

Direct Measurements of Soot/Ash Affinity in the Diesel Particulate Filter by Atomic Force Microscopy and Implications for Ash Accumulation and DPF Degradation

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ABSTRACT

Inorganic engine lubricant additives, which have various specific, necessary functions such as anti-wear, leave the combustion chamber bound to soot particles (approximately $\leq 1\%$ by mass) as ash [13], and accumulate in aftertreatment components. The diesel particulate filter (DPF) is especially susceptible to ash-related issues due to its wall-flow architecture which physically traps most of the soot and ash emissions. Accumulated lubricant-derived ash results in numerous problems including increased filter pressure drop and decreased catalytic functionality. While much progress has been made to understand the macroscopic details and effects of ash accumulation on DPF performance, this study explores the nano- and micron-scale forces which impact particle adhesion and mobility within the particulate filter.

Several recent studies have revealed several important mechanisms influencing the nature of the soot and ash deposits, which if manipulated, could yield means of actively minimizing the ash-related impact on aftertreatment system performance [1, 2, 3, 4, 5, 13]. The aim of this study is to measure and manipulate the attractive forces relevant to the soot/ash/DPF system and to identify their role in ash accumulation and catalyst aging. Interaction force measurements can be made directly in nano- and micron-scale agglomerated particle systems by use of atomic force microscopy (AFM). In this case single particles and small micron-sized particle clusters of both soot and ash are attached to AFM tipless cantilevers, where the particles act as the AFM probe tips. AFM force measurement is then used to measure several specific attractive interaction forces including those at the following interfaces: soot-soot, soot-ash, soot-DPF, ash-ash and ash-DPF. In this case, 'attractive interaction forces' includes the summation of most likely Van der Waals and electrostatic interaction. The aim of introducing this new experimental approach is to first, contribute to the fundamental understanding of the ash agglomeration process within emissions aftertreatment systems, specifically the DPF, and second, to suggest potential design characteristics and strategies for both lubricant formulations and aftertreatment system components to reduce the effects of lubricant-derived ash accumulation.

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INTRODUCTION

Stringent emissions regulations, especially those in the United States and Europe, make aftertreatment components necessary for most automotive applications. Diesel aftertreatment systems in particular, rely on several components, which may include some or all of the following: diesel oxidation catalysts (DOC), diesel particulate filters (DPF), selective catalytic reduction (SCR), or some other form of lean NO_x reduction systems to reduce emissions to the mandated levels.

Inorganic, incombustible lubricant additives, which are utilized in numerous capacities including anti-wear and detergency functions, pass through the engine and into the aftertreatment

components. In many applications, the DPF is of a wall-flow architecture, which effectively traps most of the lubricant-derived inorganic additives as ash. This ash has several negative effects on the diesel particulate filter, which may accumulate significant quantities of lubricant-derived ash over its entire useful lifetime.

After extended operation, usually around 50,000 miles of on-road use, ash accounts for the majority of material within the DPF on average [15]. Ash may significantly increase the filter-specific pressure drop, thus leading to decreased fuel economy. A shift in the balance point temperature (BPT) during filter regeneration of catalyzed filters has also been observed with ash accumulated in the DPF [16]. Research is currently

underway in both industry and academia to understand the relationship between ash (and its negative effects) and operating methods, such as regeneration strategy, lubricant formulation and DPF design [1, 2, 3, 4]. Figure 1 shows DPF pressure drop as a function of ash load with varying trends for specific additive chemistries [5].

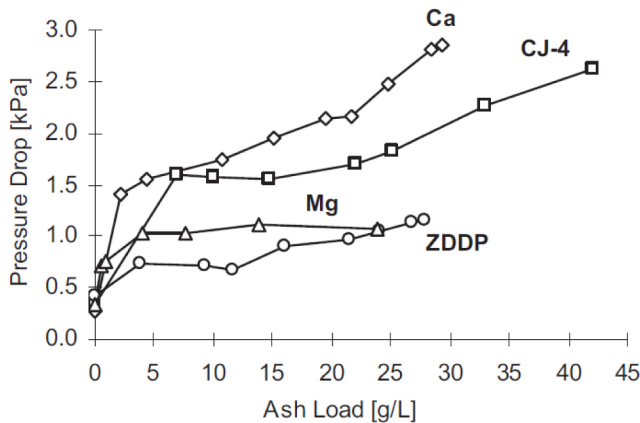


Figure 1. Pressure drop vs. ash load data for single additive lubricants and a fully formulated CJ4 lubricant for a DPF in an accelerated aging system taken from [5].

The specific formation mechanisms controlling ash agglomeration and growth in the DPF are not entirely known, but there are many theories in the literature which may explain certain parts of the overall formation and growth mechanism. In general, it is thought that ash exits the engine bound in some way to individual soot particles and that the ash accounts for approximately 1% of the total particulate matter (PM) [13]. When observed with a scanning electron microscope, that the structure of the ash is quite complex, as it forms agglomerates composed of tens or even thousands of individual particles and undergoes relatively extreme restructuring and crystalline growth within the typical temperature range of DPF operation [4].

Furthermore, the ash agglomeration and growth process in the DPF appears to occur quite rapidly, with 10-50 micron sized ash agglomerates formed following only a single regeneration event, as depicted schematically in Figure 2. In the experiment, approximately 1-2 mg of soot was collected from a Yanmar diesel engine, and subsequently oxidized at 625°C in air for 5 minutes. Although this experiment is extremely basic it illustrates an important mechanism. If the ash precursors entering the DPF are smaller than individual soot particles, the SEM image in the right hand side of Figure 2 shows that following oxidation in air for only 5 minutes, a very large, 30-50µm diameter, agglomerate of ash was formed. This suggests that, assuming the ash precursors are 5nm initially, ash particle growth by approximately four orders of magnitude occurred in a few minutes. In order for this to occur, attractive intra- and inter-particle forces are most likely at work.

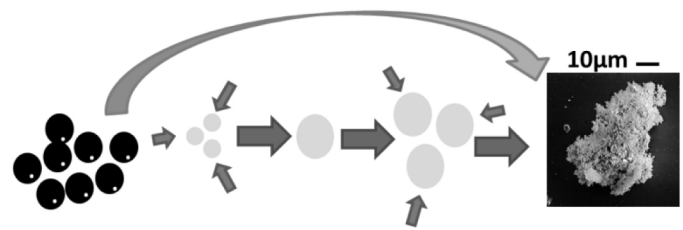


Figure 2. Schematic diagram depicting the growth process of ash particles and agglomerates which most likely occurs in several steps. The image begins with ash precursors smaller than the soot particles on the left. The SEM image on the far right shows a relatively large ash agglomerate which resulted from oxidizing approx. 1-2 mg of diesel soot in air over a 5 minute period.

The goal of this study was to investigate the fundamental attractive forces relevant to the particle accumulation processes in the diesel particulate filter, including forces between the lubricant-derived ash, soot and the DPF surface. Once understood, the fundamental attractive forces should be useful to better describe the ash formation and accumulation mechanisms. Further, understanding of the variables such as regeneration strategy or lubricant additive chemistry, which may influence the magnitude of these forces, may suggest potential means or practical solutions to mitigate the ash problem.

Attractive forces have been measured in this study for the following pairs, ash-DPF, soot-DPF, ash-ash (inter-particle) and soot-soot (inter-particle) with the hypothesis that the forces should vary among these pairs, and that the ash formation/accumulation mechanism is in some way dictated by these microscale attraction forces.

FORCE OF ATTRACTION AND MEASUREMENT

On the scale relevant to the system investigated in this study, that of soot, ash and the DPF surface, non-chemical interaction is generally assumed to consist of three primary, normal force types: electrostatic repulsion, capillary attraction and Van der Waals attraction. In this study, both electrostatic and capillary forces are ignored and it is assumed that Van der Waals forces dominate. However, high relative humidity can lead to significantly higher capillary forces. After approximately 45% relative humidity, the capillary forces may be equal to or greater than Van der Waals [6]. Capillary forces are neglected in this study as all measurements are made in air with fairly low relative humidity. In addition, the direct effects of electrostatic repulsion have not been observed, as the ash and soot agglomerates may be in the size range where Van der Waals simply dominates. The Van der Waals force is a normal force which is essentially a summation of several dipole-dipole interactions, which includes permanent-to-permanent (Keesom), permanent-to-induced (Debye) and induced-to-induced dipoles (London dispersion).

In self-organizing systems on the laboratory scale, the self-organizing mechanism can, in many cases, be understood as a dynamic balance between the above-listed forces in a strong non-equilibrium state. In addition, many such systems are self-limiting in that the growth mechanism will stop at some point, for example when the ratio of repulsive to attractive forces changes with the size of a particle or agglomerate of particles. An example of this is reported in the literature where CdSe supraparticles are created via a self-organizing mechanism and described by a dynamic balance between Van der Waals attraction and electrostatic repulsion, where the self-limiting point can be controlled to produce various sizes of supraparticles for specific purposes [7].

The CdSe study referenced here was performed in a cleanroom on a clean, flat and homogeneous surface where the growth mechanism could be observed and controlled directly. In the case of lubricant-derived ash, the growth mechanism is a very heterogeneous process, in that it is driven by soot oxidation and exhaust flow and occurs on very rough surfaces. Recently, advances in understanding the ash formation and ash/soot agglomeration processes have been made through the use of DPF samples configured to allow for in-situ optical access with a stereo-microscope, which enables a clear view of the processes occurring over a range of filter operating conditions, including regeneration modes [8,9,12].

The techniques employed in this study focused on nano- and micro-scale measurements of the particle and surface forces which control the macro-scale processes observed in the DPF. Scanning probe microscopy enables a number of very useful and exact measurements ranging from surface profiling and morphology imaging, elastic and inelastic deformation, phase mapping, to adhesion force measurements, to name a few. Atomic force microscopy was used in this study to measure the attractive forces inherent to the complex automotive aftertreatment ash-related aging process.

The basic idea behind AFM is to use a cantilever with a tip of known geometry that is controlled by a piezoelectric actuator where a narrow laser beam is reflected off of the gold coated cantilever topside into a photodetector, as described schematically in Figure 3. Several distinct AFM methods exist, however they all share the capability of a very high measurement resolution in the vertical axis, which is generally measured by a combination of the laser deflection and the piezo-actuator voltage in the z direction. Many commercial AFM systems allow for height measurement resolution in the angstrom range and force measurement resolution in the pN range. For example, typical, high-resolution pN AFM force measurements include separating receptors from ligands, unfolding proteins, (which will give a characteristic saw-like force curve for each fold) and breaking single H-H bonds. The force measurements presented in this study are in the nN range and AFM is, therefore, a suitable tool.

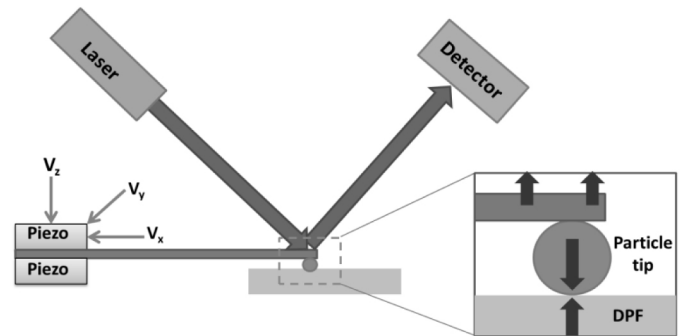


Figure 3. Schematic diagram of Atomic Force Microscopy (AFM) where a particle is used as the cantilever tip.

The AFM force measurement is conceptually fairly simple and needs only two measured parameters before attraction forces can be directly measured. The tip parameters are the *inVols*, or deflection sensitivity which is calculated from a force measurement on a smooth glass surface and expressed as *nm/V*, and *k*, the spring constant which is a measure of the free movement of the cantilever tip in air due to Brownian motion and is expressed as *nN/nm*. In this way, the attractive/repulsive force is measured directly by measuring the deflection voltage in the z direction giving the following relationship,

$$F = k \left[\frac{nN}{nm} \right] * inVols \left[\frac{nm}{V} \right] * V_{z,piezo}$$

Equation 1

The AFM force measurement is made by slowly bringing the cantilever particle tip in contact with the surface of interest until it stabilizes, and then retracting the particle tip from the surface. These steps will be discussed as 'approach' and 'retract' respectively and are described in Figure 4.

For particle-surface systems with sufficient attraction, the cantilever tip will actually make a nm-scale jump to the surface which can give information of the surface energy of the particle-surface system. After the approach, the cantilever reaches a stable height position before it is retracted. The retraction process results in flexing of the cantilever due to the normal attraction force between the tip and the surface, and the amount of flexure in the cantilever results directly in the force of attraction through Equation 1. Therefore, once the spring constant, *k*, and the deflection sensitivity, *inVols*, are known, the force of attraction is directly measured.

In addition to the force measurement, there is useful information in the portion of Figure 4 where the approach line changes slope. This change in slope is due to the tip coming in contact with the sample surface with a given amount of force making the cantilever flex. If this response is linear, as in the case of Figure 4, there is very little-to-no sample or tip deformation. All sample/tip combinations in this study did not show any signs of deformation, however several force measurements of soot agglomerate tips on a glass slide resulted in some deformation.