

Engine Exhaust Solid Sub-23 nm Particles: I. Literature Survey

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ABSTRACT

In the current diesel vehicle exhaust emissions legislation Particle Number (PN) limits for solid particles >23 nm are prescribed. The legislation was extended to include Gasoline Direct Injection (G-DI) vehicles since September 2014. Target of this paper was to investigate whether smaller than 23 nm solid particles are emitted from engines in considerable concentration focusing on G-DI engines. The literature survey and the experimental investigation of >15 vehicles showed that engines emit solid sub-23 nm particles. The average percentage over a test cycle for G-DIs (30-40%) is similar to diesel engines. These percentages are relatively low considering the emission limit levels (6×10^{11} p/km) and the repeatability (10-20%) of the particle number method. These percentages are slightly higher compared to the percentages expected theoretically not to be counted due to the 23 nm cut-off size (5-15%). Higher fraction can be measured with high ethanol content fuels, at sub-zero ambient temperatures and when additives are added in the fuel or lubricant. Based on the information today, the PN legislation should remain the same. However measurements of particles <23 nm should go on in order to monitor the sub-23 nm fraction of current and future engine technologies.

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INTRODUCTION

Figure 1 gives a simplified overview of the processes from the combustion in the cylinder of the engine until the sampling point at the full dilution tunnel (CVS). In the combustion chamber primary soot particles (spherules, around 20 nm) form via the pyrolysis of fuel (and lubricant) molecules when there is not sufficient oxygen for complete oxidation. In this stage fuel (and lubricant) molecules can completely escape combustion and/or be partly modified; however at this stage they remain in the gas phase. The primary particles agglomerate and most of them are oxidized at the high temperatures in the cylinder. As the piston moves downward, the system cools rapidly. At this stage if there are other non-volatile species (like metals) with very high concentrations, they will deposit on the carbon particles or may alternatively self-nucleate.

In the exhaust tailpipe and the transfer tube from the vehicle to the full dilution tunnel the exhaust gas temperature is still high and usually agglomeration goes on. Agglomerates have an impure form of near-elemental carbon with a graphite-like structure. Also previously "stored" material on transfer tube walls can be released. Semi-volatiles such as Polycyclic Aromatic Hydrocarbons (PAHs) can condense on particles.

In the full dilution tunnel the exhaust gas is mixed with room air dilution air. Some volatile material (from unburned fuel and/or lubricant) condenses on the agglomerates and/or creates

nucleation mode particles (droplets). Thus at the end of the dilution tunnel there is a tri-modal number distribution (see upper right panel of Figure 1) [66]:

- The *nucleation mode*, which contains mainly volatile droplets, but solid cores¹ can also exist.
- The *accumulation mode*, which consists mainly of the agglomerates (soot) and the condensed on them volatile material.
- The *coarse mode*, which consist of deposited particles that reenter in the full dilution tunnel.

Most particles, by mass, reside in the accumulation mode, while by number sometimes the nucleation mode can dominate [66]. During mixing in the dilution tunnel semi-volatile gaseous species, organics and sulfates partition to the aerosol phase, depending on the local temperature and species concentrations, both of which are a function of dilution ratio (ratio of air to exhaust gas). This partitioning occurs in the form of adsorption and condensation onto existing soot agglomerates or as nucleation of separate particles (droplets), usually between 10-30 nm in diameter. Extensive condensation can change the structure of the agglomerates [148, 122]. Whether a separate nucleation mode forms, as well as its magnitude, depends on a number of factors. These include the engine characteristics, the aftertreatment devices utilized [50, 9, 68, 69, 144, 40], the pre-conditioning and history of the test

1. The term *core mode* is used for a separate solid size distribution with peak <23 nm to avoid confusion with the nucleation mode which is typically volatile

[41, 139], the fuel and the lubricant used [67, 70], the sampling conditions [62, 64, 103], adsorption phenomena along the sampling lines [95], and the amount of soot present, since this promotes the competing process of condensation and adsorption instead of nucleation [63, 64, 146]. In order to avoid the variability of the volatile nucleation mode, the European legislation introduced a particle number (PN) method based on the thermal pretreatment of the aerosol and the measurement of the accumulation mode only (agglomerates).

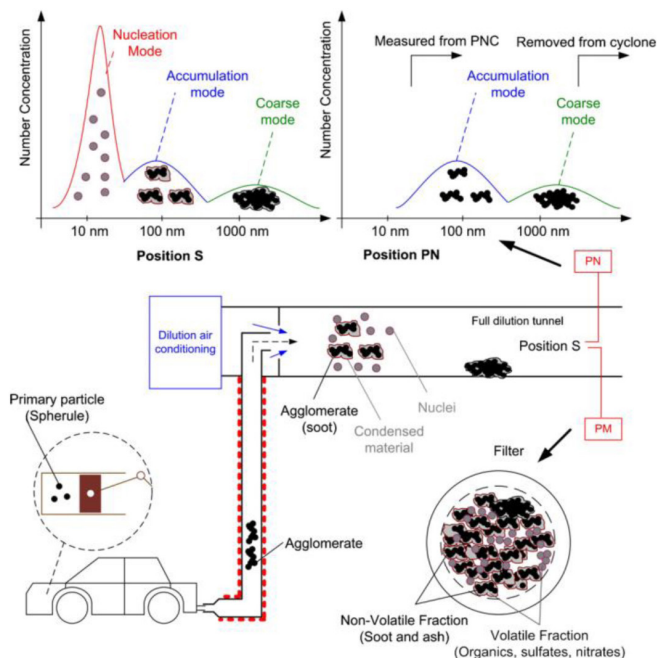


Figure 1. Typical sequence of particle transformation from the engine to the measurement location (from [36]).

Particle Number (PN) Method

The PN method is based on the findings of the Particle Measurement Program (PMP) [3, 37]. When the exhaust gas enters the volatile particle remover (VPR) of the PN system it is diluted with filtered air at temperature $>150^{\circ}\text{C}$, then heated up to $300\text{--}400^{\circ}\text{C}$ and most volatiles and semi-volatiles evaporate and the particle number distribution is affected (see Figure 1). Thus at the exit of the VPR only non-volatile particles should remain. In this paper, particles after thermal pre-treatment at approximately 350°C are called 'solid'.

The particle number counter (PNC) of the PN system measures particles $>23\text{ nm}^2$; this means that the particle number system measures only the accumulation mode and (depending on whether there is a cyclone or not) the coarse mode. The coarse mode in terms of number doesn't contribute much. Note also that even if the volatiles from the accumulation mode are not completely evaporated the total number concentration is not affected. If the nucleation mode is not completely evaporated, there will be an effect on the number concentration. The 23 nm cut-off size of the PNC ensures that this effect will be small. Note however, that if there is a solid core mode $<23\text{ nm}$, this will not be counted.

2. Actually the PNC has a counting efficiency of $50\%\pm 12\%$ for particles of 23 nm and $>90\%$ for 41 nm . The 50% cut-point is called cut-off size $d_{50\%}$.

The PN standard was introduced for Diesel Light Duty vehicles in September 2011 (Euro 5b) limiting the number of solid particles emitted over the NEDC to $6\times 10^{11}\text{ p/km}$. The new standard effectively necessitated the installation of high-efficient wall-flow DPFs in all diesel vehicles. The same standard was introduced to gasoline vehicles utilizing direct injection (G-DIs) at Euro 6 stage (September 2014) initially with a limit of $6\times 10^{12}\text{ p/km}$ and from September 2017 with $6\times 10^{11}\text{ p/km}$. This 3 year delay was decided in order to allow the manufacturers sufficient time to investigate the possibility of compliance through improvements in the combustion process without the need of Gasoline Particulate Filter (GPF). The PN standard has also been introduced for heavy-duty engines since the beginning of 2014 (Euro VI). Particle number limits will also be introduced for most categories of Non-Road Mobile Machinery (NRMM) engines in the near future.

Note that it is important to distinguish solid particles $<23\text{ nm}$ that are part of the lognormal soot accumulation mode from a separate small solid core particle mode. Sub- 23 nm accumulation mode particles are already regulated with the current 23 nm cut-off size, at least to an extent, even if they are not explicitly counted. For example for typical size distributions with means around $50\text{--}70\text{ nm}$, approximately 5-15% of the total particles are not counted. However, one could theoretically manipulate the size distribution to lower sizes and thus avoid part of the emitted particles to be measured (e.g. with a mean of 30 nm , 40% of the particles are not counted). Lowering the cut-off size ensures that most of the particles will be measured and is necessary when a separate core mode exists. However, at the same time the measurement uncertainty due to different losses in the commercial PN systems can increase.

Objectives

Target of this report is to investigate whether it is necessary to measure $<23\text{ nm}$ particles (i.e. to change the current legislation). In other words it will be investigated whether smaller than 23 nm solid particles are emitted by engines in considerable concentration focusing on Gasoline Direct Injection (G-DI) engines. High sub- 23 nm fraction could exist either because the mean size is lower than from diesel vehicles or because there is a separate solid core mode. Initially the health effects of sub- 23 nm particles will be examined. Then the typical solid emissions of vehicles will be investigated based on the literature and experimental tests.

HEALTH EFFECTS OF VEHICLE EXHAUST PARTICLES

Initially a short overview of the adverse health effects of small particles will be given. Target is to see whether sub- 23 nm particles are more harmful than the $>23\text{ nm}$ particles and whether the nature (physical and chemical composition) is also important.

The residence time of particles in the atmosphere depends mainly on their size. Owing to the effect of gravity, coarse particles are rapidly removed from the air by sedimentation

(residence time between some minutes and some hours); also, particles in the nucleation mode are transformed into coarser particles by coagulation processes. The highest residence time in the atmosphere (up to some weeks) is shown by particles in the accumulation mode, which can be easily transported by the wind up to thousands of kilometers from the area where they are formed. Thus, due to their lower residence time in the atmosphere, the sub-23 nm particles should have fewer possibilities to be inhaled. However, it should be kept in mind that in cities people are close to cars and the diluted exhaust gas can reach them in a few seconds/minutes.

Particulates are considered to have a negative impact on the human health. Epidemiological (e.g. [125]) and toxicological studies (e.g. [120]) have associated urban air quality and air pollution, and specifically particulate matter, with adverse health effects. Vehicle exhaust particles have long been considered a significant source of anthropogenically generated particles. In the most extensive and current review of the literature [26], it was concluded that adverse health effects are still best linked to exposure to Particulate Matter (PM) below 2.5 μm . However, pioneering studies [119, 22] suggested that the inflammatory response to particles from non-toxic materials correlates better with the particle surface area rather than the mass. Thus it is assumed that nanoparticles are more harmful than bigger particles because they will have larger surface area (for the same mass). A number of health effect studies suggested that ultrafine particles, particles whose diameter is <100 nm, might be more hazardous than fine particles [28, 93, 134, 130] but maybe this is not true for all materials [60]. Two are the main reasons for the possibly higher danger of smaller particles: Higher deposition fraction of smaller particles and higher surface area in contact with the human cells (for the same mass).

The three main regions of the respiratory tract are: 1) the extrathoracic region that consists of the oro- and naso-pharyngeal region and the larynx; (2) the tracheobronchial region, the system of the conductive airways; and 3) the pulmonary region that contains the fully alveolated alveolar sacs and different types of alveolated airways. Hence, the lung consists of the tracheobronchial and the pulmonary regions. The deposition fraction, defined with respect to the inhaled total particle number concentration, is shown in Figure 2 as a function of particle diameter [1]. The deposition fractions in the three characteristic regions of the respiratory tract are presented separately. The deposition location of an inhaled particle is a sensitive function of its diameter since diffusion is the main deposition mechanism, inertial impaction contributing as well, for particles in the size range of emitted diesel-exhaust distributions. The deposition fraction in the extrathoracic and tracheobronchial region is lower for the accumulation mode (particle size around 50-100 nm) but increases for smaller particles. In the pulmonary region the deposition efficiency curve has a maximum around 30 nm and decreases for smaller sizes. Generally the total deposition increases with decreasing size in the size region emitted by vehicles (particles <600 nm).

The deposition location of an inhaled particle is a determining factor in assessing its health effect. Cancers in mouth, larynx, trachea, bronchus and other regions of the lung can be traced to exposure to particles. In the bronchial and bronchiolar airway generations mucociliary clearance eliminates a significant fraction of deposited particles within 24 hours [54]. In deeper lung regions the majority of deposited particles remain long enough to interact with lung fluid and epithelial cells. During this interaction mutagen and carcinogen agents such as oxidative radicals are generated [10, 58, 120]. Inflammatory [132], allergic immune response [123, 133], or cardiovascular consequences [21] have also been reported.

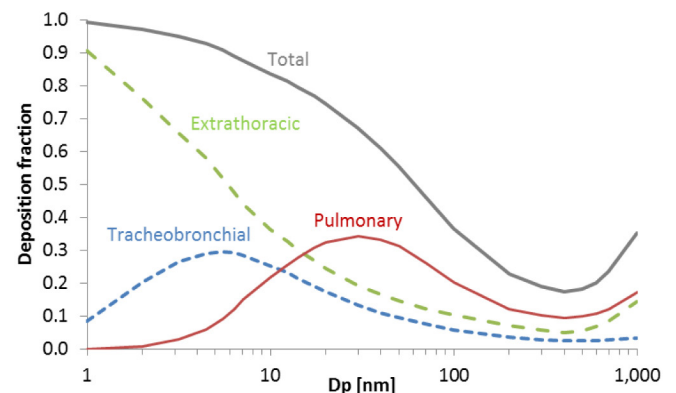


Figure 2. Calculated deposition fraction of inhaled particles as a function of particle diameter for the three region of the human respiratory system: extrathoracic, tracheobronchial, and pulmonary. From [1].

Some authors suggest that the soot is the component that stimulates the most adverse reaction [31, 87, 112]. Many studies have concluded that the toxicity response of PM primarily depends on its chemical composition (e.g. organics) [14, 15, 42, 81, 114, 151]. Transition metals (like iron, copper, vanadium and zinc) and metal oxides [55] also contribute to the oxidative stress resulting from exposure to PM [32] and maybe even more than soot [130]. The high surface activity of metals, which are used in emission control catalysts, seem to increase their adverse health effects [20]. Moreover, these insoluble nanoparticles can transport other surface adhered toxic substances, a phenomenon that is described as the 'Trojan horse' effect [85].

It should also be added that the concept of translocation proposes that inhaled solid nanoparticles pass through the lungs' alveolar membrane and go via the blood to the heart and other organs where they exert a directly toxic effect [121]. They can cross the blood-brain barrier and can also cross the placenta and enter into the fetus. This doesn't apply for volatile nanoparticles which will dissolve in lipid and aqueous bodily fluids.

Conclusions

From the available studies the main conclusions are:

- Total mass still correlates best with adverse health effects.

but other metrics like surface area (for the same mass) might be proven more important in the future.

- Both soluble and insoluble fractions have been identified as potential contributors. Metal oxides were also identified as potential contributors to adverse health effects.
- The size of particles determines the deposition location and deposition fraction. Generally, it increases with decreasing size in the range of particle sizes emitted by vehicles.
- Thus in the presence of excessive sub-23 nm solid particle fractions, the regulated procedure might fail to quantify the number concentration of potentially harmful (i.e. owing to their chemical nature) particles.
- Next chapters will focus on the concentration of vehicle emitted solid sub-23 nm particles and their nature, since volatile particles are out of the European regulation scope at the moment.

LITERATURE SURVEY ON SOLID PARTICLE EMISSIONS FROM VEHICLES

In this chapter it will be examined whether the 23 nm cut-off size makes sense based on studies of primary particles formed inside the combustion chamber, typical vehicle size distributions and specific studies of solid sub-23 nm particles.

Primary Particles

The cut-off size of the PNC was chosen to be 23 nm in order to include the primary soot particles and at the same time avoid any artifact from volatile nucleation mode particles, which, if they still exist after thermal pretreatment, are <20 nm. This section will examine the first assumption i.e. the size of primary particles for different engine categories.

Several studies have investigated the morphology of soot particles from combustion processes using Transmission Electron Microscopy (TEM). Diesel engine soot is composed of agglomerated carbonaceous primary particles [8, 136, 72, 124, 108]. The soot particle nanostructure is highly dependent on conditions such as temperature, time, and fuel properties [147]. The diameter of primary soot particles determined by TEM analysis has been reported to be 23 nm for diesel soot in a smog chamber [149]. In [75] the primary particle size ranged from 16 to 28 nm. The primary soot particle diameter ranged from 19 to 33 nm for a light-duty engine and from 28 to 35 nm for a heavy-duty engine [77, 78, 80]. Similar results were found in [102] with sizes ranging from 18 to 32 nm and in [113] with sizes between 20 and 35 nm. For diesel engines solid sub-23 nm particles can be found when additives are added [76].

Regarding G-DI engines, primary particles from 16 nm to 23 nm were found in [30] and from 10 to 30 nm in [126]. In [101] an image of a nanoparticle agglomerate with about 27 nm primary particle was shown. In [7] it was shown that primary particles were distributed in a range of 7 to 60 nm in diameter, which is somewhat wider than the size range of diesel

particulates. In [79], for early fuel injection strategy, liquid droplets were prevalent, and the primary particle diameter was between 20 and 25 nm with graphitic structure. For a fuel injection strategy which produced low particle number concentration there were many single solid sub-25 nm particles and fractal like agglomerates with primary particle size between 10 and 15 nm with more amorphous structure. In [101] it was observed that the 20 nm particles of a G-DI vehicle evaporated within 60 s of exposure to the electron beam.

Conclusions

The mean value of the primary particles is around 25 nm for both diesel and G-DI engines. However the following points should be considered for G-DIs: The distribution of particles and primary particles can be wider, so larger percentage of particles can exist <23 nm. The structure of primary particles is sometimes different (more amorphous) and more unburned hydrocarbons or volatile organics can be found. This means that differences in the thermal pre-treatment (temperature, residence time of the PN systems) might lead to different results. High concentration of smaller than 23 nm solid particles could also exist from fuel or lubricant additives as with diesel engines.

Typical Size Distributions

Typical PN size distributions of various engine technologies were summarized in [38]. The results were based on more than 15 light-duty diesel vehicles without DPF, 5 with DPF, 10 G-DI vehicles and 30 G-PFI vehicles [35, 44, 46, 61, 88, 89, 96, 98, 100, 109, 110, 111, 115, 117, 126, 143]. The HD results were based on more than 20 engines without DPF and 5 with DPF [4, 35, 39, 46, 142, 145]. The standard deviations were derived from approximately the 1/3 of the vehicles for which there was information in the texts. The size distributions had count median diameters in the range of 50-75 nm (light-duty) and 60-85 nm (heavy-duty) with standard deviations around 1.8-1.9, with no separate core modes <23 nm.

Conclusions

The PMP legislation was based on typical engine exhaust size distributions with means of 50-85 nm and standard deviations of 1.8-1.9. It was also observed that DPFs trap almost equally all particle sizes.

Solid <23 nm Particles Studies

Although it was believed that there were no solid particles <23 nm (except when additives were present), the last years many studies showed that this is not the case. Table A1 in the Appendix summarizes the studies that have investigated solid particles <23 nm. Only the studies with thermal pre-treatment and those that measured both >23 nm and <23 nm solid particles were considered. Some studies with lower temperatures than 250°C were included in grey. Studies without any thermal pre-treatment that typically found the volatile nucleation mode formation were not considered at all. It

should be also mentioned that many of these studies that found a soot-like solid nucleation were conducted with thermodenuders which have been found to form artifacts at small particle sizes [138]. It should be also noted that in many studies it was recognized that the 'solid' nucleation mode [57, 150] was actually volatile, thus an artifact of the PMP method and the dilution factors employed (e.g. [91, 153]). This will be topic of a separate publication. Focusing on the studies that found solid sub-23 nm particles, and were considered reliable, the following conclusions can be drawn. In brackets the number of engines or vehicles that were found with sub-23 nm solid particle fraction.

Diesel (41 Engines and Vehicles)

A solid core mode has been measured with older and modern diesel engines without exhaust aftertreatment [68, 128] or with low particle collection efficiency filters [49] and/or DOCs [19, 73, 74]. It appears mostly at idle and low loads [19, 106] but even at high [73]. It becomes more prominent when the EGR is forced low. The solid core mode increases along with NO and overall NO_x emissions, in contrast with the accumulation mode [74]. The solid core could consist of soot, metal oxides or low volatility organic compounds [68, 71, 128, 131]. The nature of these particles will be discussed below.

Low Volatility Components

Chemical analysis of nucleation mode particles of a heavy-duty engine showed that although organic carbon was the primary component (79%) elemental carbon (8%), elements (4%) and ions (9%) existed as well [29]. The authors also found that lubricating oil was the primary component of the nuclei particles. Recently it was also measured high concentration of sub-23 nm oil particles (20-30% of total) during deceleration and engine braking [129].

Metal Oxides (Lubricant)

Elements such as S, Ca, Zn and P have been found in high concentrations in diesel nanoparticles <30 nm [29]. These elements are used as antioxidants (e.g. ZnDTP) and detergent-dispersants (e.g. CaCO₃). The assumption is that metal particles from the lubricant are partially vaporized during combustion and nucleate. Emissions can reach 1 mg/km (or 1 mg/kWh) [106]. High solid nucleation mode is found when the soot mode is low and at idle. The lube oil consumption is high in this case because the engine blow-by gas flow from cylinder to oil sump, which usually pushes back the lubrication film, is weak. Thus more lubrication oil intrudes in the combustion [106]. Metals from the coatings of catalytic converters and particulate filters (e.g. Pt, Va) are assumed to be low (ng/km) and in the μm range. Similarly for abrasion metals (e.g. Fe, Cr, Ni, Cu, Pb) from piston rings, valves and bearings. They will probably be washed away by the oil film and may end up in the lubrication oil sump or oil filter, however it cannot be excluded that they can re-entrain in the combustion chamber and thus be vaporized and form solid nucleation mode particles [106].

Metal Oxides (Fuel)

Fuel additives (fuel borne catalysts, like Fe and Ce) can also result in a solid core mode [59]. Additives are added in small concentrations to promote regeneration in DPFs. At low concentrations no solid core peak is observed [11, 137]. The additives are deposited on larger soot particles to catalyze the soot combustion. Overdosing the additives (fuel born catalyst) results in a separate solid core mode peak [106] due to self-nucleation and reduced soot surface for condensation [84]. Additives that are used for the regeneration of DPFs are typically captured in the DPF and don't escape in the environment. However, sometimes they can escape filtration [83].

Soot

Another assumption is that the solid core mode consists of soot-like particles. In light-duty diesel TEM images were unsuccessful and only by defocusing the TEM could faint roughly 10 nm smudges be seen [19]. The explanation was that these solid nuclei were amorphous and couldn't be distinguished from the carbon substrate. The lack of a clear TEM image, their low volatility and the charge distribution ruled out that these particles derived from ash or sulfate and suggested rather that they had composition similar to the incipient soot mode observed at <10 nm in rich flames [135, 94], or derived from heavy hydrocarbons that nucleated already in the engine cylinder [19, 73]. How the two solid particle modes (core and accumulation) can originate during diesel combustion is currently not known. Possibly the multiple fuel injection pulses per engine cycle used in new engine technology diesel engines to control soot formation and noise can produce separate particle populations [19].

An important finding from many studies is that DPFs remove the solid nuclei with an efficiency comparable or higher than accumulation mode particles [45]. However, regeneration can also result in increased emissions of sub-23 nm solid particles [13]. It is suggested that they originate from the fragmentation of the soot cake of the DPF. However, they could also be metal oxide particles previously adhered to soot particles [106].

G-PFI (8 Vehicles)

Solid nucleation mode is often observed in Gasoline Port Fuel Injection (G_PFI) engines and it is assumed to originate from the metals of the lube oil [106]. Big differences can be found between old and new engines. A solid core mode has been observed when fuel additives were used [33]. The fuel additives were Mn, Fe and Pb in concentrations up to 18 ppm and very high metal oxide emissions at a size of 10 nm were measured. This case is still realistic in some countries.

G-DI (12 Engines and Vehicles)

A shoulder at 20 nm appears quite often at G-DIs [56, 140]. A separate solid nucleation mode is not typical, but the size distribution can peak at small sizes (20 nm or lower) in some engine operation modes [99, 48] with EGR and high speed.