Influence of Metal Oxide Ashes on Soot Oxidation Kinetics and Nanostructure using Electron Microscopy and Thermogravimetric Analysis

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Abstract. According to increasingly stringent regulations on particulate emission from automotive vehicles, diesel engine must be equipped with Diesel Particulate Filter (DPF) to trap the Particulate Matter (PM) which are very harmful to human health. Diesel particulate matters are composed primarily of unburned hydrocarbon (soot) and metal oxide ashes as solid fraction. DPF can trap PM with higher filtration efficiency and the process which can burn the soot into carbon dioxide is called regeneration process. Although regeneration process can burn the soot effectively, incombustible ashes will be remained inside the DPF channel causing engine back pressure. These metal oxide ashes are mainly derived from lubricant additives, engine wear and trace metals from diesel fuel. In this article, different nanostructures of diesel soot and metal oxide ash derived by diesel blending lube oil condition were briefly compared using Transmission Electron Microscopy (TEM) image analysis. Electron Dispersive X-ray Spectroscopy (EDS) analysis was introduced to investigate the chemical composition of particulate matters. Thermogravimetric Analysis (TGA) was also conducted to compare the oxidation kinetics of pure diesel soot and the influence of metal oxide ash on soot oxidation kinetics. Contamination of metal oxide ashes promoted soot oxidation rate due to the presence of metallic additives from lube oil acting as a catalyst on soot oxidation kinetics.

1. Introduction

Particulate Matter (PM) emitted from diesel engines are very harmful to human health and must be removed due to stringent emission regulations. PM are mainly composed of solid fraction (soot and ash) and soluble organic fraction such as (sulfates and nitrates) organic compounds. Diesel Particulate...
Filter (DPF) is one of the most effective aftertreatment system which can perform higher PM trapping efficiency. There are honeycomb rectangular channels where the exhaust gas flows through its porous walls. The trapped PMs must be burned out during vehicle running and a chemical oxidation process which can oxidize the trapped soot into carbon dioxide is called regeneration process. Although regeneration process can burn the soot effectively, the unburned metal oxide ashes will be remained along the inlet channels causing engine back pressure. These metal oxide ashes are originated mainly from lubricant additives and a very few amounts from engine wear and fuel trace metals{1 ,4}.

Conventional lubricant additives such as anti-oxidants, rust and corrosion inhibitors, viscosity index modifiers, anti-wear (AW) agents, detergents and dispersants are well known additives which all are responsible to get better performance of engine lubricating oil. Among them, detergents help to prevent the high temperature deposits on the surface of metal walls, and it assists to neutralize acids that form in the lube oil. They are typically composed of calcium and magnesium as chemical metallic compounds. During engine combustion, lube oil can also participate, and these metallic compounds leave as an ash deposit when the oil is burned{5, 6}.

P. Karin et al., mentioned that nanostructure and oxidation kinetics of biodiesel PM compared to Diesel PM. A primary soot particle has two distinct parts: an inner core and an outer shell. The size of each crystallite and agglomeration might be strongly related to Brownian force of gas molecule, drag and shear forces of fluid dynamics, electrostatics forces of charge elements. Nanostructure of soot is composed of curve line crystallites while the ash nanostructure shows straight line structures{7, 8}.

During engine combustion, the lubricants can also participate, and the contamination of lube oil can vary the morphology and oxidation kinetics of particulate matters. Some literatures have already investigated not only physical characterization like morphology and particle size distribution but also chemical composition focusing on lube oil related particulate matters{9-11}. Y. Wang et al., found that the anti-wear lubricant oil additives changed the nanostructure of emitted particles and led to particles with a more disordered nanostructure. Moreover, oil-related particles have larger aggregate size than diesel particles{12}.

In the previous literatures, oxidation kinetics of carbon black and engine’s PMs were briefly compared. Engine’s PMs are easier to oxidize than carbon black nanoparticles because of containing unburned hydrocarbon. Oxidation kinetics of PM is dependent upon both physical shape of reactant substance and chemical composition (oxygen, unburned hydrocarbon and others). The calculated apparent energy of diesel engine’s PMs were in the range of 117-130 kJ/mol. H. Jung et al., also investigated that the influences of metals derived from lube oil on oxidation kinetics of soot particles by dosing 2% lube oil and determined apparent activation energy. By using Arrhenius equations, frequency factor of oil dosed PM were about twice as large as without dosing{13, 14}.

This research mainly compares nanostructure of diesel soot and metal oxide ash which are mainly derived from lubricant additives. The designed lube oil consisting excess amount of Calcium (Ca) additives was blended 10%, directly into diesel fuel to obtain more ash formation among PM composition. Oxidation kinetics of diesel PM and diesel blending lube oil PM were also investigated to compare the influence of metal oxide ash on soot oxidation kinetics.

2. Experimental

A direct injection compression engine (Kubota – RT140) was used to generate the particulate matter. Engine specification are described in Table 1. Eddy Current Engine Dynamometer was used to control the desired engine speed and load conditions. LabView program controlled the engine dynamometer. A soot collector which contains metal netting inside was used to collect the PM powders.
Table 1 Engine specification

| Items               | Details                          |
|---------------------|----------------------------------|
| Engine Type         | 1-cylinder, Direct Injection, CI engine |
| Bore x Stroke       | 97 x 96 mm                       |
| Displacement        | 709 cm³                          |
| Compression ratio   | 18:1                             |
| Power               | 9.2 kW @ 2400 RPM                |
| Injection Timing    | 19ºCA bTDC                       |
| Injection Pressure  | 22 MPa                           |

Table 2 Properties of test fuel

| Fuel Properties      | Unit | Result |
|----------------------|------|--------|
| Chemical Formula     | -    | C₁₄₂H₂₈ |
| Auto Ignition Temperature | °C  | 288   |
| Calorific Value      | kJ/kg| 46180  |
| Heat of Vaporization | kJ/kg| 250   |
| Viscosity            | mm²/s| 30    |
| Stoichiometric A/F ratio | - | 12.3  |
| Density              | kg/m³| 844.8 |

Table 3 Properties of blending lubricant

| Test                | Method    | Unit | Result |
|---------------------|-----------|------|--------|
| Density @15°C       | ASTM D4052.15 | g/mL | 0.8960 |
| Density @30°C       | ASTM D4052.15 | g/mL | 0.8866 |
| Viscosity @40°C     | ASTM D445.15a | mm²/s | 154.8 |
| Viscosity @100°C    | ASTM D445.15a | mm²/s | 150.5 |
| Magnesium           | ASTM D6481  | %wt  | 0.1816 |
| Zinc                | ASTM D6481  | %wt  | 0.0798 |
| Phosphorous         | ASTM D6481  | %wt  | 0.0856 |

Schematic diagram of the engine setup is shown in figure 1. To conduct the experiment, commercial diesel containing \( (C_{142}H_{28}) \) was used as an ideal fuel and secondly, designed lube oil was blended 10% by mass directly into diesel fuel to obtain more ash formation among PM composition. This blending lubricant was supported by Bangchak Corporation and it contains excess amount of Calcium (Ca) additives since CaSO₄ is the most abundant sulfate compound found in diesel ashes inside used DPF. The fuel properties and blending lubricant oil properties are briefly described in Table 2 and 3. Density and viscosity of blending lubricants were tested under ASTM D4052.15 and ASTM D445.15a respectively. According to ASTM, viscosity is measured as kinematic viscosity and usually described in data sheets at 40°C and 100°C. For the engine lubrication system, conventional lubricating oil 15W-40 API CI-4 SL synthetic engine oil was used.

3. Results and Discussion

3.1 Morphology of ultrafine agglomerate particles

Transmission Electron Microscopy (TEM) image analysis was used to determine the ultrafine agglomerate primary particle nanostructures as shown in figure 2. Soot powders were collected under 2400 RPM engine full load condition since this engine condition is properable to generate the soot efficiently according to previous smoke intensity results. TEM image results showed that the agglomerate structure of ultrafine particles from diesel blending lube oil condition were not significant different compared to neat diesel engine’s ultrafine particle. The primary particles from both conditions were grouped each other with similar agglomerate structures and results have not shown much differences.
3.2 Nanostructures of soot and metal oxide ash

Figure 3 compare TEM images of different nanostructures of soot (pure carbon) obtained from the neat diesel condition and metal oxide ash which is derived from diesel blending lube oil condition. The nanostructure of diesel soot primary particle is a spherical shape composed of curve line crystallites as described in figure 3 (a).

Different from soot, in figure 3 (b), metal oxide ash nanostructure is not a spherical shape composed of parallel straight line hatch patterns which shows similar nanostructures among metals. Due to the fact that blending lubricant oil contains metallic additives and these additives cannot be burned during engine combustion and finally it might be changed into metal oxide ashes. Therefore, particulate matters from diesel blending lubricant condition shows distinct straight lined patterns of ash collaborating with unburned hydrocarbon (soot).

3.3 Elemental composition of particulate matters

To investigate the chemical elemental composition of particulate matter, electron dispersive x-ray spectroscopy collaborating with SEM was introduced. X-ray spectrum detect the sample and distinguish the elements according to their particular atomic number. Regarding to the results of SEM-EDS as described in figure 4, particulate matters from neat diesel condition shows only carbon (soot) and oxygen as elemental composition. However, particulate matters from diesel blending lube oil condition contain not only carbon and oxygen but also unburned metallic elements such as Calcium (Ca), Phosphorous (P), Sulfur (S), Silicon (Si) and Zinc (Zn) respectively. Among metallic additives, elemental composition amount of Ca expressed highest weight percentage due to the fact that the blending lubricant was designed with excess Ca additives. Therefore, EDS result pointed out that metallic additives from engine lubricating oil cannot be burned by engine combustion and these unburned metallic additives might be transformed into metal oxide ash which cannot be burned by regeneration process inside diesel particulate filter. On the other hand, these incombustible ashes might promote soot oxidation kinetics since ash are mainly originated from metallic additives of lube oil.

![Figure 2. TEM images of ultrafine agglomerate particles from small engine (a) diesel and (b) diesel blending lubricating oil condition under 2400 RPM engine full load condition](image_url)
Figure 3. TEM images of nanostructure of (a) diesel soot and (b) metal oxide ash

Figure 4. Elemental analysis of (a) Diesel PM and (b) Diesel blending lube oil PM by using electron dispersive x-ray spectroscopy (SEM-EDS) showing unburned metallic lubricant additives derived from engine lubricating oil
3.4 Oxidation kinetics of particulate matters

Thermogravimetric analysis (TGA) was conducted to investigate the influence of contamination of metal oxide ash on soot oxidation kinetics. Mass conversion results of diesel particles and diesel blending lube oil particles were compared under different operating temperatures (600 °C and 625 °C). Mass conversion rates can be calculated to describe the faster oxidation kinetics of diesel blending lube oil PMs. Isothermal method was used to maintain the operating temperature. Nitrogen was introduced before air is injected and the sample was oxidized until 90 minutes. Particles were treated with increasing temperature about (20 – 30) minutes by nitrogen atmosphere in order to occur vaporization process. After vaporization, air (oxygen and nitrogen) was start injected and the system was maintained under isothermal to initiate PM oxidation process. Chemical oxidation reaction of PM mass conversion results can be expressed by Eq.1 and the amount of mass conversion over time can be

![Graphs showing mass conversion and rate of PM oxidation at different temperatures.](image)

**Figure 5.** Thermogravimetric analysis of mass conversion graphs of diesel PM and diesel blending lube oil PM at (a) 600°C and (b) 625°C, mass conversion rate of diesel PM and diesel blending lube oil PM at (c) 600°C and (d) 625°C.
\[ C + O_2 \rightarrow CO_2 \]  
(1)
\[ \frac{d[C]}{dt} = k[C]^n[O_2]^m \]  
(2)

Calculated as mass conversion rate by using Eq.2, where \( C \) is represented as PM mass, \( t \) is time, \( n \) and \( m \) are reaction order of PM and oxygen during oxidation process.

Regarding to thermogravimetric analysis results as described in figure 5 (a and b), particles from diesel blending lube oil condition (represented as Diesel+A) were easier to oxidize than neat diesel’s particles. The unburned lube oil metallic additives might be participated as an oxidative catalyst resulting faster oxidation kinetics under both operating temperatures 600°C and 625°C. As shown in figure 5 (c and d), mass conversion rates were also calculated to mention sharply for the higher mass conversion rate of diesel blending lube oil PMs.

4. Conclusion

Morphology of ultrafine agglomerate particles, different primary particle nanostructures of lube oil derived metal oxide ashes compared to diesel soot and influence of incombustible metal oxide ashes on soot oxidation kinetics were briefly discussed. The agglomerate structure of ultrafine particles from diesel blending lube oil condition has not shown significant difference compared to agglomerated ultrafine particles from neat diesel condition. Nanostructure of primary soot particle is a spherical shape composed of curve line crystallites while the metal oxide ash has not shown a spherical shape composed of parallel straight-line hatch patterns. Nanostructure of metal oxide ash is like the nature of common metals’ nanostructures since these metal oxide ashes are also derived from unburned metallic additives of engine lubricating oil.

According to the chemical characterization results, PM from neat diesel condition composed mainly of carbon and oxygen as elemental composition while PM from diesel blending lube oil condition contained not only carbon and oxygen but also unburned metallic additives from engine lubricating oil. Particulate matters from diesel blending lube oil condition were easier to oxidize than PMs from neat diesel condition. Metallic additives from engine lubricating oil cannot be burned by engine combustion and it might be changed into metal oxide ash. These metal oxide ashes promote oxidation kinetics resulting faster mass conversion rate. Moreover, although accumulated metal oxide ashes tend to reduce effective filtration length of diesel particulate filters, on the other hand, these incombustible ashes might assist to promote the soot oxidation kinetics during regeneration process of diesel particulate filter.

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