Applied Energy 160 (2015) 442–455

Contents lists available at ScienceDirect

Applied Energy

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

Impact of intake hydrogen enrichment on morphology, structure and oxidation reactivity of diesel particulate

J.H. Zhou [a,b,*], C.S. Cheung [b], W.Z. Zhao [a], Z. Ning [c], C.W. Leung [b]

[a] College of Energy and Power Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, Jiangsu, China
[b] Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
[c] School of Energy and Environment, City University of Hong Kong, Hong Kong

HIGHLIGHTS

- Primary particle exhibits four types of nanostructure with and without H_2 addition.
- Effect of H_2 on size of primary/aggregate particle is majorly engine load dependent.
- Oxidation reactivity of primary particle is evaluated with and without H_2 addition.
- Oxidation reactivity of primary particle is morphology-controlled.

ARTICLE INFO

Article history:
Received 27 May 2015
Received in revised form 31 August 2015
Accepted 7 September 2015
Available online 2 October 2015

Keywords:
Diesel particulate
Hydrogen
Morphology
Microstructure
Oxidation reactivity

ABSTRACT

Experimental investigations were conducted on a 4-cylinder natural-aspirated direct-injection diesel engine with naturally aspirated hydrogen, focusing on the effects of hydrogen addition on the physico-chemical properties of the diesel particulate. Diesel particulates were sampled for off-line analysis, with the aid of TEM and TGA facilities. Hydrogen addition promotes particle oxidation at low engine load and speed due to the increase of exhaust temperature, resulting in smaller particles, but it inhibits particle oxidation at high engine load due to the competition of oxygen between hydrogen and diesel fuel which results in larger primary particles. The replacement of injected diesel fuel by hydrogen inhibits the formation of soot nuclei and decreases its volume density, hence reduces the size of aggregate particles which are more spherical as indicated by an increase of fractal dimension and a decrease of radius of gyration. With increase of engine load, primary particles exhibit more graphitic structure, changing from "onion like" to "shell–core" structure. Hydrogen addition promotes and inhibits primary particle oxidation at low and high engine loads, respectively, and the corresponding primary particles are "turbostratic interlayer" and "shell-amorphous" in structure, respectively. The results of recognized fringe length, tortuosity and fringe separation distance are consistent with the observed morphology. The oxidation reactivity is related to equivalence ratio, being higher at low engine load and speed, which is indicated by the variation of activation energy and ignition temperature. The oxidation reactivity is validated to be related to the nanostructure of primary particles.

1. Introduction

Diesel engines are widely used in both mobile and stationary applications owing to the high fuel efficiency and low HC/CO emissions. However, the inborn heterogeneous combustion process of a diesel engine contributes to particulate matter (PM) emission which becomes the major source of ambient particles, especially those with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$), accelerating environment degradation and greenhouse effect [1,2]. Moreover, many epidemiological studies reported that the exposure to $PM_{2.5}$ may contribute to respiratory health problems, such as asthma, lung function decrements and cancers and these diseases area more closely related to the number, size and structure of PM emission rather than its mass concentration [3].

Applying gaseous fuel including natural gas [4], liquid petroleum gas [5], hydrogen [6], syngas [7] in diesel engine is a promising way to reduce PM emission. Among these gaseous fuels,

* Corresponding author at: College of Energy and Power Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, Jiangsu, China. Tel.: +86 13851665643; fax: +852 2365 4703.

E-mail addresses: zhoujianhao@nuaa.edu.cn, jianhao.zhou@connect.polyu.hk (J.H. Zhou).

http://dx.doi.org/10.1016/j.apenergy.2015.09.036
0306-2619/

Nomenclature

k_f	constant prefactor term
D_f	fractal dimension
d_p	the average of primary particle diameter (nm)
n	number of primary particles within a single aggregate particle
A_a	projected area of an aggregate particle (nm^2)
A_p	projected area of the primary particles (nm^2)
R_g	the radius of gyration of an aggregate particle (nm)
r_i	distance between the center of *i*-th individual primary particle (nm)
m_0	instantaneous mass of the soot sample during oxidation (μg)
t	time (s)
A	frequency factor (s^{-1})
E	activation energy (kJ/mol)
T_{ig}	ignition temperature (°C)
R	molecular gas constant, using 8.314 $J/mol^{-1}\ K^{-1}$
T_0	instantaneous heating (TGA furnace) temperature (K)
N	reaction order
L_f	fringe length (nm)
T_f	tortuosity
S_f	fringe separation distance (nm)

Abbreviations

BTDC	before top dead center
CPC	condensation particle counter
DR	dilution ratio
DMA	differential mobility analyzer
DSC	differential scanning calorimetry
EGR	exhaust gas recirculation
PNSDs	particle number and size distributions
EC	elemental carbon
GMD	geometric mean diameter
HRTEM	high-resolution transmission electron microscopy
HACA	H-abstraction–C_2H_2-addiction
SMPS	scanning mobility particle sizer
TGA	thermogravimetric analyzer
TEOM	tapered element oscillating microbalance
ULSD	ultra low sulfur diesel
VS	volatile substance
SD	standard deviation

hydrogen is a notable fuel, being carbon-free and possesses many favorable physicochemical properties [8], it has attracted great interest in its application as a clean and renewable alternative fuel for diesel engine recently [9–13]. Previous studies showed hydrogen addition affected the combustion process of diesel fuel and hence the engine performance; and the effects were engine load-dependent [9,10]. The direct replacement of diesel fuel by hydrogen contributed to the reductions of CO_2, CO, HC and PM emissions [11]. Diesel–hydrogen dual-fuel operation was usually coupled with EGR (exhaust gas recirculation) in order to reduce the in-cylinder gas temperature due to hydrogen combustion and accordingly reduce NO_x emission [12,13].

It is generally accepted that hydrogen addition in diesel engine could reduce the mass concentration of PM emission while further studies have been conducted on understanding its influence on particle number and size distributions (PNSDs). Tsolakis et al. [14] and Cho et al. [15] investigated the effect of EGR containing hydrogen-enriched gas on diesel particulate emission. The results indicated that the total number of particle increased, but the particle mass decreased since the increased particles were those with lower aerodynamic diameter. Bika et al. [16] examined the impact of hydrogen addition on PNSDs at all load ranges without EGR. Their results revealed that 10–40% hydrogen replacement could reduce the total number of PM by 10–50%. An increase of nuclei particles (<20 nm) was noticed, especially at light and medium engine loads. It can be found that the PNSDs of PM were affected by engine operating conditions (in-cylinder gas temperature and pressure), hydrogen addition amount (influence on total H–C ratio of fuels) and intake charge composition (CO_2). The measurement of PNSDs of PM conducted by previous studies were based on the aerodynamic diameter, however, the effects of hydrogen addition on size and structure of primary and aggregate particles were not well elucidated.

High resolution transmission electron microscope (HRTEM), thermogravimetric analyzer (TGA), etc., have been widely employed to analyze the physico-chemical properties of diesel particulate. Zhu et al. [17] and Yehliu et al. [18] focused on the effects of operating conditions on diesel particulate. They concluded that the primary particle diameter and the radius of gyration of aggregate particles were ranged from 19.4 nm to 32.5 nm and 77.4 nm to 134.1 nm, respectively, at various engine operating conditions and it was mainly dependent on the exhaust temperature (engine load and speed). Mustafi et al. [19,20] investigated the effects of diesel–biogas dual-fuel operation on diesel particulate. They reported an increase of primary particle diameter owing to the existence of CO_2 in biogas. The particles emitted from dual-fuel engine were more spherical than those from diesel engine presenting higher fractal dimension. Their results also indicated that dual-fuel operation increased the volatile fraction of particle which may be related to the partial replacement of diesel fuel by biogas. It can be found that engine operating condition and gaseous fuel application affect the size, morphology and volatility of the diesel particulate which are related to its formation, coagulation and oxidation processes.

Some fundamental studies have been conducted on soot formation within hydrogen enriched hydrocarbon flames. Pandey et al. [21] studied the effects of hydrogen on soot size and morphology in a laminar diffusion acetylene flame. They found a decrease of primary particle size that was closer to the burner surface when hydrogen was premixed with acetylene. The fractal dimension was unaffected while the aggregate particle size decreased. They finally concluded that the reduction of soot was attributed to the interference of hydrogen on the HACA (hydrogen-addition-acety lene-addition) mechanism [22]. Zhao et al. [23] compared the effects of adding helium and hydrogen on soot emission in a diffusion acetylene flame. They found that 25% replacement of ethylene by hydrogen reduced the total soot number by 66% which was not only due to the dilution and chemical inhibition effects but also due to the reduced number of carbon atoms. However, there is lack of study related to the effect of hydrogen addition on diesel particulate properties.

The above literature survey shows that hydrogen, as a gaseous fuel can offer assistance in suppressing PM emission formation, in terms of mass and number concentrations. However, there are still very few investigations on the effects of hydrogen on diesel particulate, especially effects on the primary and aggregate particles. In this study, hydrogen was naturally aspirated to a diesel engine to substitute part of the total fuel energy at various operating conditions and the PM samples were collected and analyzed. Scanning mobility particle sizer (SMPS) was used to measure the PSNDs. TGA was employed to characterize the oxidation reactivity of the PM samples. The morphology and structure of the primary and aggregate particles were characterized by HRTEM.