Oxidation of activated carbon and methane using a high-frequency pulsed plasma

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Abstract

We have demonstrated a new method using a high-frequency pulsed plasma for oxidizing methane and activated carbon powder (1–150 μm) as two substitutes for diesel particulate matter (PM). Methane and activated carbon can be oxidized at a rate of 4–40 and 4–10 g-CH$_4$/kWh, respectively. A discussion on future development of this technology is given. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Diesel engines emit several types of pollutants into the atmosphere. In the recent years, human health concerns regarding penetration of diesel particulate matter (PM) into the deeper regions of the lungs have greatly increased. Therefore, an effective method but one with a low operational cost of reducing diesel PM is required. Today's commercial diesel catalyst controls diesel particulates only through the control of their organic fraction (SOF). Furthermore, the catalyst is unfortunately susceptible to poisoning by sulfur and phosphorus from such as lubrication oil additives [1–3]. In order to reduce the emission of PM, diesel particulate traps physically capture diesel particulates preventing their release to the atmosphere. The most common filter is from expensive ceramic materials, such as SiC. An electric heater or fuel burner is also incorporated to regenerate the filter [4]. Non-thermal plasma has been used for treatments of wastes such as acid gas, VOCs, ODSs, and PFCs from not only mobile exhausts but other sources [5–14]. However, most studies on non-thermal plasmas have focused on No$_x$ reduction.

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Study of the reduction of diesel PM emission requires analyses of size and composition of PM and their products after treatment. Since these analyses require expensive instruments only a few laboratories can perform such a study. Here, we demonstrate a new and simple method for oxidizing diesel PM using activated carbon and methane as substitutes for PM and a high-frequency pulsed plasma recently developed by the Yao et al. [15].

2. Experimental

The experiments were carried out using two reactors (Reactor 1 in Fig. 1 for activated carbon oxidation and Reactor 2 in Fig. 2 for methane oxidation) and a pulse power supply, DP-15K35, which Pulse Electronic Engineering constructed according to our specifications. The rise rate of voltage was controlled by changing the value of resistor R. Discharge currents through anode and cathode were measured with two current transformers (CT-anode, Mode 2–1.0, 35 MHz; CT-cathode, Mode 0.5–1.0, 20 MHz, Strangenes Industries) and the discharge voltage was measured with a voltage probe (V-probe, EP-50 K, 50 MHz, Pulse Electronic Engineering). The signals from the voltage probe and current transformers were recorded with a digital oscilloscope (TDS754D, Tektronix) having an analog bandwidth of 500 MHz and a maximum sampling rate of 2 GS/s.

Reactor 1 was mainly composed of a quartz tube, a stainless steel wire and a stainless steel net supported by quartz wool. Pulse voltage was applied between the stainless steel wire (anode) and net (cathode). N_2 and O_2 were supplied to the lower part of the reactor with or without water. Water was supplied at a rate of 5 μl/min with a micro-flow liquid pump to reactor 1. Activated carbon (Wako, Charcoal, 034-02125) was grounded to powder having a diameter range of 1–150 μm. The powder was set on the stainless steel net supported by quartz wool.
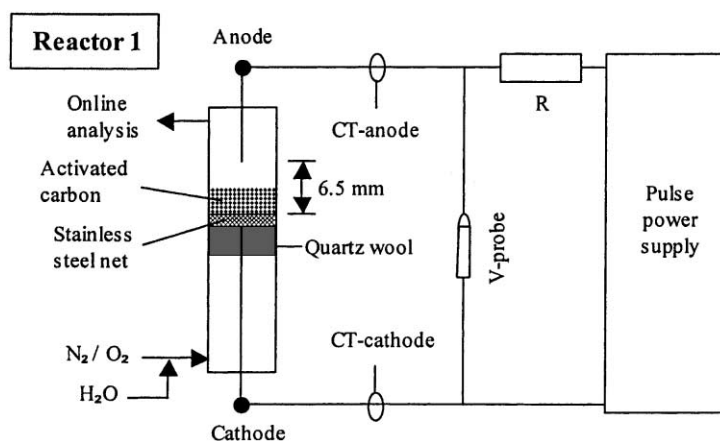

Fig. 1. Schematic of a pulsed plasma system. Thickness of activated carbon layer: 2–3 mm, stainless steel wire (anode): 1.0 mm (diameter) × 250 mm (length); gap distance between anode and cathode: 6.5 mm; quartz tube: 16 (o.d.) × 12.5 mm (i.d.) × 350 mm (length); stainless steel net: 2 mm (diameter) × 2 mm (thickness); gas flow rate: N_2: 90 ml/min, O_2: 10 ml/min; liquid water flow rate: 0 or 0.5 μl/min.
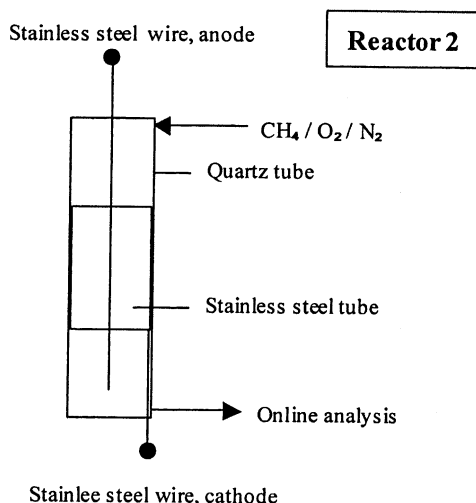
Fig. 2. Plasma reactor for methane oxidation. Stainless steel wire (anode): 0.5 mm (diameter) × 600 mm (length); stainless steel tube (cathode): 12 mm (o.d.) × 10 mm (i.d.) × 100 mm (length); quartz tube: 15 mm (o.d.) × 12 mm (i.d.) × 800 mm (length); gas flow rate: CH_4: 10 ml/min; O_2: 20 ml/min; N_2: 170 ml/min.

Reactor 2 was a co-axial cylindrical type of reactor used for methane oxidation. Methane, oxygen, and nitrogen were supplied to the upper part of reactor.

Carbon compounds in the gaseous product from the upper part of Reactor 1 or the lower part of Reactor 2 were analyzed with an online chromatograph (GC 103, Okura Riken, FID) equipped with a 2 m Porapak N column. The products were pretreated with a methanizer (MT-221, GL Science) to convert carbon compounds to related alkanes prior to detection by FID. All experiments were carried out at atmospheric pressure and under a condition without additional heating except plasma heating.

The energy P (W) injected into the background gas was calculated as the product of pulse frequency F (Hz), discharge voltage (V), anode current (A), and differential discharge time (s) obtained from waveforms of discharge voltage and anode current. For convenience of comparison, the quantity of methane in grams equivalent to carbon compounds produced per unit energy injected (kWh) was used to represent energy efficiency of the pulsed plasma.

3. Results and discussion

Typical waveforms of discharge voltage and currents are shown in Fig. 3. The rise rate of discharge voltage was 0.3 and 0.4 kV/ns when R was 408 and 110 Ω, respectively. A relatively high discharge current yielding high energy injection was observed when using a small resistance (Table 1).

Activated carbon oxidation was carried out with or without water (Table 1). Activated carbon was oxidized mainly to CO, CO_2, and partially to high carbon compounds, such as C_2H_6 and C_3H_8. The selectivity of CO and CO_2 is higher than 90%. Energy efficiency
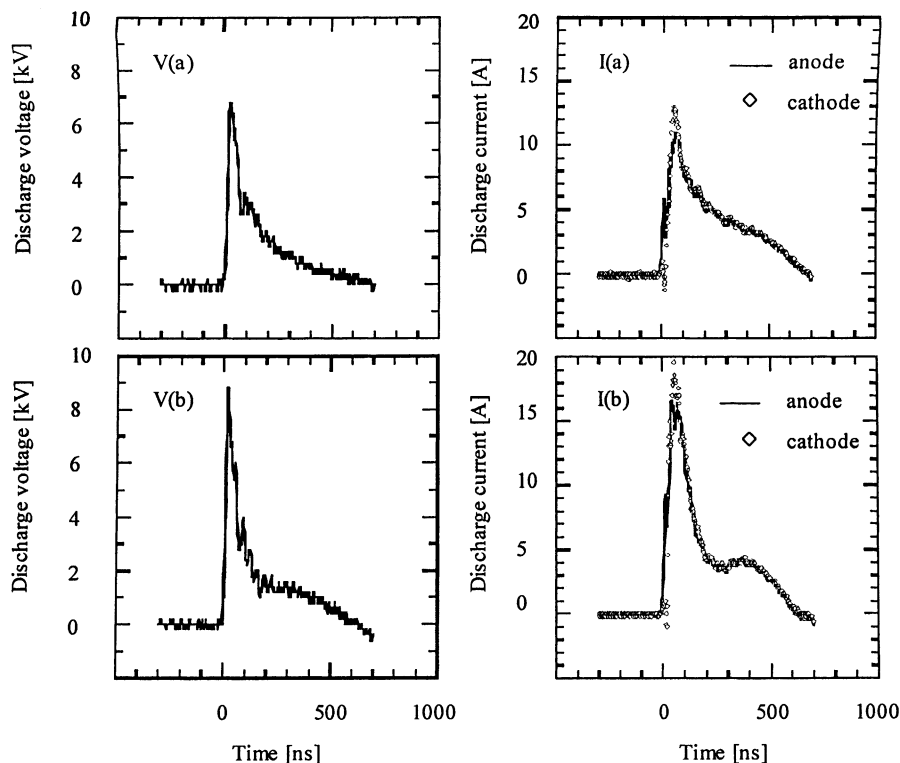
Fig. 3. Waveforms of discharge voltage and anode and cathode currents at 5080 Hz and (a) 408 or (b) 110 Ω. The rise rate of discharge voltage was (a) 0.3 and (b) 0.4 kV/ns.

increased as pulse frequency increased. This is not contradictory with our previous findings of methane conversion, indicating that a high-frequency pulsed plasma is more efficient than a low-frequency pulsed plasma [16]. The presence of water decreased the oxidation under the same experimental condition due to the high affinity of water to electrons, but promoted CO_2 formation. This finding suggested that water could affect not only discharge

Table 1
Oxidation of activated carbon using a high-frequency pulsed plasma[a]

No.	H_2O	F (Hz)	R (Ω)	P (W)	Gas production (mg-CH_4/min)	Selectivity (%)		Efficiency (g-CH_4/kWh)
						CO	CO_2	
1	−	2050	408	11	0.93	44.6	45.9	5.03
2	−	5080	408	23	3.17	14.3	83.4	8.18
3	+	5080	408	30	2.13	5.9	90.8	4.28
4	+	5080	110	45.5	7.50	6.4	92.2	9.90

[a] H_2O flow rate: −, 0 μl/min; +, 5 μl/min.

Table 2
Methane oxidation at various pulse frequencies ($R = 110$ W)

F (Hz)	CH_4 conversion (%)	P (W)	Gas production (mg-CH_4/min)	Selectivity (%)		Efficiency (g-CH_4/kWh)
				CO	CO_2	
108	6.122	1.10	0.398	50.07	34.53	21.7
500	47.66	4.7	3.10	35.61	56.69	39.6
1046	78.27	9.09	5.09	24.93	71.89	33.6
5044	97.67	45.0	6.35	5.57	92.76	8.47
10509	99.85	88.0	6.49	2.46	95.84	4.42

property but also reactions enhanced by discharge. Since water contributes the formation of H and OH radicals [17,18], CO_2 formation is possibly accelerated by H and OH related reactions such as reactions (1)–(3).

$$H + O_2 = HO_2 \tag{1}$$

$$HO_2 + CO = CO_2 + OH \tag{2}$$

$$OH + CO = CO_2 + H \tag{3}$$

The oxidation efficiency can be recovered by using a small value resistor. Generally, activated carbon can be oxidized at a rate range of 4–10 g-CH_4/kWh. This means that a pulse power supply with 0.6–1.4 kW is sufficient to oxidize PM from a diesel engine emitting PM at a rate of 0.1 g/min.

Shi and Harrison [19] recently reported that there is a size growth in PM emitted from an engine. This implied that the size of PM would be smaller at the point close to the outlet of engine cylinders. Therefore, we used methane as a substitute of a molecule carbon (smallest PM) to confirm the oxidation ability of this plasma. In this case, Reactor 2 in Fig. 2 was used. Most of methane was oxidized to CO and CO_2. The methane oxidation peaked at 500 Hz with a maximum oxidation of 39.6 g-CH_4/kWh (Table 2). This finding suggested that a pulse power supply with 0.15 kW is sufficient for oxidizing PM from a diesel engine emitting PM at a rate of 0.1 g/min. The ability to oxidize methane is higher than that for activated carbon. This finding may imply that the oxidation ability of this kind of pulsed plasma would be higher for true diesel PM than for activated carbon.

The components of diesel PM are mostly elemental carbon, heavy hydrocarbons, and aromatic hydrocarbons. Smulders et al. [20] have shown that these compounds are easily oxidized by a pulsed plasma with a relatively low rise rate of 0.9 kV/μs. For example, toluene and styrene can be oxidized at 42 and 143 g/kWh, respectively. On the other hand, the size of PM is in an average diameter order of 0.1–0.2 μm [21], rather smaller than that of the activated carbon powder used in this study. Furthermore, diesel PM is more uniform in the exhaust, not like that activated carbon powder concentrated on the stainless steel net. These data implied that the energy efficiency to oxidize actual diesel PM of a high-frequency pulsed plasma with a rapid rise rate could be better than the oxidation of activated carbon powder.

4. Conclusions

Activated carbon and methane as substitute of PM could be oxidized to CO and CO_2 using a non-thermal pulsed plasma of high-frequency at 4–10 and 4–40 g-CH_4/kWh, respectively. Since some products of oxidation of activated carbon and methane, such as CO, ethane and propane, are easily oxidized over a catalyst, a combination system of plasma and catalysis would be further powerful for diesel PM reduction. We anticipate that our technology would be useful for the realization of a PM-free vehicle. A further study is now being undertaken.

Acknowledgements

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