Bulgarian Chemical Communications, Volume 49, Special Edition K2, (pp. 54 – 58) 2017

Study on the effect of diesel blended with n-butanol on particulate matter state characteristics of a small agricultural diesel engine

L. Chen [1,2*], Z. Wang [1], S. Liu [1]

[1]*School of Automotive and Traffic Engineering, Jiangsu University, Zhenjiang, China*
[2] *CATARC Yancheng Automotive Proving Ground Ltd. Yancheng, China*

Received August 15, 2017, Revised November 15, 2017

This work studied the effect of diesel blended with n-butanol on particulate matter (PM) state characteristics of a small agricultural diesel engine which revealed the mechanism of n-butanol reducing PM emissions in diesel engine. The microstructure, oxidation characteristics, components and surface functional groups of PM with N5 (5% n-butanol and 95% diesel fuel in quality basis), N10 and diesel fuel were measured. The results indicated that n-butanol/diesel PM displayed cluster structure. With the increase in n-butanol content, the average diameter of PM gradually decreased while aggregation degree increased. Pyrolysis of PM in the air was divided into two stages - soluble organic matter evolution stage and soot combustion stage. With the increase in n-butanol content, the initial combustion temperature of soot decreased, the temperature corresponding to the mass change rate peak of weightlessness with PM dropped, soluble organic matter and soot content in particulate fractions increased, while metal and inorganic salt content decreased. The equivalent peak height ratio (IC-H-IC=C)/IC=C of aliphatic functional C-H on particulate surface increased and its relative content gradually increased.

Key words: Particulate matter, n-Butanol, Microstructure, Diesel engine

INTRODUCTION

Particulate matter (PM) is the main pollutant of diesel engine; it discharges into the atmosphere environment and suspends in the atmosphere for a long time. Besides, PM from diesel engine can involve in the formation of haze, and affect the human physical and mental health. [1-4] As alternative fuels, oxygenated fuels include alcohols, esters and ethers that are widely used in diesel engine for today's applications and effectively control the diesel PM emissions.

Many scholars have carried out studies on the characteristics of PM formed by the mixing of oxygenated fuels for diesel engine. Chen [5] has studied the particle size distribution of diesel engine with ethanol/methyl ester/diesel combustion PM. The results showed that in the oxygenated fuel, PM were essentially unchanged with a size greater than 0.5 μm, the number of PM decreased when the size was between 0.2~0.5 μm, and the number increased when the size was less than 0.2 μm. Carbon cores formed by burning of oxygenated fuels are less in comparison with diesel fuel. Tsolakis' studies showed that biodiesel PM coagulated and aggregated to spherical fundamental particulates. The PM were arranged closely in grape-like state and clusters, while the structure of the diesel PM was loose in a state of chain [6].

As a kind of alcohol fuel, N-butanol is one of the best additives for diesel engines due to its features such as high oxygen content and intersolubility with diesel. It is widely used in the blending of methanol and diesel fuel. The physical and chemical properties of n-butanol are close to diesel fuel and cause little corrosions without needing to rebuild the structure of the original fuel supply control systems. This is the particular reason for directly applying a low ratio of n-butanol blending to diesel in the diesel engine [7-9].

Great progress has been made in this field; however the effect of diesel blended with n-butanol on PM state characteristics has not been fully characterized. Compared with vehicle diesel engine, the moving range of off-road diesel engine such as the agricultural machinery, engineering machinery and so on is small, which leads to high PM emission [10-12]. In view of this, the study takes off-road diesel engine 186F as the research object which is widely applied in pump and diesel engine power generator units. n-Butanol/diesel blended fuel was studied with the aid of scanning electron microscopy, thermogravimetric analysis, and infrared spectroscopy. The studies covered various aspects of microstructure, oxidation characteristics, components and distribution of surface functional groups of n-butanol/diesel combustion particulates. The study investigates the effects of n-butanol on the state characteristics of diesel engine particulates which provide a theoretical basis for revealing the mechanism of n-butanol reducing particulate emission of diesel engine, as well as the promotion

*To whom all correspondence should be sent:
E-mail: chenlin@catarc.ac.cn

of n-butanol substituted fuel for off-road diesel engine.

EXPERIMENTAL

Test for diesel engine and fuels

The experimental work was conducted on 186F diesel engine, and the main technical parameters are shown in Table 1.

Table 1. Main parameters of 186F diesel engine

Project	Parameter
Engine type	Single-cylinder, direct injection, air cooling
Bore	86 mm
Stroke	70 mm
Rated power	5.7 kW
Rated speed	3000 rpm
Compression ratio	19
Link length	117.5 mm
Displacement	0.406 L
Supply advance angle	12°CA

Test materials for the experiment were diesel and anhydrous n-butanol, from which three kinds of fuel on the basis of diesel were prepared: diesel fuel, N5 w (5% n-butanol and 95% diesel fuel on quality basis), N10 w (10% n-butanol and 90% diesel fuel on quality basis).

The cetane number of n-butanol is less than that of diesel fuel. The mass fraction of oxygen was about 21.6% which effectively improved the oxygen concentration of the blended fuel and perfected the fuel combustion process. The calorific value of n-butanol was lower by 77% than that of diesel fuel, and the calorific value of the blended fuel slightly decreased on blending with a small amount of n-butanol.

Test scheme

The bench test was carried out on the premise of unchanged supply advance angle and structural parameters of the diesel engine. The schematic diagram of the test system is shown in Figure 1.

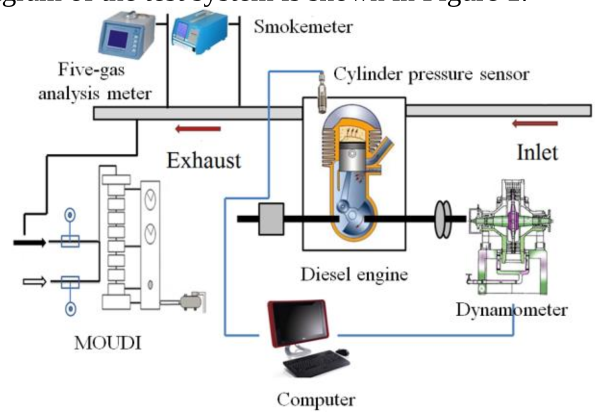


Fig. 1. Schematic diagram of the test system

For sampling, aluminum foil filter paper was used whose microporous diameter was 47 nm, the sampling rate was 6 L/min, and the sampling time lasted 30 min. The collected samples were characterized by scanning electron microscopy, thermogravimetric analysis and infrared spectra to discuss the effects of n-butanol on PM state characteristics.

RESULTS AND DISCUSSION

Soot emission

The change law of smoke intensity value with different loads at a speed of the diesel engine of 1800 rpm and 3000 rpm is shown in Figure 2.

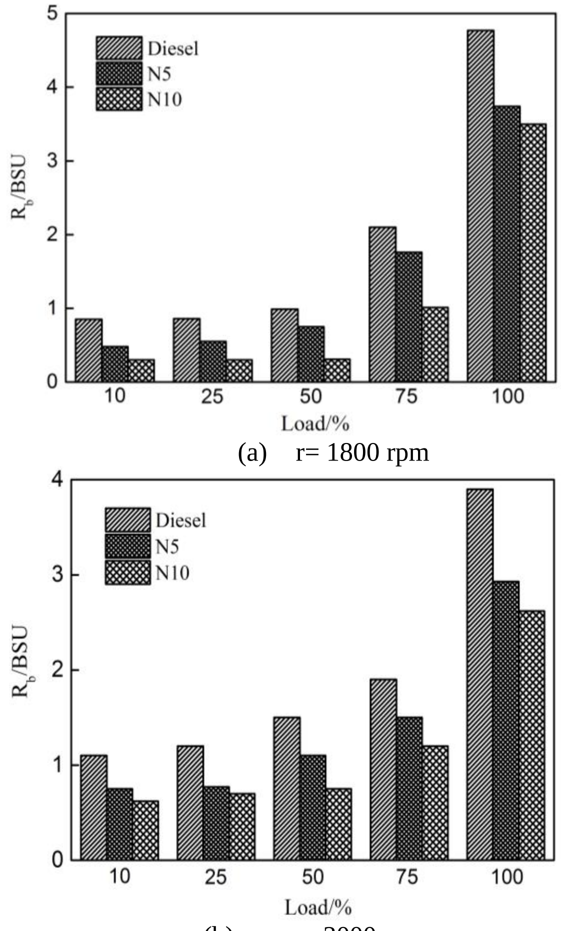
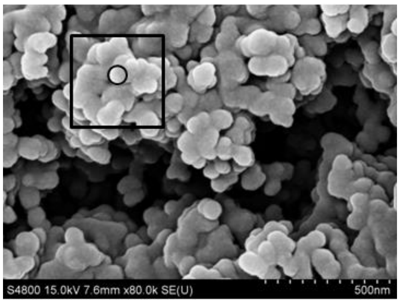


Fig.2. Effects of different n-butanol blends on soot emission

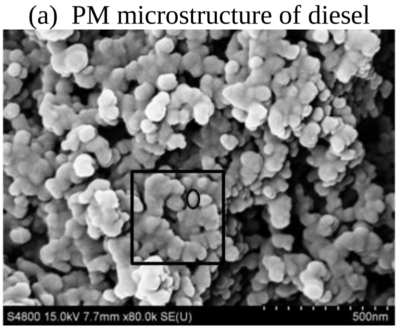
As shown in Figure 2, the trends of soot emission with the three tested fuels were basically the same. The fuel burnt completely and the possibility of soot generation was small at the low load. The smoke value obviously increased with the load increase at medium-to-high load. At the high load, the superfluous air coefficient decreased, air mixed unevenly in the combustion chamber, which resulted in a low air-to-fuel ratio in some areas, incomplete combustion of fuel and generation of a lot of soot. The smoke intensity value sharply increased. Under the same conditions, smoke intensity value gradually decreased with the increase in n-butanol content. Compared with diesel fuel, smoke intensity value of N10 obviously decreased and was reduced by 26.7% and 32.8% at the speed of 1800 rpm and 3000 rpm, respectively, with full load. Diesel blended with n-butanol could reduce soot emissions for the main factors: Compared with diesel fuel, the vaporization heat of n-butanol is high. By blending with n-butanol, the vaporization heat of the blended fuel increased which resulted in the addition of heat absorption. The time of physical and chemical reaction was prolonged and the ignition delay period was extended.

Microstructure

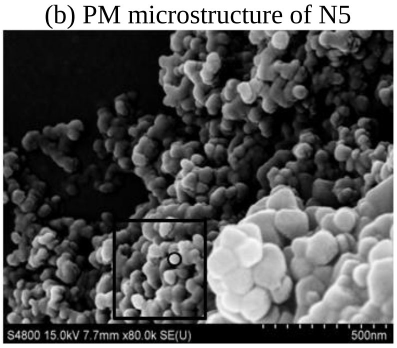
The PM microstructure of the three tested fuels was recorded by scanning electron microscopy (8×10^4 magnification). The results are shown in Figure 3.



(a) PM microstructure of diesel



(b) PM microstructure of N5



(c) PM microstructure of N10

Fig. 3. SEM images of n-butanol/ diesel combustion PM

Under the action of adhesive forces such as van der Waals force, electrostatic force, liquid bridge force and so on, the PM showed clusters as a whole and accumulated by hundreds of unequigranular spherical basic accumulations of carbon particulates which formed different density of PM. Average diameter of PM was calculated by the number of per unit area by scanning electron microscopy. The average diameters of PM with diesel, N5 and N10 were 1.43, 0.85, 0.52 μm, respectively. The average size of the PM decreased with the increase in n-butanol content. The reasons why blending n-butanol could decrease the size were as follows: (1) n-butanol could reduce the concentration of polycyclic aromatic hydrocarbons in the precursor of soot; decrease the formation of nuclear particulates; reduce the polymerization ability of carbon nuclei, and decrease the size of formed particulates [13]; (2) as an oxygenated additive fuel, n-butanol improved the combustion process and promoted the transformation of PM in the diesel engine; (3) at high temperature, n-butanol easily cracked into longer-living radicals which could oxidize PM and reduce the diameter of the carbon nuclei in the process of PM formation.

The SEM images of diesel engine PM revealed typical fractal structure, and the growth mechanism of PM determined its fractal structure characteristics. The agglomeration morphology of PM was mainly divided into settlement by gravity, diffusion of PM in the process of turbulence and irregular Brown motion [14]. For further analyzing the geometric structure characteristics of PM, the density of pellet geometry structure was quantitatively studied. At bigger fractal dimensions there was a higher degree of overlap between the primary carbon particulates and higher compactness of the PM which consisted of fundamental carbon particulates and *vice versa* [15]. Fractal characteristics of PM with different n-butanol/diesel blends were studied in this article by self-similar fractal dimension which is known as the box-counting dimension. The algorithm of box-counting dimension could be expressed as described in [16].

By calculating the box-counting dimension of the SEM image of PM in the diesel engine, the threshold binarization and the relationship lgN(r)-lgr of diesel PM were obtained. After fitting curve, the results are shown in Figure 4. It can be seen that the linear regression coefficient of the fitting curve is 0.9981, and the box-counting dimension of diesel PM is 1.942. Calculating box-counting dimensions of PM (N5, N10) used the same method. The results are shown in Table 3.

It can be seen that the linear regression coefficient of lg*N(r)*-lg*r* fitting curve of PM is higher than 0.99 which signifies a good fitting. The calculated box-dimensions were 1.975 and 1.995, respectively. With the increase in n-butanol content, the box-dimension of the PM gradually increased which indicated that the agglomeration degree of PM gradually increased, and the structure arrangement was more compact.

Table 3. Box dimensions of n-butanol/diesel combustion PM

Test sample	Fitting line	R^2	D_B
Diesel	y=-1.942+13.647	0.9981	1.942
N5	y=-1.975+13.781	0.9987	1.975
N10	y=-1.995+12.058	0.9947	1.995

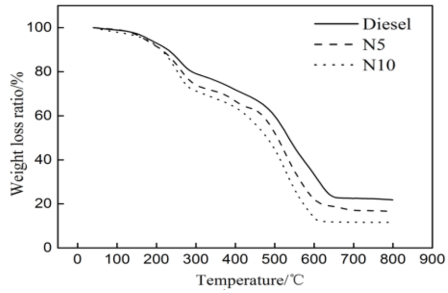
With the increase in *w* (n-butanol) content, the proportion of the single molecule decomposition reaction in n-butanol gradually increased, generating more propyl (-C_3H_7), hydroxymethyl (-CH_2OH) and other active radicals which accelerated the chain propagation reaction rate. In addition, O and C formed stable C-O bonds in the molecular structure of n-butanol which promoted PM oxidation and reduced the produced quantity of polycyclic aromatic hydrocarbon material in the soot precursor [17]. Each carbon and hydroxyl of the n-butanol molecules easily participated in dehydrogenation and non-bridging agglomeration reactions, which generated trace amounts of water molecules; promoted the attraction by the van der Waals force between PM, and made the reunion more compact.

Thermogravimetric analysis

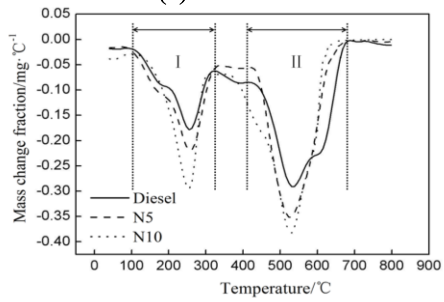
Thermogravimetric analysis studied a series of physical and chemical changes such as volatility, pyrolysis, oxidation, combustion and other physical and chemical changes of PM samples by controlling the temperature. It measured the quality of PM with the temperature change in the thermogravimetric curve (TG curve). The derivative TG curve reflected the derivative thermogravimetric curve of PM samples mass rate (DTG curve). Through the combination of TG curve and DTG curve, the relative content of soluble organic matter, soot, metals, inorganic salts, etc. in the particulates was determined [18]..

Figure 4 shows the TG-DTG curves of PM fuelled with n-butanol/diesel.

As can be seen from the TG curve, with the rise of temperature, the mass of PM gradually decreased. When the temperature reached around 640°C, the mass of PM no longer changed. What could be seen from the DTG curve was that each



(a) TG curve



(b) DTG curve

Fig. 4. Effects of w (n-butanol) on TG-DTG of PM

curve had two peaks which could be considered as the two main reaction stages corresponding to the temperature range. The first stage was the low-temperature zone. The temperatures of the mass change rate peak of weightlessness of the PM samples (diesel, N5, N10) were 254℃, 250℃ and 247 °C, respectively. The main reaction in this section was the evolution of soluble organic matter. At the initial heating stage, the moisture in PM and low boiling point components of HC volatilized with the increase in temperature. When the temperature gradually reached the boiling point of HC, evaporation and oxidation reaction with oxygen occurred in the air. When the moisture of PM and HC basically volatilized and completely oxidized, the weight loss ratio was equal to the content of soluble organic matter in the PM. With the increase in n-butanol content, the initial combustion temperature TSOF decreased. As a small molecular oxygenated fuel, the carbon chain length of n-butanol was short; more oxygen groups were adsorbed on the particulate surface after burning which resulted in soluble organic matters oxidizing and burning easily in air atmosphere. The second stage was the high-temperature zone; main reactions in this stage were the oxidation and combustion of soot. When the temperature increased and there was no change in PM mass, the remaining components were mainly metal and inorganic salt groups. With the increase in the n-butanol content, the temperature corresponding to the mass change rate peak of weightlessness decreased which indicated that the weight loss curve of PM was shifted to the low temperatures.

CONCLUSIONS

1. At the same speed, with the increase in load, the smoke intensity value gradually increased, slowly under small and medium loads and sharply under medium and high load. Under the same conditions, the formation of soot gradually decreased with the increase in n-butanol content. When the speed of the diesel engine was 1800 rpm and 3000 rpm with full load, the smoke intensity value of N10 was reduced by 26.7% and 32.8% respectively, compared with the diesel fuel.

2. The microstructure of the n-butanol/diesel PM appeared as irregular clusters, and the average diameters of the PM were 1.43, 0.85, 0.52 μm. The PM size decreased and the aggregation degree gradually increased with the increase in the n-butanol content.

3. The pyrolysis process of PM in air was divided into two stages: (i) soluble organic matter evolution stage, (ii) soot oxidation and combustion stage. With the increase in n-butanol content, the initial combustion temperature of PM decreased; the temperature corresponding to the mass change rate peak of weightlessness of PM decreased; the weightlessness curve moved toward low temperatures. The content of soluble organic matter and soot components increased, but the content of nonvolatile and nonflammable materials such as metals, inorganic salts and other decreased.

Acknowledgements: *This study was financially supported by the National Natural Science Foundation of China under Grant (No. 51376083), and the Natural Science Foundation of Jiangsu Higher Education Institutions Project (No.13KJA470001).*

REFERENCES

1. Z. H. Zhang, R. Balasubramanian, J. *Hazard. Mater.*, **264**, 395 (2014).
2. O.B. Popovicheva, E.D. Kireeva, N.K. Shonija, M. Vojtisek-Lom, J. Schwarz, *Environ. Sci. Pollut.* R., **22**, 4534 (2015).
3. L. Zhu, W. Zhang, W. Liu, Z. Huang, *Sci. Total. Environ.*, **408**, 1050 (2010).
4. Z. Liu, B. Hu, L. Wang, F. Wu, W. Gao, Y. Wang, *Environ. Sci. Pollut*. R., **22**, 627 (2014).
5. H. Chen, W. M. Chen, J. X. Wang, S. Shuai, *Transactions of CSICE*, **25**, 47 (2007).
6. A. Tsolakis, *Energy Fuels*, **20**, 1418(2006).
7. B. Choi, X. Jiang, *Fuel*, **154**, 188 (2015).
8. B. Choi, X. Jiang, Y. K. Kim, G. Jung, C. Lee, I. Choi, C. S. Song, *Appl Energ.*, **146**, 20 (2015).
9. S. S. Merola, C. Tornatore, S. E. Iannuzzi, L. Marchitto, G. Valentino, *Renew. Energ.*, **64**, 225(2011).
10. B. F. Yin, T. Guan, J. G. He, Y. Xu, *Applied Mechanics Materials*, **43**, 476 (2010).
11. M. Pietikäinen, A. Väliheikki, K. Oravisjärvi, T. Kollia, M. Huuhtanena, S. Niemib, S. Virtanenc, T. Karhuc, R. L. Keiskia, *Renew. Energ*., **77**, 377 (2015).
12. A. Chung, A.A. Lall, S.E. Paulson, *Atmos. Environ*., **42**, 2129 (2008).
13. H. Huang, Q. Liu, R. Yang, T. Zhu, Y. Wang, *Energy Convers. Manage*., **106**, 748 (2015).
14. S.K. Friedlander, C.S. Wang, *Politics Policy*, **22**, 126 (1996).
15. J. Park, J. Yoon, S. Song, K.M. Chun, *J. Aerosol Sci*., **41**, 531 (2010).
16. P. Bouboulis, L. Dalla, V. Drakopoulos, *J Approx Theory*, **141**, 99 (2006).
17. S.M. Sarathy, M.J. Thomson, C. Togbé, P. Dagaut, F. Halter, C. Mounaim-Rousselle, *Combust Flame*, **157**, 852 (2009).
18. M. M. Conceição, R. A. Candeia, F. C. Silva, A. F. Bezerrab, J. F. J. Valter, G. Antonio, *Renew. Sust. Energ. Rev*., **11**, 964 (2007).