

Measuring Diesel Ash Emissions and Estimating Lube Oil Consumption Using a High Temperature Oxidation Method

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ABSTRACT

Diesel engine ash emissions are composed of the non-combustible portions of diesel particulate matter derived mainly from lube oil, and over time can degrade diesel particulate filter performance. This paper presents results from a high temperature oxidation method (HTOM) used to estimate ash emissions, and engine oil consumption in real-time. Atomized lubrication oil and diesel engine exhaust were used to evaluate the HTOM performance.

Atomized fresh and used lube oil experiments showed that the HTOM reached stable particle size distributions and concentrations at temperatures above 700°C. The HTOM produced very similar number and volume weighted particle size distributions for both types of lube oils. The particle number size distribution was unimodal, with a geometric mean diameter of about 23 nm. The volume size distribution had a geometric volume mean diameter of about 65 nm.

Inductively coupled mass spectrometry (ICP-MS) was used to determine the ash content of different lube oils, revealing the differences in elemental compositions of

ash for a fresh lube oil and an used lube oil; the most notable changes were a 166% increase in Mg and a 194% increase in Fe concentrations. The mass penetration fraction of lube oil using the HTOM was compared to the oil ash concentrations found from the ICP-MS analysis and the results are discussed.

The HTOM was also used to measure exhaust ash concentrations from a passenger car Diesel engine during steady-state and transient engine conditions. Using known oil ash compositions the HTOM was used to estimate engine oil consumption rates from exhaust ash measurements.

INTRODUCTION

Diesel particulate matter (DPM) is mainly composed of solid carbonaceous species and ash, volatile organic compounds, and sulfur compounds [1]. The ash component of DPM is defined in this paper as the incombustible component of DPM. Metallic ash is derived from engine wear metals, metallic additives used in fuel and lubricating oil, sulfates, and phosphates [2]. Metals are added to engine lubricating oil as detergents,

anti-wear agents, anti-oxidants, corrosion inhibitors, and lubricant improvers [3]. For diesel engines operating under normal conditions, most of the metallic ash is derived from lubrication oil additives [4] and metal engine wear that enter the combustion chamber by means of reverse blow-by of the piston rings [5].

A variety of methods have been used to measure engine ash emissions but most require either a steady-state engine operating condition or are purely qualitative. Inductively coupled plasma mass spectrometry (ICP-MS) [6] and electron microscopy [7] have been used to analyze elemental mass concentrations of selected metals. Both of these methods require DPM to be collected on a media and then processed before attaining results. Single particle mass spectrometry (SPMS) and aerosol time-of-flight mass spectrometry offer real time information on particle elemental composition by examining the emittance of particles after they have been shot with a high energy laser [8, 9]. Under steady-stated conditions an aerosol time-of-flight mass spectrometer could be used in conjunction with the method described in this paper to attain compositional information about the particles in question. SPMS has been used to detect particles as small as 30 nm [8]. Another method used to analyze the ash component in DPM is time resolved laser induced breakdown spectrum (TRELIBS) [7]. TRELIBS analysis requires an exhaust sample to be collected on a filter and is able to give elemental composition without destroying the entire sample [7]. Other methods that have been used are transmission electron microscopy [5] and the real-time high temperature oxidation method (HTOM) [10] used in this study. The HTOM does not determine the chemical composition; rather the aerosol passes through a high temperature tube oven (HTO) before entering a Scanning Mobility Particle Sizer (SMPS) or other, real-time aerosol instruments to determine the aerosol particle size distribution and other physical characteristics such as mass, diameter, or number concentrations. This method has shown promise for estimating ash emissions in real-time [10].

Lubrication oil consumption occurs in the power cylinder, valve system, and crankcase ventilation system. In the power cylinder, oil is scraped by piston rings into the combustion chamber, where it is evaporated and removed with exhaust gas [11]. Another source of oil consumption is leakage of oil from valve stems into the cylinder [12]. Oil may also be delivered to the power cylinder by the crankcase ventilation system [13].

The typical four-cylinder, turbocharged diesel passenger car consumes lube oil at a rate of 8-16 g/hr[14]. The power cylinders and valve system are responsible for the majority of oil consumption [12], and about 5-10% of the oil is consumed via crankcase ventilation system [13]. Oil consumption increases with engine size [13], engine speed, and load [15]. Oil consumption may be greatest during transient conditions such as rapid changes in load [16].

Several methods are used to measure oil consumption. The simplest method is to weigh the oil in the sump before and after operating the engine [17]. However, this method does not always produce repeatable results [18]. Lubrication oil consumption is more accurately measured by performing a mass balance for a specific element, referred to as a tracer, that is found in both the oil and exhaust. Radioactive tritium was used as a tracer in several oil consumption studies, but it requires special handling and disposal [15]. Sulfur is commonly used as a tracer for lube oil consumption where a high sulfur lube oil is used with a low or zero sulfur fuel [19, 20].

Metallic additives in lubrication oil are also used as tracers because they form ash in the exhaust. Calcium, zinc, phosphate, magnesium, and manganese appear in exhaust ash in proportions similar to the composition of lubrication oil [21]. Ash analysis is most effective if the metal being studied is present in oil but not in the fuel [22]. Calcium and zinc, which make up the majority of oil ash, are good indicators because they are found in very small quantities in diesel fuel [14, 22].

TEST APPARATUS AND METHODS

Ash was isolated from engine exhaust or atomized solutions of fuel and lubrication oil using the apparatus shown in Figure 1. This system is a modification of the HTOM developed by Kim [10]. To prevent condensation, the aerosol was diluted with cleaned, compressed air using an ejector pump. The primary dilution ratio was about 20:1, and was verified by measuring the concentration of NO in engine exhaust before and after dilution. A 90-cm quartz tube, of either 1.67 or 1.03 cm internal diameter, was used to carry aerosol through the tube furnace (Lindberg/Blue M Model HTF55122A with control module Model CC58114A-1). The quartz tube was centered inside the tube furnace, with 46 cm of length inside the furnace and 22 cm exposed to ambient air on either end of the furnace. Temperatures inside the furnace ranged from 50% below the programmed temperature at the ends of the furnace to 5% above the programmed temperature at the center. The temperature inside the furnace met or exceeded the programmed temperature in a 22 cm length in the center of the 46 cm heated length. The flow rate through the quartz tube was maintained at approximately 1-2 L/min., resulting in residence times of 1 to 6 s in the oven (0.5 to 2.9 s at or above the programmed temperature). The oven flow rate was controlled by means of an ejector pump and a critical orifice downstream of the oven. The ejector pump (Air Vac TD110) was also used to dilute the post oven sample with dried and filtered compressed air. The oven was operated at room temperature and at temperatures ranging from 300 to 1200°C. Exhaust at the oven outlet passed through a stainless-steel cooling tube that was exposed to ambient air. Due to thermophoretic deposition, the expected ash penetration ratio through the cooling tube is predicted by Equation 1 [10].

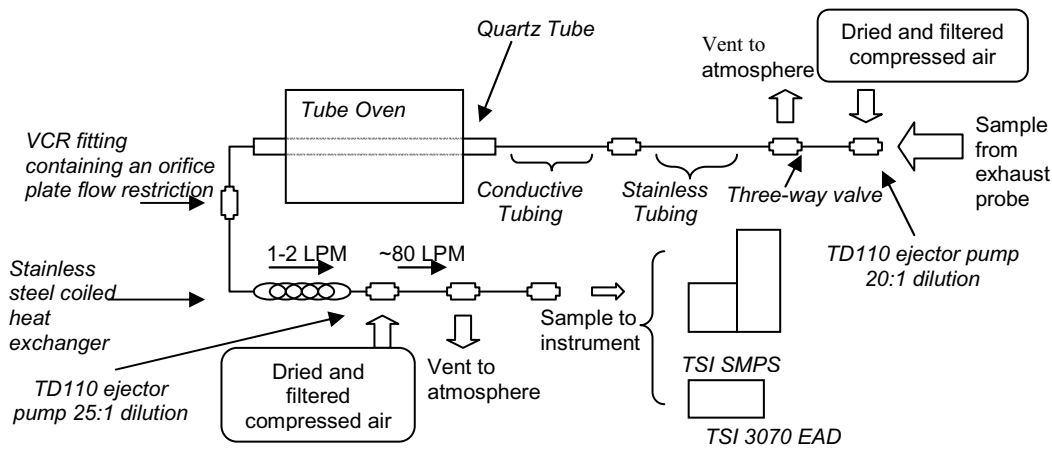


Figure 1. High-temperature oxidation system used in exhaust ash sampling

$$\text{Penetration ratio} = (T_1/T_2)^{0.38} \quad (1)$$

where

T_1 = Ambient temperature outside oven, K

T_2 = Peak temperature inside oven, K

Ash particles that remained after the high-temperature oxidation process were diluted 25:1 and then quantified by a SMPS and an electrical aerosol detector (EAD: TSI Model 3070A). The SMPS consists of a differential mobility analyzer (DMA: TSI Model 3080) and condensation particle counter (CPC: TSI Model 3025). The DMA classifies particles from 8 to 300 nm using electrical mobility and classified particles are counted by the CPC. A 90-s scan time (60-s up and 30-s down) was used. The SMPS was used as the primary measurement device for all steady-state experiments. The exhaust ash concentration and exhaust flow rate were used to determine the ash generation rate.

Transient aerosol measurements were made with the EAD, which uses a diffusion charging system to determine particle diameter concentration in real-time (up to 3.75 Hz) without bias to chemical composition. Aerosol length is defined as number concentration multiplied by the average diameter, or as d^1 weighting. This measurement falls between the number concentration (d^0) and the surface area concentration (d^2). The EAD measures particles in the range of 10 nm to greater than 1 μm . The EAD was used to verify SMPS results and to monitor exhaust ash during transient tests.

The particle size distribution of atomized lubrication oil ash was determined for different lube oils. Oil was diluted 100:1 in butanol and atomized with cleaned compressed air delivered at 415 kPa. The atomized mixture was first exposed to a vent at atmospheric pressure before passing through a charcoal scrubber and heated catalytic stripper (CS) [23, 24]. The CS removed remaining combustible butanol vapor that was not completely removed by the charcoal scrubber. Ash particles in the atomized spray were then isolated by a high temperature tube furnace and then quantified by the SMPS and EAD. Treating atomized fuel and lube oil with the HTO system simulates the particle elemental composition seen when actual engine exhaust is treated using the HTOM.

Table 1 displays a matrix of all the experiments that are reviewed in this report. Two fresh lube oils and two used oils were tested as atomized lube oils treated with the HTOM. The lube oils were diluted at a ratio of 100:1 prior to being sprayed. Baseline tests were conducted by atomizing only butanol. Engine exhaust experiments were all run on a 1.8L Volkswagen TDI engine on a dynamometer. The engine was operated with different fuels and lube oil doped fuel combinations as displayed in Table 1.

Engine specifications are shown in Table 2. Diesel fuel (BP50) containing 50 ppm sulfur was used for all oil consumption tests. Castrol 5W-40 oil was used in the engine and in oil consumption simulations. Soy methyl ester biodiesel (B100) was used in separate tests to compare oxidation characteristics of petroleum-based