PARTICLE AND NOX EMISSIONS FROM AUTOMOTIVE DIESEL AND PETROL ENGINES

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- A 2009 update, including some biofuels and additional exhaust components

The emissions from motor vehicles impact on regional and global air quality. This report shows the origins, varieties and trends of PM and NO$_X$ emission.

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PARTICLE AND NO$_X$ EMISSIONS FROM AUTOMOTIVE DIESEL AND PETROL ENGINES

A 2009 update, including some biofuels and additional exhaust components

A report for Statoil Hydro
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ABBREVIATIONS, ACRONYMS AND GLOSSARY

BTL	Biomass To Liquid
Cetane number	The ability of the fuel to ignite in compression ignition engines.
CI	Compression ignition
CRT™	Continuously Regenerating Particle filter
CVS	Constant Volume Sampling, method for exhaust emission measuring in laboratory
DMA	Differential Mobility Analyzer
DME	Dimethyl Ether
DOC	Diesel oxidation catalyst
DPF	Diesel Particle Filter
EGR	Exhaust Gas Recirculation
EPA	Environmental Protection Agency (USA)
ESC	European Stationary Cycle
ETC	European Transient Cycle
FAEE	Fatty Acid Ethyl Esters
FAME	Fatty Acid Methyl Esters
GDI	Gasoline Direct Injection
GTL	Gas To Liquid
HD	Heavy-Duty
LD	Light-duty
NEDC	New European Driving Cycle
NExBTL™	Trade mark of the Finnish oil company Neste Oil for a fuel made by hydrogenating vegetable oils and animal fats.
NO_x	nitrogen oxides
NO	nitric oxide
NO_2	nitric dioxide
PAH	Polycyclic Aromatic Hydrocarbons
PM	Particulate Matter
PMP	Particle measurements program
PN	Particulate number

SCR	Selective Catalytic Reduction, a NO_X reducing catalyst
SI	Spark Ignition
SME	Soy Methyl Ester
SOF	Soluble Organic Fraction
Stoichiometric	Stoichiometric conditions = when ratio of fuel and air is chemically correct for complete combustion. Under 'lean' conditions there is an excess of oxygen in the air:fuel ratio, under 'rich' conditions there is more fuel in the air:fuel ratio
THC	Total hydro carbons
TWC	Three Way Catalyst
WHSC	World Harmonised Stationary Cycle
WHTC	World Harmonised Transient Cycle

1   SUMMARY

The report is a literature survey to update and summarize the 2008's report *'Combustion particles and NOx from diesel and petrol vehicles'* [Alvik]. The purpose of present report is to review PM and NOx emission and how they are affected by fuel qualities, engine technologies and exhaust after-treatment systems. Biodiesel is the fuel in main focus.

It is generally recognized that using neat biodiesel and biodiesel blends leads to significant decrease in PM emissions and slightly increased NOx emissions compared to fossil diesel fuel. In addition CO, HC, aromatics, PAH and 1,3- butadiene emissions decrease with biodiesel and biodiesel blends. However contrary results were also observed as stated in the report.

The PM and PN emissions from different engine technologies follow such a sequence:
conventional petrol engine < gasoline direct injection (GDI) engine < diesel engine

High efficient DPF (Diesel Particle Filter) reduces PM and PN emissions dramatically. The DPF vehicles have similar or even lower PM and PN emissions than the conventional petrol vehicles. For the DPF vehicles most particle emissions originate from cold start, and the PM and PN emissions increase during DPF regeneration.

Further, decreasing sulphur content in diesel fuel and lubricant oil leads to decreased PM and PN emissions. Gas to liquid and biomass to liquid fuels have lower PM and PN emissions compared to diesel fuels.

Successful introduction of Three-Way Catalysts lead to significant NOx reduction in conventional petrol vehicles. The recent development of Selective Catalytic Reduction (SCR) and NOx adsorb catalysts provides the potential to cut down NOx emissions from diesel and GDI engines to similar levels as conventional petrol ones. Consequently the NOx level in the ambient air is reduced in the last years; however the NO_2 stays at the same level or even increases in some areas. This report illustrates that introduction of advanced after-treatment technology is one of the main factors leading to the increased NO_2/ NOx ratio.

2 BACKGROUND

The emissions from motor vehicles not only contribute considerably to the local air quality but also have an impact on global emissions. Although there has been a shift in focus from local emissions to global warming, local emissions are still of great concern. Many areas still have problems in meeting air quality norms, e.g. particle mass and nitrogen dioxide (NO_2) level. Diesel vehicles contribute significantly to both PM and NO_x emission, these vehicles have thus been under constant assessment during the last decades.

In order to reduce the emissions of greenhouse gases, the use of bio-components, as blending components but also as neat fuel, has gained an increasing interest. The call for the use of biofuel, particularly of biodiesel, has been made by many governments following international energy policies. However the impact of biofuels and biofuel blends on exhaust emissions is not yet fully clarified. Numerous studies have been carried out and a general trend has been found in most cases, but there have always been contrary results reported. One reason for this is the large number of different engine technologies tested, the varying operating conditions or driving cycles followed, the different biodiesel fuels used (from different feedstocks and with different qualities), and the various measurement techniques and procedures applied.

Present report is a literature survey, updating and summarizing the 2008's report 'Combustion particles and NOx from diesel and petrol vehicles' [Ahlvik], with focus upon impacts of bio components in the fuel.

As the 2008's report, the objective of this report is still on diesel powered vehicles and engines, emissions from petrol cars are also addressed. With focus upon NOx and particle emissions, the impacts of biodiesel, fuel qualities, engine and exhaust after-treatment technologies upon exhaust emissions are discussed.

The regulations and fuel specifications mentioned in this report are only limited to European standards. The test cycles such as NEDC, ETC, ESC, WHTC, WHSC used in the EU regulations are not discussed in this report rather than listed in the Appendix.

The data used in this report are mainly based upon literature searches using database of SAE Global Mobility Database (GMD), ISI Web of Knowledge and ScienceDirect.

3   ENGINES AND FORMATION OF NO$_X$ AND PARTICLES

Introduction to engine- and exhaust gas after-treatment technology

Like other combustions – combustion of fuel in an engine contributes significantly to air pollution with damaging effect to our health and environment. This chapter gives a short introduction to differences between petrol (SI) and diesel (CI) engines and description of some methods used to clean exhaust emissions from petrol and diesel engines. In short the main difference between petrol and diesel engine is that diesel engines have relatively high fuel efficiency but create difficulties in reducing of the exhaust emissions (e.g. particles and NO$_X$), whereas petrol engines have relatively low fuel efficiency but the exhaust emissions are easier to take care of.

3.1   Engine technology

The diesel engine (compression ignition, CI) and the petrol engines (Spark ignition, SI) are both internal combustion engines.

3.1.1   Petrol engine (Spark ignition engine) and diesel engine (Compression ignition engine)

A spark ignition engine (SI) starts the combustion process in each cycle by use of a spark plug. The spark plug gives a high-voltage electrical discharge between two electrodes which ignites the air-fuel mixture in the combustion chamber surrounding the plug.

The combustion process in a compression ignition engine (CI) starts when the air-fuel mixture self ignites due to high temperature in the combustion chamber caused by high compression.

A typical petrol engine is the Otto engine or four stroke engine that works as shown in *Figure 1*. The four-stroke diesel engine has similar working cycles as the four-stroke petrol engine.

- Intake stroke – intake valve opens, when the piston moves down the cylinder fills with air and petrol.

- Compression stroke – the piston moves back up and compresses the fuel/air mixture.
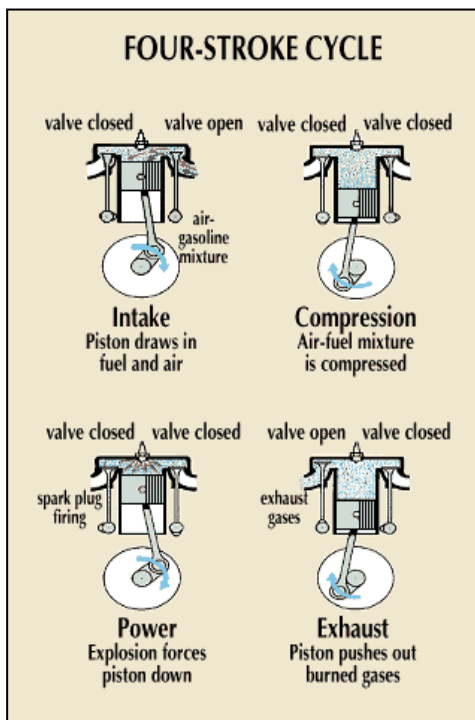

Figure 1 The Four strokes in the four-stroke spark ignition engine (Otto engine)

Source: Four-stroke engine, retrieved august 25, 2009, from Encyclopedia Britannica online

- ▪ Combustion (power) stroke – when the piston reaches the peak of compression a spark ignites the petrol that explodes and drives the piston back down again.

- ▪ Exhaust stroke – when the piston reaches the bottom, the exhaust valve opens and the exhaust leaves the cylinder

3.1.2   Main differences between diesel and petrol engines

The major differences between diesel and petrol engines can be summarized as follows:

- • Introduction of fuel in the engine:

In the case of petrol engines, a mixture of air and fuel is injected into the cylinder. In the case of diesel engines, fuel is injected into the combustion chamber towards the end of the compression stroke. The fuel starts burning instantly due to the high pressure.

- • Ignition of fuel

By nature petrol is a highly volatile liquid, but its self-ignition temperature is high. For this reason a spark is necessary to initiate the burning process of this fuel. With diesel, the self-ignition temperature is lower. When diesel fuel is compressed to high pressure, its temperature increases beyond the self-ignition temperature. Hence in the case of diesel engines there is no need for spark plugs.

- • Compression ratio for the fuels

In the case of petrol engines, the compression ratio of the fuel is in the range of 6 to 10 depending on the size of the engine and the power to be produced. In diesel engines, the compression ratio for air is 16 to 20. The high compression ratio of air creates high temperatures, which ensures the diesel fuel can self-ignite.

- • Air-fuel ratio

A petrol engine operates in a very narrow range around the stoichiometric air fuel ratio. A diesel engine works with a high air to fuel ratio (lean burn) which creates an exhaust gas with a very high surplus of oxygen.

Diesel engines are until now mostly used for heavy duty vehicles like trucks, busses and ships but recently they are also used in passenger cars due to the low fuel consumption.

3.1.3   Lean burn engine (GDI)

The petrol lean burn engine is in some ways a crossing between the petrol and the diesel engines. The lean burn engine operates with spark-plug like the petrol engine; and like the diesel engine it works with a high air fuel ratio and the fuel is not premixed with air, it is directly injected in to the combustion chamber. Therefore it is

often called Gasoline Direct Injection (GDI). The benefit of GDI is lower fuel consumption than conventional petrol engines but the downside is high NO_x and particle emission.

3.2 NO_X formation

NO_x is formed when the nitrogen reacts with the oxygen at high temperature in the engine combustion chamber. The higher the temperature, the more NO_x emissions. In addition to temperature, the formation of NO_x depends on pressure, air-fuel ratio and combustion time. Petrol exhaust contains much lower NO_x emissions than diesel exhaust mainly due to the successful introduction of the three way catalyst technology already in 1980's.

3.3   Particle formation

The particles are generated in the fuel-rich zones within the cylinder during combustion.

In petrol engines the air and fuel is premixed and more homogeneous than in a diesel engine. Therefore petrol engines have rather complete fuel combustion.

The diesel engines use diffusion combustion. The fuel is injected into a very hot combustion chamber, creating in-homogeneous air-fuel zones. This causes incomplete combustion and particle formation.

The Gasoline Direct Injection (GDI) engines (Lean burn engine) work with similar fuel injection principle as diesel engines and also has a similarly high particle formation.

4 DEVELOPMENT OF AFTER-TREATMENT TECHNOLOGY

Diesel engines and lean-burn direct injection petrol engines offer the benefit of lower carbon dioxide emissions and reduced fuel consumption. The conventional three-way catalyst technology can effectively reduce THC, CO and NO_x simultaneously for the petrol vehicles (the engine operates in a very narrow range around the stoichiometric air fuel ratio). Selective Catalytic Reduction, Lean De-NO_x catalysts, and NO_x adsorbs are technologies that can be used in lean applications such as GDI and diesel engines.

4.1 After-treatment technology for diesel engines (Compression ignition engine)

- DOC - Diesel Oxidation Catalysts

Diesel Oxidation Catalysts (DOC) remain a key technology for diesel engines. These catalysts convert CO and HC but also decrease the mass of diesel particulate emissions by oxidizing some of the hydrocarbons that are adsorbed onto the carbon particles.

- SCR - Selective Catalytic Reduction

Selective Catalytic Reduction (SCR) is now fitted to most new heavy-duty diesel engines in Europe (i.e. trucks and busses). Systems are also being introduced on light-duty diesel vehicles. In the SCR system ammonia is used as a selective reductant, in the presence of excess oxygen, to convert over 70% (up to 95%) of NO (nitrogen oxide) and NO_2 (nitrogen dioxide) to N (nitrogen) over a special catalyst system. Different precursors of ammonia can be used; one of the most common option is a solution of urea in water (e.g. AdBlue®) carefully metered from a separate tank and sprayed into the exhaust system where it hydrolyses into ammonia ahead of the SCR catalyst

- EGR – Exhaust Gas Recirculation

NO_X levels are reduced by recirculating the exhaust gas back to the engine. It gives lower combustion temperatures and more inert gas in the combustion reaction wich reduces the NO_X content.

- DPF – Diesel Particle Filter

Particulate filters are generally used with diesel engines to remove diesel particulate matter (PM), but they can be used with other types of engine/fuel combinations that produce less particulate matter. Based on engine technology and application specifics different filter technologies may be used to reduce particle emissions. The DPF needs to be regenerated, either by active regeneration or passive regeneration. In the active system a late fuel injection is used to increase the exhaust gas temperature so much that the particles in the filter incinerate. The active systems are

so far available only for light duty vehicles. In the passive system an oxidation catalyst is placed before the filter and NO_2 is used for soot burning.

- Full- Flow filters

The full-flow filters almost completely remove the carbon particulates including fine particles with an efficiency >95% in mass and >99% in number over a wide range of engine operating conditions.

- Partial-Flow filters

Partial-Flow filters offer an option for reducing PM emissions by 30-60%.

4.2 After-treatment technology for petrol engines (Spark Ignition engines)

- TWC (Three Way Catalyst)

The TWC is called a three way catalytic converter because there are three main catalytic reactions.

1. unburned carbon monoxide (CO) is oxidized to carbon dioxide (CO_2)

2. unburned hydrocarbons (HC) are oxidized to carbon dioxide and water

3. nitrous oxide (NOx) is reduced to nitric gas (N_2)

TWC converters in combination with the oxygen/hydrocarbon sensor were introduced in Europe about 20 years ago, in the late 1980'ies. Nowadays this kind of exhaust gas after-treatment systems is standard for all petrol cars. The engine systems with TWC and sensor are not affected in negative ways by using bioethanol as a fuel [Eriksson 2009].

Ecotraffics opinion is that the petrol vehicle exhaust emission problem is solved even if there is still some fine tuning that can be done. Compared with the situation 20-30 years ago a huge uplift has been achieved.

4.3 After-treatment technology for lean burn engines (GDI)

- Lean De-NO$_x$ catalysts (Hydrocarbon-SCR)

Lean De-NO$_x$ Catalysts, also known as hydrocarbon-SCR systems use advanced structural properties in the catalytic coating to create a rich 'microclimate' where hydrocarbons from the exhaust can reduce the nitrogen oxides to nitrogen, while the overall exhaust remains lean. A small amount of hydrocarbon already exists in the exhaust gas ("native"), it can also be added to the exhaust gas through injection of a small amount of additional fuel. This has the advantage that no additional reductant source (urea) needs to be carried but these systems do not, at present, offer the same performance as ammonia-SCR systems.

- NO$_x$ adsorbers (NO$_x$ traps)

NO$_x$ adsorbers (NO$_x$ traps) adsorb and store NO$_x$ under lean conditions. A typical approach is to speed up the conversion of nitric oxide (NO) to nitrogen dioxide (NO$_2$) using an oxidation catalyst so that NO$_2$ can rapidly be stored as nitrate on alkaline earth oxides. A brief return to stoichiometric[1] or rich operation for one or two seconds is enough to desorb (remove) the stored NO$_x$ and provide the conditions for a conventional three-way catalyst mounted down streams to reduce (destroy) NO$_x$.

Unfortunately, NO$_x$ adsorbers also adsorb sulfur oxides resulting from the fuel sulfur content. For that reason fuels with a very low sulfur content are required (European 'zero' sulfur fuel contains less than 10 ppm sulfur).

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[1] Stoichiometric conditions are those where the ratio of fuel and air is chemically correct for complete combustion. Under 'lean' conditions there is an excess of oxygen in the air:fuel ratio, under 'rich' conditions there is more fuel in the air:fuel ratio.

5   FUELS AND FUEL QUALITY DEVELOPMENT AND TRENDS

The improvement of diesel and petrol quality has given large environmental benefits lately. The latest fuel specifications for diesel, FAME, petrol and E85 can be found under Appendix III – Appendix VI

5.1   Diesel (EN 590:2009)

For current specification see Appendix III

During the last 20 years the quality of diesel fuel has improved.

Some of the improvements are:

- Lower sulphur content (from 2 000 ppm 1993 to 10 ppm 2009)

- Lower concentration of aromatics

- Increased blending of bio components (FAME)

Two main reasons were behind the reduction of the sulphur content in fuel, firstly for reducing environmental acidification, secondly to enable the use of advanced after-treatment technology. When removing sulphur a positive side effect occurs, the concentration of aromatics also sinks.

Another improvement is that bio components (FAME) are blended into the diesel at larger extent. In the last diesel specification (EN 590:2004) the FAME concentration in standard diesel fuel had raised from 5% to 7%.

5.2   Petrol (EN 228:2008)

For current specification see Appendix V

During the last 20-30 years the quality of petrol fuel has been significantly improved and more bio components are added. Some important matters are listed below:

- Lead is removed

- Lower sulphur content

- Lower concentration of benzene

- Increased blending of bio components (ethanol)

Bio components (ethanol) are blended into the petrol in larger extent. Since the last petrol specification (EN 228:2004) ethanol concentration in standard petrol fuel has risen from 5% to 10%.

5.3   FAME also called biodiesel or RME (SS-EN 14214:2008)

For current specification see Appendix IV

Rapeseed methyl ester (RME) also called biodiesel, is a bio based alternative fuel and in Europe it is the mostly used bio diesel. RME is very similar to standard diesel oil in flash point and cetane number and therefore it is possible to use it to replace fossil diesel oil in diesel engines, both neat (100 %) and blended with fossil diesel oil.

RME is just one of several methyl esters that can replace fossil diesel oil. RME is made of rape seed oil but other oils like soy oil or palm oil can be used. It is also possible to use fat of animal origin like for example pork fat and tallow. Lately algae oil has been up for discussion as raw material for biodiesel production. The different methylized plant oils (methyl esters) are called FAME which is an abbreviation for **F**atty **A**cid **M**ethyl **E**sters.

In biodiesel methanol is used for the etherification of the vegetable oil. Methanol is produced from fossil gas. It is also possible to use ethanol for this process. This would change the names FAME and RME to FAEE and REE.

Recent years the quality has increased, mostly due to a lower concentration of "free fatty acids" in the biodiesel. The higher quality may be due to the improvements in the production line, larger manufacturers like Perstorps may affect the product quality in a positive way. These improvements give much better winter fuel.

The fuel specification for diesel has recently changed; the maximum level of FAME blended into diesel is now 7 %.

5.4   Hydrated vegetable oils

Hydrogenation of vegetable oils gives a biodiesel that fulfills the normal diesel specification. These type of fuels can be blended with conventional fossil diesel in all ratios (from 0-100%). The Finish company Neste Oil produce this type of fuel with trade name NextBTL. Neste Oil mostly use palm oil as bio crude oil. Palm oil has been criticized by a lot of organization all over the world, the argument for the criticism is that rain forests may be turned into palm plantations.

5.5   Ethanol E85 (Swedish standard SS 15 54 80:2006)

For current specification see Appendix VI

E85 – specification has been changed to allow up to 25 % petrol in ethanol during winter time. More petrol gives better performance in winter time.

The higher petrol content in winter blend has more or less eliminated the cold start problem

5.6   Other biofuels (bio and synthetic)

- Synthetic diesel

Synthetic diesel fuels are produced from fossil gas or from coal. Sometimes this type of fuels is called GTL fuels (Gas To Liquids). The process (FT or Fischer-Tropsch) for producing synthetic diesel is an old method; it was used already in Germany during the Second World War and in South Africa during the apartheid.

Around the world there is a lot of research going on regarding use of biomass as bio crude for production of synthetic fuels. This type of fuels is often named BTL (Biomass To Liquid). The process from biomass to liquid includes gasification of biomass (it is this process step which is not fully developed yet). It may not be a significant amount of BTL fuels on the market within the next 10 years period, so far there are no commercial plants.

GTL and BTL fuels are relatively clean fuels and almost free from components as sulphur and aromatics and they fulfill the normal diesel specification. This makes it possible to use a blend ratio with normal diesel from 0 – 100 %

- DME and Methanol

Di Methyl Ether is a gaseous fuel which can be produced from synthetic gas. DME is a fuel for diesel engines. In the same process it is also possible to produce methanol that can be used as a low blending component in petrol (maximum 3 % is allowed), or in the future in neat form or as high blending component (M85 in analogue to E85).

In the same way as GTL and BTL fuels described above, it is possible to produce DME and methanol from fossil gas or from gasified coal. A lot of research is carried out to enable use of biomass as bio crude for the process. In Sweden focus is to integrate DME and Methanol production in the pulp industry (by gasification of black liquor).

- SunPine / Tall oil

A Swedish company, SunPine AB, started building a plant for producing pine diesel (a kind of FAME or biodiesel) originating from tall oil, which is a byproduct from the pulp process. The tall oil will be transported from the plant in Piteå to Preems refinery in Gothenburg where it will be used a kind of bio crude oil. The total production volume will be about 100 000 m^3 pine diesel oil per year. Pine diesel is considered to be the second generation of renewable diesel as no foodstuff is used in the production.

5.7   Trends of diesel vehicles

The market share for diesel cars has increased steadily during the last 20 years and the sales now account for approximately 50% of the market in EU. It should be noted that the diesel share of some markets with relatively low market penetration has

increased considerably during the last years. For example, the market share in Sweden has increased from some 10% in 2005 to about 35% in 2008. Similarly, the market share has increased in Norway and is now about 50% (39% in 2005).

However one may expect the rate of increase in diesel penetration would slow down in the future due to the following factors. First, the share of diesel fuel from crude oil cannot increase to an arbitrary level with contemporary refinery technology. Second an increase in the demand for diesel fuel will lead to higher prices. Further the fuel consumption of petrol-fuelled cars is anticipated to decrease more than for diesel cars, diminishing the fuel consumption advantage for the latter category. Furthermore, the more stringent emission limits will increase the cost for diesel engines. It is also likely that the current tax incentives, that currently favour diesel fuel in most EU member states, will diminish in the future.

Only few percent of the current total fleet are equipped with diesel filters. Due to the stringent regulations all new diesel passenger (from Euro 5) cars and all on road heavy duty engines from Euro 6 will be equipped with DPF.

6 CHARACETRISATION OF PARTICLE EMISSIONS

Particles emitted from combustion engines are the most complex emissions of the exhaust emissions. Unlike the gaseous emissions, the particles emissions are not well defined chemical species rather than defined by emissions standards and measurement methods. Depending upon aerosol measurement technology, particles can be characterised by total particulates mass, number concentration, size distribution, chemical composition, surface, density, morphology and structure. The technologies commonly used for characterizing the particle emissions from diesel engines were documented in two review articles [Burtscher 2005, Maricq 2007]. In this chapter we focus our discussion upon the two particle emission concepts i.e. particulate matter (PM) and particle number (PN) emissions which is/will be used in EU regulations.

The concept of particulate matter (PM) has been used in emission regulations for decades. Generally PM consists of tiny solid particles and liquid droplets, which are mixtures of elemental carbon (EC), organic materials derived from fuel and lubricant oil, sulphuric compounds, ash and water [Burtscher, 2005]. *Figure 2* illustrates an example of PM compositions from a US heavy-duty diesel engine transient test [Kittelson, 1998]. PM compositions vary depending upon fuel and lubricant oil qualities (e.g. sulphate and aromatics contents), engine technology, after-treatment technology and engine testing conditions.
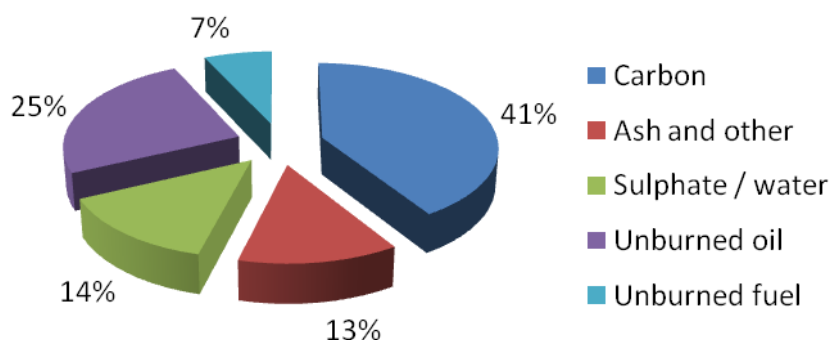

Figure 2 Composition of PM compositions from a heavy-duty diesel engine without DPF [Kittelson 1998].

PM can be divided into three main fractions like:

▪ Solid fractions including carbon and ash. This fraction is normally associated with the names EC (element carbon), soot or black carbon

▪ Organic fraction, also called OC (organic carbon)

- Sulphates

Many species in organic fractions are volatiles. Depending on the temperature and other conditions the volatiles from exhaust emissions may remain in the gas phase, condense on solid particles or nucleate and form new particles. Clearly different amount volatile species will be measured as PM emissions depending upon measurement conditions such as filter materials, dilutions, temperature, sampling locations etc.

The EU regulations concerning PM emissions have been limited only to diesel engines until 2009. From Euro 5 PM limits are also applied to GDI petrol light duty vehicle. *Table 1* summarizes the current and future EU PM emission standards for diesel and GDI petrol passenger vehicles and heavy-duty engines.

Table 1 Current and future EU Particle mass (PM) emission limits

	Year	Passenger car (mg/km)	Heavy Duty ESC (g/kWh)	Heavy Duty ETC (g/kWh)
Euro 4	2005	25[a]	0,02	0,03
Euro 5a	2009	5[b]	0,02	0,03
Euro 5b	2011	4,5[b,c]	0,02	
Euro 6	2014	4,5[b,c]	0,01[d]	0,01[e]
PM limit applies only to diesel cars.				
PM limit applies both to diesel and DI petrol cars.				
PM limit based upon PMP method.				
ESC will be replaced by WHSC				
ETC will be replaced by WHTC				

Current legislative emission standards regulate particle emissions in terms of PM, this is effective when controlling emissions of larger size particles, but particles at the smaller end of the size range contribute little to the total mass of particulate matter emitted. This is clearly illustrated in *Figure 3* [www.DieselNet.com].
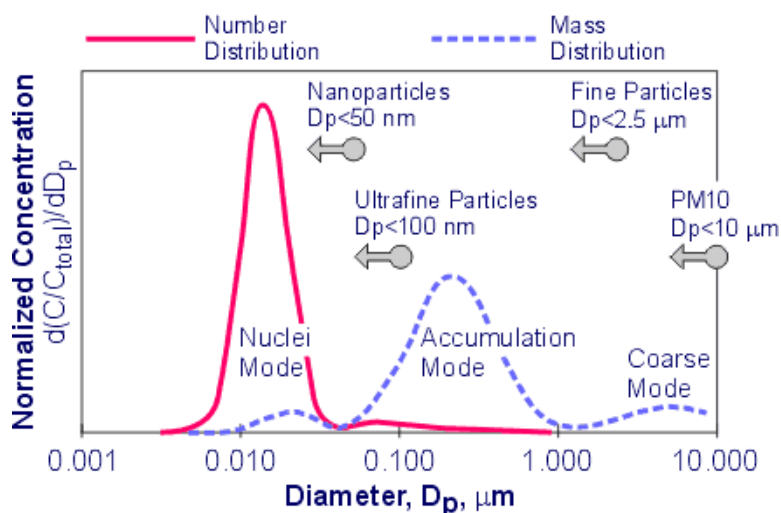
Figure 3 Diesel particle mass and number size distribution. Diesel PM is composed of numerous small particles holding very little mass. [www.DieselNet.com]

As shown in *Figure 3* the typical size distribution of diesel exhaust particulates exhibit bimodal character with two concentration peaks, which correspond to the nuclei and accumulation mode particles. The nuclei mode is usually fairly insignificant (a few percent) if mass distribution is presented. In particle number representation, however, the nuclei mode often accounts for over 90% of the total particulate count. In other words, diesel PM is composed of numerous small particles holding very little mass, mixed with relatively few larger particles which contain most of the total mass. A small fraction of diesel particulates reside in a third, coarse mode. These three particle modes have different characters, see below:

Nuclei mode: The diameters of nuclei mode particles are generally less than 40-50 nm, and they are composed mostly of volatile condensates (hydrocarbons, sulfuric acid) and contain little solid material.

Accumulation mode: The diameters of accumulation mode particles are from 30 to 500 nm. Accumulation mode particles are made of solids (carbon, metallic ash) intermixed with condensates and adsorbed material (heavy hydrocarbons, sulphur species).

Coarse mode: These particles have aerodynamic diameters above 1 μm. The coarse particles are not generated in the diesel combustion process rather than formed through deposition and subsequent re-entrainment of particulate material from walls of the engine cylinder, exhaust system, or the particulate sampling system.

With the rapid development in fuel quality, engine technology and after-treatment technology, the PM emission from modern engines have been significantly reduced. In the mean while, scientific studies have revealed that both acute and long term effects of particles are possibly of more relevance for fine particle size fractions rather than the coarse fraction. This implies that particle number (PN) may be better related to health concerns than particulate mass (PM). Further for state of the art

vehicles with low PM emissions, the standard gravimetric method using filter for PM measurement is approaching the lower limit of its practical usefulness.

Since the late 1990s, a number of emission laboratories have undertaken particle number and size distribution studies. Opposite total particulate mass quantification, there is no standard for measuring the number and size distribution yet. Due to differences in particulate sampling and the variety of used measuring methods test results from different laboratories have not been consistent.

In 2001 an EU Particle Measurement Programme (PMP) was initiated. The aim was to develop new particle measurement techniques to complement or replace the existing particulate mass measurement, with special consideration to measuring particle emissions at very low levels. An improved PM measurement method was developed, and this so called PMP PM method will be applied for Light Duty Vehicle and Heavy Duty Engine type approval testing in the future regulations 2011 [Anderson 2007]. A new method was established to measure solid particle number (PN) within the particle size range 23 nm to 2,5 µm by using sample pre-conditioning to eliminate volatile particles. Hence a new PN concept was introduced for the future regulation, for solid particle within 23 nm to 2,5 µm. Suggested PN emission limits for diesel passenger cars are shown in *Table 2*. The PN limits for HD engine is still under discussion, and the indication from EU legislators is shown in the table [Bunting 2009].

Even though the PMP (Particle measurements program) PM and PN methodology is implemented in EU regulation to improve the detection, accuracy, discrimination power and variability of the conventional PM measurement method, the PMP method still has its limitation as discussed in the Andersson's report [Andersson 2007]. Many factors contribute to the uncertainty of the measurements, such as dilution ratio and residence time in the CVS (Constant Volume Sampling) and secondary tunnels, filter face velocity, dilution temperature, CVS background, weighing room conditions, PN instrument calibration methods, etc. As stated in the report, the PMP PM method was unable to discriminate a efficiency of DPF filters, whereas PN method could. The discriminating power is approximately 20 times greater for the number method than for the mass method.

Table 2 EU PN emission limits for passenger cars and heavy duty engines

	Year	Passenger car (#/km)	Heavy Duty WHSC (#/kWh)	Heavy Duty WHTC (#/kWh)
Euro 4	2005	---	---	---
Euro 5a	2009	---	---	---
Euro 5b	2011	5×10^{11}	---	---
Euro 6[a]	2014	5×10^{11}	8×10^{11} (?)	6×10^{11} (?)
a. It is under discussion if PN limits will be applied for Euro 6 DI petrol vehicles in Euro.				

7 REGULATIONS RELATED TO PARTICLE AND NO$_x$ EMISSIONS

NO$_x$ (nitrogen oxides) refer to a mixture of NO (nitric oxide) and NO$_2$ (nitric dioxide). In engine exhaust, NO is produced as a primary by-product of the combustion process and is usually the most abundant nitrogen oxide; NO$_2$ as the secondary product forms from NO. There is an equilibrium between NO and NO$_2$, 2 NO + O$_2$ ↔ 2 NO$_2$, the equilibrium shifts to NO at high temperature. As a result NO dominates about 80-95% of total NO$_x$ from combustion engines due to the high combustion temperature.

The emission regulations for vehicles and engines are based upon NO$_x$ level, but air quality (AQ) legislations regulate NO$_2$ limit. Thanks to the ever-tightening exhaust regulations, the ambient NO$_x$ concentration is reduced; however NO$_2$ stays at the same level or rises which indicates an increase in the NO$_2$/NO$_x$ ratio in the atmosphere.

It was suggested that the increased concentration of background ozone may contribute to the increased NO$_2$/NO$_x$ ratio; however it is questioned if the atmospheric chemistry is the only one to blame. Even though the main composition of NO$_x$ emissions from automobile combustion engine is NO, the modern diesel vehicles with exhaust treatment technology may have much higher NO$_2$ percentages (30-80%) of the total NO$_x$ emission. Researchers believe that direct NO$_2$ emissions from diesel-powered vehicles both from LDV and HDV also play an important role in the new balance of NO$_2$/NO$_x$ ratio in the atmosphere.

In EU it was intensively discussed if a NO$_x$ source-specific legislation is needed. This can be achieved by specifying a limit for the NO$_2$ part (in the order of 20% at most) together with a tighter NO$_x$ limit value. For now it is agreed that the source-specific legislation for vehicle and engine emissions will not be applied with the argument that the future stringent NO$_x$ limit values (Euro 6 for LDV and HDV) will anyhow decrease the absolute level of NO$_2$ emissions.

In *Table 3* NOx emission limits for passenger cars and HD engines are presented. Clearly the NO$_x$ limits for diesel cars have been less tighten than for petrol vehicles. The differences in NO$_x$ limits between diesel and passenger cars will be reduced significantly in the coming Euro 6 regulations.

Table 3 EU NO$_x$ emission limits for passenger cars and heavy duty engines.

	Year	Passenger car (g/km)	Heavy Duty (g/kWh)
Euro 4	2005	0,08[a] /0,25[b]	3,5
Euro 5	2009	0,06[a] /0,18[b]	2,0
Euro 6	2014	0,06[a] /0,08[b]	0,5
a: Limits applied petrol vehicles. b: Limits applied diesel vehicles.			

8 FACTORS INFLUENCING PARTICLE EMISSION

8.1 Diesel fuel and particle emissions

It is well known that the fuel quality is an important factor with respect to the pollutants in the exhaust gas emission. In this report the focus of fuel effects upon particle emissions is upon sulphur content and biodiesel. The effect of fuel formulation is not discussed here.

It is recognized that decreasing sulphur contents in the diesel fuel leads to significant PM reduction. *Figure 4* presents the PM emission as a function of fuel sulphur content reported by Merkisz et al [Merkisz 2002]. The authors also stated that the PM reduction caused by less sulphur in the fuel is more significant at high temperature and high load tests.
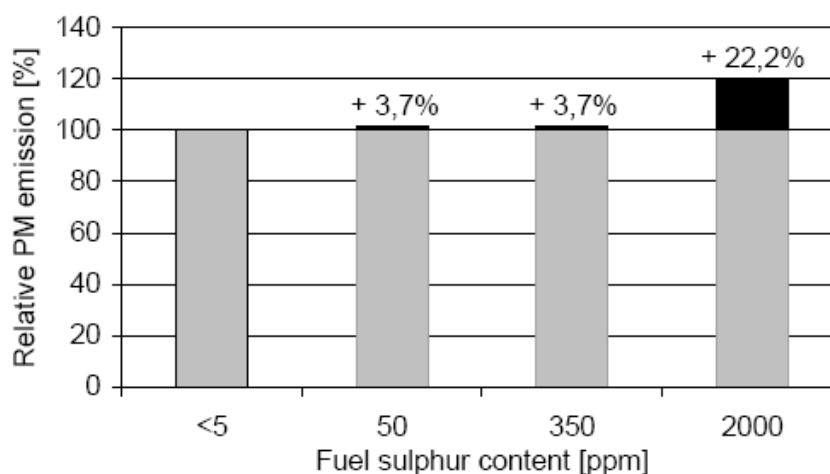

Figure 4 The PM emission percentage increase with increased sulphur content in diesel fuel. The test was performed with light duty diesel vehicles without DPF using the NEDC (New European Driving Cycle).[Merkisz 2002].

Similar results were also reported by Carbone et al in their study of PM emissions from diesel fuels with different S-contents (5 to 307 ppm S) [Carbone 2005].

The highest PM emissions occurred with fuel with greatest sulphur content during high temperature tests. And vice versa the fuel with least sulphur content produced the smallest PM emissions. The filter analysis data from this test confirmed that the high PM emissions from high sulphur fuel were associated with sulphate formation. This is in good agreement with findings reported by Kittelson et al [Kittelson 2006] in a study of a HDV with a CR-DPF (Continuously Regenerating Diesel Particle Filter) system using fuels with different sulphur levels, see *Figure 5*. Using test conditions between 300°C and 500°C, higher sulphur in diesel fuel leads to increased PM emissions, mostly due to the formation of sulphate as shown in *Figure 5.*
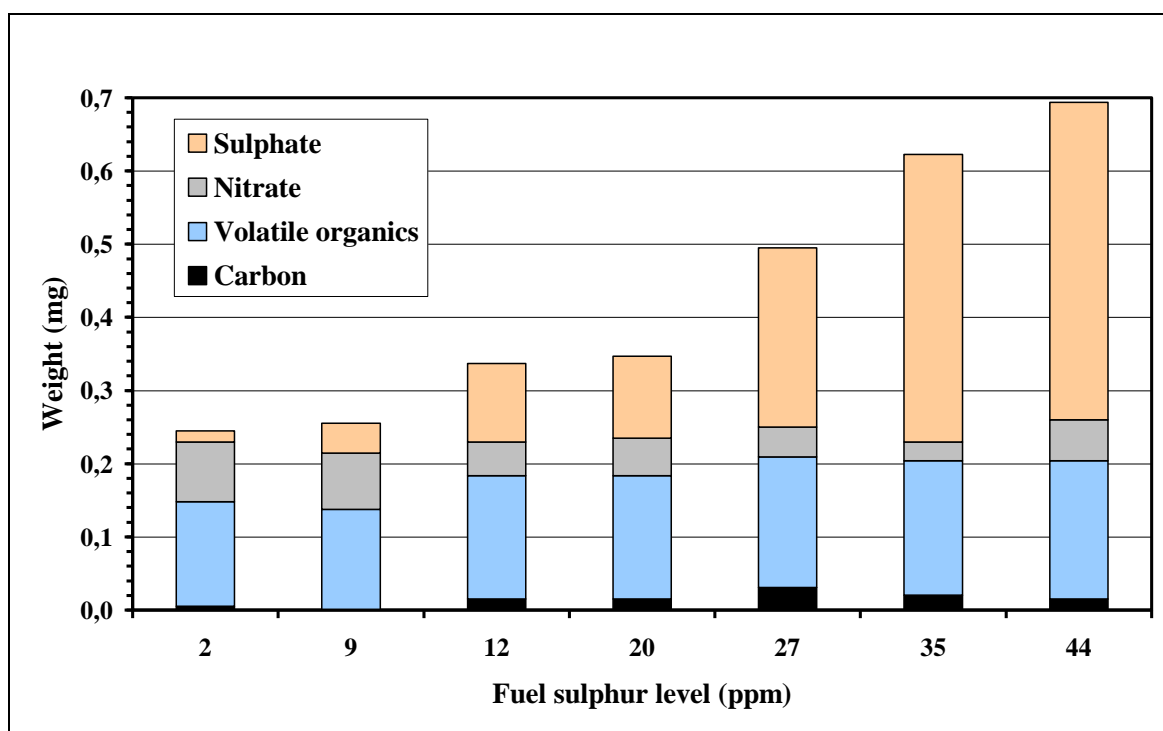
Figure 5 Compositions of PM-emissions as a function of fuel sulphur level. Test performed in a HDV CR-DPF system (Heavy Duty Vehicle Continuously Regenerating Diesel Particle Filter system) [Kittelson 2006].

Note that the results in *Figure 4* are from light duty diesel vehicles without DPF, whereas results in *Figure 5* are from HD engine with DPF, therefore the results are not directly comparable. However both results indicate increased PM emissions with higher sulphur contents in the fuel, independent of DPF.

High sulphur contents in diesel fuel also lead to a higher nanoparticle number emission. Hall et al [Hall 2000a] showed that decrease sulphur content in diesel fuel led to lower nanoparticle number emissions (< 30 nm) from HD engines. This result was supported by Kittelsson and Wedekind's study on HD engines [Wedekind 2000, Kittelsson 2006]. Kittelson showed that the presence of sulphur in fuel and engine lubricant can lead to significant emissions of sulphate particles (nanoparticles). It was demonstrated that, when using low-sulphur fuel in combination with a uniquely formulated low-sulfur lubricant and a suitable filter system, the particulate emissions of a heavy-duty vehicle were reduced to the levels already present in the ambient environment. Similar results were reported in an E-43 project [Ziemann 2002]. Ziemann et al suggested that high-sulphur fuels may cause early nucleation of sulphuric acid particles that later serve as nuclei for hydrocarbon condensation, which leads to high nuclei mode particle emissions.

Findings from the European Community 5th framework project "Particulates" also supported the above statements about sulphur effects upon nanoparticle number

emissions [Ntziachristos 2004]. The authors reported that volatile particle (nucleation mode particles) increased when the sulphur content changed from less than 5 ppm to about 350 ppm. The authors also attributed the sulphur induced volatile particle emissions to sulphur-mediated nucleation processes.

8.2   Biodiesel and particle emissions

The impact of biodiesel and biodiesel blends upon particle emissions has been investigated in numerous publications. Lapuerta et al have reviewed the effects of biofuel upon particles comparing to conventional diesel fuels [Lapuerta 2008a]. Their literature studies are summarized here together with updated information from the latest development in this field.

It is generally recognized that the PM emissions will be significantly lower with biodiesel fuel than conventional diesel fuel [Graboski 1998, Lapuerta 2002, Monyem 2001b, Staat 1995, Wang 2000, Cardone 2002, Karavalakis 2009a], even though occasionally some authors reported contrary results [Durbin 2000, Munack 2001, Alfuso 1993, Karavalakis 2009b].

Explanations to the reduction of PM emissions when using biodiesel or blends: [Lapuerta 2008a]

- The relatively high oxygen content in biofuel reduces soot formation and promotes the oxidation of the already formed soot.

- The lesser need of air in the case of biodiesel combustion reduces the probability of fuel-rich regions.

- Absence of aromatics in biodiesel fuels, species considered as soot precursors.

- The different structure of soot particles between biodiesel and diesel fuels, which may also favor the oxidation of soot from biodiesel.

- The ion sulphur content of most biodiesel fuels prevents sulphate formation.

- The lower final boiling point of biodiesel, despite its higher average distillation temperature, provides lower probability of soot or tar being formed from heavy hydrocarbon fractions unable to vaporize.

EPA summarized PM data based on emission results from HD engines of model year 1997 or earlier without EGR or after-treatment system. The results were used to adjust the following equation, statistically significant with a 95% confidence level [EPA 2002]:

$$PM_B/PM_D = e^{-0,006384\%B}$$

B = biodiesel
D = diesel
%B = biodiesel volume percentage in diesel fuel

Figure 6 Equation for maximum reduction of PM for neat biodiesel without DPF [EPA 2002].

This equation provides a maximum reduction of PM emissions of about 50% for neat biodiesel. Many studies confirmed this general trend of PM emissions, with variation in PM reduction rates with biodiesel fuels [Camden 2005, Kado 2003, Lapuerta 2002, Bagley 1998, Handbook, Karavalakis 2009c]. For example, extreme PM emission reductions of 75% and 91 % have been reported by Kado et al [Camden 2005, Kado 2003].

It is well known that the PM reduction is more effective with low biodiesel concentration in blends in agreement with the equation above [EPA 2002], e.g. Haas et al reported 20% reduction with 20% blends and only and 50% reduction with neat biodiesel [Haas 2001]. Similar findings were also reported by other researchers [Armas 2006, Lapuerta 2000]. However, some authors stated liner reductions with the biodiesel contents [Graboski 1998, Graboski 2003]. Exception was reported by Last et al that the reduction in PM emissions were around 30% with biodiesel blends independent of the proportions [Last 1995].

Some studies observed negligible reduction or even increase in PM emissions with biodiesel compared to diesel fuel [Turrio-Baldassarri 2004, Hansen 1997, Peterson 1996, Munack 2001]. In these cases it is generally explained that the reduction of soot fraction of the PM was compensated by a sharp increase of soluble organic fractions (SOF) [Graboski 1998, Lapuerta 2002, Hansen 1997, Graboski 2003, Schumacher 2006]. It is a widely accepted fact that using biodiesel favours volatile particle emissions even though it reduces soot formation. Such increase is explained by the low volatility of the unburned hydrocarbons from biofuel, which promotes their condensation and adsorption on the particle surfaces.

Parameters such as the origin and composition of biodiesel the alcohols used in transesterification process have also been studied concerning their impacts upon PM emissions.

No common conclusions have been drawn about the effects of the origin of biodiesel upon PM emissions. Some researchers reported lower PM emissions with biodiesel from animal fats than the ones from vegetable oils and indicated that biodiesel PM emissions depend somewhat on the feedstock [EPA 2002, Kado 2003]; whereas some authors showed that no differences in PM emissions between cooking oil and soybeen oil and therefore concluded that the biodiesel feedstock had no effects upon PM emissions.

Some authors suggested that the oxygen content in the biodiesel fuel is of the main factors affecting PM formation [Haas 2001, Graboski 2003]. For example somewhat

higher PM emissions was observed with oleic methyl ester when comparing to lauric and palmitic methyl ester [Knothe 2006], and the authors attributed the differences in PM emissions to the lower oxygen contents in oleic ester.

Lapuerta et al stated that the degree of unsaturation of biodiesel fuels have significant effects on PM emissions [Lapuerta 2008]. Increasing the degree of unsaturated biofuels leads to lower PM emissions. Schmidt et al reported increases in SOF (soluble organic fraction) with increased saturation level [Schmidt 1996]. Contrary results were reported by Haas [Haas 2001] that PM reductions with biodiesel showed no correlation with the saturation levels.

It was also claimed that the biodiesel density and cetane number affect somewhat PM emissions. If the density was higher than 895 kg/m3 or the cetane number lower than 45, the PM emissions with biodiesel increased considerably [Graboski 2003].

The engine load conditions, operation temperatures also influence PM emissions. Most researchers found larger decreases in PM emissions by biodiesels at high load conditions [Last 1995, Hamasaki 2001, Durbin 2002, Leung 2006, Czerwinski 2007, Di 2009]. E.g. a resent study by Czerwinski et al of a 2005 model HD engine showed that the RME fuel led to lower EC emissions in PM and higher nuclei mode particle emissions comparing to diesel fuel. Depending upon the engine working conditions, the fuel effects upon PM emissions differ, RME led to higher PM emissions when operating the engine at 1500 rpm with10 % load, but lower PM emissions with 80% load comparing to diesel fuel [Czerwinski 2007]. Some authors suggested that the load effect was due to the oxygen contents in biodiesels being more effective in reducing PM at high loads; others explained that the sharp increase in SOF at low load caused such load effects. Contrary results also reported by Lapuerta et al that larger decreases in PM emissions by biodiesel at low load conditions than the middle load operation modes [Lapuerta 2000].

Operating at a cold temperature the advantage of biodiesel in PM emissions may be reduced or even reversed [Tinaut 2005, Armas 2006, Martini 2005]. E.g. in a study of load, speed and start-up tests with a direct injection engine, PM emission were reduced with biodisels comparing to diesel fuel during all transient tests except the start up tests. The authors suggested it is more difficult for the biodiesel to atomize and evaporate in the cold conditions of the start-up period, due to its higher viscosity and lower volatility comparing to diesel fuel [Armas 2006]. Fontaras et al also observed higher PM emissions of pure biodisel fuel comparing to diesel fuel in the cold start NEDC test, and the authers concluded that PM emission benefits with biodiesel are questionable over a cold start driving cycle [Fontaras 2009].

Note that the biodiesel effects upon PM emissions presented above are mainly based upon diesel vehicles/engine without DPF[2]. A recent study by Luján et al showed that high efficient DPF led to reduction in PM emissions drastically; the potential benefits of biodiesel in PM reductions is thus hided [Luján 2009]. Contrary results were reported by William et al. in a study of HD engine with a catalyzed continuously regenerating particle filter (CCRT™) fuelled by Soy Methyl Ester (SME) and ultra-low sulphur diesel fuel [Williams 2007]. With and without the DPF, PM emissions were significantly reduced by using the SME comparing to the diesel fuel.

The effects of biodiesel upon particle number emissions have been investigated, and most studies reported increases in the number of nanoparticles with biodiesel. Krahl et al studied particle number emissions using rapeseed biodiesel and low sulphur diesel fuels [Krahl 2003]. They observed an increased number of particles in the 10-40 nm range but reduced particles above 40 nm when biodiesel was compared to the diesel fuel. Increase in particle numbers below 30 or 40 nm were again observed by the authors in a study of pure soybean, rapeseed and palm oil and their blends comparing to diesel fuel [Krahl 2006, Krahl 2005].

The effect of blending of RME in diesel upon dry particle number emissions from HD engine was reported by Mayer et al [Mayer 2005]. The solid particle number were reduced using 100% RME compared to RME blends, however RME blends tend to increase the number of fine particles as shown in *Figure 7*. The authors explained that the lower particle emissions for the RME are due to the high oxygen content of RME promoting internal particle oxidation.
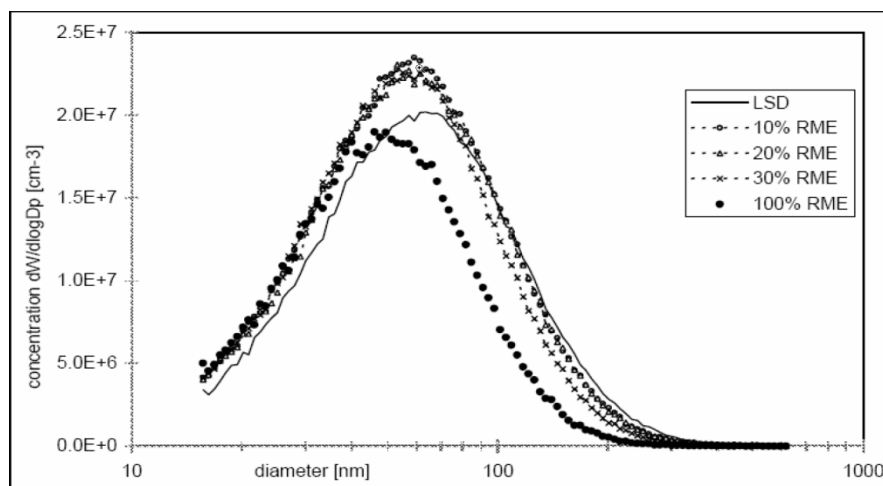

Figure 7 Particle size distribution at 1400 rpm without DPF. LSD is Low Sulphur Diesel [Mayer 2005]

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[2] Note so far no car manufacturer allow the use of pure biodiesel in diesel cars with DPF. PSA (Peugeot-Citroën) allow 30% biodiesel blends in cars using DPF.

A recent study on passenger car carried out by Fontaras showed that solid particles (PMP equivalent PN) decreases with biodiesel and biodiesel blends but total particle number increased comparing to diesel fuel [Fontaras 2009], indicating increase in volatile particles with biodiesel fuel. The authors observed an increase of dry nanoparticles in the range of 20 -55 nm with biodiesel fuels. The authors suggested that the reduction of solid particle numbers is caused by the oxygen content in biodiesels. They also proposed that the C=O bond does not lead to soot formation and thus those carbons don't contribute to soot production. The authors believed that the increase in the volatile particle emissions is associated with the reduction of the solid particle emissions. The decreased surface area of solid particles, resource for condensation of volatile species, promoted the formation of nanoparticles by homogeneous nucleation.

8.3   GTL/BTL and particle emissions

It is commonly agreed that GTL/BTL fuel led to decreased PM emissions compared to diesel. The GTL effects upon PM emissions were reviewed by Steinbach et al [Steinbach 2006]. Significant reductions (about 55% to 75%) of PM by GTL were observed for PM emissions compared to diesel fuel. The results were in good agreement with many studies [Fanick 2001, Schubert 2002, Li 2009, Oja 2006].

Czerwinski reported that PM and PN emissions from GTL were related to engine load. PM emissions from GTL fuel at the low engine load were similar to those from conventional diesel fuel but lower at the high engine load. The particle number emissions from GTL at low load were higher compared to diesel but similar at the high load.

Schubert et al reported a significant reduction of particle number emissions in the nucleation mode with the synthetic diesel fuel. The authors explained that the negligible sulphur content of the synthetic diesel led to reduction in the nucleation mode sulphate particle emissions [Schubert 2002]. The reduction of particle number emission by GTL was also reported by Li et al [Li 2009].

Reduction of PM emissions with NExBTL and GTL fuels were also reported by Kleinschek and Rothe et al [Kleinchek 2005, Rothe 2005]. The reduced aromatic content in the NExBTL fuel was claimed to be the reason for the PM reduction.

8.4   Lubricant oil and particle emissions

Effects of Lubrication oil upon PM emissions appear to be an important yet little investigated area. Long chain alkenes and sulphur in lube oil supply condensable material for the semi volatile PM fraction and thus play important roles in the nucleation mode particle formation. Calcium, zinc, phosphorus and other elements in the additives contribute to the PM ash contents. The metal emissions are of great concerns because of their potential health effects.

In a review article Johnson indicated the importance of lubrication oil to the emission of nucleation mode particles [Johnson 2003]. It is suggested that a change to synthetic oil may reduce formation of nucleation mode particles by 50%, presumably due to the higher volatilization temperature of synthetic oil [Johnson 2003].

Sakurai et al studied nucleation particle composition from a HD engine using synthetic Fischer-Tropsch fuel [Sakurai 2003], showed that 95% of the organic fraction of diesel nucleation mode particles was comprised of unburned lubricating oil, by compounds with carbon numbers in the C24-C32 range. The results are in good agreement with Jojnson's study, i.e. lube oil contributes significantly to the emissions of nucleation mode particles.

Miller reported measurable levels of metallic lube oil additives in bulk diesel particulate matter (DPM) samples, they suggested that the metals in exhaust particles originate from lubrication oil that is spread onto the cylinder walls by the piston rings or that enters the combustion chamber via reverse blow-by of the rings [Miller 2007].

Kittelsson illustrated that the presence of sulphur in the lubricant contribute to emissions of sulphate particles (nanoparticles) [Kittelsson 2006].

The emissions from crankcase vapour are not yet regulated in the current EU regulation for HD engines. For most of the present engines the crankcase emissions were directly released to ambient air. The coming Euro 6 regulation for HD engine requires either closed crankcase system or routing of the crankcase vapours into the dilution tunnel during certification tests. Due to the stringent PM and PN regulation for HD Euro 6 regulation, most probably the future HD must be equipped with DPF, by which significant soot emission reduction will be achieved. At then condensed crankcase vapours may dominate the overall PM emissions.

8.5 Diesel engine technology and particle emissions

Engine technology is of great importance in particle emissions. This chapter reports the trend of particle emissions with the development of engine technology.

A study of PM emissions with different engine technology clearly showed that PM emissions from modern car with common rail technology are significantly lower than the PM emissions from conventional diesel cars with turbo direct injection [de Serves 2002].

A comprehensive study E-43 of several engine models indicated that old and new technology engines produce nuclei particles of similar magnitude. In the new engines PM is reduced due to decreased accumulation mode particles [Kittelson 2002]. This is well illustrated in *Figure 8*. The data from the Health Effects Institute (HEI) were also included in the Figure [Bagley 1996]. The comparison showed that the model year 1999-2000 engines produced fewer nanoparticles than the 1991 engines.
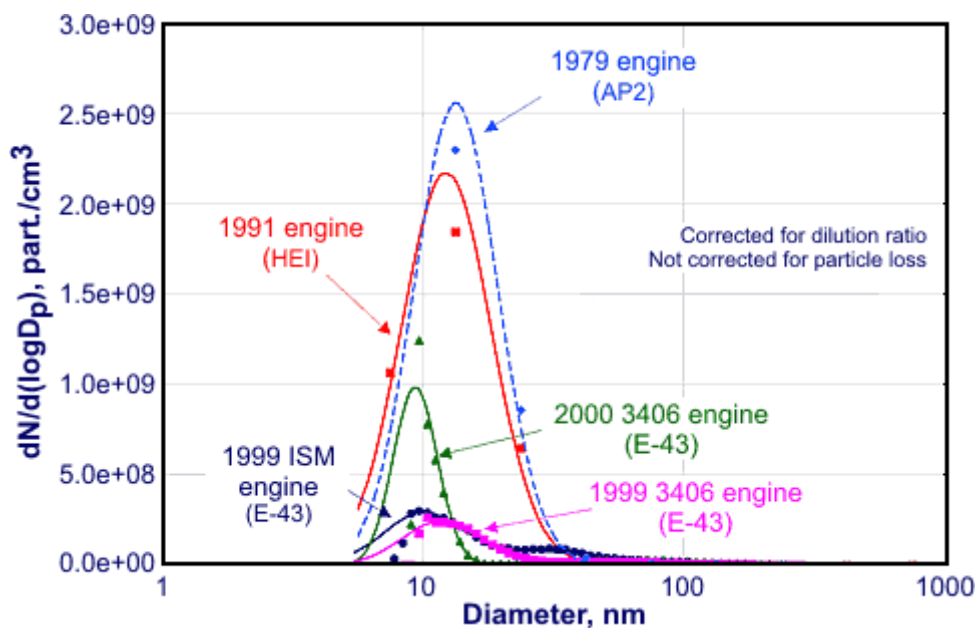
Figure 8 Particle number emissions from different engines. [Kittelson 2002].

Generally advanced engine technology led to reduction in PM and particle emissions [Wedekind 2000, Andersson 2001, ACEA 2002]. The ACEA study also showed that the size distribution of diesel particulates was similar in the older and more advanced technology vehicles and the particulate mass could be correlated with particle numbers.

8.6   Diesel particle filter (DPF) and particle emissions

Meeting future emission standards leads to rapid development and implementation of advanced after-treatment technologies. Diesel particulate filter is one of the most promising technologies used for particle reductions. This report only focuses upon the wall-flow type filter (so called full filter), other type particle reduction device will not be discussed here. It is worth to point out that when an efficient DPF is used, it will become the primary driver on tailpipe particle emissions. From the emissions point of view the properties of fuel would have only secondary importance. Thus, the primary fuel issue would be its compatibility with particular after-treatment technologies.

Note that after-treatment technologies such as EGR, oxidation catalyst, SCR etc have also significant impacts upon the particle emissions; even the primary purpose of these technologies is not for reducing particle emissions.

Modern DPF technology allows a very efficient removal of solid particles, and also of the nanoparticles. Numerous studies have been carried out to develop and characterize the DPF for PM reductions. A typical example is given here with a study of particle emissions from Euro 4 passenger cars with and without DPF [Bosteels 2006]. *Figure 9* clearly demonstrated that DPF led to significant PM, PN reductions.

The size distribution data revealed that the DPF reduced particle emissions in the whole range (*Figure 10*).
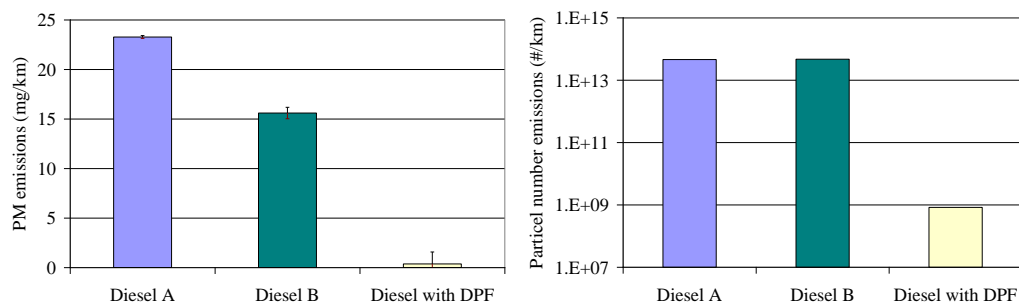
Figure 9 PM emission (mg/km) and PN emissions (#/km) from diesel cars without and with DPF. Diesel A and Diesel B are Euro 4 diesel passenger cars from two different manufacturers.
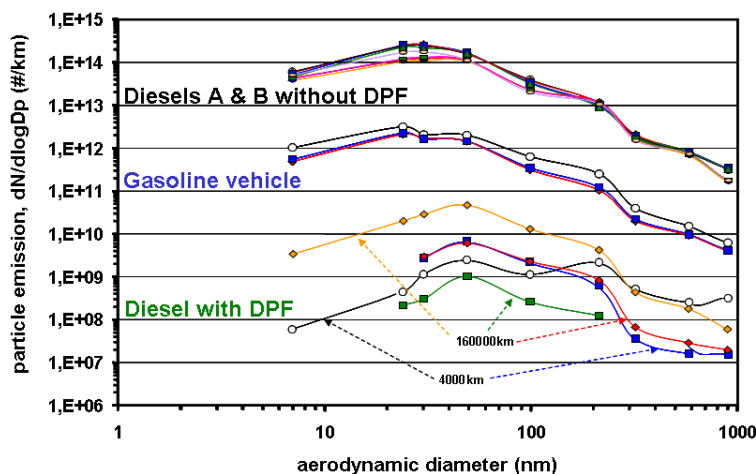
Figure 10 Particle size distribution from diesel cars with and without DPF. Diesel A and Diesel B are Euro 4 diesel passenger cars from two different manufacturers.

Further filter analysis in this study showed that DPF not only reduced elementary carbon (EC) but also organic carbon (OC) emissions see *Figure 11*. The results also indicated that the DPF changed the PM composition profile comparing that from the non-DPF diesel cars, i.e. the PM emitted from DPF car is dominated by organic compounds whereas PM from non-DPF diesel is mainly composed of black carbons. The authors also presented that the DPF reduced PM associated PAH to a very low level.
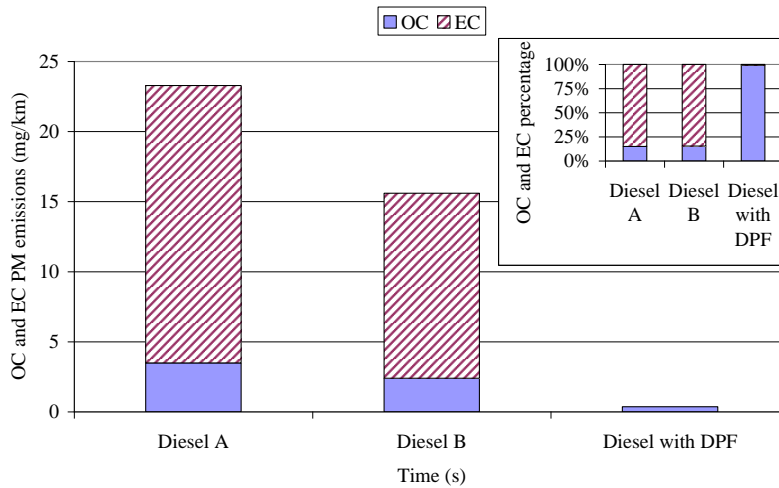
Figure 11 OC and EC emissions from diesel cars without and with DPF

Results from newly finished EU light duty Inter-laboratory Correlation Exercise showed the similar results, i.e. the DPF device reduced the PN emissions from diesel cars from ~10^{13}/km down to 10^{10} - 10^{11}/km levels and PM emissions from ~20 mg/km to less than 5 mg/km [Andersson 2007].

May et al studied particle emissions from HD engine equipped with DOC, DPF and SCR [May 2008]. The DPF led to > 99% PM, PN and elementary carbon emissions. The PN emissions were reduced by DPF from ~10^{14}/kWh to 10^{11} - 10^{12}/kWh, and PM emissions from ~ 50 g/kWh to less than 10 mg/kWh. Similar results were presented by Giechaskiel from the EU PMP HD Validation program [Giechaskiel 2009] (Figures 12 and 13).
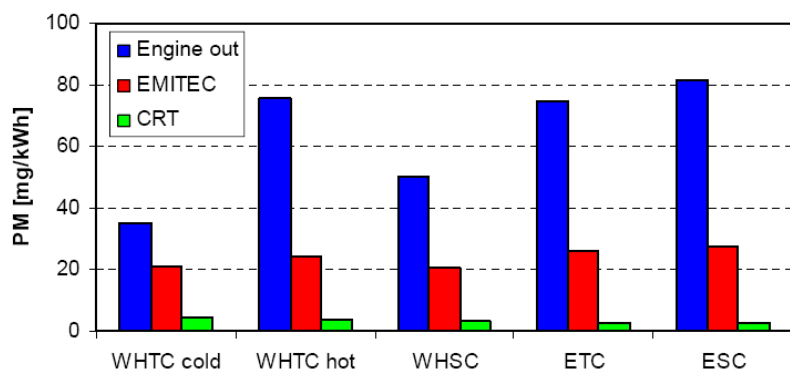
Figure 12 PM emission from Heavy Duty engine with and without filter
(engine out = emissions before catalyst, EMITEC = half filter,
CRT = continuously regenerating particle filter)
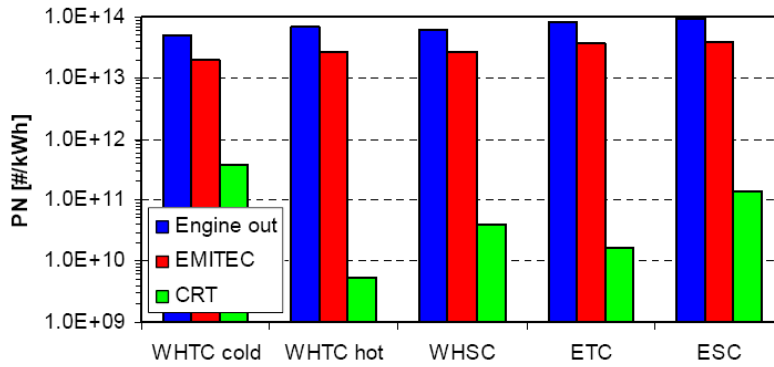
*Figure 13 PN emission from Heavy Duty engine with and without filter
(engine out = emissions before catalyst, EMITEC = half filter, CRT = continuously
regenerating particle filter).*

Andersson showed a DPF cold start effects with increased particle number emissions
in the first 200 s of the NEDC test (*Figure 14*). The results are in good agreement with
the observations reported by Rahman et al [Rahman 2007]. Rahman found that DPF
vehicles emitted about 90% of the total particle number emissions within the initial
200 s of the cold start NEDC tests. Particle emissions decreased drastically once the
vehicle and the DPF system attained operating temperature.
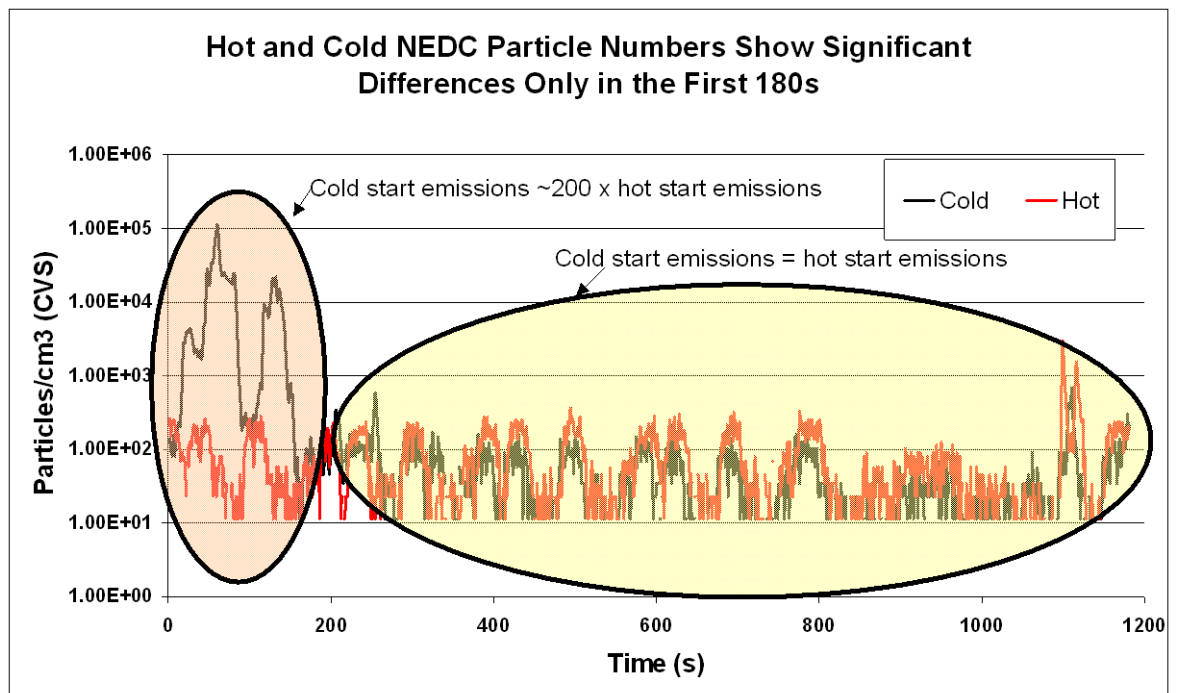
*Figure 14 PN emission cold start effect in the NEDC with a DPF diesel vehicle
[Andersson 2007].*

It is recognized that PM and PN emissions will be increased during DPF regeneration.
The results from Karlsson et al's study illustrated such 'regeneration' effects (*Table 4*)
[Karlsson 2005]. The presentation from Andersson et al showed the regeneration

promoted more nucleation particles (mainly volatiles) than solid particles (> 50 nm) [Andersson 2007]. Maik et al also observed that the majority of the particles emitted during DPF regeneration were volatiles [Maik 2009].

Table 4 PM and PN Emissions from a Euro 4 diesel-DPF passenger car with and without regeneration [Karlsson, 2005].

	PM (g/km)	P (#/km)
Test with regeneration	0,0054	1,39E+11
Test without regeneration	0,0012	2,28E+08
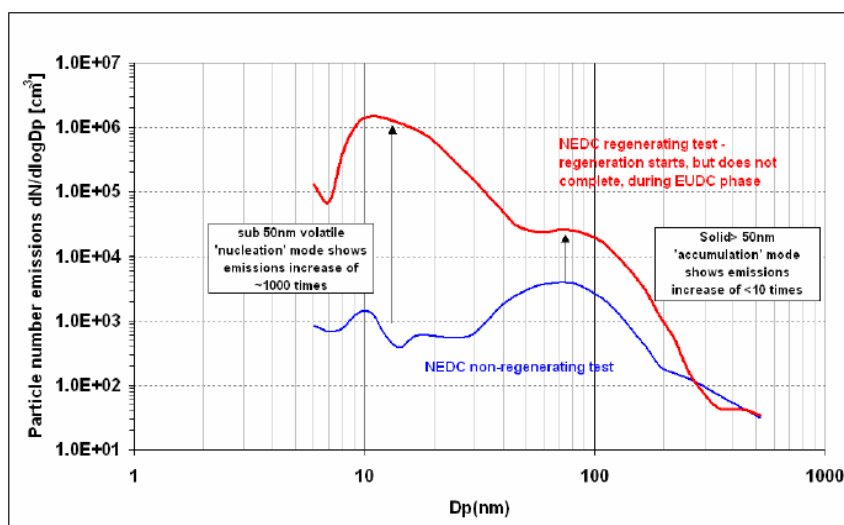
Figure 15 Particle size distribution from a DPF diesel car with (red graph) and without (blue graph) regeneration.

A recent study of metal emissions from HD vehicles equipped with DPF and SCR showed that all tested DPFs significantly reduced emissions of total trace elements; however the authors observed emissions of vanadium and titanium from vanadium-based DPF + SCR vehicle, suggesting the possible release of actual SCR wash-coat (V2O5/TiO2) from the catalyst under the higher temperatures operation [Hu 2009].

It is worth to point out most of the modern passenger cars with DPFs can not use pure biodiesel fuels. This is due to the lubrication oil dilution that happens during DPF regeneration. In the regeneration process fuel is injected to increase exhaust temperature and some of the fuel ends up on the combustion chamber surfaces and cylinder walls. With the lubrication oil, the fuel is transported to the oil sump. The high boiling range of biodiesel makes the oil dilution problem more severe. As a result, no car manufacturer allows the use of pure biodiesel in their diesel cars with DPF today. One exception is PSA (Peugeot-Citroën) who allow blendings of up to 30% biodiesel. PSA is using a different regeneration strategy for the DPF than most other car manufacturers

However, on heavy-duty vehicles/engines with DPF can be fuelled by biodiesels and blends, since HD DPF are using a different regeneration strategy for the filters (DPF) than passenger cars today (passive and continuous regeneration). The effects of biodiesel on DPF were studied by Williams et al [Williams 2006]. The results suggest significant benefits for the use of biodiesel blends in engines equipped with DPFs. The significant lowering of BPT (BPT, the DPF inlet temperature at which the rate of particle oxidation approximately equals the rate of particle collection) and increase in regeneration rate might allow passive DPFs to be used in lower temperature engine duty cycles, avoiding the need for actively regenerated filters and their associated fuel economy penalty. The author predicted that actively regenerated systems might require less frequent regeneration, also resulting in a lower fuel economy penalty.

8.7 Petrol engine, GDI technologies, ethanol fuel and particle emissions

Particulate emission research has mostly been focused on diesel exhaust. This due to the fact that particle emissions from petrol engines (SI) were much lower compared to those from diesel engines, this is clearly illustrated by Bosteels and Anderson's studies [Bosteels 2006, Andersson 2007]. However diesel vehicles equipped with DPF can reduce PM and PN emissions to similar or even lower levels than petrol cars, the interest in particle emissions from petrol engine may be an issue.

Some comments from Graskow and Greenwood's studies upon PM emissions from petrol engines can be given here [Graskow 1999, Greenwood 1996, Graskow 1998]:

- Petrol engine particulates are composed of much smaller particles than those from diesel engines. In some reports, the petrol engine particles were found practically entirely in the nanoparticle range (<50 nm).

- Particle numbers in the petrol engines are about 2 orders of magnitude lower than those in diesel engines when measured at low engine speeds or over standard engine test cycles. The particle number emissions increase significantly at rich air-to-fuel ratios. At such conditions, comparable particle numbers may be emitted from petrol and diesel engines.

- Petrol and diesel engines have different mechanism of particle formation.

- Petrol engine particles appear to be composed of ash (calcium, magnesium, copper, iron, sodium, ...), lube oil, and other volatile components, the elemental carbon content is low in comparison to diesel [Bosteels 2006].

- Three-way catalytic converters decrease the concentrations of the smallest particles. Different types of fuel additives may either increase or decrease the particulate number concentrations.

Gasoline direct injection engine (GDI) technology is already commercially available in Japan and Europe. It is well known that GDI leads to increased particle emissions. Indeed PM emission limit is applied to the GDI petrol cars from Euro 5 regulations; and it is under intensive discussion if PN limit also should be applied to petrol vehicles in Euro 6 regulations. The particle emissions from GDI vehicles were reported by numerous studies, and it was agreed by all the authors that GDI led to increased emissions both in particle mass and numbers [Lu 2000, Hall 1999]. The results from PMP projects clearly showed that GDI vehicles have lower PM and PN emissions than diesel vehicles but have significantly higher PM and PN emissions than the DPF diesel cars or conventional petrol vehicles [Andersson 2007].

The effects of ethanol fuel blends upon PM and PN emissions were investigated by de Serves, Karlsson et al [de Serves 2005, Karlsson 2008], but no conclusive comments can be drawn from their studies. Karlsson et al observed that the ethanol effects upon particle emissions were different at different test temperatures. E85 led to reduced PN emissions comparing to E5 fuel at 22°C tests, but no fuel effects upon PM emissions were found at this temperature. At -7°C, vehicles operating with E85 fuels led to significant increase in PM and PN emissions. On the contrary de Serves reported higher PM and PN emissions from E5 comparing to E85 fuels at the cold climate tests.

9 NOx EMISSIONS

Similar as particle issue the main concern of NO_x emission has been focused upon on diesel vehicles and engines, since the well developed three-way catalyst have brought down the NO_x emissions from petrol vehicles to significant lower levels than for diesel vehicles. Traditionally the EU limits for diesel NO_x emissions are significantly higher than for petrol cars. The scenario will be changed in Euro 6 regulations, the NO_x limits for diesel vehicles will be at the similar levels as petrol cars, thanks to the potential brought by the rapidly developed after-treatment technology.

The NO_x emissions from GDI vehicles are significantly higher than conventionally petrol vehicles; this is well illustrated by numerous studied [Lu 2000, Hall 1999]. The lean burn principle of the GDI requires other type of NO_x after-treatment device than TWC [Li 2009a], the development of after-treatment technology for GDI will not be further discussed here.

The focus of this chapter will be the impacts of biodiesel fuel and after-treatment technology upon NO_x and NO_2 emissions from diesel vehicles/engines.

9.1 Biodiesel and NOx emissions

Most of the studies agreed that NO_x emissions increase when using biodiesel fuel; however some work showing different effects were also reported.

In the above cited literature NO_x data based on emission results from HD engines of model year 1997 or earlier without EGR or after-treatment system were used by EPA to adjust the following equation, statistically significant with a 95% confidence level [EPA 2002]:

$$NOx_B/NOx_D = e^{0,0009794\%B}$$

B = biodiesel
D = diesel
%B = biodiesel volume percentage in diesel fuel

Figure 16 Equation describing the effects of biodiesel on NO_x (no EGR or afte-treatment system)

This equation provides an almost liner increase in NO_x emissions as the biodiesel contents. The formula was widely used to describe the effects of biodiesel on NO_x emissions [Staat 1995, McCormick 2005a, McCormick 2005b, National]. The trend of in increase of NO_x emissions with the increased biodiesel in the fuel were confirmed by numerous studies [FEV 1994, Schumacher 1994, Marshall 1995]. With pure biodiesel a 4-20 % increase in NO_x emissions was reported by different studies [Graboski 1998, Marshall 1995].

Some authors concluded that the effects of biodiesel on NO_x emissions depend upon the engine operation conditions. Hamasaki reported slight decrease in NO_x emissions

at low loads but increase at high loads when testing waste-oil biodiesel fuels [Hamasaki 2001]. This concluded that the NO_x emissions with biodiesel fuel were usually increased during engine tests but not in the vehicle tests [Ta 2003]. The reason pointed out was that the engine load was usually lower in the vehicle tests than in the engine rig tests, conclusions in consistent with some other studies [Hamasaki 2001, McCormick 2005, McCormick 2005a]. Some researcher suggested the higher cetane number of biodiesel fuel comparing to diesel fuel could explain the dependence of NO_x emissions with different loads [Li 1998].

Some researchers found that biodiesel fuel effects upon NO_x emissions were not significant [Durbin 2000, Durbin 2002, Nabi 2006, Wang 2000]. A minor number of papers have reported decrease in NO_x emissions when using biodiesel fuels [Peterson 1996, Dorado 2003, Lapuerta 2005]. About 5-10 % decrease in NO_x emissions with biodiesel and blends were reported by different studies.

Some authors reported that different types of biodiesel (carbon chain length and unsaturation degree) led to differences in NO_x emissions. Graboski et al showed that NO_x emissions increased as the mean carbon chain length decreased and as the unsaturation increased [Graboski 2003]. The latter effect led to a linear relation with the iodine number (number of double bonds in the ester molecule), .i.e. the higher iodine number the higher NO_x emissions. Graboski indicated that the iodine number is closely related to density, compressibility and cetane number.

The results from EPA and some other studies also confirmed the relationship between NO_x emissions and molecular unsaturation [EPA 2002, Ta 2003, Peterson 2000, Wyatt 2005]. In general soybean-oil biodiesel provided 15% increase in NO_x emissions as compared to the diesel fuel, rapeseed with a 12% increase, animal fats diesel only 3%, since these different types of biodiesels have different unsaturation degree.

Chapman et al studied improving soybean diesel blends with adding short chain methyl ester or hydrogenating the soybean biodiesel and showed somewhat reduction in NO_x emissions comparing to the non-modified biodiesel blends [Chapman 2004]. McCormich reported using a low aromatic content diesel fuel when blending with biodiesel to compensate increase in NO emissions by biodiesel [McCormick 2002]; however this approach was not supported by Bermúdez et al's study [Bermu 2003]. Cetane enhancers as di-tert-butyl peroxide (DTBP), ethyl hexyl nitrate (EHN), anti-oxidant additives as tert-butyl, butylated hydroxyanisol (TBHQ) were investigated to compensate increased NOx emissions with biodiesel fuel. They found that the cetane enhancers DTBP and EHN both are effective at reducing NOx from biodiesel. The antioxidant TBHQ is also effective, but may cause an increase in PM emissions. The authors proposed to investigate further antioxidants as NOx reduction additives, and suggested that it may be other antioxidants also reduce NOx but have no negative impact on PM emissions. [McCormick 2002, Hess 2005].

GTL/BTL and NO_x emissions.

Most studies showed that GTL/BTL fuel led to somewhat decreased NO_x emissions comparing to diesel fuel. In the studies of NExBTL and GTL effects upon NO_x emissions by Rothe, Kleinschek, Oja and Li, 10 to 22% reduction in NO_x emissions were observed [Rothe 2002, Kleinschek 2002, Oja 2006 and Li 2009].

Steinbach et al reviewed the GTL effects upon NO_x emissions, somewhat decreasing in NO_x emissions (2 to 6%) with GTL comparing to diesel fuel were found in their study except one case [Steinbach 2006]. Schubert et al also reported a slight increase in NO_x emission by GTL [Schubert 2002].

9.2 NO_x After-treatment technology and NO/NO_2 ratio

As presented above different after-treatment technologies can be applied in diesel NO_x reductions, e.g. SCR, NO_x adsorb, Lean De-NO_x catalysts etc.

A possible technology mix for meeting the NO_x limit in Euro 6 is shown in *Figure 17*. The Figure showed that for smaller engines Euro 6 could be met without any NO_x after-treatment. For engines up to 3 liters, NO_x adsorbing catalysts are of great interest, while the largest engines might use an SCR catalyst with urea as a reducing agent, a technology widely used on heavy-duty vehicles in Europe. Indeed Gekas reported that Euro VI NO_x emission limits could be achieved with a SCR catalyst (in combination with DOC and DPF). In the ETC cycle NO_x emissions was reduced from 10 g/kWh down to below 0.4 g/kWh, the SCR catalyst thus achieving >95% NO_x conversion [Gekas 2009].
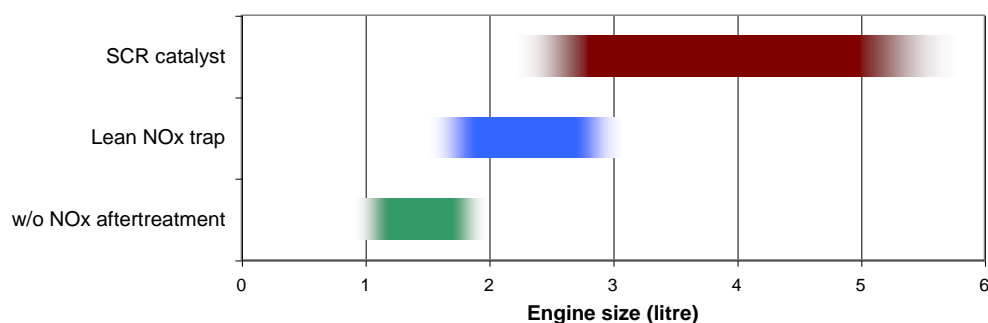
Figure 17 Potential of different technology for meeting Euro 6 NO_x limits [Alvik].

Present report will not further discuss the different NO_x after-treatment technologies and their performance in NO_x reduction. The focus will be on NO_2/NO_x ratio issue, which is a by-effect of advanced after-treatment technology and is now of great concern in EU.

As we stated in the beginning of the report, NO is the dominated composition (about 80-95%) in NO_x emissions from combustion engine. However NO_2/NO_x ratio is significantly enhanced in the modern vehicle fleets, this is a result of direct NO_2

emissions induced by the penetration of after-treatment technology [Grice 2009]. The data from the Swedish passenger car In-Use Compliance (IUC) program in 2007 confirmed the problematic of high NO_2 emissions directly from the current production vehicles (*Figure 18*).
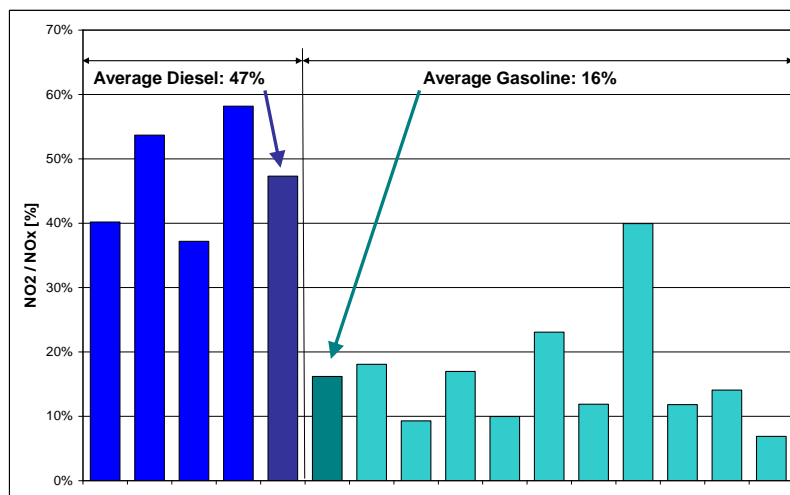
Figure 18 NO_2 /NO_x ratio, results from Swedish IUC tests in 2007. Each bar in the graph represents the average for all tested cars of the same car model. In total, the graph represents 79 individual cars. The average NO2/NOX ratio for diesel cars is about a factor 3 higher than for petrol-fuelled cars.

It is recognized that using oxidation catalysts for CO and HC oxidation led to a side effect of oxidation of NO to NO_2. For some types of after-treatment devices, the oxidation of NO to NO_2 is desired. For DPF NO_2 formed in a DOC catalyst before the DPF will strongly promote filter regeneration ("passive" regeneration), since NO_2 is a much more active species than O_2 for soot oxidation. [Cooper 1989]. The commercialized DPF under the name CRT™ is based upon this principle. NO_2 is reduced to NO by reacting with soot, but the reaction does not fully reduce the NO_2 share to pre-catalyst levels. Note that even so called "active" regeneration DPF systems use the NO_2 effect to a certain extent.

NO_2 is also a desired product for the SCR catalyst, since NO_x reaction with ammonia is promoted with a mixture of 50% NO_2 in NO_x. Another example is the so-called NO_x storage catalyst, which is used for NO_x abatement on petrol-fuelled direct injection engines. Similar catalysts are now being introduced on diesel engines. The NO_x storage catalyst relies on the oxidation of NO to NO_2 before NO_x storage.

Although the oxidation of NO to NO_2 is desired for many exhaust after-treatment systems, a high NO_2 share is not desired in the tailpipe exhaust. Some researcher reported that the tailpipe NO_2/NO_x ratios could be decreased by changing DPF coating. The effects of catalyst formulations in DPF systems upon NO_2/NO_x ratio were reported by Czerwinski et al [Czerwinski 2006] (*Figure 19*). The black line shows the NO_2/NO_x ratio without a DPF, the higher the temperature the lower NO_2/NO_x ratio

due to the NO, NO_2 equilibrium shifts. Catalyst coatings have significant effects on the NO_2/NO_X ratio. Platinum (Pt) catalysts strongly promote the oxidation of NO to NO_2, whereas base metals have little – or negative – effect on the NO_2/NO_X ratio. Using proper catalyst coating for NO_2 suppression in DPF was also reported by other researchers [Lemaire 2009, Mogensen 2009].
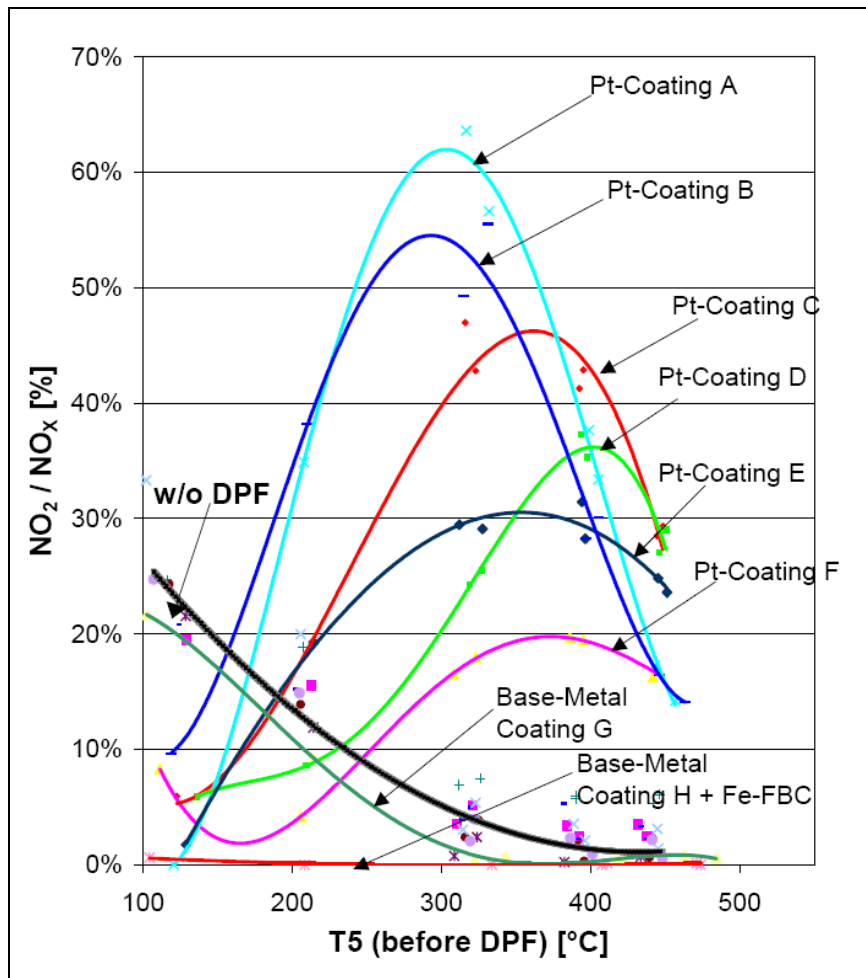
Figure 19 NO_2/NO_X ratio with different DPF coatings [Czerwinski 2006]
T5 = a temperature sensor placed before DPF.

10 BIODIESEL AND OTHER EMISSIONS

This chapter covers emissions from biodiesel beside NO_x and particles.

Since the biodiesel is the main topic of this report, some comments about other emissions than PM and NO_X, and unregulated emissions from biodiesels are given here.

10.1 HC, CO emissions

Most authors observed a sharp decrease in the THC (total hydrocarbon) and CO emission with biodiesel comparing to diesel fuel [Monyem 2001, Staat 1995, Pinto 2005, Shi 2005], a few authors have, however, reported no difference or even increased THC and CO emissions by using biodiesel fuels [Serdari 1999, Hamasaki 2001].

$$THC_B/THC_D = e^{-0,011195\%B}$$
$$CO_B/CO_D = e^{-0,006561\%B}$$

B = biodiesel
D = diesel
%B = biodiesel volume

Figure 20 Equation expressing the reduction in CO and HC emissions(no EGR or afte-treatment system)

The formulas indicate a 70% reduction in THC and a 50% reduction in CO with pure biodiesel compared to conventional diesels. Rather similar reductions in THC [Nwafor 2004, Last 1995] and CO [Krahl 2003, Peterson 1996] by neat diesels were reported, whereas some authors reported either higher or lower reductions comparing the values predicted by the equations.

Figure 21 Regulated emissions (NO$_X$, PM, CO, HC) as a function of biodiesel contents in the fuel (data from HD engine without EGR (exhaust gas recirculation) or after-treatment device) [EPA 2002].

The EPA review, already mentioned above, summarised the impact of biodiesels upon regulated emissions (*Figure 21*) [EPA 2002].

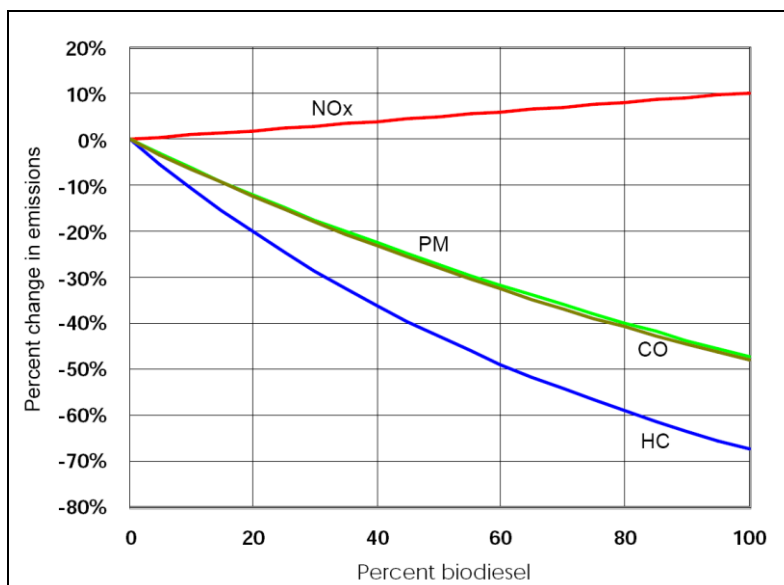The EPA equation indicates that relative larger THC reductions will be reached with lower biodiesel contents; Last et al's study of soybean biodiesel blends confirmed this statement [Last 1995]. On the contrary some authors reported liner THC reductions with biodiesel blends [Handbook, Peterson 1996]. Linear and non liner trends in CO emissions as a function of biodiesel contents were reported [Last 1995, Peterson 1996].

Engine operation mode is not a decisive factor in THC emissions with biodiesel fuel but have a remarkable effect on CO emissions. Most authors concluded that CO emissions decrease with biodiesel except at low load conditions.

Aakko reported that the biodiesel effects upon THC reduction were much sharper with an engine without DOC (diesel oxidation catalyst) than that with DOC [Aakko 2002], and biodiesel led increasing in CO emissions with the DOC equipped engine. Same conclusions were also reached by other studies [Munack 2001].

The biodiesel origin and the alcohols used in production process are not factors significantly affecting THC emissions. No conclusion could be reached concerning the effects of saturation level upon THC emissions. The presence of peroxides in the biodiesel may result in lower THC emissions [Monyem 2001a].

EPA's study of biodiesel feedstock effects upon CO emissions concluded that higher CO reduction could be achieved with animal fat biodiesel compared to rapeseed or soybeen oil biodiesel [EPA 2002], the results were supported by Graboski et al [Graboski 2003]. Knothe reported that CO emission with biodiesel was reduced with the increased chain length [Knothe 2006]. Hamasaki et al stated that CO emissions increase when the biodiesel acidity increases [Hamasaki 2001]. Monyem et al found decreased CO emissions with oxidized biodiesel [Monyem 2001a].

Some reasons have been suggested to explain the decrease in THC and CO emissions with biodiesel [Lapuerta, 2008], such as:
(1) The oxygen content in the biodiesel molecule, which leads to a more complete and cleaner combustion;
(2) The higher cetane number of biodiesel reduces the combustion delay, and such a reduction has been related to decreases in THC emissions;
(3) Higher final distillation points of diesel fuel;
(4) The advanced injection and combustion timing when using biodiesel

10.2 Unregulated emissions

The effect of biodiesel on the unregulated emission of these compounds is very limited with poor repeatability [Graboski 1996, EPA 2002]. It is generally agreed that emissions of toxic compound were lower from biodiesels than from diesel fuel.

EPA concluded that the emissions of toxic compounds were lower with biodiesel than with diesel fuel by about 16% with pure biodiesel. This reduction is lower than that of THC (70% reduction), which means that the concentration of toxics in the biodiesel emitted hydrocarbons is higher than diesel fuels [EPA2002].

Pinto and Graboski reported decreased aromatic and PAH emissions when using biodiesel, and attributed such decrease to the absence of PAH in the biodiesel fuel [Pinto 2005, Graboski 1998]

Krahl et al reported that PAH emissions decreased with rapeseed oil biodiesel independent upon engine type and operation conditions. Similar results were shown by Karavalakis et al using soy methyl blends [Krahl 1996, Karavalakis 2009a]. Karavalakis and Di observed an overall aromatic and PAH reduction with the biodiesel blend [Di 2009a], whereas Krahl reported increased emissions of benzene based aromatics during certain occasions [Krahl 1996].

Oxygenated compounds (carbonyl) like aldehydes and ketons were studied concerning the biodiesel exhaust emissions. Aldehydes and ketons appear in intermediate phases of the combustion process. These compounds are precursors of ozone formation (and other oxidative species) in the troposphere (photochemical smog). It is widely believed that biodiesel could increase emissions of these oxygenated compounds as a consequence of the oxygen content in the molecule. However no clear conclusions can be drawn from the literature survey studies [EPA 2002, Staat 1995, Pinto 2005, EPA 2002, Turrio-Baldassarri 2004].

Karavalakis et al reported decreased carbonyl emissions using soy methyl ester blends [Karavalakis 2009a]. On the contrary Lin found that neat palm-biodiesel and 20% biodiesel blend led to increased carbonyl emissions by 9.74% and 2.89%, respectively comparing to diesel. Lin observed, however, paraffinic-palmbiodiesel blends significantly reduced carbonyl emissions [Lin 2009]. Di Fontaras et al also observed increased carbonyl emissions with biodiesel and its blends [Di 2009, Fontaras 2009].

The effects of biodiesel quality upon carbonyl emissions were also investigated by some authors, and they suggested that high glycerine in biodiesel led to increased aldehyde emissions [Graboski 1998, Hamasaki 2001, Graboski 2003].

Hydrocarbon species 1,3-butadiene is one of the toxic compounds identified in the diesel exhausts. However few studied have been carried out to identify 1,3-butadiene emissions from biodiesel. The limited results indicated that using biodiesel led to reductions in 1,3-butadiene emissions comparing to diesel fuel [Di 2009, Di2009a].

11 COMMENTS ABOUT ETHANOL, BUTANOL AND PYROLYSIS OIL

Emissions from ethanol/E85 fuel vehicles/engines have been investigated by many authors. The most thoughtful study was carried by Westerholm et al [Westerholm 2008, Karlsson 2008]. The most important conclusions from their study are given here.

In the cold start NEDC tests the ethanol/petrol vehicles operating with E85 led to reductions in NOx, 1,3-butadiene, benzene, toluene, PAH and PN emissions, but increase in aldehyde emissions. The influence of using E85 fuel upon CO and HC emissions was closely related to the engine calibration strategy and catalyst converter efficiency.

At -7°C, vehicles operating with ethanol fuels led to severe increase in aldehyde emissions together with significant rise in CO, HC, PM, PAH and PN emissions. Using E85 winter fuel (about 75% ethanol contents in the fuel) had only marginal effects upon cold climate emissions compared to E85.

In the warm start tests, E85 fuel had trivial or no effects upon HC, aldehyde, HC speciation emissions, but led to reductions in CO and PAH emissions.

Using ethanol fuel improved energy consumption in all test conditions although the volumetric fuel consumption of ethanol fuels was much higher than those of the petrol fuel.

Butanol is one of the alternative fuels that can be used in both petrol and diesel engines. Until now the few existing studies are mostly focused upon its combustion characters.

There are too few results about butanol emission performance to give any general comments. An example can be given here. Scott et al studied emissions from diesel cars fuelled with butanol blend [Scott 2008]. The butanol effects upon HC, CO and NO_X emissions depend upon the blending level and driving conditions. E.g. for the urban driving, butanol blends led to increased CO and HC emissions, and NO_X emissions keep unchanged with a 20% butanol blend and decreased with a 40% butonal blend. A significant soot reduction was observed with the 40% butonal fuel.

Pyrolysis oil is a synthetic fuel that is under study as a substitute for petroleum. Murugana studied tyre pyrolysis oil (TPO) and diesel blends as a fuel in diesel engine. High smoke, HC and CO emissions were observed with TPO and blends [Murugana 2009, Murugana 2008].

REFERENCES

[Aakko 2002] Aakko P, Nylund NO, Westerholm M, Marjama¨ ki M, Moisio M, Hillamo R, et al. *Emissions from heavy-duty engine with and without after-treatment using selected biofuels*. In: FISITA 2002 world automotive congress proceedings, F02E195, 2002

[ACEA 2002]. ACEA, ACEA programme on emissions of fine particles from passenger cars, Brussels, Belgium, 2002

[Alfuso 1993] Alfuso S, Auriemma M, Police G, Prati MV. The effect of methyl ester of rapeseed oil on combustion and emissions of DI engines. SAE paper 1993, 932801

[Andersson 2001]. Andersson, J.D., Wedekind, B., DETR/SMMT/CONCAWE Particulate Research Programme, Ricardo report DP01/0515, 2001

[Andersson 2007]. Andersson J., Giechaskiel B., Muñoz-Bueno R., Sandbach E. and Dilara P. *Particle Measurement Programme (PMP) Light-Duty Inter-laboratory Correlation Exercise (ILCE_LD) Final Report*, Informal document No. GRPE-54-08 Rev.1, June, (2007)

 [Armas 2006] Armas O, Herna´ ndez JJ, Ca´ rdenas MD. Reduction of diesel smoke opacity from vegetable oil methyl esters during transient operation. Fuel 2006;85:2427-38

[Bagley 1996]. Bagley, S.T., Baumgard, K., J., Leddy, D.G., *Characterization of fuel and after-treatment Device Effects on Diesel Emissions,* Health Effects Institute, MA, Report 76

[Bagley 1998] Bagley ST, Gratz LD, Johnson JH, McDonald JF. Effects of an oxidation catalytic converter and a biodiesel fuel on the chemical, mutagenic, and particle size characteristics of emissions from a diesel engine. Environ Sci Technol 1998;32:1183–91

[Bermu 2003] Bermu´ dez VR, Martı´ nez S. Efectos de la composicio´ n del gas–oil sobre las emisiones contaminantes. Ingenierı´ as 2003;VI(21):18–24

[Bosteels 2006] Bosteels, D., May, J., Karlsson, H., and de Serves, C., "Regulated" and "non-regulated" emissions from modern European passenger cars, SAE-report, 2006-01-1516, 2006a D., May, J., Karlsson, H., and de Serves, C., *"Regulated" and "non-regulated" emissions from modern European passenger cars*, SAE-report, 2006-01-1516

[Bunting 2009]. Bunting A., www.AutomotiveWorld.com, Sep., 22, 2009

[Burtscher 2005]. Burtscher, H., *Physical characterization of particulate emissions from diesel engines: a review*, Journal of Aerosol Science, 36 (2005), 896-932

[Camden 2005] Camden Council (Australia). *Camdem Council Biodiesel Truck Trial 2005; Final report*. Available on line: /www.camden.nsw.gov.au/, 2005

[Cardone 2002] Cardone M, Prati MV, Rocco V, Seggiani M, Senatore A, Vitolo S. Brassica Carinata as an alternative oil crop for the production of biodiesel in Italy: engine performance and regulated and unregulated exhaust emissions. Environ Sci Technol 2002;36(21):4656–62.

[Chapman 2004] Chapman E, Hile M, Pague M, Song J, Boehman A. *Eliminating the NO$_X$ emissions increase associated with biodiesel*. In: The 95th AOCS annual meeting 2004, expo2004.

[Cooper 89]. Cooper B. J. and Thoss J. E. Role of NO in Diesel Particulate Control. SAE Paper 890404.

[Czerwinski 2006]. Czerwinski J., Pétermann J.-L., Comte P. Mayer A. and J. Lemaire*. Diesel NO$_2$-Emissions with Different DPF's and DOC's*. AKPF. Accessible on the Internet at: www.akpf.org, 2006.

[Czerwinski 2007] Czerwinski, J., Zimmerli, Y., Neubert, T., Heitzer, A., and Kasper, M., Injection, combus-tion and (nano) particle emissions of a modern HD-diesel engine with GTL, RME & ROR, SAE Paper 2007-01-2015.

[de Serves 2002]. de Serves, C., Particle emissions from different petrol and diesel engine technologies, AVL MTC reporrt 2002.

[de Serves 2005]. de Serves, C., Emissions from Flexible Fuel Vehicles with different ethanol blends, AVL MTC report 2005.

[Di 2009]. Di, Y., Cheung, CS., Huang, ZH., Experimental investigation on regulated and unregulated emissions of a diesel engine fueled with ultra-low sulfur diesel fuel blended with biodiesel from waste cooking oil, SCIENCE OF THE TOTAL ENVIRONMENT, 407 (2): 835-846, 2009.

[Di 2009a]. Di, Y. G., Cheung, C. S., ; Huang, Z. H., Comparison of the effect of biodiesel-diesel and ethanol-diesel on the gaseous emission of a direct-injection diesel engine., ATMOSPHERIC ENVIRONMENT, 43 (17): 2721-2730 2009.s

[Dorado 2003] Dorado MP, Ballesteros E, Arnal JM, Go´ mez J, Lo´ pez F. *Exhaust emissions form a Diesel engine fueled with transesterified waste olive oil*. Fuel 2003;82:1311–5.

[Durbin 2000] Durbin TD, Collins JR, Norbeck JM, Smith MR. Effects of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. Environ Sci Technol 2000;34(3): 349–55.

[Durbin 2002] Durbin TD, Norbeck JM. Effects of biodiesel blends and arco ECdiesel on emissions from light heavy-duty diesel vehicles. Environ Sci Technol 2002;36:1686–91.

[EPA 2002] US EPA, A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions - Draft Technical Report. EPA420-P-02-001.

[Eriksson 2009] Eriksson L, Rhenlund B, Yagci K, *Vehicle warranties and the use of biofuels*, Senter Novem, 2009

[Fanick]. Fanick E. R., Schubert P. F., Russell B. J. and Freerks R. L. Comparison of Emission Characteristics of Conventional, Hydrotreated, and Fischer-Tropsch Diesel Fuels in a Heavy-Duty Diesel Engine, SAE Paper 2001-01-3519, 2001.

[FEV 1994] FEV Engine Technology. Emissions and performance characteristics of the Navistar T444E DI engine fuelled with blends of biodiesel and low sulphur diesel. Final report to National Biodiesel Board 1994.

[Fontaras 2009] Fontaras G., Karavalakis G., Kousoulidou M., Tzamkiozis T., Ntziachristos L., Bakeas E., Stournas S., and Samaras Z., *Effects of biodiesel on passenger car fuel consumption, regulated and non-regulated pollutant emissions over legislated and real-world driving cycles,* Fuel, 88(9): 1608-1617, 2009

[Gekas 2009]. Gekas, I., NO$_X$ Reduction Potential of V-SCR Catalyst in SCR/DOC/DPF Configuration Targeting Euro VI Limits from High Engine NO$_X$ Levels, SAE 2009-01-0626

[Giechaskiel 2009], Giechaskiel, B., PMP Group meeting, 2009, London.

[Graboski 1998] Graboski MS, McCormick RL. Combustion of fat and vegetable oil derived fuels in diesel engines. Progr Energy Combust Sci. 1998;24:125–64.

[Graboski 2003] Graboski MS, McCormick RL, Alleman TL, Herring AM. *The effect of biodiesel composition on engine emissions from a DDC series 60 diesel engine*. National Renewable Energy Laboratory 2003; NREL/SR-510-31461.

[Graskow 1998]. Graskow, B.R., Characterization of exhaust Particulate Emissions from A Spark Ignition Engine, SAE 980528.

[Graskow 1999]. Graskow, B.R., Exhaust Particulate Emissions from Two Port Fuel Injected Spark Ignition Engines, SAE 1999-01-1144.

[Greenwood 1996]. Greenwood, W., Particulate Size Analysis, MIRA Automobile Abstract, 1996.

[Grice 2009]. Grice, S., Stedman, J., Kent, A., Abbott, J., Cooke, S., *Recent trends and projections of primary NO2 emissions in Europe,* ATMOSPHERIC ENVIRONMENT, 43 (13): 2154-2167 2009.

[Hall 1999] Hall D.E., Dickens, C. J., Measurement of the number and size dist-bution of particles emitted from a Gasoline Direct-Injection Vehicles, SAE 1999-01-3530.

[Hall 2000a] Hall D.E., Strandling R.J., Zemroch P.J., Rickeard D.J., Mann N., Heinze P., Martini G., Hagermann R., Rantanen L., and Szendefi J., *Measurement of the number and size distribution of particle emissions from heavy duty engines*, SAE-report, 2000-01-2000.

[Handbook] *Handbook of biodiesel: emissions reductions with biodiesel*, 1999. Available on line: /http://www.cytoculture.com/Biodiesel%20Handbook.htmS.

[Hansen 1997] Hansen KF, Jensen MG. Chemical and biological characteristics of exhaust emissions from a DI diesel engine fuelled with rapeseed oil methyl ester (RME). SAE paper 1997, 971689.

[Hamasaki 2001] Hamasaki K, Kinoshita E, Tajima H, Takasaki K, Morita D. *Combustion characteristics of diesel engines with waste vegetable oil methyl ester.* In: The 5th

international symposium on diagnostics and modeling of combustion in internal combustion engines, 2001 (COMODIA 2001).

[Haas 2001] Haas MJ, Scott KM, Alleman TL, McCormick RL. Engine performance of biodiesel fuel prepared from soybean soapstock: a high quality renewable fuel produced from a waste feedstock. Energy Fuels 2001;15:1207–12.

[Hess 2005] Hess MA, Hass MJ, Thomas AF, Marmer WN. *Effect of antioxidant addition on NO$_x$ emissions from biodiesel*. Energy Fuels 2005;19:1749–54.

[Hu 2009]. Hu,S., Herner, JD., Shafer, M., Ayala, A., *Metals emitted from heavy-duty diesel vehicles equipped with advanced PM and NO$_X$ emission controls*, ATMOSPHERIC ENVIRONMENT, 43 (18): 2950-2959 JUN 2009

[Johnson 2003]. Johnson, T.V., *Diesel emission control in review-the last 12 months*, SAE-Report, 2003-01-0039.

[Kado 2003] Kado NY, Kuzmicky PA. Bioassay analyses of particulate matter from a diesel bus engine using various biodiesel feedstock fuels. National Renewable Energy Laboratory 2003 NREL/SR-510- 31463.

[Karavalakis 2009a]. Karavalakis, G., Stournas, S., Bakeas, E., Effects of diesel/biodiesel blends on regulated and unregulated pollutants from a passenger vehicle operated over the European and the Athens driving cycles, ATMOSPHERIC ENVIRONMENT, 43 (10): 1745-1752 2009.

[Karavalakis 2009b]. Karavalakis, G., Stournas, S., Bakeas, E., *Light vehicle regulated and unregulated emissions from different biodiesels,* SCIENCE OF THE TOTAL ENVIRONMENT, 407 (10): 3338-3346 MAY 1 2009.

[Karavalakis 2009c]. Karavalakis, G., Alvanou, F., Stournas, S., Bakeas, E., Regulated and unregulated emissions of a light duty vehicle operated on diesel/palm-based methyl ester blends over NEDC and a non-legislated driving cycle, FUEL, 88 (6): 1078-1085 JUN 2009.

[Karlsson 2005]. Karlsson, H., Measurement of emissions from four diesel fuelled passenger cars meeting euro 4 emissions standards, MTC-report 5505, 2005.

[Karlsson 2008]. Karlsson, H., Regulated and Non-regulated Emissions from Euro 4 Alternative Fuel Vehicles, SAE 2008-01-1770.

[Kittelsson 2002]. Kittelson D. B., Watts W. F., Johnson J. P., Diesel Aerosol Sampling Methodology-CRC E43: Finial Report, 2002.

[Kittelsson 2006] Kittelson D. B., Watts W. F., Johnson J. P., Rowntree C. J., Goodier S. P., Payne M. J., Preston W. H., Warrens C. P., Ortiz M., Zink U., Goersmann C., Twigg M. V. and A. P. Walker. *Driving Down On-Highway Particulate Emissions*, SAE 2006-01-0916.

[Kleinchek 2005]. Kleinchek G*. Emission tests with synthetic diesel fuels (GTL & BTL) with a modern EURO 4 (EGR) engine*. 5th International Colloquium Fuels Conference, Stuttgart, January 12-13, 2005.

[Knothe 2006] Knothe G, Sharp CA, Ryan III TW. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine. Energy Fuels 2006;20:403–8.

[Krahl 1996] Krahl J, Munack A, Bahadir M, Schumacher L, Elser N. Review: utilization of rapeseed oil, rapeseed oil methyl ester or diesel fuel: exhaust gas emissions and estimation of environmental effects. SAE paper 1996, 962096.

[Krahl 2003] Krahl J, Munack A, Schro¨ der O, Stein H, Bu¨ nger J. Influence of biodiesel and different designed diesel fuels on the exhaust gas emissions and health effects. SAE paper 2003, 2003-01-3199.

[Krahl 2005] Krahl J, Munack A, Schro¨ der O, Stein H, Herbst L, Kaufmann A, et al. *Fuel design as constructional element with the example of biogenic and fossil diesel fuels*. Agric Eng Int: CIGR J Sci Res Dev 2005;VII: manuscript EE 04 008.

[Krahl 2006] Krahl J, Munack A, Schro¨ der O, Stein H, Bu¨ nger J. *Comparison of biodiesel with different diesel fuels regarding exhaust gas emissions and health effects*. Available on line: http://www.ufop.de/

[Last 1995] Last RJ, Kru¨ ger M, Du¨ rnholz M. Emissions and performance characteristics of a 4-stroke, direct injected diesel engine fueled with blends of biodiesel and low sulfur diesel fuel. SAE paper 1995, 950054.

[Lapuerta 2000] Lapuerta M, Armas O, Ballesteros R, Carmona M. Fuel formulation effects on passenger car diesel engine particulate emissions and composition. SAE paper 2000, 2000-01-1850.

[Lapuerta 2002] Lapuerta M, Armas O, Ballesteros R. Diesel particulate emissions from biofuels derived from Spanish vegetable oils. SAE paper 2002-01-1657.

[Lapuerta 2005] Lapuerta M, Armas O, Ballesteros R, Ferna´ ndez J. *Diesel emissions from biofuels derived from Spanish potential vegetable oils*. Fuel 2005;84:773–80.

[Lapuerta 2008a]. Lapuerta, M., Armas, O., and Rodríguez-Fernández, J., *Effects of biodiesel fuels on diesel engine emissions,* Progress in Energy and Combustion Science 34 (2008) 198-223.

[Lapuerta 2008] Lapuerta, M., Armas, O., and Rodríguez-Fernández, J., *Effect of the degree of unsaturation of biodiesel fuels on NO$_x$ and particulate emissions*, SAE paper 2008-01-1676.

[Lemaire 2009]. Lemaire, J., Morin, J., Johansen, K., *Catalytic Formulation for NO2 Suppression and Control,* SAE International Journal of Fuels and Lubricants April 2009 1:803-810.

[Leung 2006] Leung DYC, Luo Y, Chan TL. Optimization of exhaust emissions of a diesel engine fuelled with biodiesel. Energy Fuels 2006.

[Li 1998] Li X, Gu¨ lder O¨ L. Effects of fuel cetane number, density and aromatic content on diesel engine NO$_x$ emissions at different operating conditions. In: The fourth international symposium COMEDIA, 1998, p. 111–6.

[Li 2009]. Li, XL., Huang, Z., Emission reduction potential of using gas-to-liquid and dimethyl ether fuels on a turbocharged diesel engine, SCIENCE OF THE TOTAL ENVIRONMENT, 407 (7): 2234-2244 MAR 15 2009.

[Li 2009 a]. Li, W., Perry, K., Narayanaswamy, K., Kim, C., and NajtPassive, P., *Ammonia SCR For Lean Burn SIDI Engines, DEER conference 2009*.

[lin 2009]. Lin, Y. C., Wu, T. Y., Ou-Yang, W. C., Chen, C. B., Reducing emissions of carbonyl compounds and regulated harmful matters from a heavy-duty diesel engine fueled with paraffinic/biodiesel blends at one low load steady-state condition, ATMOSPHERIC ENVIRONMENT, 43 (16): 2642-2647 2009.

[Lu 2000]. Lu, H., Comparison of regulated and unregulated emissions from a Volvo V40 GDI, a Volvo V40, a VW Beetle TDI and a VW Lupo TDI passenger vehicles, MTC 6927A, 2000.

[Luján 2009]. Luján, J.M., Bermudez, V., Tormos, B., Pla, B., Comparative analysis of a DI diesel engine fuelled with biodiesel blends during the European MVEG-A cycle : Performance and emissions (II), Biomass and Bioenergy, 33(2009), 948-956.

[Maik 2009]. Maik, B., Kirchner, U., Vogt, R., Benter, T., On-road and laboratory investigation of low-level PM emissions of a modern diesel particulate filter equipped diesel passenger car, ATMOSPHERIC ENVIRONMENT, 43 (11): 1908-1916 APR 2009.

[Maricq 2007]. Maricq, M. M., Chemical characterization of particulate emissions from diesel engines: A review, J. Aero. Sci., 38 (2007), 1079-1118.

[Marshall 1995] Marshall W, Schumacher LG, Howell S. Engine exhaust emissions evaluation of a cummins L10E when fuelled with a biodiesel blend. SAE paper 1995, 952363.

[Martini 2005] Martini G, Astorga C, Farfaletti A. *Effect of biodiesel fuels on pollutant emissions from LD diesel vehicles*. Inst Environ Sustain, 2005.

[May 2008]. May, J., Bosteels, D., Such, C., Nicol, A. and Andersson, J., Heavy-duty Engine Particulate Emissions: Application of PMP Methodology to measure Particle Number and Particulate Mass, SAE 2008-01-1176.

[Mayer 2005] Mayer, A., Czerwinski, J., Wyser, M., Matteral, P., and Heitzer, A., *Impact of RME/diesel blends on particle formation, particle filtration and PAH emissions*, SAE Paper 2005-01-1728.

[Merkisz 2002]. Merkisz, J., Kozak, M., An investigation of influence of diesel fuel sulphur content on particulate emissions from direct injection common rail diesel vehicles, Journal of Kones Internal Combustion Engines 2002 No. 3-4, ISSN 1231- 4005.

[McCormick 2002] McCormick RL, Alvarez JR, Graboski M. *NO_x solutions for biodiesel. National Renewable Energy Laboratory*, NREL/SR-510-31465.

[McCormick 2005] McCormick RL. *Effects of biodiesel on pollutant emissions*. National Renewable Energy Laboratory, 2005. Available on line: /www.eere.energy.gov/

[McCormick 2005a] McCormick RL. *Effects of biodiesel on NO$_x$ emissions*. National Renewable Energy Laboratory, 2005. Available on line: /www.arb.ca.gov/

[McCormick 2005b] McCormick RL, Alleman TL. *Impact of biodiesel on pollutant emissions from diesel engines.* National Renewable Energy Laboratory 2005. Available on line: /www.uidaho.edu/bioenergy/BiodieselEd/ publication/05.pdfS.

[Miller 2007]. Miller, A.L., Stipe, C.B., Habjan, M.C., and Ahlstrand, G.G. *Role of Lubrication Oil in Particulate Emissions from a Hydrogen-Powered Internal Combustion Engine*, Environ. Sci. Technol., 41, 19, 6828 - 6835, 2007

[Mogensen 2009]. Mogensen, G., Johanson, K., Karlsson., Regulated and NO2 Emissions from a Euro 4 Passenger Car with Catalysed DPFs, SAE 2009-01-1083

[Munack 2001] Munack A, Schro¨ der O, Krahl J, Bu¨ nger J. Comparison of relevant gas emissions from biodiesel and fossil diesel fuel. Agricultural Engineering International: the CIGR Journal of Scientific Research and Development 2001; III: manuscript EE 01 001.

[Monyem 2001a] Monyem A, Van Gerpen JH, Canakci M. *The effect of timing and oxidation on emissions from biodiesel-fueled engines.* Trans A SAE 2001;44(1):35–42.

[Monyem 2001b] Monyem A, Van Gerpen JH. *The effect of biodiesel oxidation on engine performance and emissions*. Biomass Bioenergy 2001; 20:317–25.

[Murugana 2008]. Murugana,S., Ramaswamya, M.C. and Nagarajan, G., The use of tyre pyrolysis oil in diesel engines, Waste Management Volume 28, Issue 12, December 2008, Pages 2743-2749.

[Murugana 2009]. Murugana,S., Ramaswamya, M.C. and Nagarajan, G., Assessment of pyrolysis oil as an energy source for diesel engines, Fuel Processing Technology, Volume 90, Issue 1, January 2009, Pages 67-74

[Nabi 2006] Nabi N, Akhter S, Mhia ZS. Improvement of engine emissions with conventional diesel fuel and diesel–biodiesel blends. Bioresource Technol 2006;97:372-8.

[National] National Biodiesel Board. Biodiesel emissions. Available on line:

/http://www.biodiesel.org/pdf_files/fuelfactsheets/emissions.pdfS

[Ntziachristos 2004]. Ntziachristos L., Mamakos A., Samaras Z., Mathis U., Mohr M., Thompson N., Strandling R., Forti L., and de Serves C., Overview of the European "Particulates" project on the characterization of exhaust particulate emissions from road vehicles: results for light-duty vehicles, SAE-report, 2004-01-1985.

[Nwafor 2004] Nwafor OMI. Emission characteristics of diesel engine operating on rapeseed methyl ester. Renew Energy 2004;29:119–29.

[Oja 2006]. Oja S. *2nd Generation Biodiesel by Neste Oil*. presentation in Stockholm, August 31, 2006.

[Peterson 1996]. Peterson CL, Reece DL. Emissions testing with blends of esters of rapeseed oil fuel with and without a catalytic converter. SAE paper 1996, 961114.

[Peterson 2000] Peterson CL, Taberski JS, Thompson JC, Chase CL. The effect of biodiesel feedstock on regulated emissions in chassis dynamometer tests of a pickup truck. Trans ASAE 2000;43(6):1371–81.

[Pinto 2005] Pinto AC, Guarieiro LLN, Rezende JC, Ribeiro NM, Torres EA, Lopes EA, et al. *Biodiesel: an overview*. J Braz Chem Soc 2005;16(6B):1313–30.

[Rahman 2007]. Rahman M. M., Ashano I., Kusaka T. Nakatani S., Inoue K., Hill L. Particle and Particulate Matter from Automobile & HORIBA's Solution. International Conference on Transport and Environment: A global challenge Technological and Policy Solutions, Milan, Italy 19-21 March 2007

[Rothe 2005]. Rothe, D. Lorenz J., Lämmermann R., Jacobi E., Rantanen L. and Linnala R. *New BTL Diesel Reduces Effectively Emissions of a Modern Heavy-Duty Engine. 5th International Colloquium Fuels Conference*, Stuttgart, January 12-13, 2005

[Sakurai 2003]. Sakurai H., Tobias H.J., Park K., Zarling D., Docherty K.S., Kittelson D.B., McMurry P.H., and Ziemann P.J*., On-line measurements of diesel nanoparticle composition and volatility*, Atmos. Environ. 37, 1199-1210, 2003

[Serdari 1999] Serdari A, Fragioudakis K, Teas C, Zannikos F, Stournas S, Lois E. *Effect of biodiesel addition to diesel fuel on engine performance and emissions.* J Propul Power 1999;15(2):224

[Schumacher 1994] Schumacher LG, Borgelt SC, Hires WG, Fosseen D, Goetz W. *Fueling diesel engines with blends of methyl ester soybean oil and diesel fuel.* 1994. Available on line: www.missouri.edu

[Schumacher 2006] Schumacher LG, Marshall W, Krahl J, Wetherell WB, Grabowski MS. *Biodiesel emissions data from series 60 DDC engines*. Trans ASAE 2006;44(6):1465–8

[Shi 2005] Shi X, Yu Y, He H, Shuai S, Wang J, Li R. Emission characteristics using methyl soyate-ethanol-diesel fuel blends on a diesel engine. Fuel 2005;84:1543–9

[Schubert]. Schubert P. F., Russell B. J., Freerks R. L. DeVore J. and Fanick R. *Impact of Ultra-Clean Fischer-Tropsch Diesel Fuel on Emissions in a Light-Duty Passenger Car Diesel Engine*. SAE Paper 2002-01-2725.

[Schmidt 1996]. Schmidt K, Van Gerpen JH. The effect of biodiesel fuel composition on diesel combustion and emissions. SAE paper 961086

[Scott 2008] Scott, A., Ng, H., K. , Wallner, T., Drive Cycle Analysis of Butanol/Diesel Blends in a Light-Duty Vehicles, SAE 2008-01-2381

[Staat 1995] Staat F, Gateau P. The effects of rapeseed oil methyl ester on diesel engine performance, exhaust emissions and long term behaviour—a summary of three years of experimentation. SAE paper 1995, 950053

[Steinbach 2006]. Steinbach N., Harndorf H., Weberbauer F., und Thiel M. (Bosch): "*Engine potential for synthetic diesel fuels*. " MTZ 02/2006, Jahrgang 67, in German, 2006

[Tinaut 2005] Tinaut FV, Melgar A, Bricen˜ o Y, Horrillo A. *Performance of vegetable derived fuels in diesel engine vehicles*. Int Congr Combust Sci 2005 [PTNSS Kongres], Poland

[Ta 2003] Tat ME. *Investigation of oxides of nitrogen emissions from biodiesel-fueled engines*. PhD thesis 2003, Iowa State University. Available on line: /http://www3.me.iastate.edu/biodiesel/

[Turrio-Baldassarri 2004] Turrio-Baldassarri L, Battistelli CL, Conti L, Crebelli R, De Berardis B, Iamiceli AL, et al. Emission comparison of urban bus engine fuelled with diesel oil and biodiesel blend. Sci Total Environ, 2004;327:147–62

[Wang 2000] Wang WG, Lyons DW, Clark NN, Gautam M, Norton *PM Emissions from nine heavy trucks fuelled by diesel and biodiesel blend without engine modification*. Environ Sci Technol 2000;34(6):933–9

[Weber 1997]. Weber S., Pischinger S., Quvinage F., and Abthoff J. (Daimler-Benz AG*). The Potential of Small DI-Diesel Engines With 250 cm^3/Cylinder for Passenger Car Drive Trains*. SAE Paper 970838

[Wedekind 2000] Wedekind B.G.A., Anderson J.D., Hall D., Strandling R., Barnes C., and Wilson G., *DETR/SMMT/CONCAWE particle research programme: Heavy Duty results*, SAE 2000-01-2851

[Williams 2006] Williams A., McCormick R.L., Hayes R., and Ireland J., *Biodiesel Effects on Diesel Particle Filter Performance*. Milestone Report, NREL /TP-540-39606, March 2006

[Wyatt 2005] Wyatt VT, Hess MA, Dunn RO, Foglia TA, Hass MJ, Marmer WN. *Fuel properties and nitrogen oxide emission levels of biodiesel produced from animal fats*. J Am Oil Chem Soc 2005;82:585–91

[Ziemann 2002] Ziemann P.J., H. Sakurai; Chemical Analysis of Diesel Engine Nanoparticles Using a Nano-DMA/ Thermal Desorption Particle Beam Mass Spectrometer, Final Report CRC Project No. E-43-4, April 2002

APPENDIX

Appendix I: Driving cycle for light duty vehicles

NEDC - New European Driving Cycle

The legislative NEDC cycle is the current year 2000 test cycle for emission certification of light duty vehicles (Shown in the Figure).
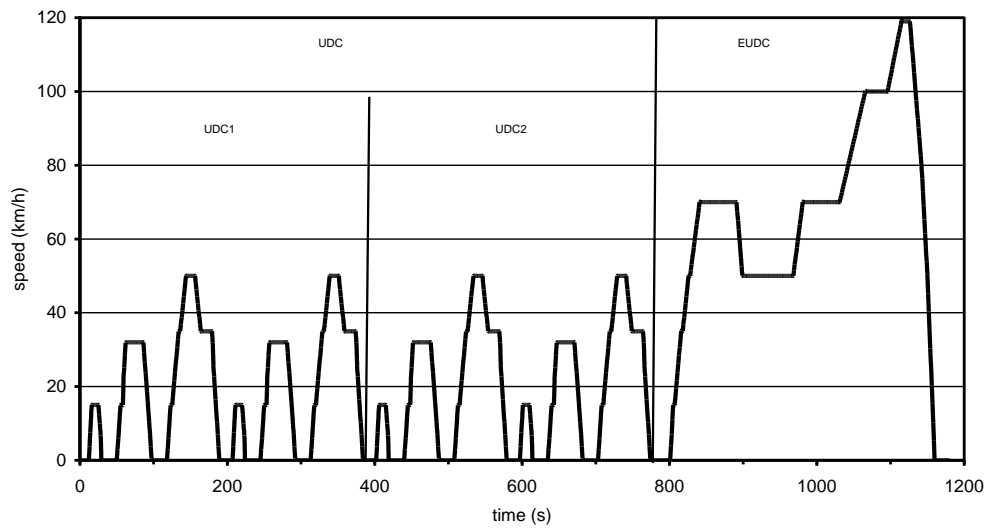
Figure A 1 The NEDC driving cycle.

Appendix II: Driving cycles for heavy duty (HD) engines

ESC - European Stationary Cycle

The ESC test cycle (also known as OICA/ACEA cycle) has been introduced for emission certification of heavy-duty diesel engines in Europe starting in the year 2000 (Directive 1999/96/EC of December 13, 1999). The ESC is a 13-mode, steady-state procedure that replaces the R-49 test as shown in the Table.

Mode	Engine Speed	% Load	Weight factor, %	Duration (min.)
1	Low idle	0	15	4
2	A	100	8	2
3	B	50	10	2
4	B	75	10	2
5	A	50	5	2
6	A	75	5	2
7	A	25	5	2
8	B	100	9	2
9	B	25	10	2
10	C	100	8	2
11	C	25	5	2
12	C	75	5	2
13	C	50	5	2

ETC - European Transient Cycle

The ETC test cycle (also known as FIGE transient cycle) has been introduced for emission certification of heavy-duty diesel engines in Europe starting in the year 2000 (Directive 1999/96/EC of December 13, 1999). The ESC and ETC cycles replace the earlier R-49 test.
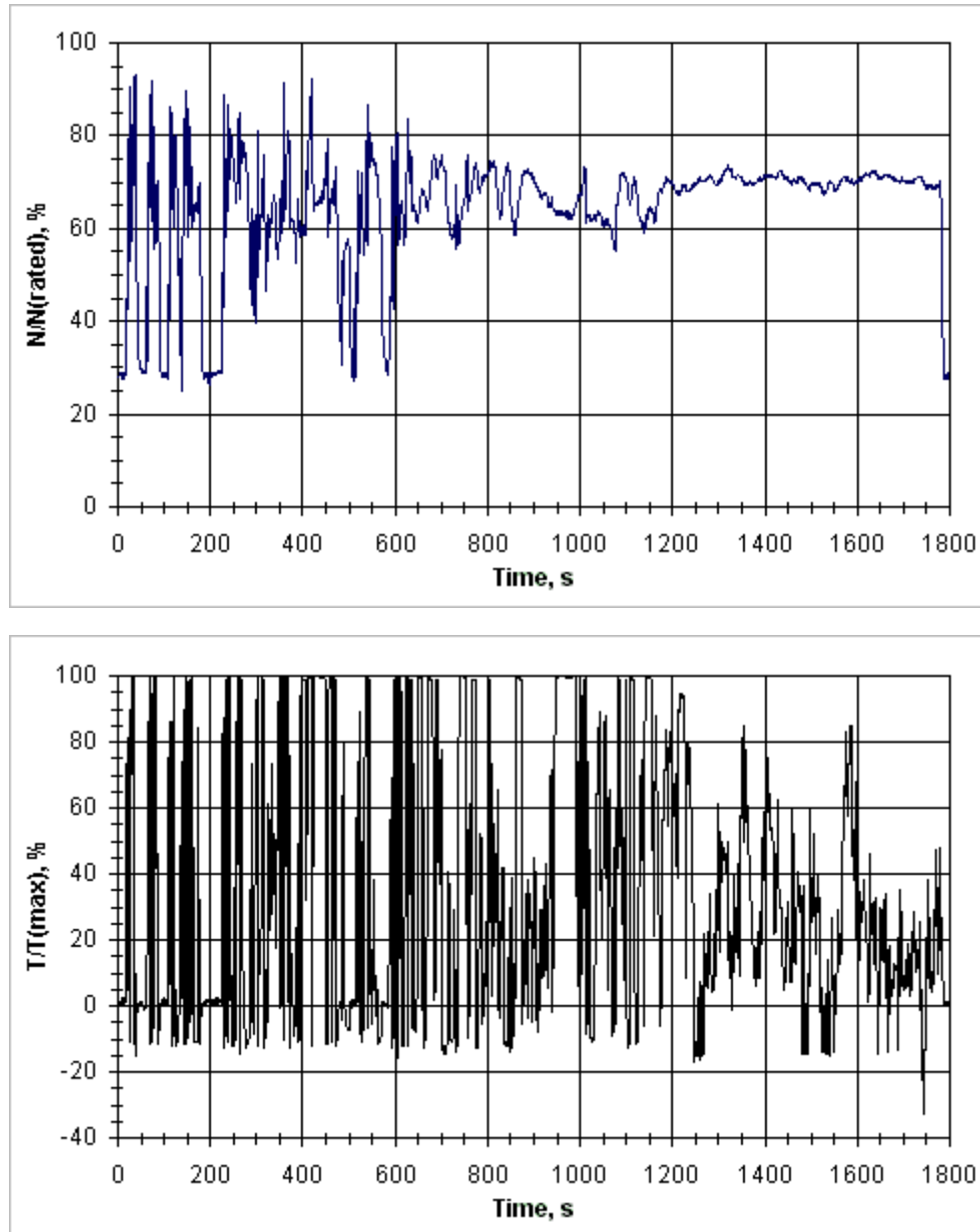
Figure A 2 Vehicle speed vs time over the duration of the cycle.

WHTC - World Harmonised Transient Cycle

The WHTC test is a transient engine dynamometer schedule defined by the proposed global technical regulation (GTR) developed by the UN ECE GRPE group. The WHTC is a transient test of 1800 s duration, with several motoring segments.
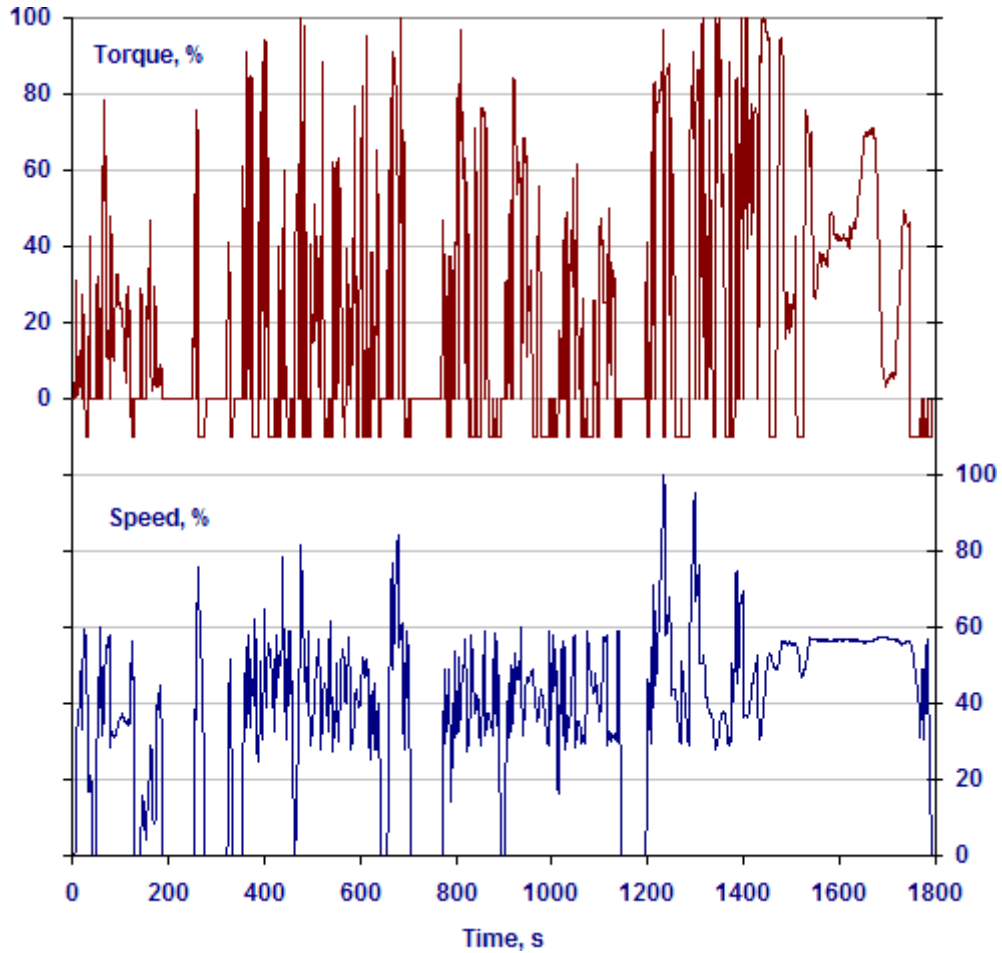
Figure A 3 Normalized engine speed and torque values over the WHTC cycle are schematically shown here in the Figure.

WHSC – World Harmonised Stationary Cycle

The WHSC test is a steady-state engine dynamometer schedule defined by the proposed global technical regulation (GTR) developed by the UN ECE GRPE group. The WHSC is a ramped steady-state test cycle, with a sequence of steady-state engine test modes with defined speed and torque criteria at each mode and defined ramps between these modes (WHSC). The parameters of the WHSC are listed in the Table.

Mode	Normalized Speed (per cent)	Normalized Load (per cent)	WF for reference	Mode length (s) incl. 20 s ramp
0	Motoring	-	0.24	-
1	0	0	0.17/2	210
2	55	100	0.02	50
3	55	25	0.10	250
4	55	70	0.03	75
5	35	100	0.02	50
6	25	25	0.08	200
7	45	70	0.03	75
8	45	25	0.06	150
9	55	50	0.05	125
10	75	100	0.02	50
11	35	50	0.08	200
12	35	25	0.10	250
13	0	0	0.17/2	210
Sum			1.00	1895

Appendix III: diesel fuel specification

Table 5 Generally applicable requirements and test methods diesel, European Standard EN 590:2009, edition 5

Property Diesel	Units	Limits Min Max		Test method [a] (See 2. Normative references)
Cetane number [b]		51,0	-	EN ISO 5165 EN 15195
Cetane index		46,0	-	EN ISO 4264
Density at 15 °C [c]	kg/m^3	820	845	EN ISO 3675 EN ISO 12185
Polycyclic aromatic hydrocarbons [d]	% (m/m)	-	11	EN 12916
Sulfur content [e]	mg/kg	-	10	EN ISO 20846 EN ISO 20847 EN ISO 20884
Flash point	°C	Above 55	-	EN ISO 2719
Carbon residue [f] (on 10 % distillation residue)	% (m/m)	-	0,30	EN ISO 10370
Ash content	% (m/m)	-	0,01	EN ISO 6245
Water content	mg/kg	-	200	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662 [g]
Copper strip corrosion (3 h at 50 °C)	rating	class1		EN ISO 2160
Fatty acid methyl ester (FAME) content [h]	% (V/V)		7,0	EN 14078
Oxidation stability	g/m^3 h	- 20	25 -	EN ISO 12205 EN 15751 [i]
Lubricity, corrected wear scar diameter (wsd 1,4) at 60 °C	µm	-	460	EN ISO 12156-1
Viscosity at 40 °C	mm^2/s	2,00	4,50	EN ISO 3104
Distillation [k,l] % (V/V) recovered at 250 °C % (V/V) recovered at 350 °C **95 % (V/V) recovered at**	% (V/V) % (V/V) °C	85	<65 360	EN ISO 3405
NOTE Requirements in bold refer to the European Fuels Directive 98/70/EC [1], including Amendment 2003/17/EC [2]				

a. See also 5.6.1
b. See also 5.6.4
c. See also 5.6.2
d. For the purposes of this European Standard, polycyclic aromatic hydrocarbons are defined as the total aromatic hydrocarbon content less the mono-aromatic hydrocarbon content, both as determined by EN 12916.
e. See also 5.6.3
f. See also 5.4.2 and Annex A
g. Further investigation into the total contamination test method to improve the precision, particularly in the presence of FAME, is being carried out by CEN.
h. FAME shall meet the requirements of EN 14214
i. For diesel fuel containing FAME above 2 % (V/V) this is an additional requirement. This is an interim requirement, under revision by CEN, when more technical data on oxidation stability and field performance of diesel fuels will be available.
k. For the calculation of the cetane index the 10 %, 50 % and 90 % (V/V) recovery points are also needed.
l. The limits for distillation at 250 °C and 350 °C are included for diesel fuel in line with EU Common Customs tariff.

Appendix IV: FAME fuel specification

Table 6 Generally applicable requirements and test methods diesel, Swedish Standard SS-EN 14214:2008, edition 2

Property FAME	Units	Limits Min Max		Test method (See 2. Normative references)
FAME content [a]	% (*m/m*)	96,5[b]	-	EN 14103
Density at 15 °C [c]	kg/m^3	860	900	EN ISO 3675 EN ISO 12185
Viscosity at 40 °C[d]	mm^2/s	3,50	5,00	EN ISO 3104
Flash point	°C	101	-	EN ISO 2719[e] EN ISO 3679 [f]
Sulfur content	mg/kg	-	10,0	EN ISO 20846 EN ISO 20884
Carbon residue (on 10 % distillation residue)[g]	% (*m/m*)	-	0,30	EN ISO 10370
Cetane number [h]	-	51,0	-	EN ISO 5165
Sulphated ash content	% (*m/m*)	-	0,02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper strip corrosion (3 h at 50 °C)	rating	class1		EN ISO 2160
Oxidation stability, 100 °C	hours	6,0	-	pr EN 15751 [i] EN 14112
Acid value	mg KOH/g	-	0,50	EN 14104
Iodine value	g iodine/100g	-	120	EN 14111
Linolenic acid methyl ester	% (*m/m*)	-	12,0	EN 14103
Polyunsaturated (≥ 4 double bonds) methyl esters	% (*m/m*)	-	1	[k]
Methanol content	% (*m/m*)	-	0,20	EN 14110
Monoglyceride content	% (*m/m*)	-	0,80	EN 14105
Diglyceride content	% (*m/m*)	-	0,20	EN 14105
Triglyceride content [a]	% (*m/m*)	-	0,20	EN 14105
Free glycerol	% (*m/m*)	-	0,02	EN 14105[l] EN 14106
Total glycerol	% (*m/m*)	-	0,25	EN 14105
Group I metals (Na+K)	mg/kg	-	5,0	EN 14108[l] EN 14109 EN 14538
Group II metals (Ca+Mg)	mg/kg	-	5,0	EN 14538
Phosphourus content	mg/kg	-	4,0	EN 14107

a. See also 5.6.1
b. The addition of non-FAME components other than additives is not allowed, see 5.2. When C17-methyl esters naturally appear in FAME this can result in a lower measured fatty acid methyl ester content. In this situation reference should be made for verification to a modified determination procedure [4], until a modified method is established within CEN.
c. Density may be measured by EN ISO 3675 over a range of temperatures from 20 °C to 60 °C. Temperature correction shall be made according to the formula given in Annex C. See also 5.6.2.
d. If CFPP is -20 °C or lower, the viscosity shall be measured at -20 °C. The measured value shall not exceed 48 mm2/s. In this case, EN ISO 3104 is applicable without the precision data owing to non-Newtonian behaviour in a two-phase system.
e. Procedure A to be applied. Only a flash point test apparatus equipped with a suitable detection device (thermal or ionization detection) shall be used. See also 5.6.2.
f. A 2 ml sample and apparatus equipped with a thermal detection device shall be used.
g. ASTM D 1160 shall be used to obtain the 10 % distillation residue. See also 5.3.4.
h. See 5.6.3.
i. See 5.6.2.
k. A suitable test method is under development by CEN [3].
l. See 5.6.2. See Annex A for precision data for sum of Na + K.

Appendix V: Petrol fuel specification

Table 7 Requirements and test methods for premium grade unleaded petrol, European Standard EN 228:2008, edition 7

Property **Unleaded petrol**	Units	Limits		Test method [a] (See 2. Normative references)
		Min	**Max**	
Research octane number, RON		95,0	-	EN ISO 5164 [b]
Motor octane number, MON		85,0	-	EN ISO 5163 [b]
Lead content	mg/l	-	5,0	En 237
Density (at 15 °C) [c]	kg/m^3	720,0	775,0	EN ISO 3675 EN ISO 12185
Sulfur content [c]	mg/kg	-	10	EN ISO 20846 EN ISO 20847 EN ISO 20884
			10,0	EN ISO 20846 EN ISO 20884
Oxidation stability	minutes	360	-	EN ISO 7536
Existent gum content (solvent washed)	mg/100 ml	-	5	EN ISO 6246
Copper strip corrosion (3 h at 50 °C)	rating	class 1		EN ISO 2160
Appearance		clear and bright		visual inspection
Hydrocarbon type content[c]	**% (V/V)**			EN 14517 EN 15553
-olefins		-	18,0	
-aromatics		-	35,0	
Benzene content [c]	**% (V/V)**	-	1,00	EN 238 EN 12177 EN 14517
Oxygen content [c]	**% (V/V)**		2.7	EN 1601 EN 13132 EN 14517
-methanol [d]		-	3,0	
-ethanol [e]		-	5,0	
-iso-propyl alcohol		-	10,0	
-iso-butyl lcohol		-	10,0	
-tert-butyl alcohol		-	7,0	
-ethers (5 or more C atoms)		-	15,0	
- other oxygenates [f]		-	10,0	
NOTE Requirements in bold refer to the European Fuels Directive 98/70/EC [1], including Amendment 2003/17/EC [2]				
a. See also 5.8.1 b. A correction factor of 0,2 for MON and RON shall be subtracted for the calculation of the final result, before reporting according to the requirements of the European Directive 98/70/EC [1], including Amendment 2003/17/EC [2]. For advice on reporting see 5.7. c. See also 5.8.2 d. Stabilizing agents shall be added. e. Shall conform to EN 15376 (see 5.2). Stabilizing agents may be necessary. f. Other mono-alcohols and ethers with a final boiling point no higher than prescribed in Table 2.				

Appendix VI: Ethanol- E85 fuel specification

Table 8 Requirements and test methods for Ethanol E85, Swedish Standard SS 15 54 80:2006, edition 1

Property E85	Units	Limits Min	Max	Test method [a] (See 2. Normative references)
Research octane number RON		95,0	-	SS-EN ISO 5164
Motor octane number MON		85,0	-	SS-EN ISO 5163
Sulfur content	mg/kg	-	10,0	SS-EN ISO 20846 SS-EN ISO 20884
Oxidation stability	minutes	360	-	SS-EN ISO 7536
Existent gum content (solvent washed)	mg/100 ml	-	5	EN ISO 6246
Appearance		clear and bright, visible free from contamination		visual inspection
alcohols, C3-C8 (volume content)	%	-	2,0	SS-EN 13132 SS-EN 14517
Methanol (volume content)	%	-	1,0	
Ethers, 5 or more C atoms (volume content)	%	-	5,2	
Water (volume content)	%	-	0,3	SS-ISO 760 SS-EN ISO 12937 ASTM E 1064
Non organic chloride	mg/l		1	SS-ISO 6227
pH $_e$		6,5	9,0	ASTM D 6423
Copper strip corrosion (3 h at 50 °C)	rating	class 1		SS-EN ISO 2160
Oxygen concentration	% (mg/l)	-	0,005 (40)	ASTM D 1613