ELSEVIER

Journal of Hazardous Materials B127 (2005) 149–155

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

An investigation of the treatment of particulate matter from gasoline engine exhaust using non-thermal plasma

Ye Dan *, Gao Dengshan, Yu Gang, Shen Xianglin, Gu Fan **

Education Ministry Key Laboratory on Clean Coal Power Generation and Combustion Technology, Southeast University, 210096 Nanjing, China

Received 23 July 2004; received in revised form 28 June 2005; accepted 29 June 2005
Available online 29 August 2005

Abstract

A plasma reactor with catalysts was used to treat exhaust gas from a gasoline engine in order to decrease particulate matter (PM) emissions. The effect of non-thermal plasma (NTP) of the dielectric discharges on the removal of PM from the exhaust gas was investigated experimentally. The removal efficiency of PM was based on the concentration difference in PM for particle diameters ranging from 0.3 to 5.0 μm as measured by a particle counter. Several factors affecting PM conversion, including the density of plasma energy, reaction temperature, flow rate of exhaust gas, were investigated in the experiment. The results indicate that PM removal efficiency ranged approximately from 25 to 57% and increased with increasing energy input in the reactor, reaction temperature and residence time of the exhaust gas in the reactor. Enhanced removal of the PM was achieved by filling the discharge gap of the reactor with Cu-ZSM-5 catalyst pellets. In addition, the removal of unburned hydrocarbons was studied. Finally, available approaches for PM conversion were analyzed involving the interactions between discharge and catalytic reactions.

Keywords: Particulate matter; Hydrocarbons; Non-thermal plasma; Dielectric barrier discharge; Gasoline engine

1. Introduction

Gasoline and diesel engines are major sources of urban air pollution. They emit a large amount of pollutants, including particulate matter (PM), carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen monoxide (NO). Particulate matter may cause respiratory and mutagenic diseases, such as lung and bladder cancer. Hydrocarbons may react with nitrogen monoxide in the presence of sunlight forming ozone that irritates lungs [1,2]. Thus, suppressing the emission of these contaminants from engines is important.

The PM in raw exhaust gas emitted by engines primarily consists of soot which is a complex material with a complex structure. According to Johnson et al. [3] and Kittelson [4], soot consists of a carbonaceous core with an agglomerate structure that is formed in the combustion chamber by incomplete combustion. According to Klingenberg [5], the core has a graphite-like structure. Ashes from the metals present in the lube oil or from engine wear are enclosed in the carbonaceous core. Volatile organic compounds (VOCs) originating from unburned fuel and lube oil are adsorbed on the surface of the carbonaceous core. Components of sulfur present in the fuel and in the lube oil can also be adsorbed on the carbonaceous core, but sulfur components also form particles (partially sulfuric acid aerosol droplets). Water from the combustion process is also present on the surface of the carbonaceous core. The relative amounts of these compounds may differ considerably with different engines and engine operating conditions [6].

Few studies on soot suppression have been published. The conventional methods of soot suppression that have been performed include: (a) dust collection using a filter and (b) soot oxidation (combustion). However, these methods have the disadvantage of lowering the efficiency of soot suppression. [7] As a result, a non-thermal plasma (NTP) reactor

* Corresponding author. Tel.: +86 25 3793612 0; fax: +86 25 3793612 6.
** Corresponding author.
E-mail addresses: heretofore@seu.edu.cn (D. Ye), fangu@seu.edu.cn (F. Gu).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.06.040

was utilized in this study to evaluate the removal rate of PM and HC as a possible new approach for exhaust gas treatment.

The use of plasmas in various industries has increased in recent years. Plasma processes are used widely in the electronics industry to dope semiconductors and in microcircuit fabrication to etch and deposit thin films. Plasma processes are now being considered in air purification systems to remove trace contaminants by converting them to less harmful species via reactions in a plasma reactor. In NTP, free electrons gain energy from an imposed electric field and lose energy through collisions with neutral gas molecules. This transfer of energy to the molecules leads to the formation of a variety of new species, including ions, metastables, atoms and free radicals. These products are all chemically active and lead to the formation of new stable compounds. Thus, in plasma reactors, the applied electric power is spent in breaking the bonds in the parent molecules. As there is no appreciable heating of the gas (the electron temperature is of the order of a few thousand degrees Kelvin and the atomic species are near room temperature), energy is not lost either in heating up the gases (as in pyrolysis) or to the surroundings [8].

The primary aim of this paper is to investigate the removal rate of the PM emitted by a gasoline engine using NTP. In addition, the HC removal from exhaust gas was also investigated and the treatment results of HC by NTP were compared with those of PM.

2. Experimental apparatus and method

2.1. Experimental setup

Fig. 1 shows the sketch of the experimental setup. A commercial unleaded gasoline was used to produce an exhaust gas. The engine was kept running at an idle condition. The exhaust gas sampled from the engine was first passed successively through a condensator and a dryer filled with $CuSO_4$ to remove its moisture content. It was noted that the cooling and drying process could influence the exhaust gas contents to some extent due to particle deposition, HC-condensation, etc. However, this step is inevitable, so all of the experiments were carried out under similar cooling and drying conditions so as to reduce the potential error caused by this step. Second, a fraction of the dried exhaust gas was forced to flow into a NTP reactor at a certain flow rate, which was located in a constant temperature electric oven to maintain constant reaction temperature and was treated by NTP in the reactor. Third, the HC concentration of the treated exhaust gas was measured by an exhaust gas analyzer (model FGA-4100) at the outlet of the reactor. Fourth, to accommodate the requirement of a particle counter (handheld laser particle counter (model 3886 GEO-), Kanomax Japan Inc., 2-1 Shimizu, Suita, Osaka 565-0805, Japan), the treated exhaust gas was diluted in a mixer by N_2 with a content of 98%. Finally, the diluted exhaust gas was passed through the particle counter to measure its PM concentration and then the gas was vented. The measurable particle sizes ranged from 0.3 to 5.0 μm. The data from the exhaust gas analyzer and the particle counter were collected by an online data acquisition system.

2.2. Plasma reactor

As shown in Fig. 2, the plasma reactor consists of a 2 mm diameter stainless steel rod electrode, a grounded plate type electrode and a piece of glass on the surface of the plate as a dielectric barrier. The discharging gap distance is about 3 mm and the effective discharging length is 70 mm. Pulsed voltages with a frequency of 15 kHz and adjustable amplitudes from 0 to 15 kV were applied to the electrodes to produce NTP. Input power was measured with a wattmeter connected to the low voltage side of a step-up transformer [9,10]. The input power

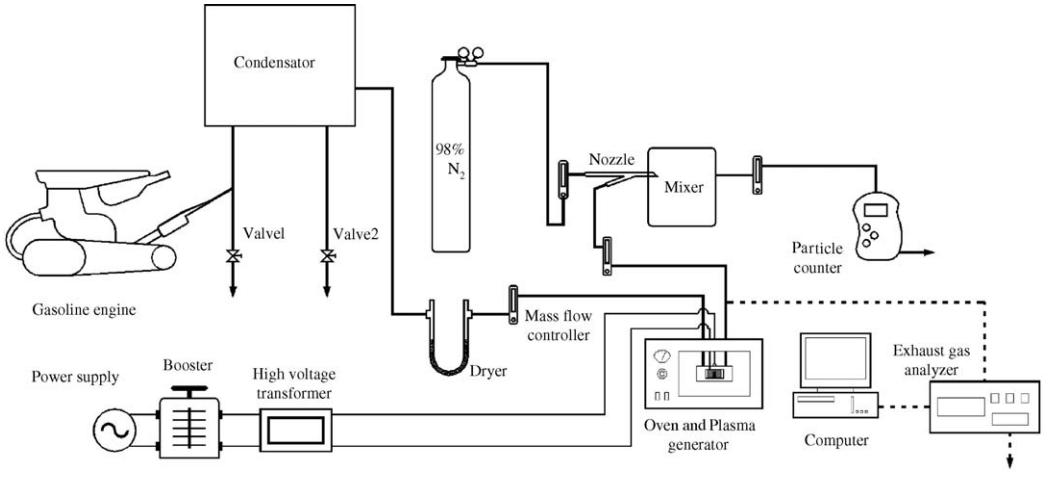


Fig. 1. Schematic diagram of the experimental setup.

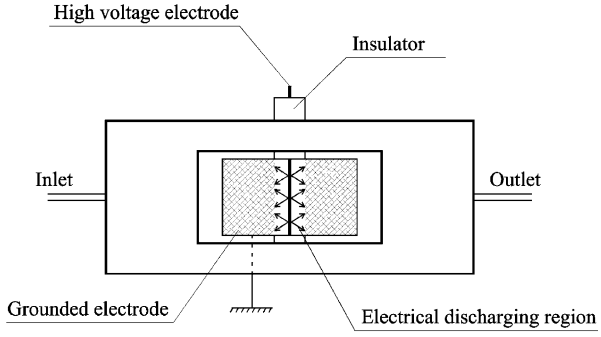


Fig. 2. Sketch of the plasma reactor.

Table 1
The concentrations of each component in the tail gas

Parameter	Concentration
HC (ppm)	3836
NO (ppm)	63
CO (%)	3.6
CO_2 (%)	2.4
O_2 (%)	4.8

of the dielectric barrier discharge is obtained by subtracting the transformer loss from the wattmeter reading.

2.3. Measurement of original exhaust gas

Table 1 shows the HC, NO, CO, CO_2 and O_2 contents of the dried and untreated exhaust gas when the gasoline engine was in the idle running condition at the air/fuel ratio of 1.352. Fig. 3 shows the PM concentration (count/m^3) spectrum of the exhaust gas as well as those for the outdoor air and the dilute N_2 for comparison. The dilution ratio of 1:50 was taken in the experiment, i.e., the flow rates of the dilute N_2 and the dried exhaust gas were 1800 and 36 L/h, respectively. As can be seen from Fig. 3, the PM concentrations of the dilute N_2 are much less than those of the exhaust gas, so the effects of PM content of the dilute N_2 on the measure results can be neglected.

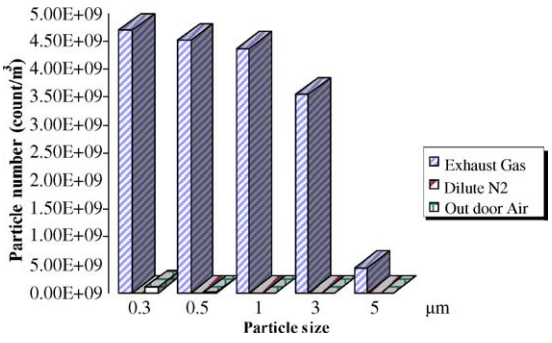


Fig. 3. Result of the numbers of PM from the exhaust gas in different sizes and its comparison to other testing condition.

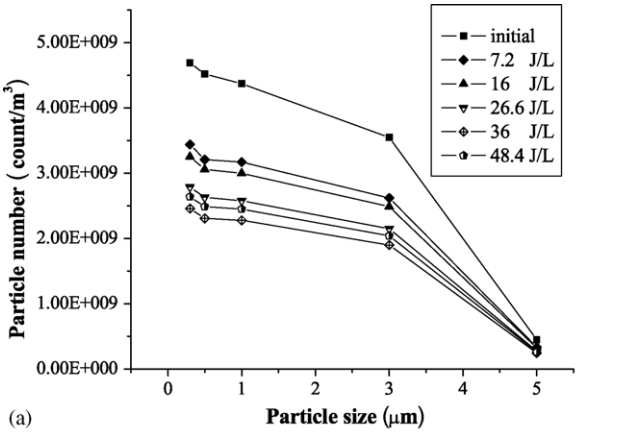
3. Experimental results and discussions

3.1. Effect of input power on PM and HC removal rate

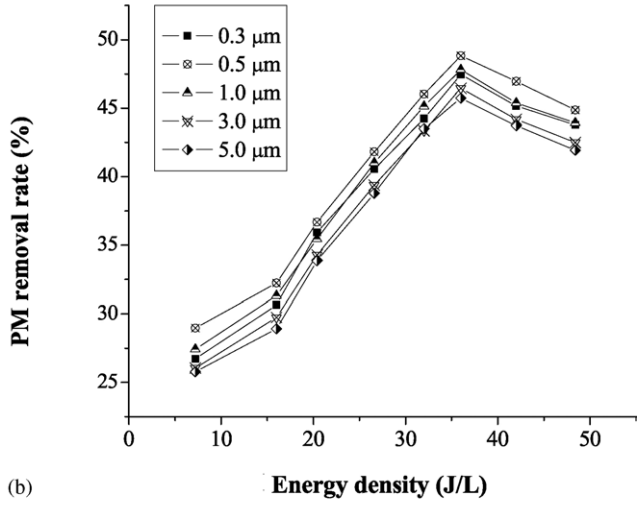
Fig. 4 shows the effects of NTP on the removal of PM and HC at an exhaust gas flow rate of 0.6 L/min and room temperature. In Fig. 4(a), the PM concentration decreased with increasing energy density in the range of lower energy densities. However, when the density was raised from 36 to 48.4 J/L, the PM concentration increased. This can be seen more distinctly in Fig. 4(b), which shows that the PM removal rates (based on changes in PM concentration) of the exhaust gas increased gradually with increasing energy density until reaching a maximum and then decreased with further increasing energy density. In general, the PM removal rate in the NTP reactor is primarily based on the number of activated radicals, such as O, O_2^*, O_3, N, etc. Formation of active components as radicals is induced by electron impacts with the main components of the exhaust gas: nitrogen, oxygen and carbon dioxide. The efficiency of production of chemically active species in the NTP is determined by the reduced electric field or E/N, where E is the electric field and N is the density of gas. Because the electric field relates to the energy density, it can be suggested that the number of the activated radicals rises with increasing energy density when the energy density is less than a certain threshold, and then the activated radicals decrease with the further increasing in energy density due to the change in discharging condition. In the experiments, it was observed that the color of the discharging region in the reactor changed from violet to salmon pink when the energy density exceeded the threshold. This observation implies that in this case, the electric field strength in the reactor was so high that some local arcs occurred, which consumed some electric energy and reduced the net energy deposited in the exhaust gas.

According to Sato et al. [7], soot suppression resulted from the oxidation of soot particles. Kimula et al. [11] further concluded that smaller size soot particles burn faster than larger size particles in a high-temperature oxidizing atmosphere. However, Fig. 4(b) shows that the highest PM removal rate occurs for the 0.5 μm diameter particles versus the smaller 0.3 μm diameter particles, which is unexpected. In fact, this apparent contradiction was caused by the residence time of exhaust gas in the reactor. Because of the limitation of reactor size, the residence time of exhaust gas in the reactor is not long enough for the larger particles to be completely oxidized by NTP and their residuals become smaller particles, which increase the number of smaller particles and causes the feint that the smaller particle has lower removal rate.

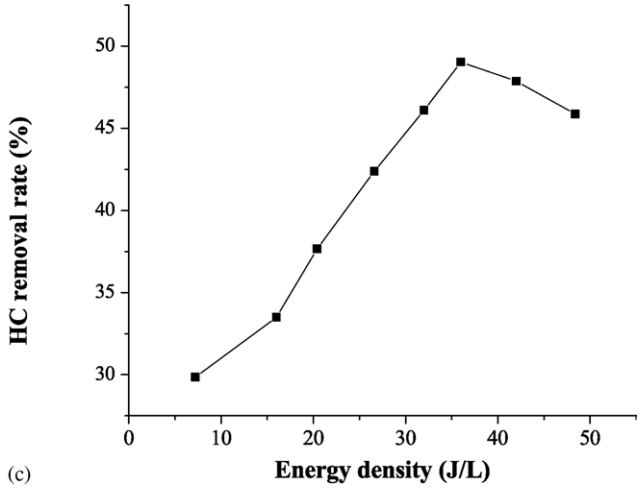
There are only a few studies on the mechanisms for PM removal using plasma. Based on the experiments, a two-step process could be proposed for the removal of the engine-emitted PM in NTP. First, the VOCs on the surface of the carbonaceous core of the PM [5] are released due to the heat produced by NTP and then the released gaseous VOCs are oxidized immediately by the oxidants produced by NTP. Sec-



(a)



(b)



(c)

Fig. 4. Effect of the input power on PM and HC removal rates. The flow rate was 0.6 L/min and the temperature was held at room temperature. (a) Particle-size distributions of PM in variable energy density; (b) PM removal rate vs. energy density; (c) HC removal rate vs. energy density.

ond, the carbonaceous core is exposed to NTP and reacts with the activated radicals of plasma as described by Cuesta et al. [12] and Perez-Mendoza et al. [13].

Fig. 4(c) shows the relationship between HC removal rate (based on its changes in weight) and energy density. According to Tonkyn et al. [14], HC plays an important role in the plasma oxidation of NO to NO_2. Nevertheless, in our experiments, the concentration of NO is much less than that of HC (see Table 1), because the HC is oxidized mainly by the activated radicals produced by NTP. So, the HC is oxidized by activated radicals, such as O, O_2^*, O_3, N, etc., produced by NTP in the reactor in a similar manner as the PM, and the removal rate of the HC mainly depends on the number of the activated radicals. Consequently, the relationship between the HC removal rate and energy density (in Fig. 4(c)) is similar to that between PM removal rate and energy density (in Fig. 4(b)).

3.2. Effect of exhaust gas flow rate on PM and HC removal rate

In Fig. 5, the effect of exhaust gas flow rate on PM and HC removal at an energy density of 36 J/L and room temperature is shown. As shown in Fig. 5(a), the PM concentration decreased with increasing flow rate. As shown in Fig. 5(b and c), the removal rates of both PM and HC decrease apparently with the increase in flow rate. The decrease of the removal rate results from the reduction of residence time of the exhaust gas in the plasma reactor, such that there is not sufficient time for the removal reactions for PM and HC.

3.3. Effect of reacting temperature on PM and HC removal rate

Fig. 6(a) shows the size distributions for the PM in the exhaust gases at five different ambient temperatures before and after NTP treatment. The experiments were carried out at an energy density of 36 J/L and a flow rate of 0.6 L/min. Fig. 6(b) shows the PM removal rate as a function of the ambient temperature. The removal rates of different sizes of PM increase as the temperature increases. Higher ambient temperature may reduce the heat loss of plasma, thereby, ensuring a more stable state to NTP. Consequently, VOCs adsorbed on the surface of the particle carbonaceous core are released more rapidly at a higher temperature and upon being released, they are oxidized by plasma more completely. On the other hand, the removal rate of HC has a similar tendency to that of PM as shown in Fig. 6(c).

3.4. Effect of catalyst on PM and HC removal rate

The effect of catalyst on PM removal at an energy density of 36 J/L, a flow rate of 0.6 L/min and room temperature is shown in Fig. 7(a). The experiment was carried out in a packed reactor that was full of the catalyst pellets of Cu-ZSM-5 between its two electrodes. Comparing Fig. 4(b) with

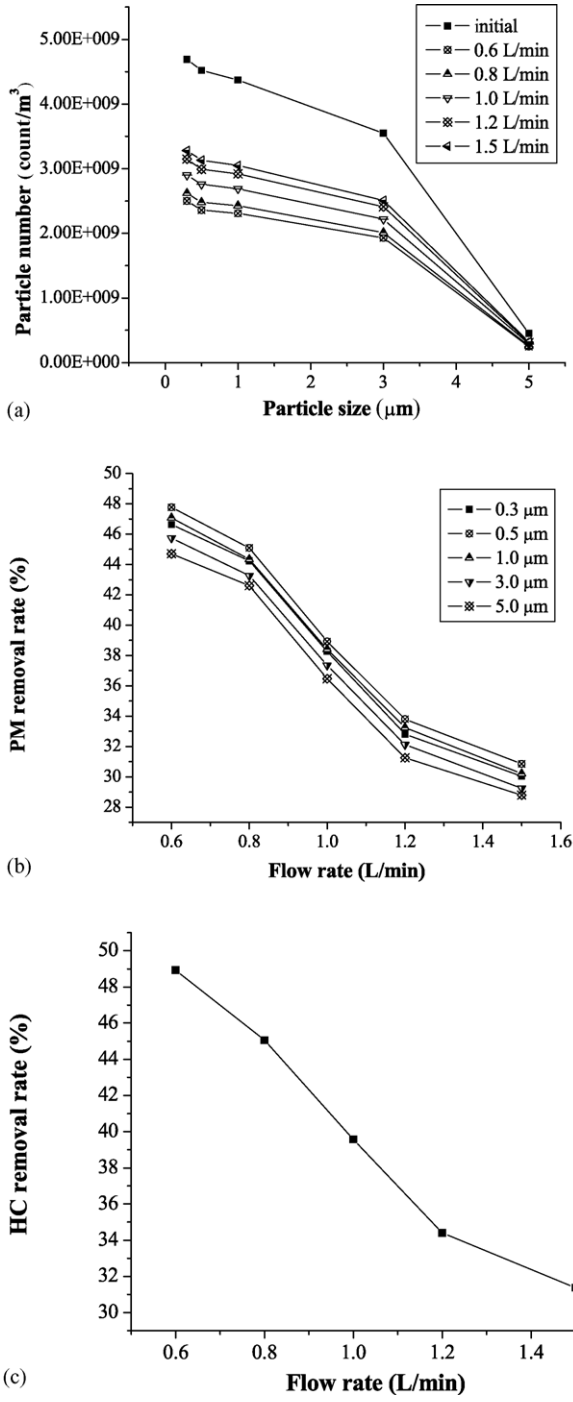


Fig. 5. Effect of the exhaust gas flow rate on PM and HC removal rates. The energy density was 36 J/L and the temperature was held at room temperature. (a) Particle-size distributions of PM in variable flow rate; (b) PM removal rate vs. flow rate; (c) HC removal rate vs. flow rate.

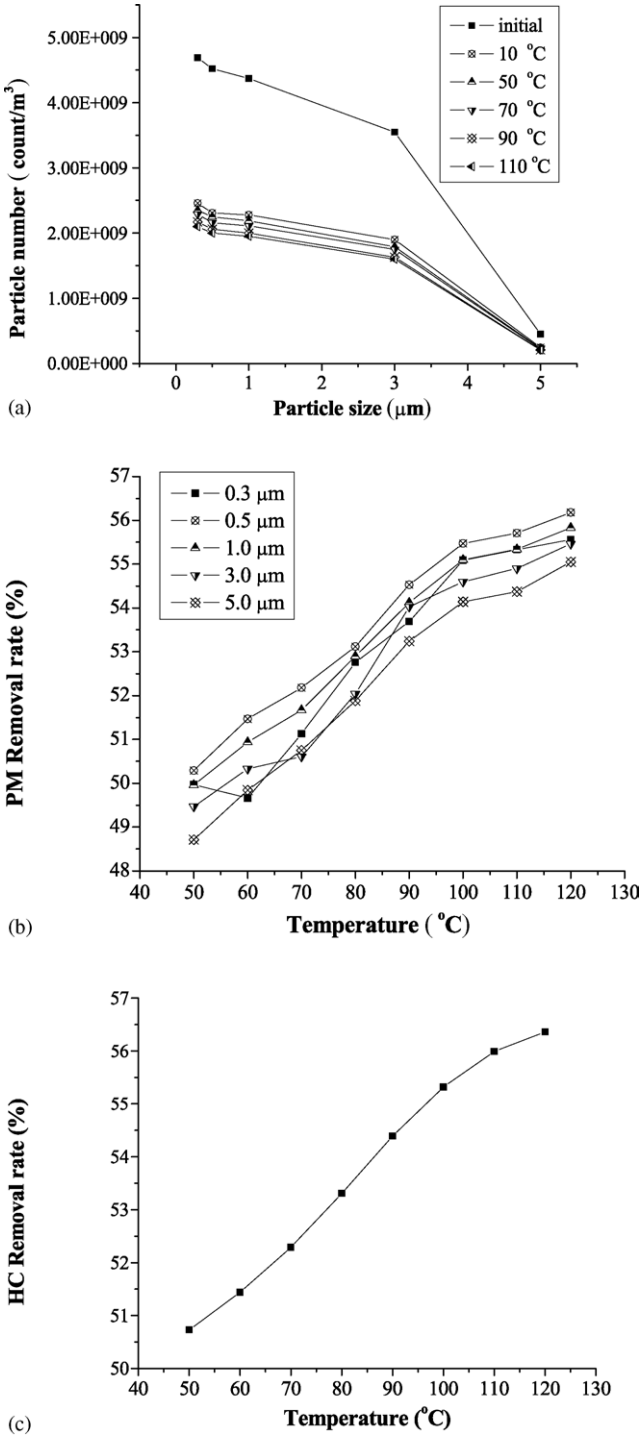


Fig. 6. Effect of the reacting temperature on PM and HC removal rates. The energy density was 36 J/L and the flow rate was 0.6 L/min. (a) Particle-size distributions of PM in variable temperature; (b) PM removal rate vs. temperature; (c) HC removal rate vs. temperature.

Fig. 7(b), the enhanced plasma in the packed reactor has higher PM removal efficiency than that in non-packed reactor. Mizuno et al. [10] and Lang and co-workers [15] reported that the surface discharges on the catalyst pellets, which were also observed in this experiment, could enhance the electric field strength and electron density in the packed-bed reactor. The enhanced electric field strength and electron density increases the number and power of the activated radicals of NTP, which results in higher PM removal rate. Fig. 7(c) shows the removal rate of HC under the same condition. The gaseous HC oxidization is enhanced by the catalyst directly and its removal rate rises.

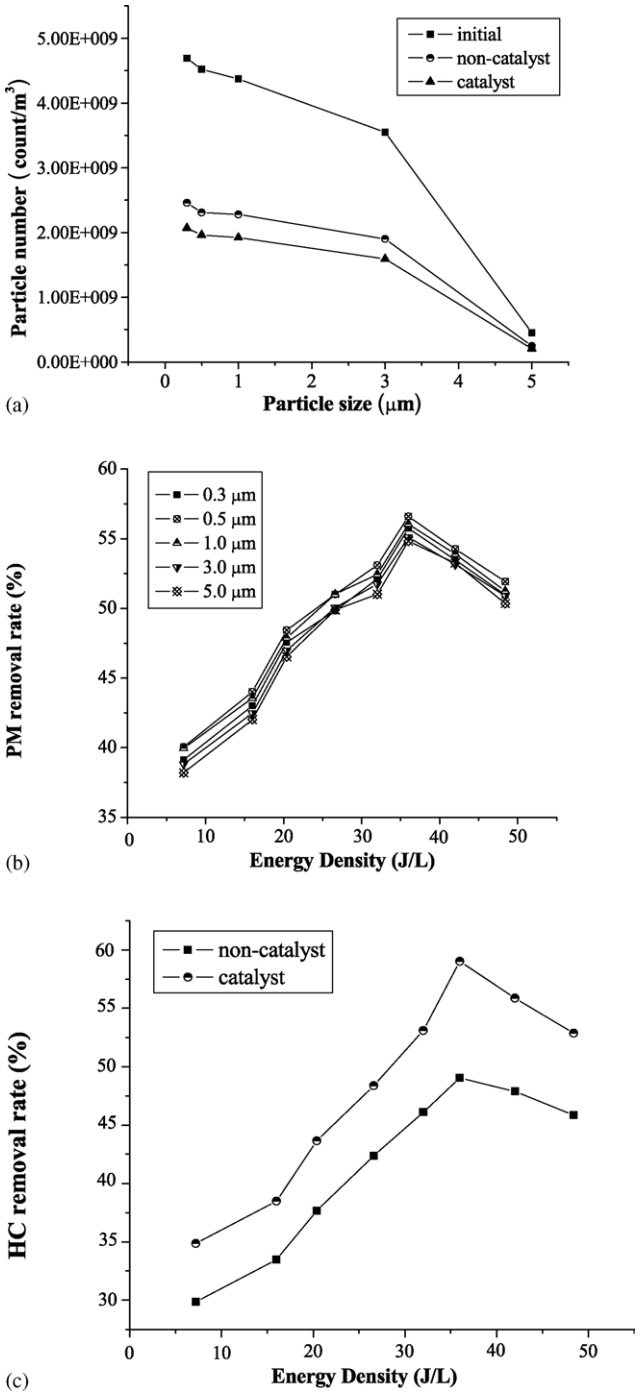


Fig. 7. Effect of catalyst on PM and HC removal rates. The flow rate was 0.6 L/min and the temperature was held at room temperature. (a) Particle-size distributions of PM with or without catalyst, the energy density was 36 J/L; (b) PM removal rate vs. energy density; (c) HC removal rate vs. energy density.

4. Conclusion

An experimental study on the removal of harmful particulate matter and hydrocarbons emitted by a gasoline engine using non-thermal plasma was conducted. Non-thermal plasma was found to remove the PM and HC effectively. However, there is a threshold of the energy density applied to the NTP reactor such that increasing the energy density below the threshold promotes the removal rate of PM and HC, whereas increasing the energy density above the threshold hinders the removal rate of PM and HC. Increasing reaction temperature, prolonging the residence time of exhaust gas in the reactor and using appropriate catalysts are beneficial to the removing of the PM and HC.

Acknowledgements

The authors wish to gratefully acknowledge the financial support of the National Key Basic Research and Development Program of China, Grant No. 2002CB211600 and the National High Technology Research and Development Program of China, Grant No. 2002AA529130.

References

[1] M. Moldovan, M.A. Palacios, M.M. Gomez, G. Morrison, S. Rauch, C. Mclcod, R. Ma, S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, P. Schramel, M. Zischka, C. Pettersson, U. Wass, M. Luna, J.C. Saenz, J. Santamaria, Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters, Sci. Total Environ. 296 (2002) 199–208.
[2] J. Wang, L. Fu, W. Li, Motor Vehicle Emissions Control and Catalytic Converter, Chemical Industry Publishing Company, 2000.
[3] J.H. Johnson, S.T. Bagley, L.D. Gratz, D.G. Leddy, A Review of Diesel Particulate Control Technology and Emission Effects, SAE Paper No. 940233, 1992 Horning Memorial Award Lecture, Presented at SAE International Congress and Exposition, February 28–March 4, 1994.
[4] D.B. Kittelson, Engines and nanoparticles: a review, J. Aerosol Sci. 29 (1998) 575–588.
[5] H. Klingenberg, Automobile Exhaust Emission Testing, Springer, Berlin, 1996, pp. 7–15.
[6] C. Van Gulijk, J.J. Heiszwolf, M. Makkee, J.A. Moulijn, Selection and development of a reactor for diesel particulate filtration, Chem. Eng. Sci. 56 (2001) 1706–1712.
[7] M. Saito, M. Sato, K. Sawada, Variation of flame shape and soot emission by applying electric field, J. Electrostatics 39 (1997) 305–311.
[8] S. Mukkavilli, C.K. Lee, K. Varghese, L.L. Tavlarides, Modeling of the electrostatic corona discharge reactor, IEEE Trans. Plasma Sci. 16 (6) (December 1988) 652–660.
[9] R. Feng, G.S.P. Castle, S. Jayaram, Automated system for power measurement in the silent discharge, IEEE Trans. Ind. Appl. 34 (1998) 563–570.
[10] A. Mizuno, Y. Yamazaki, S. Obama, E. Suzuki, K. Okazaki, Effect of voltage waveform on partial discharge in perroeletric pellet layer for gas cleaning, IEEE Trans. Ind. Appl. 29 (2) (March/April 1993) 262–267.
[11] H. Ohisa, I. Kimula, H. Horisawa, Control of soot emission of a turbulent diffusion flame by DC or AC corona discharges, Combust. Flame 116 (4) (March 1999) 653–661.
[12] A. Cuesta, A. Martinez-Alonso, J.M.D. Tascon, Carbon reactivity in an oxygen plasma: a comparison with reactivity in molecular oxygen, Carbon 39 (2001) 1135–1146.
[13] M. Perez-Mendoza, M. Domingo-Garcia, F.J. Lopez-Gazon, Modifications produced by O_2 and CO_2 plasma treatments on a

glassy carbon—comparison with molecular gases, Carbon 37 (1999) 1463–1474.

[14] R.G. Tonkyn, S.E. Barlow, J.W. Hoard, Reduction of NO_x in synthetic diesel exhaust via two-step plasma-catalysis treatment, Appl. Catal. B Environ. 40 (2003) 207–217.

[15] H. Russ, M. Neiger, J.E. Lang, Simulation of micro discharges for the optimization of energy requirements for removal of NO_x from exhaust gases, IEEE Trans. Plasma Sci. 27 (1) (February 1999) 38–39.