6. RELATIONSHIP BETWEEN THE SULFUR CONTENT OF DIESEL FUELS AND THE NUMBER OF ULTRAFINE PARTICLES IN DIESEL EMISSIONS.

This part of the literature review establishes the current knowledge on the relationship between fuel sulfur content and the number of ultrafine particles in diesel emissions. Before tackling the question of the influence of the fuel sulfur level on particle emission it is necessary to first develop an understanding as to what constitutes diesel exhaust, the complex issues of nanoparticles in diesel exhaust, their physical properties, chemical composition and formation. The first section of this chapter explains the general characteristics of emissions from diesel vehicles without a special focus on any of the pollutants. In the second part, an attempt is made to address the questions of why is it important to know the size distribution of diesel particulate matter (DPM) and what is the role of nanoparticles as part of the DPM. The current state of knowledge on the mechanisms governing nanoparticle formation, physical and chemical properties is presented. It is important to stress that the mechanisms governing nanoparticle formation are still not fully understood and the theories presented here still have to be confirmed by more hard scientific data. A short description of what constitutes diesel fuel is given with a focus on sulfur content. It is worth mentioning that one of the most useful, and up-to-date source of data on this topic was the Dieselnet Technology Guide (Majewski, 2003) from which larger parts were taken in these first few general sections.

The fourth section focuses on the main topic of our literature review, the influence of the fuel sulfur level on diesel emissions with a special attention to nanoparticle emissions. It is surprising how little information is available on this topic. The initial search has led to more than 150 references (journal articles, conference presentations, reports, etc.) on the fuel sulfur level and diesel emissions, but only a small number of them covered the topic of nanoparticle emissions. From those only the relevant references were chosen that lead to some definite conclusions.

Finally, in the last section, the main conclusions are presented regarding the current state of knowledge and the scale of the problem. Recommendations are provided for the appropriate way of addressing the gaps in knowledge as well as for adequate management responses.

6.1 GENERAL CHARACTERISTICS OF EMISSIONS FROM DIESEL ENGINES

Diesel engines, like other internal combustion engines, convert chemical energy contained in the fuel to mechanical power. Diesel fuel is a mixture of hydrocarbons, which theoretically produce only carbon dioxide (CO_2) and water vapour (H_2O) during combustion. Indeed, diesel exhaust gases are primarily composed of CO_2, H_2O and the unused portion of engine charge air. Concentrations of these gases in diesel exhaust vary depending on the engine and its load and speed conditions, typically in the following ranges:

CO_2 - 2 ... 12%
H_2O - 2 ... 12%
O_2 - 3 ... 17%
N_2 - balance.

None of these diesel combustion products, with the exception of CO_2 for its greenhouse gas properties, have adverse health or environmental effects. The same cannot be said of other products such as sulfur oxides and unburned hydrocarbons (see sections 6.1.1 to 6.1.4).

Diesel emissions include also pollutants, which are toxic to humans and/or cause other detrimental environmental effects. The diesel pollutants, which are by-products of diesel combustion, originate in several non-ideal processes occurring during real combustion. These processes include incomplete combustion of fuel, reactions between mixture components under high temperature and pressure, combustion of engine lubricating oil and oil additives. They also include combustion of non-hydrocarbon components of diesel fuel, such as *sulfur compounds* and various fuel additives. The total concentration of pollutants in exhaust gases from today's new diesel engines, however, amounts to a fraction of a percent.

Some diesel emissions are regulated in the U.S., Europe, and several other countries. Regulated emissions include the following compounds:

- Diesel Particulate Matter (DPM) also referred to as PM (particulate matter) or TPM (total particulate matter), regulated by the mass of emitted particles
- Nitrogen Oxides (NO_x)
- Hydrocarbons (HC) including either the total hydrocarbons (THC) or only the non-methane hydrocarbons (NMHC)
- Carbon Monoxide (CO).

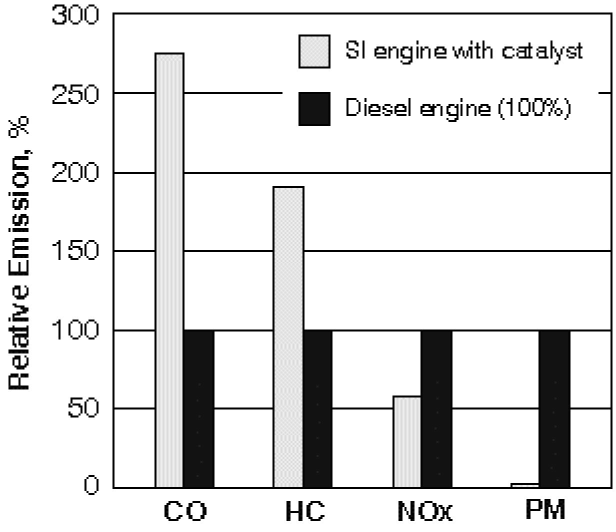


Figure 6.1 Comparison of Regulated Emissions - Spark Ignited and Diesel Engines

Because diesel engines operate with "internal" mixture formation and with compression ignition, where combustion takes place during and after fuel injection, diesel emissions are somewhat different from those observed in spark-ignited engines. An example comparison of regulated emissions from a light-duty diesel engine with those from a gasoline engine is shown in Figure 6.1 (Bosch, 1994). Both engines were tested on the European test cycle (4-cylinder MY1992 engines, 1.7L displacement). Emissions of carbon monoxide and hydrocarbons from diesel engines are significantly lower than those from gasoline engines. Diesel NO_x emissions are also usually lower than those from gasoline engines. However, if a gasoline engine is equipped with a three-way catalyst, then its emissions could be lower than those for diesel engines. A real drawback of the diesel engine is its high particulate matter mass emissions that are practically absent from gasoline exhaust gases. Reduction in the emissions of particulate matter and NO_x are the focus of today's diesel emission control technologies.

Several non-regulated pollutants or suspected pollutants can be found in diesel exhaust, usually at concentration levels much lower than the regulated emissions. Some of them are part of the complex diesel particulate matter emission; others are totally separate species in the gas phase. The list of unregulated diesel emissions includes the following compounds:

- PAH – poly-nuclear aromatic hydrocarbons, heavy organic compounds found mostly in the DPM but some of PAHs are also present in the gas phase.
- SOF - "soluble organic fraction" constituting part of DPM.
- Aldehydes, R-CHO, derived from hydrocarbons (formaldehyde, HCHO, is regulated in some applications).
- Sulfur dioxide, SO_2, from sulfur present in the fuel.
- Nitrous oxide, N_2O (nitrous oxide is not included in NO_x).
- Dioxins - diesel emissions are suspected to be a source of dioxin emissions.
- Metal oxides - several engine lubricating oil additives include organo-metal-compounds resulting in some metal oxide emissions including such metals as copper zinc, and calcium and non metals like phosphorus. Fuel additives as a means of diesel emission control may result in emissions of iron, copper, cerium, or other metals.

6.1.1 Nitrogen Oxides – NO_x

Nitrogen oxides as defined by emission regulations include nitric oxide NO and nitrogen dioxide NO_2. Concentrations of NO_x in diesel exhaust are typically between 50 and 1000 ppm. If concentrations are given in mass units, NO_x is usually expressed as NO_2 equivalent. Nitric oxide is a colourless and odourless gas that may be synthesised directly from nitrogen and oxygen under high temperature and pressure:

$$(1)\ N_2 + O_2 = 2NO - 182.4\ \text{kJ/mole}$$

The negative heat effect represents an endothermic reaction. NO is produced according to reaction (1) in the engine cylinder, where temperature and pressure are high. At low temperature and pressure, the chemical equilibrium moves to the left side of equation (1). Thermodynamically, nitric oxide has a tendency to decompose to nitrogen and oxygen under conditions in diesel exhaust. The rate of decomposition, however, equals practically zero and NO_x control from diesel engines remains an unsolved problem.

In older technology engines, approximately 95% of nitrogen oxides were composed of NO and only 5% of NO_2. The proportion of NO_2 in total NO_x in newer, turbocharged diesel engines can be as high as 15% and more. NO can be easily oxidised by oxygen into nitrogen dioxide at ambient conditions:

$$(2)\ 2NO + O_2 = 2NO_2 + 113.8\ \text{kJ/mole}$$

The above reaction occurs spontaneously (but not instantaneously) in the NO - air mixture after exhaust gases are discharged into the atmosphere. NO_2 is a very toxic red-brown gas with an unpleasant irritating odour. NO_2 is extremely reactive and exhibits strong oxidation properties. NO_2 reactions, which occur in various types of emission control catalysts, may include oxidation of hydrocarbons, carbon monoxide as well as diesel particles.

Nitrogen oxides are highly active ozone-generating precursors playing an important role in the smog chemistry. Besides diesel particles, NO_x is one of the most critical pollutants found in diesel exhaust.

6.1.2 Hydrocarbons – HC

Hydrocarbons found in the gas phase of diesel exhaust are a mixture of many hydrocarbon species derived from diesel fuel and from lubricating oil. Shorter carbon chains characterize fuel hydrocarbons while lube oil hydrocarbons contain the heavier material. C_nH_m, the generic chemical formula for hydrocarbons, represents a molecule with n atoms of carbon and m atoms of hydrogen.

In engine emission standards, hydrocarbons are commonly regulated as either total hydrocarbons (THC), or as non-methane hydrocarbons (NMHC): the latter category excluding the simplest hydrocarbon methane (CH_4) due to its different atmospheric reactivity to longer chain hydrocarbons. Even though the concentration of methane in diesel exhaust is very low, certain HC emission standards from diesel engines are expressed as NMHC for the sake of compatibility with other emission regulations.

Hydrocarbons, especially those with longer carbon chains, may have a characteristic or irritating odour. Some of them, such as benzene, are toxic and/or carcinogenic. Various hydrocarbon derivatives, e.g. aldehydes, are also present in diesel exhaust gases. Many aldehydes have an irritating odour and/or are toxic. Some of them, such as formaldehyde, are classified as carcinogens. Concentration of gaseous hydrocarbons in diesel exhaust ranges from approximately 20 to 300 ppm.

Diesel exhaust hydrocarbons are divided between the gas phase and the particle (liquid or adsorbed) phase. There is no clear distinction between volatile and non-volatile hydrocarbon species. As a guideline, compounds with vapour pressure of above 0.1 mmHg in standard conditions (20°C, 760 mmHg) can be considered volatile. Volatile diesel hydrocarbons contain aliphatic and aromatic species with up to approximately 24 carbon atoms in their molecule. *Hydrocarbon emission regulations refer to the volatile gas phase HCs.* The particle phase hydrocarbons are referred to as SOF.

Hydrocarbons may be oxidised by oxygen to produce carbon dioxide and water (3), which is one of the fundamental reactions occurring in emission control catalysts. Under mild oxidizing conditions hydrocarbons form aldehydes or ketones (4).

$$C_nH_m + (2n + m/4)O_2 = nCO_2 + (m/2)H_2O \tag{3}$$

$$R\text{-}CH_3 + O_2 = R\text{-}CHO + H_2O \tag{4}$$

In the atmosphere, hydrocarbons undergo photochemical reactions with NO_x leading to formation of smog and ground level ozone. Different hydrocarbons exhibit different activity as ozone precursors. Methane (CH_4), the simplest hydrocarbon, does not exhibit any activity and is not considered an ozone precursor. This is the reason why many regulations exclude methane from regulated hydrocarbon emission by setting standards for non-methane hydrocarbons (NMHC).

6.1.3 Carbon Monoxide – CO

Carbon monoxide (CO) is an odourless, colourless, and a very toxic gas of about the same density as that of air. At high concentrations CO is very flammable, burning in air with a bright blue flame.

CO emissions from today's new diesel engines are relatively low. Carbon monoxide concentrations in diesel exhaust range from approximately 10 to 500 ppm.
At elevated temperatures, or over an oxidation catalyst, carbon monoxide can be oxidised by oxygen to form carbon dioxide, as follows:

$$2CO + O_2 = 2CO_2 + 565.6 \text{ kJ/mole}$$

The reaction produces a high heat effect, which, in the case of CO-rich exhaust gases, can cause a significant increase of the gas temperature in catalytic reactors designed to oxidize CO. Adiabatic oxidation of 1% of CO in the exhaust stream raises the gas temperature by approximately 100°C.

6.1.4 Sulfur Dioxide - SO_2

Although sulfur dioxide is an unregulated diesel emission it plays a critical role in nanoparticle formation and therefore will be discussed in this review. Sulfur dioxide originates from the sulfur in fuel and in engine lubricating oil. SO_2 is a colourless gas with a characteristic, irritating odour. Sulfur dioxide can be oxidised to sulfur trioxide (SO_3), which is the precursor of the sulfuric acid responsible for sulfate particle emissions. The majority of sulfur in raw diesel exhaust exists as SO_2. Only approximately 2 - 4% of fuel sulfur is emitted as SO_3 from the engine.

The exhaust concentration of sulfur dioxide is in direct proportion to the fuel sulfur level. In fact, SO_2 concentrations can be calculated from the fuel consumption and its sulfur content with good accuracy. Such calculations are based on an air to fuel ratio of 20:1, which is typical for diesel engines operating at full load conditions. Diesel fuels of 500 ppm S produce exhaust SO_2 levels of about 20 ppm.

As the levels of sulfur in fuels decrease, engine lubricating oils become an important source of SO_2 in diesel exhaust. Diesel lube oils typically contain 4,000 - 10,000 ppm sulfur, primarily as part of their additive package. Anti-wear additives typically contain zinc, sulfur and phosphorus in the form of zinc dithiophosphates. Many detergent additives also contain alkyl sulfonates (DECSE, 1999).

6.1.5 Diesel Particulate Matter

Particulate matter—perhaps the most characteristic of diesel emissions—is responsible for the black smoke traditionally associated with diesel-powered vehicles. The diesel particulate matter emission is usually abbreviated as PM or DPM, the latter acronym being more common in occupational health applications. Diesel particles form a very complex aerosol system. *Despite a considerable amount of basic research, neither the formation of DPM in the engine cylinder, nor its physical and chemical properties or human health effects are fully understood.* Nevertheless, on the basis of what is already known, DPM is perceived as one of the major harmful emissions produced by diesel engines. Diesel particles are subject to diesel emission regulations worldwide and, along with NO_x, have become the focus in diesel emission control technology.

Contrary to gaseous diesel emissions, DPM is not a well-defined chemical species. The definition of particulate matter is in fact determined by its sampling method, the detailed specification of which is an important part of all diesel emission regulations. DPM sampling involves drawing an exhaust gas sample from the vehicle's exhaust system, diluting it with air, and filtering through sampling filters. The mass of particle emissions is determined based on the weight of DPM collected on the sampling filter. It is quite obvious that any changes in the procedure, for example using a different type of sampling filter or different dilution parameters, may produce different results. Standardization of sampling methods is of the utmost importance if results from different laboratories are to be comparable. Such standards have been developed for the measurement of *PM mass* in the area of public health regulations (i.e., emission standards for diesel engines and vehicles) worldwide. Ongoing research in Europe is aimed at developing standardised measuring methods based on particle number emissions, rather than mass, for the inclusion in future emission standards in addition to the PM mass metric (Andersson, 2002). So far no common standard has been reached in the area of diesel occupational health regulations, where a number of different measuring methods and corresponding DPM definitions exist in parallel.

Diesel particles are composed of elemental carbon particles, which agglomerate and adsorb other species to form structures of complex physical and chemical properties. Diesel particles have a bimodal size distribution. They are a mixture of *nucleaction mode* and *accumulation mode* particles, schematically shown in Figure 6.2. Nucleaction mode particles are very small: according to most authors, their diameters are between approximately 0.007 and 0.04 μm. More recent studies redefined the nucleaction mode particle size range to be even smaller, from 0.003 to 0.03 μm (Kittelson, 2002), thus making them comparable to certain large molecules. Nucleaction mode particles are often referred to as *nanoparticles*, although these two terms are not the same. Nanoparticles are usually defined as particles below 50 nm in diameter (0.05 μm). This is an arbitrary definition, not related to the physical properties of diesel exhaust; nanoparticles include practically all nucleaction mode particles, but may also contain a certain fraction of the accumulation mode particles.

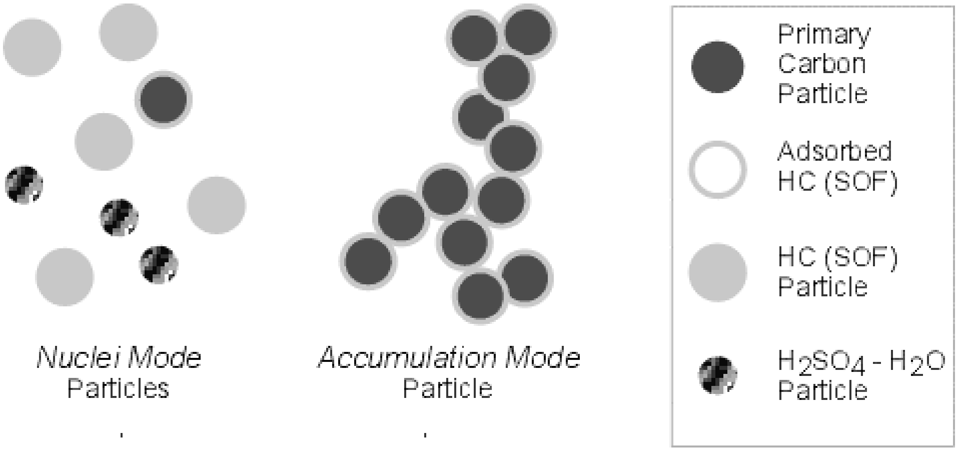


Figure 6.2 Schematic of Diesel Particulate Matter

The nature of nucleaction mode particles is still studied in research laboratories. It is believed that nucleaction mode particles are primarily volatile: they consist mainly of hydrocarbon and hydrated sulfuric acid condensates. These are formed from gaseous precursors as temperature decreases in the exhaust system. After mixing with cold air, be it in the laboratory dilution tunnel or in the ambient air, these volatile particles are very unstable: their concentrations strongly depending on dilution conditions such as dilution ratio and residence time. A small amount of nucleaction mode particles may consist of solid material, such as carbon or metallic ash from lube oil additives (Tobias, 2001; Kittelson, 1998). Nucleaction mode particles constitute the majority of particle number – of the order of 90% - but only a few percent of the PM mass.

Agglomeration of primary carbon particles and other solid materials, accompanied by adsorption of gases and condensation of vapours, form accumulation mode particles. They are composed mainly of solid carbon mixed with condensed heavy hydrocarbons (Figure 6.2), but may also include sulfur compounds, metallic ash, cylinder wear metals, etc. Diameters of the accumulation mode particles are between approximately 0.04 and 1 µm with a maximum concentration between 0.1 and 0.2 µm (Brown, 2000; Kittelson, 1998). Most PM mass emission (but only a small proportion of the total particle number) is composed of agglomerated particles.

Particles leaving the engine are composed primarily of solid phase, carbon material (SOL). Both individual (nucleaction mode) and agglomerated carbon particles are formed in the combustion chamber. In the exhaust system, depending on the temperature, the particles undergo limited oxidation and further agglomeration. Some particles are deposited on the exhaust pipe walls due to thermophoretic forces (i.e., mass transfer driven by temperature gradient). Other PM precursors including hydrocarbons, sulfur oxides, and water are present in the hot diesel exhaust as gases or vapours.

Another source of solid material in diesel exhaust is metal ash compounds derived from lubricating oil additives as well as from engine wear. Nucleation of volatile ash constituents is believed to take place during expansion stroke in the engine cylinder. The ash nucleaction can then agglomerate to form accumulation mode particles. The relative proportion of ash generally increases in new engines, due to less carbon particles and lower total PM mass.

Physical and chemical properties of DPM change once the exhaust gases enter the dilution tunnel, are mixed with air and cooled to below 52°C. Heavy hydrocarbons, which are derived from lubricating oil and unburned fuel, condense or adsorb onto the surface of carbon particles forming the organic portion of DPM (SOF). If the amount of carbon particles that can act as a “sponge” is insufficient, hydrocarbons will nucleate, forming increased numbers of volatile (liquid) nucleaction mode particles. In the dilution tunnel, the total hydrocarbon material from the combustion chamber becomes finally proportioned between particle (SOF) and gas phase hydrocarbons (at least in theory; in practice a portion of diesel hydrocarbon material may be measured and accounted for twice: in the particle phase and in the gaseous phase).

Sulfate particles are formed in the dilution tunnel through a hetero-nucleation process from the molecules of H_2SO_4 and water. During PM measurements, sulfate particles are deposited on the filters together with the carbonaceous material. It was once believed that sulfuric acid is attached to or associated with carbon particles. Later research found that sulfate particles may also be separate from carbon particles (Walters, 1988). It is now envisioned that sulfate particles, while existing in the accumulation mode, mixed with carbon and organic SOF material, are also an important source of volatile (H_2SO_4 - H_2O) nucleaction mode particles (Kittelson, 2002). Depending on the availability of metal-based compounds, sulfuric acid may also form solid (non-volatile) sulfate salts.

6.2 PARTICLE SIZE DISTRIBUTIONS AND NANOPARTICLE EMISSIONS

Interest in particle size distributions and nanoparticle emissions from diesel engines was sparked by reports that newer technology engines - designed for low PM mass emissions - may still generate high particle numbers. The most significant study indicating such possibility (involving measurement of particle size distributions from an older and a newer generation heavy-duty diesel engine) was published by the Health Effects Institute (HEI) (Bagley, 1996). As indicated by later research which was based on more comprehensive data, from several engine models, old and new technology engines produce, in general, nucleaction modes of similar magnitude; the PM mass reductions in new engines are due to a smaller number of particles in the accumulation mode (Kittelson, 2002; Ristovski, 2002; Andersson, 2002). It is believed that emissions from the new engine in the HEI study - an experimental 1991 design - have not reflected general emission trends in new technology engines. That study, however, must be credited with prompting quality research by the diesel industry, academia, and governments, leading to a greatly increased understanding of particle emissions from internal combustion engines. In a later chapter, we will discuss the results of this study in more detail.

6.2.1 Diesel Particle Size Distribution

Since the mid-1990’s, particle size distributions from internal combustion engines have been receiving increased attention due to the possible adverse health effects of fine and ultrafine particles. Diesel emission control strategies, based on both engine design and aftertreatment, are being examined and re-evaluated for their effectiveness in the control of the finest fractions of diesel particles and particle number emissions. However, a fair performance assessment of various control technologies can be possible only if the research community reaches a consensus on the definition and the measurement techniques of the smallest fractions of diesel particles. The determination of particle sizes and numbers is much more sensitive to the measuring techniques and parameters than the quantification of particle mass emissions. Dilution and sampling methods are key variables that must be taken into consideration to ensure accurate and repeatable results. On the other hand, particle-sizing instruments exist that have significantly better sensitivities than the gravimetric measurement: these present an attractive alternative for the PM emission measurement in future engines, provided standardised measuring methods are developed.

A typical size distribution of diesel exhaust particles is shown in Figure 6.3 (note that a logarithmic scale is used for particle aerodynamic diameter). Nearly all diesel particles have sizes of significantly less than 1µm. As such, they represent a mixture of fine, ultrafine, and nanoparticles. Due to the current PM sampling techniques (diluted exhaust, temperature <52°C), diesel particulate matter includes both solids (such as elemental carbon and ash) and liquids (such as condensed hydrocarbons, water, and sulfuric acid). Formation of particles starts with nucleation, which is followed by subsequent agglomeration of the nuclei particles. The nucleation occurs in both the engine cylinder (carbon, ash) and the dilution tunnel (hydrocarbons, sulfuric acid, water), through homogeneous and heterogeneous nucleation mechanisms.

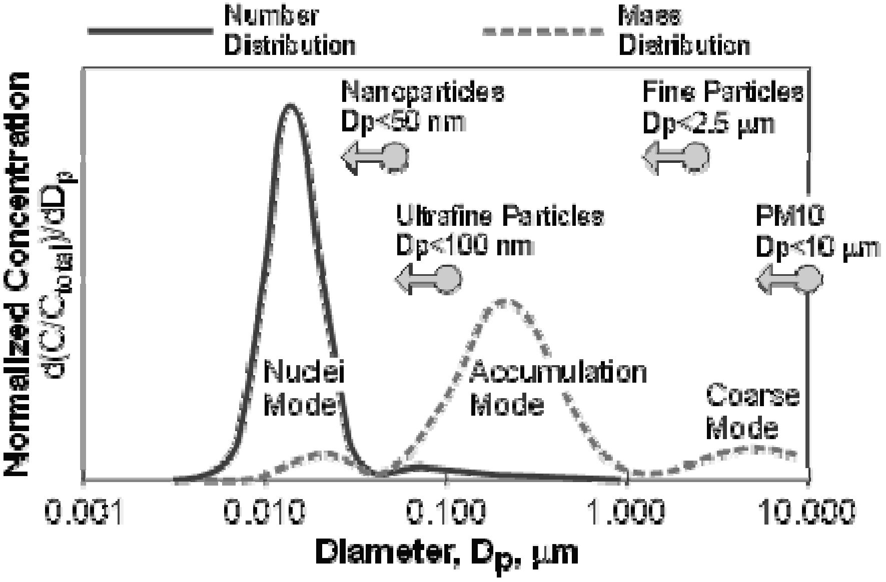


Figure 6.3 Diesel Particle Size Distribution (Kittelson, 2002)

Size distributions of diesel particles have a well-established bimodal character, which corresponds to the particle nucleation and agglomeration mechanisms, with the corresponding particle types referred to as the *nucleaction mode* and the *accumulation mode*. Size distributions are usually presented using either particle mass or particle number weighting. In each representation normal-logarithmic distribution curves are produced, as shown in Figure 6.3. Both the maximum particle concentration and the position of the nucleaction and accumulation mode peaks, however, depend on which representation is chosen. In mass distributions, the majority of the particles (i.e., the particle mass) are found in the accumulation mode. In number distributions, on the other hand, most particles are found in the nucleaction mode. In other words, diesel particulate matter 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 particles resides in a third, coarse mode (Figure 6.3). These three particle modes can be characterised as follows:

Nucleaction mode: The diameter of the original nucleus, such as formed during sulfuric acid nucleation, is about 1 nm (Abdul-Khalek, 1999). Today's measuring techniques are capable of detecting a minimum particle size of approximately 3 nm. According to various definitions, the diameters of nucleaction mode particles were generally less than 40-50 nm (0.04-0.05 μm). Based on particle size research in the 1990's technology heavy-duty diesel engines, it has been postulated that the nucleaction mode extends through sizes from 3 to 30 nm (0.003-0.03 μm) (Kittelson, 2002; Hall, 2001). All of the above size ranges place nucleaction mode particles entirely within the nanoparticle range. The maximum concentration of nucleaction mode particles occurs at 10-20 nm. The nucleaction mode, depending on the engine technology and particle sampling technique, typically contains only 0.1-10% of the total PM mass; however it often includes more than 90% of the total particle count. Sometimes the nucleaction mode particles present as much as 99% of the total particle number. Nucleaction mode particles are composed mostly of volatile condensates (hydrocarbons, sulfuric acid) and contain little solid material.

Accumulation mode: The accumulation mode is made of submicrometre particles of diameters ranging most often from 30 to 500 nm (0.03-0.5 μm), with a maximum concentration between some 100-200 nm (0.1-0.2 μm). As shown in Figure 6.3, the accumulation mode extends from the upper end of the nanoparticle range through to the ultrafine and fine particle range. Accumulation mode particles are made of solids (carbon, metallic ash) intermixed with condensates and adsorbed material (heavy hydrocarbons, sulfur species).

Coarse mode: These particles with aerodynamic diameters above 1 μm (1000 nm) contain 5-20% of the total PM mass and practically no contribution to particle numbers (Kittelson, 2002). The coarse particles are not generated in the diesel combustion process. Rather, they are formed through deposition and subsequent re-entrainment of particle material from walls of the engine cylinder, exhaust system, or the particle sampling system.

6.2.2 Current Theories on Nanoparticles: Composition and Formation

Generally, diesel nanoparticles include the same constituents that are found in the total particulate matter emissions including elemental carbon, ash, hydrocarbons, sulfuric acid, and water. Contrary to the total PM emission, diesel nanoparticles cannot be chemically analysed to precisely determine their composition. There is no sampling/analytical procedure that would allow for separation of a sufficient mass of the nanoparticle material for such an analysis. As a result, the exact formulation of diesel nanoparticles has to be studied through indirect experiments. A consensus has been forming that diesel nanoparticles are mostly volatile. In most cases, they are composed primarily of hydrocarbon and sulfuric acid condensates with small contribution of solid material, such as ash and carbon.

The nanoparticle composition can be dramatically changed by exhaust emission control measures, such as diesel particle filters or fuel additives. Very high numbers of nanoparticles were measured downstream of particle filters in the VERT study

(Verminderung der Emissionen von Realmaschinen im Tunnelbau), a study set up by the Swiss EPA to evaluate the possibility of curtailing emissions with after-treatment of exhaust-gases from existing engines (Mayer, 1997). A special sampling technique was developed to distinguish between solid particles and volatile condensates. The diluted sample passed through a heated vapour trap (thermodenuder), filled with active carbon, before entering the particle size analyser. Depending on the vapour trap temperature, different fractions of particle condensates were driven off the sample. An example of such condensate analysis is presented in Figure 6.4. The data were generated on a 100 kW DI diesel engine equipped with a particle filter at full load with low sulfur fuel (< 0.04% S). The exhaust gas temperature in the particle trap was 460°C. The temperature in the active carbon vapour trap was changed between 120 and 250°C, as shown in the graph.

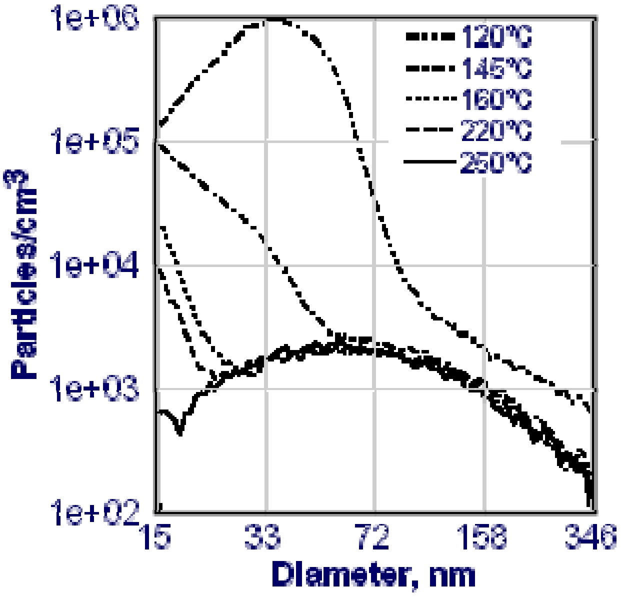


Figure 6.4 Solid Particles and Condensates in Diluted Diesel Exhaust

The high peak of 30 - 40 nm particles disappears from the graph when the sample is heated to 145°C. It is an indication that these particles included volatile materials, presumably hydrocarbons and hydrated sulfuric acid. As the temperature was increased to 250°C, the high nanoparticle emissions disappeared almost completely (note the logarithmic scale in the graph). It can be concluded that high nanoparticle emissions observed downstream of particle filters were composed primarily of condensates (strictly speaking, this conclusion was valid only within the measuring system detection limit of 15 nm, below which solid particles still could be found).

In the same study, particle distributions with iron-based fuel additive were analysed from an engine without a particle filter. Distributions were found with two particle concentration peaks: (1) the additive ash particle peak at about 20 nm and (2) the carbon particle peak at about 90 - 100 nm. As shown in Figure 6.5, the additive caused substantial increase of nanoparticle emissions. Analysis with the heated vapour trap did not significantly change these results, confirming the mostly solid character of nanoparticles in that case. These results indicate that metallic fuel additives, if used, may be a significant contribution to solid ash nanoparticle emissions.

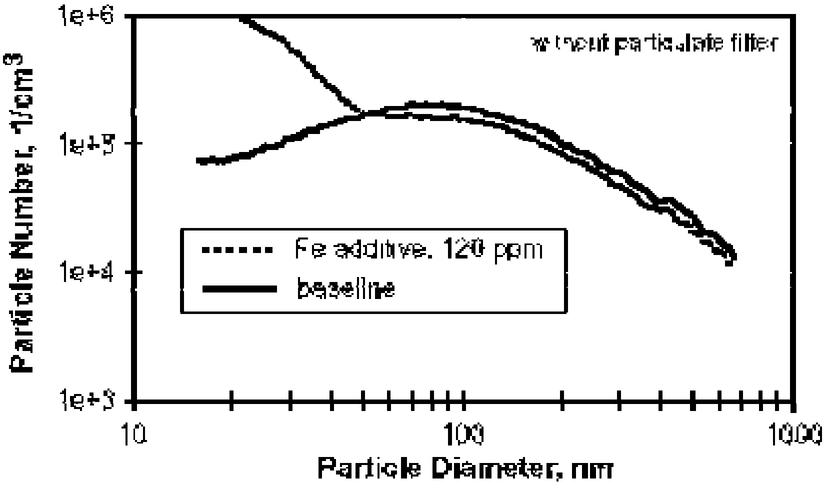


Figure 6.5 Nanoparticle Emissions with Fuel Additive

Nanoparticle volatility experiments were also conducted in the CRC E-34 study (Kittelson, 2002). The set-up involved a Cummins ISM engine and a nano-tandem differential mobility analyser (nano TDMA). The instrument consisted of two differential mobility analysers (DMA) with a heating section between the two DMAs. It allowed a single particle size to be selected with the first DMA, which was then heated, and the resulting size change determined with the second DMA.

Several particle sizes representing the bottom size end of the accumulation mode (50 nm) and the nucleaction mode (down to 7 nm) were subjected to the experiment. It was expected that in this size range, representing the overlap between accumulation and nucleaction modes, a mix of solid and liquid particles would be found. Upon heating, solid particles consisting primarily of carbon and volatile particles consisting primarily of hydrocarbons would be differentiated. Volatile particles would shrink until they would totally disappeared. Solid particles, on the other hand, would shrink only a little as any volatile material on their surface would be removed and then their sizes would stabilize. The results of the experiment, for initial sizes of 50, 30, 12 and 7 nm, are shown as a function of temperature in Figure 6.6. The 50 nm particles split into a mainly solid mode that shrinks to a diameter of 43 nm, and a volatile mode that rapidly shrinks to 15 nm. The 30 nm and 12 nm particles show a similar behaviour, being differentiated into solid and volatile fractions. However, the 7 nm particles continued shrinking upon heating, not showing evidence of containing any solid material. (Volatile particles do not disappear due to a possible instrument artefact around its detection limit.)

The volume fraction that remained in the 12-30 nm particles after heating was also determined in the study. It was found that the volatile fraction amounted to 97-98% of the particle volume, leaving only 2-3% for possible non-volatile, solid cores in the tested particles. Similar heating experiments, as well as evaporation calculations, were conducted for particles made of pure alkanes of different carbon chain length. It was determined that the shrinkage of particles from diesel engines was in the same range as for C28-36 normal alkanes, thus corresponding to the hydrocarbons in the engine lube oil. These results suggest that hydrocarbons that make up diesel nanoparticles are derived mostly of the engine lube oil. It should be mentioned, however, that some fuel effect studies found increased nanoparticle numbers with more volatile fuels, indicating that fuel derived HCs may also present a noticeable contribution (Wedekind, 2000).

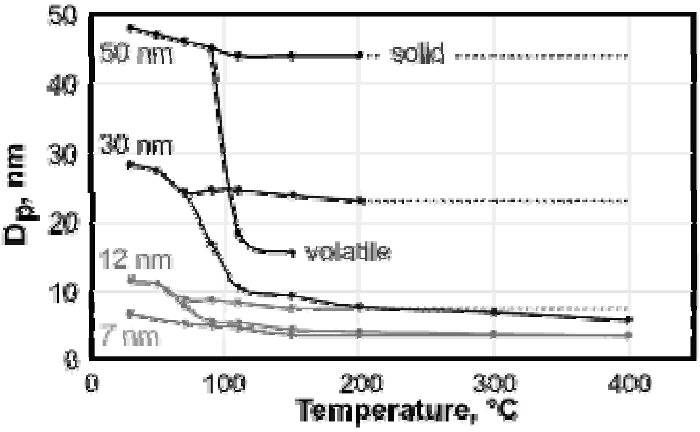


Figure 6.6. Volatility of Diesel Nanoparticles

Various hypotheses have been formulated to explain the increased particle numbers that were seen in certain studies with new diesel engines. It was once suspected that the high particle numbers were related to high injection pressures, which are used by engine manufacturers as a strategy for meeting emission targets. That theory, however, has not been confirmed. On the contrary, a continuous decrease in mass and number emissions was shown when injection pressure increased from 400 to 1000 bar. In another study, the injection pressure had only a small influence, and only under some engine operating conditions, on the particle size distribution (Pagan, 1999).

It is believed that increased number emissions are a simple consequence of:

(1) high concentration of nanoparticle precursors (HC, SO_4), combined with
(2) decreased mass of accumulation mode particles.

Normally, the accumulation particles act as a “sponge” for the condensation and/or adsorption of volatile materials. In the absence of that sponge, gas species that are to become liquid (or solid) will nucleate to form large numbers of small particles. The driving force for the gas to particle conversion is the saturation ratio, defined as the ratio of the partial pressure of a species to its saturated vapour pressure. For the constituents of the SOF or sulfuric acid, the maximum saturation ratios occur during dilution and cooling of the exhaust and are typically achieved at dilution ratios between 5 and 30 (Abdul-Khalek, 1998).

The above nucleation theory explains the high number emissions seen downstream of particle traps (which remove solid accumulation mode particles, but not necessarily nanoparticle precursors), as well as high number emissions from engines of high SOF fraction, such as the ’91 Cummins engine in the HEI study (Bagley, 1996). It is also consistent with the observation of high particle numbers from gasoline engines, which are believed to be composed primarily of liquid condensates (Graskow, 1998). In all of these cases, the low quantities of agglomerated particles present in the gas cannot provide enough surface area for the condensation/adsorption of volatile material. As the species approach saturation, high numbers of small particles are produced through nucleation.

A similar nucleation mechanism may apply to the formation of ash particles. In that case, the ash nucleation takes place inside the engine during the expansion stroke rather than in the dilution tunnel. Once these ash nuclei are formed, they may serve as heterogeneous nucleation sites for SOF and other species during dilution and cooling in the exhaust. It was suggested that some particles in the high SOF nucleaction mode might include ash cores (Abdul-Khalek, 1998).

6.3 AFTERTREATMENT TECHNOLOGIES

The two main particulate matter control technologies are Diesel Oxidation Catalyst and Diesel Particle Trap. Although there are a variety of other techniques that are used in reducing PM emissions, such as SCR (selective catalytic reduction with ammonia/urea) catalyst systems, chemical aftertreatment (with cyanuric acid), Plasma Exhaust Treatment, the majority of them are still under development and not in extensive use.

6.3.1 Diesel Oxidation Catalyst

In general, the overall effect of the DOC on the total PM emission could be a decrease as well as an increase. The total diesel particulate matter (TPM) emission is composed of three major fractions including the carbonaceous particles, the organic particles (SOF), and sulfates (SO_4). Each of these fractions behaves differently over the diesel oxidation catalyst. Oxidation catalysts reduce the SOF fraction and have little effect on the carbonaceous portion of PM in diesel exhaust. This limits the reduction in PM emissions that an oxidation catalyst can achieve. Typical transformations of the three fractions and the resulting total PM emissions are schematically illustrated in Figure 6.7. As apparent from the graph, PM emissions can be reduced in the DOC through the removal of their organic fraction (SOF). The maximum total particle matter reduction is dependent on the magnitude of the SOF (compared to the carbonaceous portion) in the engine-out exhaust, and is usually between 20 and 30% (Harayama 1992). The sulfate fraction of diesel particles (SO_4) is increased in the DOC due to the oxidation of SO_2 with subsequent formation of sulfuric acid. Under certain conditions, however, the SOF decrease can be more than off-set by an increase of sulfate PM, leading to an overall increase in TPM emission (if high sulfur fuels are used, sulfate particle emissions may be much higher than shown in Figure 6.7). Therefore low sulfur fuels and special catalyst formulations are required to limit the catalytic generation of sulfate particles from sulfur dioxide present in the exhaust gas.

Reports on changes in PM carbon fraction over DOCs (Lylykangas 2002, Brueck 2001) must be always approached with careful scrutiny. The magnitude of change in many of such reports is on the threshold of detection. Measurement error can be magnified due to the analytical methods that determine insolubles only indirectly, by subtracting sulfate and SOF from total PM. If sulfuric acid reacts with metals, such as with calcium from lube oil additives, the resulting sulfate salts may be accounted for as insoluble material.

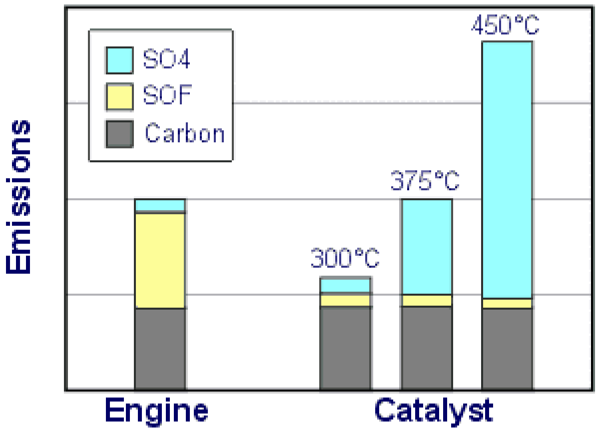


Figure 6.7 Impact of Diesel Oxidation Catalyst on PM Emission

Impact on Particle Number Emission

Contradictory published reports exist on the effect of diesel oxidation catalysts on particle number emissions. Since diesel particle number emissions can be attributed primarily to nucleaction mode particles which are composed mostly of hydrocarbon and sulfuric acid condensates, one can easily explain the performance of the DOC by analysing its effect on nucleaction mode particle precursors. If the catalyst removes hydrocarbons (gas phase and SOF), it prevents their subsequent nucleation, thus reducing the particle number emission. If, however, the catalyst produces sulfates, an effect more prominent with high sulfur fuels and more active, noble metal catalysts, the particle numbers may be increased due to sulfuric acid nucleation.

Experiments which attempt to quantify the impact of DOCs on particle numbers must be very carefully designed. Catalysts can be a source of additional error, such as sample loss due to thermophoretic forces or sample additions due to solid particle blow-off and/or release of condensates from the washcoat.

6.3.2 Diesel Particle Trap

Diesel particle traps are devices that physically capture diesel particles to prevent their release to the atmosphere. Some of the diesel filter materials which have been developed show quite impressive filtration efficiencies, frequently in excess of 90%, as well as acceptable mechanical and thermal durability. In fact, diesel traps are the most effective control technology for the reduction of particle emissions with high efficiencies. More precisely, due to the particle deposition mechanisms utilised in these devices, traps are effective in controlling the solid fraction of diesel particles, including elemental carbon (soot) and the related black smoke emission. It must be remembered that traps may have limited effectiveness, or be completely ineffective, in controlling the non-solid fractions of PM, such as the SOF or sulfate particles. For this reason, trap systems designed to control the total PM emission are likely to incorporate additional functional components targeting the SOF emission (e.g., oxidation catalysts) and sulfate particles (e.g., ultra low sulfur fuels).

Currently available filters for diesel engines are either ceramic wall-flow monolith filters or filter tubes covered with multiple layers of a yarn-like ceramic fibre material.

The filter material contains many pores, or small holes, that allow the exhaust gases to pass through while collecting the particles from the raw exhaust.

The particulate matter that is collected by the filter eventually needs to be removed. This process is called regeneration. Two general approaches for regeneration of the trap have been investigated. One approach employed, called a passive system, is the use of catalytic material on the filter, which causes regeneration, in a continuous or periodic manner, during the regular operation of the system. The other approach, known as an active system, includes an electric heater or fuel burner to periodically raise the filter temperature, oxidise the particle and regenerate the trap, as dictated by an electronic control unit.

Diesel traps are very effective in reducing PM emissions. Their drawbacks are durability/reliability problems and a decrease in fuel economy due to high exhaust gas pressure drop and, in the case of active systems, due to the operation of the heater or burner.

All diesel particle traps of practical importance are diesel particle filters (DPF). Even though the term “trap” covers a wider range of devices, it is often used as a synonym for “diesel filter”. Such use of the term “diesel trap” in reference to filter devices was more common in older literature. In recent years, there is a trend to replace it with the more precise term “diesel particle filter”.

The impact of particle filters on PM composition is illustrated in Figure 6.8 (Andersson and Wedekind, 2001). The filter, a two-stage system incorporating an oxidation catalyst and a wall-flow DPF, was installed on an Euro 1 engine and tested on the R-49 schedule, which is dominated by the full speed - full load mode, resulting in high average exhaust gas temperature. It is clear from the graph that the DPF is extremely effective in removing elemental carbon particles (black, bottom portion of each bar). SOF fractions from fuel and oil are somewhat reduced by the catalyst portion of the filter system. Despite the use of ultra low sulfur fuels, sulfate particles are increased (especially so in the test with UKULSD fuel of higher sulfur content). The increase in the sulfate particles could be due to the catalyst portion of the filter system, which is known to produce sulfates by oxidation of SO_2 with subsequent formation of sulfuric acid. This effect is more prominent if a fuel has higher sulfur content, such as the UKULSD, which has higher sulfur content than the SWCL1.

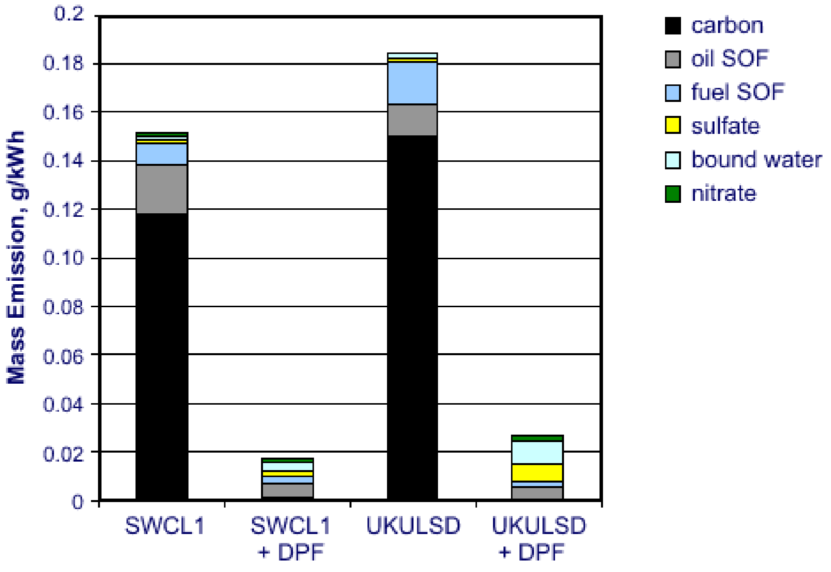


Figure 6.8 Effect of Particle Filter on PM Composition Euro 1 engine on R-49 cycle; SWCL1 (Swedish Class 1) fuel <10 ppm S; UKULSD (UK ultra low sulfur diesel) fuel - 50 ppm S

Impact on Particle Number Emission

While most PM mass emissions are composed of solid matter (or solid particles with adsorbed vapours), liquid material constitutes a very significant part of diesel nanoparticles which are the main contributor to particle number emissions. If the liquid material, including sulfates and SOF, is formed in the PM sampling system, i.e., downstream of the filter, the DPF will be ineffective in reducing nanoparticle and particle number emissions. Even worse, by retaining carbon particles, the DPF removes the material, which otherwise acts as a “sponge” for condensates formed in the sampling system. Therefore, particle filters tend to increase the formation of nanoparticles through nucleation. In effect, DPFs reduce the numbers of mostly solid agglomeration mode particles, replacing them by mostly liquid nucleaction mode nanoparticles, as shown in Figure 6.9 (Burtscher, 2001).

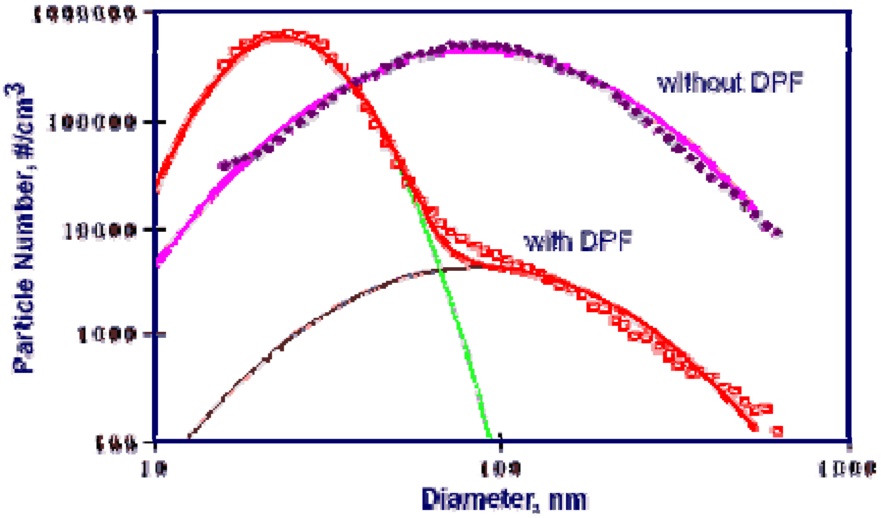


Figure 6.9 Typical Particle Size Distributions with and without DPF

As a result, several studies measured increased particle numbers with particle filters, as illustrated in Figure 6.10 (Andersson, 2001). The data were generated on the hot ECE R-49 test cycle and with a catalytic filter system. High particle number emissions are clearly related to sulfates, which are generated at high exhaust temperatures in the catalyst, as indicated by the higher particle numbers in tests with higher sulfur content in the fuel.

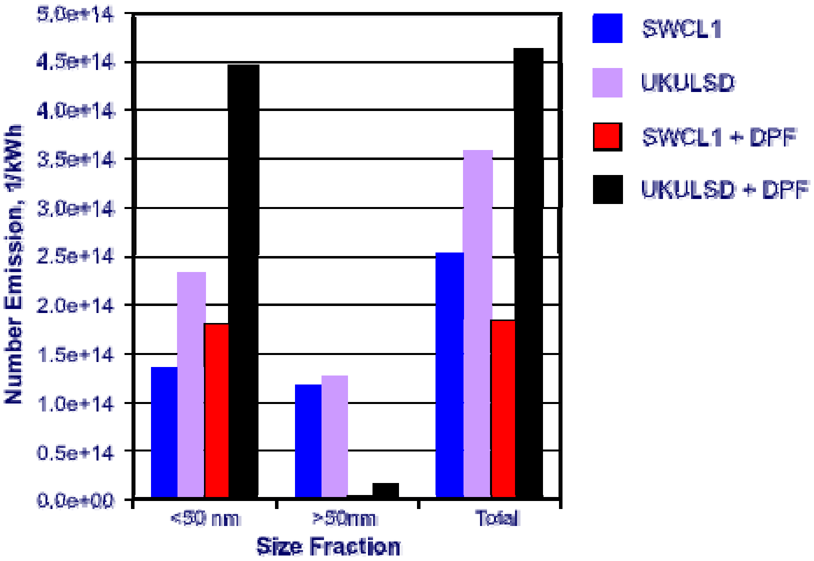


Figure 6.10 Effect of Particle Filter on Particle Number Emissions. Euro 1 engine on R-49 cycle; SWCL1 fuel <10 ppm S; UKULSD fuel - 50 ppm S

In the general case, however, the impact of DPFs on particle number emissions has to be described as inconclusive; the particle numbers may be either increased or decreased. The main parameters influencing the DPF performance or the performance assessment can be listed as follows:

- *Presence of nanoparticle precursors*. This includes SO_3/sulfuric acid which may be catalytically generated from sulfur precursors in the fuel. Hence, lower fuel sulfur content will result in less nanoparticle emission. Hydrocarbons are another nanoparticle precursor. If HCs are removed from the system, e.g., by using a catalyst, lower nanoparticle emissions may be expected. Such phenomena as adsorption/desorption of HCs on accumulated soot in the exhaust system may also contribute to the overall particle number emission.
- *Exhaust gas temperature*. Sulfate particles are formed at high temperature conditions, such as at full engine load. Therefore, in catalytic systems, higher particle numbers will be measured over hot engine test cycles.
- *Particle sampling parameters*. In the absence of standard measuring methods of particle number emissions, laboratories are free to choose any measuring set-up and parameters. As discussed previously, the choice of parameters, such as dilution ratios or dilution tunnel residence times, can critically influence the measurement. Measurements are particularly unstable and irreproducible in systems with high rates of particle nucleation and condensation (as opposed to testing configurations that attempt to measure exclusively solid nanoparticles).

The above discussion was based on an assumption that liquid condensates are counted as particles. As standards are being developed to quantify diesel particle number emissions, a controversy exists as to the inclusion of liquid condensates in particle number measurements (Burtscher 2001). Several laboratories use sample-conditioning techniques that "dry" the gas sample by removing volatile nanoparticle precursors before particle number measurements are taken. If particle filters are evaluated using this technique, they show consistently good particle number reduction performance, as shown in Figure 6.11 (Mayer 2000). This is an indication that solid nanoparticles are retained with high efficiency in a variety of DPF media.

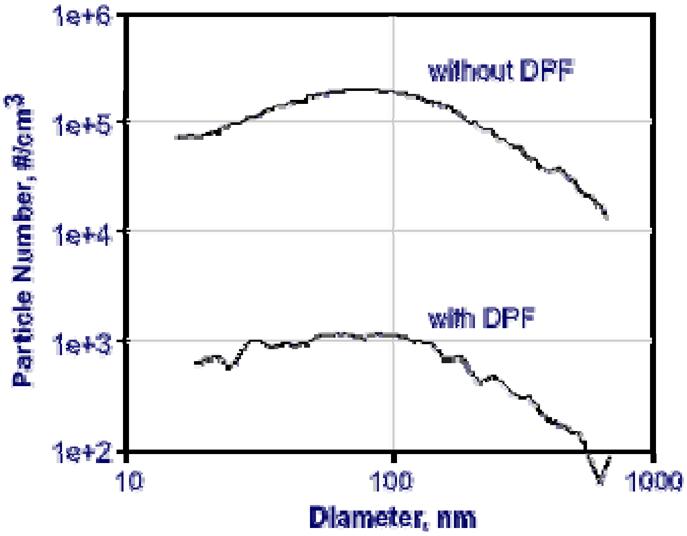


Figure 6.11 Particle Size Distribution with and without DPF - Solid Particles. Ceramic monolith filter on Caterpillar construction engine

6.4 DIESEL FUELS

Diesel fuels are mixtures of hydrocarbons with boiling points in the range of 150 to 380°C. They are obtained from the distillation of crude oil. Refineries are increasingly blending conversion products (cracked components) with the primary distillation streams in order to meet the appropriate product specifications as well as to meet the market demands for different proportions of gasoline, diesel fuel, and other petroleum products.

6.4.1 Diesel Fuel Properties

The requirements placed on diesel fuels are specified in standards, such as the ASTM D975 in the US and EN 590 in the European Union. The most important parameters specified by the standards include: Cetane number, Viscosity, Cold behaviour, Flash point, Volatility, Lubricity, Sulfur, and Additives. As this review will concentrate only on the effects of sulfur we shall not discuss other fuel properties.

Sulfur in diesel fuel and its impacts

Diesel fuels contain chemically bound sulfur. The amount of sulfur depends on the crude oil quality and the components used in blending the fuel. In particular, some crack components have high sulfur content. Refineries can reduce the sulfur content of diesel fuel by treatment with hydrogen. Sulfur increases the lubricating properties of diesel fuels. Therefore, fuels of low sulfur levels typically require lubrication additives to avoid potential damage to fuel injection equipment (Batt, 1996).

There are a number of negative effects of sulfur in diesel fuel, which can be categorised as follows (Ruzicka, 1999):

Emissions

- Sulfur dioxide emissions — most of the sulfur is converted in the engine into sulfur dioxide, a substance of a negative environmental impact.
- Sulfate particle emissions — a fraction of the sulfur is oxidised to sulfur trioxide. The SO_3 binds with water, forms sulfuric acid, and contribute to the total PM emission.

Corrosion and wear

- Corrosion of exhaust system components by sulfur condensates — especially troublesome in exhaust gas recirculation coolers (McKinley, 1997; Kreso, 1998).
- Increasing wear of engine parts through the corrosion of internally formed acid.

Exhaust aftertreatment

- The SO_2/SO_3 shift is increased very significantly if oxidation catalysts are used in the emission control system, resulting in increased PM emissions.
- Sulfate particles are also generated in catalytic particle filters, both the CRT and catalysed traps. Under certain conditions, the benefit of reducing the carbon fraction of diesel PM can be more than offset by the generated sulfates.
- Deactivation of NO_x adsorbers by sulfur is one of the most important obstacles in implementing this technology.
- Many catalysts are poisoned by sulfur (reversibly or otherwise). There may be interferences with future emission control systems that are currently unknown.

In order to minimise these adverse effects, there are strong pressures to reduce the level of sulfur in diesel fuels worldwide. Until early 1990’s, the sulfur level in diesel fuel was not subject to environmental regulations. The maximum sulfur level in good quality fuels, as listed by fuel specifications, was at about 0.5% (5000 ppm = 5000 mg/kg). In the 1990’s, environmental regulations limited the maximum sulfur level to about 500 ppm; this type of diesel fuel was typically referred to as “low sulfur diesel”. Further pressures from the increasingly stringent diesel emission standards, such as the Euro 4 and US2007, will require the use of aftertreatment devices such as DPF. In order to implement these technologies the maximum sulfur levels have to be limited to 50 or 10 ppm. Diesel fuels of typically 15 ppm S (but not more than 50 ppm) are commonly referred to as “ultra low sulfur diesel” (ULSD). In Europe, diesel (and gasoline) fuels of maximum sulfur content of 10 ppm are termed “sulfur-free” fuels.

More recently, fuel quality has been further influenced by national and local regulations aimed at reducing emissions. Many countries introduce tax incentives for cleaner burning, better quality fuels (primarily lower sulfur, but also lower density, aromatics, higher cetane) to offset their higher production costs. Examples of fuel specifications and tax incentives in the 1990’s are listed in Table 6.1 (Lee, 1998).

Table 6.1 Diesel Fuel Specifications

	Sulfur	Cetane No.	Total Aromatics	Density	T90/95	Tax Incentive
	max ppm	Min	max % vol.	g/cm3	max °C	$/ton
US No.2 (ASTM D975)	500	40	-	-	338	-
CARB[a]	500	40	10	-	338	-
EU 1996 (EN 590)	500	49	-	0.82-0.86	370	-
Japan No.2	500	45[b]	-	-	350	-
Japan No.3	500	45[b]	-	-	330	-
Sweden Class I	10	50[b]	5	0.80-0.82	285	97[c]
Sweden Class II	50	47[b]	20	0.80-0.82	295	54[c]
Finland Sw II	50	47[b]	20	0.80-0.82	295	34
Denmark Sw I	10	50/47[b]	5	0.80-0.82	285	85
Denmark City Bus	500	50	-	0.82-0.855	325	50
UK City Diesel	10	49[b]	-	0.80-0.83	-	37.5

a - or fuel must show emissions equivalent or better compared to CARB reference fuel of 500 ppm S, 48 cetane number, 10% aromatics, 1.4% polyaromatics, 0.83-0.86 g/cm3 density, max T90 of 321°C.
b - cetane index
c - initial tax incentive at introduction (1991), current tax incentive lower (e.g. $76/ton Swedish Class I in 1998)

Sulfur content in Australian diesel fuels

The level of sulfur both in diesel and petrol fuels is regulated by the Fuel Quality Standards Act 2000. The Act provides a legislative framework for setting national fuel standards for Australia. The main object of the Act is to regulate the quality of fuel supplied in Australia in order to:

(a) reduce the level of pollutants and emissions arising from the use of fuel that may cause environmental and health problems;
(b) facilitate the adoption of better engine technology and emission control technology; and
(c) allow the more effective operation of engines.

More details of the Act can be found on the following website:
http://www.ea.gov.au/atmosphere/transport/fuel/index.html

The first standards made under the Fuel Quality Standards Act 2000 were environmental standards for petrol and diesel fuels. The first suite of national fuel

standards, which came into force on 1 January 2002, regulates petrol and diesel parameters that have a direct impact on the environment ('environmental' standards). A second suite of national fuel standards came into force on 16 October 2002. These standards address those parameters of petrol and diesel that do not have a direct impact on emissions but, if not controlled, can have adverse impacts on the efficient operation of the engine ('operability' standards). Both environmental and operability standards are summarised in Table 6.2. More details including the Petrol Standards can be found on the Australian Department of Environment and Heritage web site at:
http://www.ea.gov.au/atmosphere/transport/fuel/standardstable.html

The level of sulfur in Australian diesel fuel was set to 500ppm effective from 31st December 2002. Future standards to be implemented from 1st January 2006 will further reduce the fuels sulfur level below 50 ppm.

Table 6.2 Diesel Standard

Parameter	**Proposed standard**	**Date of effect**
Sulfur	500 ppm 50 ppm	31 Dec 2002 1 Jan 2006
Cetane Index	46 (min) index	1 Jan 2002
Density	820 (min) to 860 (max) kg/m^3 820 (min) to 850 (max) kg/m^3	1 Jan 2002 1 Jan 2006
Distillation T95	370°C (max) 360°C (max)	1 Jan 2002 1 Jan 2006
Polyaromatic hydrocarbons (PAHs)	11% m/m (max)	1 Jan 2006
Ash and suspended solids	100 ppm (max)	1 Jan 2002
Viscosity	2.0 to 4.5 cSt @ 40°C	1 Jan 2002
Carbon Residue (10% distillation residue)	0.2 mass % max	16 Oct 2002
Water and sediment	0.05 vol % max	16 Oct 2002
Conductivity @ambient temp	50 pS/m (Min) @ambient temp (all diesel held by a terminal or refinery for sale or distribution)	16 Oct 2002
Oxidation Stability	25 mg/L max	16 Oct 2002
Colour	2 max	16 Oct 2002
Copper Corrosion (3 hrs @50°C)	Class 1 max	16 Oct 2002
Flash point	61.5°C min	16 Oct 2002
Filter blocking tendency	2.0 max	16 Oct 2002
Lubricity	0.460 mm (max) (all diesel containing less than 500ppm sulfur)	16 Oct 2002

6.5 INFLUENCE OF THE FUEL SULFUR LEVEL ON DIESEL EMISSIONS

6.5.1 Regulated Emissions

During combustion, the organic sulfur compounds in diesel fuel are first degraded to molecules or radicals such as H_2S, HS, S, or S_2 and then oxidised via SO radical to SO_2. The reactions are very fast, resulting in practically complete conversion of sulfur to SO_2.

Other than the changes in the levels of exhaust SO_2, changing fuel sulfur content does not cause any observable effects on gaseous engine-out emissions. The emissions of HC, CO, and NO_x are practically independent from the fuel sulfur level. This can be illustrated by the data shown in Figure 6.12, where emissions of CO were constant at all sulfur levels, HC increased slightly (3-8%) with increased sulfur level, and NO_x slightly decreased (DECSE, 2000). Average fuel consumption (BSFC) increased with increased sulfur, but the data showed considerable scatter. Similar results were obtained in a local study conducted by QUT in collaboration with BP and BCC (Ristovski, 2002).

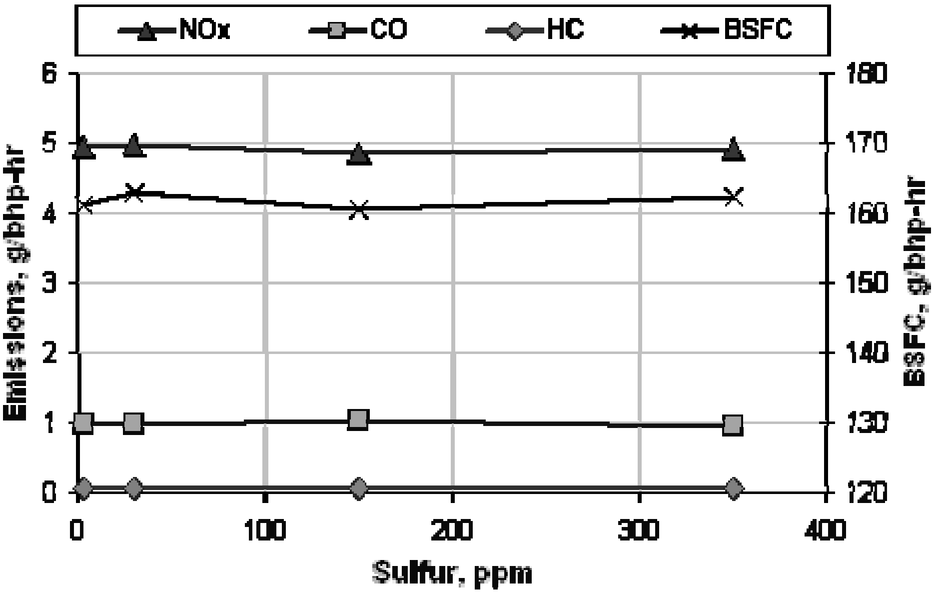


Figure 6.12 Fuel Sulfur Effects on Gaseous Emissions and BSFC

Direct impact of fuel sulfur on emissions is limited to emissions of particulate matter. A fraction of the fuel sulfur is converted to sulfur trioxide and sulfuric acid that, due to the current definition of diesel particulate matter by regulatory authorities, is accounted for as PM emission. That emission is known as “sulfate particles”. Studies have shown that the amount of sulfur converted to sulfate is usually about 2% of the fuel sulfur content (Cowley, 1993), and rarely exceeds 4%. This conversion rate depends only slightly on the engine technology. It should be emphasised that the impact of sulfur is limited to sulfur particles. There is no evidence that reduced sulfur levels have any influence on the carbonaceous portion of PM and on the black smoke.

Since sulfates are just one of several components of the DPM emissions, lowering fuel sulfur levels has only limited potential as a means of PM control. The reduction of diesel fuel sulfur levels from 0.30% to 0.05%, as legislated in the U.S. in 1994, yielded relatively large benefits of about 0.04-0.08 g/bhp-hr PM reduction. However, further reductions of fuel sulfur from the current 0.05% to lower levels has only a small incremental PM reduction benefit of about 0.008-0.016 g/bhp-hr.

6.5.2 Nanoparticle Emissions

Of the150 publications, which refer to the influence of fuel sulfur level on nanoparticle emissions, only a few are directly focused on this topic. Most of the studies concentrate on particle mass and not number emissions. Overall, these studies have limitations, which makes it difficult to provide robust conclusions on the influence of sulfur levels on nanoparticle emissions. Most studies do not utilise a large sample size of vehicles and usually investigate only one or a few engine types. Furthermore, some of the studies were conducted on engine dynamometers while others investigated vehicles on chassis dynamometers. This added additional uncertainties when comparing different studies. It should also be noted that there is still not a clear consensus in the scientific community on the procedures for particle number size distribution measurement during vehicle emission testing. Different studies have used different sampling methods, which are often not described in full detail. Since sampling method itself affects particle formation processes, a meaningful comparison of the results of different studies is not always possible.

One of the largest studies conducted so far (final report submitted in June 2001) has been the Diesel Emission Control – Sulfur Effects (DECSE) program (DECSE, 2001). This program was a joint effort of the U.S. Department of Energy (DOE), two national laboratories, manufacturers of heavy-duty compression ignition (CI) engines, and manufacturers of emission control systems. The objective of DECSE was to conduct tests to determine the effects of various levels of sulfur in fuel on the emission exhaust control systems that could be used to lower nitrogen oxides and particulate matter from diesel vehicles in the years 2002 to 2004. As the sulfur content in diesel fuel is known to adversely affect the operation of diesel exhaust emission control systems, DECSE had also documented the need for low-sulfur fuel. The tests were conducted on a Caterpillar 3126 engine, Cummins ISM370 and Navistar T444E with nominal fuel sulfur levels of 3 ppm, 30 ppm, 150 ppm and 350 ppm. Four emission control technologies were tested:

1. NO_x adsorbers,
2. diesel particle filters (DPF)
3. lean NO_x catalyst, and
4. diesel oxidation catalyst.

Tests were conducted for NO_x concentrations, hydrocarbons, carbon monoxide, and particle mass. Although no work has been done on particle number emissions, the authors recommended that future work should be conducted on investigation of the influence of fuel sulfur level on particle number emissions with various emission control technologies.

Historically, the first and largest program was conducted by the Health Effects Institute (HEI) (Bagley, 1996). They analysed the influence of fuel sulfur content on the emissions from two heavy-duty diesel engines with two types of fuel with sulfur level of 0.32% High Sulfur (CS), and 0.01% (100ppm) or Low Sulfur (LS). The two analysed engines were a 1988 LTA 10-300 (L10) equipped with a ceramic particle trap and a 1991 LTA 10-310 equipped with an OCC. Cummins Engine Co. manufactured both engines. The tests were conducted on an engine dynamometer. The engines were analysed for modes 9, 10 and 11 corresponding to 25%, 50% and 75% load at rated speed. The measurements were conduct without the aftertreatment devices, in baseline mode, and with the aftertreatment devices, trap mode. Although the investigators observed a reduction in SO_4 below the detection limits, a significant difference in TPM levels between the CS and LS fuels was found only at mode 9 base-line. For mode 11 and 9 trap, there was little difference in TPM levels even when the SO_4 component decreased.

They have conducted a limited number of measurements of particle size distributions. Their main finding was a significant reduction of the number of smaller (nuclei-mode) particles when the sulfur levels were reduced from 3200ppm to 100ppm. The study recommended further investigation of the influence of the fuel sulfur level and aftertreatment devices on particle number and size distribution.

Only recently several reports have been published on the influence of fuel specification on particle number, mass and size of emitted particles (Andersson, 2001; Andersson, 2001; Kittelson, 2002; Wedekind, 2000; Ristovski, 2002).

A recent European study conducted within the DETR/CONCAWE/SMMT Particle Research Programme has concentrated on the influence of the sulfur level on nanoparticles emissions (Andersson, 2001; Andersson, 2001). The Anderson and Wedekind (2001) study investigated only 3 heavy duty diesel vehicles (EURO I, EURO II and EURO III) for 3 different sulfur fuel levels: 340-ppm, 53-ppm, and less than 10-ppm. Measurements were conducted for both steady state (R49) and transient cycles (ETC).

For the steady state R49 cycle they found that the changes in accumulation mode particles could be attributed to changes in engine technology. However, the variation in nanoparticles might be influenced by fuel properties. The effects of engine technology proved larger on regulated particle mass emissions than those of fuel specification. With both engines, fuel with highest sulfur content (340 ppm) emitted highest and fuel with lowest sulfur content (<10ppm) lowest weighted cycle nanoparticle emissions. In chemical terms although hydrocarbon and sulfate masses were small, the influences on nanoparticle formation can be significant.

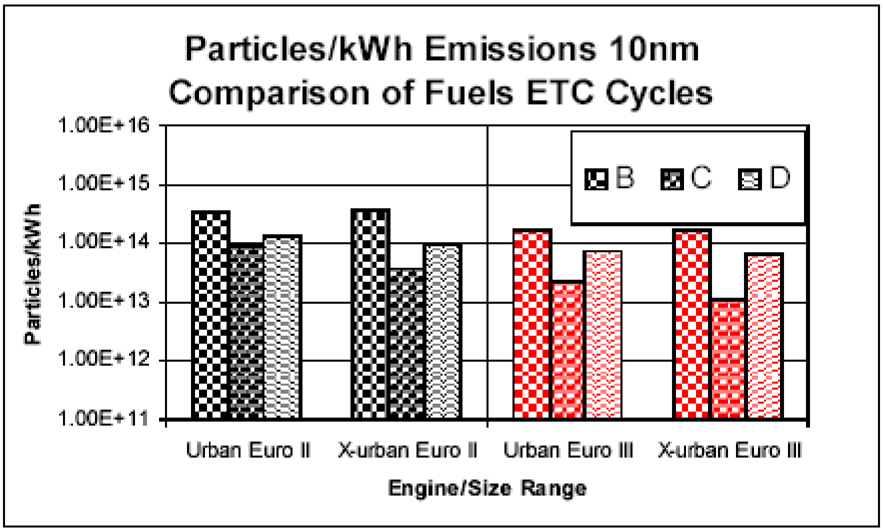


Figure 6.13 Emissions of 10nm Particles During the Urban and Extra-urban Phases of the ETC (Wedekind, 2000)

In Figure 6.13, the emissions of 10nm particles during the Urban and Extra-urban phases of the ETC as a function of fuels sulfur level are presented for EURO II and EURO III type engines. Fuels B, C, and D correspond to 300, <10 and 53 ppm sulfur levels respectively. Although 10nm particles may be more sensitive to transient events with the <10ppm fuel, absolute production is still higher for fuels with higher sulfur level content, e.g., 300 and 53 ppm fuels. It is possible that this effect is related to the differences in nucleation sites provided by fuel specific sulfation. However, as an influence, the sulfur content of the fuel cannot be fully decoupled from other chemical and physical effects within the tested fuels, such as the total aromatic content, which was 21.2, 4.4, and 16.4 % for fuels B, C, and D, respectively.

The light duty part of their program (Andersson, 2001) studied three different vehicles (EURO II and EURO III class equipped with a DPF) over four different sulfur fuel levels (500, 300, 50 and <10 ppm sulfur content) and transient and steady state conditions. They found that the lowest numbers of nucleation mode particles were emitted by the fuel with less than 10ppm sulfur, which resulted in the lowest total number of particles. They concluded that the engine technology effects dominated the accumulation mode (particles larger than 50nm), while the fuel dominated the nucleation mode particles.

Main findings and recommendation from these 2 studies were:

- The changes in accumulation mode particles could be attributed to changes in engine technology. However, the variation in nanoparticles might be influenced by fuel properties.
- The effects of engine technology proved larger on regulated particle mass emissions than those of fuel specification.
- The lowest numbers of nucleation mode particles were emitted by the fuel with less than 10ppm sulfur, which resulted in the lowest total number of particles.
- This study also showed that regulated PM and particle number emissions do not necessary correlate, therefore the focus of the future work should be upon particle number and particle number weighted size distributions.

The recommendations for future work from this study can be summarised:

1. As this program examined only several vehicles from a limited fleet an investigation should be extended to better represent the current and future fleets.
2. New engines and aftertreatment technologies may present new particle production challenges and solutions. These should be investigated.
3. The specific influence of fuel and lubricants should be studied by testing matrices where key parameters of interest, such as sulfur, volatility, and aromatic content are decoupled.
4. The effect of fuel and lubricant sulfur should be studied to determine the influence of this parameter as a source of the condensation sites when nucleation modes form.
5. Moves toward cycles that more closely represent real world driving and measurements methods including dilution parameters should be investigated.
6. Further work is required to develop sampling and measurement standards for particle size and number so that comparable data sets can be produced. Within this new instrumentations should be tested.

A recent study (Bertola, 2001), from collaboration between two Federal Laboratories in Switzerland, analysed the influence of fuel properties and injection parameters on the particle number size distribution. For the fuel composition, five different fuels including low sulfur diesel, zero-sulfur and zero aromatics diesel, two blending portions of oxygenated diesel additive and rapeseed-methylester (biodiesel produced locally in Switzerland) were used. Measurements were carried out on a single-cylinder research engine focusing on exhaust particulate matter emissions. Unfortunately, the levels of sulfur in all tested fuels were not presented and there is a significant difference in the composition of the fuels used, so any changes in emissions could not be attributed only to the sulfur level content. The interesting result from this study is that a nucleation mode is present with all fuels tested when the engine is operated at extremely high injection pressures. At higher injection pressures, a dependency seems to be present between oxygen content in the fuel and formation of nanoparticles. Compared to the reference fuel with 50 ppm sulfur, the blends containing Butylal and the zero aromatics zero sulfur diesel showed lower particle concentrations.

The main findings of this study are:

- A nucleation mode is present with all fuels tested, independent of the sulfur content, when the engine is operated at extremely high injection pressures.
- At higher injection pressures, a dependency seems to be present between oxygen content in the fuel and formation of nanoparticles.
- Compared to the reference fuel with 50 ppm sulfur, the blends containing Butylal and the zero aromatics zero sulfur diesel showed lower particulate concentrations.

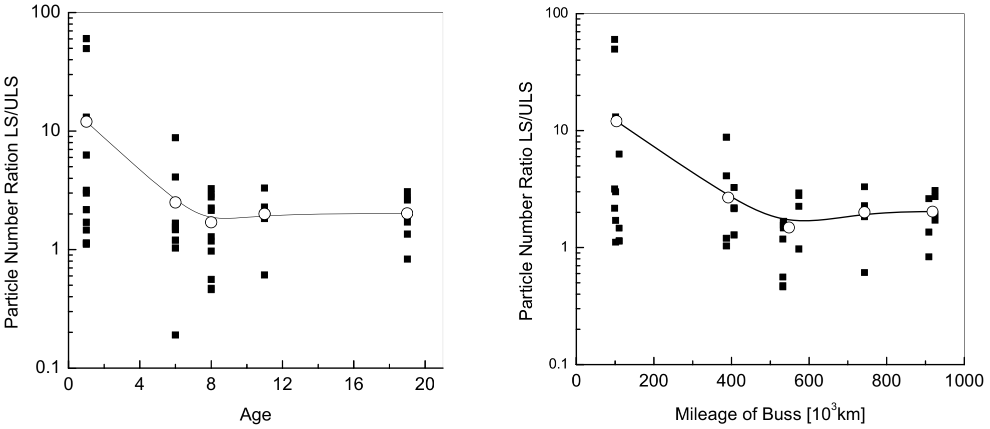
Another study concentrating only on a single engine and on an engine dynamometer was conducted by Wei et al (2001). Wei et al (2001), who studied the emissions from a 1995 model medium-range diesel engine operating at 50% load. Two fuel sulfur contents were used: 440 ppm (low sulfur) and 10 ppm (ultra low sulfur). They found that increasing the fuel sulfur content increased the formation of nucleation mode particles, but did not significantly influence the accumulation mode. The 10 ppm sulfur fuel gave smaller concentrations of nucleation mode particles than the 440 ppm sulfur fuel. The peak particle number concentration in the nucleation mode was much higher with the low sulfur fuel than with the ultra low sulfur fuel. The number of particles in the nucleation mode was also strongly influenced by temperature, with larger concentrations formed at lower dilution temperatures. For both types of fuel, many more nanoparticles were formed during dilution of engine exhaust in the atmosphere at an ambient temperature of 10°C than at 20°C. The total number concentration produced by the two fuels was quite similar at temperatures above 30°C, but, as the temperature was reduced further, the total number produced by the higher sulfur fuel increased much more rapidly. At 15°C, the total number concentration produced by the low sulfur fuel was nearly 7 times higher than that produced by the ultra low sulfur fuel.

The main findings of the study are:

- Increasing the fuel sulfur content increased the formation of nucleation mode particles but did not significantly influence the accumulation mode.
- The number of nanoparticles produced depended strongly on the temperature of the dilution air with the highest number produced for both types of fuel during dilution of engine exhaust in the atmosphere at an ambient temperature of 10°C than at 20°C.

Although the CRC-43 Diesel Aerosol Sampling Methodology project (Kittelson, 2002) did not directly concentrate on the influence of the sulfur level on nanoparticles emissions, the influence of specially formulated fuel and lube oil was studied. Measurements were conducted only on one engine on the engine dynamometer and a CVS facility. Nanoparticle emissions for fuels with 3 different levels of sulfur (1, 49 and 325 ppm) and 2 different lubricating oils (4000 ppm and 385 ppm sulfur) were analysed. They observed that for conventional lube oil (385 ppm) and both 1 ppm and 49 ppm sulfur fuel, there is no significant formation of a nucleaction mode. When present, most of the nucleaction mode was removed when the TD was connected to the SMPS, suggesting that the nucleaction mode is composed of volatile particles. But the most surprising result was the large influence of specially formulated lube oil. Contrary to expectations low sulfur oil led to an increase in nanoparticles formation in nearly all cases. It is possible that the increase in nanoparticles formation by low sulfur oil was related to the formulation of the oil necessary to compensate for the removal of sulfur. It could also be due, in part, to the release of volatile components from the oil, related to the lack of oil break- in. Increasing fuel sulfur also increased nanoparticle emissions, especially at high load. They point out the importance of lube oil on nanoparticles formation a result previously observed by others (Sakurai, 2001).

Recent local studies conducted by Ristovski et al. (Ristovski, 2002; Ristovski, 2002) examined particle emissions from a fleet of twelve in-service buses fuelled by low (500 ppm) and ultra low (50 ppm) sulfur diesel at four driving modes on a chassis dynamometer. The examined busses were between 1 and 12 years old (pre EURO I, EURO I and EURO II). Both size and number as well as particle mass were measured. They found that the particle mass emission rates were not significantly different for the two fuel types. However, the particle number emission rates were 30-60% higher with the LS fuel over the ULS fuel. Most of the excess particles were smaller than 50 nm (nanoparticles) and resided in the nucleation mode.



a) b)

Figure 6.14 Ratios of particle number emission rates with LS and ULS diesel fuel in all four modes as a function of the a) age and b) mileage of the buses (Ristovski, 2002)

The study further investigated whether the age or mileage of a bus had an influence on the particle emissions and how, if at all, they are affected by the sulfur content of the fuel. Figure 6.14 presents the ratio of the particle number emission rates with LS fuel to ULS fuel for each bus and mode as a function of the age/mileage of the busses. The buses were classed into five groups according to their age/mileage. The interesting observation is that the ratio was highest for the more modern engines and decreased with age and mileage until the age of 8 years, and with mileage until about 500,000 km, after which remained constant. In other words, the reduction of particle number emissions with reduced fuel sulfur content was highest for the modern buses. It decreased with age and mileage but did not show any difference between the emissions with the two types of fuel after they passed a certain age and mileage.

In the engines of newer design, there is a decrease of particle mass emission and therefore a decrease in the number and the surface of particles in the accumulation mode. The accumulation particles act as a "sponge" for the condensation and/or adsorption of volatile materials. In the absence of that sponge, gas species, which are to become liquid or solid, will nucleate to form large numbers of small particles. The driving force for the gas to particle conversion is the saturation ratio, defined as the ratio of the partial pressure of a species to its saturated vapour pressure, in this case sulfuric acid. By reducing the sulfur level the partial pressure is reduced and nucleation prevented. If there are more particles in the accumulation mode, as in the case of older type engines, the available surface area will be larger and the process of adsorption will dominate over the process of nucleation. When the process of adsorption of volatile components onto accumulation mode particles becomes dominant, the formation of nucleation mode particles will be partially suppressed. For newer types of engines the number of particles, and therefore the available surface, in the accumulation mode is lower, and the process of nucleation becomes dominant. Reducing the available surface in the accumulation mode will lead to the increase in the number of particles in the nucleation mode. In these types of engines the number fraction in nucleaction mode is 99%, that is, the majority of particles are in the nucleation mode.

As in newer types of engines, the majority of particles are in the nucleation mode: preventing the formation of this mode will result in a significant decrease of the total number of particles, in some cases up to two orders of magnitude. Therefore, the reduction of the particle number would be much more prominent in the engines that have lower particle mass emissions, such as Euro 2 type engines.

In the instances where the formation of the nucleation mode was already suppressed with 500ppm (LS) fuel (i.e. possibly due to a greater particle surface area being available in the accumulation mode) there was only a small reduction, if any, in the total particle number emission with 50 ppm (ULS) fuel.

It is interesting to note that the nucleation mode in this study was also not totally suppressed with the ULS fuel and in a small number of cases (only in 3 cases out of around 50) the nucleation mode was observed with ULS fuel but not with LS fuel. This indicates that the sulfuric acid inhibits the formation of the nucleation mode, but is not the only component responsible for the formation of this mode.

A similar finding that lubricating oil, unburned hydrocarbons from the fuel as well as PAH could also play a critical role in the formation of the nucleation mode was confirmed by Kittelson et al 2002. (Kittelson, 2002)

The main findings of this study are:

- The reduction of particle number emissions (mainly in the nucleation mode) with reduced fuel sulfur content, from 500 ppm to 50 ppm, was highest for the newer type of engines (Euro 2) that have smaller particle mass emissions than the other tested engines (Euro I and pre Euro I).
- The reduction of particle number emission decreased with the age and mileage of the tested vehicles, but did not show any statistically significant difference between the emissions with the two types of fuel for vehicles older than 8 years, and with mileage above 500,000 km.
- In the instances where the formation of the nucleation mode was already suppressed with 500 ppm (LS) fuel, there was only a small reduction, if any, in the total particle number emission with 50 ppm (ULS) fuel.
- The formation of the nucleation mode was also not totally suppressed with the 50 ppm (ULS) fuel and in a small number of cases the nucleation mode was observed with ULS fuel but not with LS fuel. This indicates that the sulfuric acid inhibits the formation of the nucleation mode but is not the only component responsible for the formation of this mode.

6.6 SUMMARIES AND RECOMMENDATIONS FOR FUTURE WORK

6.6.1 Summary: Nanoparticle Formation and Emissions

1. Size and concentration of nucleaction mode particles

    a. The nucleaction mode extends through sizes from 3 to 30 nm (0.003-0.03 µm). All of the above size ranges place nucleaction mode particles entirely within the nanoparticle range.
    b. The maximum concentration of nucleaction mode particles occurs at 10-20 nm.
    c. The nucleaction mode, depending on the engine technology and particle sampling technique, typically contains only 0.1-10% of the total PM mass, but it often includes more than 90% of the total particle count. Sometimes the nucleaction mode particles present as much as 99% of the total number of particles.

2. Chemical Properties:

    a. The nature of nucleaction mode particles is still being studied in laboratories.
    b. Nucleaction mode particles and accumulation- mode particles are externally mixed across a wide size range, with the chemical components being distributed between two particle types: (a) “less volatile” particles, probably comprised of an elemental carbon core with a small organic component; and (b) “more volatile” particles.
    c. The volatility of the Diesel nanoparticles was found to resemble that of C24-C32 normal alkanes, which implies a significant contribution of lubricating oil to these particles.
    d. The organic component of total Diesel particles and nucleaction mode particles appears to be comprised predominantly of unburned lubricating oil, whereas the contribution of fuel to the total organic component appears to be relatively small, no more than 20 % and probably much less.

3. What influences the nucleaction mode particles:

    a. The nucleaction mode is much more sensitive to engine operation, dilution and sampling conditions than is the accumulation mode.
    b. Cold temperatures favored nucleaction mode formation.
    c. The formation of nanoparticles from particle precursors is influenced by the residence time in the dilution tunnel or exhaust system. Short residence time in the exhaust and sampling system prior to dilution favor nanoparticle formation, while short residence time in the dilution system suppresses nanoparticle growth.

    d. Storage and release of volatile material in the exhaust system, and prior engine operating history influence the formation of nucleaction mode particles.

4. Control and mitigation:

    a. Engine technology effects were observed to be larger than fuel effects for accumulation mode particles, which reflected the observations for particle mass. Fuel effects were observed to be larger than engine technology effects for nucleation mode particles, which reflected the observation for particle number.
    b. Diesel particle filters can effectively remove accumulation mode (solid) particles from the exhaust, but can emit volatile precursors that lead to nanoparticle formation and a large nucleaction mode under high load conditions.

6.6.2 Summary: Influence of the fuel sulfur level on nanoparticle formation

1. Sulfuric acid nanoparticles form as a result of condensation of hydrated sulfuric acid. They are formed from gaseous precursors as temperature decreases in the exhaust system, and after mixing with cold air, be it in the laboratory dilution tunnel or in the ambient air. The diameter of the original nucleus is believed to be about 1 nm.

2. Fuel sulfur enhances nucleation but is not the major component of the nucleaction mode. The C24-C32 normal alkanes, from the lubricating oil, have a more significant contribution to these particles (see 6.6.1 point 2).

3. Nanoparticles are more easily formed when fuels with high sulfur content (500ppm and above) are used, but under some engine conditions, such as light load, nucleaction mode formation is independent of fuel sulfur content and heavy hydrocarbons like those in lubricating oil could play a major role.

4. It has been observed that in some engines particle number emissions with low sulfur fuels (below 50ppm) can be up to 100 times lower than with higher sulfur fuels (500ppm). For these engines the reduction in particle mass emission was negligible.

5. The reduction of particle number emissions with reduced fuel sulfur content is greater in engines that emit a smaller concentration of accumulation mode particles, smaller mass emissions (new technology vehicles or vehicles with DPFs).

6. The reduction in particle number emission with the reduction of sulfur level will not show any statistically significant change as the vehicles reach an age of 8 years.

6.6.3 Recommendations for Future Investigations

All of the studies except one (Ristovski, 2002) examined only a few vehicles/engines from a limited fleet with most of the engines of a newer design. In order to assess the magnitude of the problem, a more extensive investigation should be designed to better represent the current and future fleets.

New engine designs and aftertreatment technologies may present new particle production challenges and solutions. These should be investigated.

The reduction of fuel sulfur level is very often accompanied by a significant change in other fuel properties such as aromatic content and volatility. In many of the studies so far these parameters were not decoupled. The specific influence of fuel and lubricants should be studied by testing matrices where key parameters of interest, such as sulfur, volatility and aromatic content are decoupled.

The effect of not only fuel sulfur content but also lubricant sulfur content should be studied to determine the influence of this parameter on the formation and emissions of nanoparticles.

Further work is required to develop sampling and measurement standards for particle size and number so that comparable data sets can be produced. For this purpose assessment and adoption of the existing instruments and techniques should be conducted.

6.6.4 Recommendations on Management Response

Since sulfates are just one of several components of the particle mass (PM) emissions, lowering fuel sulfur levels has only limited potential as a means of PM control. The reduction of diesel fuel sulfur levels from 3000 ppm to 500 ppm, as legislated in the U.S. in 1994, yielded relatively large benefits of about 0.04-0.08 g/bhp-hr PM reduction. However, a further reduction of fuel sulfur from the 500 ppm to lower levels has only small incremental PM reduction benefit of about 0.008-0.016 g/bhp-hr. The main benefit in reducing sulfur levels further below 500 ppm towards 50 ppm and lower will be in the reduction in particle number emissions. This reduction will be in the number of particles emitted in the nanoparticle range. Further to achieve EUROIV and even EUROIII standards of emissions new diesel emission control technologies have to be implemented (aftertreatment devices such as DOC, DPF, etc.). The influence of the sulfur level on the emission of nanoparticles with aftertreatment devices is still unknown.

Previous studies have shown that the reduction of nanoparticle emission with the reduction of fuel sulfur level below 500 ppm depends on the age/mileage of the vehicle. In order to assess the scale of the problem on the whole Australian diesel fleet, more data are needed on the dependence of the reduction of nanoparticle emission as a function of age/mileage of the vehicles. The available scientific data, which is from a single study, cannot give us this information as that study has been conducted on only one type of vehicle present in the diesel fleet (buses).

6.7 REFERENCES

Abdul-Khalek, I. S. and D. B. Kittelson (1999). “The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements.” SAE Technical Paper Series 1999-01-1142.

Abdul-Khalek, I. S., D. B. Kittelson, et al. (1998). “Diesel Exhaust Particle Size: Measurement: Issues and Trends.” SAE Papers 980525: 133-145.

Andersson, J. (2002). “UK Particle Measurement Programme: Heavy-Duty Methodology Development”, Ricardo Consulting Engineers, Report DP02 / 2493, 31 July 2002, http: //www.ricardo.com/ chemistry/ UK_PMP_HD_Programme.pdf

Andersson, J. and B. Wedekind (2001). “DETR/SMMT/CONCAWE Particulate Research Programme”, Ricardo Consulting Engineers, Summary Report DP01/0515, May 2001, http: // www.ricardo.com /downloads/ SummaryReport.pdf

Andersson, J., B. Wedekind, et al. (2001). “DETR/SMMT/CONCAWE Particulate Research Programme: Light Duty Results.” SAE Technical Paper Series 2001-01-3577.

Bagley, S. T., K. J. Baumgard, et al. (1996). “Characterization of Fuel and After-Treatment Device Effects on Diesel Emissions”, Health Effects Institute, Report #76, 1996, http://healtheffects.org/Pubs/st76.htm

Batt, R., J. A. McMillan, et al. (1996). “Lubricity Additives - Performance and No-Harm Effects in Low Sulfur Fuels.” SAE Technical Paper Series 961943.

Bertola, A., R. Schubiger, et al. (2001). “Characterization of Diesel Particulate Emissions in Heavy-Duty DI-Diesel Engines with Common Rail Fuel Injection Influence of Injection Parameters and Fuel Composition.” SAE Technical Paper Series 2001-01-3573.

Bosch (1994). “Diesel Fuel Injection”, Robert Bosch GmbH, 1994,

Brown, J. E., M. J. Clayton, et al. (2000). “Comparison of the Particle Size Distribution of Heavy-Duty Diesel Exhaust Using a Dilution Tailpipe Sampler and an In-Plume Sampler During On-Road Operation.” J. Air Waste Management Association 50: 1407-1416.

Burtscher, H. (2001). "Literature Study on Tailpipe Particulate Emission Measurement for Diesel Engines", Report for Particle Measurement Programme, BUWAL/GRPE, March 2001, http://www.akpf.org/pub/burtscher_bericht.pdf

Brueck, R., P. Hirth, M. Reizig, P. Treiber, J. Breuer. (2001). "Metal Supported Flow-Through Particulate Trap; a Non-Blocking Solution", SAE 2001-01-1950

Cowley, L. T., S. R.J., et al. (1993). “The Influence of Composition and Properties of Diesel Fuel on Particulates Emissions from Heavy-Duty Engines.” SAE Technical Paper Series 932732.

DECSE (1999). “Diesel Emission Control Sulfur Effects Program, Phase I Interim Report No. 1”, U.S. DOE, August 1999, http://www.ott.doe.gov/decse/pdfs/interim.pdf

DECSE (2000). “Phase I Interim Data Report No. 4: Diesel Particulate Filters”, U.S. DOE, January 2000, http://www.ott.doe.gov/decse/pdfs/interim4.pdf

DECSE (2001). “Diesel Emission Control - Sulfur Effects (DECSE) Program, Final Report”, U.S. DoE, 2001, http://www.ott.doe.gov/decse/pdfs/decserpt.pdf

Graskow, B. R., D. B. Kittelson, et al. (1998). “ Characterisation of Exhaust Particulate Emissions from a Spark Ignition Engine.” SAE Paper 980528: 155-165.

Hall, D. E., et al. (2001). “Measurement of the number and mass weighted size distributions of exhaust particles emitted from european heavy duty engines”, CONCAWE, Report 01/51, January 2001, http://www.concawe.be/Download/Reports/Rpt_01-51.pdf

Kittelson, B. D. (1998). "Engines and Nanoparticles: a Review." Journal of Aerosol Science 29(5): 575-588.

Kittelson, D. B., W. F. Watts, et al. (2002). "Diesel Aerosol Sampling Methodology - CRC E-43: Final Report", University of Minnesota, Report for the Coordinating Research Council, 19 August 2002, http://www.crcao.com/reports/recentstudies00-02/UMN%20Final%20E-43%20Report.pdf

Kreso, A. M., J. J.H., et al. (1998). "A Study of the Vapor- and Particle-Phase Sulfur Species in the Heavy-Duty Diesel Engine EGR Cooler." SAE Technical Paper Series 981423.Lee, R., P. J., et al. (1998). "Fuel Quality Impact on Heavy Duty Diesel Emissions: A Literature Review." SAE Technical Paper Series 982649.

Lylykangas, R., T. Maunula (2002). "Particle Oxidation Catalyst for Heavy-Duty Diesel Engines", AutoTechnology, 5/2002, pg. 57-59

Majewski, W. A. and K. H. Breuer (2003). Technology Guide, Dieselnet. 2003.

Mayer, A. (1997). "VERT - Curtailing Emissions of Diesel Engines in Tunnel Sites", TTM Report W11/12/97, 1997,

Mayer, A. (2000). "Particulate traps for heavy duty vehicles", Swiss Agency for the Environment, Forests and Landscape (SAEFL), Environmental Documentation No. 130, http://www.akpf.org/pub/bericht_um130_en.pdf

McKinley, T. (1997). "Modeling Sulfuric Acid Condensation in Diesel Engine EGR Coolers." SAE Technical Paper Series 970636.

Pagan, J. (1999). "Study of Particle Size Distributions Emitted by a Diesel Engine." SAE Technical Paper Series 1999-01-1141.

Ristovski, Z. D., E. R. Jayaratne, et al. (2002). Influence Of The Fuel Sulfur Content On The Particulate Emission From A Bus City Fleet. CASANZ 2002, Christchurch, New Zealand.

Ristovski, Z. D., L. Morawska, et al. (2002). "Final Report of a Comparative Investigation of Particle and Gaseous Emissions From Twelve In-Service B.C.C Buses Operating on 50 and 500 ppm Sulfur Diesel Fuel", QUT, Report prepared for BCC and BP Australia, August 2002,

Ruzicka, N. and T. Liebscher (1999). "Possible Exhaust Gas Aftertreatment Concepts for Passenger Car Diesel Engines with Sulfur-free Fuel." SAE Technical Paper Series 1999-01-1328.

Sakurai, H., et al. (2001). Hygroscopicity and Volatility of Diesel Nanoparticles Studied by Nano TDMA. AAAR Annual Conference.

Tobias, H. J., D. E. Beving, et al. (2001). "Chemical Analysis of Diesel Engine Nanoparticles Using a Nano-DMA / Thermal Desorption Particle Beam Mass Spectrometer." Environmental Science & Technology 35: 2233-2243.

Walters, R. B., et al. (1988). "A Generator for the Production of Sulfuric Acid Coated Diesel Soot Aerosols." Atmospheric Environment 22(1): 17-23.

Wedekind, B., J. Andersson, et al. (2000). "DETR/SMMT/CONCAWE Particle Research Program: Heavy-Duty Results." SAE Technical Paper Series 2000-01-2851.

Wei, Q., D. B. Kittelson, et al. (2001). "Single-stage dilution tunnel performance." SAE Technical Paper Series 2001-01-0201.