Physical Characterization of Biodiesel Particulate Matter by SEM

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Abstract

A diesel engine is a principle choice in transportation, because of its high thermal efficiency, durability and low maintenance. However, in-use diesel engines produce high concentration of particulate matter (PM) which affects air pollution and human health. This paper describes a part of an ongoing research project in diesel particulate matter reduction as emitted from diesel engines. In order to achieve the particulate matter reduction, physical structure and aggregation behavior should be investigated for better understanding. The physical characteristics such as micro- and nano- structure of particulate matter were studied by a scanning electron microscope (SEM) and a scanning transmission electron microscope (TEM). The primary and accumulate size distributions as well as particulate structures were presented by means of scanning images. From this study, the primary particle size of biodiesel was found that smaller than that of diesel because the oxygen content in biodiesel might have effects on particle combustion. Therefore, the biodiesel particulate removing is necessary to study in detail in an actual engine for more understanding. The particulate matter generation is based on the application of on-road conventional diesel vehicles. Particulate matter emitted from biodiesel combustion was compared with the results of diesel. Finally, the expected results will be used to design and develop a diesel particulate filter (DPF) which is proper for in-use diesel engines for using in both diesel and biodiesel fuels.

Keywords*:* diesel engine, biodiesel, particulate matter, diesel particulate filter

1. Introduction

Recently, the liquid fuel is limited in the world. The increasing usage of diesel engine is the way to increase the efficiency of liquid fuel, because it has the highest thermal efficiency when compared with other internal combustion engines. In addition, using diesel engine also reduce the carbon dioxide emission which is the cause of global warming. However, the main pollutants from diesel engine are solid particles

(Particulate Matter: PM) and nitrogen oxide (NO_x). The pollutants should be removed from exhaust gas because they affected environment and human health such as lung cancer.

From the reviewed literatures, they found that the average size of primary particles was approximately 20 – 60 nm while the agglomerated size of soot was approximately 100 – 300 nm. Moreover, some soot particle was also agglomerated with ash (calcium), which included in lubricant oil [1].

The diesel is fossil fuel which is consumable and limited in the earth. The alternative fuels, such as biodiesel, are the good choice for usage instead of diesel fuels. The main advantages of biodiesel over diesel fuel are its very low sulfur and aromatic hydrocarbon content. In addition, it includes oxygen molecule and also acts like environmental friendly fuel. Due to environmental benefits, there has been increasing interest in utilizing biodiesel fuel in transportation. The biodiesel fuel can substantial reduce the net global warming gas (CO_2). The combustion of biodiesel emits greenhouse gas to atmosphere as same as diesel fuel. However, in theoretical the net emission of carbon dioxide is zero while diesel combustion is 100 % emitted to atmosphere. Due to the biodiesel is produce from biomass, as plants. The growth of plants pulls out of the atmosphere to be a carbon by photosynthesis. So the carbon dioxide emitted from bio-combustion and the carbon dioxide absorption of the bio-plants is balance, the increasing of greenhouse gas in the atmosphere can assume to be zero. The biodiesel fuel results in more complete combustion than that of diesel, because it has oxygen content in its molecule. The complete combustion of biodiesel emits less and smaller size of particulate matter than that of diesel fuel. The reduction of biodiesel particulates are approximately 38% when compared with diesel. The size is around 80 to 62 nm at 75% load. These results were measured by scanning mobility particle sizer (SMPS) and high – temperature oxidation – tandem differential mobility analyzer (HTO – TDMA) system [2]. Another one, the particles size at peak value decreased from 61 nm to 39 nm with increasing the biodiesel blend ratio. The values, noted in this reviewed paper, were measured by an Engine Exhaust Particle Sizer (EEPS) device which was based on the development of the electric aerosol spectrometer [3]. In the present day, biodiesel is alternative fuels, promoted by Thai government. It can be produced in country by palm oil, jatropha oil, and etc.

The diesel particulate matter has a complicated physical and chemical structure. Two main elements of diesel particulate matter are Solid Organic Fraction (SOL), consisting of carbon and metallic ash, and the Soluble Organic Fraction (SOF), consisting of hydrocarbon. The idealized of diesel particle number and size distributions were reported by Kittelson [4] as shown in Fig.1. Most of the particle mass exists in the accumulation mode which consists of carbonaceous agglomerates and associated absorbed materials reside. The diameter ranges from 100 to 300 nm. The nucleation mode usually consists of volatile organic and sulfur compounds that formed during exhaust dilution and cooling process. In addition, it may contain solid carbon and metal compounds of size 5 – 50 nm. Figure 1 is also illustrated the definition of size of atmosphere particles: PM10, D (*diameter*) < 10 μm; fine particles, *D* < 2.5 μm; ultrafine particles, *D* < 0.10 μm; and nano- particles, *D* < 0.05 μm or 50 nm. However, the physical and chemical structure depends on engine conditions. In this research, the scanning by SEM and TEM method were used to analyze the particle structure for understanding in particle structure in order to design the high efficiency particulate filter.

2. Experimental Methodology

2.1 Test Engine

A single cylinder, four stroke, direct injection diesel engine was used in the experiment. The detailed specifications of the engine are shown in Table 1. The fuel injection pressure was kept constant at 19.6 MPa throughout the study.

2.2. Fuels

Biodiesel, derived from palm-olein, was used and compared with the results of commercial grade diesel. The significant physical and chemical properties are listed in Table 2.

2.3. Test Method

The engine speed was fixed at 2400 rpm and no load condition on the engine dynamometer. The exhaust pipe was connected to the particulate trapping devices which divided into two parts. The first part is a paper filter used for scanning accumulated particle mode by SEM. The sample gas was drawn from exhaust pipe by the vacuum pump. The paper filter was used to trap particulate matter from combustion in accumulate mode while it suspend in the exhaust gas. For primary particle measurement, the particulate matter cannot be separated from paper filter to take image for primary size by TEM. The metal net was used to capture the soot particle in the exhaust pipe, soot particle was trapped to be a powder by metal net, as shown in Fig.2. The trapped soot was removed from the metal net and taken an image by TEM in order to investigate the size of single/primary particle.

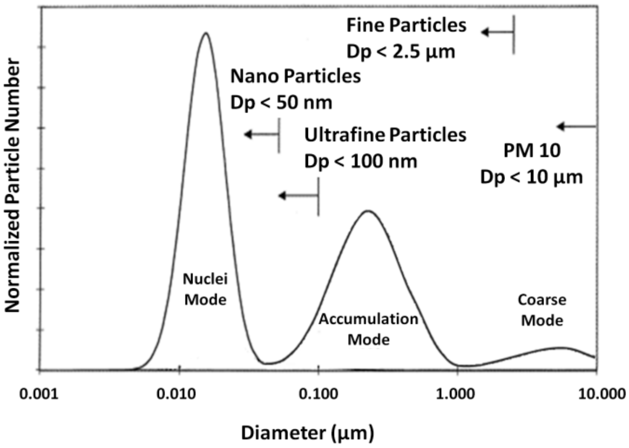


Fig.1. The idealized of diesel particle size distribution by Kittelson [4]

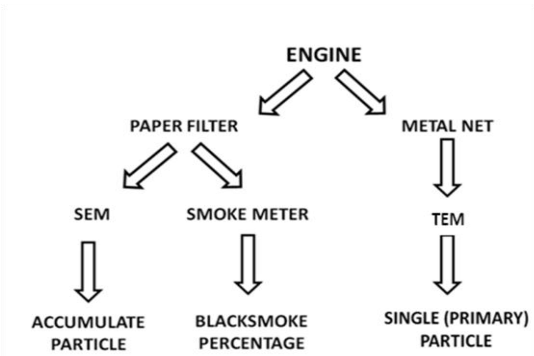


Fig.2. Schematic diagram of testing experimental

Table 1. Test engine specifications.

Type	Direct Injection (D.I.)
Number of cylinder	1
Bore x stroke (mm.)	92 x 96
Displacement (lite)	0.638
Compression ratio	16.1 : 1
Injection pressure (kg/cm²)	200
Injection timing (degree)	BTDC 19.0
Max. output (kW/rpm.)	8.8 /2400

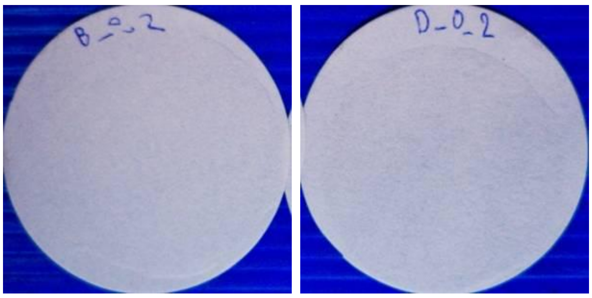
Table 2. Test fuel properties (from Department of Energy Business, Thailand)

PROPERTIES	DIESEL	BIODIESEL
Density (kg/m^3)	844.78	874.73
Heat of Combustion (MJ/m^3)	32491.826	30170.98
Cetane Number	48	55
Viscosity Centistrokes	3	5.7
Flash point (C)	64	70
Chemical formula	$C_{12}H_{22}$	$RCOOCH_3$
Carbon Concentration	82	78
Heating value (kJ/kg)	46800	39550

3. Results and Discussion

3.1. Particle Concentration

The soot particle is formed in the fuel spray cores, in which the rich fuel is contained, whereas the fuel vapor is heated by mixing with hot burned gases in the flame regions. The particle is oxidized in the flame zone when it contacts with available oxygen, resulting in yellow luminous flame character [5]. The remaining soot particle is emitted in the exhaust pipe. The paper filter was used to trap the emitted diesel and biodiesel soot particle at any time. Subsequently, smoke meter was applied to measure the concentration of trapped particulate on the paper filter by light emitting method, the zero percentage black smoke is mean no particulate



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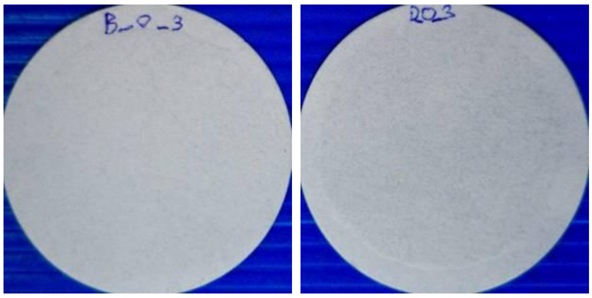

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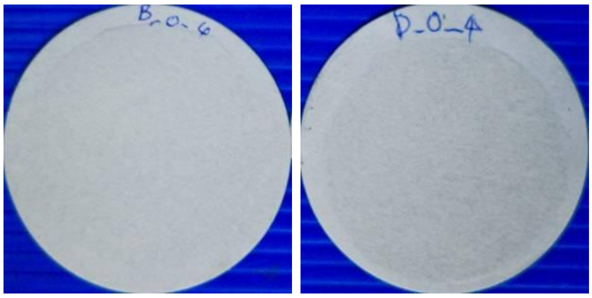


(c)

Fig.3. The paper filter of trapped biodiesel (left) and diesel (right) particulate with trapping duration for (a) 2 second (b) 3 second and (c) 4 second

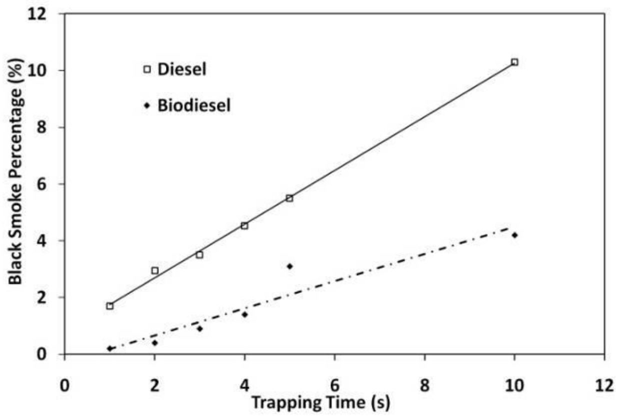
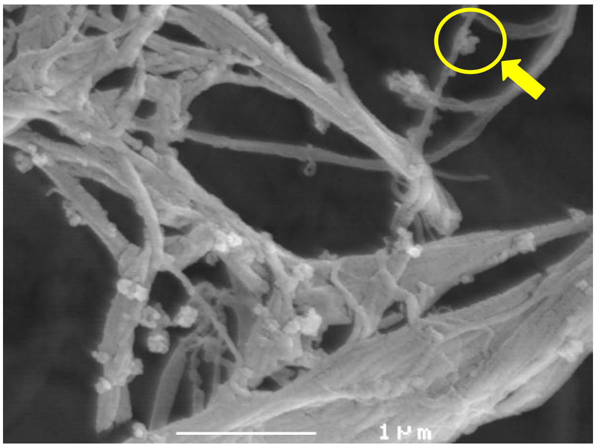


Fig.4. Particle concentration measure by black smoke meter

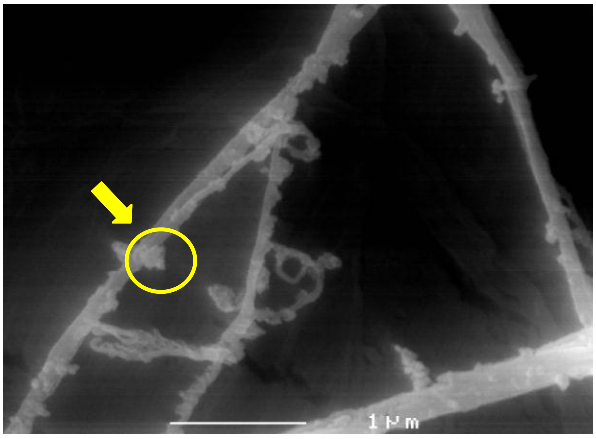
on filter and the other hand 100 percentage is mean the filter is covered by particulate all of area. The results were reported as black smoke percentage. The particle from diesel combustion was emitted more than those of biodiesel combustion for the same duration of trapping. Figure 3 shows the concentration of the soot particulate on paper filters. The concentration of biodiesel particle, on the left column, is slightly lower than that of diesel (on the right column) for all cases. Figure 4 shows the percentage of black smoke of diesel and biodiesel when varying the trapping period. The result showed that the percentage of black smoke of diesel increased faster than biodiesel did. Hence, diesel particulate formation was higher than biodiesel. This could be explained that more soot particulate was remained in diesel combustion than those of biodiesel. Because it contains oxygen molecule, biodiesel is readily oxidized with available oxygen in the flame zone. Particulate filter trapping duration of biodiesel fuel has longer than that of diesel fuel because of particulate concentration emitted from biodiesel combustion frame is lower than that of diesel combustion

3.2. Particle Structure

According, the kittelson idealized of particle size distribution. The particulate matter from diesel and biodiesel combustion was verified size for 100 particles size in each fuel. The measurement of particle diameter is calculated by average of two diagonal lengths. It is divided in two structure modes.



(a)



(b)

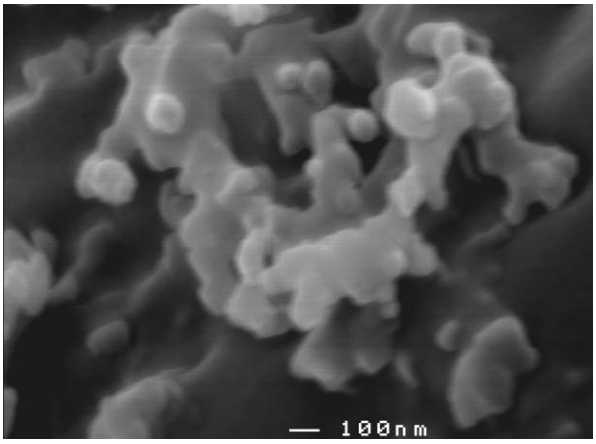
Fig.5. Accumulate particle size of (a) Diesel and (b) Biodiesel in range of fine particle

3.2.1. Fine Particles

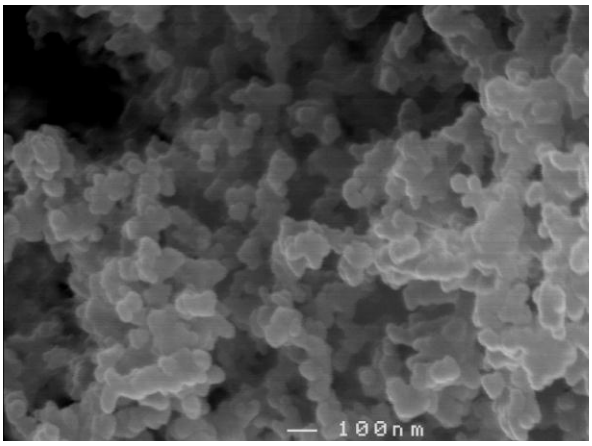
The fine particle size, as shown in Kittelson chart, is less than 2.5 μm diameter. Figure 5 is shown micro-image of diesel and biodiesel particulates by SEM in range of fine particles. In this study, the diesel and biodiesel particles size showed in result approximately 80 - 320 nm.

3.2.2. Ultrafine Particles

In this research, the particle image is taken to verify the diesel and biodiesel particle size by micro- and nano- image. Figure 6 shows a particle size of diesel (a) and biodiesel (b) respectively in range of ultrafine particles by SEM image. The image showed that the biodiesel particle size is slightly smaller than that of diesel particle. The diesel particulate size is approximately 120 – 150 nm whereas the biodiesel particle size is around 80 – 100 nm. The particulate matter is difficult to measure actual primary size by SEM method. The particulate matter emitted from engine could be covered by hydrocarbon (HC) around the particle surface.



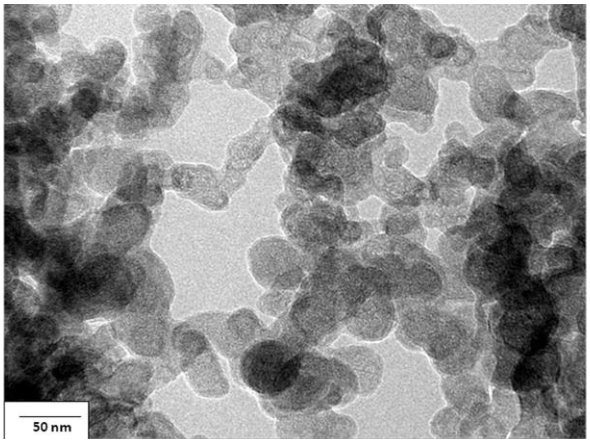
(a)



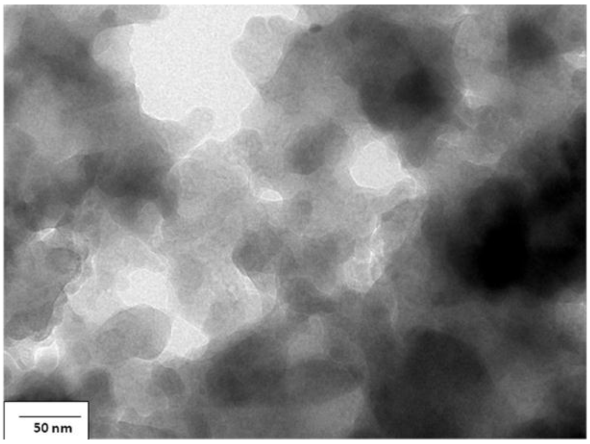
(b)

Fig.6. Primary particle size of (a) diesel and (b) biodiesel in range of ultrafine particle by SEM

The TEM method was used to measure primary particle size from diesel and biodiesel fuel. The primary particles size, be shown in TEM image as Fig. 7, is approximately 60 nm which is in range of ultrafine particles (the diameter size < 100 nm). The biodiesel primary sizes are slightly smaller than that of diesel primary sizes.

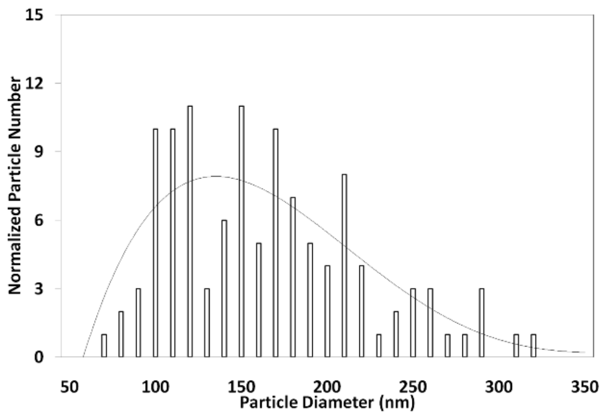


(a)

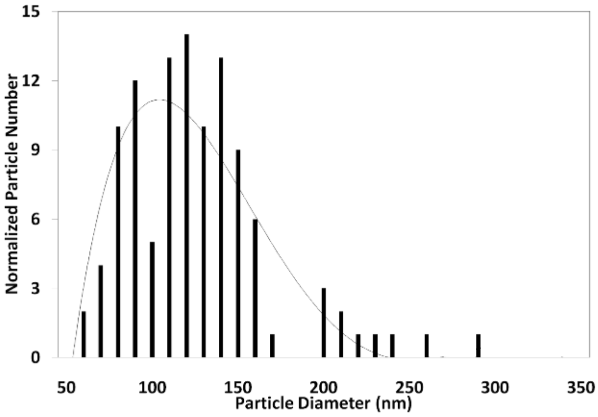


(b)

Fig.7. Primary particle size of (a) diesel and (b) biodiesel in range of ultrafine particle by TEM



(a)



(b)

Fig.8. Diesel (a) and biodiesel (b) accumulate size distribution

3.3. Particulate Size Distributions

The accumulated particulates were trapped by paper filters for 3 second. The SEM method was used to visualize the particle diameter. The particulate size distribution in accumulated mode of approximately 100 particles, taken from SEM image, was shown in Fig.8. Most of diesel particle size is around 120-160 nm while the biodiesel particle size is in range between 100-120 nm, slightly smaller than that of diesel particle. The accumulated particle is the aggregation of primary size. Due the primary particle of biodiesel was smaller than diesel primary particle. Consequently, when the primary particle were aggregated or were form in accumulate mode, biodiesel particle which were less space between the primary than that of diesel particle, the accumulate size of diesel and biodiesel might be shown in different result.

4. Conclusions

The diesel and biodiesel particulate characteristics were investigated in this experimental study. The particulate concentration of diesel and biodiesel combustion was analyzed by the black smoke meter. In addition, the particulate size was verified by SEM and TEM images. Subsequently, the size distribution chart was created for analyzing average of diesel and biodiesel accumulate particle size. The main conclusions can be summarized as follows:

1. The remaining soot particle in diesel combustion is emitted more than that of biodiesel. The oxygenated fuel properties of biodiesel should improve combustion of CI engine.

2. The SEM method measured primary particle size of diesel and biodiesel particulate matter bigger than that actual particle because of the particulate matter could be covered by hydrocarbon from engine combustion. The actual primary particle size can be measured by TEM image.

3. The primary size of diesel particles is larger than that of biodiesel. This is due to the lower concentration of biodiesel particle, which is readily oxidized with more available oxygen, in combustion flame due to oxygenated biodiesel fuel.

4. The accumulate particle size of diesel particle is larger than that of biodiesel particle. The smaller primary size of biodiesel is aggregated with small gap, resulting in smaller accumulate size.

The oxygen content in fuel has a strongly effect on the soot particle, emitted from combustion. Consequently, using the biodiesel instead of diesel can help to reduce the net global warming gas, emitted to atmosphere. The biodiesel combustion also decreases accumulate particle size and reduces the concentration of particulate, emitted from the exhaust pipe. Furthermore, biodiesel usage extends the filtration duration of the conventional particulate filter system than that of diesel fuel. Therefore, the engine back pressure from particulate filter system should be decreased, resulting in the reduction of the filter regeneration energy.

5. Acknowledgement

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6. References

[1] P. Karin, Microscopic Visualization and Characterization of Particulate Matter Trapping and Oxidation in Diesel Particulate Filters and Membrane Filters. Doctor thesis, Tokyo Institute of Technology, Japan, 2010

[2] Jung H, Kittelson D B, Zachariah M R, Characteristics of SME Biodiesel-fueled Diesel Particle Emissions and the Kinetics of Oxidation. Environmental Science & Technology, 2006, 40(16): 4949-4955.

[3] Pi-qiang T, Zhi-yuan H, Di-ming L,Bo L, Particle Number and Size Distribution from a Diesel Engine with Jatropha Biodiesel Fuel, SAE Paper 2009-01-2726, 2009.

[4] D.B. Kittelson, Engines and nanoparticles: a review, *Journal of Aerosol Science,* Vol.29, pp.575-588, 1998.

[5] J.B. Heywood, Internal Combustion Engine Fundamental, McGraw-Hill series in mechanical engineering, 1998.

[6] Shigeyuki T and Toshio S, A Study of Composition and Size Distribution of Particulate Matter from DI Diesel Engine, SAE Paper 1999-01-3487

[7] Jaime P, Study of Particle Size Distributions Emitted by a Diesel Engine, SAE Paper 1999-01-1141.