Thermo-gravimetric Analysis of Biodiesel Diffusion Flame's Particulate Matter

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Abstract

The problem of particulate emissions from diesel engine can be reduced in many ways, for example: engine design, development of fuel additives and using the diesel particulate filter (DPF). This research has two parts. First is studied about the physical properties of diesel (B0) and bio-diesel (B100) particulate matter (PM), such as nanostructure, microstructure and size distribution by using a scanning electron microscope (SEM) and transmission electron microscope (TEM). The primary and agglomerated size distribution of each particulate matter can be estimated by using the image of TEM and SEM. The primary sizes of diesel and biodiesel particulate matter are approximately 50-60 nm and 40-50 nm, respectively. Oxygen content inside bio-fuel may be affected to biodiesel particulate combustion. Second, chemical kinetics of particulate matter oxidation are studied by using Thermo-gravimetric analysis (TGA). The apparent activation energies of diesel and biodiesel PM oxidation in the first stage (hydrocarbon) are approximately 133 and 96 kJ/mol. In the second stage (carbon), apparent activation energies of diesel and biodiesel PM are approximately 176 and 158 kJ/mol, respectively. Because of oxygen content inside unburned fuel and nanostructure may be affected to biodiesel particulate combustion, resulting in low apparent activation energy.

Key words: Emissions, Particulate matter, Apparent Activation Energy, Thermo-gravimetric analysis

1. Introduction

Nowadays, energy consumption and global warming problems are mainly issue of our community. In order to overcome such problems, high efficiency engines should be widely used. Among internal combustion engines, diesel engines have the highest thermal efficiency. However, particulate matters (PMs) must be removed from exhaust gases that are emitted by diesel engines to protect the environment and human health (lung cancer).

Diesel particulate matter consists of a solid fraction (SOL) and a soluble organic fraction (SOF). Primary particles composed of solid carbon and metallic ash, are coated with SOF and sulfate. The mean diameter of primary and agglomerated particles is usually in the range of 20-60 nm and 60-200 nm, respectively. The composition of particles from a diesel engine is widely depending on the operating conditions and fuel composition [1-5].

The advantages of biodiesel are renewable energy and oxygenate fuel. Photosynthesis of plants can be considered biodiesel is carbon neutral. As a result, biodiesel can reduce emitted CO_2 because it is derived from vegetable oil. The oxygen contained within molecule of fuel can promote complete combustion.

This research studies about oxidation of diesel and biodiesel particulates. The oxidation temperature, chemical reaction rate and activation energy are successfully explained in this paper.

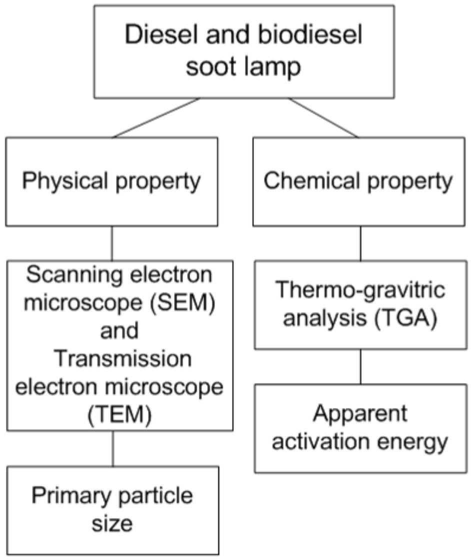


Fig. 1 Experimental procedure

Table1 Properties of diesel and biodiesel fuel (From Department of Energy Business)

Properties / Fuels	Diesel	Biodiesel
Density (kg/m^3)	844.78	847.73
Heat of combustion (MJ/m^3)	140,000	130,000
Cetane Number	48	55
Viscosity (centistokes)	3.0	5.7
Flash point °C	64	70
Chemical formula	$C_{12}H_{22}$	$RCOOCH_3$
Carbon fraction	82	78
Heating value (kJ/kg)	46,800	39,550

2. Experimental setup

2.1 Experimental procedure

Figure1 shows a schematic diagram of the experimental procedure for investigation of chemical and physical properties of diesel and biodiesel diffusion flame particulate matters. Particulates were generated by diesel and biodiesel lamps. This research separated in two parts. The first is studying about diesel and biodiesel primary particle size by the TEM and SEM images. Second, chemical kinetics of particulate matter oxidation are studied by using Thermo-gravimetric analysis (TGA).

Table 1 shows the properties of diesel and biodiesel fuels. The carbon fraction of diesel (82) is higher than that of biodiesel (78). It might be that high carbon fraction plays an important role in high soot emitted quantity of diesel fuel diffusion flame.

2.2 Diesel and biodiesel diffusion flames

Figure 2 shows diesel diffusion flame and biodiesel diffusion flame by Schlieren method. It can explain core of diesel diffusion flame darker than that of biodiesel. It may be biodiesel is oxygenated fuel and some chemical properties of biodiesel fuel.

According to the previous study, the result shows biodiesel particulate matter is approximately 30 percent of diesel particulates [7]. Figure 3 shows diesel diffusion flame longer than that of biodiesel because it may be diesel has carbon content more than biodiesel and biodiesel has oxygen content can promote complete combustion.

Figure 4 shows SEM and TEM images of (a) diesel particulate matters and (b) biodiesel particulate matters collected from diffusion flame combustion. The average primary particles sizes

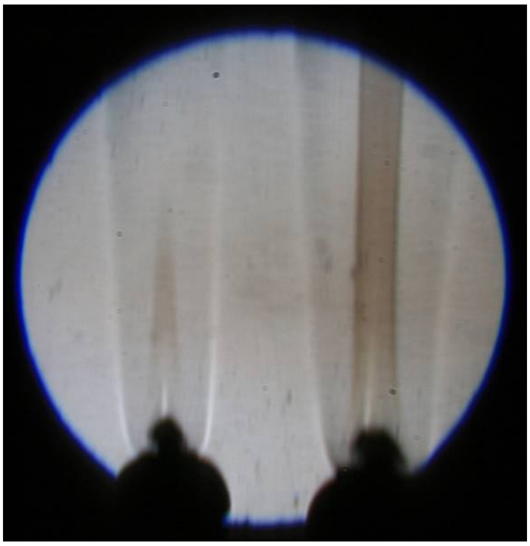
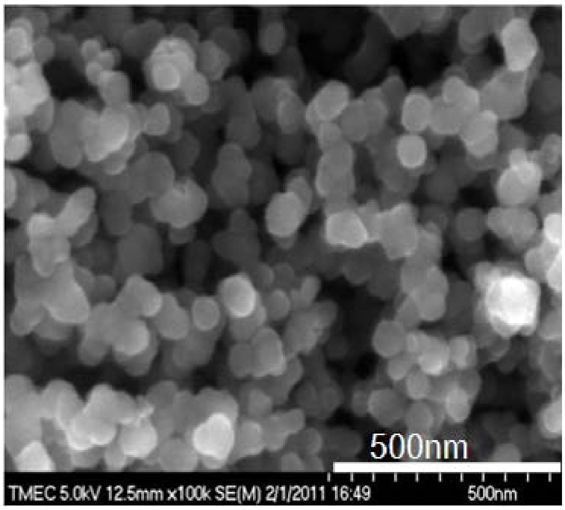
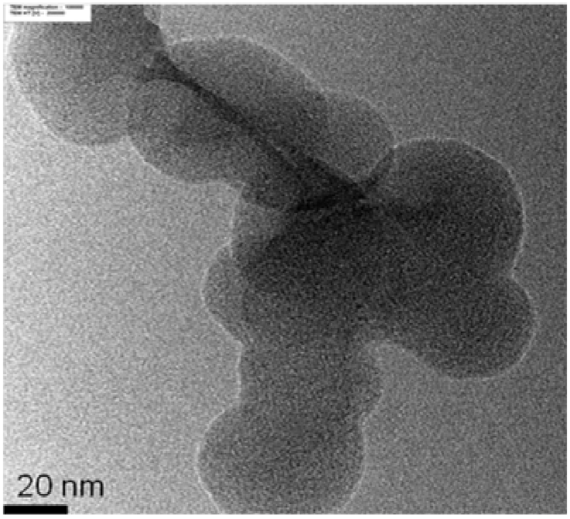


Fig. 2 Biodiesel (left) and diesel (right) captured by Schlieren method

Fig. 3 Biodiesel (left) and diesel (right) diffusion flame by conventional digital camera.



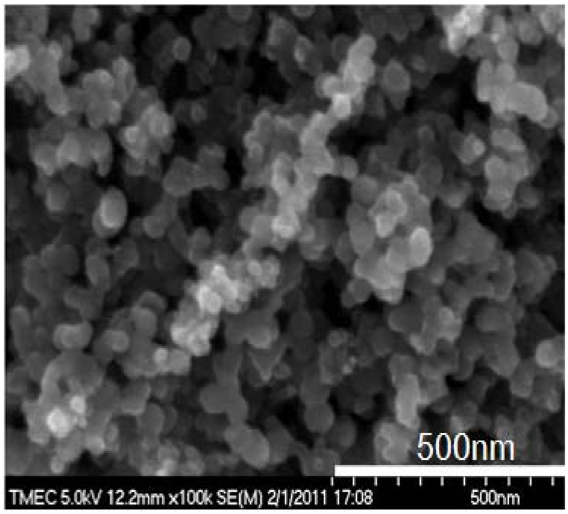
(a) SEM image of diesel PM [7]



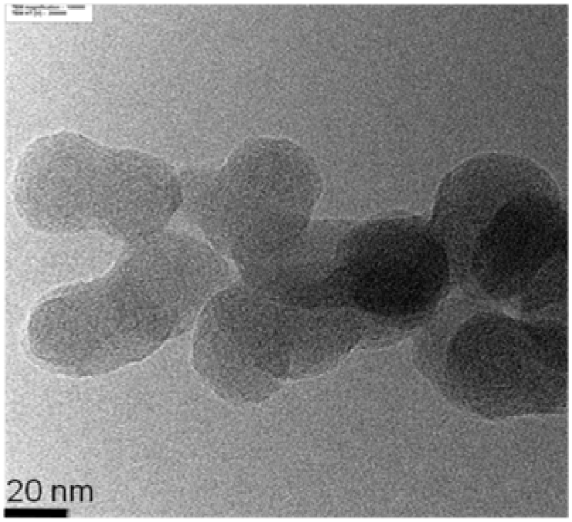
(b) TEM image of diesel PM

Fig. 4 TEM and SEM [7] images of (a and b) diesel particulate matter and (c and d) biodiesel particulate matter for primary particle study.

are approximately 50-60 nm and 40-50 nm for diesel and biodiesel particulates, respectively. It may be discussed that low concentrations of biodiesel particle have more opportunity to contact with oxygen, in the air and molecule of fuel itself in combustion flame.



(c) SEM image of biodiesel PM [7]



(d) TEM image of biodiesel PM

2.3 Thermo-gravimetric analysis

Chemical kinetics of particulate matter oxidation is studied by using Thermo-gravimetric analysis (TGA).

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

The chemical reaction rate in eq.1 can calculate from the TGA curve based on the chemical kinetic in eq.2

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

where C is particulate matter mass, t is time, k is specific rate constant, *m, n are the reaction order*. The dependence of the specific rate constant k is expressed by eq.3

$$k = Ae^{-E_a/RT} \quad (3)$$

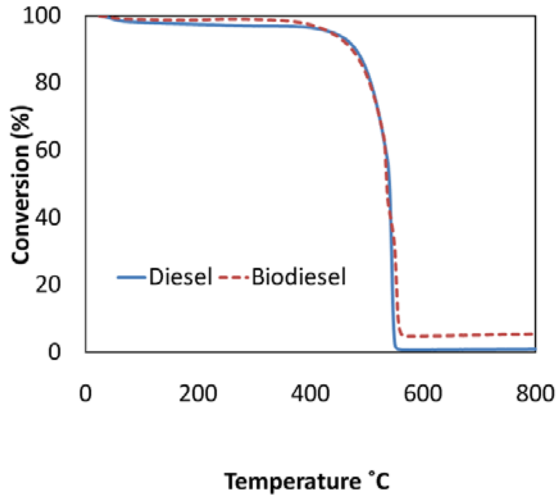
where A is the frequency factor, E_a is the activation energy, R is the gas constant. The apparent activation energy can be calculated by eq.4 [6].

$$\ln\left[\frac{-1}{[C]^n}\frac{d[C]}{dt}\right] = -\frac{E}{RT} + (\ln A + m\ln[O_2]) \quad (4)$$

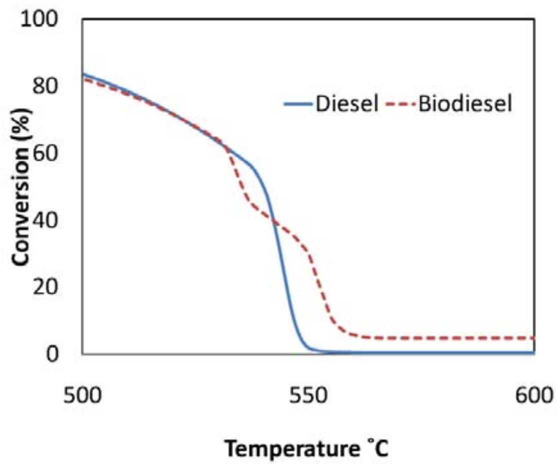
3. Results and discussions

Figure 5 shows TGA curve of (a) diesel and biodiesel particulate matter emitted from diffusion flame. Test condition starts from temperature of 25 °C to 800 °C with oxygen. For temperature 25 °C to 100 °C is considered that evaporation of moisture. After that 100 °C to 400 °C is assumed to be unburned fuel oxidation. Then 400 °C to 600 °C is assumed to be some hydrocarbons and carbon oxidation, as shown in Fig. (5b). Finally, above 600 °C biodiesel has ash more than that diesel. It means the unburned additive of biodiesel more than diesel. The oxidation rate of biodiesel is faster than that of diesel. It may be biodiesel has oxygen content.

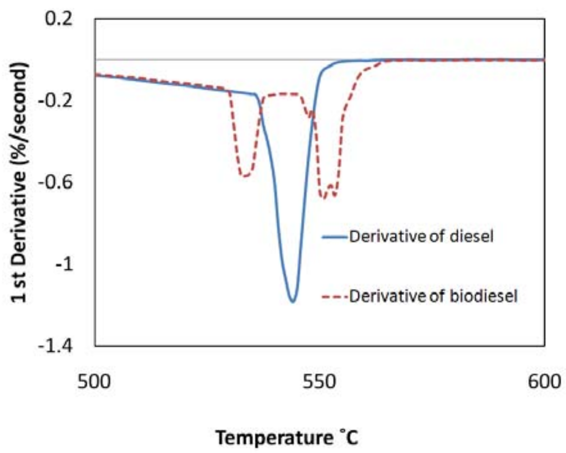
Figure (5c) shows derivative of particulate matter oxidation. Biodiesel has 2 peaks, the first



(a) Conversion of diesel and biodiesel PMs

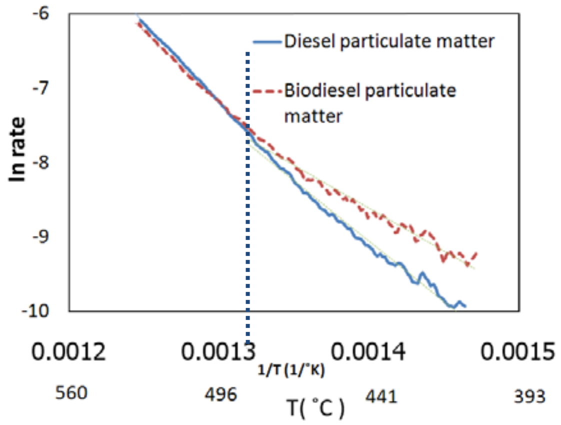


(b) Conversion of diesel and biodiesel PMs

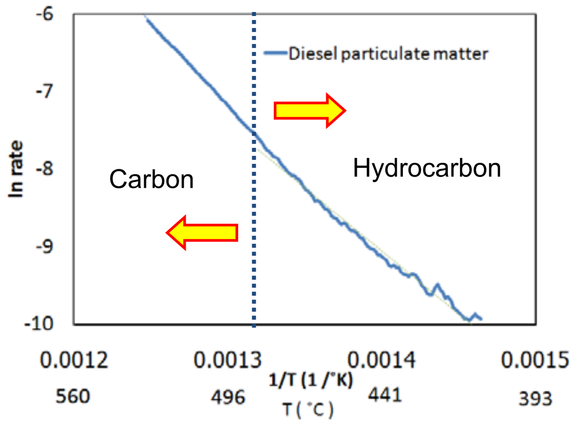


(c) Derivative of diesel and biodiesel PMs

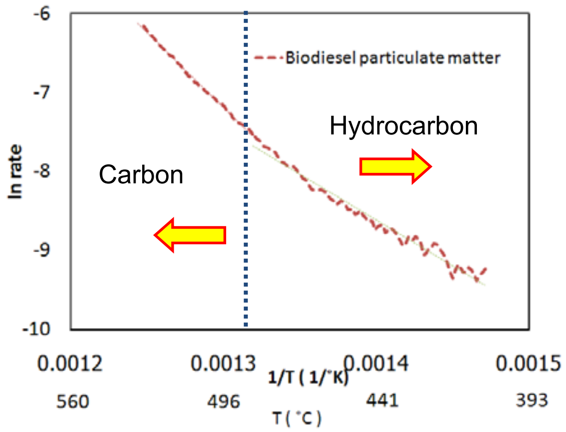
Fig. 5 TGA curves of (a and b) and (c) derivative of diesel and biodiesel PMs oxidation.



(a) Arrhenius plot of PMs oxidation



(b) Arrhenius plot of diesel PM oxidation



(c) Arrhenius plot of biodiesel PM oxidation

Fig. 6 Arrhenius plot of (a) diesel versus biodiesel PMs (b) diesel PM (c) biodiesel PM oxidation.

is may be hydrocarbon oxidation and second is may be carbon oxidation. Whereas diesel has only 1 peak and have peak of length longer than that of biodiesel. It may be diesel have carbon content more than that of biodiesel.

Figure 6 shows apparent activation energies of (a) diesel and biodiesel PM oxidation in temperature of 406 °C to 484 °C is assumed to be hydrocarbon oxidation that can calculate apparent activation energies of 158 and 96 kJ/mol for (b) diesel and (c) biodiesel, respectively. Temperature of 485 °C to 530 °C is assumed to be carbon oxidation. The apparent activation energies are 176 and 133 kJ/mol for diesel and biodiesel, respectively. Table 1 summarizes the apparent activation energy of each PM oxidation.

Table 2 Apparent activation energy calculated from oxidation rate of each PM.

PM Type	E_a (kJ/mol)	
	406-484 °C	485-530 °C
Diesel	158	176
Biodiesel	96	133

4. Conclusion

(1) Primary particle size of biodiesel particulate matter smaller than that of diesel particulate. It may be biodiesel has oxygen content within fuel molecule. It can be oxidized better than that of diesel particulate matter.

(2) Apparent activation energies of particulates oxidation are divided into two groups, unburned hydrocarbon and solid carbon.

(3) Apparent activation energy of diesel unburned hydrocarbon is higher than that of

biodiesel because unburned biodiesel hydrocarbon composes of oxygen atom within itself. On the other hand, apparent activation energy of diesel and biodiesel solid carbon are not significantly different because it is carbon.

(4) The results of this research can be used for base of designing and developing the particulate filtration system. The biodiesel may consume much filtration duration than that of diesel fuel. Therefore the engine back pressure from filter system may be decrease and also reduces the filter regeneration energy.

5. References

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