



European automotive fuel evolution and additive solutions

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Abstract

Over the last decades, European regulations have dictated the evolution of engines and their fuels. The European standards for petrol (EN 228) and diesel (EN 590) have substantially changed since their introduction in 1993, with sulphur levels falling from 8,000 ppm in 1970 to 10 ppm today for both diesel and petrol. Passenger cars and heavy duty engines have also undergone substantial modifications following the introduction of regulated emission requirements and the introduction of Euro 1. Biofuels emerged in the fuels market at the start of the 21st century. The nature of these biofuels and the breadth of new fuel product streams lead to vehicles and fuels being adjusted again as new problems emerged. These changes impacted the fuel specifications and vice versa. Additionally, problems experienced in the field have influenced the specifications and the profile of the car parc that we have today. Fuel additives have long contributed to bringing workable solutions to real problems in the field. The relevance of multifunctional additive packages for diesel and petrol and single additive components are well known and are continuously evolving, bringing solutions to the market in an ever-changing environment.

European Directives and European norms

The European regulatory environment dictates the emissions regulations and fuels specifications of cars and fuels through mandates and Directives. One could ask the question, “have fuels influenced engine design or has the engine influenced fuel composition?”. In today’s landscape, we see more and more evolution in fuels and a spread in new fuel components that can be used. Engine manufacturers and additive companies must respond to this highly changing and challenging market with existing technologies, and also develop new technologies and possibilities.

The fuel is an engineering element, an essential part in the engineering process of vehicles. It will influence the choice of materials such as metallic material, polymers, lubricants... The fuel properties will also dictate limits for engine calibration and the optimisation of emissions, power output, drivability, exhaust systems, fuel combustion efficiency and so on.

Automotive fuel quality in the European Union (EU) is addressed at two levels: binding legislation and non-mandatory technical specifications. All requirements of a mandatory nature are established by the Fuel Quality Directive (FQD, Directive 98/70/EC as amended). European Standards are established by the European Committee for Standardisation (CEN), the only recognised organisation in the EU empowered to elaborate and adopt standards with fuel quality requirements. Quality standards (referred to as ENs) are technical specifications with which compliance is not compulsory. These technical specifications are characteristics required of a product for reasons of safety, engine and vehicle performance, drivability, air pollution mitigation, health and environmental protection, etc. This is why the lists of parameters included in European standards for fuels are longer than those covered by the directive.

Harmonised and standardised fuel specifications have existed in Europe since the introduction of EN 228 for unleaded petrol and EN 590 for diesel in 1993. These specifications are established by the

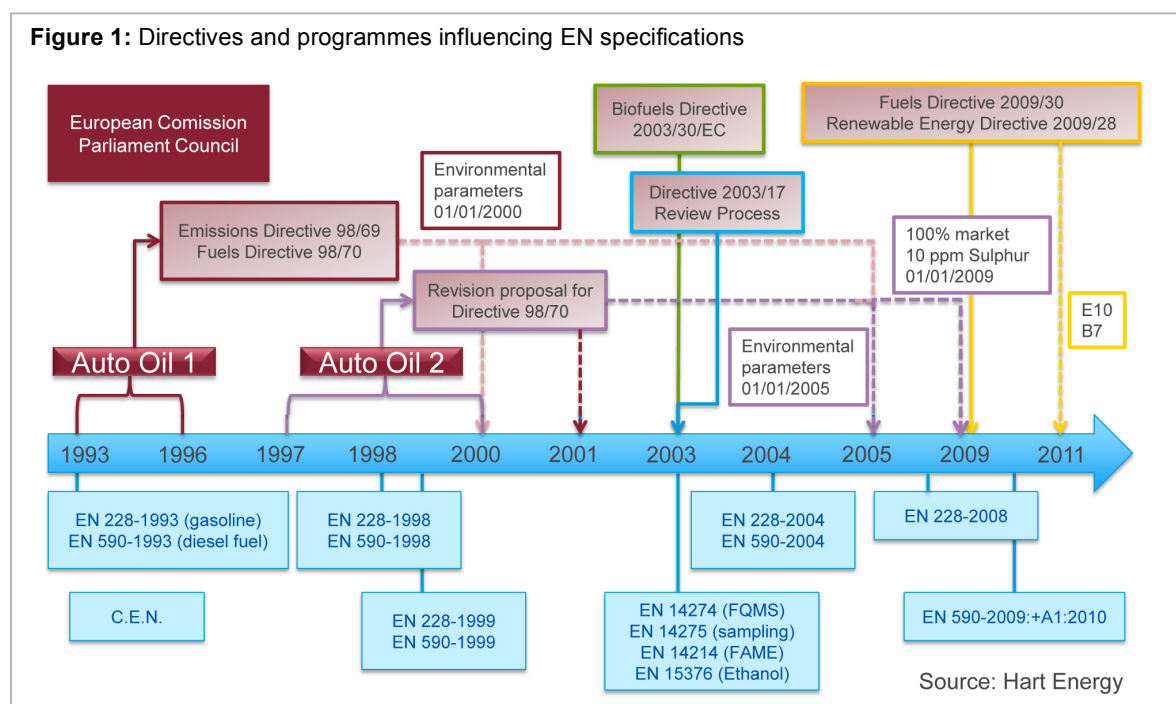
European automotive fuel evolution and additive solutions *Chevron Corp., November 2012*

CEN and can be influenced and shaped by interested stakeholders. Until the mid 1980s, only national standards or exchange agreements existed in Europe. From late 1980 to the early 1990s, quality awareness increased due to very cold winter periods (diesel cold flow), problems with lack of detergency in some European markets, lead phase out and vehicle emissions control coming into focus via the Euro 1 regulation in 1993. Therefore, CEN was tasked by the European commission in 1988 to create quality standards for diesel, petrol and automotive LPG. This led to the first EN norms for petrol (EN 228), diesel (EN 590) and automotive LPG (EN 589) in 1993.

From 1990 to 2000 onwards, the emphasis of European regulations centred on emissions, which lead to increasingly stringent emissions requirements through Euro 1 (1993), Euro 2 (1996) and Euro 3 (2000). Auto-Oil I, including the European Programme on Emissions, Fuels and Engine Technologies (EPEFE), examined the effect on emissions of vehicle technology and fuels characteristics, while Auto-Oil II programmes recognised that fuel quality has to match emerging emissions technology.

The programme Clean Air for Europe (CAFE) was developed alongside Auto Oil II. CAFE resulted in the adoption of the next Thematic Strategy on Air Pollution in 2005. Airborne particulates and ozone (formed by reaction between HC and NOx) emitted by road transport were identified as being of most concern to human health. Euro 5 and Euro 6 emissions standards were proposed. Clearly, the fuel quality had to keep up pace with the changing and emerging emissions technology, which led to the first European Directive in 1998 (Dir 98/70/EC). Since then, EN 228 and EN 590 standards were improved to match the new emissions specs.

Figure 1 shows the various directives and programmes that have influenced the EN specifications since their introduction up until 2011. The various regulations are indicated above the arrow. Meanwhile, below the arrow, the consecutive EN revisions are highlighted.



The second FQD, (Directive 2003/17/EC) led to mandatory values of 50.0 mg/kg max sulphur for both petrol and diesel (and max 10.0 mg/kg as of Jan 1, 2009). In addition to those sulphur limits, both fuels with a maximum of 10ppm sulphur also had to be marketed. Furthermore, mandatory values for olefins (18.0% (V/V)), aromatics (18.0% (V/V)), benzene (1.0% (V/V)) and oxygen content (2.7% (m/m)) were specified, and a maximum Reid Vapour Pressure for summer of 60 kPa was imposed. For diesel, a minimum cetane number of 51.0 and maximum polyaromatic hydrocarbon content of 11.0% (m/m) became mandatory.

From the 2000s to the present day, the European emphasis has shifted with CO₂ reduction, the introduction of biofuels, crude oil availability, greenhouse gas emissions, sustainability and renewable energy gaining more attention.

The revision process undertaken by the European Commission in 2007 resulted in fuel specifications meeting stricter EU air quality targets and future auto emissions requirements, and – for the first time – greenhouse gas (GHG) emissions from transportation fuels.

The outcome of the review process has been incorporated in a new directive: Directive 2009/30/EC of the European Parliament and of the Council of April 23 2009, amending Directive 98/70/EC. This directive constitutes part of the EU Climate Change and Energy Package, adopted by the European Union in April 2009, whose aim is to reduce GHG emissions by 20%, increase renewable energies in the total energy mix to 20% (and to 10% in the transportation sector) and improve energy efficiency by 20%. All of this should be achieved by 2020.

Major features of the third FQD, Directive 2009/30/EC, are:

- The introduction of E10 (petrol with up to 10.0% (V/V) ethanol and 3.7% (m/m) oxygen; increased levels of oxygenates, with the exception of methanol, which remains at the current level of 3.0% (V/V); EU Member States must ensure availability of E5 (petrol with ethanol content no higher than 5.0% (V/V) and oxygen content no higher than 2.7% (m/m)) at least until 2013. Member States may decide to keep E5 for a longer period if considered necessary.
- Different RVP limits: 60.0 kPa max; 70.0 kPa max is allowed in countries with low summer ambient temperatures under the condition that the European Commission will not raise objections. The UK and Ireland among other countries are granted this 70.0 kPa by the European Commission; the waiver (0 kPa to 8 kPa) for ethanol blends is directly linked to the percentage of ethanol blended into petrol. It is allowed in countries with no low ambient summer temperatures under the condition that the ethanol used is a biofuel. In this case, the European Commission will not raise objections.
- With the introduction of B7 (diesel with up to 7.0% (V/V) FAME), however, Member States may permit higher FAME content and there is no limit for other biofuel components; PAH levels reduced to 8.0% (m/m) for on-road diesel.
- The presence of MMT (methylcyclopentadienyl manganese tricarbonyl) in fuel has been limited to 6 mg manganese per litre from January 1st 2011, and will be limited to 2 mg/L starting January 1st 2014 (these limits will be revised based on the results of an assessment conducted by the European Commission by the end of 2012).
- Fuel suppliers are required to reduce life cycle GHG emissions per unit of energy from fuel and energy supplied for the transportation sector by 6% by 2020 compared with the 2010 baseline standard.

Also introduced in 2009, a second directive, the Renewable Energy Directive (Directive 2009/28/EC) requires member states to meet a 10% renewable energy target in the transport sector by 2020. Each member state had to outline a National Renewable Energy Action Plan (NREAP) and submit it to the commission. Certain sustainability criteria need to be respected in order to count towards this target. This includes the sustainable cultivation, production and certification of biofuels as well as minimum GHG savings per unit of energy. Biofuels produced from waste, residues, non-food cellulosic and lingo-cellulosic materials count double compared to other biofuel sources.

In addition to the EN 228-petrol and EN 590-diesel specifications, other fuels such as B10, B20, B30, E85, are used at member state level too. Currently, no EN norm is available for those fuels. National specifications are used. Examples include E10 in France, Germany, Finland, Spain and Poland, B30 in France and the Czech Republic for captive fleets, E85 in Austria, France, Germany, Sweden and B20 in Poland. This could lead to non-harmonised fuel specifications in the various member states.

CEN is currently working on a B30 and an E85 specification. Once EN 228:2012 (likely to be published 4th quarter 2012) is published, member states have six months to adopt this at a national level and the E10 national specifications will be redrawn and replaced by EN 228:2012.

In recent years, the objective of the European Directives has been energy security and CO₂ reduction, through the introduction of renewable biofuels and advanced emission control systems. In the past, the emphasis was on controlling emissions of traditional air pollutants, e.g. lead removal, sulphur reduction, olefins/aromatics content limits, volatility control and catalytic converters.

Some of the important revisions of the EN 590 standard since 1993 include (see *Figure 2* and *Figure 3*):

- EN 590:1993 – the first EU diesel fuel specification. It established a sulphur limit of 0.2% (m/m) (2000 mg/kg) for on road and off-road diesel fuels.
- EN 590:1999 – this standard reflected the sulphur (350.0 mg/kg) and cetane (51.0) specifications by Directive 98/70/EC.
- EN 590:2004 – Sulphur limits of 50.0 mg/kg (so called Euro 4) and 10.0 mg/kg (Euro 5) as regulated by Directive 2003/17/EC. FAME (Fatty Acid Methyl Ester) content of maximum 5.0% (V/V).
- EN 590:2009 – FAME content (EN 14214) of maximum 7.0% (V/V) as regulated by Directive 2009/30/EC. This Directive also adopts mandatory biofuel requirements for refiners and introduced a sulphur limit of 10.0 mg/kg in off-road fuels, effective from 2011.
- EN 590:2009+A1:2010: PAH (Polycyclic aromatic hydrocarbons) maximum 8.0% (m/m) - this version includes all legal parameters from Directive 2009/30/EC.
- Currently, CEN is working on a B10 specification. This B10 may be subject to a new EN norm, rather than sitting under EN 590.

Some of the important revisions of the EN 228 standard since 1993 include (see *Figure 2* and *Figure 3*):

- EN 228:1993 – the first EU unleaded petrol fuel specification. It established a sulphur limit of 500 mg/kg.
- EN 228:1999 – this standard reflected sulphur level (150.0 mg/kg), lead (5.0 mg/l maximum), benzene, aromatics, olefin, oxygen content, ethanol (max 5.0% (V/V)) vapour pressure, E100 and E150 specifications by Directive 98/70/EC.
- EN 228:2004 – Sulphur limits of 50.0 mg/kg (so called Euro 4) and 10.0 mg/kg (Euro 5) as regulated by Directive 2003/17/EC. Aromatics maximum 35.0% (V/V).
- EN 228:2008 – from January 1st 2009, the maximum Sulphur allowance has been 10.0 mg/kg. This is the recognised standard for ethanol when used as a blending component for petrol. EN 15376 was included following the mandate M/344 given to the CEN by the European Commission. This is not incorporated in *Figure 3*, as emphasis in this figure was given to the Fuel Quality Directive.
- EN 228:2012(*) – Oxygen content maximum 3.7% (m/m), 10.0% (V/V) ethanol, increased levels of other oxygenates. Distribution of petrol with oxygen content of 2.7% to be ensured at least until 2013. At the time of writing, this EN 228 has not yet been published. It should be published during 2012. This version includes all legal parameters from Directive 2009/30/EC. This revision features two tables, one for unleaded petrol with a maximum oxygen content of 2.7% (m/m), known as E5 or protection grade, and one for unleaded petrol with a maximum oxygen content of 3.7% (m/m), known as E10. This E10 will have slightly different volatility parameters compared to E5. The E70-range (% evaporated at 70°C) for an E10 fuel in the case of class A, will range from 22.0% to 50.0% (V/V) while for an E5, a range of 20.0% to 48.0% has to be respected. So the E70-range is the same for E5 and E10, however for an E10, the lower and upper limits are increased with 2% (V/V). The E100max (E100 is % evaporated at 100°C) is increased by one unit to 72.0% (V/V). The volatility index is updated accordingly. MMT limited by Mn maximum 6.0 mg/l from 2011 and maximum 2.0 mg/l from 2014.

Figure 2: Changes of key fuel properties since 1970

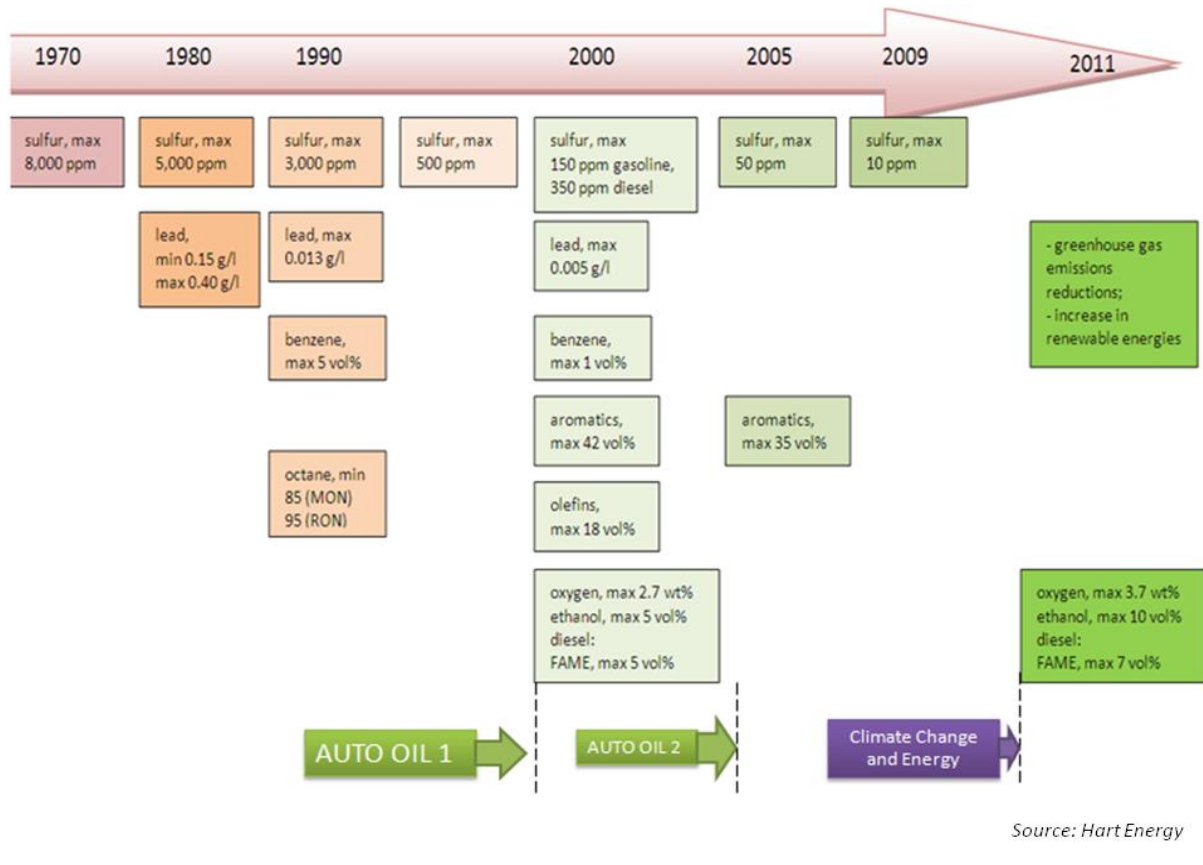


Figure 3: Key changes in fuel properties as regulated by the directive

Gasoline				
	EN 228: 1993 Euro II	FQD - Dir 98/70/EC EN 228:1999 2000 Euro III	FQD - Dir. 2003/17/EC EN 228:2004 2005 Euro IV	FQD - Dir. 2009/30/EC EN 228:2012(*) 2009 Euro V
Aromatics, vol%, max	-	42	35	35
Olefins, vol%, max	-	18	18	18
Benzene, vol%, max	5,0	1,0	1,0	1,0
Oxygen, wt%, max	-	2,7	2,7	2,7 3,7
Sulfur, ppm, max	500	150	50(10)	10
RVP, kPa	35 - 100	60,0/70,0	60,0/70,0	60,0/70,0
Lead, g/l, max	0.013	0.005	0.005	0.005
Use of additives	-	-	-	MMT limited by Mn max 6,0 mg/l from 2011, max 2,0 mg/l from 2014
Diesel				
	EN590: 1993	FQD - Dir 98/70/EC EN 590:1999	FQD - Dir. 2003/17/EC EN 590:2004	FQD - Dir. 2009/30/EC EN 590:2009:+A1:2010
Poly Aromatics, vol%, max	N/A	11,0	11,0	8,0
Sulfur, ppm, max	2,000	350	50/10	10
Cetane number, min	49	51	51	51
Density @ 15°C, kg/m ³	820 - 860	820 - 845	820 - 845	820 - 845
Distillation, T95 °C, max	370	360	360	360
FAME content	-	-	5%	7%

(*) EN228:2012 likely to be published in 4th quarter 2012

Source: Hart Energy

Some examples (first five from the EPEFE-programme) of how fuel parameters can influence vehicle emissions. With today's engine technologies, vehicle emissions can be affected through various parameters and should be tested in order to quantify any changes.

- Lowering aromatics decreases hydrocarbons (HC) and carbon monoxide (CO)
- Lowering Sulphur in petrol reduces HC, CO and nitrogen oxides NOx
- Decreasing density of diesel reduces HC, CO and particulate matter (PM)
- Decreasing Poly Aromatics of diesel reduces light-duty NOx and PM and for heavy diesel HC, NOx and PM
- Increasing cetane rating reduces HC and CO
- Introducing biofuels to increase share of renewables and reducing green house gas emissions

EN 14214, the European FAME specification, was introduced in 2003 and has evolved since then due to issues being observed in the field, newer car design requiring tighter limits and the variety of possible FAME sources that can be used as blending components into EN 590 up to 7.0% (V/V), or as neat fuel in B100 for dedicated engines. In 2008, a first revision (including a phosphorous reduction) was carried out, followed in 2012 by a second revision (likely to be published 4th quarter 2012). This revision was conducted with a view to blending up to 10% (V/V) of FAME in automotive diesel fuel. Changes include an increase of the rancimat oxidation stability (from 6 to 8 hours). Additional requirements on FAME were solving precipitation problems observed in the market during cold periods and an extension towards distillate heating fuels. The FQD (Fuel Quality Directive) limits the FAME content to maximum 7.0% (V/V) in diesel for technical reasons and such a limit is not required for other biofuel components, such as pure diesel-like hydrocarbons made from biomass using the Fischer-Tropsch process, or hydrotreated vegetable oil, which can be blended in to diesel at any chosen content as long as the final blend meets EN 590. The FAME task force under CEN WG 24 (working group for diesel) is also working towards a B30 specification for captive fleet.

EN 15376, the European ethanol specification as blending component for petrol was introduced in 2007 for up to a maximum 5.0% (V/V) in automotive fuel. This version was amended in 2009 (including an electrical conductivity limit, phosphorous and inorganic chloride content limits which were reduced) and revised in 2011. This last version specifies ethanol for automotive fuels of up to 10.0% (V/V) ethanol. For the other oxygenates used in EN 228, no European specification exists.

Regulated vehicle emissions including CO₂ emissions restrictions placed stringent requirements on light duty and heavy duty vehicles. Light duty (LD) passenger cars will move further with Euro 5/5b to 2014 and Euro 6 from 2015. Heavy duty (HD) vehicles will move further with the implementation of Euro V to 2013 and Euro VI from 2014 onwards. As for CO₂ emissions, LD passenger cars must respect a new fleet average of 130 g/km by 2015 and light commercial vehicles a fleet average of 175g/km by 2015. The consecutive Euro norms have substantially changed the engines and after-treatment designs to much more advanced technology and diversification in engines and fleet.

For petrol engines, compliance with Euro 3 legislation was achieved through port fuel injection and three-way catalysts. Euro 4 introduced direct injection gasoline (GDI) and Euro 5 turbo charged GDI. Petrol particulate filters will be introduced to meet Euro 6 in 2014.

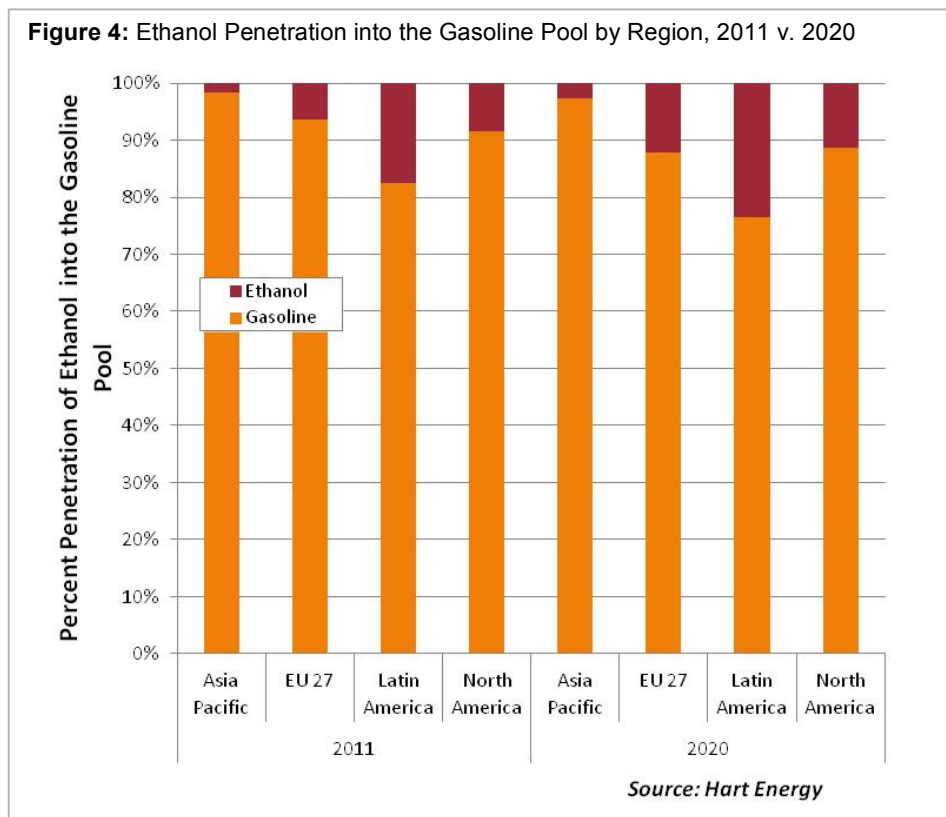
For diesel engines, Euro 3 was achieved by indirect injection diesel and direct injection diesel with exhaust gas circulation (EGR). For meeting Euro 4 and Euro 5 in addition to EGR, diesel particulate filters (DPF) are needed and to meet Euro 6 requirements EGR, DPF and selective catalyst reduction systems will be required.

Petrol

Sulphur reduction and ethanol

Sulphur is found naturally in crude oil and has decreased substantially over the last decades. Low sulphur petrol and low sulphur diesel production is achieved primarily by hydrotreating and hydrorefining processes that convert organic sulphur molecules to hydrogen sulphide gas, which in turn is removed by distillation and a “steam stripping” process. There is concern that the typical refinery hydrotreating process that is being used more often may be removing the “beneficial sulphurs” and leaving, or even creating, “harmful sulphurs” (“beneficial sulphurs” can actually coat metal surfaces and protect against “harmful sulphurs”). Interactions may play a role as well; this means that while two separate batches of petrol may each meet spec, a problem may occur when mixed together. Corrosion inhibitors can help in addressing this.

- Increasing levels of petrol will be displaced by ethanol and other oxygenates in fulfilling mandates in the various member states.
- With the new EN 228 revision (likely to be published in 2012) up to 10.0% (V/V) ethanol can be included in petrol, which will alter the petrol composition even further.
- According to Hart Energy, (see *Figure 4*), there was an average penetration of slightly more than 6% ethanol (including ETBE recalculated to ethanol) in 2011, with a sharp growth identified towards 2020 and a penetration of more than 10%.

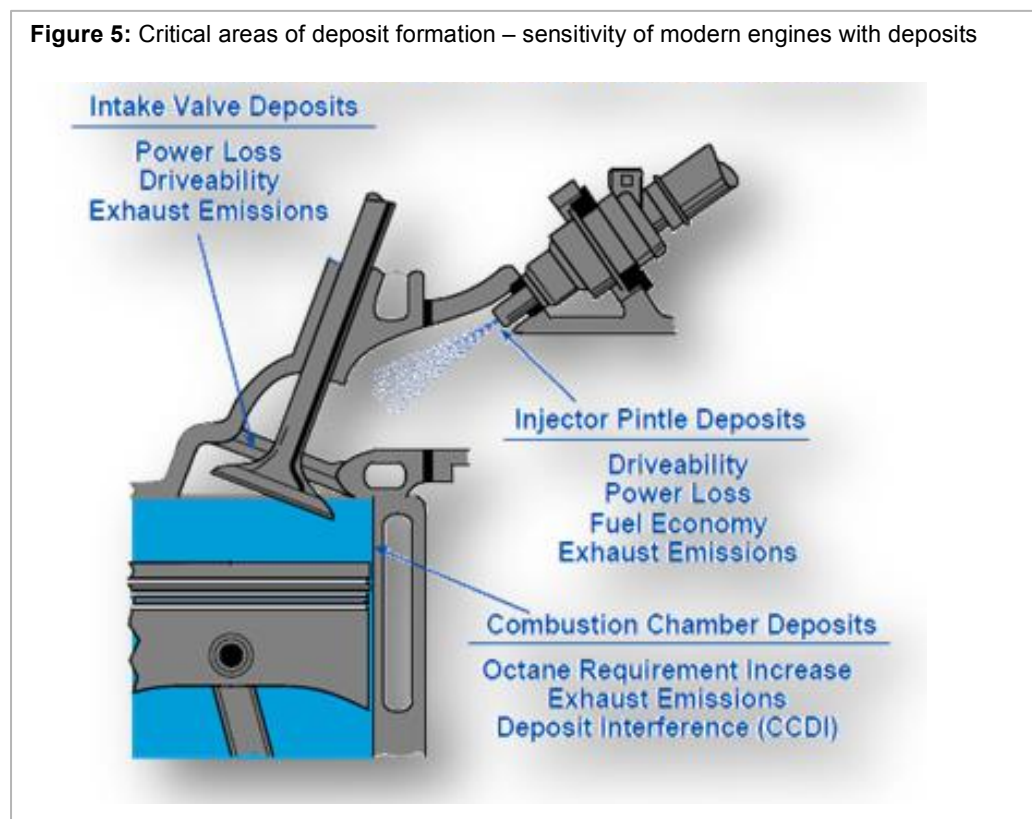


Petrol deposit control additives

Almost without exception, harmful sediment and residue would build up inside an engine if commercial petrol did not contain effective deposit control (DC) additives. The best of today's additives not only keep an engine clean, they also remove existing deposits to help restore the engine's original performance. Because almost all base petrol is formulated to a regulated specification, the performance of the DC additives is a key distinguishing feature.

Engine deposits and performance

Figure 5 shows the critical areas of deposit formation in an engine and the associated impact on performance.



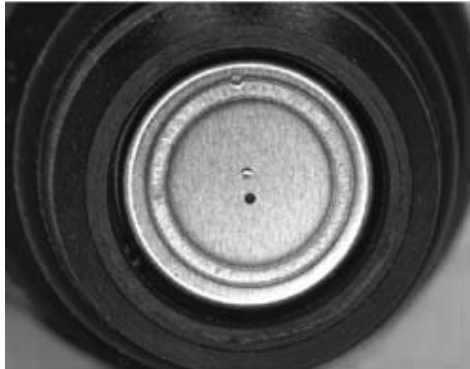
Fuel injectors and carburettors

Fuel injectors are designed to accurately meter fuel into an engine's airstream in a precise pattern of fine droplets. Because of their narrow fuel passages, injectors are highly sensitive to small deposits in the regions where fuel is metered and atomised. These deposits, which may be any combination of dirt, rust, or degraded petrol, can reduce fuel flow and alter the spray pattern, degrading driveability, decreasing power and fuel economy, and increasing exhaust emissions. Deposits cause similar problems for carburetted engines because carburettors also use a number of small channels and orifices to meter fuel.

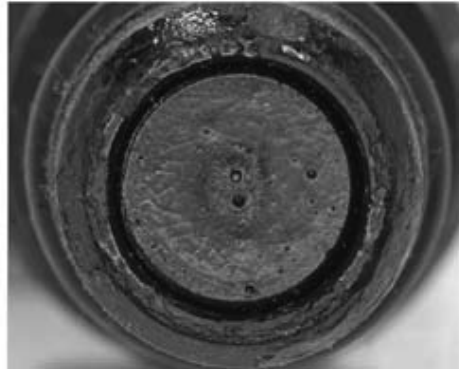
Port fuel injector (PFI) deposits form during the *heat soak* period after an engine has been turned off. The petrol trapped in an injector tip is exposed to a higher temperature for a longer time than the petrol that flowed through the injector when the engine was running. The heat degrades the petrol into a hard varnish, initiating deposit formation. In the absence of an effective additive, injector deposits

form quite rapidly if a base petrol is relatively unstable and if a vehicle is used predominantly for short trips. *Figure 6* shows a close-up of deposits on the director plate of a petrol injector tip.

Figure 6: Port Fuel Injector Director Plate Deposits (High detergency / No additive)



High detergency



No additive

Deposits restrict fuel flow and disrupt spray pattern

Direct injection

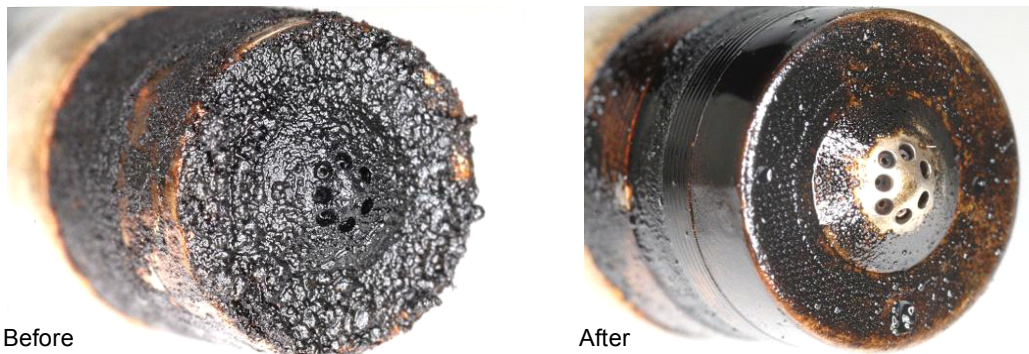
The automotive industry already produces some direct fuel injection petrol engines in which each fuel injector is mounted directly into a cylinder head combustion chamber, as shown in *Figure 7*. This approach results in higher thermal efficiency (lower fuel consumption and lower CO₂ emissions) than is possible with a conventional engine that has port fuel injection. These engines are called direct injection spark ignition (DISI) engines. DISI injectors utilise very small nozzle hole sizes and require fuel at much higher pressure than port injectors can provide (to overcome in-cylinder air pressure).

Figure 7: Typical direct injection engine



Figure 8 shows how deposits formed on the injector can be removed with a concentrated aftermarket DC additive.

Figure 8: Direct injection clean-up with aftermarket DC additive



Intake valves and ports

Because valves and ports operate at high temperatures in the very reactive environment of a running engine, they are susceptible to deposit formation. Heavy deposits on valves and ports restrict air flow and alter air flow patterns within a cylinder, which reduces engine power. In some sensitive fuel-injected engines, even low levels of intake valve deposits (IVD) can damage performance. Cold-start and warm-up driveability can be adversely affected and exhaust emissions increase. In fact, the emissions increase can be surprisingly high (Figure 9) because deposits momentarily absorb and then release fuel, which upsets the delicate air-fuel ratio (A/F), particularly during transient cycles. The altered A/F not only increases emissions from the engine but also impedes the conversion efficiency of the catalytic converter. Other valve deposit problems include valve sticking (when deposits interfere with a valve stem sliding in its guide) and burned valves (when severe deposits prevent a valve from seating properly). Figure 10 shows different levels of IVD common in today's engines.

Figure 10: Typical intake valve deposits

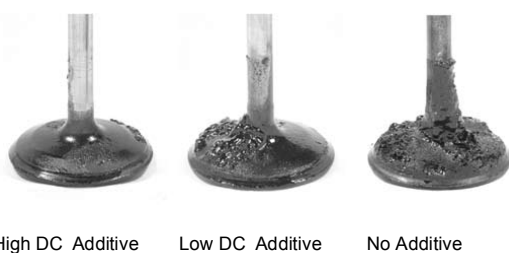
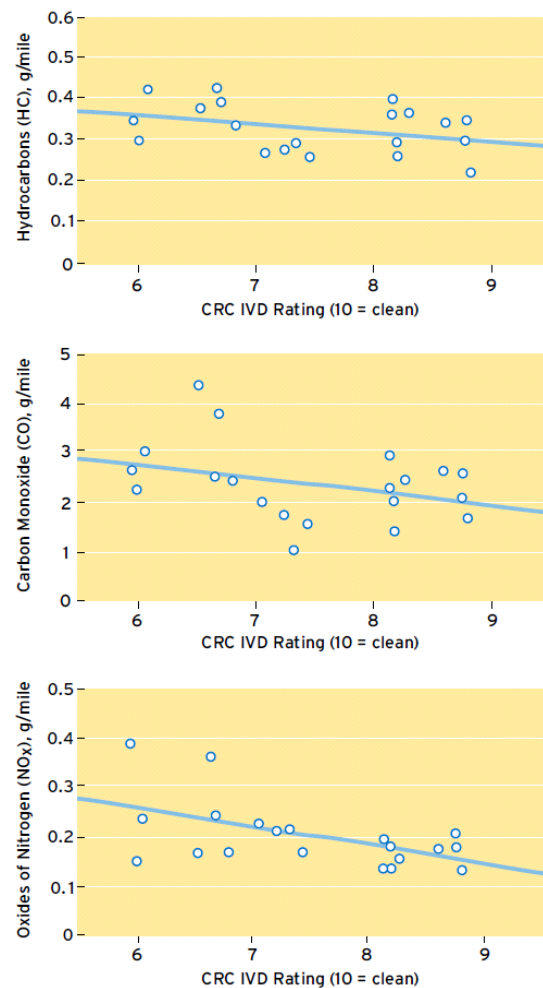


Figure 9: Intake Valve Deposits Increase Tailpipe Emissions

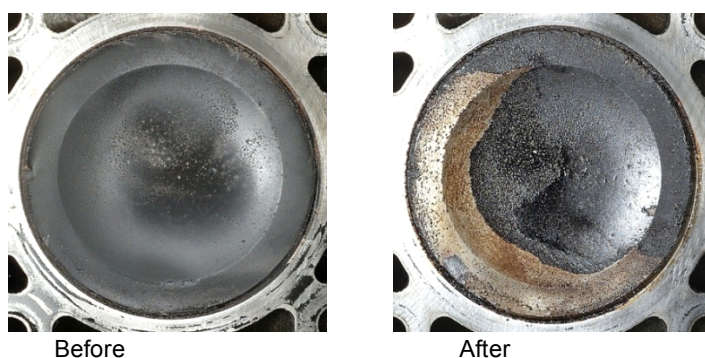


Emissions were measured by Federal Test Procedure Cycle (FTP 75); results are average results for a 20-car fleet. Reprinted with permission from SAE Paper No. 922259. © 1992 Society of Automotive Engineers, Inc.

Combustion chamber

When an engine is brand-new, its octane number requirement (ONR) is determined by the quality of its design and manufacture. Generally, the engine will not knock while operating on petrol with the antiknock quality prescribed by the manufacturer. The engine's ONR increases, however, as combustion chamber deposits (CCD) form during the first several thousand miles of operation (*Figure 11*). If the ONR increase is large enough, the recommended petrol Antiknock Index (AKI) may not prevent knocking or, if the vehicle is equipped with a knock sensor, the loss of power that accompanies knock suppression.

Figure 11: Deposits accumulated on a piston top after several thousand miles and the effect of using an aftermarket DC additive for deposit clean-up



Combustion chamber deposits increase ONR in two ways: they increase combustion temperature by transferring heat to the incoming air-fuel mixture and by slowing heat transfer from the combustion gases (thermal insulation). In addition, they increase the compression ratio because their bulk volume reduces the volume of the combustion chamber when its piston is at top dead centre (TDC). The increase in compression ratio has a much smaller effect on octane requirement increase (ORI) than the rise in combustion temperature.

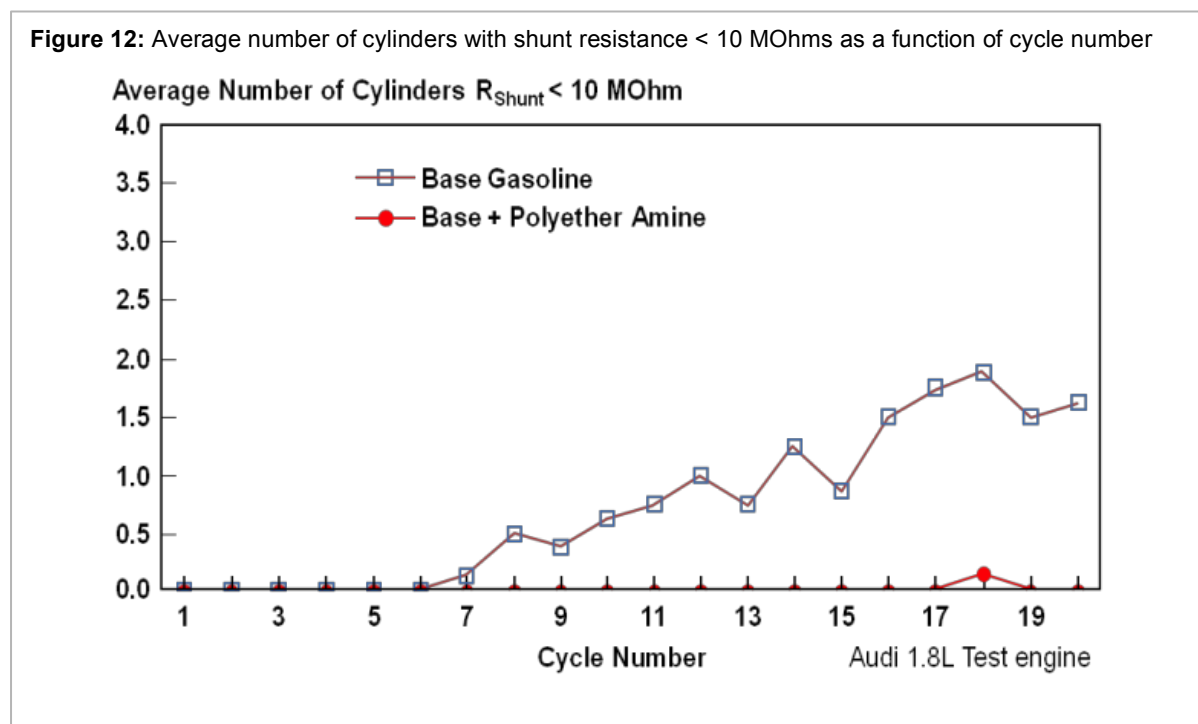
Research shows that precursors for CCD come from fuel, some fuel additives, and engine oil, and that certain fuel and engine oil components form more deposits than others. To date, the only quick, effective means of removing these deposits is to treat petrol with an aftermarket DC additive concentrate based on polyether amine chemistry. Aftermarket DC additive concentration in a treated tank of petrol is 10 to 20 times higher than that of petrol station petrol. With such a change in chemistry, one tankful of treated petrol can decrease ORI 30 percent to 40 percent. Periodic treatment is required because deposits reform with additional driving and the ONR gradually returns to the previous equilibrium level.

Combustion chamber deposit interference (CCDI) and combustion chamber deposit flaking (CCDF) are two other problems that sometimes occur in certain modern engines. CCDI is the result of physical contact between deposits on a piston top and the cylinder head, and is manifested as a loud, metallic banging sound when an engine is cold. CCDI is limited to engines that have been designed with minimal clearance (one millimetre or less, primarily to reduce emissions) between some areas of the piston tops and the cylinder head (*squish* areas) when the pistons are at TDC. CCDF causes low compression pressures when flakes from deposits lodge between a valve's face and its seat, preventing the valve from sealing properly. Engine symptoms of CCDF are difficulty in starting and rough running when cold.

Spark fouling

Carbon spark fouling is another phenomenon that can result in engine start failure due to inadequate voltage to the firing tip and consequently the cylinder is not fired properly. A spark plug is considered fouled when the insulator nose at the firing tip becomes coated with a foreign substance such as fuel, oil or carbon. This coating makes it easier for the voltage to follow along the insulator nose, leach back down into the metal shell and ground out rather than bridging the gap and firing normally. Prolonged idling or continuous low speed driving may keep the spark plug from reaching its optimum operating temperature. Using too cold a spark plug can lead to the same problem. The NKG cold start test sequence measures spark plug shunt resistance for evaluation against spark fouling. This test begins with new spark plugs properly gapped and verified to have infinite shunt resistance. Each cycle of the test includes a sequence of intermittent idle, short duration low speed operation and concluding with a cold soak to a coolant temperature of 10°C. Shunt resistance is measured for each spark plug at the beginning and end of each cold soak for a total of 16 measurements per cycle. Many European OEMs consider the completion of 15 cycles (one cycle is one hour) as acceptable performance. The engine will not start if the average shunt resistance of any cylinder during a cycle drops below 10 MOhms. Low shunt resistance in one or two spark plugs may still allow the engine to start, but with a high probability of poor driveability. Performance in this test may be determined by observing average shunt resistance as a function of the cycle number, or by observing the average number of cylinders with shunt resistance < 10 MOhms as a function of the cycle number (see *Figure 12*).

Figure 12: Average number of cylinders with shunt resistance < 10 MOhms as a function of cycle number



Historical development of deposit control additives¹

Carburettor detergent

This class of additives consists of relatively inexpensive low-molecular-weight surfactants used at low concentrations. When introduced in 1954, they were effective in preventing, and in many cases removing, deposits from carburettor throttle bodies. These detergents could not, however, handle deposits in other carburettor parts, such as air bleeds, or other intake system sections. The introduction of positive crankcase ventilation (PCV) and exhaust gas recirculation (EGR) emission control systems in the vehicles of the 1960s and 1970s increased deposit levels throughout their intake systems. As a result, carburettor detergents were not as effective as they were in the simpler vehicles of the 1950s.

Detergent dispersants

This class of additives consists of polybutene succinimides. Additives with similar chemistry had been used widely as engine oil dispersants before this chemistry was applied to petrol in 1968. Detergent dispersants are higher-molecular-weight materials used at concentrations three to five times higher than that of carburettor detergents. Their performance is sometimes improved by using them in combination with a petroleum carrier oil. They provide keep-clean performance for the intake manifold and intake ports. However, they cannot control IVD and have poor carburettor and fuel injector clean-up performance.

Deposit control additives

The first additive of this class was introduced in 1970. It is based on polybutene amine chemistry and is used in combination with a carrier fluid. While they have to be used at higher concentrations than detergent dispersants, DC additives provide benefits throughout an engine's intake system. They clean up, and keep clean, the throttle body and upper areas of the carburettor, fuel injectors, intake manifold, intake ports, and intake valves.

Lead salts are a combustion catalyst for carbon, so the shift to unleaded petrol changed the nature of CCD. When first generation DC additives were used in unleaded petrol, they continued to control intake system deposits but increased CCD. Consequently, a second-generation DC additive designed specifically for use with unleaded petrol was developed and introduced in 1980. It was based on new¹ polyether amine chemistry, which provides excellent deposit control performance throughout the intake system without contributing to CCD or causing any other adverse side effects.

No harm and compatibility

DC additives are used at concentrations that are 20 to 50 times higher than the concentrations of other petrol additives (such as oxidation inhibitors, corrosion inhibitors and demulsifiers). At these higher concentrations, they have the potential to affect petrol properties, fuel system materials, and engine oils. Therefore, DC additives are tested for the absence of negative attributes (*no harm*) as well as for the positive attribute of controlling deposits. Additised fuel must be fully compatible with the elastomers and metals it will contact. In addition, it must be compatible with other petrol additives, tolerate water well, and not contribute to spark plug fouling, crankcase sludge formation or intake or exhaust valve sticking.

¹ L.M. Gibbs, *Petrol Additives – When and Why*, Paper No. 902104, Society of Automotive Engineers, October 1990

Emissions

At some level, carburettor, injector, intake port, valve and combustion chamber deposits all increase engine emissions. For example, *Figure 9* illustrates that hydrocarbon, CO and NO_x tailpipe emissions are lower when the intake valves are cleaner.

Aftermarket additives

Engine deposits are affected by engine design, driving conditions, petrol base fuel quality and petrol additives. Although petrol may contain a DC additive, some additives are less effective than others or are used at minimum concentration levels that are not very effective. In addition, some engine designs promote heavier deposits than others, and some engine designs are extremely sensitive to deposits that do form. Aftermarket DC additives can clean up deposits that form as a result of these factors. Treating one tankful of petrol with an aftermarket additive is often sufficient. However, chemistry and dosage greatly influence the effectiveness of an additive. Polyether amine-based aftermarket additives have been shown to be particularly effective at providing both excellent intake system and CCD clean-up.

Additive solution

Deposit control additives, by removing deposits, could reduce exhaust emissions and increase fuel economy. The benefits of deposit control additives were recognised by both the automotive and oil industries. So in 1985, when the fuel injector deposit problem was recognised, many oil companies adopted the use of deposit control additives. However, their use was and is still voluntary and no regulatory standards exist in Europe by which to gauge their effectiveness. In the US, regulatory standards exist to ensure minimum and premium performance.

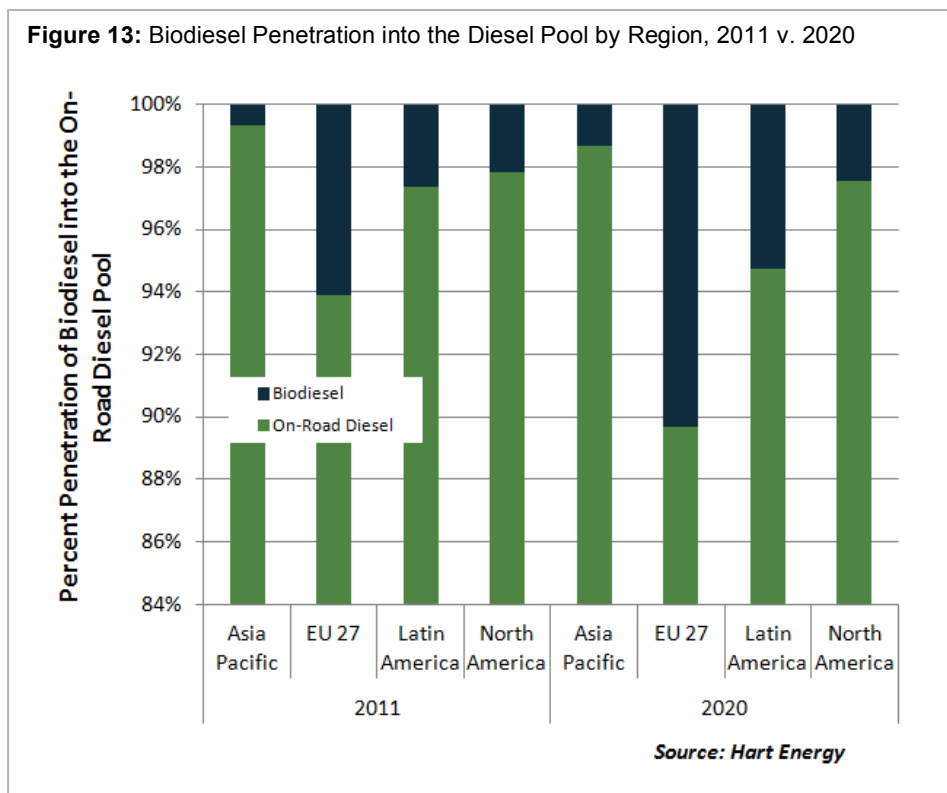
Industry performance tests to evaluate intake valve, combustion chamber deposits, port fuel injector and spark plugs are in place to evaluate performance additives and their benefit over non-additised fuel. In Europe for instance, CEC (Coordinating European Council for the development of performance tests for transportation fuels, lubricants and other fluids) petrol tests are in place for inlet valve sticking (CEC F-16-96, VW Waterboxer Intake Valve sticking of Petrol Engine), including M111E for Deposit Forming Tendency on Intake Valves (CEC F-20-98) and Inlet Valve Cleanliness in the MB M102E Engine (CEC F-05-93). Multifunctional additives, well tested in standard engines, lab tests and multiple non-harm testing, and complemented with proven field performance, can overcome problems such as deposits, wear, corrosion, spark plug fouling, dirty valves, pistons, and combustion chambers, and can provide other benefits such as emission reduction and fuel economy improvement.

Diesel

Sulphur reduction and biofuels

Sulphur has decreased substantially over the last few decades, to 10 mg/kg in European diesel fuel. This has altered the ability to keep deposits in solution. Biofuels increased the variability of the biological constituent parts of diesel. Due to the increasing focus in Europe on fulfilling renewable mandates towards 2020, more and more biodiesels (including FAME) will find their way into the diesel. Other advanced renewable biodiesels such as hydrogenated vegetable oils, animal fats and biomass-to-liquid will increase too.

- This means that depending on the original biological source, the chemical make-up and long term rate at which deposits build up is difficult to predict. The diesel specification EN 590 allows up to 7% (V/V) FAME and other biodiesel (not limited by the FQD in EN 590) at the pump.
- According to Hart Energy,(see *Figure 13* below) the average on-road diesel contains 6% in the EU27, which is projected to grow to more than 10% in 2020 in order to fulfil the European directives.
- Biodiesel is a different product with different by-products and combustion products resulting in different types of deposits.



Diesel injection common rail DW10

Diesel injectors have always been prone to injector coking. In 2008, a new diesel injection test was approved by CEC. This was a 2nd industry test alongside the existing indirect injection (IDI) Peugeot CEC F-023 (XUD-9, 1993) standard coking test that has proven its relevance for many years.

There was clearly a need, as modern passenger car engines have evolved from indirect injection to direct injection in order to meet the new emission standards requirements. This led to a shift in the fuel injection equipment to high-pressure common-rail technology. The Euro 5 (2009) standard requires sophisticated after-treatment systems, such as particulate filters, to meet tighter emissions regulations. There is also extreme pressure from European regulators to reduce CO₂ emissions. Euro 6 (2014) will even require more modern systems. A key part of meeting those requirements is through further improvements of the fuel injection equipment. For the DW-10 injector, six holes of 110 microns in size are used per injector.

For Euro 6, injector holes of even smaller sizes are expected. Also, increasing fuel injection pressures and temperatures and growing levels of biodiesel are likely to increase the coking severity. As a result of all these changes, the new DW-10 diesel fuel injection fouling test was introduced to monitor the performance of market quality fuels. This ensures that modern passenger cars are protected against deposits that can result in engine losses such as power loss and spray pattern degradation, leading to increased emissions.

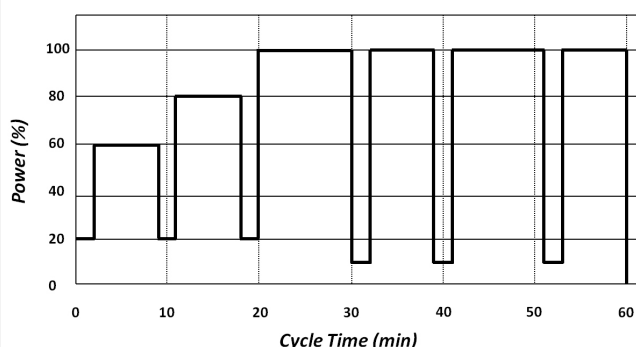
CEC has developed CEC F-98-08 Peugeot DW10 diesel fuel injector fouling test. The engine profile of the DW-10 is presented in *Figure 14*.

A high speed, high load one-hour test cycle forms the basis of this test. After every test cycle (*Figure 15*) an engine power measurement is logged. A cumulative engine run of 32 hours in a 60-hour test (including running in and soak periods) is performed on the tested fuel. Part of testing with the DW-10 method includes the use of 1 ppm zinc salt (zinc neodecanoate), which is added to the test fuel to simulate high fouling fuels. Zinc can also arise from other zinc-containing parts such as fuel injectors within the fuel system of some vehicles, or fuel distribution systems in some geographic regions.

Figure 14: DW-10 Engine Profile

- **Direct injection, 2.0L, 4 cylinder, 4 valves per cylinder, in-line, turbocharged, intercooled**
- **1,600 bar, common rail**
- **6-holes (110 μ), Euro 5 Siemens injectors**
- **EGR disabled for the test**
- **100kw @ 4,000 rpm**
- **32Nm @ 2,000 rpm**

Figure 15: High load one-hour test cycle

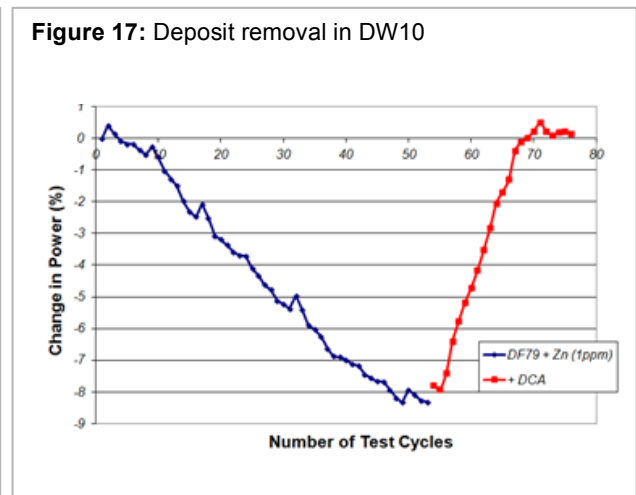
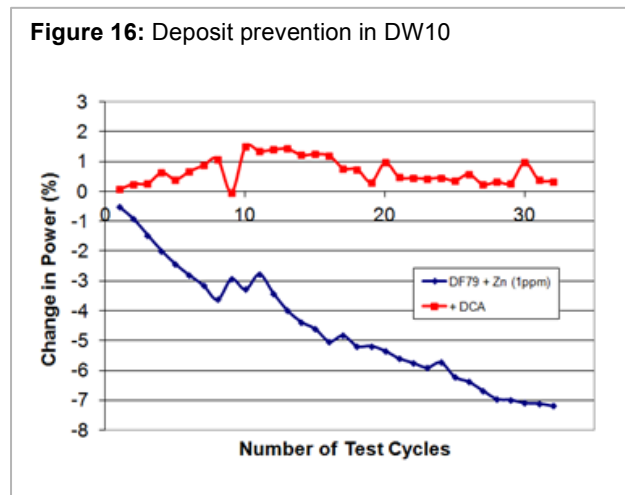


Test runs on DF-79-07 (unadditised reference fuel without zinc) typically results in 1% power loss. With one ppm of zinc salt added to DF-79-07, power losses up to 12% can be produced. Fuels with 10% FAME can result in an even higher power loss.

A formal pass/fail limit has not yet been established in the industry. However, a 2% power loss is considered to be the target for deposit control additives to prevent injector fouling in real life.

Meeting the previous XUD-9 injector fouling test will not guarantee a good result in the DW-10. Nor is the opposite always true.

- Well balanced additives and aftermarket additives can completely prevent power loss (see *Figure 16*) and restore and/or clean up dirty injectors (see *Figure 17*).

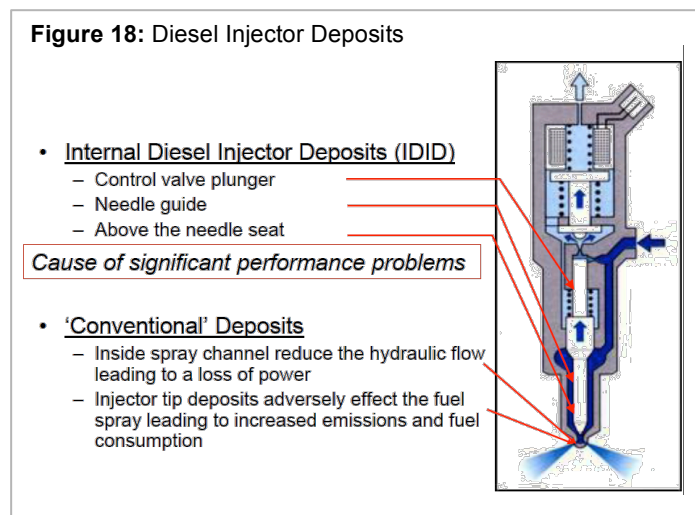


Internal Diesel Injection Deposits (IDID)

One of the latest challenges in the industry is that of Internal Diesel Injection Deposits (IDID). The problem is widespread. These deposits are different from the deposits that occur at the tip of the diesel injector, known as nozzle coking, disrupting the fuel spray patterns and resulting in inefficient fuel deliveries. CEC's DW-10 and XUD-9 tests evaluate this type of deposits and additive solutions to prevent it. To comply with the latest regulatory requirements, modern common rail injector systems operate at much higher pressures (up to more than 2,000 bar) and elevated temperatures (exceeding 200°C) are more complex, with lighter, smaller and faster moving components leading to a build-up of internal deposits.

Internal deposits are different in nature and are observed at control valve plungers, needle guides and above the needle seats (see *Figure 18*), causing significant performance problems including:

- Hard starting
- Preventing motion of internal parts, disrupting timing and fuel delivery
- Rough idling
- Reduced fuel economy
- Reduced power
- Increased emissions
- In extreme cases, engine failure.



There appear to be several types of IDID:

- White, waxy or soap deposits defined by the presence of sodium or calcium and carboxylic acid functionalities.
- Lacquer deposits often associated with an amide peak in Fourier Transfer Infrared Spectroscopy.
- Brown carbonaceous deposits that are more degraded and not easily tied to the original components.

As there are various types of IDID, several chemical causes and multiple possible factors have been proposed:

- In terms of the mechanical aspect, it is known that modern injection equipment has tighter tolerances, multiple injections per cycle, and lower inertia available for the moving parts as the injectors are becoming lighter, smaller and thinner.
- The base fuel changes over the recent years, including poorer solubility in lower sulphur, lower aromatics and a variety of biodiesel types.
- Refinery carry-over (saltic driers and caustic washers) and distribution pick-up of certain components such as sodium and calcium.
- Single component additives such as certain types of corrosion inhibitors, lubricity additives and even deposit control additives.

Solving the issue would mean identifying means of tackling the possible factors listed above. Newer and more robust injection equipment is able to cope with IDID. Adjusted or improved housekeeping practices in fuel refining, terminals and distribution are also needed. Further additives could be part of the solution. Currently, there is no standardised test available to detect the problem or to evaluate additive solutions for IDID. Several additive companies, injection equipment manufacturers and fuel producers are investigating by simulating the problem in proprietary in-house test facilities. It seems that some of the problems can be mitigated by switching to other components, e.g. some acidic corrosion inhibitors that cause IDID in the presence of sodium are solved by changing to another type of corrosion inhibitor. Modern new deposit control additives have been identified and evaluated in real situations and are proved to be helpful in addressing IDID.

Conclusion

Emission regulations have changed the world of vehicles and fuels. Vehicles and their associated hardware must evolve and adapt to meet the continuous more stringent requirements. This is due to increasingly stringent regulatory requirements including fuel economy, CO₂ reduction, emissions reduction and other regulations. Consequently, more modern materials and vehicles are brought into the market.

EN 228 and EN 590 in consecutive revisions became more stringent over the years. Some of the changes are due to European Directives, other changes address issues between stakeholders, as they shape and influence those standards, leading to a requirement for more fit-for-purpose fuels.

European norms for blend components FAME (EN 14214) and ethanol (EN 15376) have been introduced in the 2000s and have undergone substantial changes since their introduction to safeguard the market.

Injector issues and deposit formation problems have existed for quite some time but have also changed due to the introduction and increasing levels of ethanol, FAME and other blend components.

Other problems are more recent and new tests are being developed to detect and evaluate solutions to those problems.

Individual additive components and multifunctional petrol and diesel packages have been able to successfully address deposits (intake valve, combustion chamber, injection, spark fouling), IDID, nozzle cooking, etc.

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- Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC