Fuel 218 (2018) 218–226

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Study on status characteristics and oxidation reactivity of biodiesel particulate matter

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ARTICLE INFO

Keywords:
Diesel engine
Biodiesel
PM
Status characteristics
Oxidation reactivity

ABSTRACT

Biodiesel is a kind of clean and renewable fuel for diesel engine. The source of biodiesel affects the component and physicochemical properties of biodiesel, and it also influences the formation of particulate matter (PM) during the combustion process. In this paper, the PM of diesel and 5 kinds of biodiesel from different sources were collected. In addition, the effects of biodiesel from different sources on morphology and PM diameter were analyzed. Taking the biodiesel made from waste cooking oil as the research object, the PM of diesel engine fueled with diesel/biodiesel blend ratio of 0%, 20%, 50%, 100% were collected by the test bench at engine speed 2000 r/min and engine torque 12.27 N·m. The effects of biodiesel on morphology, diameter, elements, functional groups and component of PM were analyzed. Results show that the average PM diameter of biodiesel from different sources is between 20 and 90 nm. The PM diameter of biodiesel made from cottonseed is larger than that from other different sources. From the test, the average PM diameter of diesel is 26.27 nm. With the increase of biodiesel blend mixing ratio from 0% to 20%, 50% to 100%, the diameter of PM is decreased by 7.9%, 17.2% and 24.2% compared with that of diesel respectively and the microscopic morphology of PM changes from ring to cluster. The analysis of X ray energy spectrometer shows that the content of C in PM is reduced. However, the content of O, Na, Cu, Al, Ba and Zn is increased. The analysis of X-ray absorption near edge structure shows that the content of "graphite" C = C, phenol C–OH, ketone C = O, aliphatic C=C in PM is decreased gradually, and the content of aliphatic hydrocarbon C–H and carboxyl C=O is increased. With the increase of biodiesel blend mixing ratio, the content of volatile organic compounds (VOF) is increased and the content of soot is decreased. When biodiesel mixing ratio reaches 50%, T_i, T_m, T_b and E of PM are decreased obviously from thermo-gravimetric analyzer test, it means that oxidation of PM was more actively.

1. Introduction

In 2016, China's dependence on foreign oil has reached 65.4% [1]. Finding clean alternative fuels for diesel engines has become an important topic among scholars. Biodiesel is prepared by transesterification of vegetable oils or animal fats. The raw materials of biodiesel don't contain sulfur, aromatic compounds and other harmful substances. Diesel engine fueled with biodiesel fuel could reduce particulate matter (PM) emission, and it can relieve haze and air problems. Besides, the degradation rate of biodiesel is as high as 98%, which is 2 times of that of mineral diesel. It is a kind of high quality green environmental protection renewable energy [4–7]. In China, waste cooking oil is the main source for biodiesel. At present, Chinese biodiesel has achieved large-scale production and increased year by year. In 2016, China had more than 50 biodiesel product companies with a total capacity of more than 3.5 million tons.

Biodiesel can be mixed with diesel or used directly in diesel engines. Compared with diesel, biodiesel can effectively reduce the emission of unburned hydrocarbons (HC), carbon monoxide (CO) and PM in diesel engine [2–6]. PM is mainly composed of VOF, soot and metal components. The component and structure of PM have a great influence on the oxidation activity of PM, and the oxidation activity of PM influences on the regeneration of diesel particulate filter (DPF) carrier. For the PM with higher oxidation activity, the regeneration temperature is lower and the regeneration efficiency is higher [7].

Biodiesel made from different raw materials contains different types of esters, and the physicochemical properties will be different from each other, leading to different combustion parameters of biodiesel and different oxidation activity of PM. Abdalla [8] studied the properties for diesel, biodiesel and blended fuels. The results indicated that a linear increase with increasing the biodiesel percentage in the blend. Sulphur content decreased continuously with increasing the biodiesel percentages in the blend while the acid content increased with increasing biodiesel ratio. Madheshiya [9] studied the soot emissions of diesel

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https://doi.org/10.1016/j.fuel.2018.01.041
Received 7 November 2017; Received in revised form 2 January 2018; Accepted 11 January 2018
0016-2361/

engine fueled with diesel, waste cooking oils and mustered oil. The results showed that soot emissions were alike for diesel, waste cooking oils, and mustered oils at low load, but at higher load diesel had an exponential increment in soot emissions. Zhao [10] studied analysis of fuel structures on engine soot particles' mass and size using diesel and different levels of unsaturated biodiesel fuels through the numerical simulation. The results showed that the biodiesel fuel with a higher fraction of unsaturated fatty acid methyl esters (more double carbon bonds C=C) contributed more to the formation of soot precursors, thus producing a higher amount of soot particles in mass and numbers, accelerating soot particle nucleation and soot surface growth.

Giakoumis [11]studied the effects of diesel/biodiesel blends on the exhaust emissions of diesel engines operating under transient conditions. The results showed that the use of biodiesel blends, regardless of their source material, resulted in dramatic PM mass reductions ranging from 67% to 74%. These reductions could be attributed to the increased oxygen concentration in the biodiesel blend, which reduced locally fuel-rich regions and limits soot nucleation in the formation process. Grigoratos [12]tested diesel as well as three blends of rapeseed methyl ester at 10%, 30% and 50% v/v with three Euro 4+ compliant vehicles. The result showed higher oxidative activity with increasing biodiesel blending when testing two light-duty vehicles with and without a DPF over the NEDC and Artemis cycles. Agudelo etc. [13] compared the oxidation activity of PM produced by diesel, palm oil biodiesel and jatropha oil biodiesel. The results showed that PM oxidation activity of Jatropha curcas oil biodiesel was the highest, followed by palm oil biodiesel, and diesel. Karavalakis [14] assessed PM on two heavy-duty trucks fueled with ultra-low sulfur diesel and biodiesel blends as well as the oxidative potential of the PM measured by means of the dithiothreitol assay. The results showed a reduction on oxidative potential of PM with the use of biodiesel blends relative to ultra-low sulfur diesel.

The oxidation activity of PM is closely related to the microstructure of PM. Disordered carbon atoms, which are located in PM microcrystalline graphite layer, have unpaired sp^2 electrons, are more easily to form a covalent bond with the chemical adsorption oxygen. However, the ordered carbon atoms in microcrystalline graphite layer only with sharedπelectron, are difficult to combine with oxygen. The surface functional group on the edge of the PM carbon layer is more likely to react with the oxidized gas to form CO or CO_2, and to make the carbon atoms fall off the original chemical bond. Cain etc. [15]studied the distribution of functional groups on soot PM. The results showed that many types of functional groups were present on the surface of the soot PM, including aliphatic C—H functional group, aromatic C—H functional group and oxygen-containing group (C=O, C—OOH, C—OH, C—O—C). Among these functional groups, the relative content of aliphatic C—H functional group was the highest. Nabi [6]studied PM and particulate number (PN) of biodiesel/diesel blends in a six-cylinder turbocharged diesel engine with a high-pressure common rail injection system in compliance with a 13-Mode European Stationary Cycle. Results showed that with the addition of biodiesel, a significant reduction in both PM and PN emissions was observed relative to those of diesel. A maximum reduction of 84% PM and 88% PN was observed by using the biodiesel blends. Wei [16] studied the influence of waste cooking oil biodiesel on particulate emissions of a direct-injection diesel engine. The results showed that the addition of biodiesel reduced the weighted particle mass concentration and the weighted geometric mean diameter of the particles. The influence of biodiesel on the investigated emissions was proportional to the biodiesel content in the tested fuels. Gali [17] studied the chemical components of solid and semi-volatile PM from diesel and biodiesel blend. The results showed that PM emission was lower for biodiesel/diesel blend (30% biodiesel added) in general. PM for biodiesel/diesel blend contained 19% higher organic compounds in semi-volatile PM compared with diesel, which on the other hand noted 24% more solid PM. Shukla [18] studied the trace metals and ions in particulates of engine fueled with Karanja biodiesel blend (20% v/v biodiesel in the blend fuel), and 9 commonly present trace metals (Ca, Fe, Cr, Cu, Mn, Pb, Ni, Ba and Cd) and inorganic anions (such as nitrates, chlorides, fluorides and sulphates) were compared for biodiesel/diesel blend and diesel. The results showed that biodiesel origin particulate contained slightly lower amount of trace metals and inorganic ions compared with diesel for similar operating conditions except nitrates. According to the analysis above, biodiesel has a wide range of sources and complex components, and it will influence the formation of PM from diesel engine. The oxidation activity of PM is closely related to the microstructure, such as elements, component, and functional group. However, the PM oxidation activity has most important effect on exhaust emission of the engine, and it affects after-treatment of diesel engine. There are no enough reports to explanation the status characteristics and oxidation activity of biodiesel PM. From this view points of biodiesel sources and fuel characteristics, it is necessary to carry out the research on the status characteristics and oxidation reactivity of biodiesel PM.

Friendly environment and stricter engine emission stander requires lower diesel engine particulate emissions. DPF is one of the effective way to reduce the PM. With the time going on, the PM adsorbed in the DPF will cause problems such as blockage of the DPF, etc. Performance of diesel engine will be reduced. This involves the problem of DPF regenerated. The objective of this research is to study the influence of biodiesel on the status characteristics and oxidation reactivity of PM. In this paper, the PM diameter distribution of diesel oil and biodiesel made from five different sources were investigated by the combustion test at normal temperature and pressure. Then the waste cooking oil biodiesel was selected to add into diesel, and PM of diesel/biodiesel blend with different blending ratio were collected on engine bench test. By means of high resolution transmission electron microscopy (TEM), X ray energy spectrometer, thermogravimetric analyzer and X-ray absorption near edge structure (XANES) test, the micro morphology, element type, chemical component and functional group of the PM were measured, and the effect of biodiesel on the formation of PM characteristics was discussed.

2. Analysis of biodiesel quality and PM formation factors

6 kinds of fuel were used in this test, including $0^{\#}$ diesel, waste cooking oil biodiesel, rapeseed oil biodiesel, soybean oil biodiesel, cottonseed oil biodiesel and palm oil biodiesel. $0^{\#}$ diesel is commercial diesel, soybean oil biodiesel is produced by Hainan positive and Bio Energy Limited, waste cooking oil biodiesel is produced by Jiangsu Carter Petroleum New Energy Co., Ltd. The remaining 3 kinds of biodiesel are prepared in Jiangsu biodiesel power machinery application engineering center. The physicochemical parameters of the fuels are listed in Table 1.

The formation mechanism of PM is complex, which is greatly affected by the combustion process. It is generally believed that soot size and amount of formation are related to temperature, pressure, time, oxygen content, fuel properties and so on. Local high temperature, hypoxia, cracking and dehydrogenation are benefit for the generation of PM. The carbon structure of PM has an important effect on the oxidation of PM. The PM whose carbon atoms are arranged orderly, like in a graphite structure, are difficult to be oxidized in the combustion process [19]. Thus, the properties of the fuel which will influence the formation of PM are analyzed below.

2.1. Oxygen content

The area in front of the burning flame is rich of oxygen, and soot is mainly generated on the side of the flame front. The average oxygen content in biodiesel is around 11%. The oxygen in biodiesel can improve the situation of oxygen deficiency and promote combustion. So, combustion condition of biodiesel is better compared with diesel and less soot is formed. Bedjanian's study showed that fuel quality played an important role in the formation of PM. Oxygen in the fuel could