problems like preignition and “superknock” [2, 3] more likely. Increasing the anti-knock quality of the fuel enables a higher efficiency to be reached in SI engines.

This paper focuses on the fuel requirements of spark ignition engines. The emphasis will be on liquid fuels since they are expected to be dominant. The next section reviews the effects of gasoline properties on engine performance and emissions. Section 2 discusses the anti-knock properties of gasoline and how this can be defined and measured, while Section 3 discusses the volatility of gasoline. Some additional fuel properties are mentioned in Section 4 and Section 5 is focussed on autoignition and anti-knock properties of gasolines and their effects on knock, preignition and “superknock” or mega-knock.

Fuel composition and fuel properties can affect SI engine performance and emissions [4, 5, 6] and in most countries fuel specifications ensure that these properties are within an acceptable range. In general, the engine has to start reliably when cold, warm-up rapidly, run smoothly and as efficiently as possible, deliver adequate power and generate low emissions. The fuel must enable all this to happen over long periods of use and must not have side effects that might harm the engine. For instance it must not lead to excessive wear, contaminate or corrode the fuel system, harm after-treatment systems or cause harmful deposits to be formed. Gasolines for SI engines are made by blending components from oil refineries and might contain other components such as ethanol, which might be mandated for use by regulations and produced from bio sources. Higher alcohols (such as propanol and butanol, that ideally would be bio-derived) might be added because they act as co-solvents with water to prevent phase separation when moisture is present. Methanol can also be added - sometimes in breach of legislation if its cost is lower than gasoline. The fuel will also most likely contain gasoline additives [7] which are usually at concentrations of well below 1% by volume. Gasoline will contain over 100 identifiable components and the major constituents of a typical gasoline (albeit with no alcohols) are shown in Table 1.

Table 1 Typical gasoline volumetric composition (%), with identification of some of the 100+ individual components

n-alkanes (C_nH_{2n+2})	9	n-Butane	4.3
		n-Pentane	1.9
		n-Hexane	1.5
		other n-alkanes	1.3
iso-alkanes (C_nH_{2n+2})	43	2-Methylpentane	14.3
		Isopentane	5.8
		3-Methylpentane	4.1

		Isooctane	3.5
		2-Methylhexane + 2,3-Dimethylpentane	3.5
		2,3-Dimethylbutane	3.3
		other iso-alkanes	8.5
aromatics	34	Xylene ($C_6H_5.2CH_3$)	10.2
		Toluene ($C_6H_5.CH_3$)	8.0
		1,2,4-Trimethylbenzene ($C_6H_5.3CH_3$)	2.6
		Ethylbenzene ($C_6H_5.C_2H_5$)	2.2
		m-Ethyltoluene ($C_6H_5.CH_3.C_2H_5$)	1.7
		other aromatics	9.3
alkenes	11	2-Methylbut-2-ene	1.9
(C_nH_{2n})		Pent-2-ene	1.5
		other alkenes	7.6
cyclo-alkanes	3		
(C_nH_{2n})			

The following sections will consider important gasoline properties that feature in fuel specifications because they have been shown to affect engine performance, efficiency and emissions. These are defined by the European Standards Organisation (CEN) in EN228 for gasoline in Europe [8] The two most important properties are the anti-knock rating (the octane number) which will be discussed in Section 2 and its volatility which will be discussed in Section 3.

2 GASOLINE ANTI-KNOCK PROPERTIES

2.1 Development of the Octane Scale

The first scientific study of gasoline combustion in an engine was by Hopkinson and Ricardo in the years around 1906 [9.10] when in-cylinder pressure measurements were made using an 'optical engine indicator' in which cylinder pressure rotated a small mirror. These tests showed that combustion was rapid but not instantaneous (as some people had assumed), and that turbulence could increase the rate of combustion. This work also established that 'knock' (or detonation as it was then known as) was associated with a much more rapid pressure rise, and that the onset of knock limited the power output and efficiency of engines.

It was also known that different fuels had a different propensity for knock, for example, Bert Skinner (co-founder of SU Carburettors) reported in 1912 that Benzole (a mixture principally of benzene and toluene that was a by-product of coke manufacture from coal) would "stand a more advanced ignition without engine knocking than is the case with petrol" [11]

This was also known to Ricardo and in 1917 it led to tests being conducted on behalf of the Asiatic Petroleum co. (now well known as Shell). The tests examined pure components found in gasoline as well as gasolines of different compositions, resulting in a very comprehensive report that was in due

course published as part of the 'Report of the Empire Motor Fuels Committee' in 1924 [12]. Ricardo and his colleagues conducted tests with a supercharged engine and a variable compression ratio engine. The quality of the fuel was expressed in terms of the highest useful compression ratio, defined as the compression ratio that led to the onset of knock with the ignition timing and air fuel ratio adjusted for maximum efficiency. Ricardo also introduced the toluene number, having found that 'the addition of 40% by weight of, say, toluene to hexane would raise the detonation point exactly four times as much as the addition of 10%'; the result was not linear if volume % was used. He also noted that there was not always a correlation between the anti-knock performance in the supercharged engine and the variable compression ratio engine, and this was attributed to the different in-cylinder pressure temperature histories – a result of significance that will be discussed further in Section 5.1.

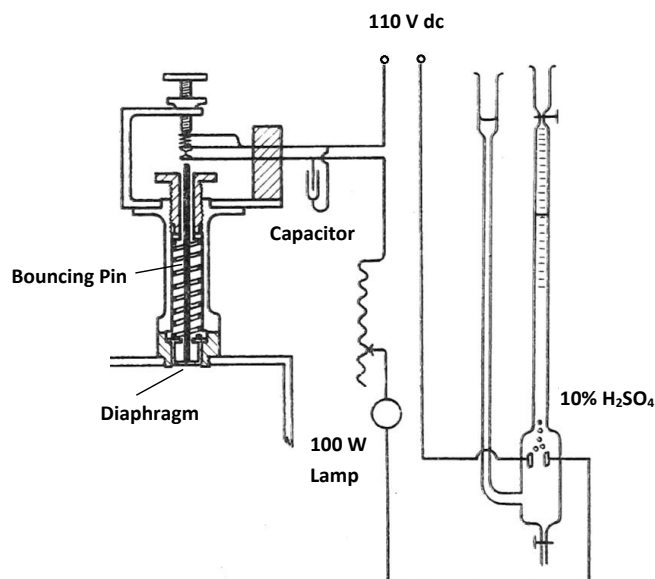


Fig. 2 The Midgley and Boyd bouncing pin apparatus for knock detection, adapted from [12].

To quantify knock, Midgley and Boyd [13] in the USA developed a bouncing pin apparatus, as illustrated in Fig. 2. The pressure oscillations made the diaphragm vibrate, and the bouncing pin would then cause closure of the electrical contacts. There are of course significant cycle-by-cycle variations in knock intensity, so timing the evolution of gas over a fixed time gave an averaged value of knock intensity. Subsequently a hot wire ammeter (in which the elongation is measured of a heated wire) was used to give a smoothed real-time indication of the knock intensity. Midgley had previously (during World War 1) developed an aviation gasoline with improved anti-knock properties that was 70 per cent cyclohexane and 30 per cent benzene [14] – it was ironic that the cyclohexane was manufactured from benzene, as the benzene has a higher anti-knock rating.

Edgar [15] recognized that combustion researchers were using different reference fuels for an anti-knock rating, and this limited the scope for data being shared. Edgar proposed the use of n-heptane and iso-octane, and described how each could be manufactured to a high level of purity. This led to the octane rating scale with n-heptane and iso-octane being used as reference fuels. As yet there was no

standardization of the test engine, but this changed with the introduction of the Cooperative Fuel Research (CFR) Committee engine.

Ricardo had designed and built a number of engines in which the compression ratio could be varied while the engine was running. He had also established a useful collaboration with Harry Horning, president of the Waukesha company – a well-established engine manufacturer. This led to Waukesha manufacturing the CFR engine [9]. The first commercial CFR engine was designed and built in forty-five days, beginning in December 1928, as a standardized single-cylinder variable compression ratio engine to be used for a gasoline knock-test method [16]. The basic system was unchanged for many decades, and the diaphragm and bouncing pin are still the basis of measuring the knock intensity with test procedures defined by ASME and adopted throughout the world.

2.2 The Measurement of the Research and Motor Octane Numbers, RON and MON

Thermal efficiency of SI engines is limited by knock [5, 17, 18], since for practical liquid fuels a higher compression ratio increases the engine efficiency but such an increase is limited by the onset of knock.

Knock is determined by the pressure and temperature history of the end-gas and the anti-knock or auto-ignition quality, which is traditionally measured by Research and Motor Octane Numbers, RON and MON, of the fuel used [5]. The tests are conducted in the single-cylinder CFR variable compression engine, as summarized in Table 2, in strict accordance with the procedures set in ASTM D2699 for RON and ASTM D2770 for MON [19].

The most significant differences are that the RON test is run at an engine speed of 600 rpm and an intake air temperature of 52° C while the MON test is run at 900 rpm and an intake air temperature of 38° C with a high specified mixture intake temperature of 149°C.

Table 2 CFR engine test conditions for the RON and MON tests

Test conditions	Research octane number ASTM D2699	Motor octane number ASTM D2770
Engine speed (rpm)	600	900
Coolant temperature (°C)	100 ±1.5	100 ±1.5
Intake air humidity (g of water per kg of dry air)	3.6 – 7.2	3.6 – 7.2
Intake air temperature	52 ±2.8	38 ±2.8
Mixture temperature (°C)	See ASTM Standards	149 ±1.1
Spark advance, (°btdc)	13	14–26 inversely dependent on the compression ratio

As already mentioned, the octane scale is based on two paraffins, n-heptane and iso-octane (more specifically the 2,2,4-trimethylpentane isomer). Blends of these two primary components are referred to as primary reference fuels (PRFs) and define the intermediate points in the RON or MON scale. The RON or MON is the volume percent of iso-octane in the PRF. Thus a blend of 95% of isooctane and 5% of n-heptane by volume is assigned the octane number of 95 in both the RON and MON scales. The compression ratio of the engine has to be adjusted to give a standard knock intensity, and this gives an

indication of the octane rating. Two mixtures of the primary reference fuels (with octane numbers either side of the test fuel) are prepared, and the knock intensity of the three fuels (the test fuel and the 2 PRFs) is measured, and if they are sufficiently similar, then linear interpolation is used to find the octane rating of the test fuel. The manufacture and marketing of transport fuels is profoundly influenced by the requirements to meet RON and MON specifications and hence RON and MON are amongst the most important properties of a practical gasoline.

The auto-ignition chemistry of practical gasolines, which are mixtures of aromatics, olefins, naphthenes and oxygenates as well as paraffins, is different from that of PRF. A typical gasoline has a higher RON number than MON number, and the difference between RON and MON is known as the sensitivity. Practical fuels for SI engines have RON ranging from 90 to 100 with sensitivity in the range of 7 to 12; the most common fuels in Europe have RON ~ 95 and MON ~ 85. However, the anti-knock quality of a fuel is best described by an Octane Index, $OI = RON - K S$, where S is the sensitivity and K is an empirical constant which depends only on the engine design and operating conditions. In most modern engines, K is negative so that, for a given RON, a higher sensitivity (or a lower MON) fuel has better anti-knock quality. These issues will be discussed in much greater detail in Section 5.1.

2. VOLATILITY

The distillation (volatility) characteristics of fuels can affect their safety and performance. The boiling range of fuels is determined by distillation at atmospheric pressure according to the procedure specified in ASTM D86 [19]. The test yields the total volume percent of the fuel that is recovered at a given temperature as shown for a typical European gasoline in Fig. 3.

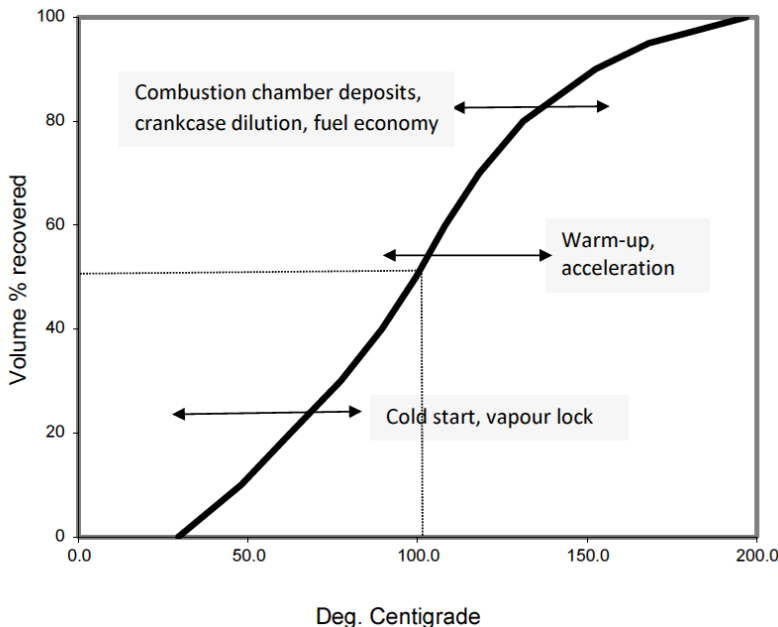


Fig. 3 Volatility characteristics of a typical European gasoline from the ASTM D86 tests and effects of volatility on performance

It should also be noted that the distillation data are based on the volume that is condensed, so some light fractions (such as butane) may only be partially recovered. Two measures are used to define volatility – the E number, E_{yy}, which is the volume percent of the fuel that is evaporated at a temperature of yy or the T number, T_{xx}, which is the temperature at which xx% volume of the fuel is evaporated. Thus in the example shown in Fig. 3, E₁₀₀ = 50% and T₅₀ = 100°C. Different parts of the volatility curve influence different aspects of engine operation as indicated in Fig. 3.

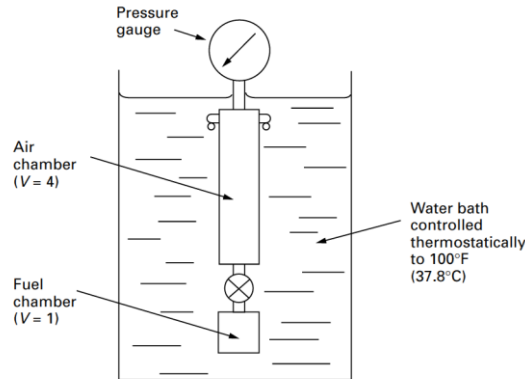


Fig. 4 Apparatus for measuring the Reid Vapor Pressure (RVP)

Another important parameter related to volatility is the Reid Vapor Pressure (RVP) which is the absolute vapor pressure exerted by the fuel at 100° F (37.8°C) and is measured according to ASTM D5191 [19]. The Reid apparatus is shown in Fig. 4, and it consists of a fuel chamber connected to an air chamber of four times its volume. The fuel chamber is filled with chilled fuel, connected to the air chamber, and then immersed in a water bath at 37.8°C and shaken. The final pressure has to be corrected for atmospheric pressure and the effect of heating the air in the air chamber, and the result is an absolute value.

EN 228: 2012, from the European Standards Organisation (CEN), includes eight different volatility specifications. Members of CEN can then use their national standards (BS EN 228:2012 [8] in the case of the UK), to specify particular volatilities for different seasons, as seen in Fig. 5. The vapour pressure is expressed in terms of Dry Vapour Pressure Equivalent (EN 13016-1) which differs very slightly from the RVP as allowance is made for the effect of dissolved air in the fuel and moisture in the air. In the case of the UK, BS EN 228:2012 [8] requires the percentage evaporated at 100°C (E₁₀₀) to be between 46% and 71% regardless of season, with only very small variations in E₇₀ (winter: 22-50%, summer 20-48%), so it is the front end volatility that determines the seasonal variations in the vapour pressure. Europe also uses a Vapour Pressure Index with a maximum permitted value of 1264 in BS EN 228:2012:

$$\text{Vapour Pressure Index} = 10 \times \text{VP (kPa)} + 7 \times \text{E70 (\%)} \quad (1)$$

kPa	100 kPa max		100 kPa max	100 kPa Max
100		70 kPa max		
70				
45	45 kPa min	45 kPa min	45 kPa min	70 kPa Min
0				
	Spring 16 April to 31 May	Summer 1 June to 31 August	Autumn 1 Sept. to 15 Oct.	Winter 16 October to 15 April

Fig. 5 Seasonal upper and lower vapour pressure limits in the UK, BS EN 228:2012 [8]

In general, volatility at the lower temperatures affects cold start and hot fuel handling. If, for instance, RVP is too low or E50 is too small, there might be problems starting the engine at cold conditions. In contrast, if the vapour pressure is too high there might be problems with vapour lock in the fuel system when the engine gets too hot. A higher RVP will also cause evaporative emissions to increase in older vehicles [20, 21]. However, U.S. vehicles, which were adapted to federal regulations in 1996, showed very little effect of RVP on evaporative emissions [21]. Addition of low molar mass alcohols and other oxygenates such as MTBE increases the volatility at low temperatures [4]. Low mid-range volatility can cause poor warm-up and acceleration. If the volatility is too low at high temperatures, because the fuel contains high concentrations of high boiling point materials, there might be problems with oil dilution or excessive deposit formation [15]. High boiling point components will also persist longer in fuel droplets, and these can cause locally rich mixtures that can be a source of hydrocarbon and particulate matter emissions. If, on the other hand it is too high, fuel economy could suffer but this might be because the density of the fuel will be low in such a case.

In 1908 an analysis of commercially available gasolines indicated that they had high initial boiling point (60-65°C) – higher than current fuels with an initial boiling point (30-35°C) and appreciable amounts (say 15% to 20%) boiling below 50°C. Figure 6 shows some historical distillation data, with the data presented by Ricardo [12] in 1924 indicating similar levels of volatility. In the 1940s the increased demand for gasoline led to a wider cut from the crude oil being used, and this could cause problems for older vehicles in which the carburettor body was directly heated by the exhaust manifold. The volatility in winter is raised by increasing the butane content, and this is fortunate, since in winter the butane content of LPG has to be reduced (so as to maintain a saturation pressure of a few bar at ambient temperatures

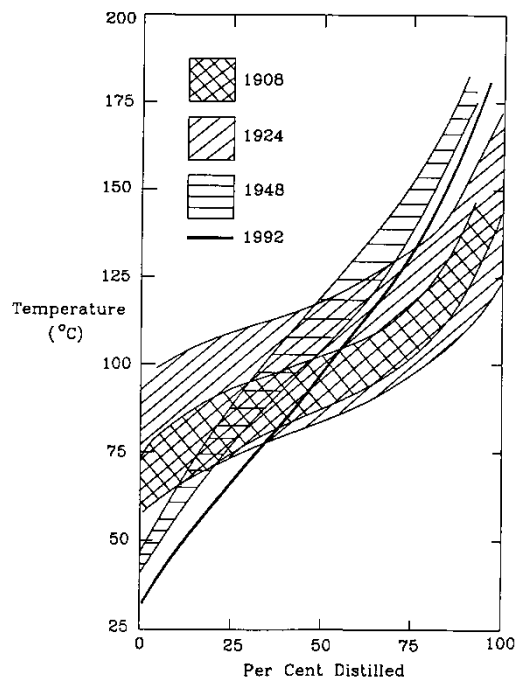


Fig 6 Trends in gasoline volatility

A Drivability Index (DI), which is a combination of different volatility parameters, is often used to consolidate volatility effects on vehicle operation. The drivability of the vehicle itself is based on subjective ratings by trained raters who drive it through a specified test cycle. The raters give demerit points on stumble (intermittent loss of power), idle roughness, surge (cyclic pulses of power), hesitation (lack of response to opening the throttle), difficulty of starting and engine stalls [21, 22]; these ratings are aggregated. Drivability demerits usually show a correlation with DI. The ASTM specification of DI is given by

$$DI = 1.5 \times T_{10} + 3.0 \times T_{50} + 1.0 \times T_{90} + 2.4 \times (\text{Ethanol vol}\%) \quad (2)$$

where the T numbers are in °F. The term with the ethanol concentration was included following a research program conducted on behalf of the Coordinating Research Council (CRC) in 2003 [23]. The maximum value set for DI in ASTM D4814 is 1250 [19]. In addition to these parameters, high values of T_{70} and T_{30} have also been found to contribute to a deterioration of driveability and driver dissatisfaction [24]. Poor cold start and warm-up driveability also results in increased HC emissions [25, 26].

4 ADDITIONAL FUEL PROPERTIES

4.1 Density

Low density will lead to increased volumetric fuel consumption while high density (which will be attributable to less volatile components) could lead to oil dilution and excessive combustion chamber deposits. The EN228 specification in Europe requires gasoline density to be in the range between 720 kg/m³ and 775 kg/m³.

4.2 Gum Specifications

Gum is a generic name for high boiling point products of oxidation that are soluble in gasoline, and these are usually from the olefins (unsaturated hydrocarbons, C_nH_{2n} ; section 4.4). High gum levels could lead to deposit formation in different parts of the engine. Hence the maximum gum level is usually specified. Paradoxically, a significant increase in unwashed gum level could be caused by detergent additives used for deposit control because they contain relatively non-volatile components. The procedure set out in ASTM D381 [19] specifies the method for measuring unwashed gum by evaporating a sample of gasoline and weighing the residue. Unwashed gum is washed with a solvent to get washed gum. A maximum limit of 5 mg/100 ml for washed gum is set by the EN228 specifications and the Worldwide Fuels Charter [6].

4.3 Aromatic Content

Aromatics, fuel molecules containing at least one benzene ring, usually have a high anti-knock quality and high volumetric energy content. Studies have shown that toxic benzene emissions in vehicle exhausts are reduced by lowering aromatic levels [27, 28, 29] but other air toxics like acetaldehyde, formaldehyde and 1,3-butadiene could increase [28]. Heavy aromatics can also increase combustion chamber deposits. In both U.S. and Europe, the maximum level of aromatics in gasoline is set at 35% by volume. Aromatics also have higher carbon- to- hydrogen ratios and hence produce more CO_2 for a given energy content. In addition, benzene levels are controlled [30] – in Europe the maximum allowable is 1% by volume.

4.4 Olefin Content

The maximum level in European gasolines is set at 18% by volume. Olefins (alkenes, C_nH_{2n}) are unsaturated hydrocarbons and are thermally unstable. They generally have a good anti-knock quality but could cause increased deposit formation, particularly in fuel injectors. Their combustion can cause increased toxic emissions [28] and they have high ozone forming potential [31].

4.5 Sulfur Content

The maximum level allowed in Europe by the EN 228 specification is 10 ppm. Sulfur is naturally present in crude oil and active steps have to be taken to reduce its concentration in the finished fuel because it reduces the efficiency of three-way catalysts and hence increases all emissions [27]. The fleet average HC, CO, and NO_x were reduced by 16, 13, and 9 percent, respectively on reducing the sulfur level from 466 ppm to 49 ppm in the AQIRP study [36]. In the European EPEFE study, fleet average emissions of CO, HC, and NO_x were reduced by approximately 10% when fuel sulfur level decreased from 382 ppm to 18 ppm [33]. These trends are confirmed by other studies conducted on more modern fleets of cars which conform to more stringent emissions standards [34, 35, 36]. In fact, the percentage deterioration of emissions performance is much more marked when sulfur is increased in modern cars, since the baseline is low, than in the older AQIRP and EPEFE tests. Sulfur also adversely affects oxygen sensors [4]. Hence fuel sulfur levels have been very significantly reduced in most developed markets in the past two decades [37].

4.6 Oxygenates

Oxygenates such as ethanol and MTBE (methyl tertiary butyl ether) have excellent anti-knock properties and are used extensively as gasoline components. However, the use of MTBE has been stopped in some countries because of concerns about contamination of the water table. Ethanol can be made from bio sources and is attractive for reasons of energy security and could also have a lower greenhouse gas footprint under some circumstances. Brazil has used ethanol made from sugarcane extensively since the late 1970s. Gasoline in the U.S. contains 10% by volume of ethanol. The U.S. EPA has allowed up to 15% by volume of ethanol to be used in gasoline (E15) from October 2010 [38]. A number of companies are now investigating technologies that could enable butanol to be produced at commercial quantities from bio sources [39]. The higher alcohols (such as propanol and butanol) can be used to prevent hazing – when moisture that has contaminated gasoline leads to phase separation in the form of very small droplets that remain in suspension.

Oxygenates have a much lower volumetric energy content compared to gasoline – the lower heating value of ethanol is 21.1 MJ/litre compared to around 32 MJ/litre for gasoline. They also affect volatility and hence evaporative emissions and driveability as discussed in Section 3.2. In modern cars CO and HC are increased but NO_x is reduced upon adding MTBE and ethanol to gasoline [20, 27]. Similar trends have been found in a study with low-emission vehicles in California [40] which also found that benzene, acetaldehyde, formaldehyde and 1,3- butadiene (all considered air toxics) increased on the addition of ethanol. A California Air Resources Board (CARB) study reports that a gasoline containing 10% ethanol by volume decreased toxic emissions by 2% and CO by 10% but increased NO_x by 14%, total HC by 10% and Ozone Forming Potential by 9%, relative to a gasoline containing 11% MTBE by volume [41].

Currently ethanol provides about 2% of the total global transport energy though its use is increasing, primarily driven by energy security concerns.

4.7 Metal Content

Metal additives like tetraethyl lead and, to a lesser extent, MMT (methylcyclopentadienyl manganese tricarbonyl) and an iron compound, Ferrocene (dicyclopentadienyliron) have been used as anti-knock additives. In general, metallic additives reduce the efficiency of three-way catalysts used for emission control in modern vehicles and auto manufacturers oppose their use [4, 42]. Lead additives have been banned in many developed markets for automotive fuels (but not aviation) since it also has known adverse effects on health. Engine manufacturers would like to ban the use of MMT [4, 42] but the manufacturers of MMT have put up a spirited defence of their product [43]. The U.S. EPA assessed potential health risks of particulate manganese emitted from the combustion of MMT in gasoline and as of September 2011, still allowed its use in U.S. gasolines at a maximum level of 1/32 g of manganese per US gallon – around 11 ppm manganese [44]. MMT is in the process of being phased out of EU market fuels, with a limit of 2 ppm from 2014 according to EN228 [8]. Ferrocene, like MMT is also used in some markets.

4.8 Relevance to future engines and fuel specifications

Gasoline specifications, which determine the fuel quality, evolve over time and always lag developments in engines. Large-scale studies on fuel effects on emissions involving auto and oil industries and rule-making bodies have greatly influenced current specifications on fuel composition. The Auto/Oil Program [45] also known as the Air Quality Improvement Research Program (AQIRP), ran from 1989 to 1992 in the U.S. and mostly considered U.S. vehicles made between 1983 and 1989. The European program on

Emissions, Fuels and Engine Technologies (EPEFE) used early 1990s European vehicles [46]. A similar program was also run in Japan [47]. However, engines and after-treatment systems have evolved significantly and modern (and future) engines have to meet stringent emissions standards. Modern engines also in general run at higher pressures for a given in-cylinder temperature as their efficiency has improved [5, 48]. Such trends will continue in the future.

Fuel standards also have evolved. For instance gasoline has much lower sulfur levels and virtually no lead. The absolute changes in tail-pipe emissions in modern engines, because of changes in bulk fuel properties like aromatic and olefin content, will be very much smaller compared to older engine designs. Similarly fuel volatility effects on drivability in direct injection engines or on evaporative emissions, in modern cars equipped with canisters to absorb these, will be far less than in the previous generation of engines. Many of the fuel specifications may not be appropriate for modern and future engines. This is particularly true for fuel anti-knock quality as discussed in the next section.

There are also newer concerns. For instance particulate emissions from SI engines were not of concern in the past. However, direct injection leads to more particulate emissions compared to port fuel injection and nano particles and particle numbers from modern SI engines are of increasing concern and new regulations are coming in to control these and fuel effects on these need to be studied. As engine designers seek ever increasing efficiency small fuel effects such as the effect of burning velocity on efficiency may need to be considered. As fuel components like ethanol find increasing use, their effects on currently unregulated emissions such as aldehydes need to be considered. The challenges of avoiding deposit formation in critical components like fuel injectors will change as engine designs change and additive technology to control such deposits will need to keep pace with these changes. So fuel effects on engine performance and emissions will continue to be important and will need to be studied as engine designs evolve and fuels change.

5. FUEL EFFECTS ON KNOCK, PREIGNITION AND SUPERKNOCK

5.1 Fuel anti-knock quality

Fuel anti-knock quality, as defined by RON and MON, is of great importance to the transport sector (since low octane number fuels limit the thermal efficiency of SI engines) and has a dominant impact on the refining industry. As engine designers seek higher efficiency their demands for higher fuel anti-knock quality will increase. It is also important to understand the relative significance of RON and MON and how modern engines have very different operating conditions from those of the RON and MON tests, so that fuel specifications are set appropriately.

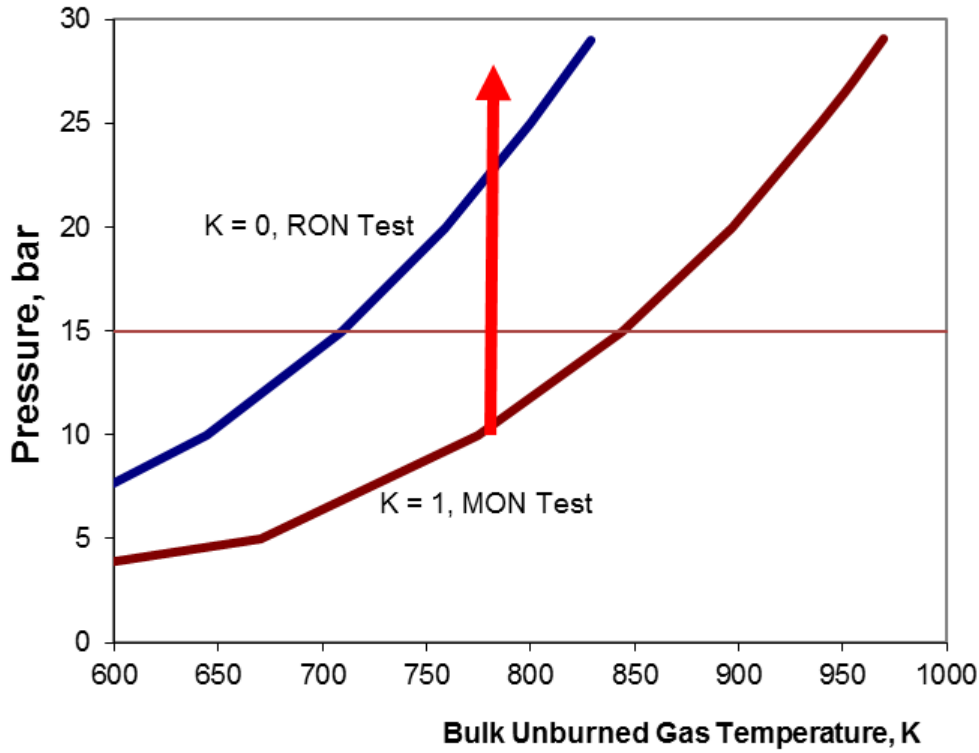


Fig. 7 Pressure vs bulk unburned gas temperature in the RON and MON tests. SI engines have evolved along the direction of the arrow as efficiency and power density have increased over the past century.

Figure 7 shows the pressure (P) variation with unburned gas temperature (T) in the RON and MON test conditions. Compared to the MON test, in the RON test, pressure is higher for a given temperature or alternatively, temperature is lower for a given pressure. The P/T trajectory such as the one shown in Fig. 7 that is followed by the end-gas during an engine cycle is determined by the engine design and operating condition. The fuel will match a PRF of different octane number defined by the Octane Index,

$$OI = (1-K) \text{RON} - K \text{MON} = \text{RON} - KS, \quad (3)$$

where K depends on the P/T trajectory and S is the sensitivity (RON-MON).

Thus at the MON test condition when $K = 1$, the fuel will match a PRF of the same octane number as the MON but at the RON test condition, with $K = 0$, the fuel will match a PRF of the same octane number as the RON of the fuel. All practical fuels have RON higher than MON and the difference between the two is known as sensitivity. The primary reason for sensitivity is that chemical kinetic response of the PRFs to changing pressure and temperature is different from that of practical fuels which are complex mixtures of aromatics, olefins, oxygenates and paraffins. All fuels become more prone to autoignition and knock as pressure and/or temperature are increased – the ignition delay measured in shock tubes decreases. However for PRF fuels, the reduction in ignition delay with increasing pressure for a fixed temperature is much more pronounced than for sensitive fuels [3, 5, 48].

The value of temperature when the pressure is 15 bar, T_{comp15} , was introduced in [48] to place such a trajectory with respect to the RON test condition. If T_{comp15} is lower than for the RON test, the condition

is said to be “beyond RON”. Engine designers have always striven to increase pressure while holding temperature down in order to increase power density and efficiency and SI engines have moved away from the MON test condition over the past century and the importance of MON has decreased [49]. In fact modern engines, including boosted engines, have moved “beyond RON” so that K is negative, and a fuel of lower MON for a given RON has better anti-knock quality, at operating conditions where knock limits their performance [48-56]. This behaviour is consistent with observations on the pressure effects on ignition delay.

However in many parts of the world high MON is assumed to be beneficial for anti-knock quality. For instance in Europe there is a minimum MON specification of 85 while in the U.S. anti-knock quality is defined by $(RON+MON)/2$. Such specifications described fuel quality in the engines at the time they were set several years ago and push gasolines in the direction of increased paraffin content. However, engines have changed and high MON, for a given RON, is detrimental to anti-knock quality and with downsizing and turbocharging, the mismatch between such fuel specifications and engine requirements will grow. Such specifications will need to change to ensure that future fuels match the requirements of future engines. One simple approach might be to specify anti-knock quality only by RON and have a minimum RON requirement as in countries like Japan. Another suggestion [57] has been to change the scale in the RON test from PRF to one based on toluene and n-heptane – toluene reference fuels (TRF). TRF have sensitivities comparable to gasolines and will be far better surrogates for gasolines.

However a mixture of toluene, iso-octane and n-heptane toluene primary reference fuel (TPRF) can be found to match *both* RON and MON [58] and can be used as an appropriate surrogate to predict knock onset in engines running on a gasoline of the same RON and MON [58, 59]. Such a surrogate will have the same OI as the gasoline at all values of K , i.e. at all operating conditions. Ignition delay, τ_i , as a function of pressure and temperature can be found using a chemical kinetic model for such a surrogate [58] and can be calculated at a given crank angle or a given cycle in an engine running on gasoline, using the measured pressure and the estimated temperature. Knock onset is predicted to occur when the integral, I , (Livengood-Wu integral) of the reciprocal of τ_i with time, t , reaches unity (Eq. 4).

$$I = \int_0^{te} \frac{dt}{\tau_i(P,T)} = 1 \quad (4)$$

It was demonstrated that the predicted crank angle at knock onset using this approach agreed very well with the observed value using different gasolines and different operating conditions in two different engines [58, 59].

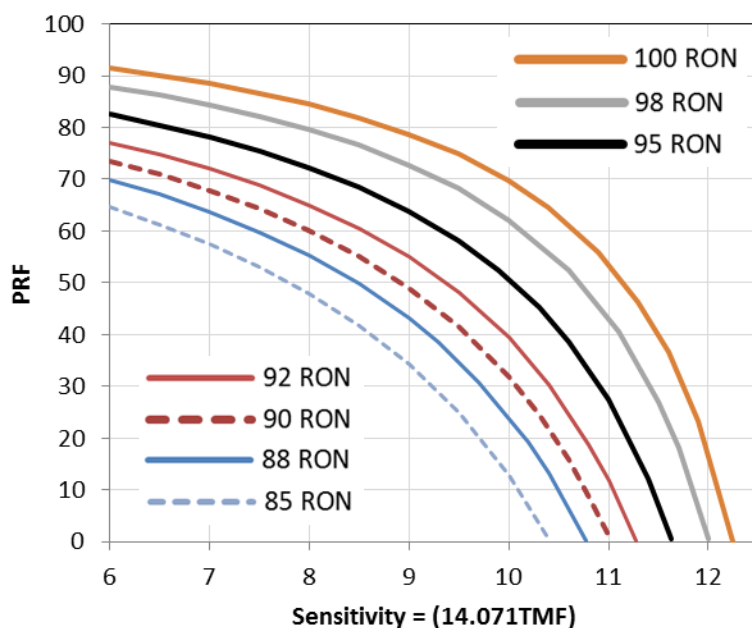


Fig. 8 Octane number of the PRF needed in the toluene/PRF (TPRF) blend vs sensitivity for different target RON values of the TPRF blend [58]. TMF is the toluene molar fraction in the TPRF blend and Sensitivity = RON - MON

Figure 8, from [58] shows how blends of toluene, iso-octane and n-heptane (TPRF) allow control over both RON and MON. For example, a TPRF with 98 RON and 88 MON (sensitivity, S , of 10), will be a mixture of toluene and a primary reference fuel, PRF with 60 octane number (60% iso-octane and 40% n-heptane). Moreover, the toluene mass fraction, TMF, in this blend is determined by the sensitivity and will be 0.71. Then, as outlined in [58], using the octane number of the PRF and the value for TMF, three algebraic equations need to be solved to get the volume percent of the components in this TPRF blend. For the TPRF blend in question, the volume percent of toluene, iso-octane and n-heptane is respectively, 62.4, 22.4 and 15.2. Figure 8 shows that toluene concentration in the TPRF has to be increased to get higher sensitivity if the octane number of the PRF is fixed but this will also increase the RON of the blend. The earlier mixing model of Smallbone et al [60] for TPRF also allows the composition of the TPRF surrogate to match RON and MON to be calculated. However, the model in [58] was based on more extensive experimental data of RON and MON measurements of TPRF blends and also used molar fractions as opposed to the volume fractions of the components to build the models. This makes the blending rules linear and hence reduces errors.

5.2 Preignition and Superknock

Preignition is an abnormal combustion phenomenon where an expanding flame front is established before the spark plug fires in the engine. It was a major area of concern in the 1950s and has again become a concern with the increasing trend in downsizing and turbocharging [61-66]. The pressure and the temperature of the end-gas can rise more rapidly compared to normal spark timing because of the

early start to combustion, from preignition. This can lead to extremely heavy knock, informally described as “superknock” or “megaknock”, with knock intensities of 10 MPa or more if autoignition occurs in the end-gas at high pressure and temperature. These are stochastic processes and are difficult, if not impossible, to model quantitatively but general trends could be understood in probabilistic terms [3, 5, 61].

Three links in the probability chain have to be completed in order to get super (or mega) knock.

1. A turbulent flame has to be initiated during the compression stroke to lead to preignition, but this initiation cannot happen by means of autoignition of the fuel/air mixture because the temperatures and pressures are too low [61, 62, 66]. Hence the probability of preignition does not depend on RON and MON. An inhomogeneity, a local “hot spot”, has to be formed first. The hot spot can be from local hot surfaces e.g., on the spark plug tip or on the exhaust valve. However in modern DISI engines, it seems that preignition is provided mainly by the combustion of oil/fuel droplets [62, 63, 64]. Autoignition reactions aided by some catalytic reactions caused by metallic lubricant additives (especially calcium) lead to the combustion of such droplets as they evaporate and mix with oxygen. These mechanisms are not really understood. This stochastic process will depend on engine design (crevice geometry etc.), operating conditions, lubricant/fuel properties and flow fields and will be difficult, if not impossible to model quantitatively.

2. However, the formation of a hot spot does not guarantee the establishment of a self-supporting flame. A laminar flame needs to grow to a critical size of the order of the laminar flame thickness because of the hot spot for it to be self-supporting. The smaller the flame thickness (higher the laminar flame speed) the more likely it is that a flame will be established all else being equal. Tests with an artificially heated hot spot were conducted by Downs and Theobald [67] who assigned a Preignition Rating value of 100 to iso-octane and zero to cyclohexane, and as expected there was no correlation with either RON or MON. However (see Fig. 9) there is an inverse relationship between the Preignition Resistance and the laminar burning velocity [5, 61].

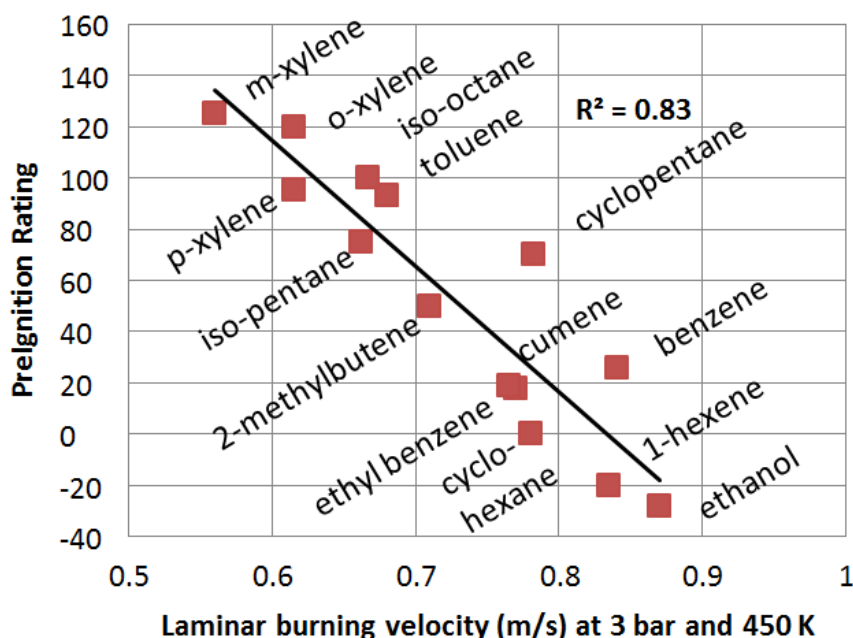


Fig. 9 The inverse relationship between the Preignition Rating and the laminar burning velocity, using data from Table 5.1 in [5]

3. Autoignition of the fuel/air mixture could then occur but at the higher than normal pressure and temperature caused by early combustion from preignition. Conditions in the end-gas are never homogeneous and autoignition always starts at a local hot spot caused by temperature gradients because of turbulence. The pressure wave from the initial autoignition can couple with the autoignition front and be greatly amplified under some circumstances to result in developing detonation [68, 69, 70]. The very high pressure pulses associated with superknock can be explained by developing detonations [3, 5, 61, 65, 71]. The probability of a developing detonation depends on the size of the hot spot in the end-gas, the temperature gradient and also on the autoignition resistance of the fuel. The likelihood of developing detonations decreases as the autoignition resistance of the fuel increases [68, 71].

5.3 Implications for fuels

Higher efficiencies in SI engines will be enabled by high RON, and lower MON (for a given RON) fuels. Such fuels will also help mitigate superknock even if preignition occurs. For instance ethanol is likely to promote preignition because of its high laminar burning velocity but could be resistant to developing detonation because of its high resistance to autoignition. Fuel specifications which assume that high MON is necessary for high anti-knock quality are inconsistent with the requirements of modern and future SI engines. Such specifications force fuel composition to evolve in a direction away from that required by future engines, usually at a greater cost in terms of energy and CO₂ in the refinery, and will require to be changed. Fuel components which have high anti-knock quality such as ethanol, methanol, butanols, MTBE and diisobutylene will be increasingly in demand in the future.

6. CONCLUSIONS

Gasoline specifications have evolved over the last 100 years, and will continue to do so. Changes are (and will continue to be) as a result of legislation and changing engine technology. Changes to fuel specifications also have to accommodate the existing vehicle fleet, so this can limit change unless new grades are introduced – for example the introduction of unleaded gasoline in the 1980s. Changes to fuel composition have also reduced both the benzene levels and sulfur levels. Oxygenate components added to gasoline increase the emissions of aldehydes; unlike the USA these are not currently regulated in Europe.

For direct injection engines fuel volatility effects on drivability or on evaporative emissions are much less critical. Modern cars are equipped with canisters to absorb evaporative emissions, and vehicles with fuel injection normally have pumps located in the engine compartment so are much less prone to vapour lock than carbureted engines with suction pumps mounted on the engine.

The most significant recent change in SI engine technology has been the move towards down-sized and boosted direct injection engines so as to improve part load efficiency. Such engines increase the importance of resistance to knock, and the existing RON and MON scales are becoming less directly

relevant. Highly boosted engines are also subject to pre-ignition and the underlying mechanisms remain unclear.

However there are newer concerns such as particulate matter emissions from SI engines. Direct injection leads to more particulate emissions compared to port fuel injection. Nano particles emissions from SI engines now subject to regulations in Europe, and the limit on the number (as opposed to mass) can be a challenge for direct injection engines. Fuel compositional effects on particulate matter emissions need to be studied further. Small fuel effects such as the effect of burning velocity on efficiency may need to be considered in the future. Deposit formation in critical components (like fuel injectors) will evolve as designs change and additive technology to control such deposits will need to keep pace with these changes. So fuel effects on engine performance and emissions will continue to be important and will need to be studied as engine designs evolve and fuels change.

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