AVL Instrumentation & Test Systems

AVL Tech Days 2012



Physical Background - particle structure, particle distribution, particle formation, loss mechanisms

21.03.2012





Agenda

- Ø Schematic of the Particulate Matter
- Ø Particle Composition
- Ø Organic Fraction
- Ø Sulfate Fraction
- Ø Carbonaceous Fraction
- Ø Ash Fraction
- Ø Typical particulate composition
- Ø What Happens in the Engine
- Ø What Happens in the Exhaust
- Ø Mechanisms of PM Transport and Transformation
- Ø Effects of Sampling Conditions on PM Measurements

- hipitwith

"How do you want to be known in my chronicle—as the discoverer of fire, or as the first man to pollute the atmosphere?"

Introduction



Particulate matter is the most characteristic of diesel emissions

Diesel particulates form a very complex aerosol system

Contrary to gaseous emissions, PM is not a well defined chemical species







The definition of particulate matter is in fact determined by its sampling method



Schematic of the Particulate Matter



Diesel Particulate can have a bimodal size distribution. The bimodal size distribution is not the standard case. "classical" Diesel particulates consist only of the agglomeration mode

Nuclei Mode Particles:

- Ø The nature of nuclei mode particles is still studied, consist mainly of hydrocarbon and hydrated sulfuric acid
- Ø These volatile particles are very unstable
- Ø Diameter between 3 and 30 nm

Accumulation Mode Particles:

- Ø they consist of a collection of much smaller primary particles (spherules 20- 50 nm)
- Ø The spherules number is what decides the size of the whole particle
- Ø Diameter between 40 and 1000 nm





Accumulation mode Particles

These spherules are simply the "building blokcs"

Their number is what decides the size of the wall or rather, the size of the whole particle

Nor is there any clearly defined morphology: there are highly elaborate and interlinking chains, and clusters of widely varying compactness.



Originator, location of data storage, date of creation



High specific surface areas The agglomerate surface is coated by a layer of liquid or semi-liquid material 6





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Carbonaceous Fraction



The non volatile fraction of diesel particulates is composed primarily of *elemental* carbon

The carbonaceous PM fraction results from the heterogeneous combustion process in diesel engines, where solid particle precursors are formed in both diffusion and premixed flame



Ash Fraction



This fraction contains different inorganic compounds or elements, predominately metals, but a few nonmetals

Diesel exhaust ash consists of a mixture of the following components:

- Ø Sulfates, phosphates, or oxides of calcium (Ca), zinc (Zn), magnesium (Mg)
- Ø oxides of iron (Fe), copper (Cu), chromium (Cr), and aluminum (Al).
- Ø Iron oxides resulting from corrosion of the engine exhaust manifold and other exhaust system components.





a) SEM Picture of ash and b) EDS spectrum for ash



Material	Ash A	Ash D
CaO	29.6	27.6
ZnO	9.9	8.22
MgO	5.5	1.66
SO3	38.8	-
P ₂ O ₅	15.8	10.4
Al ₂ O ₃	-	1.28
SiO ₂	-	3.81
Cr ₂ O ₃	-	0.14
CuO	-	0.22
Fe ₂ O ₃	0.41	1.57
CeO ₂	0.0	-

Example composition of various diesel particulate ashes



Organic Fraction

If assayed by extraction or dissolution in an organic solvent, this is the **soluble organic fraction (SOF)** and if assayed by heating or volatilizing, this is the **volatile organic fraction (VOF)**.

The SOF fraction becomes liquid only after cooling to below 52°C in the laboratory dilution tunnel

The proportion of SOF in the total PM may vary significantly between engines

The SOF is strongly dependent on the operating conditions (i.e., test modes and duty cycles).

This temperature trend was also confirmed by cold-start emission tests, which were reported to produce approximately 25% higher SOF levels than hot-start emissions





The SOF is typically composed of lube oil derived hydrocarbons, with a small contribution from the higher boiling end diesel fuel hydrocarbons



Most of the major chemical families are represented into the SOF

- Ø Alkenes Ø Alkanes
- Ø Ketones Ø Alcohols
- Ø Acids Ø Esters

Ø Aromatics

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Sulfate Fraction

Sulfate particulates are composed primarily of hydrated sulfuric acid

Formation of particles in dilution tunnel depends on H_2SO_4 and H_2O vapor pressures which are functions of:

ØFuel sulfur level
ØConversion of fuel SO₂ to SO₃
ØAir/fuel ratio
ØDilution tunnel temperature
ØDilution tunnel relative humidity

Various sulfates may be also produced in reactions between sulfuric acid and exhaust system components

Particulates may also include sulfate salts



Typical particulate composition

Diesel



Carbon
∎Ash
Sulfate and Water
Lube Oil SOF
Fuel SOF



Gasoline







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What Happens in the Engine



What Happens in the Exhaust



Transformation and Mutation:

Mutation leads to continual modification in terms of particle size, form and composition according to the conditions

These mutative processes are conveniently conceived as being of two types: ØGas-to-Particle (or particle-to-gas) conversion: The volatile species are primary contributors to this mutability à Adsorption & Nuncleation

ØParticle-to-Particle (or Particle-to-Surface) interaction: No new material is acquired from the gas phase .





Number V/S Mass



Mutative processes that affect the nucleation mode will modify the number distribution, and that affect the accumulation mode will modify the mass distribution

Generally, the accumulation mode is more likely to represent what the engine has emitted, the nucleation mode by contrast, is notoriously dependent on the way the exhaust has been handled

What Happens within the Exhaust



At the exhaust ports, only the carbonaceous and ash fraction are solid

When the exhaust temperature fall, volatile components begin transferring into the particle phase Particulate characteristics inevitabily



The most problematic fraction to model is the organic one, because the species within it posses such remarkable diversity

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Mechanisms of PM Transport and Transformation

Transport and Deposition

Particle transport does not necessarily follow the passage streamlines of sample aerosol. Some transport mechanisms that could make particles divert from the streamlines include: ØInterception à the simples ØSedimentation ØInternal impaction

ØDifussion

ØThermophoresis

ØElectrostatic attraction







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Effects of Sampling Conditions on PM Measurements

It is also important to understand the effects of testing conditions on the nature of the exhaust PM being investigated. The identified key environmental or test parameters include

ØDilution ratio (DR) and the resulting saturation ratio

ØDilution rate

ØTime the particles spend at varying dilution ratios or sampling conditions (residence time)

ØHumidity and temperature

ØBackground particle and gas concentrations



Conditions of high dilution ratio and high relative humidity (RH) and low temperature tend to favour the production of nano-size particles or a higher nucleation rate

Longer residence time favours further nucleation and thus tends to increase total particle number concentration; at low dilution ratio and low temperature, the influence of residence time is the strongest and causes highest concentration in nano-size particles





Total particle number concentration decreases as the dilution ratio increases for the same dilution temperature and residence time. For a constant DR, temperature increase can cause a decrease in number concentration. However, a shorter residence time (such as 100ms) makes DR and dilution temperature have insignificant effects on PM number concentration







Comment to slide 5:

Diesel particulates are composed of elemental carbon particles which agglomerate and adsorb other species to form structures of complex physical and chemical properties. Diesel particulates have a bimodal size distribution. They are a mixture of *nuclei mode* and *accumulation mode* particles, schematically shown in Figure 1.

Nuclei Mode: historically they have been less studied, indeed, prior to the mid-1990s, hardly anything was known about them, and this is understandable, as they lie at the limit of detection for many instrument

Most , but not all, research suggest that the nucleation mode particles consist of volatile material. This is why they are depicted as spherical in figure. Other research suggest that some nucleation mode particles are in fact solid, or at least possess minute solid kernels

Nuclei mode particles are very small—according to most authors, their diameters are between approximately 0.007 and 0.04 μ m (micron). More recent studies redefine the nuclei mode particle size range to be even smaller, from 0.003 to 0.03 μ m [*Kittelson 2002*], thus making them comparable to certain large molecules. Nuclei 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 μ m). This is an arbitrary definition, not related to the physical properties of diesel exhaust; nanoparticles include practically all nuclei mode particles, but may also contain a certain fraction of the accumulation mode.

The nature of nuclei mode particles is still studied in research laboratories. It is believed that nuclei mode particles are primarily volatile and consist mainly of hydrocarbon and hydrated sulfuric acid condensates which 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. These volatile particles are very unstable; their concentrations strongly depend on dilution conditions such as dilution ratio and residence time. A small amount of nuclei mode particles may consist of solid material, such as carbon or metallic ash from lube oil additives *[Tobias 2001][Kittelson 1998]*. Nuclei mode particles constitute the majority of particle number—on the order of 90%—but only a few percent of the PM mass.

Accumulation ModemParticles: they have received by far and away the greatest attention. The most immediately obvious feature of accumulation-mode particles is that they consist of a collection of much smaller primary particles. These primary particles are sometimes referred to as "spherules", meaning that, while not exactly spherical, they nonetheless quite closely approximate sphericity. The size range for spherules is typically 20-50 nm. Accumulation –mode particles vary in size because they contain greater or fewer number of spherules, and not because the spherules themselves vary in size. These spherules are simply the "building blokcs", but because they do vary a little in size, they are not so much like house brick as like the stones in a dry stone wall. Some slightly smaller, some slightly larger. Their number is what decides the size of the wall or rather, the size of the whole particle.

This assemblage of spherules, which forms the skeleton, or backbone, of an accumulation mode particle is an agglomerate or an aggregate. The number of spherules that may combine seems not to be subject to any natural law: it ranges from tens, through hundreds, to thousands.

Nor is there any clearly defined morphology: there are highly elaborate and interlinking chains, and clusters of widely varying compactness. And, sometimes, the two ends of the chain of spherules will link up, to form a necklace-like ring. All that can really be said is that, since spherules are seldom seen in isolation, they presumably possess an astonishing proclivity for combining.

The agglomerate surface is coated by a layer of liquid or semi-liquid material: this is viscid, and penetrates into the pores and internal voids of the agglomerates . Significant compositional dissimilarity thus exists between the surface and the bulk. Agglomerates, since they rejoice in high specific surface areas, are effective at accreting and scavenging gas-phase material. The adherence of this volatile or semi volatile layer is what leads to the expression WET particulate, in contradistinction to the solid core that remains after a heating process, which is the DRY particulate

Accumulation mode particulates are formed by agglomeration of primary carbon particles and other solid materials, accompanied by adsorption of gases and condensation of vapors. They are composed mainly of solid carbon mixed with condensed heavy hydrocarbons (Figure 1), 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 μ m with a maximum concentration between 0.1 and 0.2 μ m *[Brown 2000][Kittelson 1998]*. Most PM mass emission (but only a small proportion of the total particle number) is composed of agglomerated particles.

Comment to slide 7:

Little has been said thus far about chemical composition . This can be defined according to the fourl-layered conceptual model depicted in xxxxxxx :

At the first level everything is included that might be captured when the exhaust gas is passed through a filter, with the sole exception of condensed water, this is the legislative definition of "particulate". Obviously, to impose statutory limits on water per se would hardly be sensible, but from a health standpoint, there are no 'pure' droplet as such. Water droplets contain minute solid particles, and also absorb soluble combustion products such as aldheydes and ketones

As already hinted, upon heating, some material evaporates, and some does not; or alternatively, some material dissolves in certain solvents, and some does not. This divides the particulate into that which is VOLATILE or SOLUBLE, and that which is nonvolatile or insoluble. Thereafter there are 5 clear sub groups or fractions. These 5 fractions are defined principally according analytical methods.

Comment to slide 8:

The solid fraction of diesel particulates is composed primarily of *elemental carbon*, sometimes also referred to as the "inorganic carbon". This carbon, not chemically bound with other elements, is the finely dispersed "carbon black" or "soot" substance responsible for black smoke emissions. The carbonaceous PM fraction results from the heterogeneous combustion process in diesel engines, where solid particle precursors are formed in both diffusion and premixed flame. Hexagonal arrays of carbon atoms in soot

particles form platelet-like structures. The platelets are arranged in layers, typically 2 to 5, to form leaf-shaped graphite crystallites. The crystallites are randomly packed with their planes generally parallel to the surface of the primary (i.e., nuclei mode) particle. These three structures are shown schematically in Figure 3

The primary particles agglomerate in the cylinder, while traveling through the exhaust system, and after discharge into the atmosphere. The structure of an agglomerated diesel particle is shown in the transmission electron microscope (TEM) picture, Figure 4 *[Dreher 2002]*. A primary particle in an agglomerate can be seen in picture (a). The particle if formed of numerous graphite crystallites, few nanometers in size, ordered to yield an onion-like structure. Both the size and the arrangement of the crystallites are in reasonably good agreement with the representation in Figure 3. The agglomerated particle in Figure 4 (b) exhibits a grape-like structure formed of hundreds of nuclei mode particles.

Comment to slide 9:

This fraction contains different inorganic compounds or elements, predominately metals, but a few metals; it is a mixture of high variable composition, for which clearly defined chemical compounds are difficult to pin down. A well-used method of characterization is to burn all the particulate, and then examine what remains: that is the "incombustible ash". This, strictly speaking, denotes the condition immediately after the burning, which cannot be quite the same as before, because the burning inevitably causes partial decomposition and other chemical alterations among the ashing elements.

In new engines producing less carbon particulates, the relative importance of non-carbon solid particulate emissions increases. Particulate matter from US post-1994 HD diesel engines may contain as much as 10% and more ash [Abdul-Khalek 1998]. This proportion may increase even further in future engines.

Ash emissions receive a lot of attention from the developers of diesel particulate filter materials, which must be formulated to resist corrosion by ash compounds. In general, diesel exhaust ash consists of a mixture of the following components:

Sulfates, phosphates, or oxides of calcium (Ca), zinc (Zn), magnesium (Mg), and other metals that are formed in the engine's combustion chamber from burning of additives in the engine <u>lubricating oil</u>. These chemicals are present in lube oil as detergents, dispersants, acid neutralizers, anti-oxidants, corrosion inhibitors, anti-wear and extreme pressure additives, etc. Lube oil ash emissions can be modeled based on the known oil ash content (typically around 1.5% in older oils; below 1% in newer oil formulations) and oil consumption rate (typically 0.1-0.2% of the diesel fuel consumption).

Metal oxide impurities resulting from the engine wear, which are carried into the combustion chamber by the lube oil. These include oxides of iron (Fe), copper (Cu), chromium (Cr), and aluminum (Al).

Iron oxides resulting from corrosion of the engine exhaust manifold and other exhaust system components. Depending upon the metallurgy of the exhaust system materials, these particles may also include chromium, nickel, and aluminum

Furthermore, if metallic <u>fuel additives</u> are used to facilitate the regeneration of particulate filters, exhaust gases will contain the corresponding metal oxide ash. Metals used for that purpose include cerium, iron, and strontium. Metallic additives could become a source of high numbers of solid nuclei mode particle emissions [Kittelson 2002].

Example composition of various diesel particulate ashes are shown in Table 1. Ash "A" was collected from a particulate filter over a 100,000 km long experiment in a heavy-duty diesel vehicle [Merkel 2001]. Ash analysis revealed the presence of $(Zn,Mg)_3(PO_4)_2$ and CaSO₄, as agglomerates of primary particles of 100-500 nm in size. The BET surface area of the ash was 10 m²/g. Ashes "B" and "C" were prepared by doping ash A with iron and cerium, respectively, to simulate the use of additives for filter regeneration. The amount of additive was modeled based on the assumed concentrations of 10 ppm Fe and 40 ppm Ce in the fuel.

Ash "D" is a mix of engine generated ashes obtained from field tests [<u>Young 2004</u>]. The BET surface area was 45.58 m²/g, and the median particle size d_{50} was reported at 8.5 μ m. The ash density was 0.4 g/cm³ (theoretical density of 2.5 g/cm³ at 85% porosity).

Comment to slide 11:

Organic Fraction

In some laboratories, however, the evaporated fraction may also include water-soluble material. The VOC should be then adjusted for sulfates, which are determined by chemical analysis. If no such adjustment is made, the interpretation of VOC should rather be the sum of SOF and sulfate particulates, SO4.

It should be emphasized again that the SOF fraction becomes liquid only after cooling to below 52°C in the laboratory dilution tunnel. At the temperatures in diesel exhaust, most of the SOF compounds exist as vapors, especially at higher engine loads when temperatures are high. One needs to keep this realization in mind to understand the changes that occur to diesel particulates in such aftertreatment devices as oxidation catalysts or particulate filters.

The proportion of SOF in the total PM may vary significantly between engines. Particulates with low SOF content are called "dry" particulates. PM of high SOF content is called "wet" particulate. In wet particulates, the organic fraction may constitute over 50% of the total PM, indicating a multi-layer hydrocarbon adsorption on the surface of the particles. In dry particulates, the SOF content may be as low as 10% and less. In a given engine, the SOF is strongly dependent on the operating conditions (i.e., test modes and duty cycles). Typically, SOF content is highest at light engine loads when exhaust temperatures are low. This is illustrated in Figure 5, which presents total PM emissions (represented by the size of the circles) and their SOF content, as measured at a number of steady state conditions from a 2.8 liter DI diesel engine [Horiuchi 1990]. All measurements at exhaust temperatures up to 200°C (measured at the inlet to a catalyst) showed SOF content in excess of 50% of total PM. At high engine loads of above 70% and temperatures of 400°C and more, the SOF dropped to less than 5%.

This temperature trend was also confirmed by cold-start emission tests, which were reported to produce approximately 25% higher SOF levels than hot-start emissions [Wachter 1990]. Two-stroke engines also tend to have higher SOF emissions than their four-stroke counterparts. The fluctuations in SOF with engine technology and with engine test cycle may be extremely important in developing PM control strategies, since solids behave differently from the SOF in both diesel oxidation catalysts (approfondire)and in particulate filters.(approfondire)

These quiddities aside, the organic contingent is possibly the most complex of the five fractions, as it contains several hundred, or perhaps several thousand compounds, many

of which lie at the threshold of detection. Most of the major chemical families are represented, although their proportions vary widely.:

Alkenes Alkanes

Alcohols

Esters

Ketones

Acids

Aromatics

Since lighter C4 to C8 compounds are also found – which, theoretically, should be in the gaseous state – then, presumably, surface interactions are strong

Comment to slide 13:

Sulfate particulates are composed primarily of hydrated sulfuric acid and, as such, are mostly liquid. Formation of sulfate particulates requires an interaction between molecules of H_2SO_4 and H_2O . The process is theoretically modeled as *heteromolecular nucleation [Baumgard 1996]*. According to this theory, both sulfuric acid and water vapor can be undersaturated and still produce particles. The nucleation starts with small molecular clusters, which then grow into more stable nuclei particles. Most stable sulfate particulates are formed when the molar ratio of H_2O to H_2SO_4 equals 8:3 (i.e., 2.67:1 or 0.49:1 by weight). Nuclei sulfate particles are composed of approximately 8000 molecules of H_2O and 3000 molecules of H_2SO_4 . It is believed that sulfate particulates are separate from carbon particles and are present in the exhaust gas primarily as nuclei mode particles.

Formation of particles in dilution tunnel depends on H_2SO_4 and H_2O vapor pressures which are functions of:

fuel sulfur level

conversion of fuel sulfur to SO₃

air/fuel ratio

dilution tunnel temperature

dilution tunnel relative humidity.

Dilution tunnel sampling variability can be, thus, minimized by maintaining a constant relative humidity and using a constant sulfur level fuel. It should be noted that PM sampling procedures which are currently in place do not have any special requirements regarding the relative humidity in the dilution tunnel, while, according to the heteronucleation theory, the rate of sulfate particulates nucleation strongly depends on that parameter.

In addition to sulfuric acid, sulfate particulates may also include sulfate salts. The most common salt is calcium sulfate (CaSO₄), which can be formed in reactions between H_2SO_4 and calcium compounds originating from lube oil additives. Various sulfates may be also produced in reactions between sulfuric acid and exhaust system components. Sulfate particulates of high salt content would bound less water, as most sulfate salts are less hydrophilic than sulfuric acid.

As discussed earlier, the TPM emission is determined by weighing the total mass of material collected on the sampling filter. As a consequence, the sulfuric acid, sulfate salts, and combined water are all counted as part of TPM. The exact amount of water which is

combined with sulfate particulates changes as sulfuric acid on the filter reaches equilibrium with moisture in the surrounding atmosphere. Sampling filters are typically pre-conditioned at controlled conditions until their mass stabilizes. Assuming that sulfate particulates are pure sulfuric acid, the amount of combined water may be determined from Figure 9 depending on the relative humidity during pre-conditioning of the sampling filter *[SAE 1995]*. If filters are pre-conditioned at typical conditions of 50% relative humidity and 25°C, each gram of sulfuric acid is associated with 1.32 gram of water. This corresponds to an average hydration ratio of 7.19, i.e., the chemical composition of sulfate particulates would be $H_2SO_4 \times 7.19 H_2O$ (the molecular mass of H_2SO_4 and H_2O is 98.08 and 18.016, respectively).

Comment to slide 14:

Some figures for a typical diesel engine are: Ash fraction < 1-2% Organic fraction 10-90% Carbonaceous fraction 10-90% Sulphate fraction <5% Nitrate fraction < 1% GDI engines

Thermo-gravimetric analysis showed that the composition of the emitted PM was dominated by volatile material. The elemental carbon fraction did not exceed c30 percent of the total PM by mass. y Transmission electron microscopy confirmed the presence of a variety of solid particles, ranging from a c20 nm in diameter for single particles to a few bundred nm for aggregates. Elemental carbon particles of both amorphous and partly

hundred nm for aggregates. Elemental carbon particles of both amorphous and partly graphitised microstructures were detected. y Following a cold start from -10 °C, PM number concentration generally decreased with increasing coolant temperature, by up to an order of magnitude. y Summary: PM emissions were dominated by condensed material and having particle sizes of generally less than 100 nm. A number of researchers have shown that gasoline engines produce much smaller particles (nanoparticles) than diesel engines. Hence, should particle size be a more relevant toxicological metric than the total mass of particulate matter, then gasoline vehicles may pose a greater hazard in public health terms than diesels (Mohr et al., 2006). During steady-state driving, cruise or light loads, port-injection engines emit little particulate matter, however, they become great emitters during other driving conditions requiring fuel enrichment, such as cold starts, hard acceleration and full load (Kayes et al., 1999; Andrews et al., 1998). Even when they are operating on globally stoichiometric air-fuel ratios, fuel droplets could enter the cylinder due to inadequate fuel vaporisation, which can favour soot formation. The greater volatility of gasoline, compared with diesel, implies a lesser contribution to the organic fraction. In fact, this fraction is suspected to consist predominantly of unburned lubricant oil. Analysis of the particulates from SI engines showed that the bulk of the mass was ash and the second largest fraction was unburnt lubricating oil. Soot emissions were only significant at high power WOT with fuel enrichment, at other conditions soot was less than 10% of the total mass (Andrews et al., 1998) Accumulation mode particles emitted from port-injection engines are agglomerates of approximately mono-disperse spherules. At rich air-fuel ratios, port-injection engines tend to produce more carbonaceous fraction with the filter in the dilution tunnel being black, whereas at lean air-fuel ratios, they are likely to emit more organic fraction with the filter being yellow. On statutory driving cycles, vehicles emit particulate mass at 1-2 mg/km, and 1012-1013/km in number. Instantaneous measurements show particulate emissions increase duringacceleration mode, but then fall back when the cruise condition has been reached (Mohr et al., 2000). Studies on particulate emissions from Direct Injection Spark Ignition (DISI) gasoline engines have revealed that they are significantly higher than port fuel injected engines due to the reduced time available for mixture preparation and increased incidence of fuel impingement onto pistons and combustion chamber surfaces (Price et al., 2007). The current project is with DISI engines, therefore the literature on DISI engines regarding particulate emissions has been reviewed, the results of which are summarized in the next section.

Comment to slide 15:

The carbonaceous fraction forms in the engine via pyrolysis Of the fuel molecules, ie when there is insufficient oxygen available for the complete oxidation.

The organic fraction arises either from fuel molecules that completely escape combustion or from fuel molecules that are partly modified, the reactions which form the carbonaceous fraction having been for some reasons interrupted. Ash compounds present in the fuel, either deliberately or naturally, give rise to the ash fraction. Each of the principal four fractions can also arise from the lubricant, and for similar reasons; but the organic one is probably the most significant in mass terms. Other contributions to the ash fraction may be the induced air and material disintegration, but these are small under normal circumstances

Carbon

When there is insufficient oxygen for complete oxidation, the carbonaceous fraction forms in the engine by pyrolysis of fuel, by which fuel molecules, containing a mere handful of carbon atoms, are converted into soot particles, containing tens of thousands of carbon atoms. However, the greatest sooting tendency is seen not in the complete absence, but in the presence of a certain amount of oxygen, which is attributed to a 'sensitising' role in the pyrolytic reactions (Griffiths and Barnard, 1995). The nuclei formed in this process are of one or two nanometres in size and contain as few as fifty carbon atoms, upon which spherules are created by surface growth into a certain size range of 20-50 nm (Richter and Howard, 2000). Spherules then continue growing by physical collision and adherence to one another. This process is described as agglomeration, by which the number of particles decreases but the mass of soot keeps constant. Due to the lower temperature of the wall than that of the bulk gas, soot can deposit onto the wall without oxidation. Once temperatures have fallen, reentrainment of deposited soot could happen. Thermophoresis is well known as the chief deposition mechanism in fostering particle transport in a thermal boundary layer. This will be discussed in the next section.

Organic

The organic fraction arises from fuel in two ways: The direct path is when fuel escapes combustion and passes through the engine; The indirect path is when pyrolytic reactions are interrupted in their conversion of fuel to soot: for example, if they are quenched by continued mixing, and molecules of fuel partly undergo modification with carbonaceous fraction formation being interrupted (Fujiwara et al., 1993; Kweon et al., 2002).

In fact, the organic fraction is the feedstock for the carbonaceous fraction, which can explain a widely observed trend in the particulate emission from diesel engines: the composition is organic at low load, and carbonaceous at high load. At low load, temperatures are too low to initiate pyrolytic reactions to form carbonaceous fraction, instead, the organic fraction will be emitted from engines. After the exhaust gas leaves the engine, PAH in the exhaust will play a significant role in chemical reactions of organic fractions. Ongoing chemical reactions are thought to underpin the conversion of PAH to more mutagenic NPAH, although genuine reactions are poorly distinguished from artifactual ones (Barale et al., 1992). Organic fractions are also subject to the gas to particle conversion during the late stages in the emission process, i.e. in the exhaust plume or the dilution tunnel. Adsorption and desorption of organic fractions in the exhaust system could change the number of particles markedly (Eastwood, 2007).

Ash Ash compounds in the fuel give rise to the ash fraction. These inorganic components are sometimes deliberately added to the fuel to improve various aspects of the combustion; at other times they are introduced through contamination in the fuel distribution network (Akinlua et al., 2007). The exact chemical reaction pathways in the combustion are poorly reported.

Sulphur

The sulphur component of both fuel and oil gives rise to sulphate fraction emissions in the exhaust. Initially, SO2 is emitted from the engine with only a few percent of SO3 attached. Oxidation catalysts and existing oxidative particles start the conversion reaction from SO2 into SO3, which promptly undergoes hydrolysis to sulphuric acid, H2SO4. This acid undergoes gas to particle conversion by absorbing additional water

Comment to slide 16:

Mutation leads to continual modification in terms of particle size, shape, form and composition according to the conditions. The volatile species are primary contributors to this mutability, since these species are readily subject to gas-to-particle and particle-togas conversion. The gas-to-particle conversion is governed by saturation, which denotes the maximum amount of any volatile species that is able to exist in a gas. The saturation can be mathematically expressed by the ratio of partial pressure to saturation vapour pressure (Hinds, 1982, p.250), which is termed the saturation ratio. Condensation into the particle phase occurs when saturation ratio is above a certain value; in contrast, adsorption for gas-to particle conversion occurs when saturation is below the threshold. For lower values of saturation ratio (<1.0), the increasing saturation ratio causes increase in the organic adsorption to available surface area (of carbonaceous particles). As the saturation ratio approaches 1.0, condensation of organic matter starts. If it is sufficiently high (3 to 4), which is likely if there is insufficient particle surface available in the exhaust for extensive adsorption, new particles may form by homogeneous nucleation of gaseous species. Nucleation is one type of condensation which contributes to the generation of new particles with "on-off" property: it takes place on pre-existing kernels which are too tiny to be commonly thought of as particles. The greater the availability of condensable material, or the higher the saturation ratio, the smaller the kernel needed to commence nucleation. Depending on whether the particle formation is mediated by the nucleating substance itself or foreign material, two types of nucleation are possible: homogeneous nucleation and heterogeneous nucleation. Heterogeneous nucleation is the more usual type because it requires less supersaturation. For instance, the value of the saturation ratio is normally found to be less than 1.0, for the hydrocarbons associated with SOF of diesel PM and thus heterogeneous nuclei in the form of sulphuric acid and possibly metallic ash are the likely precursors to the formation of hydrocarbon containing nano-particles. It is also reported that sulphuric acid may nucleate in mini-dilution systems at dilution ratios ranging from 10 to 50 (Kittelson et al., 1999).

In the right conditions, a massive upsurge occurs in particle formation. Nucleation is boosted by high volatile/non-volatile ratio, while if it is low, condensation and adsorption are more likely to occur. The adsorption of volatile materials onto carbonaceous particles (when the exhaust is cooled) depends on the particle surface area available as well as the value of the saturation ratio. Thus an engine producing a large amount of volatile material with a high level of carbonaceous particles (in the case of older engines) is likely to have less particle nucleation and growth compared to an engine producing an equal amount of volatile matter but a low amount of carbonaceous matter (as in the case of newer engines) (Kittelson, 1998).

Comment to slide 17:

In Section 2.2.2 it was stated that aerosol science spans five orders of magnitude in particle size. Fortunately, to study the particles emitted by internal combustion engines, three orders of magnitude are normally sufficient, while much of the important information resides in just two orders of magnitude.

The size range of interest is situated between the largest viruses and the smallest bacteria, and in terms of electromagnetic radiation, this overlaps with light in the visible and ultraviolet. If we were to take any sample of exhaust gas and examine the size distribution of particles suspended therein, the demographic information would not greatly differ from that depicted in Figure 2.17 (after Kittelson, 1998). This figure plots, using the mathematical functions developed in Section 2.2.2, the size distribution in three ways: according to number, area and mass. The particles fall readily into three groups, known as modes, and these are designated, in order of increasing size. nucleation'.

accumulation" and 'coarse". The exact position of each peak on the x-axis varie, and the distribution is usually dominated by one node, but the trimodality appears to be generic: this parallels the picture developed earlier for atmospheric aerosols in Section 2.3.1.

Each of the three modes, when plotted on a logarithmic x-axis. appears normally distributed, and this distribution is described as lognormal. Actually, lognormality is not always the case, but mathematical curves generated from Gaussian distributions usually fit the data quite well. A fundamental aspect, the profundity of which cannot be overemphasised, is the domination of different ranges by mass and number. Most of the particles, according to number, reside in the nucleation mode: while most of the particles, according to mass, reside in the accumulation mode.

Each of the two functions, then, inherently emphasises different modes and different ranges of size.

This understanding can be extended to the two distributions developed in Section 2.2.2 for mass (m(Dp). μ gcm~3 μ m~l) and number (n(Dp), cT-^T"1). Since transport and transformation are determined fundamentally by particle size, then mass and number are inevitably affected by these phenomena in completely different ways. If one were solely interested in mass concentration (M, μ gem-3), then inaccuracies in measuring the nucleation mode might not appreciably alter the end result.

If, on the other hand, one just wished to investigate the number concentration (TV, cm-3), then inaccuracies in measuring the accumulation mode would be of lesser concern. Diffusion governs particle transport particularly strongly in the nucleation mode, and so potentially affects the number distribution, whereas inertial deposition has greater implications for the accumulation mode.

It turns out that nucleation-mode particles are vastly more vulnerable to measurement falsifications than accumulation-mode particles; indeed, measurement artefacts can completely overwhelm number concentrations. Much of the blame for this can be laid on the volatile component and the highly nonlinear nature of nucleation, as we saw in Section 2.2.4. It is, therefore, notoriously difficult to measure the nucleation mode in a meaningful, reliable or consistent way. The nucleation-mode

Comment to slide 18:

At completion of combustion, or opening of the exhaust valve, the particulate phase is still a very, very long way from its final form; and in the exhaust process that follows, continuing transformations take place, the repercussions of which are profound and farreaching. Initially, exhaust temperatures are still high enough for ongoing reactions, between gases or between particles and gases. Particles grow by agglomeration, and other particles lodge on internal surfaces. The volatile components, i.e. the sulphates, organics and nitrates, adhere to existing particles or nucleate into new particles.

Gas- particle partitioning is absolutely central to the emissions process. At the exhaust ports, where the temperature is high, only the carbonaceous and ash fraction are solid, but as the exhaust temperature continues to fall, volatile components begin transferring into the particle phase. THIS IS THE FOREMOST PROBLEM IN PARTICULATE MEASUREMENT: Particulate characteristics inevitably depend on how the exhaust gas been conditioned. The volatile species are, so to speak, the "floating voters". Samples of particulate extracted from various points in the exhaust system demonstrate that most gas-to-particle conversion happens quite late in the emissions process- often post-tailpipe. Pivotal in the emissions process is the dilution ratio, as this control saturation, through cooling (heat transfer) and mixing (mass transport) This is where the real-word emissions process diverges from that in the laboratory; both dilutions see figure. In the real world, dilution continues to an infinite ratio, whereas in the laboratory, dilution converges to a fine ratio- where it stays until the gas reaches the filter. Identically, therefore, in particulate emissions, between the real world and the laboratory, seems rather unlikely. And, perhaps less obviously, the laboratory sampling point is also influential: gas drawn from just upstream of the tailpipe has already cooled significantly, during transit through the exhaust system, whereas gas drawn from the exhaust manifold is still hot, and denied this opportunity. Moreover, the real word emissions process is influenced by shifting parameters such as wind speed, vehicle speed and ambient humidity. But some consistent method of dilution is needed in the laboratory, just as

some practical limits needs to be set on the possible permutations in these extraneous parameters.

The importance of the curve traced by the dilution ratio, as a function of the distance from the tailpipe, is currently much discussed. The upshot , however, is that, initially, cooling is the dominant factor : this decreases the saturation vapour pressures of volatile components , and encourages gas-to-particle conversion. Eventually, however mixing catches up and becomes the dominants factor . There is a temporal dimension , since gas –to-particle conversion (and vice versa)has a kinetic aspects, and is no universal experience , since each pocket in the exhaust plume mixes an cools differently.

Water is the chief condensable components, and its condensations is immediately triggered when the exhaust temperature finally falls below the dew point whenever conditions os saturation are broached. Typically dew points are in the range of 45-55°C, depending on the air-fuel ratio, and taking ½ as a typical carbon-hydrongen ration in the fuel. As a diesel engines always burn lean mixtures , their exhaust- gas dew points are lower than for gasoline engine burning stoichiometric mixtures. But, normally, the dew point is not transgressed within the exhaust system, except perhaps in a cold start or in outstandingly cold water , in these instances a dribble of water may be see issuing from the tailpipe. In other circumstances, if the dilution into the ambient air is slow I comparison with the rate of fall temperature, then the water droplets will appear in the vicinity of the tailpipe, which case a visible exhaust plume forms.

The same physics drives gas-to-particle conversion in the other volatile components of the exhaust . The most problematic fraction to model is the organic one, because the species within it possess such remarkable diversity. Each species, of which there are thousands, is characterized by its own set of parameters e.g boiling point, concentration and saturation. The lightest organics compounds remain predominantly in the gas phase; the middling ones become partitioned between the gas phase and the particulate phase, and the heaviest ones reside predominately in the particulate phase.

If unburned fuel is discharged in substantial quantities, then the fuel droplets, manifested as withe smoke, will form. A plume of fuel droplets is easy to confuse with a plume of the water droplets, because their interactions with the light are the same. Water droplets tend to be less overtly white and less opaque than fuel droplets, and are not generally seen once the power train is warm; nor are they associated with the malodorous that always accompanies fuel droplets. An exhaust plume of water droplets is shorter, suggesting swifter evaporation, and more vigorosouly swirling, suggesting the droplets are more faithful to the eddies.

Sulphates are the other principal volatile, component in the exhaust gas . There are seldom of an issue of the absence of the catalytic converters, because most of the sulphur is emitted as SO2, and, as such, this makes no difference to the amount of particulate, since it remains in the gas phase. However any oxidation catalyst will readily convert, according to well-understood thermodynamic law, the SO2 to SO3; this SO3 is rapidly hydrolysed into sulphuric acid H2SO4; and this acid, in turn, and with equal rapidity, undergoes gas-to-particle conversion. Importantly, shulpuric acid is notorious for shifting the dew point, so that condensation now begins earlier, within the exhaust system, rather than in the plume – creating a corrosion hazard for metal components.

Ash more usually exist as metal oxides or salts. It is possible that, owing to shifting equilibria, chemical compositions change as the exhaust cools, but, because this cooling

occurs with such formidable rapidity, full equilibrium may not be possible, in which case these compounds remain in some quenched or nonequilibrate state. This issue has not been well researched, The ash fraction is not noted for its volatility, and is rightly viewed as effectively non volatile in the exhaust system; most of the gas-to-particle- conversion probably happens within the engine, or close to the exhaust ports. However, one should be alert to the possibility that the some ash compounds are not entirely in the particulate phase when transit through the exhaust system.

Ash Particles formed from their respective vapours should not be confused with the others arising from processes of disintegration. Wear particles are still assigned to the ash fraction, on the grounds of commonality in their elemental composition, but they different distinctly in nature, being lager sometimes much lager (microns instead of ten or hundred namometres). This is the case with rust and scale, which, through the combination action of oxidation, thermal cycling, vibrations and corrosionby suphuric acid, exfoliate from the walls of the exhaust system. Various wera particles are also released from the catalytic converters or other afthertreatmet devices, and from mufflers. Exhaust system exhibit a remarkable proclivity for particle storage and release. The

sudden and unexpected release of the walls deposit, as triggered by vibrations, temperature cycling, etc , is behind spikes, pulses or burstsof particles, and this randomness easily leads to frictitous measurement .

THE TAILPIPE EMISSIONS IS NOT, IN THIS RESPECT A FAITH FUL REPRESENTAION OF THE ENGINEN OUT EMISSIONS; AND PERPHAS THE AS-MEASURED PARTICLES WAS ACTUALLY EMITED BY THE ENGINE IN THE PREVIOUS HOUR, PREVIOUS DAY,-.....

Comment to slide 19:

Transport and Deposition

Sometimes, particles are designedly caught; at other times, their capture by surfaces is inconvenient, and must be avoided. But, to be captured, particles must first be transported, and various mechanisms account for this transport, of which the six most relevant to the present topic are depicted in Figure 2.3.

The simplest case, 'interception', is virtually a truism: when a gas is in motion, that is, undergoing convection the particles suspended within it will follow, quite naturally, the streamlines, and, purely by serendipity, pass sufficiently close to a surface to be captured. For a spherical particle, for example, should its centre lie on a streamline, the critical distance for the interception is the sphere's radius. Whit non spherical particle, of course, the picture is more complex, but the geometrical principle is the same. Given the fortuitous nature of the geometry required, interception is not normally a significant Transport as ordinarily understood, seldom concerns this simplest case, as particles are subject to a gamut of forces, the action of which ensures motion relative to the gas, that is, the streamlines are not respected. These other mechanisms of particle transport are frequently of greater importance than the simplest case; indeed, without them, particles would regularly evade capture merely by sailing triumphantly past intercepting objects.

The predominant force is, in the main, decided by particle size. At one end of the spectrum, particles are massive enough to experience significant inertial and even

gravitational forces. At the other end of the spectrum, particles approach molecular dimensions, so that motion is influenced, and indeed dominated, by collisions with gas molecules. In this diminutive regime, the surrounding gas can no longer be considered a continuous fluid, and must, instead, be treated as rarefied with respect to the particles. The gas is, in effect, an assemblage of still smaller particles, namely molecules. The mean free path in exhaust gas, for example, is comparable with the size of many particles. There are thus, as outlined in Table 2.1, three regimes of behaviour; these regimes are defined nondimensionally by the Knudsen number $2\lambda/Dp$, where Λ is the mean free path of the particles, which is difficult to define, and of less use analytically (Plagan and Seinfeld. 1988, p. 294).

"The drag force depends on the relative velocity between particle and gas and this is described by the drag coefficient, which depends, in turn, on the Reynolds number Re. For Re>1000, Newton's resistance law applies - derived originally for a ballistic evaluation of cannonballs where inertial forces are much larger than viscous forces. At the opposite extreme, when Re<1 Stokes s law applies, where viscous forces are more important than inertial forces. For particle sizes approaching the mean free path, Stokes's law is modified by the 'Cunningham slip correction', as the key assumption, that the relative velocity of the gas at the particle surface is zero, no longer applies; this ensures faster transport than otherwise predicted (Hinds, 1999, pp. 48-51)."

When a particle is situated in a temperature gradient, so that one side is hotter than the other, the high-temperature side experiences more vigorous collisions with gas molecules than the low-temperature side. Since molecular collisions at a surface are manifested as pressure, a force imbalance arises; and this imbalance pushes the particle towards the lower temperature, that is, down the temperature gradient. This transport mechanism is called 'thermophoresis'. Clearly, appreciable rates of heat transfer are the controlling factor here. For $Dp < \lambda$, thermophoresis is independent of particle size; for $\lambda < Dp$, the situation is more complicated, because the particle, in acting as a thermal conduit, carries its own temperature gradient (Hinds, 1999, pp. 171-176). The practical outcome, however, of this size dependency is that, for particles of a few hundred nanometres, thermophoresis is often the only significant deposition mechanism.

Many particles are electrically charged; indeed, in the atmosphere, this situation is inevitable since air contains $\sim 10^{-3}$ ions per cubic centimetre, courtesy of natural ionising radiation and these ions attach themselves to particles (Hinds, 1982, p. 302). Charged particles migrate inexorably towards oppositely charged surfaces or away from similarly charged surfaces. For this reason, materials susceptible to charge build-up (such as Teflon) should be avoided in the construction of sampling lines. From an opposite standpoint, particles are sometimes deliberately charged in order to catch them:

Particle transport operating even in the complete absence of bulk flow, that is without any bulk-gas convection, is what chiefly distinguishes browbian notion. This transport mechanism is notable for its stochastic rather than deterministic nature, and for its inherent homogenising action. Brownian motion arises from random buffeting by gas

molecules, so that particles shudder, and trace out erratic, intoxicated trajectories. But, since particles are not generally influenced by single collisions with gas molecules - indeed, huge numbers of collisions take place per unit time - the motion is continuous and meandering, rather than, as with gas molecules, characterised by jumps and bounds (Flagan and This Brownian motion **is What drives Partide diffusion . as expressed by the diffusion coefficient, and this is strongly size-dependent**: the diffusion of a 10 nm particle is 2000-fold faster than a 10µm particle. The continual retention of particle by surface sustains a concentration gradient: this diffusion-mediated capture mechanism is immensely significant for particles smaller than ~50nm; indeed it is sometimes thought, intuitively although erroneously as it turns out, that smaller particles are harder to capture. In fact the smallest are caught easily because they diffuse rapidly towards surfaces.

As all particles possess a mass, they ipso facto experience forces of inertia. Consequently, whenever streamlines change direction abruptly, only the lighter particles remain faithful; the heavier ones retain their original velocity vector. In turbulent flow, particles of middling size are flung out of eddies; the heaviest particles, unable to respond to rapid velocity fluctuations, move sluggishly and phlegmatically, in accordance with the average, bulk flow. The result depends on the mass of the particle in relation to the streamline geometry, and is modelled by the dimensionless Stokes number (Hinds, 1982, pp. 113-114). As this number approaches zero, the particles follow the streamlines with ever greater assiduity. Particle deposition occurring via this means, such as at bends or contractions in the flow, is termed 'inertial impaction' or 'inertial impingement'. Inertia is also behind the concept of 'isokinetic sampling' (Hinds, 1999, pp. 206-212). This describes the way a sample of aerosol is drawn off through a probe. The ratio of flow rates and the ratio of cross-sectional areas between the sampling probe and the conduit must be equal; otherwise, the streamlines are locally distorted, and the particle size distribution of the sample is not a faithful reproduction of the population from which the sample is taken. But inertial effects are usually negligible for particles smaller than one micron.

Mass also ensures some influence from the force of gravity - this, after all. is the principle behind winnowing: separation of grain from chaff. The rate at which a particle falls merely by virtue of its own weight is termed the 'gravitational settling velocity'. If this velocity is to become significant, the size must be several microns at least, and few of the particles we shall be studying are this large.

Comment to slide 20:

Contrary to the gravimetric measurements of total diesel particulate emissions, which are a well established routine measurement of good repeatability, size distributions measured at different laboratories show considerable variability. Reported distributions, especially those weighted by particle numbers, frequently disagree by several orders of magnitude. That spread of experimental results is related to the following issues:

different measuring equipment and measurement errors,

the influence of exhaust gas sampling and dilution parameters on the properties and size distributions of diesel particulates.

The measurements of diesel particle size distributions is a relatively new analytical discipline. As increasingly more experience is being accumulated, the analytical methods and instruments are becoming more reliable and accurate. The precision, repeatability, measuring ranges, response to transient conditions, and, generally, the quality of measurement has been improving and will continue to improve.

The exhaust gas sampling issues and their influence on the particles are a more serious consideration. There is a wide agreement that sampling parameters, such as dilution ratio, dilution rate and residence time have a critical impact on the properties and sizes of the particulates [Ahlvik 1998][Andersson 2000][Hall 2001], to the point that different setups of the same measurement system can produce conflicting data. That influence is especially strong in regards to the number concentrations and distributions, as opposed to the mass/volume particle concentrations. Another consideration is that exhaust gas dilution which takes place in the dilution tunnel(s) is not a good simulation of atmospheric dilution. In effect, conditions in the dilution tunnel may easily produce artifacts, or artificial particulates, which are not normally encountered when dilution takes place in the atmosphere.

Exhaust particulates in the tailpipe are very much different from those sampled in dilution tunnels or those present in the ambient atmosphere. At high exhaust temperatures the particles are composed primarily of solids, including elemental carbon and ash. When the gases are discharged to the atmosphere and mixed with ambient air, the particulate phase increases through nucleation, adsorption and condensation, which are driven by decreasing temperatures. Nucleation is a formation of new particles, solid or liquid, from gas phase components. The rate of nucleation rapidly increases when gas components approach their saturation. Although the nucleation is usually not very significant for mass concentrations, it can increase the number concentrations of particulates by an order of magnitude. The nuclei particles may grow due to coagulation, which occurs both in the hot exhaust gas and during the dilution. Other mechanisms of particle size growth include adsorption of gas molecules and condensation of vapors on the surface of particles.

Once finally released into the atmosphere, the particles are by no means stable. The processes that occur include atmospheric evaporation and desorption of the volatile particulate fractions, as well as changes in the particle sizes. It was found in several independent studies that the nanoparticles disappear with aging and their ambient concentrations quickly decrease with time. Particle lifetimes, $\tau 90$ and $\tau 99$, are defined as the times necessary for the reduction of the total number concentrations from their initial plume values by 90% and 99%, respectively. An investigation of the lifetime of diesel aerosol found that for typical urban conditions $\tau 90$ is on the order of a few minutes and $\tau 99$ is on the order of 20-30 min (during these time periods, particulates can travel with the wind over the distance of 100-1000 m, and 0.5-10 km, respectively) [Capaldo 2001]. Important factors which influence gas to particle conversions, including nucleation and adsorption/condensation, as well as coagulation, are:

Dilution ratio, Cooling, Residence time,

Temperature,

Humidity,

Ambient aerosols.

As a consequence, the gas to particle conversion processes are very sensitive to correct simulation of atmospheric dilution. The critical parameters include saturation ratios of volatile components, which influence the nucleation of new particles, and residence times, which influence particle coagulation. Typical atmospheric dilution ratios of vehicle exhaust gases are between 500 and 1000. Since dilution tunnels used for PM sampling operate at dilution ratios of about 10, the simulation is far from being perfect. The dilution tunnel saturation ratios are much higher than those in the atmospheric dilution, while the dilution rates are slower and the residence times are longer. As a result, particulate size distributions measured in a dilution tunnel may be very different from what would be seen in the atmosphere. Furthermore, different number concentrations and distributions may be measured whenever dilution ratios or residence times are changed. Low dilution ratios lead to an increase in the total particulate mass due to increased SOF fraction. That effect has been known for quite a long time /Ahlvik 1998/. The influence of dilution ratio and dilution tunnel residence time on number weighted size distributions can be illustrated by the results of a study with a Perkins diesel engine (Abdul-Khalek 19997. Diesel particulates were sampled from a Perkins T4.40, 4 cylinder, DI, turbocharged and aftercooled engine operated with low sulfur fuel (< 0.05% S). The particulate sampling system included a primary and secondary dilution tunnel of adjustable dilution ratio. The influence of dilution ratio on size distributions was measured by changing the primary dilution rate between 4 and 84 at a fixed secondary dilution rate. For dilution ratios above 60, both the number and volume concentrations were found to be essentially independent from dilution ratio. For smaller dilution ratios, number and volume concentrations increased with decreasing dilution ratio. Particles smaller than about 30 nm were more strongly influenced than the larger ones. For example, the number concentration of 8 nm particles increased 2.8 times when the dilution ratio was decreased from 59 to 4. The increased number concentrations of small particles can be explained by nucleation of hydrocarbons, sulfur compounds and water in the dilution tunnel. Particle nucleation is favored by higher saturation ratios which occur at lower dilution ratios.

Comment to slide 22:

Test conditions that favour the formation and measurement of increased diesel particle number concentrations are: low dilution ratio, long residence time, high RH, and high fuel sulphur content.