Korean J. Chem. Eng., **25**(1), 84-88 (2008)

Reduction of NO_x in diesel engine emissions by using a plasmatron fuel reformer

Vadim Yu. Plaksin, Heon-Ju Lee†, Valentin A. Riaby, Young Sun Mok, Sang Hoon Lim* and Ji Hun Kim

College of Engineering, Cheju National University, Ara-1 dong, Jeju 690-756, Korea
*Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Korea
(*Received 20 December 2006 • accepted 2 May 2007*)

Abstract−An experimental study of diesel exhaust cleaning by means of the plasma chemical pretreatment of fuel is described. Some portion of the fuel was activated in an arc discharge and turned into hydrogen-rich synthesis gas. Plasma chemical reformation of fuel was carried out by using a DC arc plasmatron that was fabricated to increase the ability of gas activation. The yield of diesel fuel reformation reached about 80-100% when small quantities of fuel (flow rate up to ~6 ml/min) were reformed. The synthesis gas, containing H_2+CO, was supplied into the engine together with the rest of the fuel-air mixture, and the NO_x content in its emissions reduced up to 23%.

Key words: Plasma Chemistry, Arc Discharge, Fuel Reformation, Synthesis Gas, NO_x Reduction, CO, H_2

INTRODUCTION

As regulations of emissions from diesel vehicles are becoming more stringent, research in the field of in-cylinder processing technology (pretreatment) is becoming a more important issue as well as the catalyst after-treatment.

In this work, a pretreatment approach consisting of plasma chemical fuel reformation was investigated. Some fraction (10…20%) of the diesel fuel was reformed by the plasma in a high durability plasmatron and the hydrogen-rich synthesis gas, in which the H_2, CO, CO_2, N_2 and hydrocarbons are generated as the result of MIT group [1,2]. The synthesis gas is formed by the partial oxidation of fuel:

$$C_{12}H_{26}+6\,O_2+22.3\,N_2 \rightarrow 13\,H_2+12\,CO+22.3\,N_2+1{,}000\ kJ \quad (1)$$

Here $C_{12}H_{26}$ is an average chemical formula of diesel fuel, which is a complex mixture of numerous hydrocarbons. The necessary quantity of air flow rate in order to complete the reaction (1) can thus be calculated. The partial oxidation of 1 mole=170 g of diesel fuel having molar volume $V_M \approx 170/0.8 \approx 212$ ml takes 28.3 mol of air that has a volume of about $28.3 \times 22.4 \approx 634$ litres at the standard condition. An ideal stoichiometric relationship between air and fuel flow rates shows a very simple form as given below.

$$Q_{Air}\ [nl/min] \approx 3Q_F\ [ml/min] \quad (2)$$

The use of high durability plasmatron has the following characteristics, such as the low plasma contamination, the low anode erosion rate, the low plasma temperature, and the effective activation of the process gas. The details of the plasmatron are presented in the other articles [3,4].

When the produced synthesis gas was introduced into the engine as an additive, the fuel combustion efficiency increased and the NO_x content in the vehicle exhaust decreased. When a small amount of hydrogen was added to a gasoline engine, the lean limit of the engine increased due to the higher flame speed [5].

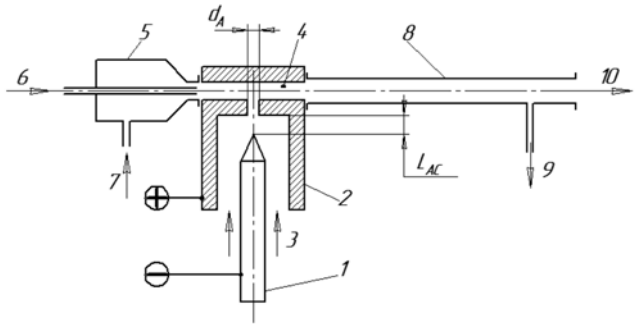

Fig. 1. Diesel fuel reformation system with the T-plasmatron.

EXPERIMENT

1. Plasma Chemical Fuel Reformation System Using T-Plasmatron

Fig. 1 shows a schematic diagram of the experimental apparatus for the plasma chemical fuel reformation that incorporates the DC arc T-plasmatron. In this case, the argon gas is heated by arc discharge to form plasma which is connected vertically to the middle of the technologic channel where the process gas flows. As the connection forms with T-junction, we called the plasmatron a T-plasmatron.

Though the reformation process follows the main ideas of the previously published studies by the MIT group in Ref. 1 and 2, the type of plasmatron which constitutes the major unit of the system used in the present study differs from those works and has increasing chemical activity. The details of the plasamatron are described in other articles [3,4]. It consists of a rod cathode, 1 and a nozzle anode, 2. Between these two electrodes, argon gas, 3 is supplied to protect a hot tungsten cathode, 1, and serve as a plasma forming gas. The hot argon plasma produced by the discharge passes through a hole, mixed with cold process gas, consisting of atomised diesel

†To whom correspondence should be addressed.
E-mail: hjlee@cheju.ac.kr
‡This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

fuel mixed with air, and performs the plasma chemical interaction in the technologic channel, 4. This process gas is supplied into the technologic channel by the diesel fuel atomisation injector, 5, having a fuel feeding connector, 6, and an air inlet, 7. In the present work, a standard atomising injector, 1/4AU Automatic Air Actuated Nozzle Assembly was used (manufactured by Spraying Systems Co., USA). The technologic channel, 4, has a rectangular cross section of 3×8 mm.

The anode orifice is connected to the middle of the wide side of the technologic channel. The hot argon plasma meets with the cold technologic gas flow at this region, turns 90º in its flow direction and forms a vortex across the technologic channel. Previous experiments showed that such kind of gas mixture flow resulted in very low anode erosion rate (~10^{-10} g/C) and almost spectrally clean plasma because the only noticeable source of plasma contamination was the hot tungsten cathode that operated nearly in the thermion mode. The difference in the anode erosion rate as compared to conventional plasma torches reached five orders of magnitude, which indicates the change in the anode spot mechanism: this arc root was attracted by the vortex at the turning point of the argon plasma flow which is quite natural for arc plasmatrons in general; then, it was distributed over a large surface, lowering the anode current density significantly. This phenomenon is responsible for such a dramatic decrease of the anode erosion rate. In addition, as the vortex filled all the cross-section of the technologic channel, the chemical reaction throughout the entire space of the technologic channel can be enhanced. Using the plasmatron for the purpose of diesel fuel reformation could result in good performance.

The elongated reformation chamber, 8, was used in this system because the reformation process took time and space. The chamber was made up of a steel pipe of 550 mm length with an internal diameter of 11.5 mm. The length of the tubular reformation chamber was selected as 550 mm, because when its length was shorter than that, a long bright flame could be seen at its exit. When the chamber length was over 550 mm, only a gleaming gas flow without any flame was observed. Beside its exit, 10, a sleeve, 9, was provided to be connected to the gas analysers, so the gas samples for the subsequent composition measurements could be taken as the main chemical reactions were completed.

In the process of fuel reformation, the plasmatron parameters were selected and adjusted as follows: anode orifice diameter d_A=1.5-2.0 mm, inter-electrode distance L_{AC}~1.5 mm, argon flow rate in the cathode channel Q_{AR}~1 nl/min, arc current I=100 A, arc voltage U≈12 V, arc power P≈1.2 kW.

2. Plasma Chemical Fuel Reformation System Using A-Plasmatron

All experiments show the importance of a more or less uniform temperature distribution in the area where the process gas interacts with the hot argon plasma, and this uniform temperature level has to be made as high as possible. The solution of the problem was found when the technologic channel of the plasmatron was made circular with an exit hole at the axis of the device, as shown in the schematic diagram in Fig. 2.

This axisymmetric technologic plasmatron is called the "A-plasmatron"; the azimuthally uniform process gas supply was arranged around the hot argon plasma jet at the exit of the anode orifice. In this case, all elementary stream-lines of the process gas meet and

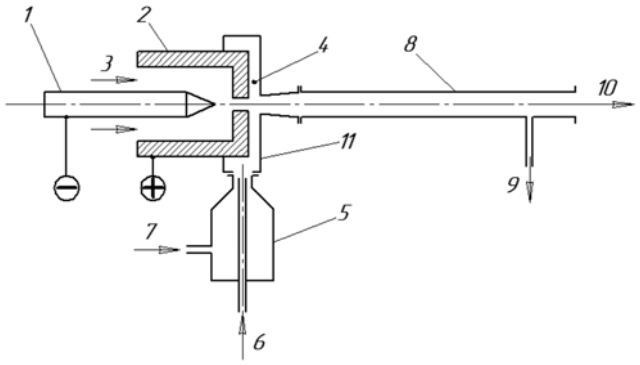

Fig. 2. Diesel fuel reformation system with the A-plasmatron.

interact with the hot argon plasma jet rather effectively. A circular gas collector at the inlet of this circular technologic channel was used to realize the idea. These elements are present in the new exit cap, 11, that changed the outlook of the device. All other components are same as that of the T-plasmatron. In the A-plasmatron, all of the technologic gas was forced to pass through the single exit hole together with the hot argon plasma coming from the arc discharge space. By considering the turbulent character of the gas flow in both the cathode and technologic channels and their collision at right angles just before the outlet nozzle, it seems easy to imagine how intensively they interact. The character of the interaction between plasma forming and process gases allowed us to expect a higher degree of process gas activation, which was confirmed in the subsequent reformation experiments.

The anode erosion rate of the A-plasmatron was checked in order to make sure that the vortex nature of the anode arc spot did not change in the new design, as the distributed character of the anode spot had remained, then the erosion rate of the anode and plasma contamination with anode material vapours would be low. The measurements of the anode erosion rate by the weight method showed the same order of the specific anode erosion rate at $m_A \approx 4 \cdot 10^{-10}$ g/C [3]. Therefore, all positive qualities of the previous model of the plasmatron remained unchanged. Additionally, some new attractive features of the device appeared. It could be operated without any water-cooling of the exit cap up to 1.5 kW of arc power. As a result, the plasmatron became more compact and reliable.

3. Fuel Reformation and Addition of Reformed Gas into Engine

The diesel fuel was reformed by the system containing the plasmatron described above. The fuel was converted into a hydrogen-rich synthesis gas mixture, which mainly consists of H_2, CO, CO_2, N_2 and hydrocarbons, by the partial oxidation of the plasma chemical reaction. While varying the parameters like fuel flow rate, air flow rate and plasmatron power, we checked the reformed gas components.

The scheme of the reformation system is presented in Fig. 3. The diesel fuel is supplied to the injector of the plasmatron by a diaphragm pump. The fuel is mixed with compressed air in the injector and atomized through a nozzle connected to a plasmatron. A part of the reformed gas was sampled for the analysis. The components of the gas were measured by the RBR-Ecom KD analyser (CO, CO_2, O_2, NO_x, and C_xH_x content) and the ATI PortaSens II

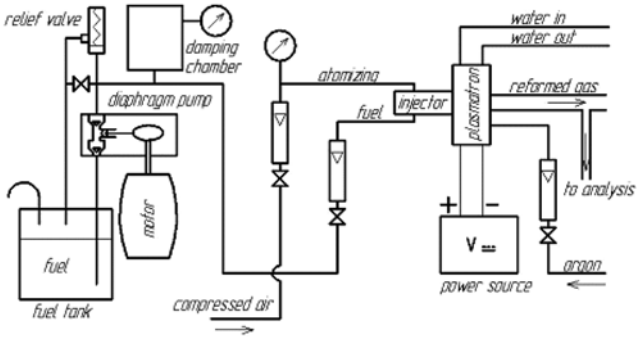

Fig. 3. Schematic diagram of a fuel reformation system.

C16 analyser (H_2 content).

The amount of the fuel for reformation was selected at about 15-20% of the fuel consumption of the diesel engine. Because the fuel consumption of the engine can reach around 150 ml/min, the plasma chemical reformation system had to be tuned to deal with the reformation fuel flow rate, Q_F≈25 ml/min≈20 g/min≈0.12 mol/min.

For a reformation fuel flow rate of 25 ml/min, the stoichiometric air flow rate should be adjusted to Q_{Air}≈75 nl/min according to Eq. (2). If 100% of this fuel quantity is reformed into synthesis gas, then the hydrogen product of the reaction can reach 13×0.12=1.56 mol/min≈35 nl/min (27%) and the CO product is 12×0.12=1.44 mol/min≈32nl/min (25%). These figures are ideal limits; real results should depend on the quality of the plasma chemical process of fuel reformation. The content of CO in the reformed gas was measured as an indicator of fuel reformation because the hydrogen content can be affected by the inclusion of water vapour in air.

The hydrogen-rich reformed gas was then introduced into the diesel engine as an additive to the air supply, and its effect on the NO_x content in the exhaust gas was checked. In the present work, a diesel engine, Kookje Kumins 3T90LT-AC, was used for the experiment. The water-cooled 4-cycle type engine has a total displacement of 1,794 cc and a power of 32 kW. The tubular reformation chamber was connected to the engine through the heat exchanger, DOVER B10Hx20/1P-SC-S. Its cooling jacket was connected in series with the cooling system of the plasmatron. At the exit of this device, the gas temperature did not exceed ~40°C even when the plasmatron power was increased up to 1.5 kW.

Measurements of the engine emissions were arranged in the following manner. The engine was started and heated during some 20-30 minutes of operation at idling speed. Then an analyzer probe was inserted into the exhaust pipe of the engine to measure NO, NO_2 and NO_x content. First, the initial levels of these parameters without any additions were determined. Then, the flow of the reformed gas from the heated and stabilized reformation system was directed into the engine. The NO_x measurements by the gas analyzer were repeated and the result was compared with previous result of non-addition.

For comparison, an experiment was conducted in which only one component of the reformed gas, pure hydrogen, was added to the fuel-air inlet of the diesel engine. The addition of hydrogen seemed to the most important component for reducing NO_x emissions in a mechanism similar to the emission gas recirculation (EGR) system. The addition of hydrogen lowers the oxygen content, the combustion speed, the temperature at the flame front and consequently the NO_x emissions [6].

RESULTS AND DISCUSSION

1. Fuel Reformation

The content of CO in the reformed gas was measured as an indicator of a fuel reformation. According to Eq. (1), the fuel reformation must result in nearly equal relative contents of CO and H_2 at the level of about 25%.

The first experiment with the T-plasmatron was performed with Q_F=1.86 ml/min, while the air flow rate, Q_{Air} was varied in the range from 6 to 16 nl/min. The result is shown in Fig. 4. The maximum CO content was measured at about 6% when Q_{Air} was about 8.8 nl/min. Because the optimum air flow rate, $Q_{Air, opt}$ is 5.6 nl/min for Q_F= 1.86 ml/min according to Eq. (2), we can consider the fuel/air mixture a lean mixture in this case. The CO content is rather low compared to the upper thin line corresponding to the ideal case. Such results indicate that the plasma-chemical reactions in the experimental facility are not completed and the most probable reason for this fact would be a non-uniformity of the plasma parameters across the technologic channel of the plasmatron. The ideal CO content, CO_{ideal}, which corresponds to 100% fuel reformation in a lean mixture with fixed Q_F can be calculated as below.

$$CO_{ideal}(Q_{Air})=(25Q_{Air, opt})/Q_{Air} \quad (3)$$

The equation is valid if $Q_{Air} \geq Q_{Air, opt}$. As $Q_{Air, opt}$ is 5.6 nl/min, CO_{ideal} is 139.5/Q_{Air} and the resulting CO_{ideal} is shown by a thin curve in Fig. 4.

In the next experiment the air flow rate, Q_{Air}, was fixed at 8.8 nl/min ($Q_{F, opt}$≈2.93 ml/min) and the fuel flow rate, Q_F, was varied from 1.5 to 4.5 ml/min. The resulting dependence of CO content on the fuel flow rate is shown in Fig. 5.

When the fuel flow rate reaches 1.86 ml/min, the CO content reproduces the level of the previous experiment of 6%. With an increase in the fuel flow rate, the CO content continues to rise up to around 8.5% at 3.5 ml/min of Q_F. Such behaviour can arise from

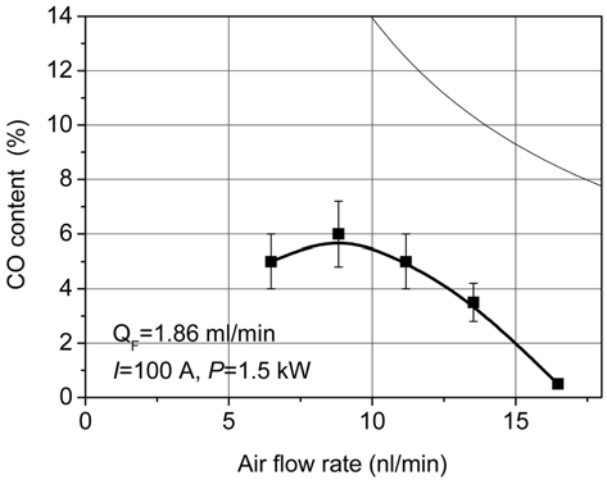

Fig. 4. CO content versus air flow rate at Q_F=1.86 ml/min with the T-plasmatron. The thin line shows the ideal obtainable CO content.

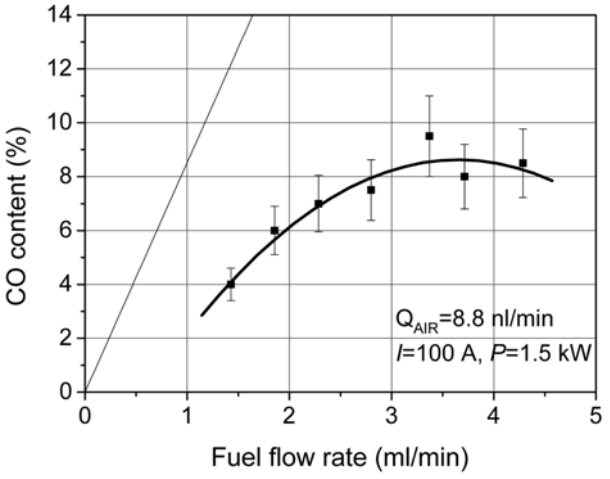

Fig. 5. CO content versus fuel flow rate at Q_{Air}=8.8 nl/min with the T-plasmatron. The thin line shows the ideal obtainable CO content.

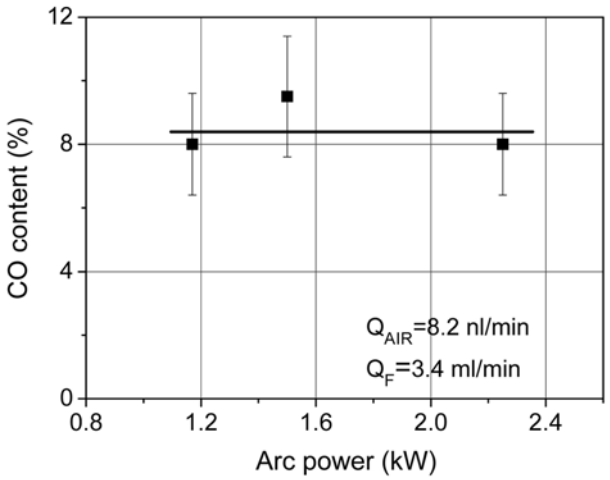

Fig. 6. CO content versus plasmatron power at Q_F=3.4 ml/min and Q_{Air}=8.8 nl/min with the T-plasmatron.

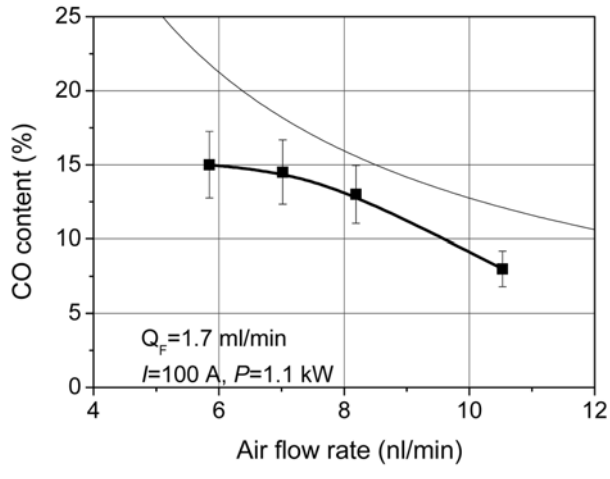

Fig. 7. CO content versus air flow rate at Q_F=1.7 cc/min with the A-plasmatron. The thin line shows the ideal obtainable CO content.

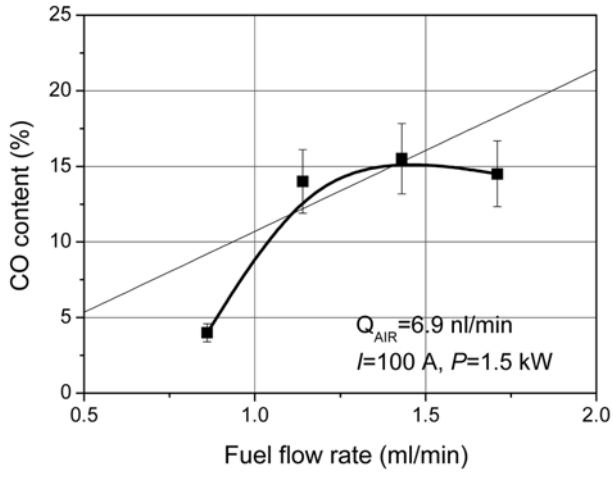

Fig. 8. CO content versus fuel flow rate at Q_{Air}=7 nl/min with the A-plasmatron. The thin line shows the ideal obtainable CO content.

the change of fuel atomization quality in the new conditions. In Fig. 4, the ideal CO content, $CO_{ideal}(Q_F)$ for lean mixtures with fixed Q_{Air} is also presented by the thin straight line.

$$CO_{ideal}(Q_F)=(25/Q_{F,opt})Q_F \quad (4)$$

The equation is valid if $Q_F \le Q_{F,opt}$. This shows once again the low level of reformation that is achieved in the initial variant of the reformation system.

Next, the CO content was measured for differing levels of arc power with fixed values of fuel and airflow rates, Q_F=3.4 ml/min and Q_{Air}=8.8 nl/min, respectively. Considering the measurement error of ±20%, the resulting value can be considered constant at the level of about 8.5% (Fig. 6). Perhaps at higher arc powers this dependence can increase the following rise of the degree of plasma ionization, but for the present project this possibility seemed impractical.

The fuel reformation was then carried out with the A-plasmatron and the results are presented in Figs. 7 and 8. Fig. 7 shows the dependence of CO content on the air flow rate, and Fig. 8 shows the dependence of CO content on the fuel flow rate. The resulting CO contents are approximately two-times higher compared to the results of the T-plasmatron as shown in Figs. 4 and 5. The yield of CO production can be found by comparing the experimental curve of the CO content with a hyperbola $CO_{ideal}(Q_F)$. This high level of CO yield demonstrates the effectiveness of the reformation process in the new design arrangement. Therefore, all of the expectations for the higher quality of the plasma-chemical process in a new plasmatron design turned out to be true. This conclusion is clearly confirmed by the upper boundaries for 100% completeness of the fuel reformation process in lean mixtures calculated according to Eqs. (3) and (4) and shown in Figs. 7 and 8 as thin lines. For a constant fuel flow of Q_F=1.7 ml/min as shown in Fig. 7, the maximum CO content of 15% was achieved at a low airflow rate of 6 nl/min. The maximum yield of CO production was of 81% at an airflow rate, Q_{Air}=8 nl/min. For the constant airflow rate of Q_{Air}=7 nl/min shown in Fig. 8, the CO yield reached 100% at the range of fuel flow rate

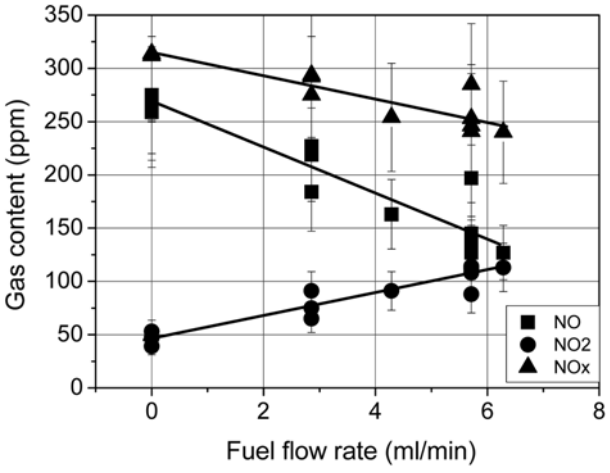

Fig. 9. Nitrogen oxide content versus fuel flow rate at Q_F=0-6 ml/min.

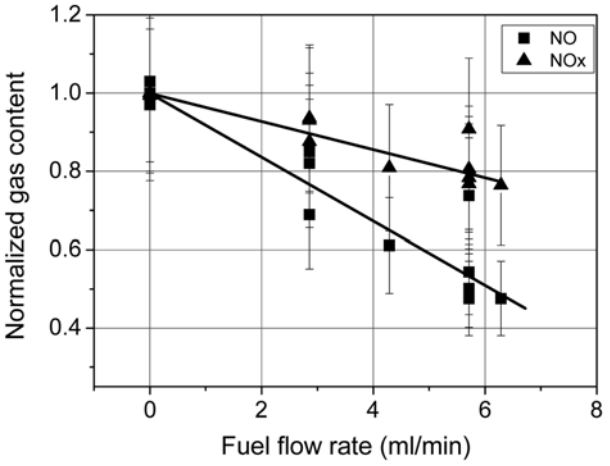

Fig. 10. Normalized NO and NO_x contents versus fuel flow rate at Q_F=0-6 ml/min.

from 1.1 to 1.4 ml/min. This means the fuel was fully reformed, which is comparable to the result of Bromberg et al. who reported 95% of hydrogen yield [7].

2. Effect of the Fuel Reformed Gas Addition into the Diesel Engine

Initially, at the trial flow rates of fuel in the range of 1.0 to 1.7 ml/min, it was found that as more fuel was supplied to the plasmatron, the NO_x content in the engine exhaust flow continued to reduce. So the fuel flow rates were increased up to 6.3 ml/min. The changes in NO, NO_2 and NO_x contents dependent on the fuel flow rate for the reformation are shown in Fig. 9. Fig. 10 shows the normalized NO and NO_x contents versus fuel flow rate ranging from 0 to about 6 ml/min. In Fig. 9, it can be seen that the NO content reduced linearly while NO_2 content increased. This is the same effect, as some parts of NO are converted into NO_2. As the content of NO decreased more rapidly than the increase of NO_2, then the net content of NO_x also decreased. The largest cut in NO_x content reached to 23% and the NO content reduced a little more than 50% when the fuel flow rate for the reformation reached a little above 6 ml/min.

3. Effect of Hydrogen Addition in the Diesel Engine Exhaust

Measurements of the exhaust gas composition showed that the reduction in NO_x about 20% and the reduction in NO was close to one order of magnitude when the hydrogen flow rate was 18 nl/min. Considering reaction (1) and the discussion of Eq. (2), we see that the tested quantity of hydrogen flow rate corresponds to a fuel flow rate of about 12 ml/min. However, in the case of our reformation experiment, an NO_x reduction of 23% could be achieved with the reformed gas from a fuel flow rate of about 6 ml/min. As all gas products from the fuel reformation process were introduced into the engine, we found that other components such as carbon monoxide play a definite positive role in cleaning diesel engine emissions.

CONCLUSIONS

The design of the DC arc plasmatron applied for the plasma chemical fuel reformation was improved by boosting the degree of fuel-air mixture activation that raised the completeness of the partial fuel oxidation reaction up to 100%. The fuel reformation was carried out with the A-plasmatron and the results showed the CO content was approximately two-times higher compared to the results of the T-plasmatron. The preliminary experiments with fuel reformation in the improved A-plasmatron at small fuel flow rates (up to about 6 cc/min) and the subsequent supply of the reformation products into a diesel engine resulted in a cut of about 23% of NO_x and about 50% of NO content in the exhaust gas flow. On the other hand, the relative quantity of NO_2 increased more than two-times. A comparison experiment with the addition of pure hydrogen to the inlet of the diesel engine showed that both components of H_2 and CO in the synthesis gas fed into the engine play a significant role in cutting NO_x content in the engine's emission.

ACKNOWLEDGMENT

This work was supported by grants R-2004-096-0-00 and 2006-C-CC02-P-05-0-000 by the Ministry of Commerce, Industry and Energy, Korea. The researchers participating in this study are supported by the grants by "the 2nd phase BK21 project" from the Ministry of Education and Human Resources Development, Korea.

REFERENCES

1. A. Rabinovich, D. Cohn and L. Bromberg, *Int. J. of Vehicle Design*, **15**, 234 (1994).
2. A. Rabinovich, D. Cohn and L. Bromberg, US Patent, 5,425,332 (1995).
3. V. A. Riaby, V. Yu. Plaksin, J. H. Kim, Y. S. Mok, H. J. Lee and C. K. Choi, *J. Korean Phys. Soc.*, **48**, 1696 (2006).
4. H. J. Lee, V. Yu. Plaksin and V. A. Riaby, *Thin Solid Films*, **515**, 5197 (2007).
5. E. Tully and J. Heywood, SAE Transactions, 2003-01-0630, 63 (2003).
6. E. Mattarelli, G. M. Bianchi and D. Ivaldi, SAE Technical Paper Series, 2000-01-0224 (2000).
7. L. Bromberg, D. Cohn, A. Ravinovich, J. Surma and J. Virden, *Int. J. of Hydrogen Energy*, **24**, 341 (1999).