รายงานการวิจัยฉบับสมบูรณ์

ผลกระทบของสารเติมแต่งน้ำมันหล่อลื่นเครื่องยนต์ต่อโครงสร้างระดับไมโครและนาโนของมลพิษเขม่าด้วยการวิเคราะห์ภาพถ่ายจากกล้องจุลทรรศน์อิเลคตรอน

Impact of Engine Oil's Additives on Particulate Matter's Micro- and Nanostructure using Electron Microscopy Image Analysis

ผู้ช่วยศาสตราจารย์ ดร.ปรีชา การินทร์

ได้รับทุนสนับสนุนงานวิจัยจากเงินรายได้ ประจำปีงบประมาณ พ.ศ. 2561

วิทยาลัยนานาชาติ
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

Research Title: Impact of Engine Oil's Additives on Particulate Matter's Micro- and Nanostructure using Electron Microscopy Image Analysis

Researcher: Asst.Prof.Dr.Preechar Karin

Faculty: International College

Department: Automotive Engineering Program

ABSTRACT

According to increasingly stringent regulations on particulate emission from automotive vehicles, diesel engine has to 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.

Keywords : Diesel Particulate Matter, Metal Oxide Ash, TEM, TGA

Acknowledgements

The author would like to acknowledge to International College, King Mongkut's Institute of Technology Ladkrabang (KMITL) for research funding and also Bangchak Corporation (BCP) for supporting designed lubricating oil to accomplish this research.

Asst.Prof.Dr.Preechar Karin

Contents

List of Tables

List of Illustration

Chapter 1
Introduction

1.1 Research Background

Direct Injection Compression Ignition Engine (DICI Engine) or Diesel Engine has the highest thermal efficiency among Internal Combustion Engines used in cars. However, diesel engines cause many pollution problems, especially particulate matter (PM) which is harmful to humans and the environment because its main components are soot (pure carbon) and metal ash, which are the main causes of cancer in the population living in the big cities.

Particulate filter (PF) is an after-treatment technology used in developed countries that enforce Euro 5 pollution control regulations such as European countries, Japan, USA, etc. The pollution control regulations in Thailand is still only Euro 4. So, such technology is not yet required to be installed. But it is expected that, within five years, there will be more stringent pollution control regulations equivalent to the Euro 5. Researchers also found that the fuel that contains oxygen, such as biodiesel and bioethanol, can reduce the amount of soot particles from combustion engines according to the proportion of biofuel mixed with diesel produced from crude oil, which is an advantage for South East Asia countries, because they can produce biofuels by themselves from palm oil and molasses from sugarcane.

Although, in the present, there is an after-treatment technology and biofuel to reduce and eliminate the pollution of soot particles from vehicles. Researchers also found that the lubricating oil used in engines that were partially coated in the combustion chamber walls, burnt and emitted pollution of soot particles that may have altered physical and chemical structures (Physicochemical Characteristics), especially metal oxide ash from engine oil additives such as Ca, Zn, Al, Fe and Mg etc. Therefore, this research sees the importance of the impact of metal oxide ash on the nanostructures of soot particles, as it directly affects the particulate matter trapping and oxidation processes. The data from this research will be the basis for lubricating oil design and the appropriate development of pollution control system for soot particles.

1.2 Research Objectives

1.2.1 To study physicochemical characteristics including micro- and nanostructure of particulate matter (PM) that contains soot from incomplete combustion and metal oxide ashes from engine oil additives.

1.2.2 To describe the effects of metal oxide ash from the oil additive to micro- and nanostructures of soot particles by analyzing image from scanning and transmission electron microscopy (SEM, TEM) including the effect of metal oxide ash on the oxidation kinetics of soot in the process of solid carbon oxidation into carbon dioxide (CO2).

1.3 Scope of Research

1.3.1 Study the physicochemical characteristics including micro- and nanostructure of the particulate matter (PM) which consists of soot from incomplete combustion and metal oxide ash from engine oil additives, by using engineering and material science analysis equipment such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Energy Dispersive X-Ray Analysis (EDX), Laser Diffraction Spectroscopy (LDS), Carbon Hydrogen Nitrogen Oxygen Analysis (CHNO), Oil and Fuel Distillation, Soot Generator and Internal Combustion Engine etc.

1.3.2 Describe the effects of metal oxide ash from the lubricant additive to the micro and nanostructure by analyzing image from the electron microscope, including the impact of metal oxide ash on the oxidation kinetics of soot by using engineering and material science analysis equipment such as Thermo Gravimetric Analysis (TGA), Transmission Electron Microscopy and Energy Dispersive Spectroscopy (TEM-EDS), Image Processing and Analysis, etc.

1.4 Research Methodology

1.4.1 Study the research that related to advanced analysis of physicochemical characteristics of micro- and nanostructures and material science testing of metal oxide ash from engine oil additives.

1.4.2 Study the physicochemical characteristics including micro- and nanostructure of particulate matter that contains soot from incomplete combustion fuels and metal oxide ash from engine oil additives using engineering and material science analysis equipment such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Energy Dispersive X-Ray Analysis (EDX), Laser Diffraction Spectroscopy (LDS), Carbon Hydrogen Nitrogen Oxygen Analysis (CHNO), Oil and Fuel Distillation, Soot Generator, Internal Combustion Engine etc.

1.4.3 Describe the effects of metal oxide ash from engine oil additive to the micro-and nanostructure by analyzing image from the electron microscope, including the effect of metal oxide ash on the oxidation kinetics of soot by using engineering and material science analysis equipment such as Thermo Gravimetric Analysis (TGA), Transmission Electron Microscopy and Energy Dispersive Spectroscopy (TEM-EDS), Image Processing and Analysis, etc.

1.5 Expected Output

The research results will be published in the international academic conference such as "The 10th International Conference on Materials Science and Technology (MSAT2018) and the 9th International Conference on Mechanical Engineering (TSME-ICoME2018).

Chapter 2

Literature Review

2.1 Diesel Particulate Matter

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, as shown in Fig. 2.1. 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, as shown in Fig. 2.2. 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, as shown in Fig. 2.3. 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. During engine combustion, lube oil can also participate, and these metallic compounds leave as an ash deposit when the oil is burned [5, 6].

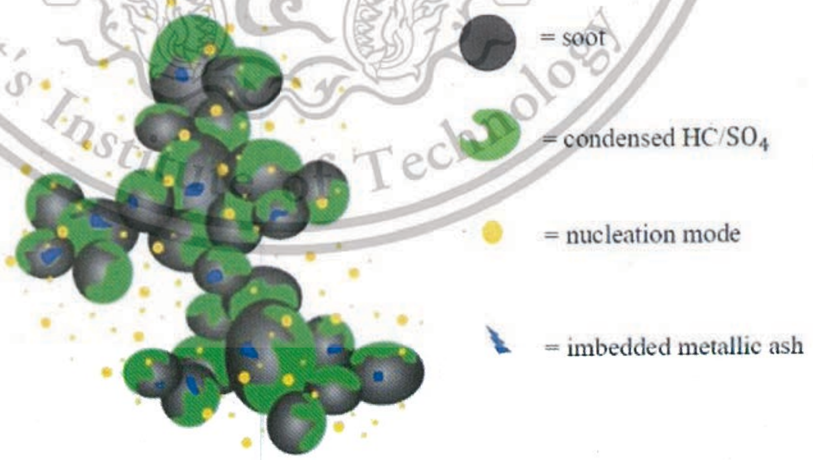


Fig. 2.1 Composition of Particulate Matter [1].

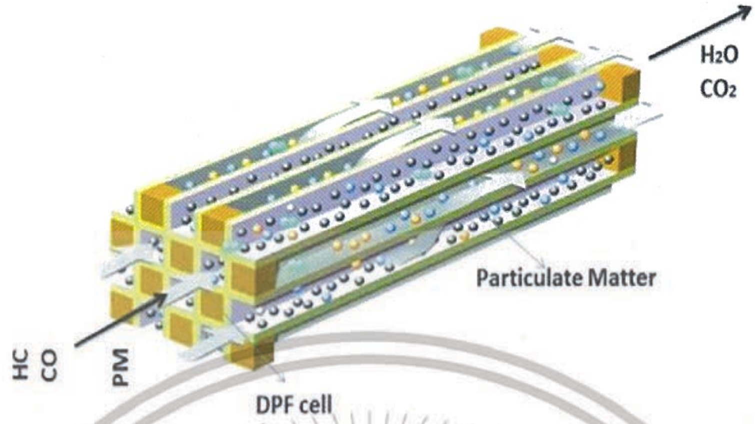
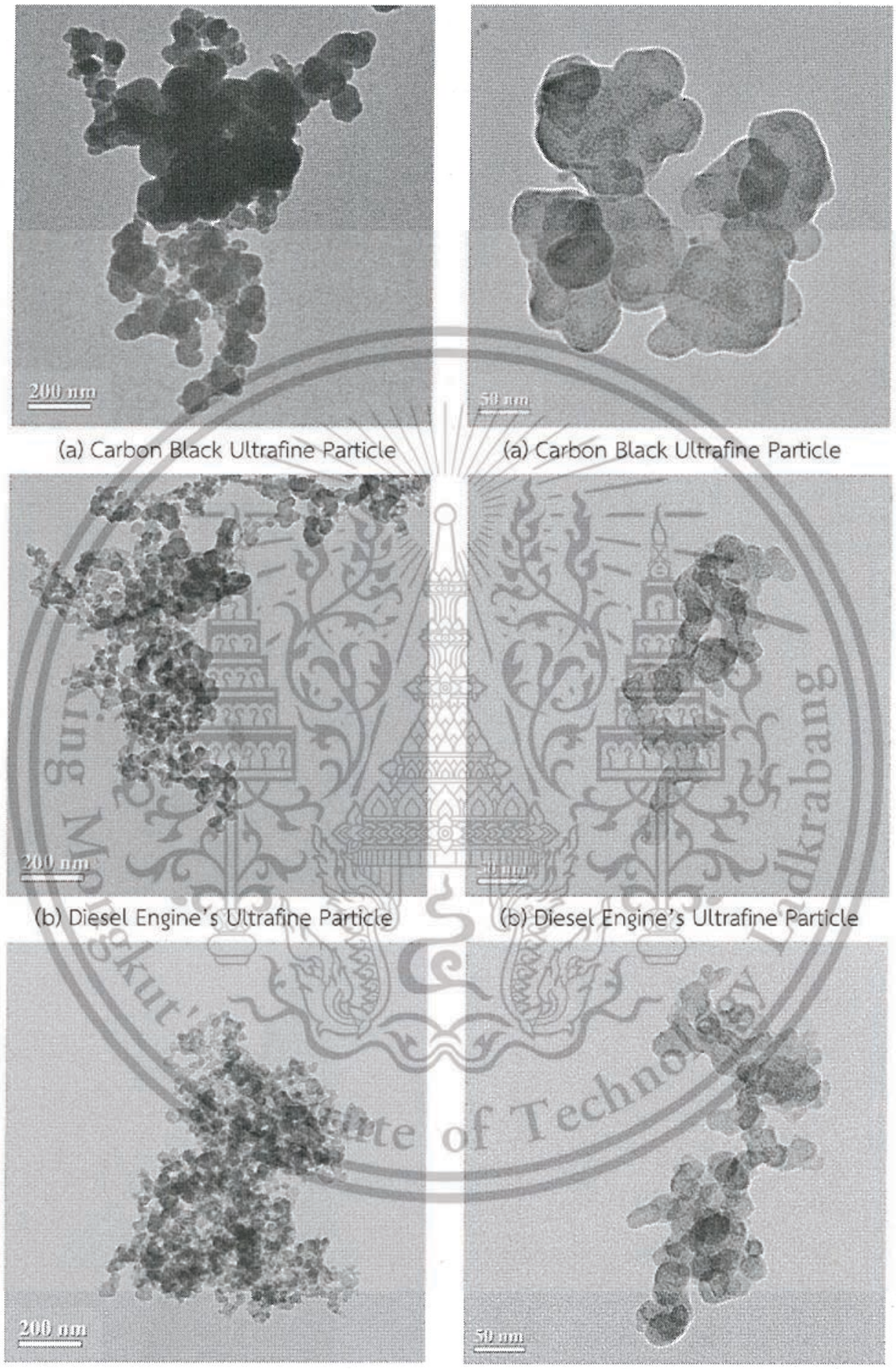


Fig. 2.1 Diesel Particulate Filter (DPF) [3].

Fig. 2.3 DPF regeneration process and remaining unburned metal oxide ash inside inlet channels [4].



(a) Carbon Black Ultrafine Particle (a) Carbon Black Ultrafine Particle

(b) Diesel Engine's Ultrafine Particle (b) Diesel Engine's Ultrafine Particle

(c) Biodiesel Engine's Ultrafine Particle (c) Biodiesel Engine's Ultrafine Particle

Fig. 2.4 TEM images of (a) carbon black, (b) diesel engine's ultrafine particles and (c) biodiesel engine's ultrafine particles in the operation conditon 80% of engine load and 2400 rpm of engine speed [7].

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. Quantity, morphology and oxidation kinetics of biodiesel engine's PMs were characterized successfully. The quantities of PMs emitted from biodiesel engine are approximately a half of diesel engine's PMs. Average primary nanoparticle sizes of carbon black particles, diesel and biodiesel engine's PMs are approximately 48, 34 and 32 nm respectively, as shown in Figs. 2.4 and 2.5. The quantity and primary particle sizes of engine's PMs decreased when increasing the engine speed and engine load because of combustion temperature is also automatically increased. Engine's PMs are easier to oxidize than carbon black nanoparticles because of unburned bio-oxygenate hydrocarbon and smaller size of particle. The oxidation rate of biodiesel engine's PMs are higher than that of diesel engine PMs because of unburned hydrocarbon and smaller size of particle, as shown in Fig. 2.6. Calculated apparent activation energies of biodiesel engine's PM engine and carbon black nanoparticles. The apparent activation energies of biodiesel engine's PM and diesel engine's PM oxidation on conventional cordierite DPF powders are 121±11 kJ/mol and 124±7 kJ/mol respectively. Oxygen atom included inside oxygenated fuel molecules might promote lower PM oxidation activation energy. However, oxidation rate of particulate matters is strongly related to not only activation energy but also physical impact, such as primary particle size which are strongly related to the reaction order and frequency factor. Smaller primary nanoparticle diameter of biodiesel engine would be an advantage of DPF regeneration process in vehicle application [7].

The amount of particulate matter emitted from CI engine depend on several variables. The result shows the parameter which has the highest effect on PM quantity is engine load, concentration of biodiesel and engine speed respectively. When increase concentration of biodiesel in fuel, PM reduce because oxygen concentration in fuel increase. Higher concentration of oxygen makes more complete combustion and higher thermal efficiency. The quantities of particulate matter emitted from biodiesel engine are approximately a half of diesel engine's particulate matter. Morphology of CI engine's PM10, PM2.5, ultrafine particle and nanoparticle was characterized using SEM and TEM successfully. The morphology of biodiesel and conventional diesel doesn't have much different in the viewpoint of particulate matter trapping using DPF micro- surface pores [8].

Nanostructures of pure carbon inside diesel lamp (external combustion) and diesel engine PMs are very similar, even though, some part of diesel engine's PM was agglomerated with metal oxide ash, which included in engine lubricating oil, as shown in Fig. 2.7 [9]. 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 [10, 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].

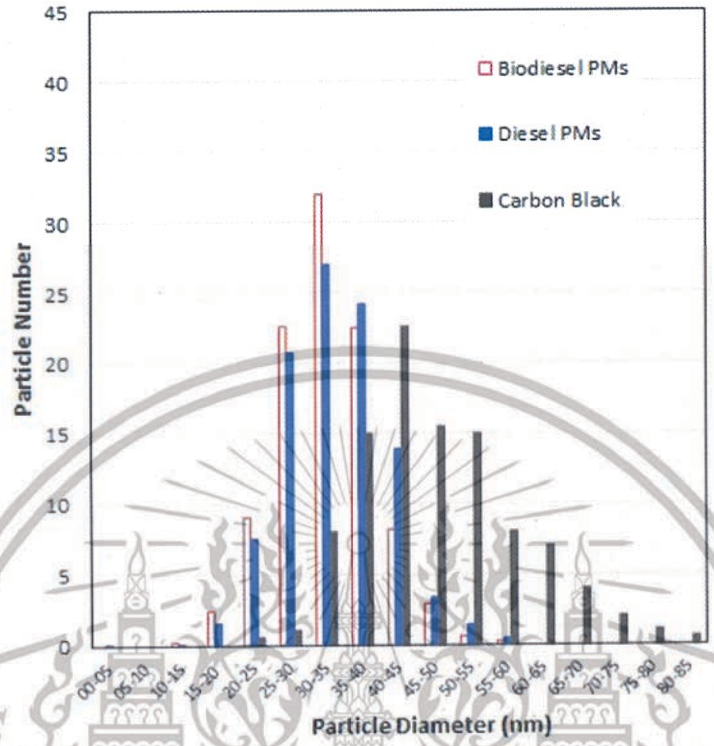


Fig. 2.5 Size distribution of carbon black, Diesel and Biodiesel engines' PMs [7].

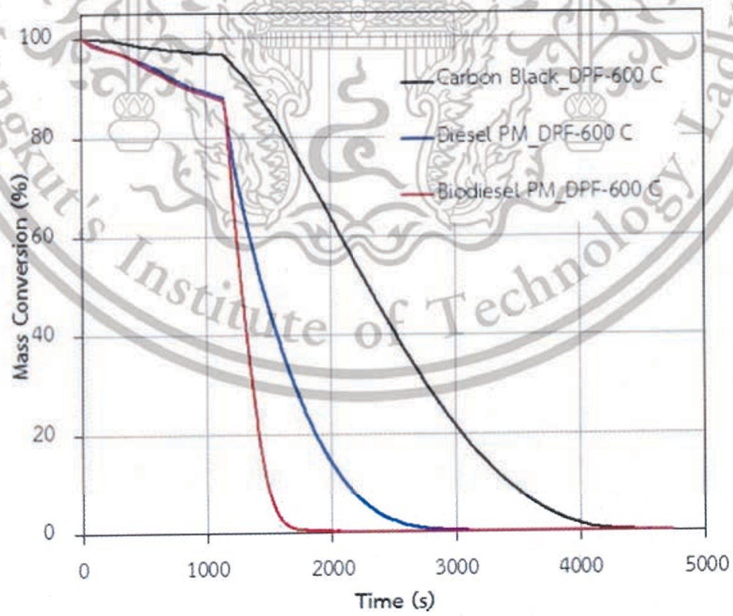


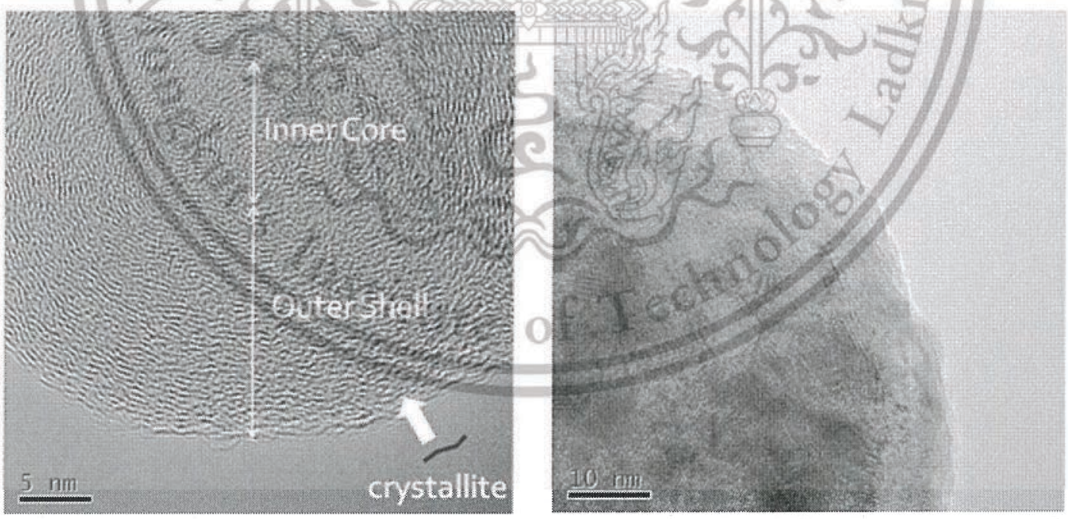
Fig. 2.6 Oxidation kinetics of carbon black, diesel and biodiesel PMs using TGA isothermal method at 600°C isothermal method with pure air [7].

2.2 Metal Oxide Ashes

A. Liati et al. investigated the physical characteristics of diesel ash particulate matter and chemical characterization of the composition of bulk ash from used DPF. The author reported that the individual ash particles are mostly crystalline with round outlines and the sizes are in the range of 10 – 200 nm, as shown in Fig. 2.8. EDX analysis of bulk ash consist mainly of Ca, Mg, P, Zn, S, O, Fe, Al and Si in the form of sulfates, phosphates and oxides, as shown in Table 3.1. The agglomerate ash sizes are in the range of 200 – 600 nm, as shown in Fig. 2.9 [13].

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 [14, 15].

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.



(a) Soot (b) Ash

Fig. 2.7 TEM images of (a) Soot and (b) ash nanostructure of PMs [9].

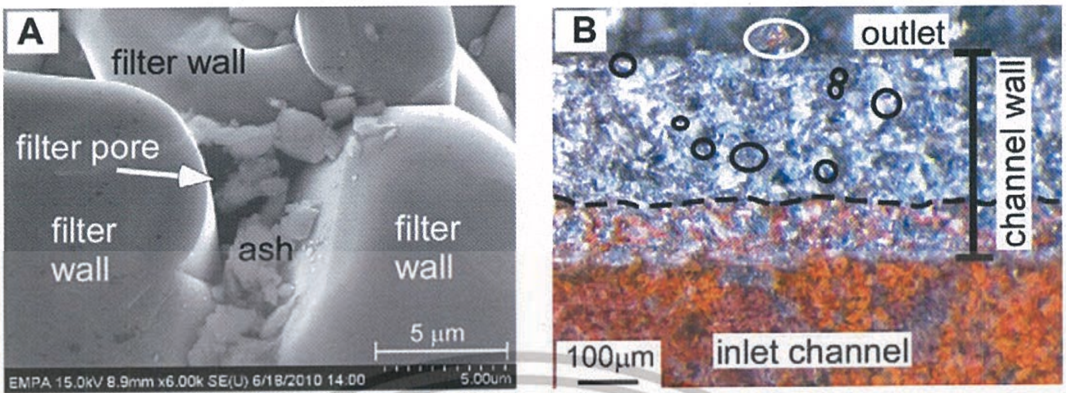


Fig. 2.8 SEM SE image of (A) ash agglomerates in the pores of the channel wall of the light truck DPF, (B) Microphotograph from the DPF showing massive ash penetration through the channel wall [13].

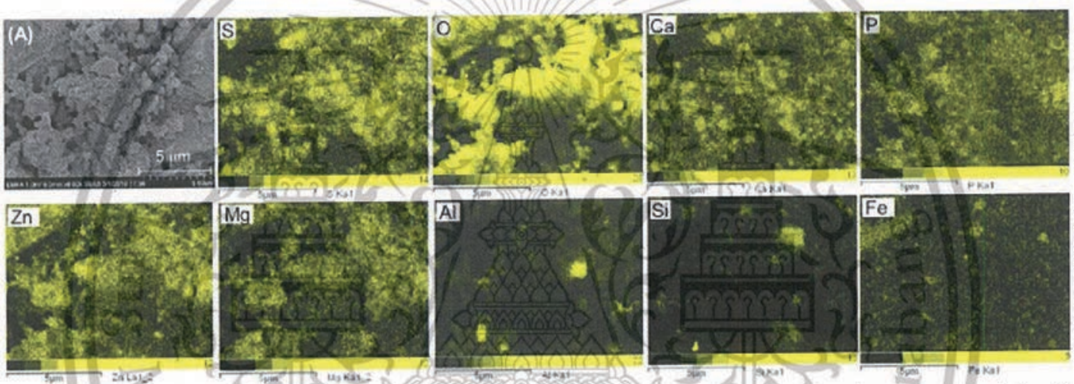


Fig. 2.9 SEM SE image of (A) ash agglomerate and distribution of elements in ash agglomerate particles [13].

Table 2.1 Chemical composition of bulk ash [13].

Element	Concentration: mol% - (wt%)		
	Light truck		Passenger car
	center	periphery	
CaO	15.7 (9.16)	17.3 (10.2)	20.9 (9.74)
ZnO	9.33 (7.94)	10.5 (9.00)	7.67 (5.20)
P_2O_5	9.50 (14.1)	8.23 (12.3)	8.17 (9.66)
MgO	22.4 (9.45)	22.6 (9.57)	2.47 (0.83)
SO_3	23.0 (19.2)	32.6 (27.5)	5.18 (3.45)
Fe_2O_3	10.3 (17.2)	4.69 (7.88)	>50 (70)
Al_2O_3	4.92 (5.24)	1.35 (1.45)	1.13 (0.96)
Cr_2O_3	1.04 (1.65)	0.49 (0.79)	0.055 (<0.1)
NiO	1.33 (1.04)	0.60 (0.47)	0.55 (0.34)
CuO	1.11 (0.86)	1.22 (0.96)	0.34 (0.21)
SiO_2	1.10 (0.69)	0.21 (0.13)	0.94 (0.47)
MnO	0.34 (0.25)	0.19 (0.14)	0.05 (<0.1)

Chapter 3

Experimental Setup and Methodology

3.1 Experimental Setup

A 1-cylinder natural aspirated direct injection compression engine (Kubota – RT140) was used to generate the particulate matter (PM). Engine specifications in details are described in Table 3.1. Eddy current engine dynamometer was used to control the desired engine speed and load conditions by the aid of Lab-view program. To investigate the smoke intensity of the exhaust emission, Opacity smoke meter (Okuda DSM – 240) was introduced at the end of the exhaust muffler and it measures the soot contamination percentage by paper filter. A soot collector containing metal netting was used to collect the soot powder. The schematic diagram of experimental setup is shown in Fig 3.1. Conventional diesel (B7) was used as an ideal fuel and secondly, designed lubricant oil which contains excess amount of Calcium (Ca) additives supported by Bangchak Corporation (BCP) was blended directly into the diesel. The blending condition is the amount of 10% by mass directly into the Diesel. Fuel properties and blending lubricant oil properties are briefly described in Table 3.2 and 3.3. Conventional lubricating oil 15W – 40 API CI – 4/SL synthetic engine oil was used for lubrication system.

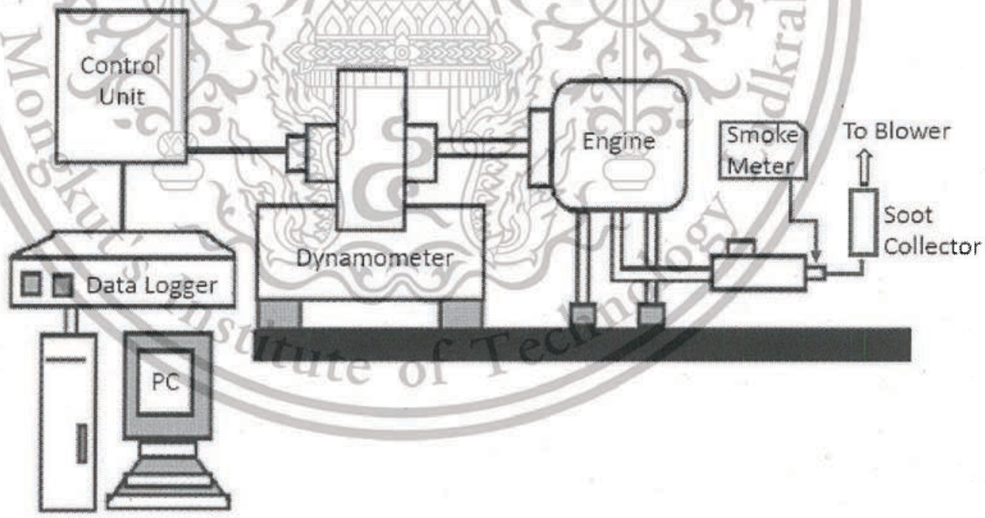


Fig. 3.1 Schematic diagram of engine setup.

Table 3.1. Engine specifications.

Items	Details
Engine Type	1 cylinder, DI, CI, Kubota (RT-140)
Bore x Stroke	(97 x 96) mm
Displacement	709 cm^3
Compression ratio	18:1
Power	9.2 kW @2400 RPM
Injection Timing	19°CA bTDC
Injection Pressure	22 MPa

Table 3.2. Properties of fuels.

Properties	Standard	Diesel
Density @30°C (g/cm^3)	ASTM D4052	0.824
Kinematic viscosity @40°C (mm^2/s)	ASTM D445	3.24
Carbon content (%)	ASTM D5291	85.73
Hydrogen content (%)	ASTM D5291	13.22
Oxygen content (%)	ASTM D5599	0.00
Cetane index	ASTM D4737	60.43
Distillation T10 (°C)	ASTM D8611b	207.7
Distillation T50 (°C)	ASTM D8611b	287.9
Distillation T90 (°C)	ASTM D8611b	352.3

Table 3.3. Properties of blending lubricant.

Test	Method	Result
Density @15°C (g/mL)	ASTM D4052-15	0.8960
Density @30°C (g/mL)	ASTM D4052-15	0.8866
Viscosity @40°C (mm^2/s)	ASTM D445-15a	154.8
Viscosity @100°C (mm^2/s)	ASTM D445-15a	15.05
Magnesium (%wt)	ASTM D6481	0.1816
Zinc (%wt)	ASTM D6481	0.0798
Phosphorous (%wt)	ASTM D6481	0.0856
Flash point (°C)	ASTM D92-12b	248
Pour point (°C)	ASTM D 6749-02	-9
Viscosity index	ASTM D2270	97

3.2 Research Methodology

3.2.1 Physical Characterization of Particulate Matters

Opacity smoke meter determined the smoke intensities of diesel and diesel blending lube oil conditions. Scanning electron microscopy (SEM) was used to investigate the agglomerate structure of particulate matters in micro- scales, as shown in Fig. 3.2.

Transmission Electron Microscopy (TEM) images were used to determine the ultrafine agglomerate primary particle nanostructures, as shown in Fig. 3.3. To investigate the different skeletonized nanostructure of diesel soot and metal oxide ash, ImageJ software was applied to transform the TEM images into skeletonized images. Firstly, (25nm x 25nm) TEM image was cropped into (5nm x 5nm) image. Secondly, (5nm x 5nm) image was transformed into black and white binary images by removing some outliers. Finally, black and white binary image was transformed into skeletonized image. The consequent transformation steps from TEM image to skeletonized images were briefly described in Fig. 3.4.

3.2.2 Chemical Composition Analysis of Particulate Matters

SEM-EDS analysis determined the chemical composition of PM from both blending and without blending lubricant oil condition, as shown in Fig. 3.5. The elemental composition of particulate matters from diesel condition and diesel blending lube oil condition were analyzed using electron dispersive x-ray spectroscopy (TEM – EDS). Regarding to the qualitive analysis of EDS, the electron beam is exerted onto the particles and determined the elements according to x-ray energies.

3.2.3 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 investigated under different operating temperatures (550 °C, 600 °C and 625 °C), as shown in Fig. 3.6. 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. Chemical oxidation reaction of PM mass conversion results can be expressed by Eq.1 and the amount of mass conversion over time can be 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. Activation energy (Ea) can be calculated using Arrhenius equation as in Eq.3. By using Arrhenius plot, Ea and ln (A) can be estimated. Ea is the minimum amount of energy that can overcome the bonding energy between each molecule while ln (A) deals with physical impact such as reaction order and frequency factor of particulate matters.

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$\frac{d\,[C]}{dt} = k[C]^n[O_2]^m \quad (2)$$

$$ln\left(-\frac{d[C]}{dt} \right) = \frac{-E_a}{RT} + (\ln A\,[C]^m\,[O_2]^n\,)] \quad (3)$$

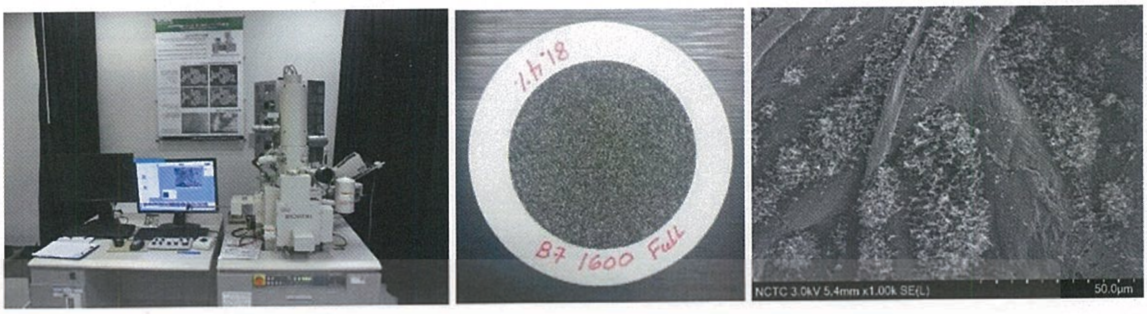


Fig. 3.2 Investigation of agglomerate structure of PM using Scanning Electron Microscopy (SEM).

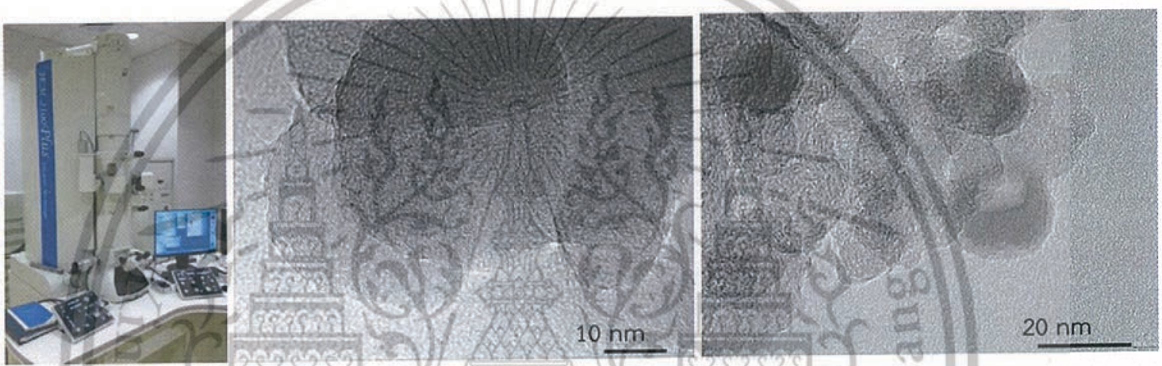


Fig. 3.3 Investigation of single primary nanostructure of PM using Transmission Electron Microscopy (TEM).

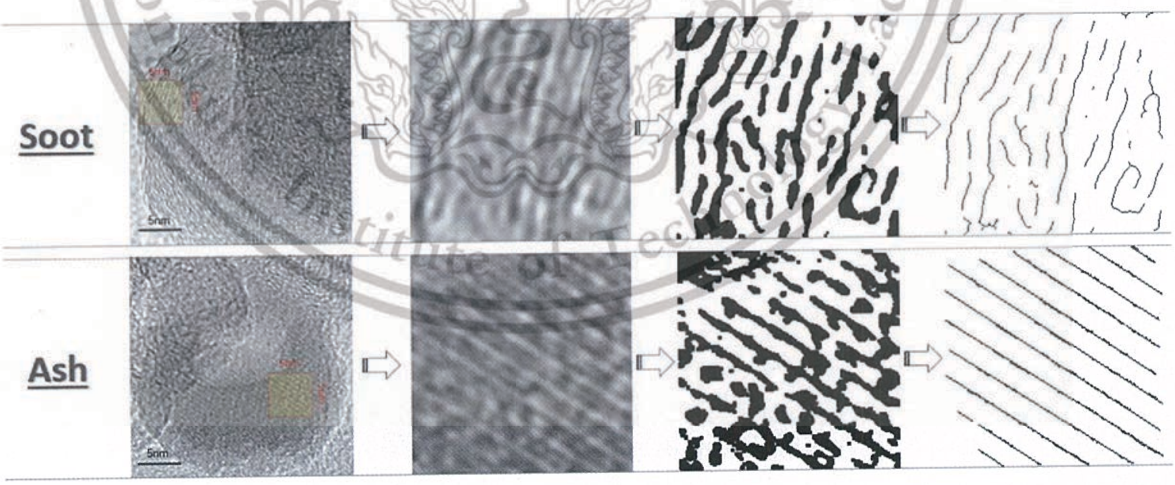


Fig. 3.4 Investigation of skeletonized nanostructure of diesel soot and metal oxide ash using ImageJ program.

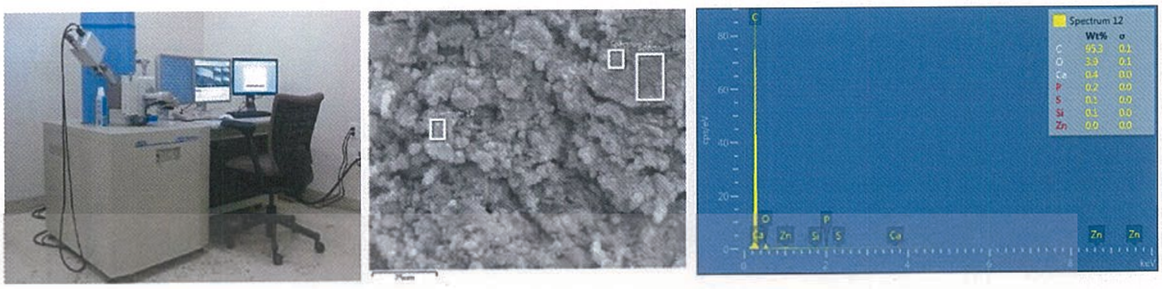


Fig. 3.5 Chemical composition analysis of diesel blending lube oil PMs showing unburned metallic additives by using Electron Dispersive X-ray Spectroscopy (SEM-EDS) analysis.

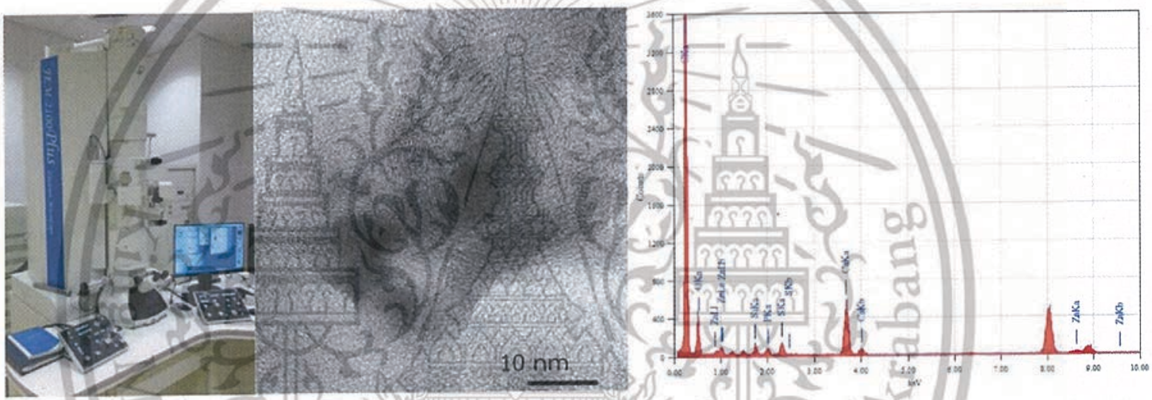


Fig. 3.6 Elemental analysis of EDS spectra focusing on metal oxide ash showing additional metallic elements.

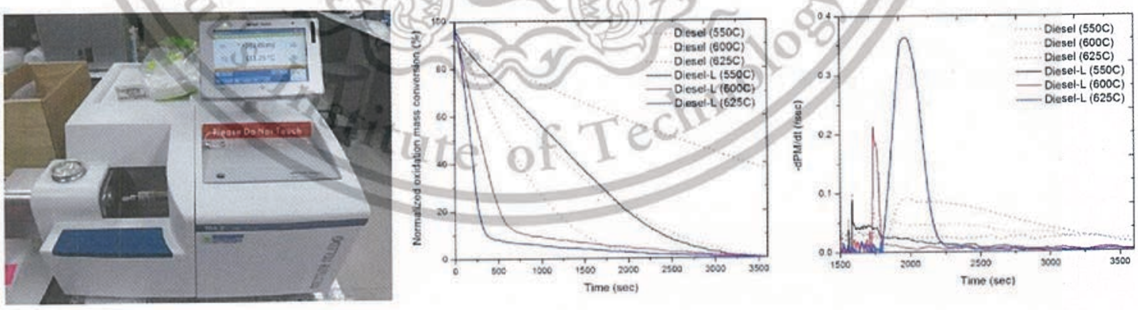


Fig. 3.7 Thermogravimetric analysis of diesel blending lube oil PMs showing faster mass conversion rate due to the influence of metal oxide ash acting as catalysts on soot oxidation kinetics.

Chapter 4

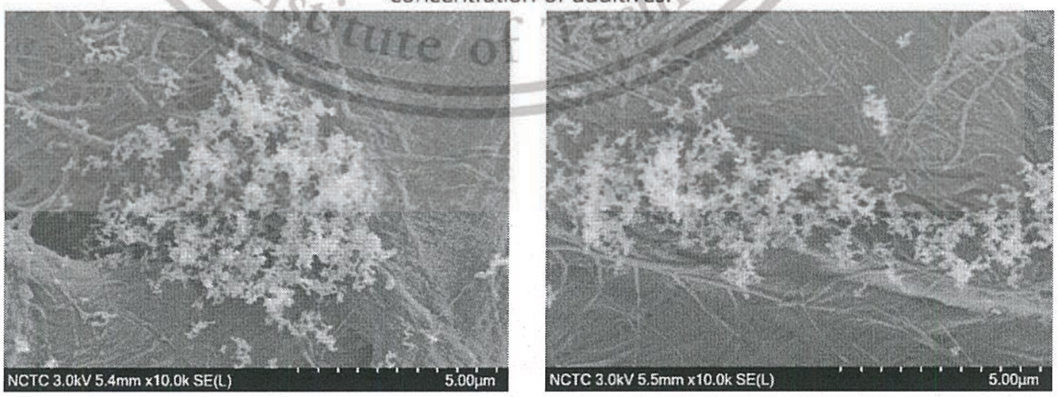
Results and Discussion

4.1 Physical Characterization of Particulate Matters

Opacity smoke meter determined the smoke intensities of diesel and diesel blending lube oil conditions. Diesel blending lubricant condition showed less smoke intensity compared to diesel condition especially in high engine load condition, as shown in Fig. 4.1. The effect of excess metallic acidic composition from blending lubricating oil might promote more complete reaction of fuel and oxygen molecules inside engine combustion chamber. Scanning electron microscopy (SEM) was used to investigate the agglomerate structure of particulate matters in micro- scales. Figure 4.2 (a) describes the agglomerate microstructure of particulate matter from diesel condition and Fig. 4.2 (b) shows the agglomerate microstructure of particulate matter derived from diesel blending lube oil condition respectively. According to the SEM images, the agglomerate structure of lubricant oil related particles has not shown significant different in micro- scales. In other words, the agglomerate structure of lubricant oil related particles was like agglomerate structure of diesel PM.

(a) Diesel black smoke (b) Diesel blending lube oil black smoke

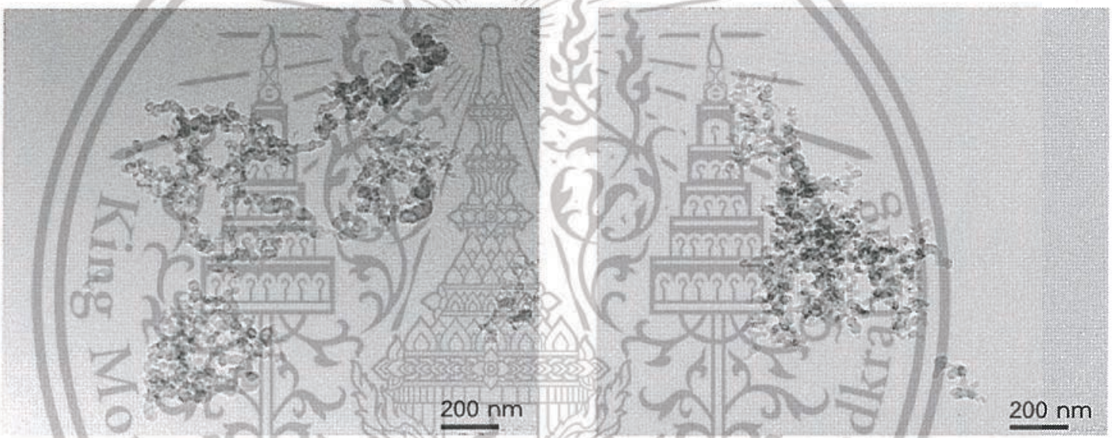
Fig. 4.1 Smoke intensities in the engine's exhaust emission of (a) diesel and (b) diesel blending lube oil with high concentration of additives.



(a) Diesel PM (b) Diesel blending lube oil PM

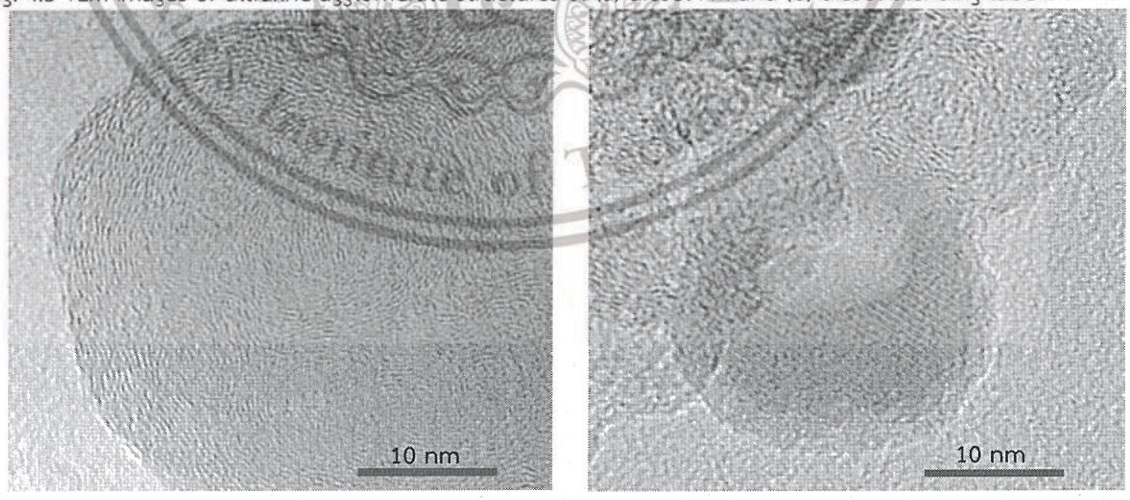
Fig. 4.2 SEM images of agglomerate structure of (a) diesel PM and (b) diesel blending lube oil PM.

Transmission Electron Microscopy (TEM) images were used to determine the ultrafine agglomerate primary particle nanostructures. Soot powders were collected under 2400 rpm engine full load condition since this engine condition is proper able to generate the soot efficiently according to previous smoke intensity results. TEM images 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 particles, as shown in Fig. 4.3. As described in Fig. 4.4 (a), nanostructure of diesel soot is a spherical shape composed of curve line crystallites and the particle sizes are in the range of 10 – 60 nm. Particles from diesel blending lube oil conditions were combined with soot and metal oxide ash as briefly described in Fig. 4.4 (b). Unlike soot, nanostructure of metal oxide ash has shown small crystallites composed of lattice fringes. According to the skeletonized images, primary particle nanostructure of soot is composed of curve line crystallites while the metal oxide ash is composed of lattice fringes, as shown in Fig. 4.5.



(a) Diesel PM (b) Diesel blending lube oil PM

Fig. 4.3 TEM images of ultrafine agglomerate structures of (a) diesel PM and (b) diesel blending lube oil PM.



(a) Diesel PM (b) Diesel blending lube oil PM

Fig. 4.4 TEM images of single primary nanostructure of (a) diesel PM (b) diesel blending lube oil PM.

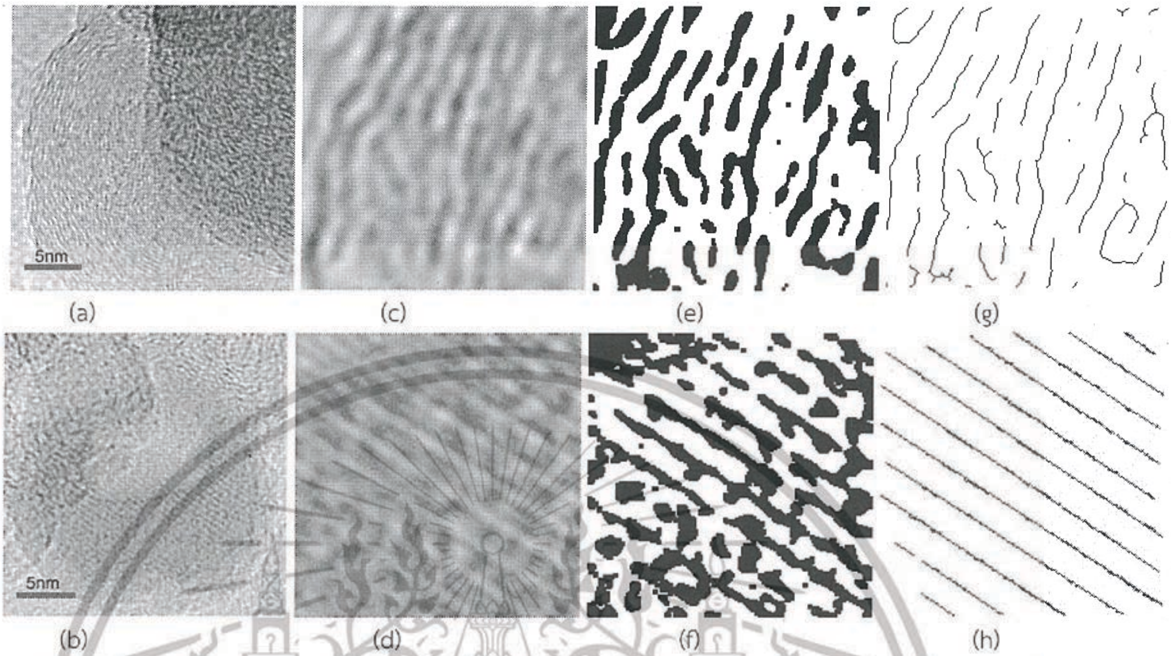
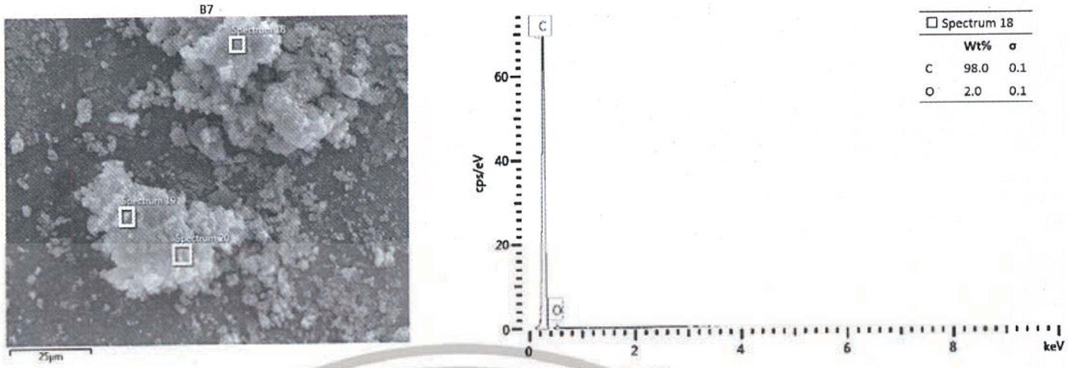


Fig. 4.5 TEM images of (a) soot from diesel, (b) metal oxide ash from diesel blending lube oil, (5nm x 5nm) cropped images of (c) soot, (d) metal oxide ash, black and white binary images of (e) soot, (f) metal oxide ash, skeletonized images of (g) soot and (h) metal oxide ash.

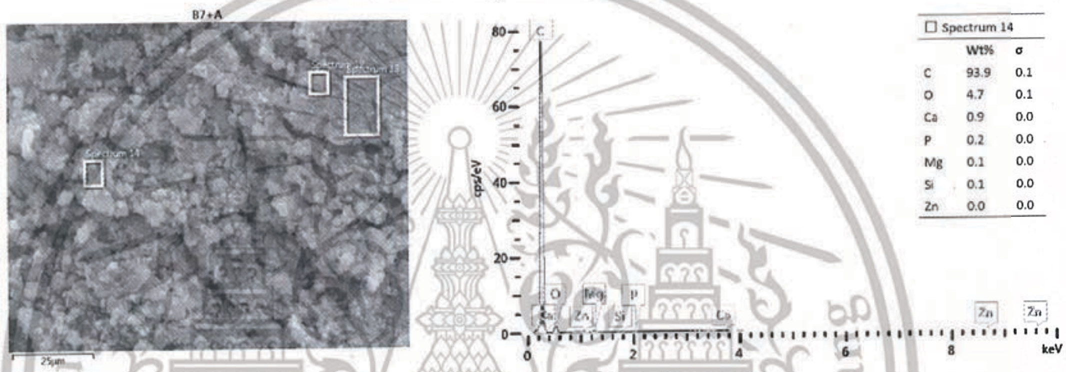
4.2 Chemical Composition Analysis of Particulate Matters

SEM-EDS analysis determined the chemical composition of PM from both blending and without blending lubricant oil condition. Results showed that diesel PM mainly contains elemental composition of Carbon (C) from soot which is unburned hydrocarbon (HC) derived from engine combustion, as shown in Fig. 4.6. However, SEM-EDS result of blending lubricant oil condition showed not only Carbon (C) but also additional metallic elements such as Calcium (Ca), Phosphorous (P), Magnesium (Mg), Silicon (Si) and Zinc (Zn) which all are originated from engine lubricant additives. Therefore, SEM-EDS result pointed out that metallic additives from engine lubricating oil cannot be burned during engine combustion and these metallic elements can be transformed into metal oxide ashes inside diesel particulate filter. Moreover, the contamination of these metal oxide ashes may affect to oxidation kinetics acting as an oxidation catalyst during DPF regeneration process.

The elemental composition of particulate matters from diesel condition and diesel blending lube oil condition were analyzed using electron dispersive x-ray spectroscopy (TEM – EDS). Regarding to the qualitive analysis of EDS, the electron beam is exerted onto the particles and determined the elements according to x-ray energies. As described in Fig. 4.7 (a), pure diesel soot are composed mainly of carbon. However, particles from blending lube oil condition as in Fig. 4.7 (b) contain not only carbon but also unburned metallic additive elements such as Calcium (Ca), Phosphorous (P), Zinc (Zn) and Silicon (Si) which all are derived from incombustible engine lubricating oil additives. Therefore, these unburned metal oxide ashes are composed of metallic elements from lubricants and oxygen as oxides.

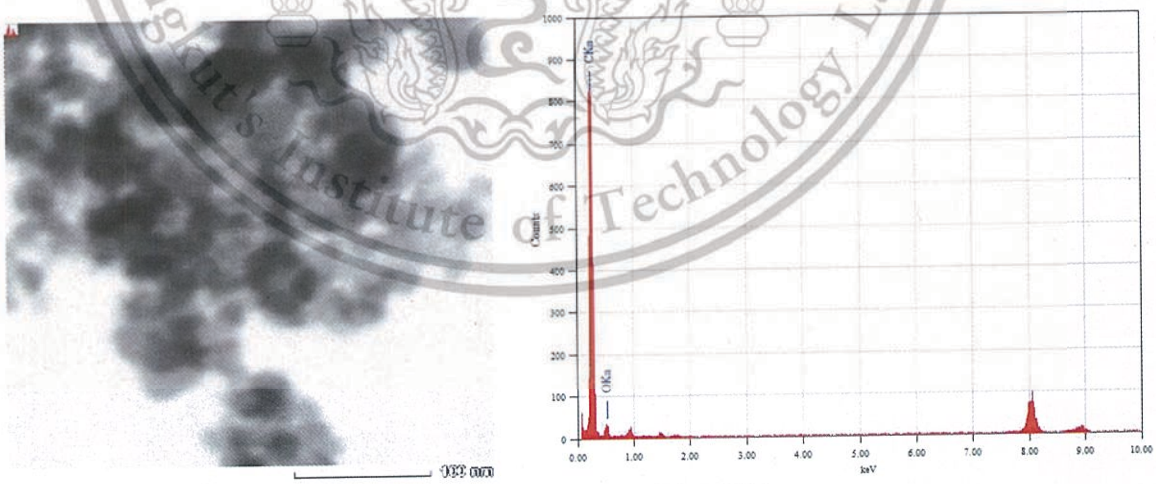


(a) EDS analysis of diesel PM

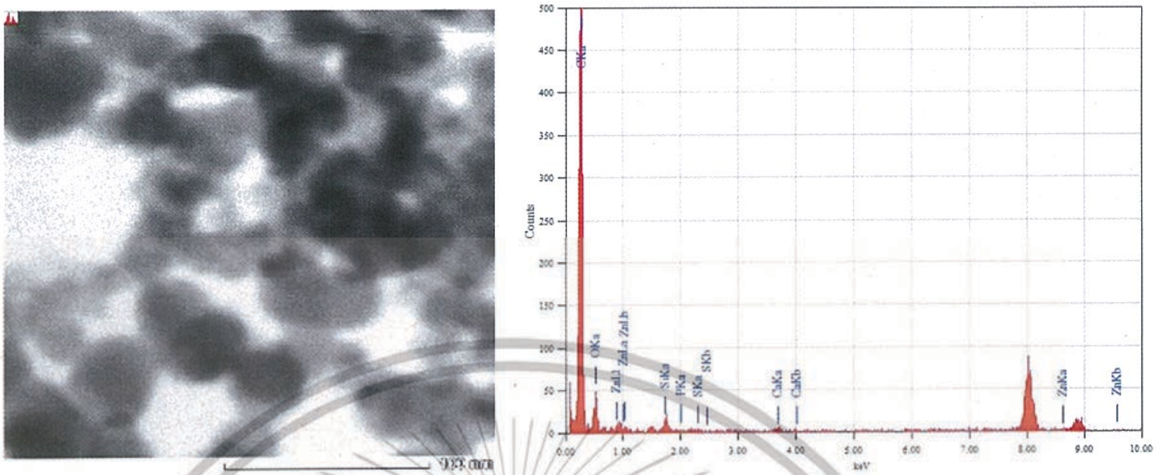


(b) EDS analysis of diesel blending lube oil PM

Fig. 4.6 Chemical composition of (a) diesel PM and (b) diesel blending lube oil PM showing unburned metallic additives from lubricating oil



(a) Elemental Analysis of diesel PM



(b) Elemental Analysis of diesel blending lube oil PM

Fig. 4.7 Elemental analysis of (a) pure diesel soot mainly showing carbon and (b) soot mixed with metal oxide ash showing carbon and incombustible metallic additives

4.3 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 investigated under different operating temperatures. Mass conversion rates can be calculated to describe the faster oxidation kinetics of diesel blending lube oil PMs, as shown in Figs. 4.8 and 4.9.

Regarding to thermogravimetric analysis as described in Fig. 4.8, particles from diesel blending lube oil condition (indicated as diesel-L) were easier to oxidize than neat diesel's particles. The unburned lube oil metallic additives promoted oxidation rate acting as catalyst on soot oxidation kinetics. As shown in Fig. 4.9, mass conversion rates can be calculated to describe the higher mass conversion rate of diesel blending lube oil PMs. Higher mass conversion means faster oxidation kinetics due to the influence of metal oxide ash on the composition of particulate matters.

Apparent activation energy (Ea) can be calculated using Arrhenius equation as in Eq.3. By using Arrhenius plot shown in Fig. 4.10, Ea and ln (A) can be estimated. Activation energy for diesel and diesel-L PMs were 135 and 186 kJ/mol respectively. Physical impact (ln A $[C]^m$ $[O2]^n$) of diesel and diesel-L PMs were 13 and 21 respectively, as shown in Table 4.1. Although the oxidation kinetics of diesel blending lube oil PM were faster, activation energy of diesel blending lube oil is merely higher than diesel PM. In fact, the physical impact (nano- primary particle size, reaction order and frequency factor) of diesel-L PM were greater than diesel PM. The pre-exponential factor ln A was dependent upon physical impact of PMs. According to the Eq.3, the more ln (A) leads to the greater the oxidation rate. Therefore, the physical impact; (ln A $[C]^m$ $[O2]^n$) play more important role than activation energy to increase the PM mass conversion rate in this research.

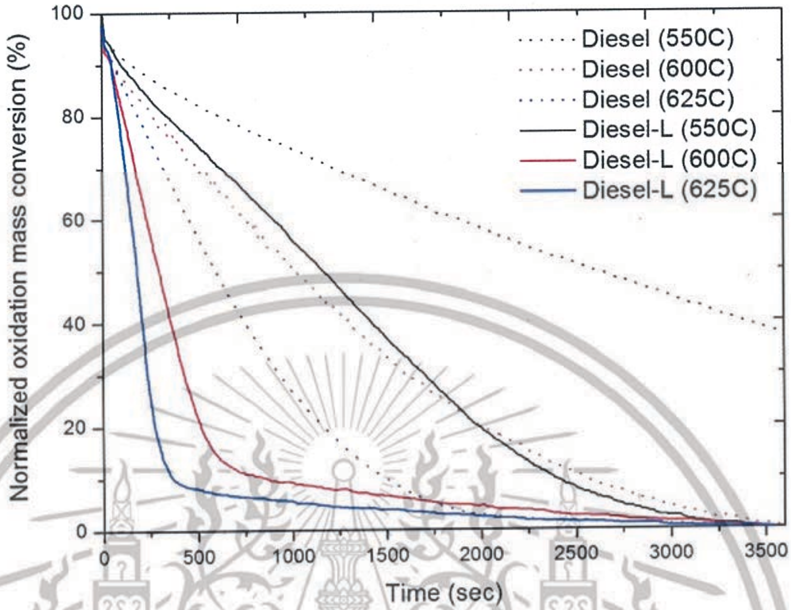


Fig. 4.8 Mass conversion of PM using TGA isothermal method with pure air.

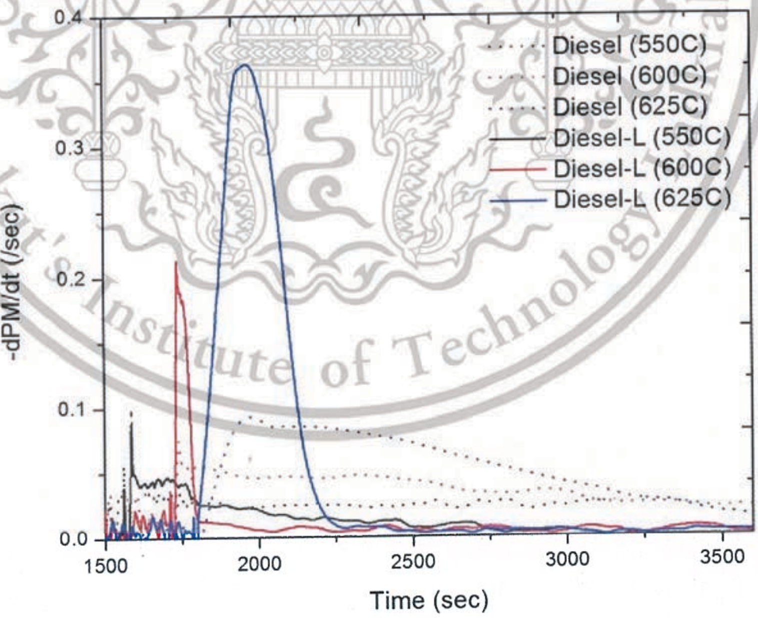


Fig. 4.9 Mass conversion rates of PM using TGA isothermal method with pure air.

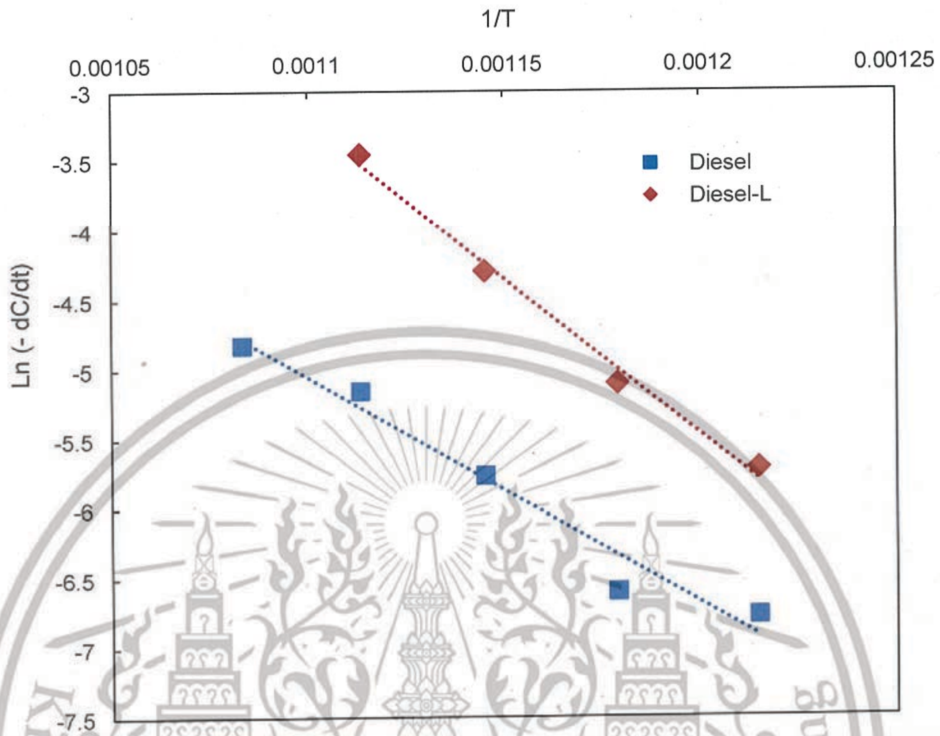


Fig. 4.10 Arrhenius plot of diesel and diesel-L PMs oxidation using TGA isothermal method with pure air.

Table. 4.1 Apparent activation energy of diesel and diesel-L PMs calculated from Arrhenius plots

50% burned	E_a (kJ/mol)	$(\ln A\,[C]^m\,[O_2]^n)$
Diesel	135.35	12.85
Diesel-L	186.18	21.40

Chapter 5
Conclusions

Physical and chemical characterization of particulate matters influenced by engine oil additives were successfully studied using electron microscopy, electron dispersive x-ray spectroscopy and thermogravimetric analysis. The designed lubricant containing higher concentration of additives were blended directly into the diesel fuel directly. The purpose of blending designed lubricant directly into diesel is to obtain the higher composition of metal oxide ash among PM composition since these metal oxide ashes are mainly originated from lubricant additives.

Smoke intensity of diesel blending lubricant condition were lower soot concentration than diesel condition. The impact of excess metallic acidic composition from blending lubricating oil might promote more complete combustion. The agglomerate structure in micro- scales and ultrafine agglomerate particles of diesel blending lube oil PMs were not significant different to diesel PM. However, single primary nanostructure of diesel soot is a spherical shape composed of curved line crystallites and the particle sizes were in the range of 10 – 60 nm. In diesel blending lube oil condition, metal oxide ashes were combined with soot since these metal oxide ashes are mainly originated from lubricant additives. Unlike soot, the nanostructure of metal oxide ash is composed of lattice fringes with round outlines. Skeletonized nanostructure of soot is composed of curve line crystallites while the metal oxide ash is composed of parallel straight-line hatch patterns.

Chemical composition analysis of SEM-EDS proved that metallic additives from lubricating oil cannot be burned by combustion and these unburned metallic additives might be transformed into metal oxide ash. Elemental analysis of TEM-EDS results showed that diesel soot mainly contain carbon while focusing spectrum on ash was composed of additional metallic elements and oxygen to become metal oxide ash. Oxidation kinetics of diesel blending lube oil PM were easier to oxidize than diesel PM. The influence of contamination of metal oxide ash on PM might promote oxidation rate acting as catalyst on soot oxidation kinetics. Although diesel blending lube oil PMs have faster oxidation rate, the activation energy needed for diesel PM is lower than diesel blending lube oil PMs due to greater physical impacts of diesel blending lube oil PM during oxidation process.

Chapter 6

Research Publications

P. Koko, P. Karin, S. Rungsritanapaisan, R. Tongsri and K. Hanamura, "Impact of Engine Oil's Additives on Particulate Matter's Micro- and Nanostructure using Electron Microscopy Image Analysis", The 10th International Conference on Materials Science and Technology, 6-7 September 2018, Bangkok Thailand, and Key Engineering Materials, Trans Tech Publications, 2019, In press.

P. Koko, P. Karin, E. Saenkhumvong, C. Charoenphonphanich, W. Phairote, N. Chollacoop and K. Hanamura, "Influence of Metal Oxide Ashes on Soot Oxidation Kinetics and Nanostructure using Electron Microscopy and Thermogravimetric Analysis", The 9th TSME International Conference on Mechanical Engineering, AME0021, 11-14 December 2018, Phuket, Thailand.

References

[1] Peter Eastwood, 2008, Particle Emission from Vehicles, John Wiley & Sons, Ltd, England.

[2] Myung C L and Park S, 2012, Exhaust Nanoparticle Emissions from Internal Combustion Engines: A Review, International Journal of Automotive Technology, Vol. 13, No.1, pp.9-22.

[3] Mohankumar S and Senthilkumar P, 2017, Particulate Matter Formation and its Control Methodologies for Diesel Engine: A Comprehensive Review, Renewable and Sustainable Energy Reviews, Vol. 80, pp.1227-1238.

[4] Myung C L, Ko A and Park S, 2014, Review on Characterization of Nano-particle Emissions and PM Morphology from Internal Combustion Engines: Part 1, International Journal of Automotive Technology, Vol. 15, No. 2, pp. 203-218.

[5] Leslie R Rudnick, 2008, Lubricant Additives Chemistry and Applications, Taylor & Franscis Group, London, New York.

[6] Tornehed P and Olofsson U, 2011, Lubricant Ash Particles in Diesel Engine Exhaust: Literature Review and Modelling Study, Proceedings of the Institution of Mechanical Engineers, Journal of Automotive Engineering, Vol. 225, Part D, pp. 1055-1066.

[7] Karin P, 2017, Morphology and Oxidation Kinetics of CI Engine's Biodiesel Particulate Matters on Cordierite Diesel Particulate Filters using TGA, International Journal of Automotive Technology, Vol. 18, No.1, pp. 31-40.

[8] Karin P, 2015, Oxidation Kinetics of Small CI Engine's Biodiesel Particulate Matter, International Journal of Automotive Technology, Vol. 16, No.2, pp. 211-219.

[9] Karin P, Oki H, Hanamura K and Charoenphonphanich C, 2012, Nanostructures and Oxidation Kinetics of Diesel Particulate Matters, Journal of Research and Applications in Mechanical Engineering, Vol. 1, No.2, pp. 3-8.

[10] Vouitsis E, 2007, Effect of Lube Oil on the Physicochemical Characteristics of Particulate Matter Emitted from a Euro 4 Light Duty Diesel Vehicle, SAE Technical Paper 2007-24-0110.

[11] Tan P, 2017, Effect of Lubricant Sulphur on the Morphology and Elemental Composition of Diesel Exhaust Particles, Journal of Environmental Sciences, pp. 354-362.

[12] Wang Y, Liang X, Shu G, Dong L, Sun X, Yu H and Wang Y, 2015, Effects of an Anti-wear Oil Additive on the Size Distribution, Morphology, and Nanostructure of Diesel Exhaust Particles, Tribology International, Vol. 92, pp. 379-386.

[13] A. Liati, P. Dimopoulos Eggenchwiler, D. Müller Gubler, Schreiber and M. Aguirre, 2012. Investigation of Diesel Ash Particulate Matter: A Scanning Electron Microscope and Transmission Electron Microscope Study, Atmospheric Environment, Vol. 49, pp. 391-402.

[14] Karin P, 2015, Oxidation Kinetics of Small CI Engine's Biodiesel Particulate Matter, International Journal of Automotive Technology, Vol. 16, No.2, pp. 211-219.

[15] Jung H, 2003, The Influence of Engine Lubricating Oil on Diesel Nanoparticle Emissions and Kinetics of Oxidation, SAE Technical Paper 2003-01-3179.

Appendix

Appendix A
Research Publications

- P. Koko, P. Karin, S. Rungsritanapaisan, R. Tongsri and K. Hanamura, "Impact of Engine Oil's Additives on Particulate Matter's Micro- and Nanostructure using Electron Microscopy Image Analysis", The 10th International Conference on Materials Science and Technology, 6-7 September 2018, Bangkok Thailand, and Key Engineering Materials, Trans Tech Publications, 2019, In press.
- P. Koko, P. Karin, E. Saenkhumvong, C. Charoenphonphanich, W. Phairote, N. Chollacoop and K. Hanamura, "Influence of Metal Oxide Ashes on Soot Oxidation Kinetics and Nanostructure using Electron Microscopy and Thermogravimetric Analysis", The 9th TSME International Conference on Mechanical Engineering, AME0021, 11-14 December 2018, Phuket, Thailand.

Impact of Engine Oil's Additives on Particulate Matter's Micro- and Nanostructure using Electron Microscopy Image Analysis

Phyozin Koko[1, a], Preechar Karin[1, b*], Sippakorn Rungsritanapaisan[1, c], Ruangdaj Tongsri[2, d] and Katsunori Hanamura[3, e]

[1] Automotive Engineering Program, International College, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
[2] National Metal and Materials Technology Center, National Science and Technology Development Agency, Pathumthani 12120, Thailand
[3] School of Engineering, Tokyo Institute of Technology, Tokyo 152-8552, Japan

[b*]preechar.ka@kmitl.ac.th

Keywords: Diesel Engine, Particulate Matter, Metal Oxide Ash, SEM-EDS, TEM

Abstract. According to increasingly stringent emission regulations on particle emissions from automotive vehicles, a diesel engine must be equipped with diesel particulate filter (DPF) to trap the particulate matters (PMs) which can be harmful to human health. Morphology and chemical composition of particulate matters were successfully studied using electron microscopy and electron dispersive x-ray spectroscopy (EDS) analysis. Microstructure of particulate matters derived from diesel blending lubricating oil were not significant different compared to diesel PM. Nanostructure of soot is a spherical shape composed of curve line crystallites and the particle sizes were in the range of 10 – 60 nm while the metal oxide ash is composed of lattice fringes. Chemical composition analysis of EDS result showed that metallic additives from lubricating oil cannot be burned during combustion and might be transformed into metal oxide ash.

1. Introduction

Diesel engine has higher thermal efficiency among internal combustion engines (ICEs) used in automobiles due to attaining higher compression ratio. However, diesel engines trail black smokes containing much amount of particulate matter (PM) resulting from incomplete combustion around single fuel droplets and are very harmful to human health such as lung cancer, asthma and so on. PM are composed primarily of unburned hydrocarbon, pure carbon (soot) and metal oxide ash as solid fractions. Each PM fraction is mainly dependent upon the chemical properties of fuel and lubricant, engine operating conditions, engine wear and exhaust after-treatment technologies [1 – 4].

One of the exhaust aftertreatment systems, diesel particulate filter (DPF) is an effective solution for reducing particle emission. DPF can trap up to (99%) of the PM emitted from the exhaust gas and a process which can oxidize the trapped soot into carbon dioxide is called regeneration process of DPF. Although regeneration process can burn the soot effectively, incombustible metal oxide ashes will be remained at the inlet channels of DPF and causing engine back pressure. These metal oxide ashes are mainly derived from lubricant additives, engine wear and a very few amounts of trace metals from the fuel [5, 6].

During combustion, lubricants can also participate inside engine cylinder and affect the composition of PM emission. Some literatures have already investigated about the impacts of lubricating oil contamination on particle emissions focusing on not only physical characterization but also chemical composition. 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. Besides, oil-related particles have larger aggregate size than diesel particles [7 – 9].

P. Karin et al., investigated that the nanostructure of soot (Carbon) and ash (Calcium) by comparing the PM from engine and diesel lamp. The pattern of soot or carbon crystallites looks like a curve line where as the ash crystallite looks like a straight cross line pattern with round outlines. The average diameter of soot single primary nanoparticles emitted from engine are in the range of 10 – 60 nm. The chemical composition and morphology of lubricant derived ash have also been reported. The individual ash particles have round shapes and sizes of approximately 10 – 200 nm [10 – 12].

The objectives of this article are to investigate the physical and chemical characterization of diesel particulate matters which are influenced by the impact of engine oil's additives using electron microscopy and electron dispersive x-ray spectroscopy (EDS) analysis. Nanostructure of metal oxide ash would be briefly discussed which is still not briefly found out among previous literatures.

2. Experimental

Table 1: Engine specification

Items	Details
Engine type	1-cylinder, DI, CI engine
Bore x Stroke	(97 x 96) mm
Displacement	709 cm^3
Compression ratio	18:1
Power	9.2 kW @2400 RPM
Injection timing	19°CA bTDC

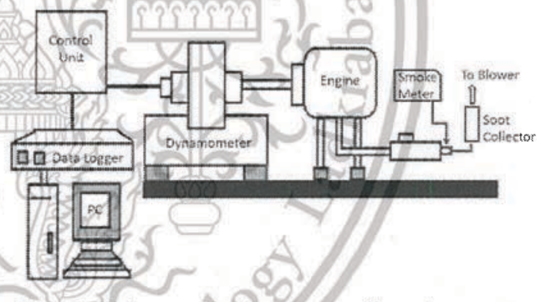


Fig. 1 Schematic diagram of engine setup

Table 2: Properties of diesel fuel

Fuel properties	Unit	Result
Chemical formula	-	$C_{14.2}H_{28}$
Auto ignition temperature	°C	288
Calorific value	kJ/kg	46,180
Heat of vaporization	kJ/kg	250
Density at 25 °C	kg/m^3	844.8
Viscosity at 40 °C	mm^2/s	3.0
Stoichiometric A/F ratio	-	14.7
Distillation temperature		
T10	°C	214.3
T50	°C	281.5
T70	°C	352.3

Table 3: Properties of 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	cSt	154.8
Viscosity @100°C	ASTM D445-15a	cSt	15.05
Magnesium	ASTM D6481	%wt	0.1816
Zinc	ASTM D6481	%wt	0.0798
Phosphorous	ASTM D6481	%wt	0.0856
Pour point	ASTM D 6749-02	°C	-9
Viscosity index	ASTM D2270	-	97

A single cylinder natural aspirated direct injection compression engine (Kubota – RT140) was used to generate the particulate matter (PM). The engine specification are described in Table 1. Eddy current engine dynamometer was used to control the various engine speed and load conditions by the aid of Lab-view program. To measure the smoke intensity of the exhaust emission, opacity smoke meter (Okuda DSM – 240) was introduced between the exhaust muffler's outlet and the blower as described in figure 1. Paper filter was inserted into the smoke meter to measure the soot contamination percentage. A soot collector containing metal netting was used to collect the soot powder.

To conduct the experiment, conventional diesel was used as an ideal fuel and secondly, designed lubricant oil containing excess amount of Calcium (Ca) additives were blended directly into the diesel fuel. The blending condition is the amount of 10% by mass directly into the diesel fuel. The purpose of blending designed lubricant containing excess additives is to obtain more ash formation among PM composition since these metal oxide ashes are mainly originated from engine oil's additives. Chemical properties of diesel fuel and blending lubricating oil are briefly described in Table 2 and 3. For the engine lubricating system, conventional lubricant 15W-40 API CI-4/SL synthetic engine oil was used.

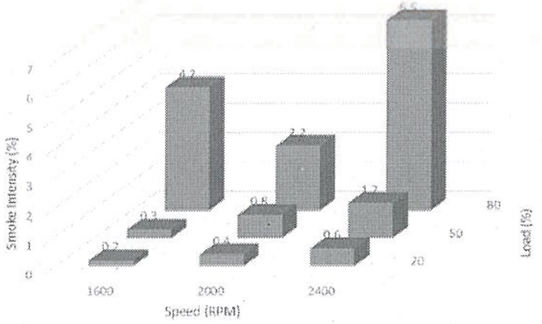
3. Results and Discussion

3.1 Smoke Intensity

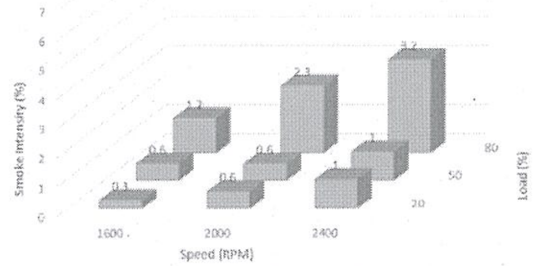
Opacity smoke meter determined the smoke intensities of diesel and diesel blending lube oil conditions as shown in figure 2. Diesel blending lubricant condition showed less smoke intensity compared to diesel condition especially in high engine load condition. Less smoke intensity means less soot contamination. Lubricating oils are basically formulated with metallic additives and acidic compositions. During engine combustion, the effect of excess metallic acidic composition from blending lubricating oil might promote more complete reaction of fuel and oxygen molecules.

3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to investigate the agglomerate structure of particulate matters in micro- scales. Figure 3 (a) describes the agglomerate microstructure of particulate matter from diesel condition and figure 3 (b) shows the agglomerate microstructure of particulate matter derived from diesel blending lube oil condition respectively. According to the SEM images, the agglomerate structure of lubricant oil related particles have not shown significant different in micro- scales.

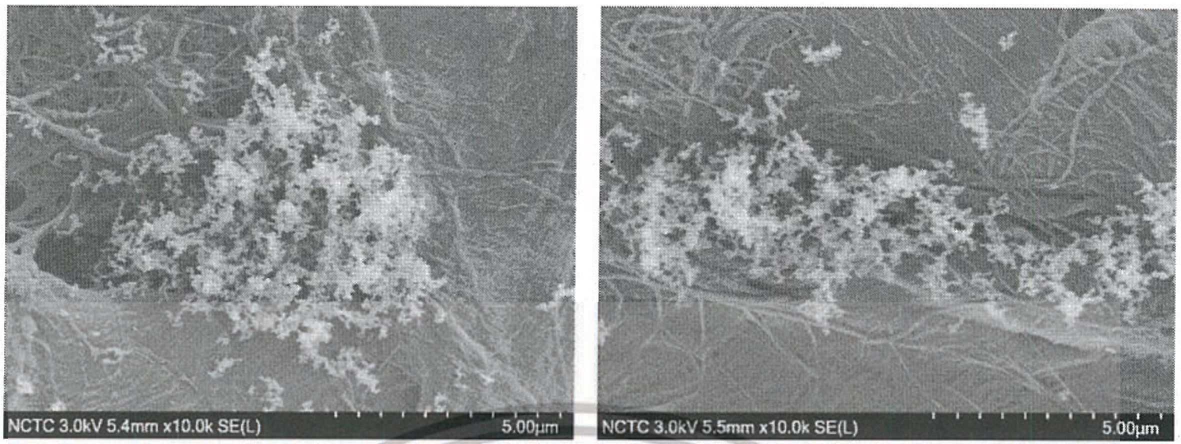


(a) Diesel black smoke



(b) Diesel blending lube oil black smoke

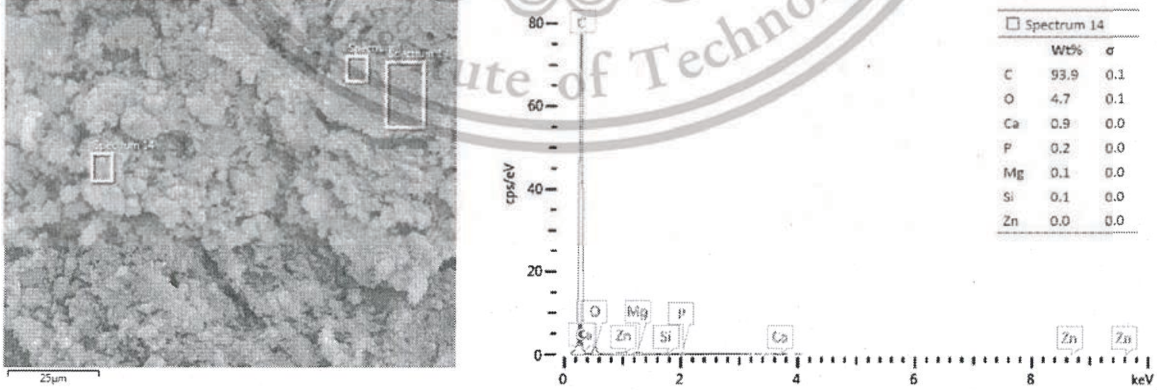
Fig. 2 Smoke intensities in the engine's exhaust emission of (a) diesel and (b) diesel blending lube oil with high concentration of additives



(a) Diesel PM (b) Diesel blending lube oil PM

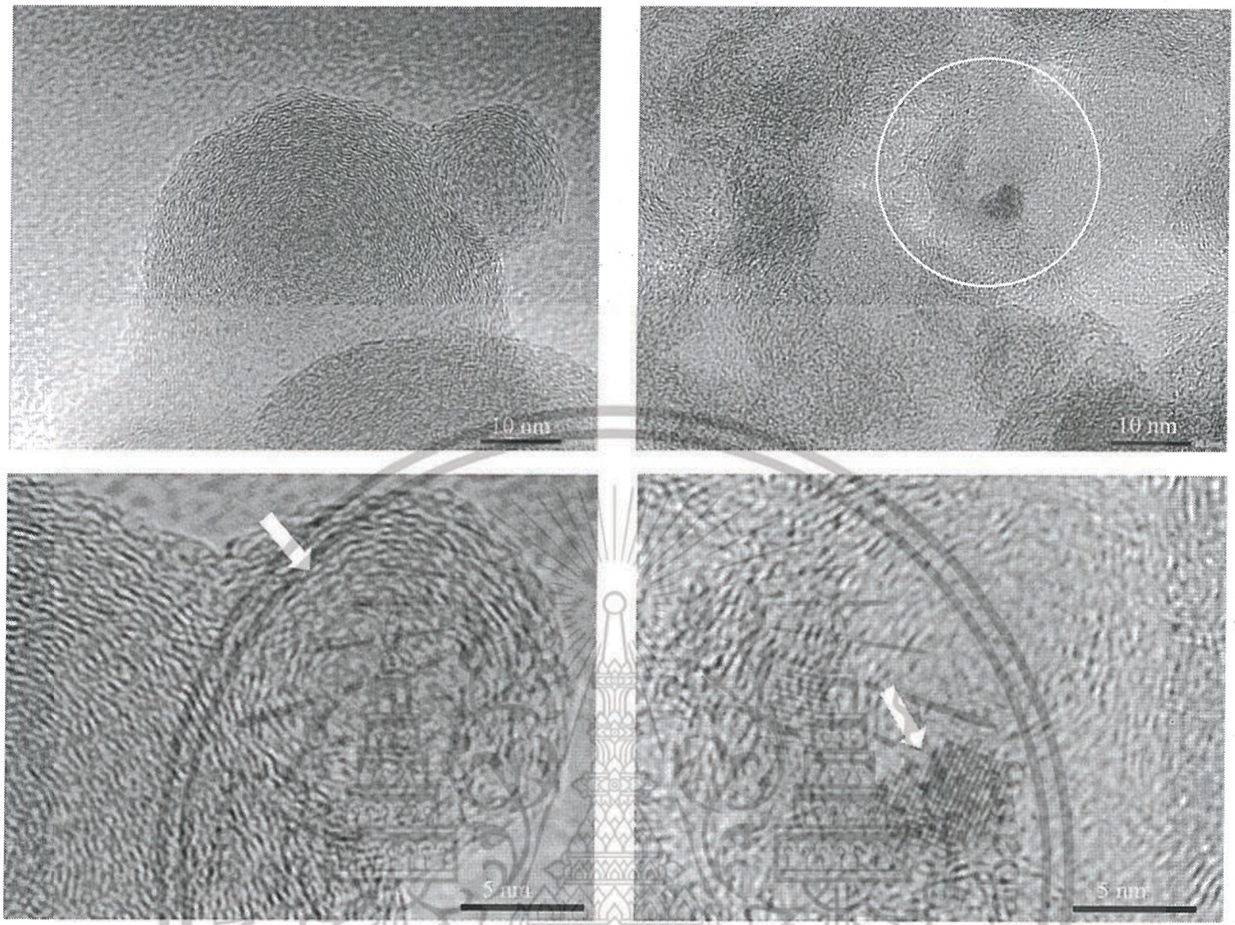
Fig. 3 SEM images of agglomerate structure of (a) diesel PM and (b) diesel blending lube oil PM under 2000 rpm engine full load condition

(a) EDS analysis of diesel PM



(b) EDS analysis of diesel blending lube oil PM

Fig. 4 Chemical composition of (a) diesel PM and (b) diesel blending lube oil PM showing unburned metallic additives from lubricating oil.



(a) Diesel PM (b) Diesel blending lube oil PM

Fig. 5 TEM images of (a) diesel soot nanostructure showing curve line crystallites and (b) nanostructure of metal oxide ash showing lattice fringes

3.3 Electron Dispersive X-ray Spectroscopy (SEM-EDS)

SEM-EDS analysis determined the chemical composition of PMs from diesel and diesel blending lube oil conditions as shown in figure 4 (a and b). Diesel PMs were mainly composed of chemical composition of Carbon (C) from soot. However, chemical composition of particulate matters from diesel blending lube oil conditions contain not only Carbon (C) but also unburned metallic elements such as Calcium (Ca), Phosphorous (P), Magnesium (Mg), Silicon (Si) and Zinc (Zn) which all are derived from lubricant additives as shown in figure 4 (b). Therefore, SEM-EDS results pointed out that metallic additives from engine lubricating oil cannot be burned during combustion and these metallic elements can be transformed into metal oxide ashes.

3.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) was used to investigate the single primary nanostructures of diesel and diesel blending lube oil PMs as shown in figures 5 (a and b). Particulate matters were collected under 2400 rpm engine full load condition and 800k magnification was introduced to observe the nanostructure of primary particles. As described in figure 5 (a), nanostructure of diesel soot is a spherical shape composed of curve line crystallites and the particle sizes are in the range of 10 – 60 nm. Particles from diesel blending lube oil conditions were combined together with soot and metal oxide ash as briefly described in figure 5 (b). Unlike soot, nanostructure of metal oxide ash has shown small crystallites composed of lattice fringes.

4. Conclusion

Soot contamination of blending lubricant oil condition showed lower percentage than neat diesel condition especially in high engine load conditions. The effect of excess metallic acidic composition from blending lubricating oil might promote more complete reaction of fuel and oxygen molecules inside engine combustion chamber. As physical characterization, the agglomerate structures of diesel PM and diesel blending lube oil PM are not significant different in micro- scales. However, the single primary nanostructure of soot is a spherical shape composed of curve line crystallites and particle sizes are in the range of 10 – 60 nm while the nanostructure of metal oxide ash is composed of lattice fringes. Chemical composition of particulate matters from diesel blending lube oil condition showed that metallic additives from engine lubricating oil cannot be burned by engine combustion and these unburned metallic components might be transformed into metal oxide ash.

5. Acknowledgements

The author would like to acknowledge to International College, King Mongkut's Institute of Technology Ladkrabang (KMITL) for research funding and also Bangchak Corporation Public Company Limited (BCP) for supporting designed lubricant to accomplish this research.

6. References

[1] J. B. Heywood. (1998). Internal Combustion Engine Fundamentals, McGraw-Hill series in mechanical engineering, Singapore.

[2] Peter Eastwood. (2008). Particle Emission from Vehicles, John Wiley & Sons, Ltd, England.

[3] C. L. Myung and S. Park (2012). Exhaust Nanoparticle Emissions from Internal Combustion Engines: A Review, International Journal of Automotive Technology, Vol. 13, No.1, pp.9-22.

[4] C. L. Myung, A. Ko and S. Park. (2014). Review on Characterization of Nano-particle Emissions and PM Morphology from Internal Combustion Engines: Part 1, International Journal of Automotive Technology, Vol. 15, No. 2, pp. 203-218.

[5] S. Mohankumar and P. Senthilkumar. (2017). Particulate Matter Formation and its Control Methodologies for Diesel Engine: A Comprehensive Review, Renewable and Sustainable Energy Reviews, Vol. 80, pp.1227-1238.

[6] K. Hanamura, P. Karin, L. Cui, P. Rubio, T. Tsuruta, T. Tanka and T. Suzuki. (2009). Micro- and Macroscopic Visualization of Particulate Matter Trapping and Regeneration Processes in Wall-flow Diesel Particulate Filters, International Journal of Engine Research, Vol. 10, pp. 305-321.

[7] P. Tornehed and U. Olofsson. (2011). Lubricant Ash Particles in Diesel Engine Exhaust: Literature Review and Modelling Study, Proceedings of the Institution of Mechanical Engineers, Journal of Automotive Engineering, Vol. 225, Part D, pp. 1055-1066.

[8] Y. Wang, X. Liang, G. Shu, L. Dong, X. Sun and H. Yu. (2015). Effects of an Anti-wear Oil Additive on the Size Distribution, Morphology, and Nanostructure of Diesel Exhaust Particles, Tribology International, Vol. 92, pp. 379-386.

[9] Y. Wang, X. Liang, G. Shu and L. Dong. (2015). Impact of Lubricating Oil on Morphology of Particles from a Diesel Engine, Energy Procedia, Vol.75, pp. 2388-2393.

[10] P. Karin, H. Oki, K. Hanamura and C. Charoenphonphanich. (2012). Nanostructures and Oxidation Kinetics of Diesel Particulate Matters, An International Journal of the Thai Society of Mechanical Engineers, Vol. 1, No.2, pp. 3-8.

[11] P. Karin, J. Boonsakda, K. Siricholathum, E. Saenkhumvong, C. Charoenphonphanich and K. Hanamura. (2017). Morphology and Oxidation Kinetics of CI Engine's Biodiesel Particulate Matters on Cordierite Diesel Particulate Filters using TGA, International Journal of Automotive Technology, Vol. 18, No. 1, pp. 31-40.

[12] A. Liati, P. Dimopoulos Eggenchwiler, D. Müller Gubler, Schreiber and M. Aguirre. (2012). Investigation of Diesel Ash Particulate Matter: A Scanning Electron Microscope and Transmission Electron Microscope Study, Atmospheric Environment, Vol. 49, pp. 391-402.

AME0021

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

P. Koko[1,*], P. Karin[1], E. Saenkhumvong[2], C. Charoenphonphanich[2], W. Phairote[2], N. Chollacoop[3] and K. Hanamura[4]

[1]Automotive Engineering Program, International College, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520, Thailand
[2]Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
[3]National Metal and Materials Technology Center, National Science and Technology Development Agency, Pathumthani 12120, Thailand
[4]Department of Mechanical Engineering, School of Engineering, Tokyo Institute of Technology, Tokyo 152-8550, Japan

* Corresponding Author: E-mail: phyozin.mech@gmail.com

Abstract. According to increasingly stringent regulations on particulate emission from automotive vehicles, diesel engine has to 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.

Keywords: Diesel Particulate Matter, Metal Oxide Ash, TEM, TGA

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 also a very few amount 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 also 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 - 15].

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

Table 1: Engine Specification

Items	Details
Engine Type	1-cylinder, Direct Injection, CI engine
Bore x Stroke	(97 x 96) mm
Displacement	709 cm^3
Compression ratio	18:1
Power	9.2 kW @2400 RPM
Injection Timing	19°CA bTDC
Injection Pressure	22 MPa

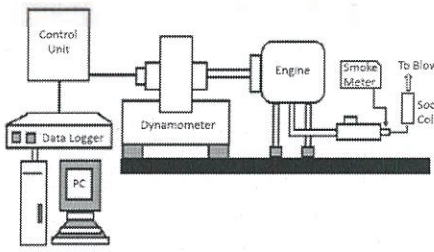


Fig. 1. Schematic diagram of engine setup

Table 2: Properties of fuel (Diesel)

Fuel Properties	Unit	Result
Chemical Formula	-	$C_{14.2}H_{28}$
Auto Ignition Temperature	°C	288
Calorific Value	kJ/kg	46180
Heat of Vaporization	kJ/kg	250
Viscosity	mm^2/s	3.0
Stoichiometric A/F ratio	-	12.3
Density	kg/m^3	844.8

Table 3: Properties of 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	mm^2/s	154.8
Viscosity @100°C	ASTM D445-15a	mm^2/s	15.05
Magnesium	ASTM D6481	%wt	0.1816
Zinc	ASTM D6481	%wt	0.0798
Phosphorous	ASTM D6481	%wt	0.0856

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. Lab-View program controlled the engine dynamometer. A soot collector which contains metal netting inside was used to collect the PM. The schematic diagram of the engine setup are shown in figure 1. To conduct the experiment, commercial diesel containing ($C_{14.2}H_{28}$) 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 $CaSO_4$ 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

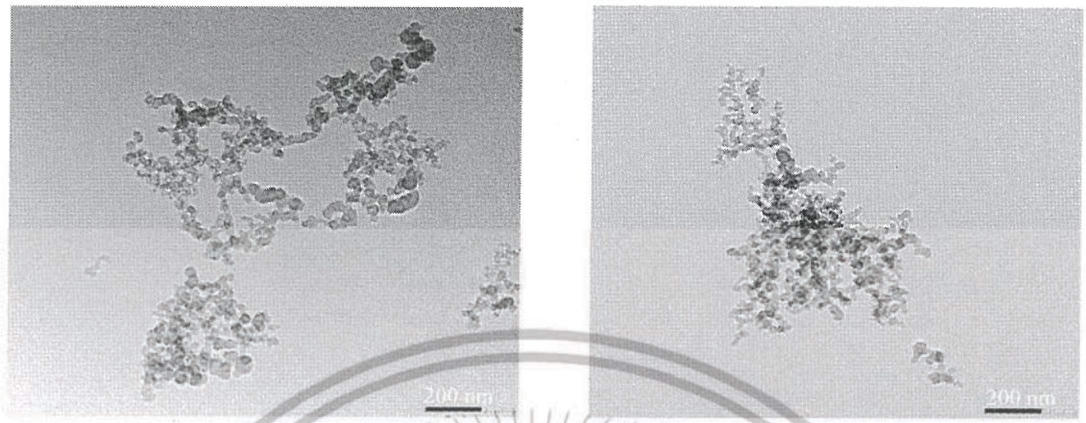
3.1 Morphology of ultrafine agglomerate particles

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

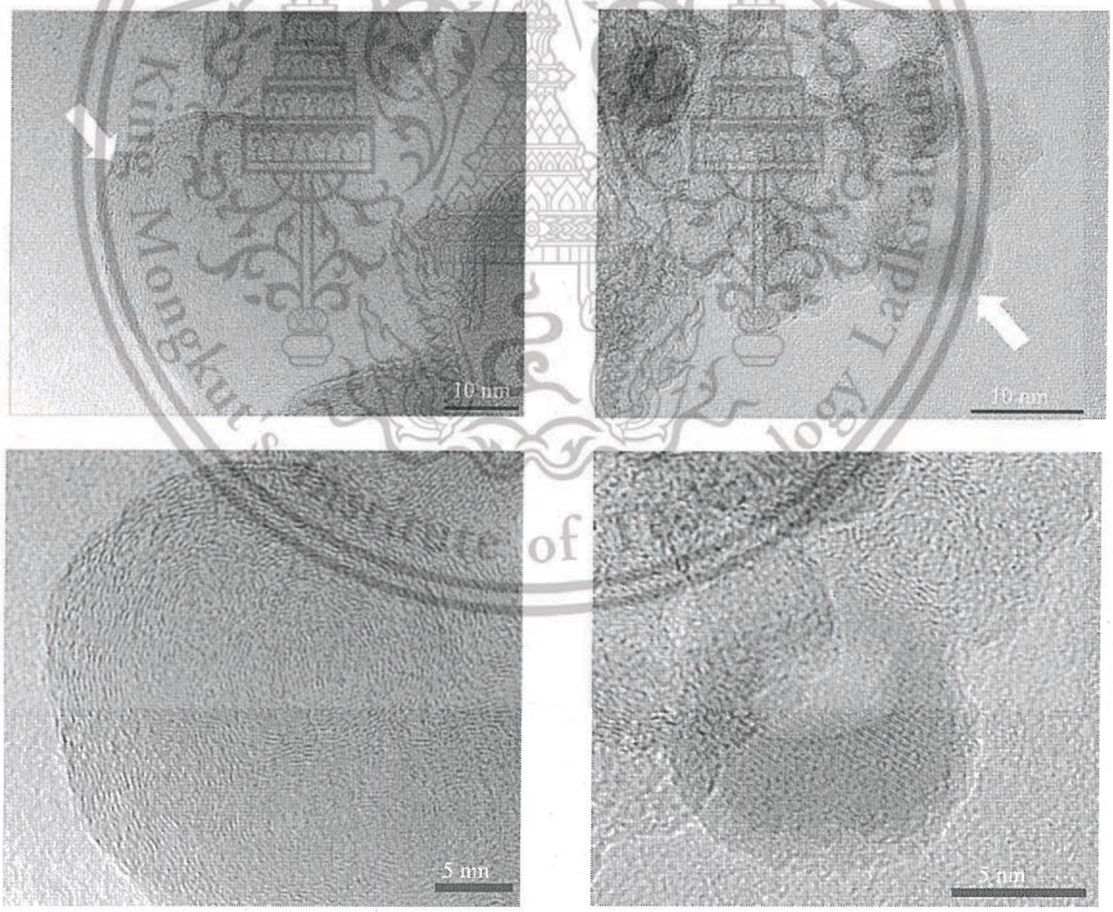
Figure 3 compare TEM images of different nanostructures of soot (pure carbon) obtained from the neat diesel condition and metal oxide ash which is derived from diesel blending lube oil condition. The nanostructure of diesel soot primary particle is a spherical shape composed of curve line crystallites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



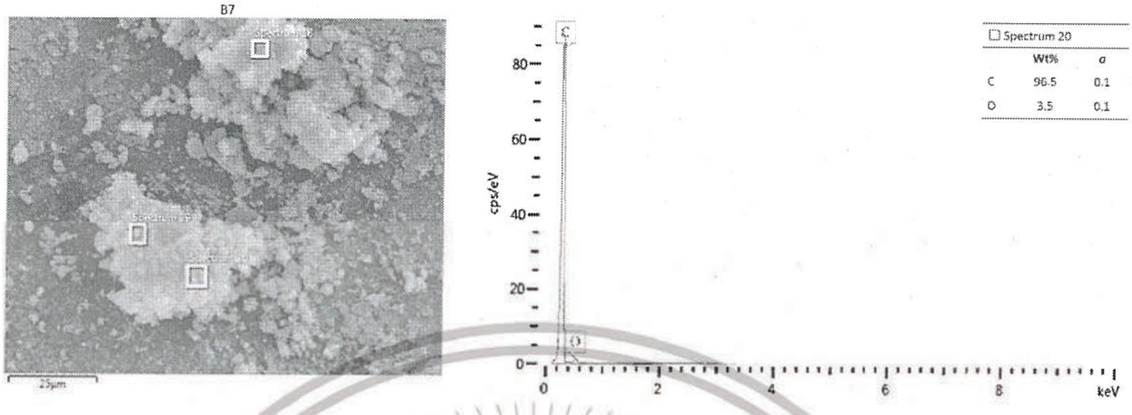
(a) PMs from neat diesel (b) PMs from diesel blending lube oil

Fig. 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

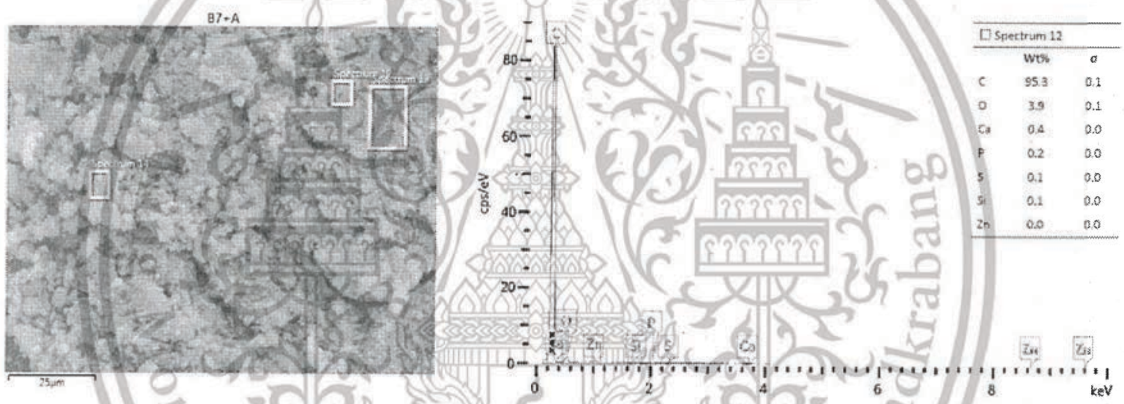


(a) Nanostructure of diesel soot (b) Nanostructure of metal oxide ash

Fig. 3 TEM images of nanostructure of (a) diesel soot and (b) metal oxide ash



(a) Chemical composition of diesel PM



(b) Chemical composition of diesel blending lube oil PM

Fig. 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

3.3 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 conditon 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.

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

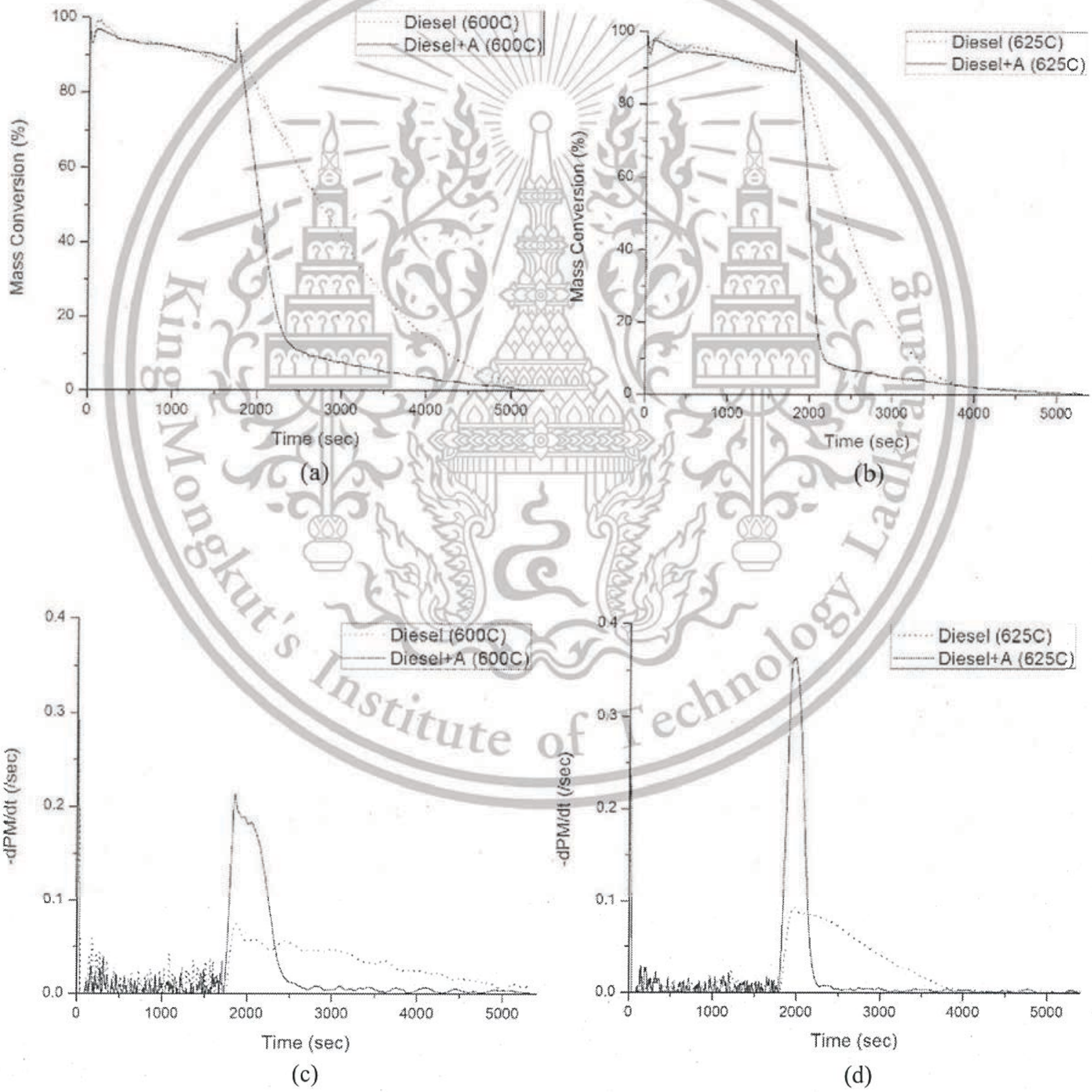


Fig. 4 Thermogravimetric analysis of mass conversion graphs of diesel PM and diesel blending lube oil PM at (a) 600°C and (b) 625°C, mass conversion rate of diesel PM and diesel blending lube oil PM at (c) 600°C and (d) 625°C

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.

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$-\frac{d\,[C]}{dt} = k[C]^n[O_2]^m \quad (2)$$

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 and Discussion

Morphology of ultrafine agglomerate particles, different primary particle nanostructures of lube oil derived metal oxide ashes compared to diesel soot and also 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 similar to 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.

5. Acknowledgements

The author would like to acknowledge to International College, King Mongkut's Institute of Technology Ladkrabang (KMITL) for research funding and also Bangchak Corporation (BCP) for supporting designed lubricating oil to accomplish this research.

6. References

[1] Peter Eastwood 2008 Particle Emission from Vehicles, John Wiley & Sons, Ltd, England.

[2] Myung C L and Park S 2012 Exhaust Nanoparticle Emissions from Internal Combustion Engines: A Review, International Journal of Automotive Technology, Vol. 13, No.1, pp.9-22.

[3] Mohankumar S and Senthilkumar P 2017 Particulate Matter Formation and its Control Methodologies for Diesel Engine: A Comprehensive Review, Renewable and Sustainable Energy Reviews, Vol. 80, pp.1227-1238.

[4] Myung C L, Ko A and Park S 2014 Review on Characterization of Nano-particle Emissions and PM Morphology from Internal Combustion Engines: Part 1, International Journal of Automotive Technology, Vol. 15, No. 2, pp. 203-218.

[5] Leslie R Rudnick 2008 Lubricant Additives Chemistry and Applications, Taylor & Franscis Group, London, New York.

[6] Tornehed P and Olofsson U 2011 Lubricant Ash Particles in Diesel Engine Exhaust: Literature Review and Modelling Study, Proceedings of the Institution of Mechanical Engineers, Journal of Automotive Engineering, Vol. 225, Part D, pp. 1055-1066.

[7] Karin P, Oki H, Hanamura K and Charoenphonphanich C 2012 Nanostructures and Oxidation Kinetics of Diesel Particulate Matters, Journal of Research and Applications in Mechanical Engineering, Vol. 1, No.2, pp. 3-8.

[8] Liati A, Dimopoulos Eggenchwiler P, Müller G, Schreiber D and Aguirre M 2012 Investigation of Diesel Ash Particulate Matter: A Scanning Electron Microscope and Transmission Electron Microscope Study, Atmospheric Environment, Vol. 49, pp. 391-402.

[9] Vouitsis E 2007 Effect of Lube Oil on the Physicochemical Characteristics of Particulate Matter Emitted from a Euro 4 Light Duty Diesel Vehicle, SAE Technical Paper 2007-24-0110.

[10] Karin P, Supanamok C and Hanamura K 2016 Impact of Soot on Metal Wear Characteristics using Laser Diffraction Spectroscopy, Journal of Research and Applications in Mechanical Engineering, Vol. 4, No.2, pp. 126-134.

[11] Tan P 2017 Effect of Lubricant Sulphur on the Morphology and Elemental Composition of Diesel Exhaust Particles, Journal of Environmental Sciences, pp. 354-362.

[12] Wang Y, Liang X, Shu G, Dong L, Sun X, Yu H and Wang Y 2015 Effects of an Anti-wear Oil Additive on the Size Distribution, Morphology, and Nanostructure of Diesel Exhaust Particles, Tribology International, Vol. 92, pp. 379-386.

[13] Karin P 2015 Oxidation Kinetics of Small CI Engine's Biodiesel Particulate Matter, International Journal of Automotive Technology, Vol. 16, No.2, pp. 211-219.

[14] Karin P 2017 Morphology and Oxidation Kinetics of CI Engine's Biodiesel Particulate Matters on Cordierite Diesel Particulate Filters using TGA, International Journal of Automotive Technology, Vol. 18, No.1, pp. 31-40.

[15] Jung H 2003 The Influence of Engine Lubricating Oil on Diesel Nanoparticle Emissions and Kinetics of Oxidation, SAE Technical Paper 2003-01-3179.

Appendix B

Research Budget

บันทึกรายการรับ-จ่ายเงิน โครงการวิจัย สัญญาเลขที่ 2561-0111005 ตั้งแต่วันที่ 1/4/2561 ถึงวันที่ 30/9/2561

แหล่งทุน: เงินรายได้ วิทยาลัยนานาชาติ สจล.
ชื่อโครงการ :การวิเคราะห์โครงสร้างไมโครและนาโนของคาร์บอนไฟเบอร์ด้วยการประมวลผลภาพถ่ายจากกล้อง จุลทรรศน์อิเลคตรอน
ชื่อหัวหน้าโครงการ: ผศ.ดร.ปรีชา การินทร์

ว/ด/ป	รายการ	เลขที่อ้างถึง	รายการรับ - จ่าย			รายรับ	รายจ่าย						รวม รายจ่าย
			รับ	จ่าย	คงเหลือ	ดอกเบี้ยรับ	งบบุคลากร	งบดำเนินงาน				งบลงทุน	
							ค่าจ้างชั่วคราว	ค่าตอบแทน	ค่าใช้สอย	ค่าวัสดุ	ค่าสาธารณูปโภค	ค่าครุภัณฑ์	
	งบประมาณที่ได้รับการอนุมัติ (ตามแผน)		100,000.00										-
	จำนวนเงินที่ได้รับ (งวดที่ 1 = 85%)		85,000.00			24.13							
	จำนวนเงินที่ได้รับ (งวดที่ 2 = 15%)		15,000.00			0							
	หัก ค่าใช้จ่าย (ครั้งที่ 1)			103,775.54			-	-	56,232.50	47,543.04	-	-	103,775.54
	ค่าใช้จ่าย (ครั้งที่ 2)			-			-	-	-	-	-	-	-
	งบประมาณคงเหลือ		100,000.00		- **3,775.54**	**24.13**							
	รายละเอียดค่าใช้จ่าย												
ครั้งที่ 1													
19 ก.ค. 61	Carbon Fiber	C61070637								6,896.15			6,896.15
4 ก.ค. 61	ใยเสริมความหนา	C61070133								5,378.89			5,378.89
16 ส.ค. 61	Carbon Fiber	C61080505								8,025.00			8,025.00
7 ส.ค. 61	SEM Analysis	353								7,757.00			7,757.00
6 ก.ย. 61	SEM Analysis (susan)	27								5,136.00			5,136.00
14 ก.ย. 61	XRD Analysis	244								6,000.00			6,000.00
17 ก.ย. 61	TEM Analysis	40							8,613.50				8,613.50
18 ก.ย. 61	TGA Analysis	373							14,980.00				14,980.00
26 ก.ย. 61	SEM EDS Analysis	400								8,350.00			8,350.00
9 พ.ย. 61	TEM EDS Analysis	178							8,346.00				8,346.00
9 พ.ย. 61	TEM EDS Analysis	179							7,597.00				7,597.00
9 พ.ย. 61	TGA Analysis	439							7,276.00				7,276.00
9 พ.ย. 61	TGA Analysis	438							6,420.00				6,420.00
9 พ.ย. 61	TSME-ICoME-IOP								3,000.00				3,000.00
	รวมครั้งที่ 1		-	-	-	-	-	-	56,232.50	47,543.04	-	-	103,775.54
ครั้งที่ 2													
													-
	รวมครั้งที่ 2		-	-	-	-	-	-	-	-	-	-	-

ลงชื่อหัวหน้าโครงการ .... วันที่ 2/9/62

Investigator

หัวหน้าโครงการวิจัย

ชื่อ-สกุล (ภาษาไทย)	ผศ.ดร. ปรีชา การินทร์		
ชื่อ-สกุล (ภาษาอังกฤษ)	Asst.Prof.Dr.Preechar Karin		
ตำแหน่งทางวิชาการ	ผู้ช่วยศาสตราจารย์	สัดส่วนการวิจัย	100
ภาควิชา/สาขาวิชา	วิศวกรรมยานยนต์	หน่วยงานต้นสังกัด	วิทยาลัยนานาชาติ
โทรศัพท์	085-128-5024		
E-mail	preechar.ka@kmitl.ac.th		
ประวัติการศึกษา	D.Eng. (Mechanical Engineering), Tokyo Institute of Technology, Japan		

สาขาวิศวกรรมศาสตร์และอุตสาหกรรมวิจัย

- Automotive Engineering, Internal Combustion Engines and Powertrain Engineering

หัวหน้าโครงการวิจัย : 2015-2017

- Conducting, TRFRSA60: The Impact of Biofuels on Soot Emission Nanostructure Oxidation Kinetics and Engine Wear Mechanisms, 2017-2019.
- Finished, KMITL2560-0111002-4: Impact of Morphology and Nanostructure on Particulate Matters Oxidation Kinetics from Bio-fuel Combustion, Combustion Characteristics of HVO and Diesel Blended Fuels in CVCC under EGR conditions and Low Temperature Combustion, Impact of Biodiesel Contamination and Soot on Engine Wear using Four-ball, Laser Particle Distribution, 2016.

ผลงานวิจัยที่ตีพิมพ์ในวารสารวิชาการระดับนานาชาติ : 2015-2017

- P. Karin et al., "Oxidation Kinetics of Small CI Engine's Biodiesel Particulate Matter", Springer, International Journal of Automotive Technology, Vol. 16, No. 2, pp. 211–219, 2015.
- P. Karin et al., "Impact of Soot on Metal Wear Characteristics using Laser Diffraction Spectroscopy", Journal of Research and Applications in Mechanical Engineering, Transactions of the TSME Vol. 4, No. 2, pp.126-134, 2016.
- P. Karin et al., "Morphology and Oxidation Kinetics of CI Engine's Biodiesel Particulate Matters on Cordierite Diesel Particulate Filters using TGA", Springer, International Journal of Automotive Technology, Vol. 18, No. 1, pp. 31–40, 2017.
- P. Karin et al., "Impact of Biodiesel on Small CI Engine Combustion Behavior and Particle Emission Characteristic", SAE International, SAE Technical Paper No. SAE 2017-32-0094, 2017.
- P. Karin et al., "Effect of Biofuel and Soot on Metal Wear Characteristic using Electron Microscopy and 3D Image Processing", SAE International, SAE Technical Paper No. SAE 2017-32-0095, 2017.