

The Influence of Engine Lubricating Oil on Diesel Nanoparticle Emissions and Kinetics of Oxidation

Heejung Jung, David B. Kittelson and Michael R. Zachariah
University of Minnesota

Copyright © 2003 SAE International

ABSTRACT

Earlier work [1] shows that kinetics of Diesel soot oxidation is different from that of ethylene diffusion flame soot oxidation [2], possibly due to metals from lube oil. This study investigates the influence of metals on soot oxidation and the exhaust particle emissions using lube oil dosed fuel (2 % by volume). This method does not simulate normal lube oil consumption, but is used as a means of adding metals to particles for oxidation studies. This study also provides insight into the effect of systems that mix lube oil with fuel to minimize oil change service.

The HTO-TDMA (High Temperature Oxidation-Tandem Differential Mobility Analyzer) technique [1] was used to measure the surface specific oxidation rate of Diesel particles over the temperature range 500-750 °C. Diesel particles sampled from the exhaust stream of a Diesel engine were size segregated by differential mobility and oxidized in situ in air in a heated flow tube of known residence time and temperature profile. The change in particle diameter after oxidation took place was measured and converted into the surface specific oxidation rate. The pre-exponential factors increased by about a factor of two, whereas the activation energy determined for the lubrication oil dosed Diesel particles was very close to that of undosed Diesel particles (108 kJ mol⁻¹, [1]). This suggests that the increase of active sites by the presence of Ca (and possibly by other metals included in the additive package of the lube oil) results in the faster oxidation rate.

Particle size measurements show that particle volume emissions, which are roughly proportional to particle mass, decreased by about a factor of two, but that particle number emissions increased by an order of magnitude with lube oil dosed fuel.

INTRODUCTION

The regulations for Diesel particulate emissions are becoming more stringent with a strong emphasis being placed on possible adverse health effects. A lot of work has been done to reduce Diesel emissions by improving aftertreatment devices, such as DPFs (Diesel Particulate Filters) [3, 4], and by enhancing the oxidation of Diesel particulate matters using fuel additives [5, 6]. Although the oxidation rates of Diesel particles have been measured numerous times in the past [7, 8], the influence of engine lube oil metals on the kinetics of Diesel particle oxidation has previously been overlooked. Understanding the role of lube oil in Diesel particle oxidation may be very important in developing new lube oil formulations, as well as new fuel borne catalysts.

It is often assumed that the oxidation kinetics of carbon particles in Diesel exhaust are similar to the kinetics of carbon oxidation in diffusion flame studies [9, 10]. However, a recent study by Higgins et al. [1] showed that the kinetics of oxidation of carbon particles in Diesel exhaust were quite different from that of carbon particles from an ethylene diffusion flame, and from the Nagle and Strickland-Constable kinetic model [11]. Higgins et al [1] suggested this might be due to the presence of metal compounds in Diesel exhaust particles. Engine lube oil is continuously consumed in the combustion chamber. Although oil consumption typically is only about 0.2 % of fuel consumption, it contributes disproportionately to the exhaust particulate matter. The combustion efficiency of lube oil is considerably lower than that of Diesel fuel and lube oil contains metals that form solid particles. Engine lube oil is composed of a base oil and an additive package. In general, the base oil is composed of petroleum-derived mineral oils, whereas the additive package is composed of various chemicals, including metal compounds (such as Ca, Mg, and Zn) [12]. Most of these contribute to lube oil ash. The typical ash content of lube oil is about 1 % [13, 14]. A material balance based on 1 % lube oil ash content, 0.2 % relative lube oil consumption rate, 250 g/kWh fuel

consumption rate and 0.13 g/kWh PM (Particulate Matter) (US PM standard for 2004) gives 0.005 g/kWh ash emissions. Under these conditions, the ash would constitute 4 % of the current PM, assuming that all of the ash appeared in the PM standard. Published results show up to 10 % ash by mass [15]. For 2007, the PM standard drops to 0.013 g/kwh. If lube oil ash consumption is assumed at the same level as in the material balance above, it could constitute 40 % of the PM emissions. This suggests growing importance of the lube oil to PM emissions.

It is still not entirely clear which mechanism is the main contributor in oil consumption due to the complexity of the phenomenon. However, recent research shows a clearer picture of oil consumption. Lube oil may leave the cylinder wall by either vaporization or atomization. De Petris et al. [16] showed that oil mist (or oil atomized by a reverse blowby) was a main contributor to oil consumption under their test conditions. Audette III and Wong [17] found that oil vaporization from a cylinder liner is a small contributor to consumption unless more volatile lube oil is used. Lube oil can also get into the combustion chamber by other pathways. It can come through a valve stem seal, a throw-off of accumulated oil above the top ring, etc. Flynn et al. [18] recently described the Diesel combustion process in terms of burning fuel jets that rapidly entrains surrounding combustion chamber air. Some of the lube oil entering the combustion chamber also will be entrained by the burning fuel jets. In this manner, species from the lube oil may have an influence on the kinetics of DPM (Diesel Particulate Matter) formation and oxidation.

Lube oil mixed with Diesel fuel is combusted directly along with the fuel, and is processed somewhat differently by the flame than lube oil consumed by the usual path. Thus, lube oil mixed with fuel is likely to be more involved in the early stages of combustion where soot is being rapidly formed and oxidized. The primary focus of this study is to investigate the role of lube oil on the kinetics of DPM in the exhaust, not in the combustion chamber. We have used fuel dosing as a relatively easy way to add additional lube oil metals to the exhaust PM. It is assumed that metal compounds added in this manner will have a similar influence on oxidation kinetics of the PM in the exhaust and in aftertreatment systems to metals originating from normal oil consumption.

In some cases, lube oil is intentionally mixed with fuel to extend lube oil change intervals. An on-board continuous oil management system called CENTINEL™ was recently developed by Cummins [19, 20]. The system takes a small amount of used oil out of the lubrication system and sends it to the fuel tank, where it is blended with Diesel fuel. At the same time, fresh oil is sent from a makeup tank to the engine, replacing the used oil. This system has been shown not to increase

PM mass emissions. However, its influences on unregulated emissions, e.g. metals and aftertreatment systems should be examined. Although our approach of dosing fuel with lube oil is very similar to the CENTINEL™ system, the primary purpose of this work is not to emulate CENTINEL™ system, but rather to estimate the influence of metal species in the lube oil on the kinetics of DPM in the exhaust. However, as a part of this study we have also looked at the influence of lube oil dosing on the exhaust particle size distribution.

In this study the Diesel fuel was dosed with engine lube oil (2 % by volume). This has done to intentionally increase the oil consumption rate and the loading of metal components from lube oil on the DPM with combustion, in order to better observe the effect of lube oil (specifically metal components from lube oil) on the oxidation of Diesel particles downstream of the engine and on the exhaust size distribution. The oxidation rate of 2 % lube oil dosed Diesel particles was compared to that of undosed Diesel particles measured in the previous study [1]. The size distribution was also compared with that for undosed Diesel particles.

EXPERIMENTAL

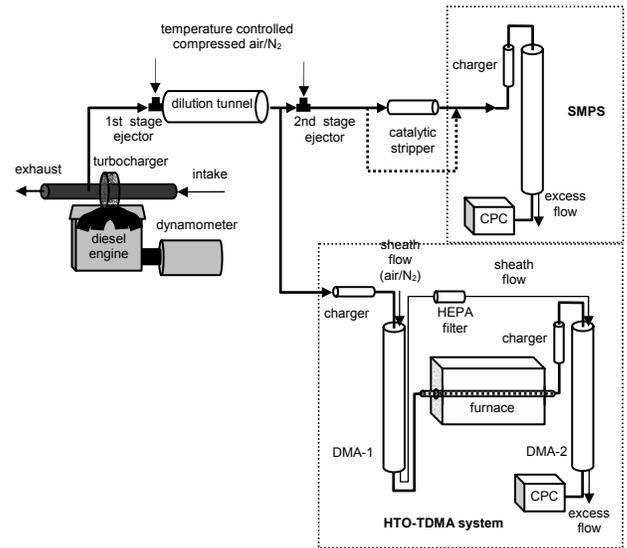
TEST FUEL AND LUBRICANT

Standard EPA No. 2 on-road Diesel fuel (300-500 ppm sulfur) was used as a base fuel. Two barrels of fuel from the same batch were used to provide consistency in the amount of sulfur content and in chemical composition. One barrel of fuel was used to measure the base size distribution when lube oil was not blended in the fuel. The other barrel was dosed with engine lube oil. Table 1 shows recent fuel analysis for fuel from the same supplier, but not the same batch as used in this study.

The lube oil used in this study was SAE15W-40 (John Deere TY6391). The elemental composition of the same type of lube oil used in this study is shown in Table 2. Calcium is typically the most abundant metal species present in lube oil. Calcium is normally in the form of a sulphonate (e.g. calcium sulphonate) and is used as a detergent to keep engines clean [12]. The lube oil used in this study contains about 2500 ppm Ca. The dosing level of 2 % by volume in the fuel results in about 50 ppm Ca content in the mixed fuel. Although the zinc content of the oil adds another 14 ppm metal to the mixed fuel, Zn has not been studied as a fuel borne oxidation catalyst. Metal contents of 20-100 ppm have typically been used to examine the effect of fuel additives [3, 5, 21, 22]. Also, a dosing level of 2 % lube oil was used to measure the effect of lube oil on Diesel particulate emissions by Kytö et al. [23].

Table 1: Fuel analysis of No.2 on-road Diesel fuel

Property	ASTM	Results
Distillation	D86	498.0 °F 50% Rec. 617.7 °F 90% Rec.
Flash point	D93	71 °C
Heat of combustion	D240	18111 BTU/lb
Kinematic viscosity	D445	2.740 cSt @40 °C
Ash	D482	0.000 mass %
Cetane number	D613	44.9
Spedific gravity	D1298	0.8479 g/ml @ 15 °C
Aromatics by FIA	D1319	27.6 vol. %
Sulfur	D2622	0.0305 mass %
Water and sediment	D2709	0. vol. %
Carbon, hydrogen and nitrogen	D5291	86.2 mass % C 13.00 mass % H
Cloud point	D5773	-29 °C
Pour point	D5949	< -60 °C

**Fig. 1: Schematic diagram of the experimental setup. The bold line indicates the path taken by the Diesel soot particles.****Table 2: Lube oil analysis of SAE 15W-40 (John Deere TY6391)**

Element	Weight (%)
S	0.260
Ca	0.250
N	0.160
Zn	0.068
P	0.061
B	0.018
Mo	0.011
Mg	0.001

ENGINE

The engine used in this study was a medium-duty, direct injection, 4 cylinder, 4 cycle, mid-90's turbocharged Diesel engine (John Deere T04045TF250) of 4.5 l displacement, with a peak power output of 93 kW at 2400 RPM and a peak torque output of 400 N·m at 1400 RPM. The engine was coupled to a dynamometer and operated at 1400 RPM under 75 % load (300 N·m). The exhaust temperature measured at the exhaust manifold downstream of the turbocharger was 530 °C, and the air-fuel ratio was measured as 27 for regular fuel at 1400 RPM under 75 % load (300 N·m).

SAMPLING AND DILUTION

Fig. 1 shows a schematic diagram for the engine bench, sampling system, SMPS (Scanning Mobility Particle Sizer) [24] system and HTO-TDMA system. The exhaust was sampled 25 cm downstream of the turbocharger exit and diluted in a two-stage air ejector variable residence time dilution tunnel, similar to one described by Abdul-Khalek and Kittelson [25].

For the oxidation study, particles were extracted after the first stage of dilution, which was operated with a fixed residence time of 0.8 seconds at a dilution ratio of 26-28:1 for 75 % load at 1400 RPM.

The dilution ratio was determined by comparing the NO_x concentration in the exhaust gas and diluted exhaust gas after the first stage of dilution after subtracting the background NO_x concentration. The first stage dilution air temperature was maintained at a temperature of 32°C at the exit by employing feedback control of a band heater wound around the copper tube for the compressed air to the ejector.

For the size distribution studies, samples were taken after the second stage of dilution to prevent saturation of the SMPS system used for particle sizing. Flow measurements were used to determine the second stage dilution ratio to be 31:1. Thus, the overall dilution ratio after the second stage was thus 810-870:1, calculated by multiplying the dilution ratios from each stage.

SCANNING MOBILITY PARTICLE SIZER (SMPS)

The SMPS measures mobility equivalent particle diameter in the diameter range of 7 to 300 nm during a 4-minute (2 minutes up, 2 minutes down) scan time. This particle measurement system consists of a neutralizer, a mobility section (long column DMA similar to TSI model 3934) with a sampling flow rate of 1 lpm and a sheath flow rate of 10 lpm, a CPC (TSI model 3010) and a computerized control and data acquisition system. This system has been described in more detail by others [25, 26].

HIGH TEMPERATURE OXIDATION-TANDEM DIFFERENTIAL MOBILITY ANALYZER (HTO-TDMA)

The HTO-TDMA method was described in detail in a previous study done by Higgins et al. [1]. Briefly, in the HTO-TDMA method, the sample is sent through a bipolar diffusion charger to establish a known charge distribution. Next, a specific particle size is selected with DMA-1. The DMA (Differential Mobility Analyzer) selects mono-area particles based on electrical mobility, which is related to the drag and charge on a particle, rather than on absolute particle size. The mono-area particles then undergo oxidation in the air while traveling through a quartz flow tube enclosed in a tube furnace of known residence time and temperature profile. The particles are recharged in a bipolar diffusion charger, and the size change resulting from the high temperature processing (which includes oxidation, thermal restructuring and evaporation processes) is measured using DMA-2. Three initial particle sizes of 41, 94 and 130 nm mobility diameters were selected at DMA-1 to match the previous study done by Higgins et al. [1] on Diesel particle oxidation. Furnace temperature settings ranged from room temperature (25-34 °C, depending on the day) to 800 °C.

In order to check for particle size decreases due to thermal effects (evaporation and restructuring), additional experiments were conducted with the air for the first dilution stage and DMA sheath flows replaced with nitrogen (Airgas, industrial grade) in the previous work by Higgins et al [1].

RESULTS AND DISCUSSION

The sampled aerosol stream from the first stage of the dilution tunnel was either introduced to the HTO-TDMA system for the oxidation study, and/or the sampled aerosol stream from the second stage of the dilution tunnel sent to a SMPS system for size distribution measurements as illustrated in Fig. 1.

THE INFLUENCE OF LUBE OIL ON SIZE DISTRIBUTION

Fig. 2 and Table 3 show the effect of lube oil on the number and volume size distributions with a dosing rate of 2 % under a fixed engine condition, 75 % engine load (300 N·m) at 1400 RPM. The data have been fit to a bimodal lognormal distribution. Most of the number is found in the nuclei mode ($D_p < \sim 30\text{nm}$), most of the volume in the accumulation mode ($D_p > \sim 30\text{nm}$). The volume concentration of accumulation mode particles was reduced by nearly a factor of two while the total number increased by about a factor of 10, mainly as a result of the formation of a large nuclei mode. The same trend was observed by Kytö et al. [23] when they blended 2 % of lube oil with Diesel fuel. They discovered that the dosage of lube oil that gave the lowest particulate mass (meaning the reduction of accumulation mode particles), produced the highest

Table 3: Number concentrations and volume concentrations of the nuclei mode and the accumulation mode particles for regular fuel and 2 % lube oil dosed fuel. Base and 2 % indicate regular base fuel and 2 % lube oil dosed fuel, respectively. The units of number and volume concentration are $\#/cm^3$ and $\mu\text{m}^3/cm^3$, respectively.

		Total	Nuclei	Accumulation
Base	Number	$3.08 \cdot 10^7$	$6.13 \cdot 10^6$	$2.47 \cdot 10^7$
	Volume	$2.70 \cdot 10^4$	$4.16 \cdot 10^2$	$2.66 \cdot 10^4$
2 %	Number	$3.57 \cdot 10^8$	$3.48 \cdot 10^8$	$8.93 \cdot 10^6$
	Volume	$1.48 \cdot 10^4$	$4.56 \cdot 10^2$	$1.43 \cdot 10^4$

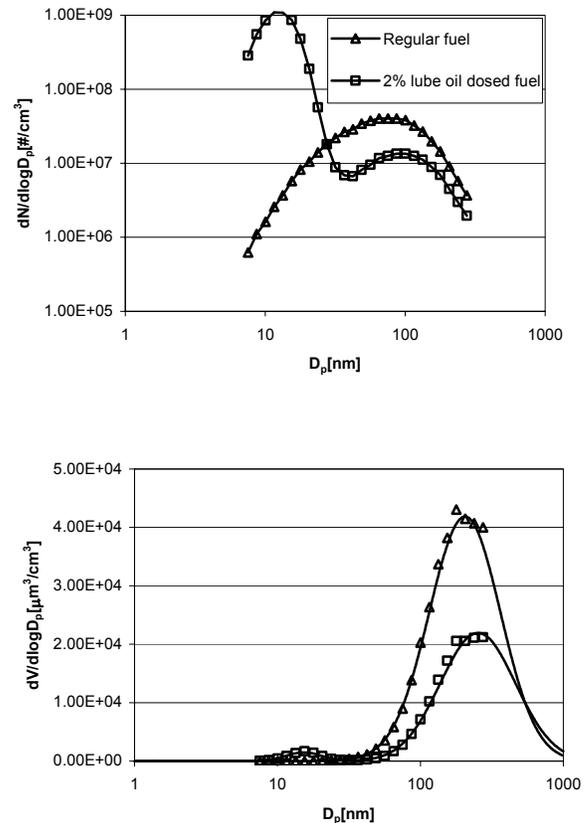


Fig. 2: Size distributions at 1400 RPM, 75 % (300 N·m). (a) (Top) Number weighted size distributions of 2 % lube oil dosed Diesel particles in comparison with base fuel. (b) (Bottom) Volume weighted size distributions of 2 % lube oil dosed Diesel particles in comparison with base fuel.

number of particles (which means the appearance of large nuclei mode).

Calcium is the most abundant species present in the lube oil used in these tests, and is known to suppress the formation of carbonaceous Diesel particles [27] and to enhance their oxidation [27, 28] when it is blended with fuel. Miyamoto et al. [27] concluded that Ca and Ba are the most effective additives for enhancing oxidation and suppressing the formation of soot among the

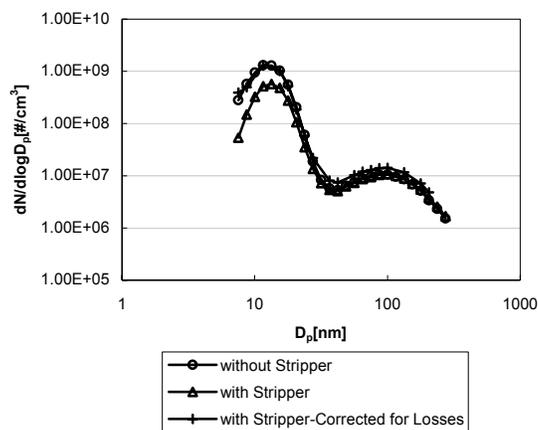


Fig. 3: Size distributions of 2 % lube oil dosed Diesel particles with and without the catalytic stripper at 1400 RPM, 75% load [29].

metallic additives (Ca, Ba, Mg, Fe, Ni, Mn, Cu) they investigated. Other studies [5, 21, 30-32] have shown that metal additives may simultaneously reduce the accumulation mode and increase the nucleation mode. This study shows that metals in lube oil blended with fuel may play a similar role.

When a large nuclei mode is present for Diesel engines operating with typical fuels without additives, the nuclei mode consists primarily of volatile particles [33-38]. However, when metals are present in the fuel, a large solid nuclei mode may form [5, 21, 30-32]. Stenitzer [29] examined Diesel particles with 2 % lube oil dosed fuel from the same engine used in this study using a catalytic stripper operating at 300 °C. The catalytic stripper was designed to remove volatile materials from Diesel particles [34]. If the nuclei mode particles are mainly composed of volatile materials, they will almost disappear completely when passing through the stripper. Fig. 3 compares size distributions for 2 % lube oil dosed fuel with and without the stripper operating at 300 °C [29]. After correcting for transport losses (thermophoretic loss and diffusion loss) in the catalytic stripper, there is no significant reduction in nuclei mode particles. This demonstrates that the nuclei mode particles with lube oil dosed fuel under our test condition are solid.

The formation of a nuclei mode from metal compounds derived from lube oil is not unexpected. Abdul-Khalek et al. [33] performed a chemical equilibrium calculation for both calcium and zinc during Diesel engine combustion to determine the possible fate of metals in lube oil. They found that NASA Program “Flame” [39] predicts that the lube oil metals in the fuel are initially transformed into gas phase compounds at high temperature (~2500K). As the combustion products cool during the expansion stroke to ~1500 K, metal compounds transform into solid

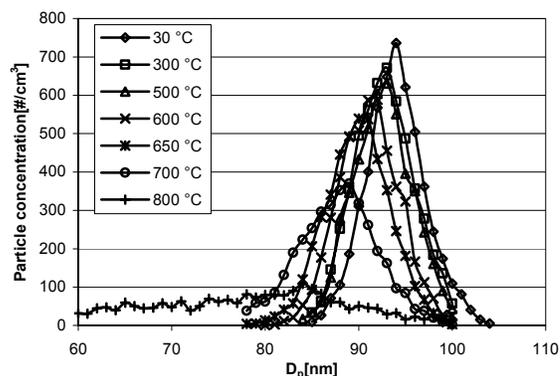


Fig. 4: TDMA Diesel particle oxidation results in air for furnace set temperature of 30-800 °C.: 94 nm initial size with 2 % lube oil dosed fuel.

compounds. When high concentrations of metals are present, some of the compounds nucleate to form a solid nuclei mode. This is consistent with Stenitzer’s [29] observation using the catalytic stripper.

RESULTS FOR HTO-TDMA EXPERIMENT

Fig. 4 shows representative HTO-TDMA data for particles with a selected mobility diameter of 94 nm, generated using 2 % lube oil dosed fuel under 75 % engine load (300N·m) at 1400 RPM. Results for other particle sizes selected at the same engine operating condition are similar to those in Fig. 4. Fig. 4 shows that particles shrink as the furnace set temperature increases, with a mobility diameter decrease of 1 nm at 500 °C and 5 nm at 700 °C. The initial shrinkage in size below 500 °C is likely due to the evaporation of semi-volatile materials condensed onto the Diesel particles. In our previous study [1] the total particle size decrease due to non-oxidative effects at 500 °C, was measured using nitrogen as the carrier gas for both the DMA sheath flow and the reactor flow. It amounted to ~1 nm for 75 % load particles using regular Diesel fuel. This is consistent with the amount of shrinkage we observed at 500 °C. Above 500 °C, most of the change in diameter results from particle oxidation. In addition to a decrease in particle size with increasing oven temperature, we also observe a spreading of the particle size distribution believed to be due to the wide distribution in particle residence time in the laminar flow reactors, as well as loss of particles due to thermophoresis.

DETERMINATION OF THE OXIDATION RATE

We used the measured decrease in particle size to obtain kinetic parameters following the procedure detailed in our previous studies [1, 2]. The size decrease rate is modeled using a modified Arrhenius expression,

$$\dot{D}_p = -A_{nm} \cdot T^{1/2} \cdot \exp\left[-\frac{E_a}{RT}\right] \quad (1)$$

where A_{nm} is an initial-size-dependent pre-exponential factor and E_a is a size-independent activation energy. Values of the A_{nm} 's and E_a are determined by integrating

$$\Delta D_p = \int_0^X \frac{\dot{D}_p(x)}{u(x)} dx, \quad (2)$$

where x is the horizontal position in the tube, X is the length of the tube and u is the flow velocity over the heated length of the flow tube. Minimizing the differences between calculated and measured ΔD_p 's is done using a non-linear least squares method. The dependence of the size decrease rate and flow velocity on horizontal position is a result of their dependence on temperature, as shown in Eq. (1) and

$$u(x) = \frac{4}{3} u_m \frac{T(x)}{T_o}, \quad (3)$$

where u_m is the mean flow velocity calculated from the volume flow rate and the cross-sectional area of the flow tube, and $4/3 u_m$ is the peak volumetric flow velocity assuming laminar flow. Decreases in size due to oxidation are determined relative to the size of the particles at 500 °C.

COMPARISON WITH PRIOR STUDIES

Fig. 5 shows the experimental size reduction data of the current study with 2 % lube oil dosed fuel (Fig. 5a) compared to our previous work [30] with 25 ppm cerium dosed fuel (Fig. 5b). The size reductions are very similar.

Light-off temperature of an oxidizing particle is defined in our previous study [30]. It is analogous to ignition temperatures in the DPF studies. The light-off temperature is defined as the peak flow tube temperature where the particle shrinks ~1 nm in size from that of a particle where the entire evaporation process has occurred. The light-off temperature of 640~690 °C with 2 % lube oil dosed fuel (Fig 5a) was lower than 840 °C with undosed Diesel particles [1], but higher than 590 °C with cerium dosed fuel, as shown in Fig. 5b. This is qualitatively consistent with observations (Miyamoto et al., [27]) on ignition temperatures of their bulk samples. They found the ignition temperature was lowered as they increased the amount of calcium in the fuel.

The data plotted in Fig. 5a was fitted to the Arrhenius expression of equation (1) to determine a different set of parameters for each of sizes studied. Table 4 shows the fitted parameters. Fig. 6 shows the Arrhenius plot of the surface specific oxidation rates for our measurements compared to other studies. The activation energy of surface specific oxidation rates for our measurements compared to other studies. The activation energy of

Table 4: Arrhenius fit parameters for oxidation rate of particles with 2 % lube oil dosed.

2% lube oil dosed	
E_a [kJ mol ⁻¹]	101
A_{41} [10 ⁵ nm K ^{-1/2} s ⁻¹]	1.0
A_{94} [10 ⁵ nm K ^{-1/2} s ⁻¹]	1.2
A_{130} [10 ⁵ nm K ^{-1/2} s ⁻¹]	1.1

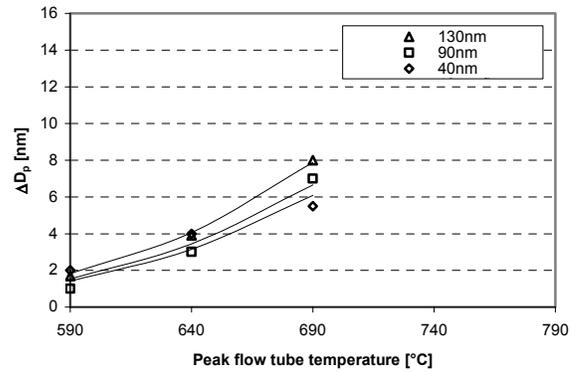
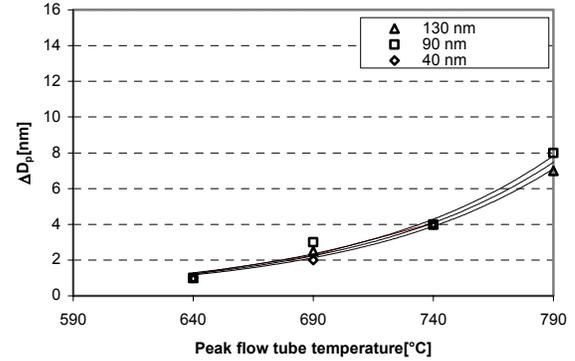


Fig. 5: Particle size change as a function of peak flow tube temperature for the three initial particle sizes. Note: The peak flow tube temperature is approximately 40 °C higher than the furnace set temperature. (a) (Top) 2 % lube oil dosed fuel. (b) (Bottom) 25 ppm cerium dosed fuel [30].

Diesel particle oxidation for 2 % lube oil dosed fuel ('a' in Fig. 6) is 101 kJ mol⁻¹, which is very close to 108 kJ mol⁻¹, the activation energy for particles using (undosed) regular fuel ('b' in Fig. 6) at the same engine operating condition. The frequency factors A_{nm} 's of the Arrhenius equation for the particles with 2 % lube oil-dosed fuel are about two times larger than that of the particles with undosed fuel. It is noteworthy that our previous studies show that the oxidation rate of diffusion flame soot using ethylene ('d' in Fig. 6, [2]) agrees well with the oxidation rate of pyrographite rod ('e' in Fig. 6) by NSC [11], whereas the oxidation rate of the undosed Diesel particle ('b' in Fig. 6, [1]) is not like the NSC (1962) model. Many modelers have used and believed that the NSC [11] model simulates the oxidation of Diesel particles. Our previous study [1] showed the oxidation of Diesel soot is different from the NSC model.

Miyamoto et al. [28] reported oxidation rates of Diesel particles for undosed ('h' in Fig. 6) and calcium dosed fuel ('f' and 'g' in Fig. 6). They found that the beginning of the particle oxidation is rapid ('g' in Fig. 6), whereas the remaining particle oxidation is relatively slow ('f' in Fig. 6) when Ca is blended in the fuel. They found the same trend when other kinds of metal additives (Ba, Ni, Fe) were used. This rapid early stage is similar to that referred to as auto-acceleration by Lahaye et al. [6] and catalytic oxidation of VOF (Volatile Organic Fraction) by Stratakis and Stamatelos [40]. While our current experiments are unable to resolve transients such as described above, we do note that, in general, addition of metals does not seem to change the activation energy, but does increase the oxidation rate significantly. In our experimental setup, suspended particles are oxidized directly, with little heat or mass transfer limitation. Essentially all volatile material is expected to have desorbed before any significant oxidation takes place. Thus, volatiles do not play a role. The auto acceleration observed in the TGA experiments may be due to limitations of heat and mass transfer in bulk soot samples. Catalytic oxidation of VOF is likely associated

with mass transfer processes within the TGA sample. The relative change between this study and our previous study [1], due to dosing with Ca (see curve 'a' and 'b' in Fig. 6), is similar to the relative change observed by Miyamoto et al. [28] (see curve 'f' and 'h' in Fig. 6). In both cases, the frequency factor increases, whereas the activation energy is nearly unchanged compared to the undosed case.

DISCUSSION

Our results clearly show that lube oil constituents increase the rate of oxidation of exhaust soot particles. This should help to improve our understanding of soot oxidation in the engine itself, as well as in aftertreatment systems. Clearly, there is a trade-off between the gains associated with lube oil metal catalyzed oxidation of exhaust particles and emissions of metal compounds. Without aftertreatment, these materials are emitted into the atmosphere and might constitute an environmental hazard. Most aftertreatment systems (filters) are very effective at removing solid particles and would trap metal

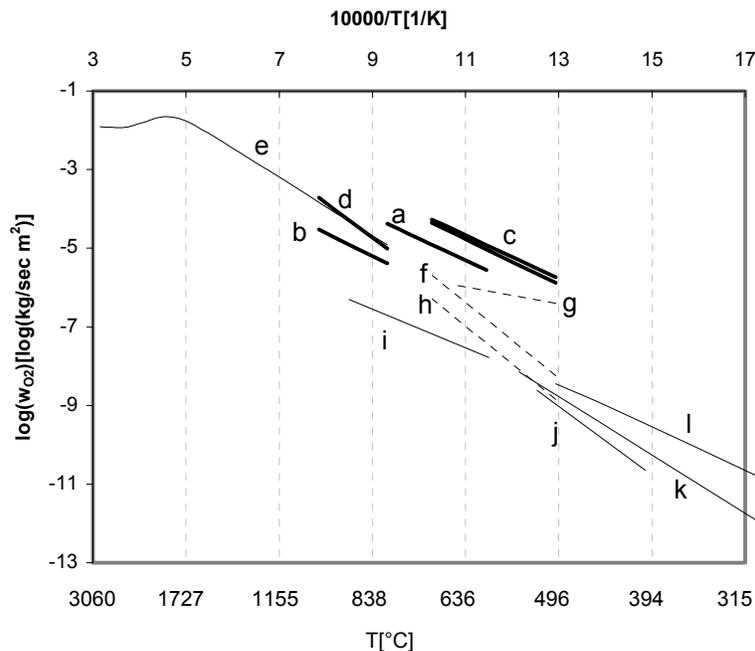


Fig. 6: Arrhenius plot of the surface specific rates of Diesel particle oxidation for the current study and for other relevant prior studies. Previous studies include oxidation rates of various soots (Diffusion flame soot and Carbon black) and pyrographite rod. Rates are presented for 21 % O₂. (a) Current study using 2 % lube oil dosed fuel. (b) Higgins et al. [1] using regular Diesel fuel. (c) Jung et al. [30] using 25 ppm and 100 ppm cerium dosed fuel. (d) Higgins et al. [2] using diffusion flame generated soot. (e) Nagle and Strickland-Constable [11] using a pyrographite rod. (f) Miyamoto et al. [28] TGA of catalyzed (Ca added to fuel) Diesel soot in slow oxidation. (g) Miyamoto et al. [28] TGA of catalyzed (Ca added to fuel) Diesel soot in rapid oxidation. (h) Miyamoto et al. [28] TGA of uncatalyzed Diesel soot. (i) Gilot et al. [41] thermogravimetric analysis (TGA) of carbon black. (j) Neeft et al. [9] flow reactor study of Printex-U flame soot from Degussa AG. (k) Otto et al. [7] TGA of Diesel particles. (l) Ahlström and Odenbrand [8] flow reactor study of Diesel particles. Note: The surface specific rates are obtained for 130 nm initial sizes assuming the density of 1.8 g/cc for (a), (b), (c) and (d).

particles [32]. While this might enhance the oxidation of carbonaceous materials in the filter, the metal compounds remain in the filter leading to gradual plugging. Future oil formulations might be optimized to enhance oxidation while minimizing ash emissions.

A somewhat surprising outcome of this study is the significant reduction of PM volume emissions (which are proportional to mass) with lube oil dosing. These experiments were done with clean lube oil. It would be interesting to examine the effects of aged lube oil, like that used in the CENTINEL™ system, and to further investigate the kinetics of oxidation at a lower level of lube oil dosing.

A disturbing result of lube oil dosing is the formation of a large solid nuclei mode. A number of studies [42, 43] suggest that very small particles, especially solid particles, may be more toxic than larger ones.

CONCLUSION

The main objective of this study was to determine the influence of metals in lube oil on the kinetics of oxidation of soot particles in the exhaust and in aftertreatment systems. This was done by dosing the fuel with 2 % lube oil and comparing the results with previous studies done using undosed fuel. A secondary objective was to examine the influence of dosing the fuel with lube oil on exhaust particle emissions. All testing was done at peak torque speed and 75 % load.

The effect of lube oil metals on the kinetics of Diesel particle oxidation was examined using the HTO-TDMA method. The light-off temperature (which is defined as the peak flow tube temperature to observe ~1 nm size reduction by oxidation) was reduced about 150-200 °C with 2 % lube oil dosed fuel compared to when using regular fuel. The oxidation rate was increased significantly by adding lube oil to the fuel. The activation energy for 2 % lube oil dosed fuel is 101 kJ mol⁻¹, which is very close to the 108 kJ mol⁻¹ activation energy for particles using undosed fuel. However, the frequency factors (A_{nm} 's) of the Arrhenius equation with 2 % lube oil-dosed fuel are about twice as large as those for undosed fuel.

The kinetics of oxidation of Diesel particles, especially activation energies are quite different from those of ethylene diffusion flame soot (164 kJ mol⁻¹) and the well-known NSC model (143 kJ mol⁻¹). Our results suggest that Diesel particles are metal catalyzed to some extent, even when using regular undosed Diesel fuels, by the small amount of metals available from normal lube oil consumption. The addition of lube oil in the fuel increases the number of catalytic sites (an increase in frequency factors), but the activation energy is barely lowered, implying that Diesel particles are already catalyzed to some extent by natural consumption of lube oil.

Particle size distribution measurements show that particle volume emissions, which are roughly proportional to particle mass, were decreased by about a factor of two with dosed fuel but that particle number emissions increased by an order of magnitude. Most of the particle number was found in tiny, solid nuclei mode particles ($D_p < \sim 30$ nm). These experiments indicate that lube oil metals influence Diesel particle formation, oxidation and the performance of aftertreatment systems. Future lube oil formulations may have to take these effects into consideration.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Deere & Company for providing information about their lube oil, and Cummins Incorporation for providing information about their CENTINEL™ system.

CONTACT

Heejung Jung: heejung@me.umn.edu

David B. Kittelson: kitt001@umn.edu

Michael R. Zachariah: mrz@me.umn.edu

DEFINITIONS, ACRONYMS, ABBREVIATIONS

CPC: Condensation Particle Counter

DMA: Differential Mobility Analyzer

DPF: Diesel Particulate Filter

DPM: Diesel Particulate Matter

HTO-TDMA: High Temperature Oxidation-Tandem Differential Mobility Analyzer

NSC: Nagle Strickland and Constable [11]

PM: Particulate Matter

SMPS: Scanning Mobility Particle Sizer

TDMA: Tandem Differential Mobility Analyzer

TGA: ThermoGravimetric Analyzer

VOF: Volatile Organic Fraction

REFERENCES

1. Higgins, K.J., H. Jung, D.B. Kittelson, J.T. Roberts, and M.R. Zachariah, *Kinetics of Diesel Nanoparticle Oxidation*. Environ. Sci. Technol., 2003. **37**: p. 1949-1954.
2. Higgins, K.J., H. Jung, D.B. Kittelson, J.T. Roberts, and M.R. Zachariah, *Size-Selected Nanoparticle Chemistry: Kinetics of Soot Oxidation*. J. Phys. Chem. A., 2002. **106**: p. 96-103.
3. Pattas, K., N. Kyriakis, Z. Samaras, T. Manikas, A. Mihailidis, W. Mustel, and P. Rouveiolles, SAE TECHNICAL PAPER SERIES, 1998: p. 980543.
4. Quigley, M. and T. Seguelong, SAE TECHNICAL PAPER SERIES, 2002: p. 2002-01-0436.
5. Skillas, G., Z. Qian, U. Baltensperger, U. Matter, and H. Burtscher, *The Influence of Additives on the Size Distribution and Composition of Particles Produced by Diesel Engines*. Combust. Sci. and Tech., 2000. **154**: p. 259-273.
6. Lahaye, J., S. Boehm, P.H. Chambrion, and P. Ehrburger, *Influence of Cerium Oxide on the Formation and Oxidation of Soot*. Combustion and Flame, 1996. **104**: p. 199-207.
7. Otto, K., M.H. Sieg, M. Zinbo, and L. Bartosiewicz, SAE TECHNICAL PAPER SERIES, 1980: p. 800336.
8. Ahlström, A.F. and C.U.I. Odenbrand, Carbon, 1989. **3**: p. 475.
9. Neeft, J.P.A., T.X. Nijhuis, E. Smakman, M. Makkee, and J.A. Moulijn, Fuel, 1997. **76**: p. 1129.
10. Song, H., N. Ladommatos, and H. Zhao, *Diesel soot oxidation under controlled conditions*. SAE TECHNICAL PAPER SERIES, 2001: p. 2001-01-3673.
11. Nagle, J. and R.F. Strickland-Constable. in *Fifth Carbon Conference*. 1962: Pergamon: Oxford.
12. Caines, A. and R. Haycock, *Automotive Lubricants Reference Book*. 1996: SAE.
13. Winsor, R.E., John Deere, Editor. 2003.
14. Thorne, C.J., Castrol, Editor. 2003, Castrol.
15. Farrar-Khan, J.R., G.E. Andrews, P.T. Williams, and K.D. Bartle, SAE TECHNICAL PAPER SERIES, 1992: p. 921649.
16. De Petris, C., V. Giglio, and G. Police, *Some insights on mechanisms of oil consumption*. SAE TECHNICAL PAPER SERIES, 1996: p. 961216.
17. Audette III, W.E. and V.W. Wong, *A model for estimating oil vaporization from the cylinder liner as a contributing mechanism to engine oil consumption*. SAE TECHNICAL PAPER SERIES, 1999: p. 1999-01-1520.
18. Flynn, P.F., R.P. Durrett, G.L. Hunter, A.O. Loye, O.C. Akinyemi, J.E. Dec, and C.K. Westbrook, *Diesel combustion: an integrated view combining laser diagnostics, chemical kinetics and empirical validation*. SAE TECHNICAL PAPER SERIES, 1999: p. 1999-01-0509.
19. Graham, J.P., J.C. Wang, L.A. Roettgen, D.P. Carver, C.I. Black, D.M. Stehouwer, and R.C. Hatton, *Electronically controlled continuous lubricating oil replacement system*. 1998: United States Patent. p. 5,749,339.
20. Cummins, *CentinelTM*. 2003: www.cummins.com/au/pages/en/products/genuine_artsandservices/extendedlifeproducts/centinel.cfm.
21. Kittelson, D.B., D.F. Dolan, R.B. Diver, and E. Aufderheide, *Diesel Exhaust Particle Size Distributions-Fuel and Additive Effects*. SAE TECHNICAL PAPER SERIES, 1978: p. 780787.
22. Stanmore, B., B. J.-F., and P. Gilot, *The ignition and combustion of cerium doped diesel soot*. SAE TECHNICAL PAPER SERIES, 1999: p. 1999-01-0115.
23. Kytö, M., P. Aakko, N.-O. Nyland, and A. Niemi, *Effect of Lubricant on Particulate Emissions of Heavy Duty Diesel Engines*. SAE TECHNICAL PAPER SERIES, 2002: p. 2002-01-2770.
24. Wang, S.C. and R.C. Flagan, Aerosol Sci. and Technol., 1990. **13**: p. 230-240.
25. Abdul-Khalek, I., D.B. Kittelson, and F. Brear, *The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements*. SAE TECHNICAL PAPER SERIES, 1999: p. 1999-01-1142.
26. Khalek, I.A., D.B. Kittelson, and F. Brear, *Nanoparticle Growth during Dilution and Cooling of Diesel Exhaust: Experimental Investigation and Theoretical Assessment*. SAE TECHNICAL PAPER SERIES, 2000: p. 2000-01-0515.
27. Miyamoto, N., H. Zhixin, A. Harada, H. Ogawa, and T. Murayama, SAE TECHNICAL PAPER SERIES, 1987: p. 871612.
28. Miyamoto, N., H. Zhixin, and O. Hideyuki, SAE TECHNICAL PAPER SERIES, 1988: p. 881224.
29. Stenitzer, M. 2003, Vienna - University of Technology: Vienna.
30. Jung, H., D.B. Kittelson, and M.R. Zachariah, *The Influence of Cerium Additive on Diesel Nanoparticle Emissions and Kinetics of Oxidation*. in preparation for publication, 2003.
31. Kasper, M., K. Sattler, K. Siegmann, U. Matter, and H.C. Siegmann, *The influence of fuel additives on the formation of carbon during combustion*. J. Aerosol. Sci., 1999. **30**: p. 217.
32. Mayer, A., A. Ulrich, J. Czerwinski, U. Matter, and M. Wyser, *Retention of fuel borne catalyst particles by diesel particle filter systems*. SAE Special Publication, 2003(SP-1755): p. 21-27.
33. Abdul-Khalek, I.S., D.B. Kittelson, B.R. Graskow, Q. Wei, and F. Brear, *Diesel Exhaust Particle Size: Measurement Issues and Trends*. SAE TECHNICAL PAPER SERIES, 1998: p. 980525.
34. Abdul-Khalek, I. and D.B. Kittelson, *Real Time Measurement of Volatile and Solid Exhaust Particles Using a Catalytic Stripper*. SAE TECHNICAL PAPER SERIES, 1995: p. 950236.

35. Mayer, A., J. Czerwinski, U. Matter, M. Wyser, P. Scheidegger, D. Kieser, and Weidhofer, *VERT: Diesel Nano-Particulate Emissions: Properties and Reduction Strategies*. SAE TECHNICAL PAPER SERIES, 1998: p. 980539.
36. Mayer, A., J. Czerwinski, and P. Scheidegger, *Trapping efficiency depending on particulate size*. SAE TECHNICAL PAPER SERIES, 1996: p. 960472.
37. Sakurai, H., H.J. Tobias, K. Park, D. Zarling, K.S. Docherty, D.B. Kittelson, P.H. McMurry, and P.J. Ziemann, *On-line measurements of diesel nanoparticle composition and volatility*. Atmospheric Environment, 2003. **37**: p. 1199–1210.
38. Tobias, H.J., D.E. Beving, P.J. Ziemann, H. Sakurai, M. Zuk, P.H. McMurry, D. Zarling, R. Waytulonis, and D.B. Kittelson, *Chemical Analysis of Diesel Engine Nanoparticles Using a Nano-DMA/Thermal Desorption Particle Beam Mass Spectrometer*. Environ. Sci. Technol., 2001. **35**: p. 2233-2243.
39. Gordon, S. and B.J. McBride. 1976, NASA.
40. Stratakis, G.A. and A.M. Stamatelos, *Thermogravimetric analysis of soot emitted by a modern diesel engine run on catalyst-doped fuel*. Combust. Flame, 2003. **132**: p. 157-169.
41. Gilot, P., F. Bonnefoy, F. Marcuccilli, and G. Prado, Combust. Flame, 1993. **95**: p. 87.
42. Pope, C.A., III, M.J. Thun, M.M. Namboodiri, D.W. Dockery, J.S. Evans, F.E. Speizer, and C.W. Heath, Jr., *Particulate Air Pollution as a Predictor of Mortality in a Prospective Study of U.S. Adults*. Am. J. Respir. Crit. Care Med., 1995. **151**: p. 669-674.
43. Dockery, D.W., C.A. Pope III, X. Xu, J.D. Spengler, W.J. H., F. M.E., M.E. Fay, B.G. Ferris, and F.E. Speizer, *An Association between Air Pollution and Mortality in Six U.S. Cities*. New Eng. J. Med., 1993. **329**(24): p. 1753-1759.