A global and historical perspective on traditional and new technology gasoline engines and aftertreatment systems

Impact of technology on gasoline exhaust emissions

Association for Emissions Control by Catalyst (AECC)
Manufacturers of Emission Controls Association (MECA)
Conservation of Clean Air and Water in Europe (CONCAWE)
European Automobile Manufacturers' Association (ACEA)

May, 2012

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ABSTRACT

This report reviews the technologies available to meet the exhaust emissions regulations for gasoline-fuelled passenger cars, light-duty and heavy-duty vehicles, non-road mobile machinery and motorcycles. Technologies applicable to gasoline engines (both stoichiometric and lean-burn) and to gaseous-fuelled engines are covered.

KEYWORDS

Gasoline, exhaust emissions, catalyst, emissions level, aftertreatment, PM, PN

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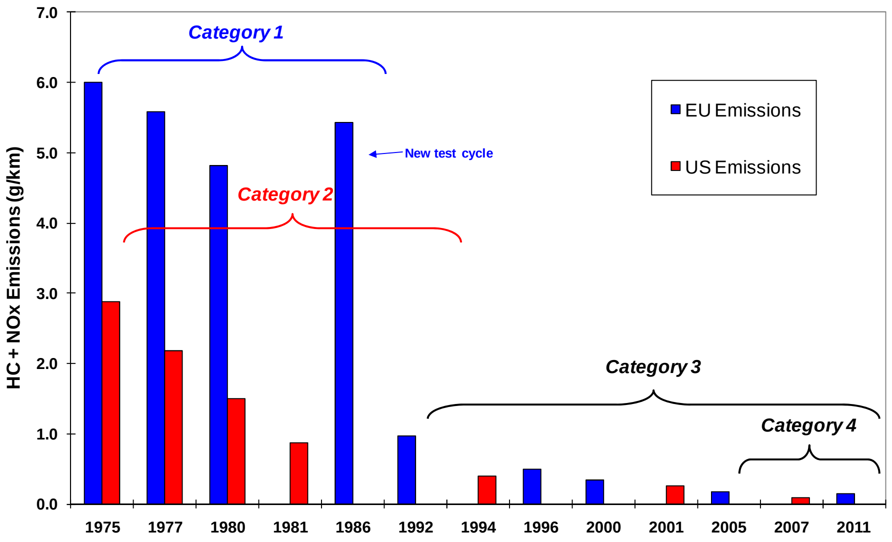
1.0 INTRODUCTION

The need for the control of the pollutant emissions from gasoline and diesel engines has long been recognised. Legislation around the world limits the permissible emissions of carbon monoxide (CO), hydrocarbons (HC), oxides of nitrogen (NOx) and particulate matter (PM). **Figure 1** shows the development of emissions legislation in the U.S. and EU. Exhaust emissions can be lowered somewhat by reducing engine-out emissions through improvements to the combustion process and fuel management, or by changes to the type of fuel or its composition, but emissions control systems – auto catalysts, adsorbers and particulate filters – in combination with good quality fuel (low sulfur content) and enhanced engine management - reduce emissions to very low levels.

Figure 1*:* Emissions regulations for light-duty engines[1]



Gasoline engines are used worldwide to power mopeds, motorcycles, cars, light commercial vehicles and machinery such as chain-saws and grass cutters. Catalyst-equipped passenger cars were first introduced in the U.S. in 1974 and three-way catalysts (TWC) are now used throughout the world as part of an integrated approach to emissions control which includes the combustion system, fuel quality and electronic control systems. Modern gasoline Direct Injection (GDI) engines require additional control equipment because of their fuel-lean operation, and technologies such as NOx adsorbers are typically used with such engines.

In recent years, particulate emissions from vehicles have become an increasing concern for human health. Particulate matter (PM) emissions from gasoline engines are usually very low

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[1] These categories do not represent industry-accepted terms but are used here to distinguish between different vintages of engines, vehicles, aftertreatment, and fuel technologies.

although GDI engines can produce small quantities of PM emissions. Ultrafine particles, that is, those having an aerodynamic diameter of greater than 23nm, can also be measured from gasoline engines. The particle number (PN) concentration is generally higher for GDI engine technology compared to Multi-Point Fuel Injection (MPFI) engine technology. In Europe, there will be controls on PN emissions from GDI engines starting in September 2014 [1] with the same PN limit as for diesel engines from 2017.

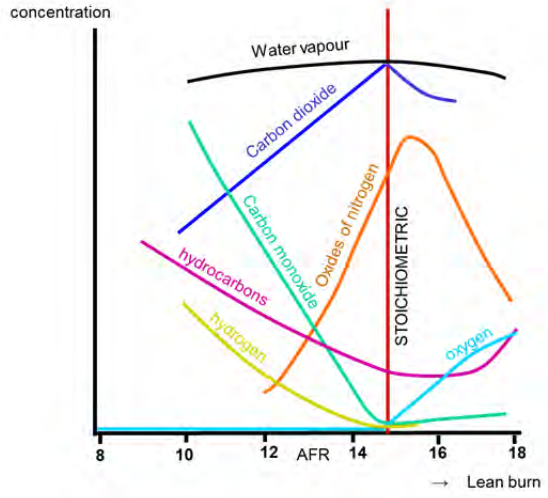
The emission control technologies discussed in this document represent state-of-the-art approaches that new vehicle manufacturers are using to meet existing and future emission regulations.

Fuels form an important part of any emissions control system. Unleaded fuel is essential for the operation of modern engines and emissions control system, and low sulfur levels are needed for their optimal operation. The effects of sulfur are described in the relevant sections on emissions control technologies and **Section 8.0** identifies other relevant parameters of current and potential future fuels.

2.0 APPROACHES FOR REDUCING GASOLINE EMISSIONS

Until the advent of emissions control technologies, most gasoline engines operated with fixed calibration carburettors or simple fuel injection systems (shown as Category 1 in **Figure 1**). Such systems are typically relatively poorly controlled in terms of achieving the stoichiometric (chemically correct) air-fuel ratio (AFR) and this ratio has a significant impact on engine-out emissions, as shown in **Figure 2**.

Figure 2: Emissions vs. air-fuel ratio



The first legislated exhaust emissions standards were promulgated by the State of California for 1966 model year cars and this was followed by the United States as a whole in model year 1968. The standards were progressively tightened year by year. The EU introduced emissions limits in 1970 [2] and these were also progressively tightened. Initially the more stringent regulations were met by improved design, combustion, de-tuning and fuelling management controls, but the invention of the catalytic converter allowed, by the U.S. 1975 model year, tighter emissions standards to be met without severe performance or fuel economy penalties. This development also forced the introduction of unleaded fuels in the U.S., as lead is a poison for the precious metal-based automotive catalysts. These original catalysts were oxidation catalysts which controlled the emissions of CO and HC, but not oxides of nitrogen (NOx).

To allow the control of NOx in addition to CO and HC, the first-generation of ‘3-way catalyst’ systems followed in the early 1980s (Category 2 in **Figure 1**). These systems utilise an oxygen sensor and an engine management system (EMS) to control the AFR to stoichiometry during normal running conditions, allowing the apparently simultaneous oxidation of CO and HC with the chemical reduction of NOx to nitrogen and water. The removal of lead from gasoline in the EU in the late 1980s [3] allowed the use of these systems in Europe, and tightening emissions legislation effectively enforced their use from 1992 [4].

Initially varying degrees of fuelling control were used to meet emissions legislation, including some systems using comparatively simple throttle-body (single point) injection but over the years the need for greater control and the benefits in performance have led to the overwhelming majority of car and light-duty commercial vehicle applications using electronically-controlled multipoint port fuel injection systems, with a general trend from banked systems (all injectors firing simultaneously) through grouped systems to sequential injection in which the injections are controlled specifically for each individual cylinder.

In modern engines, this type of system has a much more complex EMS allowing close control of operating conditions and more sophisticated exhaust aftertreatment systems (Category 3 in **Figure 1**). Such systems allow rapid 'light-off' of the catalysts, enabling to reduce emissions within seconds of engine start-up. The EMS can also include "adaptive learning" where the control system slowly "learns" the stoichiometric AFR of the fuel in the tank and corrects for changes during subsequent operation, including cold starts. The primary input to the EMS is the oxygen sensor in the exhaust system that informs the EMS of the actual engine-out combustion mixture.

More recently Gasoline Direct Injection (GDI, also known as Direct Injection Spark Ignition - DISI) has been developed and is increasingly being applied in passenger vehicles as it offers some fuel consumption benefits. This is shown as Category 4 in **Figure 1**. In this case the fuel is injected directly into the cylinder rather than into the inlet manifold. This approach provides less time for vaporisation of the injected fuel mixture and very sophisticated EMS with adaptive learning are used. The exhaust aftertreatment system used depends on whether the system operates stoichiometrically, in which case a conventional three-way catalyst is used, or under 'lean burn' conditions, where the overall AFR is to the right of the stoichiometric point shown in **Figure 2**. In this case the three-way catalyst has to be supplemented by a NOx control system as the excess oxygen precludes the use of the NOx capabilities of the three-way catalyst under lean conditions.

There are usually considered to be two generations of GDI engines that depend on how the injected air-fuel mixture is guided toward the spark plug for ignition. In the first generation approaches, the air-fuel mixture is typically guided to the spark plug by means of a specially designed piston bowl (so-called 'wall-guided') or by a combination of the piston bowl design and intake port (so-called 'air-guided'). Second generation approaches (so-called 'stratified charge') inject the air-fuel mixture into the top of the combustion chamber and directed toward the spark plug. In this approach, the air-fuel mixture is richer near the spark plug and leaner near the combustion wall. Most GDI engines today use first generation approaches although the more complicated second generation approaches are starting to appear on some higher-end vehicles.

2.1 ENGINE CONTROLS

Understanding and controlling the combustion process is the first step in reducing engine-out emissions and minimizing the burden on the emission control systems. This allows catalyst developers to design smaller, less costly exhaust controls. Engine design is an important part of controlling and facilitating the combustion process.

For gasoline engines, accurate metering of fuel is essential to minimise emissions. This must include introducing it to the combustion system at the right time in the combustion cycle and at the right position in the manifold (port fuel injection engines) or chamber (direct injection engines). The EMS plays a vital role in controlling the fuelling and engine operating strategies.

Careful design of the combustion chamber itself to direct and control charge mixing and to minimise crevice volumes plays an increasingly important part in modern engine design to minimise emissions and maximise fuel efficiency.

Variable valve timing (VVT) is used to introduce some fraction of exhaust gas into the combustion process and reduce HC and NOx emissions. Exhaust gas recirculation (EGR) can be used to dilute intake air with some fraction of exhaust gas to lower the combustion temperatures resulting in lower engine-out NOx emissions, although this technique is more common in diesel engines.

Evaporative emissions on petrol-engine vehicles are controlled by linking any vents on the system to a canister full of activated charcoal which adsorbs the hydrocarbons. The canister is also connected to the inlet manifold via a vacuum line, so that when the engine is running, hydrocarbons are desorbed from the charcoal and added to the inlet mixture for combustion. In addition, fuel hoses are designed to have low permeability, for example by using a multi-layer hose with a (relatively) impermeable inner skin of fluoroelastomer. Similarly, plastic fuel tanks need to be barrier coated, either via a fluorination treatment or, more commonly nowadays, by incorporation of a barrier layer into the tank material.

2.2 EXHAUST CONTROLS

This section provides a brief description of the available gasoline exhaust control technologies, including descriptions of their operating characteristics, control capabilities and operating experience. More detail on each control technology is provided in subsequent sections.

The majority of hydrocarbon, carbon monoxide and oxides of nitrogen emissions from gasoline engines that have exhaust catalysts occur during cold-start before the catalyst can achieve optimum operating temperatures. Engine and exhaust system manufacturers have working together with catalyst companies to develop ways to heat up the catalyst as quickly as possible. One significant benefit came from the introduction of close-coupled catalysts (CCCs). This positioned a three-way catalyst (TWC) close to the exhaust manifold to allow rapid heating and therefore ‘light-off’ of the catalytic reactions giving lower emissions within seconds of engine-start up. The exothermic heat generated by these reactions also facilitates the rapid heat up of any catalysts in the exhaust manifold.

A brief description of the major technologies employed in the reduction of pollutants from diesel exhaust is included below along with a range of conversion efficiencies that may be achieved. More detailed descriptions of their performance characteristics will be covered in subsequent sections of this report.

Oxidation Catalysts (OC), the original catalyst technology, can, in a properly optimised system, reduce CO and HC emissions by more than 90 percent. This technology is still used in some powered two-wheelers, primarily mopeds.

Three-Way Catalysts (TWC) are the main auto catalyst technology used to control emissions from gasoline engines. They operate in a closed-loop system which closely controls the AFR so that the catalyst can then simultaneously oxidize CO and HC to CO_2 and water while reducing NOx to nitrogen. Modern TWC systems can reduce these emissions by 98 percent or higher.

Lean NOx Traps (LNT, also known as *NOx adsorbers*) are used with lean-burn gasoline direct injection engines and are capable of 70 percent or more NOx reduction.

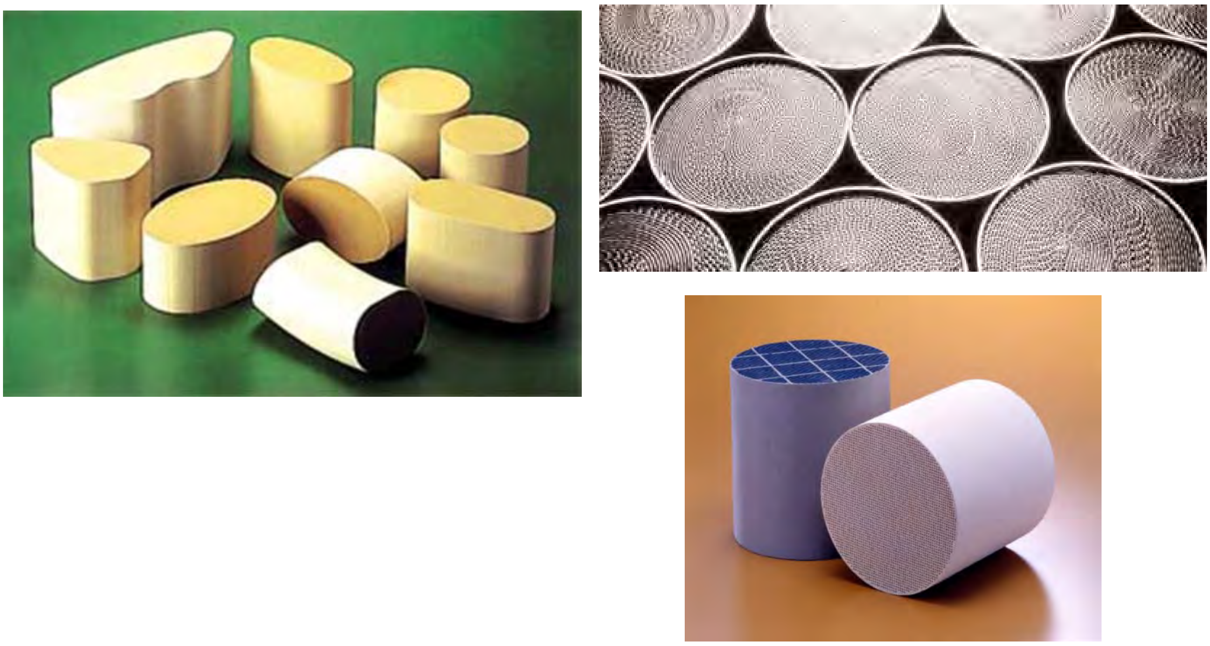
Selective Catalytic Reduction (SCR) using urea as a reducing agent is used for control of NOx from diesel engines but in principle could also be used with lean-burn gasoline direct injection engines.

Gasoline Particulate Filters (GPFs) have been demonstrated for use with GDI engines but to date have not been commercialised as current regulations can be met without them. They offer reductions in both PM and PN emissions. Changes to EU regulations from September 2014 [1] will see some GDI vehicle types being introduced with GPFs while other vehicle types may use internal engine controls to achieve the particulate limits.

3.0 SUBSTRATE TECHNOLOGIES

Catalytic converters, traps and filter technologies for the control of emissions use a ceramic (typically cordierite) or metallic honeycomb substrate (**Figure 3**). This is mounted in a can and is protected from vibration and shock by a resilient 'mat'. The catalytic converter of particulate filter then looks similar to an exhaust muffler.

***Figure 3**:* Ceramic (left) and metallic (top right) substrates and wall-flow particulate filters (bottom right)



The technology of the substrates, on which the active catalyst is supported, has seen great progress. Thin walls and increased cell densities allow a larger catalyst surface area to be incorporated into a given converter volume and this allows better conversion efficiency and durability. The thin walls reduce thermal capacity and limit pressure losses. Alternatively, the same performance can be incorporated into a smaller converter volume, making the catalyst easier to fit close to the engine as cars are made more compact. The use of additional catalytic converters close to the exhaust manifold reduces the time to light-off in the cold start and, therefore, the total emissions. Light-off times have been reduced from as long as one to two minutes to a few seconds. Improved substrate technology, combined with highly thermally stable catalysts and oxygen storage components, allows the close-coupled catalyst approach to meet current U.S., Japanese and European standards.

In the original automotive catalyst, it was only possible to apply the active coating to the whole substrate. Precision coating technologies now allow different active material compositions to be applied to different areas of the substrate to optimize the performance or, in some cases, to allow different functions. This includes, for instance, coating the inlet end of a particulate filter to act as an oxidation catalyst.

A further option that can be used for some types of catalyst is to incorporate the active materials directly into the ceramic substrate, so that the extruded ceramic matrix provides catalytic activity without further coating. Such ‘homogeneous’ catalysts are primarily used in some SCRs for reducing NOx emissions.

Wall-flow particulate filters are currently only used with diesel engines but are feasible for other applications. They also typically use a ceramic honeycomb structure of a porous wall design where every alternate channel is plugged on each end. These wall-flow filters can be made from a variety of ceramic materials, notably cordierite, silicon carbide or aluminium titanate. Technological developments in filter design include advancements in cell shape and cell wall porosity optimization aimed at minimizing engine backpressure and extending the interval between filter service. Advances such as higher pore volumes, increased pore connectivity, and thinner web designs facilitate catalyst coating while maintaining longer times between soot regeneration events.

4.0 THREE-WAY CATALYSTS (TWC)

TWCs are the main auto catalyst technology used to control emissions from gasoline engines. The catalyst uses a ceramic or metallic substrate with an active coating incorporating alumina, ceria and other oxides and combinations of the precious metals - platinum, palladium and rhodium. TWCs operate in a closed-loop system including a lambda or oxygen sensor to regulate the AFR on gasoline engines. The catalyst can then control emissions in three ways (hence the name) by simultaneously oxidizing CO and HC to CO_2 and water while reducing NOx to nitrogen.

***Figure 4**:* Automotive three-way catalytic converter

Fast light-off catalysts allow the catalytic converter to work sooner by decreasing the exhaust temperature required for operation. Untreated exhaust emitted at the start of the legislated emissions test and on short journeys in the real world is curtailed. Changes to the thermal capacity of substrates and type and composition of the active precious metal catalyst have together resulted in big improvements [5].

More thermally durable catalysts with increased stability at high temperature allow the catalytic converter to be mounted closer to the engine and increase the life of the catalyst, particularly during demanding driving conditions. Precious metal catalysts with stabilized crystallites and washcoat materials that maintain high surface area at temperatures around 1000°C are needed for this. Improved oxygen storage components stabilize the surface area of the washcoat, maximize the AFR 'window' for three-way operation and help the oxygen sensors to indicate the 'health' of the catalyst for On Board Diagnostic (OBD) systems. CCCs mounted immediately after the engine exhaust manifold allow the catalyst to start working within seconds [6].

***Figure 5**:* Close-coupled catalysts

Electrically heated catalyst systems use a small catalyst ahead of the main catalyst. The substrate, onto which the catalyst is deposited, is made from metal so that, when an electric current is passed, it will heat up quickly. This brings the catalyst to its full operating temperature in a few seconds [7].

5.0 OXIDATION CATALYSTS

Oxidation catalysts are the original type of auto catalysts and were used from the mid-1970's for petrol-engine cars until superseded by three-way catalysts. They look much the same as three-way catalysts and their construction and composition is similar but slightly less complex. Oxidation catalysts convert CO and HCs to CO_2 and water but have little effect on NOx. They are now rarely used on gasoline cars because of the advantages of TWC, but they are still used in some parts of the world where emissions legislation is less stringent. They may also be used on some buses running on Compressed Natural Gas (CNG), small motorcycles and for applications such as small gasoline engines for mopeds, hand-held equipment and recreational boats.

In most applications, an oxidation catalyst consists of a stainless steel canister that contains the flow-through honeycomb substrate or catalyst support. The substrate may be either made from a ceramic material or metal foil. As with TWCs, there are no moving parts, just large amounts of interior surface area. The interior surfaces are coated with catalytic metals such as platinum and/or palladium.

This type of device is called an oxidation catalyst because it converts exhaust gas pollutants CO and HCs into CO_2 and water by means of chemical oxidation.

Figure 6: Diagram of an Oxidation Catalyst

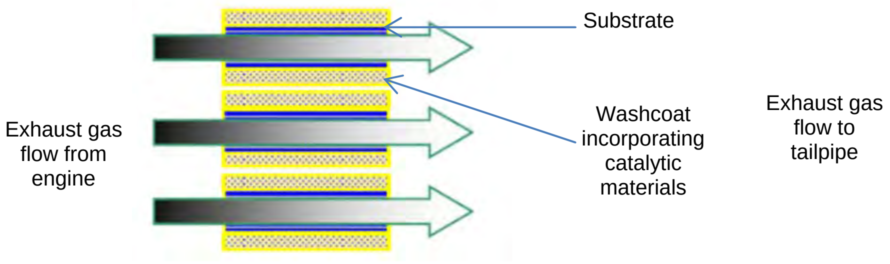


Figure 6 shows a representation of three channels of a straight through, flow path honeycomb. The engine-out exhaust gases enter the channels from the left and as they pass over the catalytic coating they are oxidized to the reaction products on the right.

5.1 IMPACT OF SULFUR ON OXIDATION CATALYSTS

The sulfur content of fuel has a significant effect on the operation of catalyst technology. In most cases oxidation catalysts can operate effectively on fuel with up to 500 parts per million (ppm) sulphur (S), however the activity and function of the catalyst components can be impacted negatively, resulting in a reduction of catalyst efficiency over time.

The U.S. Tier 2 Gasoline Sulfur program, phased in from 2004-2007 allows refiners to produce gasoline with a range of sulfur levels as long as their annual corporate average does not exceed 30 ppm S. In addition, no individual batch can exceed 80 ppm.

10 ppm S gasoline became available in the EU and Japan from 2005 and is now the only market gasoline available.

6.0 NOx REDUCTION TECHNOLOGIES

Lean-burn Gasoline Direct Injection Engines operate with air-fuel mixtures containing excess air, rather than at stoichiometry. As with diesel engines, the oxygen-rich combustion environment in a gasoline engine, in combination with high combustion temperatures, results in the formation of nitrogen oxides (NOx) in the combustion process. The higher level of oxygen in the exhaust means, however, that it is not possible to directly use a TWC to control NOx, because the oxygen content does not allow the appropriate chemical reactions to occur. Therefore, a new set of technologies have been developed by exhaust emission control manufacturers to significantly reduce NOx in oxygen-rich exhaust streams. Below is a brief overview of the types of technologies that have been developed and commercialized to reduce NOx. Most commonly, at present, NOx adsorber catalysts are used in passenger car and light-duty applications of lean-burn gasoline engines.

6.1 NOx ADSORBER CATALYSTS

NOx adsorber catalysts, also known as Lean NOx Traps (LNT), provide a catalytic pathway for reducing NOx in an oxygen rich exhaust stream.

6.1.1 Operating Characteristics and Performance

NOx adsorber technology removes NOx in a lean (i.e. oxygen rich) exhaust environment for both gasoline lean-burn direct injection and diesel engines. The mechanism involves (see **Figures 7** and **8**):

1. Catalytically oxidizing NO to NO_2 over a precious metal catalyst.
2. Storing NO_2 in an adjacent alkaline earth oxide trapping site as a nitrate.
3. The stored NOx is then periodically removed in a two-step regeneration step by temporarily inducing a rich exhaust condition followed by reduction to nitrogen by a conventional TWC reaction.

***Figure 7**:* NOx trapping mechanisms under lean operating conditions

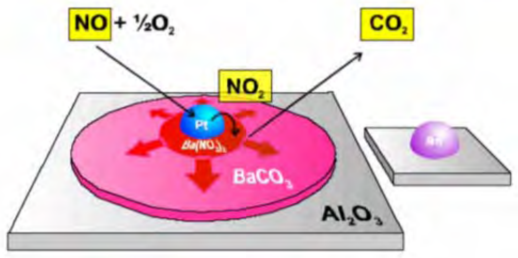
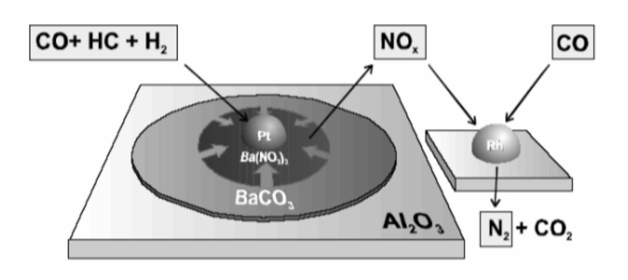


***Figure 8**:* NOx trap regeneration occurs under brief periods of rich operation



As discussed above, under normal lean engine operation, the NOx adsorber stores the NOx emissions. In order to reduce the trapped NOx to nitrogen, called the NOx regeneration cycle, the engine must be operated rich periodically for a short period of time (a few seconds). This cycling is also referred to as a lean/rich modulation. The rich running portion can be accomplished in a number of ways including:

- Intake air throttling
- Exhaust gas recirculation
- Post combustion fuel injection in the cylinder
- In-exhaust fuel injection

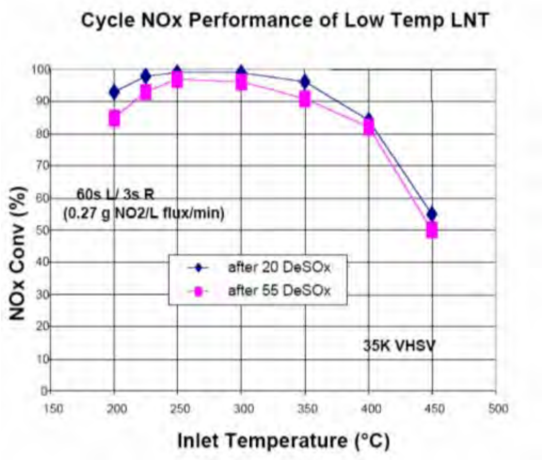
The importance of an engineered systems approach when designing an emission control system using NOx adsorber technology cannot be underestimated. Conversion efficiency of up to 90 percent is achievable over a broad temperature range and the NOx efficiency can be directly impacted by changing the lean/rich modulation of the cycle. LNTs can achieve even higher NOx reduction (>90 percent) when regenerated with on-board generated hydrogen via a fuel reforming reaction over an appropriate catalyst.

The emission control industry continues to invest considerable efforts in further developing and commercializing NOx adsorber technology. Specifically, formulations and on-vehicle configurations that improve low temperature performance and sulfur removal at lower temperatures. Advanced storage components have resulted in lower light-off temperatures and wider operating windows for NOx conversion.

6.1.2 Impact of Fuel Sulfur and Durability

The same compounds that are used to store NOx are even more effective at storing sulfur as sulfates, and therefore NOx adsorbers require ultra low sulfur fuel. The durability of LNTs is linked directly to sulfur removal by regeneration and is a major aspect of technology development. Sulfur is removed from the trap by periodic high temperature excursions under reducing conditions, a procedure called “DeSOx”. The DeSOx regeneration temperatures are typically around 700°C and require only brief periods of time to be completed. However, the washcoat materials and catalysts used in these technologies begin to deactivate quickly above 800°C and therefore methods are being developed to reduce the desulfation temperature. **Figure 9** shows how the NOx conversion window is impacted following numerous sulfation/desulfation cycles. Advanced thermally stable materials have allowed LNTs to achieve durability over their full useful life.

***Figure 9**:* Durability of advanced LNTs can be maintained over many high temperature desulfation cycles



6.1.3 Application of NOx Adsorber Technology

NOx adsorber technology is also being applied to gasoline vehicles powered by gasoline direct injection engines and the results are impressive. In fact, a number of vehicle manufacturers have commercially introduced NOx adsorber catalysts on some of their models powered by lean-burn gasoline engines in both Europe and Japan.

6.2 SELECTIVE CATALYTIC REDUCTION (SCR)

SCR has been used to control NOx emissions from stationary sources such as power plants for over 20 years. More recently, it has been applied to diesel-powered mobile sources including cars, trucks, marine vessels, and locomotives. Although it offers higher levels of efficiency, SCR is more complex than LNT and is not currently used for lean-burn GDI engines, although it remains one possible technique for this application.

SCR offers a high level of NOx conversion with high durability. Open loop SCR systems can reduce NOx emissions from 75 to 90 percent. Closed loop systems on stationary (diesel) engines have achieved NOx reductions of greater than 95 percent.

6.2.1 Operating Characteristics and Control Capabilities

An SCR system uses a metallic or ceramic wash-coated catalyzed substrate, or a homogeneously extruded catalyst, and a chemical reductant to convert nitrogen oxides to molecular nitrogen and oxygen. In mobile source applications, an aqueous urea solution is the preferred reductant. In open loop systems, the reductant is added at a rate calculated by a NOx estimation algorithm that estimates the amount of NOx present in the exhaust stream. The algorithm relates NOx emissions to engine parameters such as engine revolutions per minute (rpm), exhaust temperature, backpressure and load. As exhaust and reductant pass over the SCR catalyst, chemical reactions occur that reduce NOx emissions. In closed loop systems, a sensor that directly measures the NOx concentration in the exhaust is used to determine how much reductant to inject.

SCR catalysts formulations based on vanadia-titania and base metal-containing zeolites have been commercialized for both stationary and mobile source diesel applications. The maximum NOx conversion window for SCR catalysts is a function of exhaust gas composition, in particular the NO_2 to NO ratio. The three common NOx reduction reactions are:

$$4\ NH_3 + 4\ NO + O2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (1)$$

$$2\ NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O \qquad (2)$$

$$8\ NH_3 + 6\ NO_2 \rightarrow 7\ N_2 + 12\ H_2O \qquad (3)$$

6.2.2 Impact of Fuel Sulfur and Durability

Like all catalyst-based emission control technologies, SCR performance is enhanced by the use of low sulfur fuel.

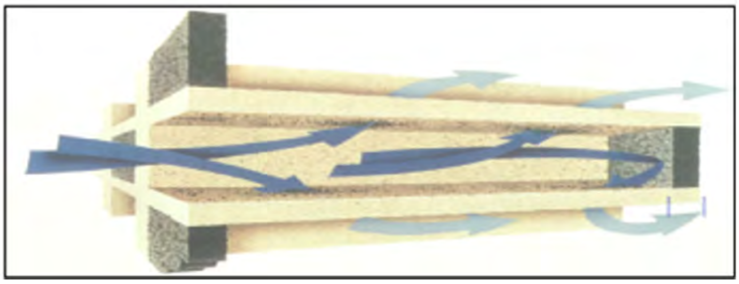
7.0 PARTICULATE FILTRATION

In Europe, diesel vehicles equipped with high efficiency diesel particulate filters to reduce PM and PN emissions have been offered commercially since 2000. Ultrafine particles, that is, those having an aerodynamic diameter of greater than 23nm, can also be measured from gasoline engines and the PN concentration is generally higher for GDI engine technology compared to Multi-Point Fuel Injection (MPFI) engine technology [8]. The low PM and PN emissions of PFI gasoline engines mean that particulate filters are not required for these engines, but the EU has introduced limits on PN emissions from GDI engines from 2014 [1]. The technologies to be used to meet the limits have yet to be announced by the automobile industry, but one possibility is gasoline particulate filters (GPFs) similar to the diesel particulate filters (DPFs) that are already in use.

7.1 HIGH EFFICIENCY FILTERS

In the most common type – wall-flow filters – PM is removed from the exhaust by physical filtration using a honeycomb structure similar to an emissions catalyst substrate but with the channels blocked at alternate ends. The exhaust gas is thus forced to flow through the walls between the channels and the PM is deposited as a soot cake on the walls. Such filters are made of ceramic honeycomb materials, typically cordierite, silicon carbide or aluminium titanate. **Figure 10** simplifies the operation of a wall-flow particulate filter.

***Figure 10**:* Exhaust gas flow through a wall-flow filter channel



Ceramic wall-flow filters remove almost completely the carbonaceous and metallic particulates, including fine particulates of less than 100nm diameter with an efficiency of >95% in mass and >99% in number of particles over a wide range of engine operating conditions. Wall-flow filters exhibit high strength and thermal durability.

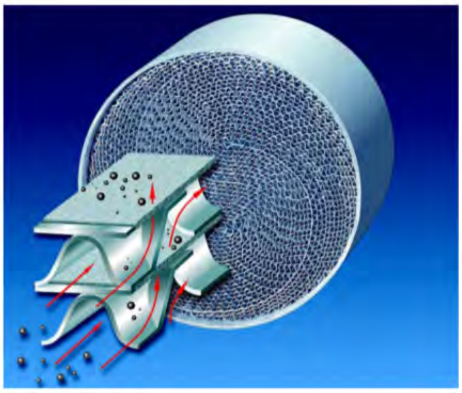
7.1.1 Operating Characteristics and Filter Regeneration

As the name implies, particulate filters remove PM by filtering the engine-out exhaust. Since a filter can fill up with soot over time, filter systems must be designed to periodically burn off or remove accumulated PM. The only practical method of disposing of accumulated PM is to burn or oxidize it within the filter when exhaust temperatures are sufficiently high. By burning off trapped material, the filter is cleaned or ‘regenerated’. Filters that use available exhaust heat for regeneration are termed ‘passively regenerated’ filters. Filters that use some kind of energy input, like injection of fuel into an upstream DOC, are termed ‘actively regenerated’ filters. Active regeneration strategies employ various engine controls to achieve filter regeneration conditions on demand.

7.2 PARTIAL FLOW PARTICULATE FILTERS

Partial-flow filters normally use a metallic substrate. The metallic partial-flow filter typically uses a special perforated metal foil substrate with a metal 'fleece' layer so that the exhaust gas flow is diverted into adjacent channels and the particles are temporarily retained in the fleece before being burnt by a continuous reaction with the NO_2 generated by an oxidation catalyst located upstream in the exhaust. It offers an option for reducing PM emissions by 30-80% depending on filter size and operating conditions [9,10].

***Figure 11**:* Metallic partial flow filter made up of corrugated metal foil and layers of porous metal fleece



7.3 IMPACT OF SULFUR ON PARTICULATE FILTERS

Sulfur in fuel affects the reliability, durability, and emissions performance of catalyst-based particulate filters. Sulfur affects filter performance by inhibiting the performance of catalytic materials upstream of or on the filter. Sulfur also competes with chemical reactions intended to reduce pollutant emissions and creates PM through catalytic sulfate formation. Catalyst-based particulate filter technology works best when the fuel sulfur level is less than 15 ppm. In general, the less sulfur in the fuel, the better the technology performs.

8.0 EFFECTS OF GASOLINE COMPOSITION ON EXHAUST EMISSIONS

Published studies on the effects of gasoline composition, including oxygenates, on exhaust emissions usually cover the following topics:

- Regulated exhaust emissions from vehicles comprising CO, HC, Volatile Organic Compounds (VOCs), NOx, PM, and PN[2];
- Unregulated exhaust emissions, including changes in benzene emissions, and emissions of various aldehydes and 1,3-butadiene; and
- Evaporative emissions of VOCs from the vehicle's fuel system.

The quantitative measurement of hydrocarbons and particles from vehicles is a complicated and specialized task because there are a wide range of pollutants emitted and the quantities of these pollutants from modern gasoline vehicles are now very small. European legislation requires HC emissions to be measured as Total Hydrocarbon Content (THC) while, in the U.S., they are regulated as Non-Methane Organic Gases (NMOG). The NMOG measurement does not include methane which can be an important fraction of the total HC exhaust emissions. In addition, the regulatory driving cycles are different, hence, European and U.S. emissions standards are not directly comparable.

While gasoline composition has some impact on vehicle emissions, the main effect of oxygenates on engine operation is to make the AFR of the injected air-fuel mixture leaner. This is because the oxygen in the ethanol (or other oxygenate) molecule increases the oxygen concentration in the air-fuel mixture. A 10% v/v ethanol/petrol blend contains about 3.7% m/m oxygen which is sufficient to alter the AFR and the combustion process. The effect, however, depends on the sophistication of the engine and aftertreatment technology which was arbitrarily defined in **Figure 1**.

Gasoline vehicle emissions can be affected by the composition of the gasoline fuel as well as by the engine and aftertreatment performance. However, there are many factors that make it especially difficult to draw robust yet simple conclusions from this extensive literature. These factors include, for example, changes over time in the emissions capabilities of test engines and vehicles; differences in research objectives; the frequently small number of vehicles or engines evaluated in a given study; differences in test cycles and measurement equipment; differences in fuel compositions; and a general lack of orthogonality among critical test variables.

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[2] PN emissions are considered to be a regulated exhaust emission because they will be included in European Euro 6b emissions regulations from 2014 for light-duty direct injection spark ignition vehicles.

At the same time, gasoline specifications have continuously changed to enable new engine and aftertreatment technologies, with the most significant change being the introduction of low-sulphur and sulphur-free gasoline and the use of oxygenated components, like ethanol and ethers. These oxygenates affect vehicle emissions and can easily mask the effects due to changes in gasoline composition in the same vehicle and aftertreatment combination. Thus, making definitive statements about the effects of fuel composition on emissions performance is a complicated task.

One of the most thorough evaluations of these effects was performed in the mid-1990’s as part of the European Programme on Emissions, Fuels, and Engine Technologies (EPEFE) [11]. This study, conducted jointly by the European auto and oil industries, confirmed that both fuels and engine technologies are important determinants of vehicle emissions performance and important relationships exist among fuel properties, engine technologies, and exhaust emissions. For gasoline fuels, the main fuel parameters investigated were sulphur content, distillation, and aromatics content and special fuel blends were created to separate the effects of these compositional parameters on emissions.

The test vehicles and engines were selected in order to reflect the wide range of engine types that were commonly used in Europe in the mid-1990’s. The vehicles selected for the study were equipped with state-of-the-art emissions reduction technologies including close-coupled catalysts. All of the gasoline vehicles exceeded the 1996 emissions limits. A strictly applied and repeatable testing and measurement protocol was used in order to reduce statistical variability.

The study concluded that reducing the gasoline’s sulfur content generally reduced the HC, CO, and NOx emissions over several driving cycles including the European reference. The effects of distillation and aromatics were more complex and generally larger than observed for changes in the sulfur content. For example, reducing the aromatics content tended to reduce the HC and CO emissions but increased the NOx emissions over the European regulatory cycle. Many effects depended on the driving cycle that was used and the test design and the orthogonality of fuel properties were instrumental in allowing the effects of fuel properties to be differentiated across the vehicle fleet.

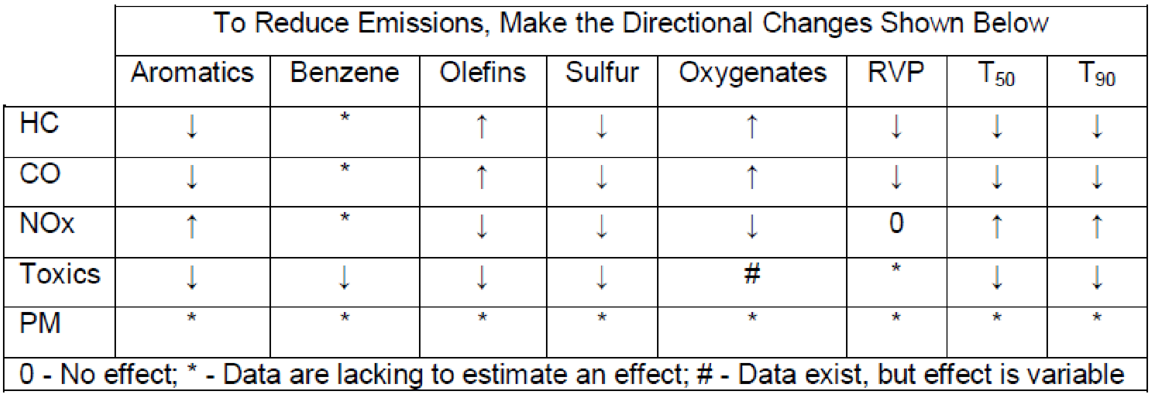
In spite of these observations, the EPEFE study provided detailed and statistically relevant information that was used as a technical basis for future policy decisions for fuels, vehicles, and emissions. The relationships developed from the EPEFE data were considered to be valid within the broad range of parameters and protocols used in the study but the authors cautioned that '*great care must be taken in extrapolating the results*' to other vehicle and aftertreatment technologies.

Clearly, this study represented a benchmark in providing internally consistent and robust information. Unfortunately, this is not always the case when one attempts to compare results from different and unrelated studies published in the peer-reviewed literature. We can assume that the results in one published study are valid but extending the interpretation of these results to another study conducted by another research group is complex.

Recognising these difficulties, extracting information from the full body of published literature is an approach that has been completed in the past. Koehl et al. [12] published a review of the published literature covering work up to 1989 on the effects of gasoline composition on vehicle emissions and Hochhauser [13] published a similar review in 2009.

The latter review was commissioned by the US CRC and covers results from 130 references on on-road and off-road vehicles. Because this reference is recent, well-referenced, and peer-reviewed, it is sufficient here to summarise the key observations that were reported in the review (**Table 1**). It should be emphasized, however, that these directional changes are not straightforward and may be complicated by the diversity of vehicles, aftertreatment systems, fuels, test procedures, and the lack of orthogonality among different test variables.

Table 1: Directional changes in gasoline composition and their impact on vehicle emissions [13]



	To Reduce Emissions, Make the Directional Changes Shown Below							
	Aromatics	Benzene	Olefins	Sulfur	Oxygenates	RVP	T_{50}	T_{90}
HC	↓	*	↑	↓	↑	↓	↓	↓
CO	↓	*	↑	↓	↑	↓	↓	↓
NOx	↑	*	↓	↓	↓	0	↑	↑
Toxics	↓	↓	↓	↓	#	*	↓	↓
PM	*	*	*	*	*	*	*	*
0 - No effect; * - Data are lacking to estimate an effect; # - Data exist, but effect is variable								

Since the elimination of tetra-ethyl lead (TEL) from gasoline in major markets in the 1980's and 1990's, sulfur is the most important property of gasoline from an exhaust emissions perspective because of its impact on the performance of TWCs and other components (see **Sections 6.1.2**, **6.2.2**, and **7.3**).

Numerous studies on modern vehicles show that reducing sulfur also reduces HC, CO, and NOx emissions. The reduction in these emissions is essentially linear for sulfur contents less than about 150 ppm. Similar reductions in benzene and emissions of 1,3-butadiene have also been reported while the impact of sulfur on emissions of formaldehyde and acetaldehyde are less certain.

Changes in gasoline composition beyond sulfur have also been investigated in numerous studies and the effects of composition and gasoline volatility are summarized in **Table 1**.

8.1 EFFECTS OF OXYGENATES IN GASOLINE

The addition of oxygenates into gasoline also has an impact on vehicle exhaust and evaporative emissions to the atmosphere [14]. These emissions may impact air quality and atmospheric chemistry but these issues are considered to be beyond the scope of this report. This assessment focuses primarily on recent published studies (1990 onwards) that highlight the effect of oxygenates on gasoline vehicle exhaust and evaporative emissions.

Several oxygenates are commonly used in gasoline, depending upon their cost, availability, and environmental performance. In Europe, ethanol and ethers, primarily Ethyl t-Butyl Ether (ETBE) and Methyl t-Butyl Ether (MTBE), are commonly used while ethers are no longer used in the United States. Other ether types, such as t-Amyl Methyl Ether (TAME), and other oxygenates, such as n-butanol, are being developed but are not widely used today.

Although ethanol and ethers have different molecular and volatility properties, their impact on vehicle exhaust emissions do not depend substantially on the oxygenate type. In studies where composition and gasoline volatility were carefully controlled, adding low levels of oxygenates to gasoline tended to reduce HC and CO emissions and increase NOx emissions. Oxygenates also tend to increase emissions of some unregulated emissions, such as aldehydes. More details on these effects are presented below. The following discussion focuses primarily on the effects of low-level blends of ethanol in gasoline and highlights effects that may be more specific to ethers or other oxygenate components where appropriate.

The evaluated studies are not comprehensive but cover sufficient studies to infer directional trends due to the impact of ethanol. A ‘weight of evidence’ approach was used to draw conclusions on this literature based on the relative change in performance between hydrocarbon-only gasoline and ethanol/gasoline blends containing less than about 20% v/v ethanol. That is, general trends have been inferred from the relative changes in emissions from published studies even though the absolute emissions levels and details regarding the vehicles, fuels, and driving cycles may be different from one study to another.

8.2 OXYGENATES AND REGULATED EXHAUST EMISSIONS[3]

There have been many studies over the years to assess the effects of low concentration ethanol blends on exhaust emissions. The main studies are summarised in **Table 2**, which shows the average percentage change in emissions found for different vehicle technology categories. Clearly, there is a wide variation in results and it is not possible to directly compare studies carried out by different groups, because the vehicles, test cycles, and ethanol/gasoline blends are all somewhat different.

The published studies typically measure percentage changes for 5 to 10% v/v ethanol in gasoline on emissions although a few studies have tested gasoline blends containing up to 20% v/v ethanol. All of the observed changes in **Table 2** are expressed as a percentage of the baseline emissions in the same study. The absolute emissions varied from one study to the next depending upon the emission standard and the four categories of engine technology shown in **Figure 1**.

The effect of ethanol in gasoline on the regulated exhaust emissions from vehicles strongly depends on the sophistication of engine and aftertreatment (catalyst) technologies. For example, for non-catalyst vehicles (Category 1), ethanol substantially reduces CO emissions with smaller reductions in HC emissions, as shown in particular by the older Australian Orbital studies [1-11,1-12]. At the same time, ethanol in gasoline substantially increases NOx compared to a similar hydrocarbon-only gasoline by about 10% in Category 1 vehicles.

For early catalyst vehicles (Category 2) tested on ethanol/gasoline blends, similar percentage changes in emissions have been reported. In general, CO emissions are reduced by about 10-20% while HC or Non-Methane Organic Gases (NMOG) are reduced by about 5-10%. The NOx emissions generally increase but with a wider variation, usually between 5 and 30%. One Australian study [1-12], however, showed greater effects of ethanol on regulated emissions after the vehicle had acquired 80,000 km of test mileage. The study concluded that this was due to higher catalyst operating temperatures on ethanol blends which increased the deterioration of the aftertreatment catalyst over time. This is a potentially important finding and similar work is in progress in the US to reproduce this finding on fuels containing up to 20% v/v ethanol in gasoline.

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[3] References for **Section 8.2-8.5** can be found in **Appendix 1**

For advanced catalyst (Category 3) vehicles, the effects of ethanol are generally (but not always) smaller and more variable and usually show the same directional change. Clearly absolute effects will be much lower for these modern low-emissions vehicles but it is surprising that significant effects of ethanol are still seen for some modern vehicles with advanced Engine Management Systems (EMS). However, most of the emissions occur during cold start before the catalyst has warmed up to operating temperature, and with the electronic control system in “open loop” mode.

There are comparatively little data available in the published literature on new DISI (Category 4) vehicles and ethanol-containing fuels [1-23,1-43]. Although the results are limited on this new technology, the studies appear to give broadly similar results on DISI vehicles compared to previously tested Category 3 vehicles.

Table 2: Summary of literature studies: effect of ethanol in gasoline on regulated exhaust emissions (These references can be found in **Appendix 1**.)

				Vehicles		% Change in Exhaust Emissions			
Programme	**Reference**	**Year**	**Fuel**	**Number**	**Technology Category**	**CO**	**THC**	**NMOG**	**NOx**
AQIRP Auto/Oil (USA)	1	1990	10%S	20 USA (1989)	2	-13.4	-	-4.9	5.1
US EPA	29	1994	10%M	36 USA – 20 Normal	2	-8.6	-7.3	-	5.7
				16 (1986-1990) - 16 High E		-25.3	-19.3		NS
US EPA	30	1994	10%M	39 USA – 27 Normal	2	-7.3	NS	-	NS
				12 (1986-1990) - 12 High E		-12.1	NS		NS
CARB Study	4	1998	10%S	12 USA (1991-1995)	3-Feb	-7	8	8	17
Toyota Study	5	2000	9%S	9 LEV/ULEVs USA	3	-6	-	-0.3	5.5
US EPA & Alaska Study	3	1998	10%(S)	11 USA (1977-1994) at – 24°C	2-Jan	-21	-14	-	-5
				3 USA (1988-1994) at -7°C		-8	-7		-1
				11 USA (1977-1994) at -21°C		-27	-24		-6
				11 USA (1977-1994) at -41°C		-17	-14		6
Thailand Petroleum Authority	31	1999	(7.5) 15(M)	5 Catalyst (1994-1996)	2	-32	-6		15
				1 Non-catalyst (1993)	1	-9	NS		12
AEAT study for UK DTLR (special cycles)	6	2002	10%S	5 EURO 3	3	-20.8	?	-	NS
Swiss EMPA study	7	2002	5%S	1 EURO 3	3	-7	-8.4	-	14.3
Shell Study	8	2002	5, 10%M	3 EURO 3 5%	3	-7	NS	-	28
				10%		-21			42
ADEME Study	10	2003	5, 10%S	3 MPI EURO 3	3	?	?		?
				1 DISI EURO 3					
Orbital Engine Company (Australia)	11	2003	20%	5 New (2002) Urban	2	-29	-30		48
				5 New (2002) Highway	2	-48	-25		unclear
				4 Old (1985-1993) Urban	1	-70	-4		9
				4 Old (1985-1993) Highway	1	-76	-10		10
Orbital Engine Company (Australia)	12	2004	20%	2x5 (2001) New Australia 80,000km	2	-13	-12		30
					2	19	33		82
IDIADA Study	13	2003	5-10%	1 2003 Euro 3	3	-6	-13	-	0
Fortum Study	14	2004	10%M	10 1999 – 2002	3	NS	NS		NS
			vs ETBE	EURO 3					
Westerholm, Egeback, Rehnlund, Henke	*17*	*2004*	*Up to 15%*	Review of various studies		*NS*	*NS*	*NS*	*NS*
Niven (Australia)	18	2005	10, 85	Review of previous studies		↓	↓	↓	↑
Coordinating Research Council (US CRC) E67	19	2006	5, 7, 10	12 CA USA LEV-SULEV	3	-6 to	NS	14	NS
						-18[1]			+5-12[1]
Environment Canada Study	21	2002	10, 15, 20	5 (1999-2001)	3-Feb	NS		NS	??
						-12 to -49		NS	
Environment Canada Study	22	2006	10, 20	3 (1998–2003) at 20°C	3	-15 to -73	**	**	-77
				1 DISI (2000) at 20°C	4	-3 to -55	-35	-39	+???
				3 (1998–2003) at -10°C	3	?	**	**	-145
				Overall statistical analysis		-16	9	14	NS

NOTES:
10%S = 10% v/v ethanol splash blend
10%M = 10% v/v ethanol matched volatility
NS = not significant
1. depends on volatility, T50 and T90
**** THC increased with 10% ethanol, decreased with 20% ethanol**
? Results variable, difficult to interpret

8.3 OXYGENATES AND UNREGULATED EXHAUST EMISSIONS

The US EPA classifies a number of organic compounds as ‘air toxics’: benzene, formaldehyde, acetaldehyde, 1,3-butadiene and polycylic organic matter (POM). In US regulations, vehicle emissions of these air toxics are not directly regulated but are controlled through fuel specifications (by means of the so-called ‘simple’ and ‘complex’ models). There have been a number of studies that have measured the exhaust emissions of these compounds. POM, however, is not easily defined and has generally not been measured in great detail.

Many studies on unregulated emissions have now been completed and the results vary substantially as shown in **Table 3**. However, the same “weight of evidence” approach can be used to draw some general conclusions from the reported results.

Benzene emissions are generally reduced with ethanol blends. Engine-out benzene has been shown to originate almost entirely from unburned benzene and from partially burned aromatics in the fuel. Ethanol normally reduces the gasoline’s aromatics content. This can occur either by simple dilution for splash blends or by reblending the base gasoline to take advantage of ethanol’s high octane blending number. Reblending can have a substantially larger impact on benzene emissions than simple dilution. The CRC [1-19] and Environment Canada [1-22,1-23] studies showed somewhat higher benzene emissions although the test fuels used in these studies were blended to have essentially constant benzene and aromatics levels. In the Environment Canada studies, benzene and aromatics levels of the summer grade ethanol blends were much higher than for the base gasoline.

1,3-butadiene emissions are either unaffected or are reduced with ethanol/gasoline blends. Again, there are exceptions such as the CRC study and the Environment Canada study which showed a significant increase in 1,3-butadiene emissions with ethanol/gasoline blends. For the CRC study, this was consistent with the 14% increase in NMOG (see **Table 2**). It should be noted, however, that these results only apply to fuels with high T90E levels. There is no clear explanation for the Environment Canada study results, which were variable and generally not statistically significant.

Formaldehyde emissions have usually been shown to be unaffected by ethanol content. This is not surprising because formaldehyde is not a partial combustion product of ethanol. Acetaldehyde however is easily formed by partial combustion of ethanol, so very substantial increases in acetaldehyde emissions have been seen at up to a factor of 10 higher values with moderate concentrations of ethanol in gasoline. However, this is one case where percentage changes can be misleading because mass emissions of acetaldehyde are very low for modern catalyst vehicles (Technology Categories 3 or 4 shown in **Figure 1**). Levels are well below 1 mg/mile, over the full emissions test cycles, and essentially zero once the catalyst is fully warmed up.

Not surprisingly, unburned ethanol emissions also increase, however, emission levels from hydrocarbon-only fuels are essentially zero so large percentage increases can be misleading. Emission rates from modern vehicles are of the order of a few mg/mile during cold start operation and well below 1 mg/mile once the catalyst has been fully warmed up.

Various other unregulated emissions have been measured in some studies, including higher aromatics, ammonia, acrolein and other aldehydes, nitrous oxide etc. However, no significant effects have been found except for aromatics which are generally reduced with ethanol for the same reasons as they are for benzene.

Table 3: Summary of effects of low concentrations of ethanol in gasoline on unregulated exhaust emissions (These references can be found in **Appendix 1**.)

				Vehicles		% Change in Exhaust Emissions				
Programme	Reference	Year	Fuel[1]	Number	Technology Category	Benzene	1,3-butadiene	formaldehyde	acetaldehyde	Ethanol
AQIRP Auto/Oil Study (USA)	1	1990	10%S	20 USA (1989)	2	-11.5	-5.8	19	159	-
US EPA and SWRI	28	1990	10%M	5 USA (1974-1990)	2-Jan	↓	NS	NS	↑	-
US EPA	29	1994	10%M	36 USA – 19 Normal	2	-27.2	No report	NS	89	
				(1986-1990) - 15 High E		-42.4		NS	138	
US EPA	30	1994	10%M	39 US – 27 Normal	2	-29.4	NS	NS	54	
				(1986-1990) - 12 High E		-36.3	NS	NS	64	
CARB Study	4	1998	10%S	12 US (1991-1995)	3-Feb	Total toxics +9%				
						Potency weighted toxics -1%				
US EPA & Alaska Study	3	1998	10%(S)	11 US (1977-1994) at – 24°C	2-Jan	-13.6	NS	NS	156	-
				3 US (1988-1994) at -7°C		-20.1			453	
				11 US (1977-1994) at -21°C		-26.5			261	
				11 US (1977-1994) at -41°C		-13.4			316	
Thailand Petroleum Authority	31	1999	(7.5) 15(M)	5 catalyst (1994-1996)	2	-1.7	NS	37	231	
				1 non-catalyst (1993)	1	-3.2	5.3	61	295	
AEAT Study for UK DTLR (special cycles)	6	2002	10%S	3 EURO 3	3	-	-27.6	NS	514	-
Shell Study	8	2002	5, 10%M	3 EURO 3 - 5%	3	-	-	-	100	-
				10%					230	
ADEME Study	10	2003	5, 10%S	3 MPI EURO 3	3	-	-	-	?	-
				1 DISI EURO 3	4					
Orbital Engine Company (Australia)	11	2003	20%	5 New (2002) Urban	2	-40	-??	NS	+~1000	-
				5 New (2002) Highway	2					
				4 Old 1985-93 Urban	1	-20	-15	NS	700	-
				4 Old 1985-93 Hway	1					
Orbital Engine Company (Australia)	12	2004	20%	2x5 (2001) Base Australia 80,000km	2	NS	NS	-60	250	-
						NS	NS	49	610	
IDIADA Study	13	2003	5-10%	1 2003 Euro 3	3	-13.6	-1.3	-68	-36	>+100
Coordinating Research Council (US CRC) E67 Project	18	2006	5, 7, 10	12 California LEV - SULEV	3	18	22	NS	73	-
Fortum Study	14	2004	10%M vs ETBE	10 EURO3 (1999–2002)	3	-22	-15	NS	180	
Westerholm, Egeback, Rehnlund, Henke	17	2004	Up to 15%	Review of various studies		↓	-	↑	↑↑	-
Niven (Australia)	18	2005	10, 85	Review of previous studies		↓	↓↑	↓↑	↑	↑↑
Environment Canada Study	22	2002	10, 15, 20	5 (1999-2001)	3-Feb					
Environment Canada Study	23	2006	10, 20	3 (1998–2003) at 20°C	3	?	?	+NS	-845	170
				1 DISI (2000) at 20°C	4	?	?	NS	+400+	300
				2 (1998–2003) at -10°C	3	?	?		108	>1000
				Overall Statistical Analysis		15	16	NS		-

NOTES:
10%S = 10% v/v ethanol splash blend
10%M = 10% v/v ethanol matched volatility
NS = not significant
1. depends on volatility, T50 and T90
**** THC increased with 10% ethanol, decreased with 20% ethanol**
? Results variable, difficult to interpret

8.4 OXYGENATES AND PARTICULATE EMISSIONS

PM exhaust emissions are increasingly a concern for human health but these emissions from gasoline engines are normally very low and difficult to measure. Somewhat higher PM emissions have been measured from DISI vehicles and ultrafine or nanoparticles (below 1 micron) can be produced in large numbers per km. These are normally counted as total or solid PN emissions rather than being weighed gravimetrically as are PM emissions.

A recent European study [1-32] showed that DISI vehicles produced 4–11 mg/km PM over the NEDC cycle while conventional gasoline vehicles produced much lower PM emissions (<3 mg/km), very near to the limit of reliable measurement for gravimetric methods. Over the same cycle, solid PN emissions were measured with an Electrical Low Pressure Impactor (ELPI) showing that diesel vehicles produced ~10^{14} particles/km while DISI vehicles were a factor of about 10-20 below this value. The PN emissions from conventional gasoline vehicles were at least two orders of magnitude (~10^{11} particles/km) lower than those from DISI vehicles and similar to diesel vehicles equipped with diesel particulate filters (DPFs). Unfortunately, this programme did not look at the effect of ethanol on particulates.

Several other studies have been carried out to determine the effects of ethanol on PM and PN emissions, as shown in **Table 4** and **Figures 12, 13,** and **14**. The overall conclusion from these limited studies is that both PM and PN emissions are reduced with ethanol blends. The Environment Canada study [1-23] did show some increases in both emissions but the results were quite variable as shown in **Figure 14**.

Table 4: Summary of effects of low concentrations of ethanol in gasoline on particulate exhaust emissions (These references can be found in **Appendix 1**.)

				Vehicles		% Change in Exhaust Emissions				
						PM	Particle Number			
Study	Reference	Year	Fuel*	Number	Technology Category	Filter	CPC^1 W/O TD^2	CPC With TD^2	ELPI^3	
EPA and Alaska Dept. Env. & Cons.	27	1997	10	EPA – 3 (1987-1994)	2	↓	-	-	-	
				5 (1977-1994)	2-Jan	↓				
AEAT Study for UK DTLR (special cycles)	6	2002	10%S	3 EURO 3	3	-39	See Fig 1	-	↓	-
EMPA Study (Switzerland)	7	2002	5%S	1 EURO 3	3	-	-8	-18		
Westerholm, Egeback, Rehnlund, Henke	17	2004	Up to 15%	1 (1985) Cat at 22°C	2	NS	-	-		
				-5°C		-11				
Fortum Study	14	2004	10%M vs ETBE	3 EURO3 (1999–2002)	3	-27 to -65	-	-	-	
Environment Canada Study	22	2006	10, 20	3 (1998–2003) at 20°C	3	↑NS	NS	-	NS	
				1 DISI (2000) at 20°C	4	↑	NS		NS	
				3 (1998–2003) at -10°C	3	↑NS	NS		NS	

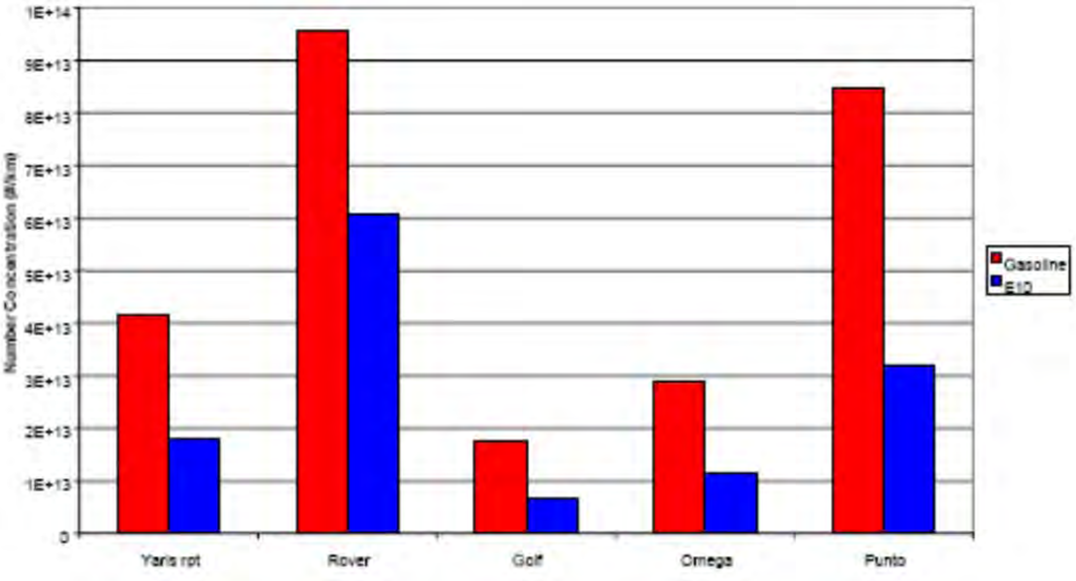
NOTES:

1. Condensation Particle Counter

2. Thermal Desorber

3. Electrostatic Low Pressure Impactor

Figure 12: PN emissions (measured with a CPC[4]) from gasoline and E10 gasoline over a cold start cycle (AEA [1-6])



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[4] Condensation Particle Counter

***Figure 13**:* PN emissions (measured with a CPC, both with and without a thermal desorber) on gasoline and E5 gasoline over the European NEDC (EMPA [1-7])

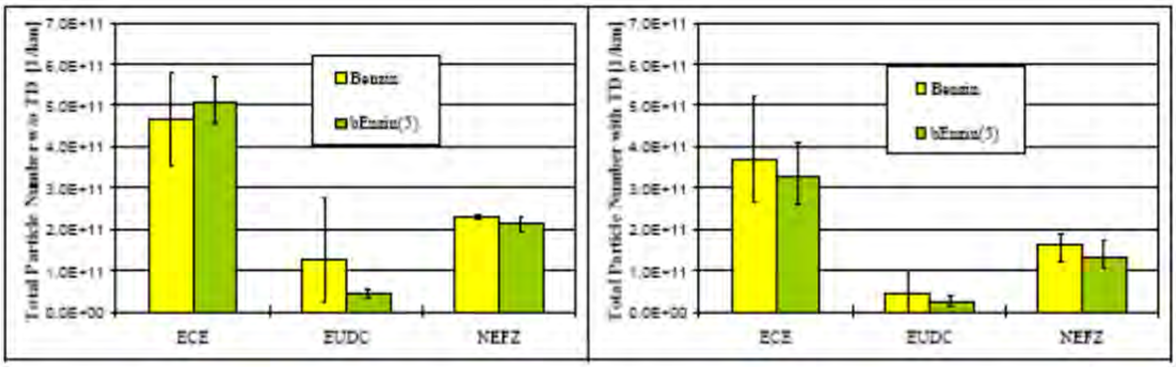
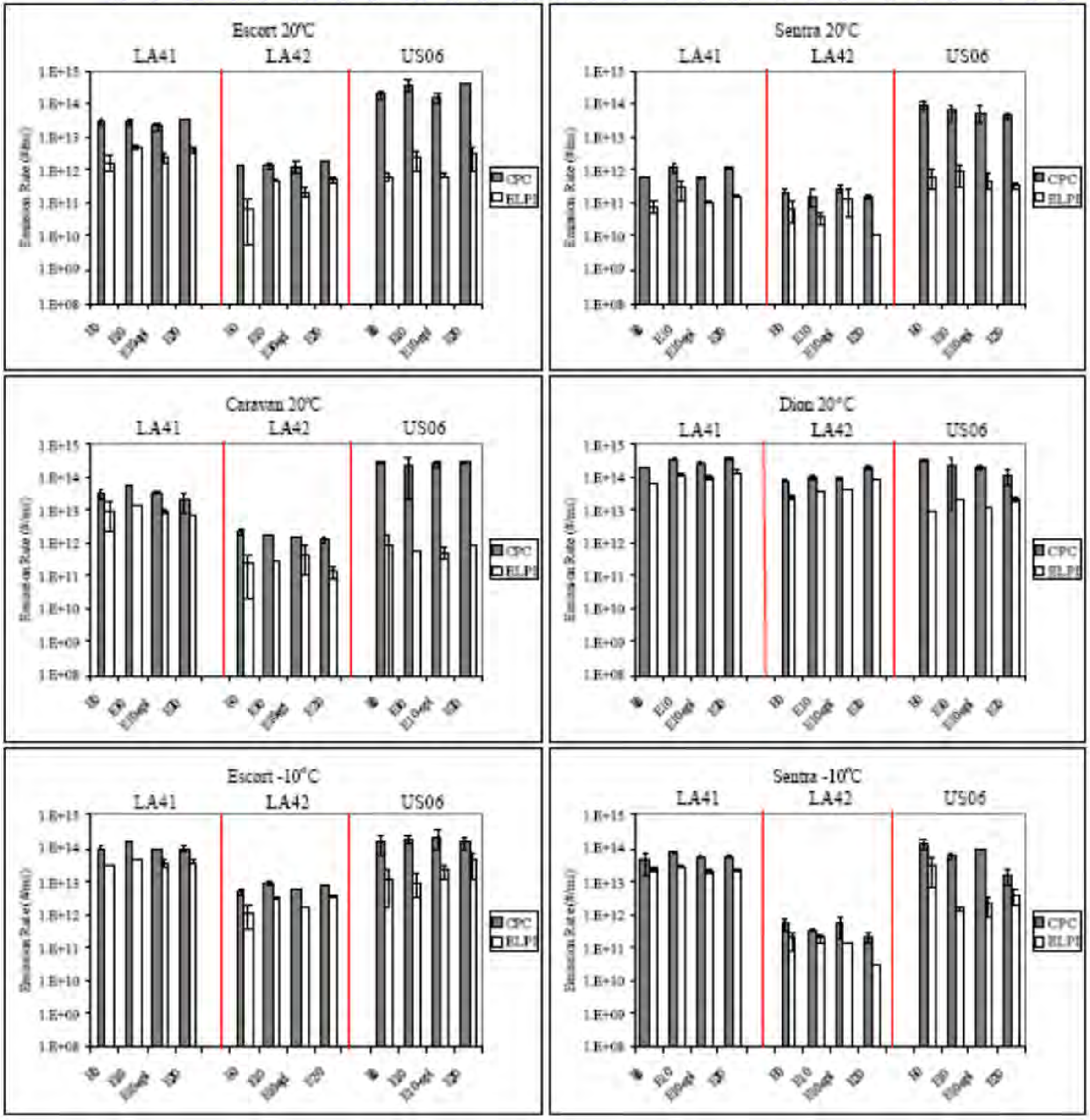


***Figure 14**:* Average PN emission rates measured using the CPC and ELPI ± 1 standard deviation (note: logarithmic scale) (Environment Canada [1-23])



8.5 OXYGENATES AND EVAPORATIVE EMISSIONS

The use of oxygenate/gasoline blends can affect several aspects of evaporative emissions and the effects are usually larger when ethanol is the oxygenate:

- Increased volatility of the blends, especially DVPE[5] and E70[6] if not controlled, will increase the amount of vapour that the evaporative control system must minimize.
- Compared to most hydrocarbon molecules in gasoline, ethanol has different adsorption and desorption characteristics on carbon canisters used for evaporative emissions control and may remain as a “heel” in the active carbon, reducing the working capacity of the carbon canister.
- Increase in the permeation of oxygenate and gasoline components through plastics and elastomers used in vehicle fuel systems.

These issues are considered in more detail below.

Vapour Generation

The mass of vapour generated will be different during normal driving (Running Losses), when the hot vehicle is resting after use (Hot Soak losses), and when the cold vehicle is resting overnight and experiencing atmospheric temperature fluctuations (Diurnal Emissions). The vapour generation will depend on the fuel system design, the permeability of the fuel system components, the fuel’s volatility, and the temperature. Evaporative control systems with carbon canisters must be designed to cope with this mass of vapour under all conditions.

Work done by CONCAWE [1-34] in the 1980s on vehicles without evaporative emission control systems showed that Reid Vapour Pressure (RVP) was the only fuel variable that significantly affected the mass of Hot-Soak and Diurnal emissions. A linear increase in evaporative emissions with increasing RVP was seen in this study but a subsequent study on cars with evaporative control systems [1-35] showed an exponential effect of both RVP and measurement temperature. Unfortunately, neither of these programmes tested ethanol blends although the first study did include methanol/t-butyl alcohol (TBA) and MTBE blends with matched volatility. Some tests showed no effect of oxygenates on evaporative emissions so that the conclusion was that only RVP was important. A second CONCAWE study [1-35] estimated vapour emissions from vehicles without canisters and from canister-

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[5] Dry Vapour Pressure Equivalent

[6] % of sample evaporated at 70°C

equipped vehicles from the late 1980s on a DVPE 93kPa gasoline at a 28°C measurement temperature:

	Hot Soak Emissions (g/test)	Running Loss Emissions(g/km)	Total Daily Loss* (g/day)
Uncontrolled cars	8.0	1.06	64.2
Controlled cars	0.9	0	3.1

*Total Daily Loss = 3.4*Hot Soak + 35*Running Loss

Diurnal emissions were not measured in this work, but other work has shown that they are the most important source of emissions for gasoline vehicles fitted with carbon canisters. In a recent test programme run at the EU's Joint Research Centre [1-36], total diurnal emissions were calculated from the weight gain of the carbon canister. The following results were obtained for one vehicle tested using the EU diurnal test procedure on a 60kPa fuel (A) and on two 5% v/v ethanol blends, one with matched volatility (A5E) and one prepared by splash blending (A5S).

Fuel	A	A5E	A5S
DVPE (kPa)	60.1	59.7	67.1
Ave. Diurnal Emissions (g/test)	18.8	21.5	22.8

In an extension of this programme [1-38], diurnal emissions up to 50 g/test were measured for higher volatility/temperature combinations but this work did not cover ethanol blends.

In the USA, a study in the 1980's [1-37] investigated emissions from gasoline/alcohol blends. The results showed that a gasoline blend with a methanol/TBA mixture gave lower mass hot soak and diurnal emissions than did a hydrocarbon-only gasoline even though both fuels had very similar distillation curves. A mathematical model of evaporation from fuel systems was developed that predicted this behaviour and showed that it was due to lower vapour pressures of oxygenated fuels at the test temperatures and the lower molecular weights of the vapours generated by these fuels. Increased emissions from gasoline/alcohol blends in other test programmes were shown to be due to their higher volatility. This work did not look at ethanol alone, although a methanol/ethanol blend was modelled. It is expected that ethanol blends would behave in the same way, however.

Thus it appears that the use of ethanol does not increase the mass of evaporative emissions for blends at the same volatility levels as hydrocarbon-only fuels. However, most ethanol blends are more volatile than hydrocarbon fuels and it is the increase in DVPE and front-end volatility due to splash blending that can increase the evaporative emissions.

Canister adsorption and desorption

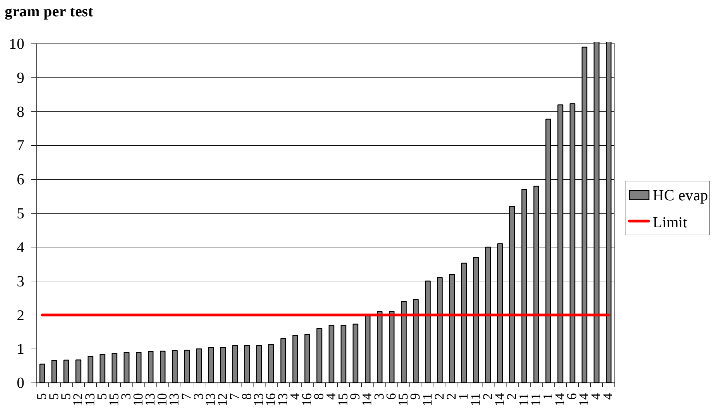
All modern vehicles are fitted with activated carbon canisters that are used to adsorb gasoline vapour emissions from the fuel system. These canisters must of course be designed with sufficient capacity to absorb all vapours generated during normal vehicle operations, and include a purging system to draw these vapours into the engine and burn them. However, the “working capacity” of a canister is only around 40–50% of its total equilibrium absorption capacity and depends on the canister design and purge conditions. A ‘heel’ of material that cannot easily be desorbed from the carbon canister can accumulate over a few operating cycles. Larger hydrocarbon molecules are less easily desorbed so the average molecular weight of the heel increases over time. For a typical one litre carbon canister, this heel of adsorbed material is about 60-90g with a working capacity of 50-60g of vapour. The canister working capacity must be adequate to adsorb all hot soak and diurnal emissions and, if this is not the case, then vapour “breakthrough” can occur and the excess fuel vapour will be emitted to the atmosphere.

Ethanol is more easily adsorbed on activated carbon than butane and other hydrocarbons. For this reason, it has been suggested that an ethanol heel may build up significantly reducing the canisters working capacity. Work by Grisanti et al. [1-2] showed that there were increased levels of ethanol in the breakthrough vapour from canisters, and a longer time to achieve breakthrough. However, recent work by Clontz et al. [1-39] on modern activated carbons showed that ethanol is easily desorbed even though it is more readily absorbed than butane. Subsequent aging tests showed no significant loss of the canister’s working capacity over 500 load/purge cycles.

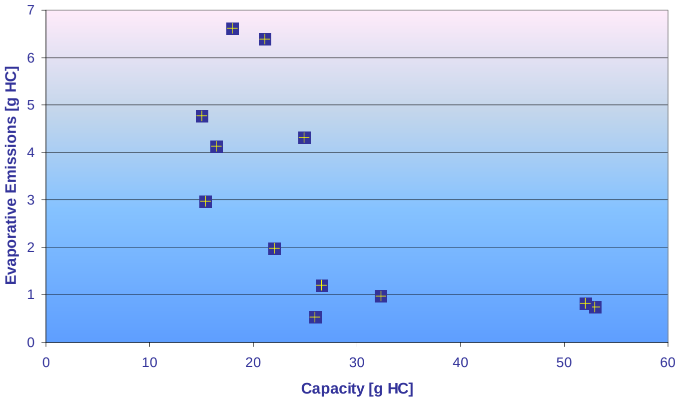
A JEC Consortium study [1-36] on the effect of ethanol on evaporative emissions did not reach clear conclusions on this question due to problems with the test procedure. It was observed that there was a clear effect of DVPE but not of ethanol as such on evaporative emissions. The canister conditioning procedure used for this programme allowed the canister weight to build up from test to test, which may have been due to increased hydrocarbon loading or a build-up of ethanol.

Thus, although ethanol is more easily adsorbed, it does not appear to build up a long term heel on the carbon canister. In-service testing in Sweden [1-40], however, has shown reduced working capacity of canisters on vehicles that fail the evaporative emissions test, which may be due to the use of ethanol blends in Sweden (see **Figure 15**). Of the 50 vehicles tested between 2002 and 2005, 40% (20 vehicles) exceeded the EU evaporative emissions limit value of 2g/test. This can be compared to the results from a similar German study where only 2 of the 19 vehicles tested (10%) failed the evaporative emissions test. The difference was thought to be due to the ethanol content that was in market fuels in Sweden and Germany at the time of the studies.

***Figure 15**:* In-service evaporative emissions testing on Swedish cars 2002-5 [1-40]



Capacity of the carbon canister affects the evaporative emissions



Permeation

Historically, fuel tanks, lines and carburettors were made of metal, with only a few flexible hoses to connect them, so fuel permeation was not an issue. In modern vehicles, however, fuel tanks are more commonly made from high-density polyethylene (HDPE), and the fuel lines and other components are made from a range of plastics and flexible elastomers.

Hydrocarbons can permeate through polymers and elastomers because permeation is a function of the solubility of the molecule in the polymer and its diffusion rate through the polymer, which is driven by the concentration gradient. The size and shape of the molecule is important because smaller molecules can pass more easily through the ‘spaces’ between polymer molecules.

Thus straight chain molecules are expected to permeate more rapidly through polymeric materials than branched chain or cyclic molecules. Although neat ethanol has relatively low solubility in HDPE, ethanol in gasoline mixtures has much higher solubility because gasoline components can increase the permeation of both ethanol and gasoline components through the polymer.

Modern fuel systems are increasingly manufactured from newer polymers that are compatible with higher ethanol concentrations. Fuel hoses are often composite materials with a fluorocarbon inner layer to control permeation and a polymeric outer layer to give greater flexibility. Fuel tanks are typically made from HDPE to facilitate molding and reduce vehicle weight but with multiple internal layers of another polymer in contact with the fuel to control permeation.

Overall Effect on Evaporative Emissions

A number of studies looked at the overall effect of ethanol blends on vehicle evaporative emissions, including all the effects described above. Only the major studies are reviewed here.

The 1992 US AQIRP programme [1-1] looked at the effect of RVP and 10% ethanol on ten 1989-model US vehicles equipped with activated carbon canisters. The study showed that splash blending of ethanol increased the diurnal emissions by 30% and hot soak emissions by 50%. Several vehicles were found to have higher than expected levels of toluene in the measured emissions suggesting that fuel permeation or leakage might be important.

Another US EPA study [1-3] at around the same time showed that, for one vehicle, diurnal emissions from a matched volatility 8% ethanol blend were 45% higher than from the base hydrocarbon fuel at low temperatures but 43% lower at higher temperatures (22–35°C). Hot soak emissions from the two fuels were similar at low and intermediate temperatures but again the ethanol blend had 20% lower emissions at 32°C.

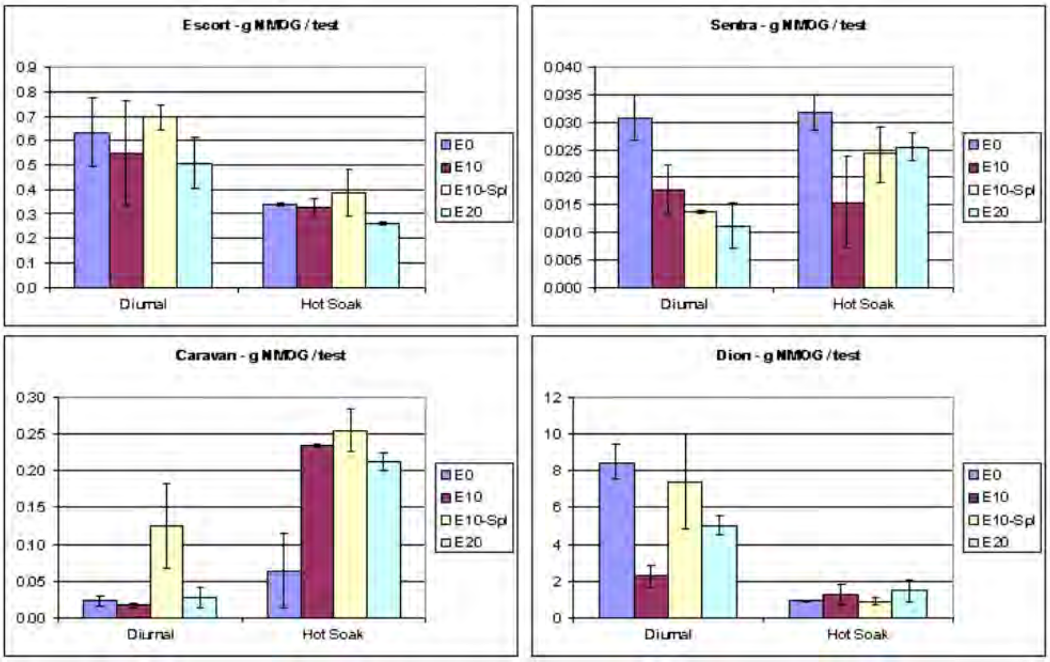
A CARB study [1-4] reported in 1998 tested six US vehicles on a base fuel and splash blends using 10% ethanol and 11% MTBE. The ethanol splash blend increased diurnal and hot-soak emissions on all vehicles tested. Running losses were not measured. Simple average emissions increased as shown in **Table 5**. Total evaporative emissions calculated using the CARB Emission Inventory process, including modelled running loss figures, increased by 54% (THC) and 84% (NMOG).

Table 5: Percentage change in THC and NMOG emissions from a 10% ethanol/gasoline blend (53.9kPa RVP) compared to an 11% MTBE/gasoline blend (47.5kPa RVP) [1-4]

Emission	**Hot Soak**	**24h Diurnal**	**24-48h Diurnal**
THC	58%	65%	86%
NMOG	89%	69%	84%

A more recent Canadian study [1-23] tested four 1998-2003 US vehicles on 10 and 20% matched volatility ethanol blends and a 10% ethanol splash blend. The study showed (**Figure 16)** that evaporative emissions on the matched volatility blends were similar to or lower than on the base fuel for three of the four vehicles. One vehicle showed higher hot-soak emissions. The 10% splash blend of ethanol into gasoline gave higher emissions on two vehicles but lower emissions on the other two.

***Figure 16**:* Diurnal and hot-soak NMOG emissions from four US vehicles [1-23]



An Australian Orbital study [1-11] measured evaporative emissions from five modern and four older vehicles on a 20% ethanol splash blend. For the modern vehicles, emission levels were very low, all below 0.5 g/test total. Diurnal emissions were lower with the ethanol blend for three vehicles, higher for one, and unchanged for one. Hot soak emissions increased for all vehicles on the E20 blend, however. Overall, the 5-car mean total emissions increased by 8%.

For the older vehicles, diurnal emissions increased in two of the oldest vehicles, one substantially, but decreased for the two more recent vehicles. Hot soak emissions increased for all four vehicles on the E20 blend. The second phase of the study [1-12] was a durability test on the five modern vehicles. All vehicles tested on base fuel and E20 fuels gave evaporative emissions below 1g/test even after 80,000 km. There was no difference in diurnal emissions between base and E20 fuels, but hot soak emissions increased by ~80%. The results were quite variable, however, and this result was not statistically significant.

The only substantial European work was the JEC Consortium study [1-36] where seven modern European cars were tested on 5 and 10% ethanol splash blends and matched volatility blends. The test protocol did not require that the canister be returned to a constant weight before each test, so canister loading increased with the number of tests making the interpretation of results difficult.

In this study, the hot soak emissions were small, generally below 10% of total emissions, with diurnal emissions comprising the other 90%. DVPE was the only fuel variable to clearly affect emissions, with high volatility ethanol splash blends having DVPE ~75kPa giving much higher emissions than the other fuels with DVPE in the range of 60-70kPa. Some diurnal tests carried out with the canisters vented outside of the measurement SHED gave similar emissions to the standard test, although levels were low, generally below 1g/test. This result suggested that leakage or permeation could be making an important contribution as has been seen previously in U.S. studies.

Overall, it is clear that ethanol does affect evaporative emissions. Although ethanol itself does not increase the total mass of emissions generated from the fuel system, the increase in DVPE caused by ethanol splash blending does. Ethanol is strongly absorbed in activated carbon canisters but is also readily desorbed, although a little more slowly than are light gasoline hydrocarbons. Finally, ethanol can increase permeation through some plastic and elastomer components. Materials that are resistant to this permeation have been developed and are widely used in the U.S. Some Australian work [1-12] has shown that canisters can readily cope with ethanol/gasoline fuel blends and maintain their performance over long periods. However, Swedish testing [1-40] suggested that this may not always be true for vehicles in-service.

9.0 ON-BOARD DIAGNOSTIC (OBD) REQUIREMENTS

Modern vehicles have to incorporate OBD requirements. These diagnostic systems must monitor the functionality of engine combustion processes including fuel injection and sensor operation as well as the proper functioning of the emissions control systems that may be on-board the vehicle. Failures of these emissions control systems must illuminate the malfunction indicator light (MIL).

Oxygen sensors are an essential part of the OBD system on gasoline vehicles today to insure that the TWC is functioning properly by monitoring any reduction in efficiency. Other monitoring requirements for vehicles with positive-ignition engines (gasoline engines) typically include detection of misfires, oxygen sensor deterioration, control system failures, and evaporative emissions purge controls.

10.0 CONCLUSIONS

- A number of technologies exist that can greatly reduce emissions from gasoline-powered vehicles and equipment.
- The widespread availability of low- and ultra-low sulfur fuels has enabled the application of more advanced emission control systems.
- Three-way catalysts provide efficient control of CO, HC and NOx emissions from stoichiometric gasoline and gas-engined vehicles.
- A combination of three-way catalysts with either NOx control technology (typically NOx traps) is being used to control emissions of lean-burn gasoline vehicles.
- Advanced sensors are already in use and continue to be developed to monitor all components of the exhaust control system.

11.0 ACRONYMS AND ABBREVIATIONS

AFR	Air/Fuel Ratio
Al_2O_3	Aluminium oxide
$Ba(NO_3)_2$	Barium nitrate
$BaCO_3$	Barium carbonate
bhp-hr	Brake horsepower-hour
CARB	California Air Resources Board (also Air Resources Board)
CCC	Close-Coupled Catalyst
CNG	Compressed Natural Gas
CO	Carbon monoxide
CO_2	Carbon dioxide
CPC	Condensation Particle Counter
CRC	Coordinating Research Council (U.S.)
Cu	Copper
°C	Degrees Celsius
DeNOx	Selective Catalytic Reduction for NOx removal
DeSOx	Procedure for SOx removal from a NOx trap
DISI	Direct Injection Spark Ignition (also Gasoline Direct Injection)
DPF	Diesel Particulate Filter
DVPE	Dry Vapour Pressure Equivalent
E70	% of sample evaporated at $70^{o}C$
EGR	Exhaust Gas Recirculation

ELPI	Electrical Low Pressure Impactor
EMS	Engine Management System
EPA	Environmental Protection Agency (US)
EPEFE	European Programme on Emissions, Fuels, and Engine Technologies
ETBE	Ethyl tertiary-Butyl Ether
EU	European Union
FBC	Fuel-borne catalyst
FTP	Federal test procedure
GDI	Gasoline Direct Injection (also Direct Injection Spark Ignition)
GPF	Gasoline Particulate (or Particle) Filter
H_2	Hydrogen (molecular)
H_2O	Water
HC	Hydrocarbon
HDPE	High Density Polyethylene
JEC Consortium	Joint Research Centre of the European Commission; European Council for Automotive R&D; and CONCAWE
LDV	Light-duty Vehicle
LNC	Lean NOx catalyst
LNT	Lean NOx trap
LTC	Low temperature combustion
mg	milligram
MIL	Malfunction Indicator Light

MPFI	Multi-Point Fuel Injection
MTBE	Methyl tertiary-Butyl Ether
N_2	Nitrogen (molecular)
nm	nanometer
NEDC	New European Driving Cycle
NH_3	Ammonia
NMHC	Non-methane hydrocarbon
NMOG	Non-methane Organic Gases
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NOx	Oxides of nitrogen
O_2	Oxygen (molecular)
OBD	On-Board Diagnostics
PAH	Polycyclic Aromatic Hydrocarbon
Pd	Palladium
PM	Particulate Matter
PMP	Particulate Measurement Programme (EU)
PN	Particle Number
POM	Polycyclic Organic Matter
ppm	Parts per million
Pt	Platinum
Rh	Rhodium

rpm	revolutions per minute
RVP	Reid Vapour Pressure
S	Sulfur
SCR	Selective Catalytic Reduction
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
SOF	Soluble organic fraction
TAME	tertiary-Amyl Methyl Ether
TBA	tertiary-Butyl Alcohol
TEL	Tetraethyl Lead
THC	Total Hydrocarbon Content
TWC	Three-way Catalyst
UN ECE	United Nations Economic Commission for Europe
V_2O_5/TiO_2	Vanadium oxide/Titanium oxide
VOC	Volatile Organic Compounds
VVT	Variable Valve Timing
WHTC	World Harmonised Transient (or Test) Cycle

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- Association for Emissions Control by Catalyst (AECC, http://www.aecc.be)
- American Petroleum Institute (API, http://www.api.org)
- Conservation of Clean Air and Water in Europe (CONCAWE, The oil companies' European association for environment, health and safety in refining and distribution, http://www.concawe.org)
- Truck and Engine Manufacturers Association (EMA, http://www.truckandenginemanufacturers.org)
- International Petroleum Industry Environment Conservation Association (IPIECA, http://www.ipieca.org)
- Manufacturers of Emission Controls Association (MECA, http://www.meca.org)
- International Organization of Motor Vehicle Manufacturers (OICA, http://www.oica.net)

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[7] International Agency for Research on Cancer (http://www.iarc.fr)

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