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Selective catalytic reduction of NO_x by diesel fuel: Plasma-assisted HC/SCR system

Byong K. Cho[a,b,*], Jong-Hwan Lee[a], Chris C. Crellin[a], Keith L. Olson[a], David L. Hilden[a], Mun Kyu Kim[b], Pyung Soon Kim[b], Iljeong Heo[b], Se H. Oh[a], In-Sik Nam[b,**]

[a] General Motors Global R&D Center, Warren, MI 48090-9055, USA
[b] Pohang University of Science & Technology (POSTECH), Pohang 790-784, Republic of Korea

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ABSTRACT

A new NO_x reduction system has been developed which can reduce NO_x emissions in diesel engine exhaust using oxygenated hydrocarbons (OHCs) generated from diesel fuel reforming as the primary reductants. The system consists of a sidestream hyperplasma reactor, a diesel fuel reformer and a dual-bed catalytic reactor. A unique feature of this system is a diesel fuel reformer that can produce highly reactive OHCs for NO_x reduction. Steady-state performance as well as simulated FTP performance of this system for NO_x reduction was evaluated in a sidestream connected to the main exhaust stream of a 4.9L, 6-cylinder Isuzu diesel engine dynamometer system. A dual-bed (BaY + CuY) catalyst yielded a mode-average FTP NO_x conversion of 61% when the catalyst volume was 3.6 times the engine displacement. NO_x reduction efficiency of the reformed diesel fuel was compared with that of an ethanol–dodecane mixture, E-diesel and NH_3 in laboratory microreactor experiments and engine dynamometer tests.

1. Introduction

The selective catalytic reduction of NO_x by urea (urea/SCR) and lean NO_x trap technology (LNT) are the two most efficient NO_x reduction technologies currently available for diesel engine emission control [1,2]. Both technologies provide good NO_x reduction performance over a wide temperature range (200–400 °C) under well-controlled conditions, but have serious drawbacks of their own that deter decision makers from adopting either technology [3–13]. In an attempt to overcome the inherent shortcomings of these existing technologies, plasma-assisted catalysis for lean-NO_x reduction through the improvement of the HC/SCR technology has emerged as a promising alternative to the more mature urea/SCR and LNT technologies [14–21]. Published literature reports on the application of the plasma-assisted HC/SCR to the lean-NO_x catalysis have focused primarily on the in situ activation by non-thermal plasma of the gas phase reactants such as NO and/or HCs. Thus, the major role of the plasma reactor in this application has been to enhance the oxidation potential of oxygen by converting it to O_3 and OH radicals, thereby to produce NO_2 from NO and partially oxidized hydrocarbons (OHC) from hydrocarbons (HC). The NO_2 and OHC then react over suitable SCR catalysts located downstream to produce N_2.

In this work, we have developed a new plasma-assisted NO_x reduction system for diesel engines based on an ex situ activation of reactants in both the gas phase and the liquid phase, in which raw diesel fuel in the liquid phase is reformed ex situ to produce oxygenated hydrocarbon (OHC) vapors that are subsequently used for NO_x reduction over suitable SCR catalysts (OHC/SCR). The NO_x reduction potential of the system has been successfully demonstrated through both steady-state and simulated FTP (federal test procedure) tests using an engine dynamometer system, achieving ~60% mode-average NO_x conversion in the Isuzu 8-mode simulated FTP tests.

2. Experimental

2.1. System description

Presented in Fig. 1 is the plasma-assisted NO_x reduction system developed and tested in this work for diesel engine exhausts. The system consists of a sidestream hyperplasma reactor [22], a diesel fuel reformer [23] and a dual-bed catalytic reactor. The

* Corresponding author at: Department of Chemical Engineering/School of Environmental Science and Engineering, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea. Tel.: +82 54 279 1325; fax: +82 54 279 8299.
** Corresponding author at: Department of Chemical Engineering/School of Environmental Science and Engineering, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea. Tel.: +82 54 279 2264; fax: +82 54 279 8299.
E-mail addresses: bbkcho@postech.ac.kr (B.K. Cho), isnam@postech.ac.kr (I.-S. Nam).

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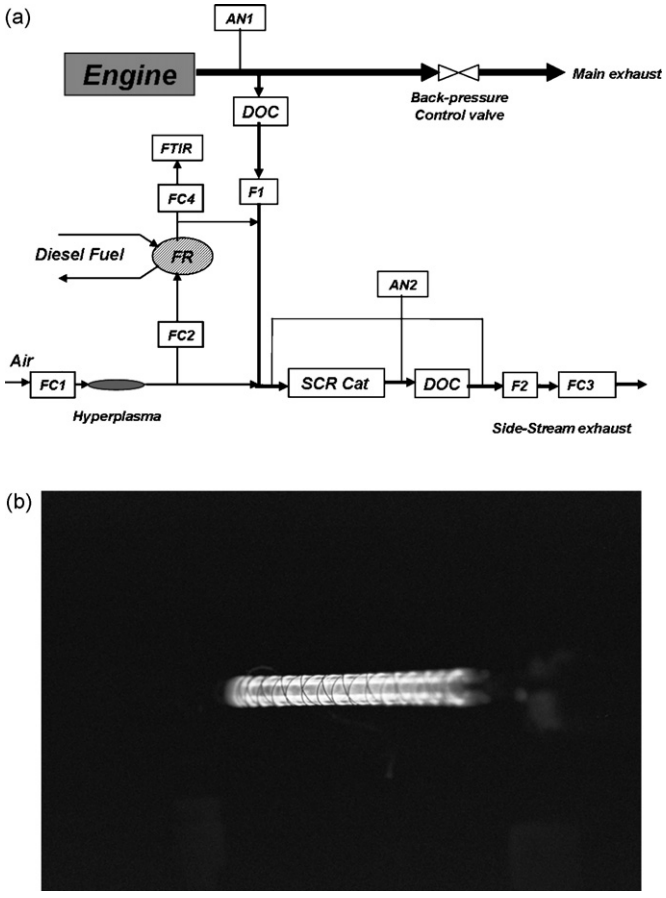

Fig. 1. (a) Schematic flow diagram for side-stream dynamometer tests of plasma-assisted HC/SCR system. (AN1, AN2 = exhaust composition analyzer; F1, F2 = filter; FC1, FC2, FC3, FC4 = mass flow controller; FR = fuel reformer.) (b) Hyperplasma reactor.

plasma-induced diesel fuel reformer can produce highly reactive OHCs from raw diesel fuel for NO_x reduction. The steady-state performance as well as the simulated FTP performance for NO_x reduction has been evaluated using a combined hyperplasma/fuel reformer/catalyst system installed in a sidestream connected to the main exhaust stream of a 4.9L, 6-cylinder Isuzu diesel engine dynamometer system. Listed in Table 1 are the experimental conditions used for the plasma-assisted HC/SCR. For comparative kinetic studies, engine dynamometer tests and laboratory microreactor experiments have also been conducted for the (HC + OHC)/SCR using E-diesel and a (simulated diesel fuel + ethanol) mixture as the reductant, respectively.

Table 1
Experimental conditions for plasma-assisted HC/SCR.

Diesel fuel	Swedish diesel and ULSD (raw)
Diesel fuel reformer	Air plasma flow rate = 15–300 cm^3/min Dilution ratio to FTIR = 20 Reformer fuel volume = 144 cm^3 Fuel feed rate = 2 cm^3/min T = 125–160 °C
Hyperplasma reactor	HV = ± 16 kV Plasma energy density = 19 J/L T = room temperature Input stream = 2.5 L/min Output stream = 15–300 cm^3/min to reformer Balance to exhaust line
Catalysts	BaY + CuY, BaY + Ag/alumina, Pt/alumina
System pressure	101.3 kPa

Table 2
Catalyst and reductants combinations.

Catalysts	1st bed	2nd bed	Reductant	Reformer
A	4BaY	1CuY	Swedish diesel	Yes
B	2BaY	2CuY	ULSD	Yes
C	2BaY	2Ag/Al_2O_3	ULSD	Yes

2.2. Catalysts and reductants

Listed in Table 2 are the three sets of catalysts tested in this work in a dual-bed configuration, which involve different combinations of SCR catalysts and reductants. The numbers before each catalyst in Table 2 denote the number of monolith bricks of the catalyst. For example, catalyst A has four bricks of BaY in the first bed and one brick of CuY in the second bed. Each piece of the SCR catalyst brick was cylindrical in geometry (1 in. long and 1.75 in. in diameter). NaY powder (10 wt.% Na) obtained from Zeolyst International (CBV-100) was washcoated onto a full-size cordierite monolith (5.66 in. o.d. × 6 in. L, 400 cells per square inch, 6.5 mil wall thickness) by Johnson Matthey, using a proprietary binder composition resulting in a total washcoat loading of slightly more than 2.5 g/in^3. Small sample cores (1.75 in. o.d. × 1 in. L) were drilled out of this full-size NaY monolith. Both the BaY (10 wt.% Ba) and CuY (7 wt.% Cu) catalysts were prepared by the aqueous ion-exchange of the NaY monolith sample cores, using aqueous solutions of $Ba(C_2H_3O_2)_2$ and $Cu(C_2H_3O_2)_2$, respectively, at room temperature. The samples were dried at 120 °C for 4 h, and calcined in air at 500 °C for 4 h. Ag/alumina containing 2 wt.% was prepared on γ-alumina powder obtained from Sasol (Catalox SBA-200) by the incipient wetness method using $AgNO_3$ (JT Baker) as the precursor. The catalyst powder was dried at 110 °C overnight, calcined at 500 °C for 10 h, and washcoated onto cordierite monoliths (1.75 in. o.d. × 1 in. L, 400 cells per square inch, 6.5 mil wall thickness) followed by calcination in air at 500 °C for 4 h. The SCR catalyst bricks were put into a flow-through reactor made of a stainless steel tube (2 in. o.d. × 1.875 in. i.d. × 20 in. L) in different combinations. The first DOC (diesel oxidation catalyst) in the sidestream exhaust in Fig. 1 was 5% Pd/alumina (0.875 in. o.d. × 2.5 in. L) obtained from Umicore, while the second DOC after the SCR catalyst was 5% Pt/alumina (1.75 in. o.d. × 1 in. L) obtained from BASF.

2.3. Engine dynamometer test conditions

NO_x reduction performances of the (plasma + fuel reformer + catalyst) system were evaluated using a sidestream taken from the main exhaust stream of a diesel engine dynamometer system connected to an Isuzu 4.9L, 6 cylinder diesel engine. NO_x reduction performance under FTP conditions was evaluated using an 8-mode steady-state FTP simulation procedure developed for this Isuzu engine. This simulated FTP performance does not include cold-start or transient operation effects, but provides an approximation of an actual vehicle certification test.

3. Results and discussion

3.1. Performance of diesel fuel reformer

Fig. 2 shows typical vapor products from the diesel fuel reformer when Swedish diesel fuel or ULSD (Ultra Low Sulfur Diesel) fuel was used as the raw diesel fuel. The reformer temperature was maintained at 140 °C for the Swedish diesel fuel, while it was 160 °C for the ULSD. This temperature difference was necessary to compensate for the difference in fuel volatility of the two diesel fuels, since the ULSD contains heavier components than the Swedish diesel. The species concentrations shown in Fig. 2 are those in the exhaust