

Comprehensive Assessment of Soot Particles from Waste Cooking Oil Biodiesel and Diesel in a Compression Ignition Engine

Joonsik Hwang, Yongjin Jung, and Choongsik Bae
Korea Advanced Inst of Science & Tech

ABSTRACT

The effect of biodiesel produced from waste cooking oil (WCO) on the soot particles in a compression ignition engine was investigated and compared with conventional diesel fuel. The indicated mean effective pressure of approximately 0.65 MPa was tested under an engine speed of 1200 revolutions per minute. The fuels were injected at an injection timing of -5 crank angle degree after top dead center with injection pressures of 80 MPa. Detailed characteristics of particulate matters were analyzed in terms of transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and elemental analysis. Soot aggregates were collected on TEM grid by thermophoretic sampling device installed in the exhaust pipe of the engine.

High-resolution TEM images revealed that the WCO biodiesel soot was composed of smaller primary particle than diesel soot. The mean primary particle diameter was measured as 19.9 nm for WCO biodiesel and 23.7 nm for diesel, respectively. WCO biodiesel showed faster mass reduction of soot particles according to surrounding temperature by TGA analysis. While the oxidation of soot particles from diesel continued until 933K, WCO biodiesel soot oxidation terminated at 833K. From elemental analysis, it was revealed that the diesel soot was mainly composed of carbon and hydrogen. On the other hand, WCO biodiesel soot contained high amount of oxygen species.

CITATION: Hwang, J., Jung, Y., and Bae, C., "Comprehensive Assessment of Soot Particles from Waste Cooking Oil Biodiesel and Diesel in a Compression Ignition Engine," *SAE Int. J. Fuels Lubr.* 8(2):2015, doi:10.4271/2015-01-0809.

INTRODUCTION

Fossil fuels have driven industrial growth for the past two hundred years, however, the security of supply and the continued sustainability of utilizing such conventional fuels are increasingly uncertain. The accumulation of carbon dioxide (CO_2) in the atmosphere from the burning of fossil fuels is resulting in global climate change, and supplies of the most easily extracted sources of liquid fossil fuels are diminishing. In this situation, many countries have paid much attention to researching and application of alternative fuels to meet the emission regulations and energy needs. Biodiesel is an alternative fuel derived from vegetable oil or animal fats by trans-esterification with alcohols. Biodiesel is a promising alternative fuel for substitution of petroleum based diesel fuel because biodiesel is an oxygenated, renewable and environment-friendly fuel. However the high production cost of biodiesel is a major barrier to its commercialization. The use of low-cost feedstock, waste resources, such as waste cooking oil (WCO) makes biodiesel competitive in price. This provides an opportunity for the utilization of WCO as production feedstock [1-2]. Reusing of WCO can reduce the costs of disposing the waste and treating the oily wastewater. It also lowers the production costs of biodiesel significantly. Therefore, many researchers are attempting to apply WCO biodiesel into compression ignition engines.

The WCO biodiesel can reduce particulate matter (PM) emissions in engine exhaust because of the oxygen content in fuel molecule. It has been reported that the oxygen content improves the oxygen availability in rich-zone flames and promote soot particles to be oxidized [3]. Although the application of WCO biodiesel to conventional compression ignition engines has a disadvantage in terms of fuel consumption, it is concluded that the application of WCO biodiesel is advantageous to reduce harmful emissions. A lot of researchers have reported that using WCO biodiesel instead of diesel fuel decreases particulate matter emissions with equivalent engine performance. Lapuerta et al. [4] studied two different WCO biodiesel-diesel blends with a reference diesel fuel in a direct injection (DI) diesel commercial engine. The results showed that the brake thermal efficiency was not significantly affected, but the fuel consumption of biodiesel was increased due to its lower volumetric heating value. However, particulate matter emissions, as well as the particle number concentration, decreased significantly as the concentration of biodiesel was increased. In terms of soot characteristics, Aizawa et al. [5] sampled soot particles directly from spray flame fuelled with US#2 diesel and soy-methyl ester. Density of sampled soot particles, diameter of primary particles, size (a radius of gyration) and compactness (fractal dimension) of soot aggregates were analyzed from transmission electron microscopy (TEM) images. The overall morphology of the biodiesel soot was similar to that of diesel, but the soot density, the primary particle size and the fractal dimension were

smaller for biodiesel. Vander Wal and Mueller [6] investigated dependence of the soot oxidation rate upon the length and curvature of the graphene segments in primary particle according to fuels. The results showed that the nanostructures of soot particle were dependent on the fuel properties. The degree of amorphous nanostructure was increased with oxygenated fuels. It was suggested that biodiesel soot particles have higher reactivity due to its smaller fringe length and larger fringe curvature.

From literature review, morphological analysis of soot particles has been studied. However, in order to reduce particulate matter more efficiently, not only morphological analysis but also compositional analysis is needed. Therefore, this study aims to compare the morphological and compositional characteristics of soot particles from WCO biodiesel and diesel fuel by means of high resolution TEM images, thermogravimetric analysis (TGA) and elemental analysis.

EXPERIMENTAL SETUP AND PROCEDURE

Biodiesel Production, Composition and Property

The biodiesel fuel used in this research was produced from WCO through trans-esterification technology with methanol (CH_3OH) catalyzed by sodium methoxide (NaOCH_3). A titration was performed to determine the amount of NaOCH_3 needed to neutralize the free fatty acids in WCO. For the trans-esterification, 220 g of CH_3OH and 18 g of NaOCH_3 were added to 1 kg of WCO at 343 K. The mixture separated into crude glycerin and biodiesel in this process. The separated crude biodiesel was washed with mildly acidic water to remove the neutralized catalysts, water-soluble glycerin and soaps.

The fatty acid composition of the biodiesel was measured by gas chromatography. The results are shown in Table 1. The fatty acids in the WCO biodiesel were identified as approximately 35% mono-unsaturated, 44% poly-unsaturated, and 17% saturated. Oleic and linoleic acid were the major fatty acids, as in other biodiesels.

Table 1. Fatty acid composition of waste cooking oil biodiesel.

Type of fatty acid	Molecular weight	Carbon chain	% (By mass)
Myristic	228	C14:0	0.24
Palmitic	256	C16:0	13.12
Palmitoleic	254	C16:1	0.82
Stearic	284	C18:0	3.23
Oleic	282	C18:1	33.4
Linoleic	280	C18:2	39.2
Linolenic	278	C18:3	4.33
Arachidic	312	C20:0	0.39
Eicosenic	310	C20:1	0.47
Behenic	340	C22:0	0.2
Unknown components			4.6
Total			100

Table 2. Properties of waste cooking oil biodiesel and diesel fuel.

Item	Diesel	Biodiesel	Analytic method
Cetane number	50.88	51.34	ASTM D4737
Lower heating value [MJ/kg]	42.98	38.85	ASTM D3338
Density (@288 K) [kg/m^3]	820	878	ASTM D1298
Kinematic viscosity (@313 K) [mm^2/s]	2.2	4.4	ASTM D445
Flash point [K]	329	463	ASTM D93
Sulfur content [mg/kg]	3.93	1.00	ASTM D5454
Surface tension (@313 K) [N/m]	0.026	0.032	[7]

The major fuel properties of WCO biodiesel were measured according to ASTM standards and compared to the conventional diesel fuel, as shown in Table 2. The viscosity and surface tension of WCO biodiesel were higher than those of diesel. The density of WCO biodiesel was 6.6% higher and the lower heating value (LHV) was 9.6% lower than those of diesel. The injection quantity of WCO biodiesel needed to be increased to produce the same amount of power. The sulfur content of WCO biodiesel was 1.0 mg/kg, which is evidently lower than that of diesel. The difference of cetane numbers between WCO biodiesel and diesel was insignificant.

Experimental Apparatus and Conditions

The test engine was a single cylinder DI diesel engine with a bore of 100 mm, a stroke of 125 mm, displacement of 980 cm^3 and compression ratio of 17.4. It was equipped with a high pressure common-rail injection system. The injection pressure, injection timing and injection quantity were controlled by a common-rail engine controller (Zenobalti, ZB-9013). An eight-hole solenoid type injector (Bosch) with a hole diameter of 0.131 mm and an injection angle of 150 ° was used. Engine speed was controlled constantly by a DC dynamometer (82 kW). A rotary encoder (Autonics, E40S) was mounted on the crankshaft. The indicated mean effective pressure of approximately 0.65 MPa was tested under an engine speed of 1200 revolutions per minute because the medium-load is a dominant engine operating regime for a commercial engine of the tested engine. The fuels were injected with injection pressure of 80 MPa and injection timing of -5 crank angle degree after top dead center (aTDC), where the maximum indicated mean effective pressure occurred. Injection quantities of each fuel were set to 30mg/cycle for diesel and 33.2mg/cycle for WCO biodiesel due to its lower caloric value. The carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxides (NOx) emissions were measured using an exhaust gas analyzer (Horiba, MEXA 1500D). A smoke meter (AVL, 415S) was used to measure the engine-out smoke emissions. Soot particles from the exhaust pipe were deposited on a glass surface, which was kept cold by circulating water. Meanwhile, the soot particles were also captured on the TEM grid which is comprised of thin branches of carbon on the copper frame. Figure 1 shows a schematic diagram of the experimental apparatus. The sampled soot particles were used to perform thermogravimetric and elemental analysis (EA).

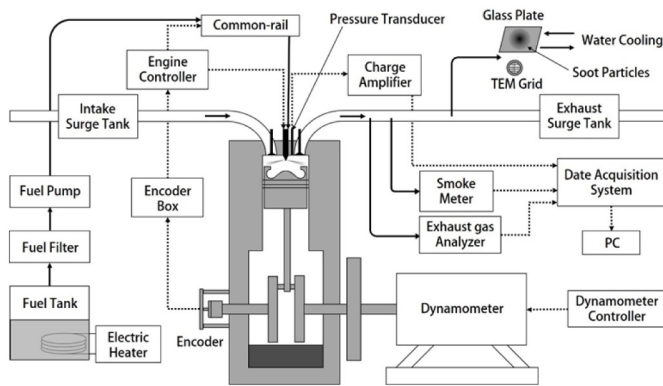


Figure 1. Schematic diagram of engine test.

Before the analysis, the samples were cured in an oven for 24 hours at 105°C to eliminate water content included in combustion products and condensed from ambient air. The cured sample was enveloped using moisture sealing film to protect soot particles from contamination. TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature or as a function of time. TGA is commonly used to determine specific characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatile. In this study, the weight of soot particles was monitored according to atmospheric temperature. The thermogravimetric analysis was conducted on the soot samples under an air atmosphere up to 1173 K by TGA analyzer (TG 209 F3 Tarsus). The temperature was raised 10 K by a minute. EA is a process where a sample of some material is analyzed for its elemental composition. The most common form of elemental analysis is accomplished by combustion analysis. In this method, a sample is burned in an excess of oxygen and various traps, collecting the combustion products which are composed of carbon dioxide, water, sulfur oxide, and nitric oxide. The masses of these combustion products can be used to calculate the composition of the unknown sample. In this research, the elemental analyzer (EA 1110-FISONS) was employed to classify soot particle components into carbon, hydrogen, nitrogen, sulfur, and oxygen by weight fraction. The soot particles captured on the TEM grid were visualized by high resolution transmission electron microscope (JEOL JEM 3010) to examine soot morphology.

RESULTS AND DISCUSSION

Combustion Characteristics

Figure 2 displays a comparison of in-cylinder pressure and heat release rate with respect to crank angle for WCO biodiesel and diesel at the injection timing of -5 CAD aTDC.

As demonstrated in Fig. 2, the combustion of the biodiesel starts slightly later than that of the diesel fuel. The main reason is a longer injection delay of the biodiesel than that of the diesel fuel. Biodiesel

has higher fuel viscosity and thus generate higher friction around the injector needle. This leads to a slow needle-lift movement and longer injection delay [8]. Although the cetane number of the biodiesel is a little higher than that of the diesel (see in Table 2), the higher viscosity and lower volatility of the biodiesel lead to poor atomization and mixture preparation with air during the ignition delay period, which results in a later start of combustion for the biodiesel. On the other hand, the peak of heat release rate with WCO biodiesel was higher than diesel. The reason is that even though the physical properties of WCO biodiesel were less favorable regarding mixing and evaporation, the presence of fuel bound oxygen enhanced combustion.

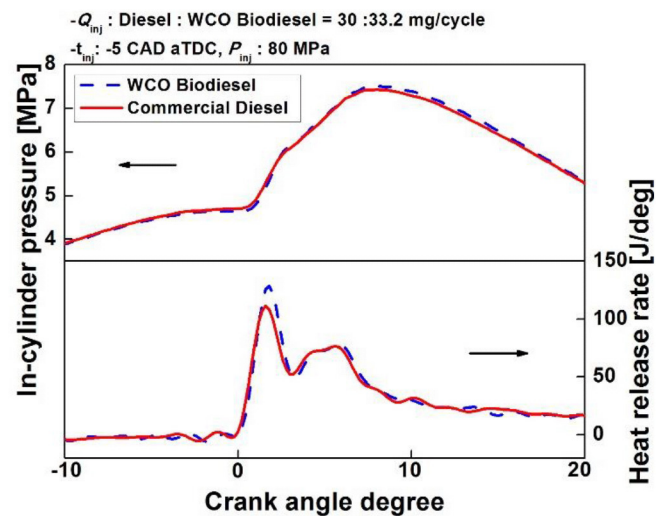


Figure 2. Comparison of combustion characteristics at injection timing of -5 CAD aTDC with injection pressure of 80 MPa for WCO biodiesel and diesel.

EMISSION CHARACTERISTICS

Figure 3 compares the emissions of WCO biodiesel and diesel combustion. WCO biodiesel was advantageous for the reduction of CO, HC and PM emissions. The reduction of these emissions has been attributed to the oxygen content of WCO biodiesel [9]. In the previous research, it was confirmed that the oxygenated fuel showed suppression effect of soot particles due to the drastic reduction of soot precursor species [10]. Venkanna et al. [11] stated that aromatics are known as a contributor of soot formation, while the oxygen molecules inherent in the biodiesel help to promote stable and complete combustion by delivering oxygen to the pyrolysis zone. NO_x levels were slightly increased with WCO biodiesel due to higher local peak temperature by forming a more stoichiometric air-fuel mixture [12]. Compared to reduction of CO, HC and PM emissions, the level of NO_x increase was not significant and it was revealed that the simultaneous reduction in NO_x and PM emission could be achieved by using double injections with appropriate injection timings and fuel distributions [13].