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Morphology and oxidation kinetics of particulate matters using TGA

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Abstract
This research is studied about physical characteristic of carbon black (N330) and diesel particulate matters (PMs) emitted from different conditions of single cylinder diesel engine. Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM) is used to investigate the nanostructures of carbon black and diesel PMs in this research for better understanding of designs and configurations of Diesel Particulate Filter (DPF). The agglomerate size distributions of diesel PMs and carbon black are average 184 nm and 313 nm, respectively. In addition, Thermo-Gravimetric Analysis (TGA) was used to investigate chemical kinetics of PMs oxidation. The apparent activation energies of diesel PMs and carbon black oxidation are approximately 126 kJ/mole and 137 kJ/mole, respectively.

1. Introduction

Among conventional internal combustion engines (ICE) diesel or compression ignition (CI) engines have the highest thermal efficiency for a given output power. However, diesel engines are an important source of particulate matters (PMs). The diesel PMs consists of two particles: i) fractal-like agglomerates of primary particles, consisting of carbon and traces of metallic ash, and coated with condensed heavier and organic compounds and sulfate, and ii) nucleation particles composed of condensed HCs and sulfate [16]. Chemical composition of diesel PMs are depending on the operating conditions and fuel composition. The PMs is consisting of three main fractions: i) solid fraction (SOL) that is elemental carbon and metallic ash, ii) soluble organic fraction (SOF) that is organic material derived from engine lubricating oil and fuel, and iii) sulfate particulates (SO_4) that is sulfuric acid and water [18]

Size distribution of diesel PMs have been reported by several researchers. Size definitions for atmospheric particles are PM10, diameter (D) < 10 µm; fine particles, D < 2.5 µm; ultrafine particles, D < 0.10 µm; and nanoparticles, D < 0.05 µm or 50 nm [18]. The particles in the size range from 20 to 200 nm are very sensitive to sudden changes of the engine power [19].

The oxidation behavior of PMs has been investigated using thermogravimetric analysis (TGA) for analysis reaction activity. The order of carbon is assumed to be 2/3(0.67) with theoretical of shrinking-core model. The order of reaction rate in oxygen is close to 1. The activation energy (Ea) of diesel PMs and biodiesel PMs oxidation is around 159±6 kJ/mole and 152±5 kJ/mole [10].

The objective of this research is to study oxidation kinetics of carbon black and diesel PMs by TGA isothermal method. The oxidation kinetics and apparent activation energies would be calculated by using chemical composition. In addition, image processing methods used to investigate micro-nanostructures of PMs for better understanding and basic information for application the conventional DPF which using in the diesel engine.

2. Methodology

2.1 PM trapping and measuring diameter size

The smoke meter, Okuda DSM-240, is shown in figure 1 used to trapping particulate matter emitted from engine combustion. The particulate matter from diesel engine combustion in 20%, 40%,60% and 80% load and 1600,200 and 2400 rpm. The diesel PMs was trapped by paper filter while it suspends on exhaust gas. The diesel PMs on paper filter was taken image by scanning electron microscope (SEM) and transmission electron microscope (TEM) for analyzed the morphology in various condition. In addition, diameter size distribution of single primary and agglomerate particle were measured by image processing method as shown in Figure 2. and would be calculated in eq.1

$$A_i = \pi \frac{d^2}{4} \quad (1)$$

where A_i is area of PMs calculated from the image processing program and d is calculated diameter of PMs

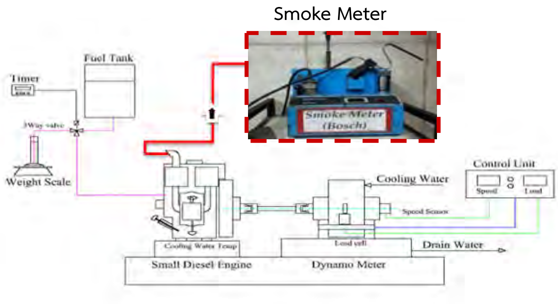
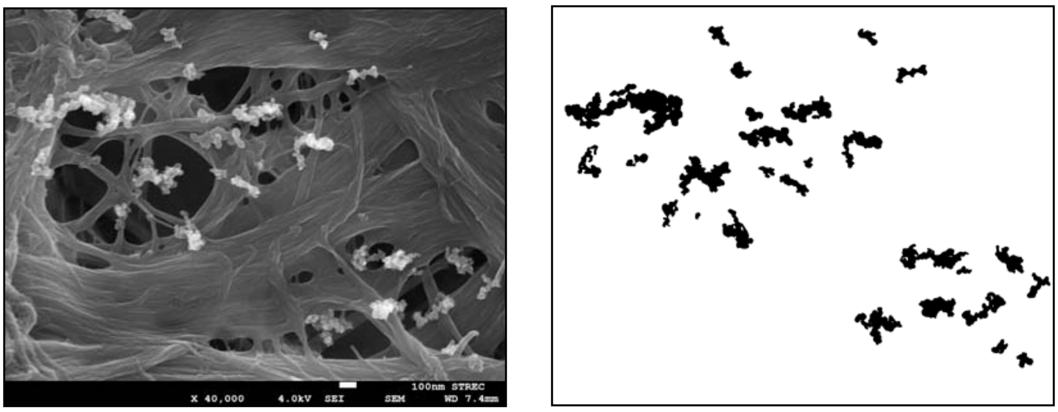


Figure 1. Schematic diagram of trapping particulate matter in smoke meter



(a) Before (b) After

Figure 2. Image processing method

2.2 Thermo-gravimetric Analysis

The oxidation kinetics behavior of PMs were investigated by using TGA with isothermal methods, sensitivity 0.1 mg, balance mass 0.1% accuracy, 2 °C of temperature error and five different of final temperatures are 525, 550, 575, 600 and 625 °C. Nitrogen was used to heat up the sample from 25 °C to desired temperature after that the air is introduced to PM oxidation for one hour.

Chemical kinetics of carbon black oxidation was studied by using mass conversion behavior from TGA. The chemical reaction rate in equation (2) can be calculated from the TGA mass conversion curve based on the chemical kinetic in equation (3). The reaction order n is assumed to be 2/3 as shrinking core model [10] because PMs is similar spherical shape.

$$PM + O_2 \longrightarrow CO_2 \quad (2)$$

$$-\frac{d[PM]}{dt} = k[PM]^n[O_2]^m \quad (3)$$

Where *PM* is mass of particulate matters, *t* is time, *k* is the rate constant of chemical reactions, *m*, *n* are the reaction orders. The rate constant of chemical reactions *k* is expressed by equation (4).

$$k = Ae^{-\frac{E_a}{RT}} \quad (4)$$

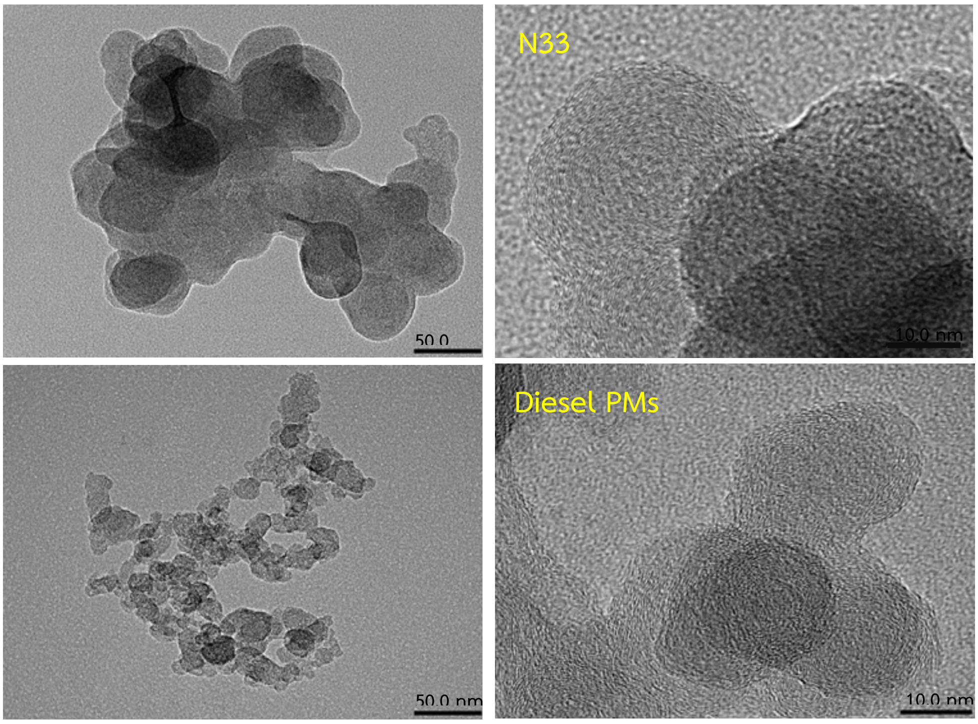
Where *A* is the frequency factor, E_a is the activation energy, *R* is the gas constant. The apparent activation energy can be calculated by equation (5).

$$\ln[-\frac{1}{[PM]^n}\frac{d[PM]}{dt}] = -\frac{E_a}{RT} + (\ln A + m\ln[O_2]) \quad (5)$$

3. Results and discussion

3.1 PMs size distribution and morphology

Figure 3 shows carbon black and diesel PMs image from Transmission Electron Microscope (TEM) in condition diesel engine is 2,400 rpm and 80% load. The morphology of particulate matter is clearly observed that is consisting of many single primary size which aggregations to agglomerate size.



(a) PMs Nanoparticle (b) PMs ultrafine particle

Figure 3. Particulate matter image from scanning electron microscope (TEM)

When focus on effect size of diesel PMs. The primary single particle and agglomerate size distribution of diesel PMs are significantly smaller than carbon black because of carbon fraction inside diesel PMs is lower than that of carbon black PMs [10]. That means HC composition and moisture content in diesel PMs have more than carbon black which expected that some of unburned HC and moisture composition might be oxidized with remain oxygen in high temperature inside the combustion resulting the size of diesel PMs is smaller than carbon black.

Figure 4 shows average agglomerate size distribution of carbon black and diesel PMs from Scanning Electron Microscope (SEM) in various diesel engine condition 20, 40, 60 and 80% of engine load and constant of engine speed 2400 rpm. The quantity PMs and agglomerate particle diameter size of diesel PMs would be increased when increased engine load due to increasing amount of fuel injection resulting in increasing of PMs.

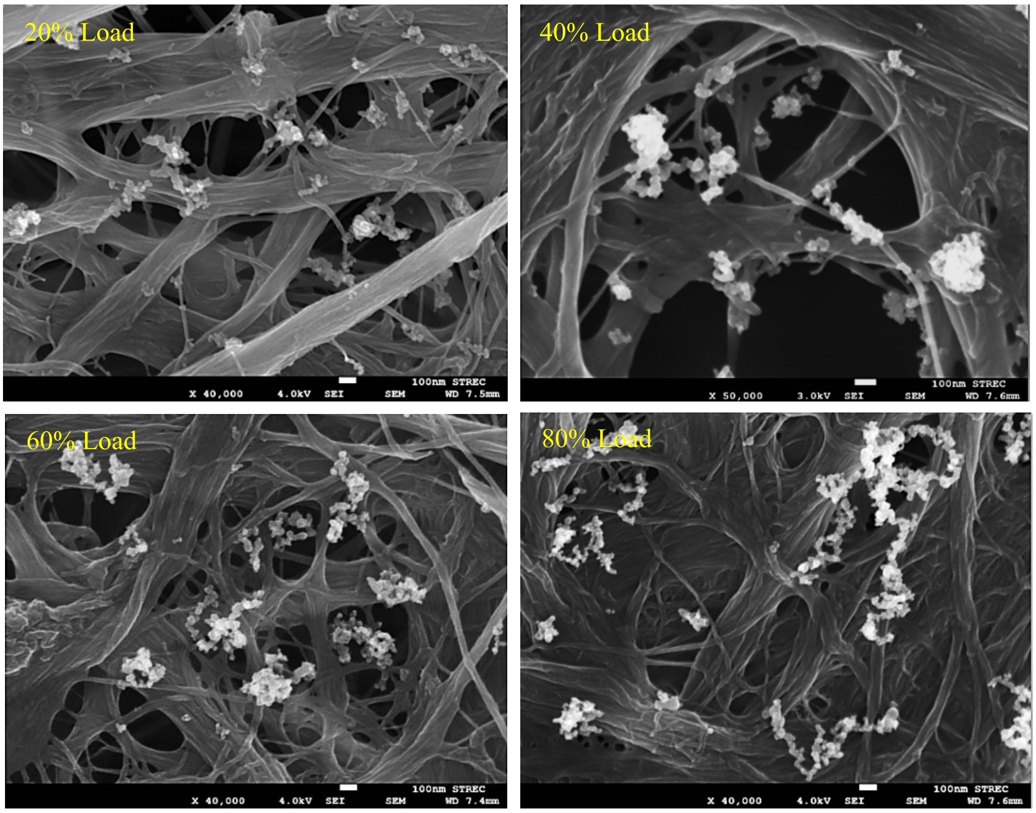


Figure 4. Size distribution of diesel PMs by SEM with constant engine speed 2,400 rpm.

Figure 5. shows the diesel PMs agglomerate size distribution when various condition of engine speed 1600 rpm, 2000 rpm and 2400 rpm and 20%, 40%, 60% and 80% of engine load which investigated by image processing methods. The particle sizes are in the range of 50-750 nm but much amount of particle sizes is in the range of 100-300 nm. When increasing engine load the results found that high of the large particle size in range 400-750 nm as Due to increasing of engine load that also increase of fuel injection quantity into the combustion chamber. While increasing the engine speed showed that not significantly different. The single particle average sizes of carbon black and diesel PMs are 52 nm and 35 nm, respectively. The agglomerate particle size of carbon black and diesel PMs are average 313 nm and 184 nm, respectively.

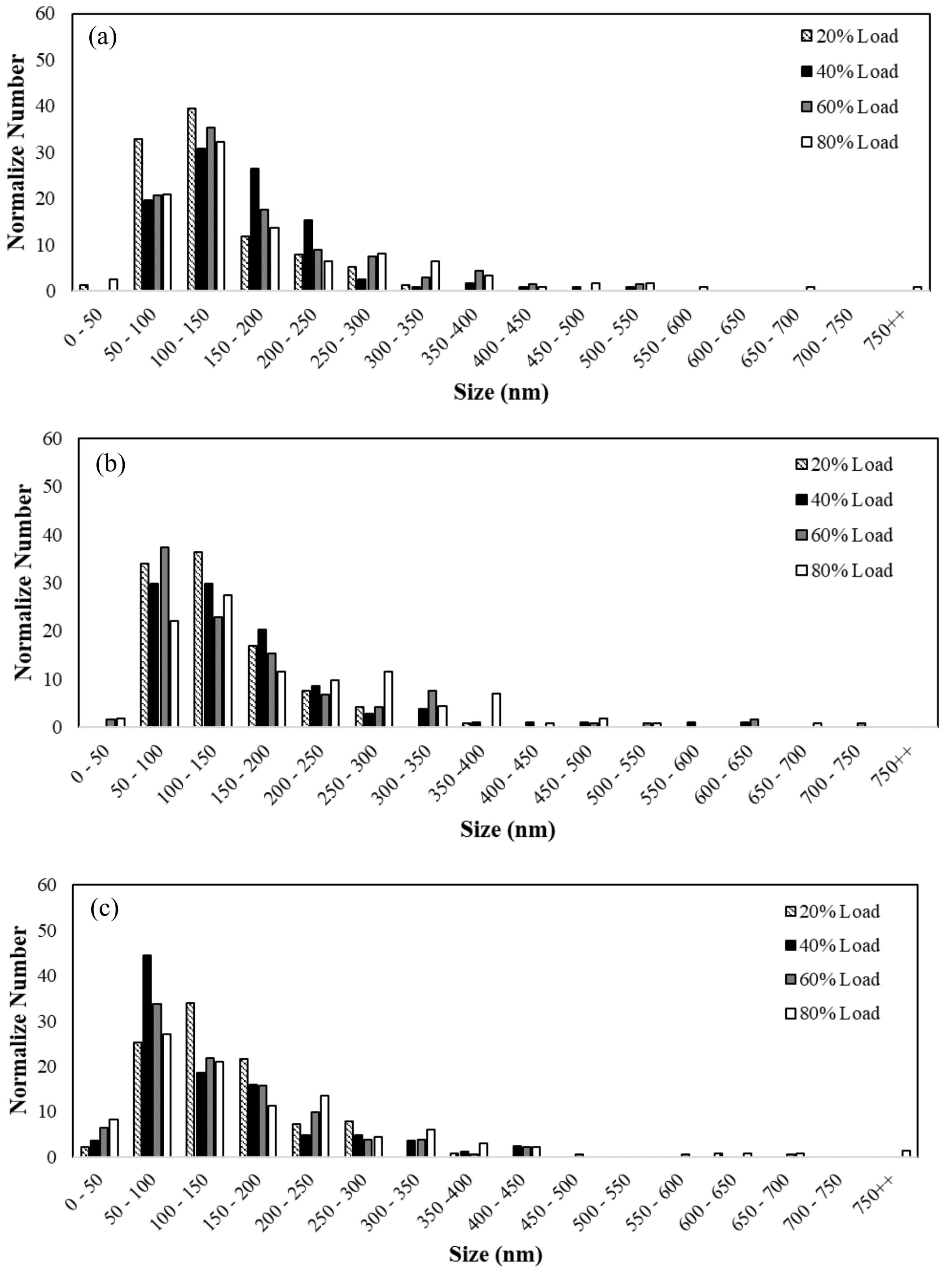
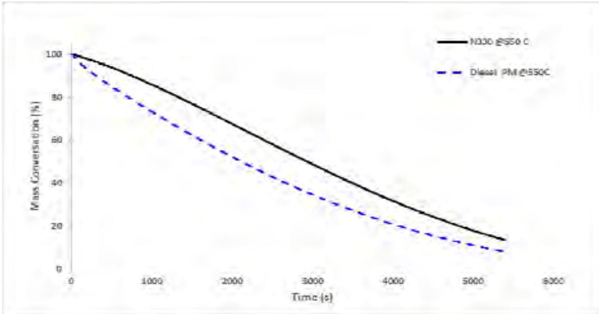


Figure 5. The agglomerate size distribution of diesel PMs using image processing with constant engine speed (a) 1,600 rpm (b) 2,000 rpm(a) 2,400 rpm

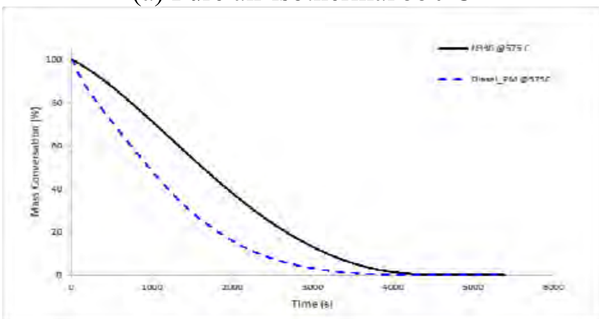
3.2 Isothermal PMs Oxidation Kinetics of PMS

The particulate matter from carbon black and diesel fuel was analyzed by TGA method to investigate oxidation behavior of the particulate matter from carbon black (N330) and diesel PMs. The results are shown that the mass conversion with pure air in the condition of 550, 575 and 600 ℃, respectively as shown in Figure 6. It was clearly observed that diesel PMs were oxidized faster than carbon black. The PMs could be oxidized fastest in the condition of 600℃ and slowest in the condition of 550℃ for both of carbon black and diesel PMs. The graph shown only isothermal stage begins, when the air is introduced the mass conversion changes to mass oxidation and the mass percentage reduces with time.

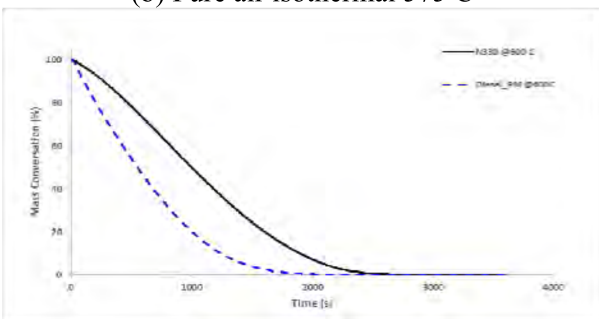
Figure 7 shows Arrhenius plots of PMs oxidation rate. PMs oxidation rate were clearly observed that the slope of carbon black is higher than diesel PMs. The apparent activation energies of carbon black and diesel PMs oxidation with pure air are 137 kJ/mole and 126 kJ/mole, respectively. It was clearly observed that apparent activation energy of carbon black oxidation is higher than diesel PMs oxidation. Due to the unburned HC and moisture fraction is support diesel PMs oxidized faster than carbon black.



(a) Pure air isothermal 550 C



(b) Pure air isothermal 575 C



(c) Pure air isothermal 600 C

Figure 6. Oxidation kinetics of carbon black and diesel PMs using TGA isothermal method

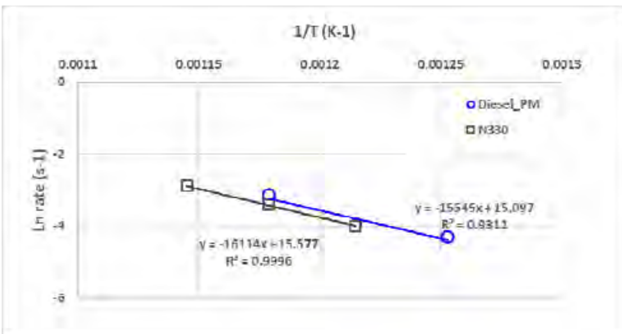


Figure 7. Arrhenius plots of PMs oxidation with air

4. Conclusion

In this research, the particulate matter from diesel PMs fuel combustion was investigated for physical and chemical characteristic to better understanding and basic information for application the conventional DPF which using in the diesel engine.

i) The size of particulate matter increases when load increases because amount of fuel injection in combustion chamber is higher. That means more of fuel injection which affected to incomplete combustion.

ii) The particle size of diesel PMs is smaller than the carbon black because of diesel PMs have unburned HC and moisture fraction higher than carbon black which support to oxidation with remain oxygen in high temperature inside the combustion. The single primary particle size of diesel PMs and carbon black are average 35 nm and 52 nm, respectively. The agglomerate size of diesel PMs and carbon black are average 184 nm and 313 nm, respectively

iii) The diesel PMs would be oxidized at apparent lower activation energy. Due to impact of unburned HC and chemical composition.

iv) The calculated apparent activation energy of diesel PMs oxidation is lower than carbon black. Because of chemical composition of diesel PMs promotes low oxidation activation energy. The apparent activation energy of diesel PMs and carbon black are 126 kJ/mole and 137 kJ/mole, respectively. However, oxidation rate of PMs not only one is strongly related to apparent activation energy but also physical impact of reaction order and frequency factor would be investigated.

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