Honeycomb discharge generated with a single high voltage power supply for activating catalyst

Tomoya Suzuki
Toyohashi University of Technology
1-1, Tempaku-cho, Toyohashi,
Aichi, 441-8580 Japan
t083820@edu.imc.tut.ac.jp

Yuki Nomura
Toyohashi University of Technology
1-1, Tempaku-cho, Toyohashi,
Aichi, 441-8580 Japan
y093834@edu.imc.tut.ac.jp

Yuichi Hinata
Toyohashi University of Technology
1-1, Tempaku-cho, Toyohashi,
Aichi, 441-8580 Japan
y103834@edu.imc.tut.ac.jp

Hideaki Hayashi
Toyohashi University of Technology
1-1, Tempaku-cho, Toyohashi,
Aichi, 441-8580 Japan
h063822@edu.imc.tut.ac.jp

Hirofumi Kurita
Toyohashi University of Technology
1-1, Tempaku-cho, Toyohashi,
Aichi, 441-8580 Japan
kurita@ens.tut.ac.jp

Kazunori Takashima
Toyohashi University of Technology
1-1, Tempaku-cho, Toyohashi,
Aichi, 441-8580 Japan
takashima@ens.tut.ac.jp

Akira Mizuno
Fellow, IEEE
Toyohashi University of Technology
1-1, Tempaku-cho, Toyohashi,
Aichi, 441-8580 Japan
mizuno@ens.tut.ac.jp

***Abstract* – Atmospheric pressure discharge plasma has been widely studied with the intention to apply for many fields, especially to environmental protection. Diesel exhaust cleaning using the non-thermal plasma is one of the most promising applications. We have studied diesel exhaust cleaning using the combination of catalyst and discharge plasma. We have developed a novel way of combining honeycomb catalyst and discharge plasma named "honeycomb discharge", in which seeding discharge generated by DBD is expanded into capillaries of honeycomb catalyst due to DC high voltage application. This paper presents a new configuration of honeycomb discharge reactor which can be operated by a single high voltage power supply. NOx reduction performance using the newly proposed honeycomb discharge reactor and simulated diesel exhaust is presented in this paper. Characteristics of the capillary discharge such as stability, uniformity, onset / flashover voltage and power consumption, were observed against various humidity and temperatures in order to evaluate influence of temperature and humidity on the honeycomb discharge.**

***Index Terms*—Diesel engine, Exhaust, Honeycomb discharge, Nitrogen oxides, NH3, SCR, Sliding discharge, Surface discharge**

I. Introduction

Diesel engine is widely used in large commercial vehicles because of its higher thermal efficiency or lower CO_2 emission compared with gasoline engine. It will be very important power source in future because alternative diesel fuel such as biodiesel can be used. However, nitrogen oxides (NOx) emission from the diesel engine is higher than that of gasoline engine and very complicated after-treatment is required to reduce NOx in the exhaust due to high oxygen concentration. Selective catalytic reduction (SCR) using NH_3 is the only technology practically used for mobile diesel engines. It requires high temperatures about 200ºC or higher to activate the catalyst but exhaust temperature is sometimes lower than this temperature range, for example, at cold start, during low speed running and idling.

Atmospheric pressure non-thermal discharge plasma is a potential technology to help activating catalyst at low temperatures. We have developed a method to generate homogeneous long-gap surface discharge on dielectric materials[1-4] called "slide discharge". We have also succeeded in generating the slide discharge inside capillaries of the honeycomb catalyst, which was named "honeycomb discharge"[5-6]. In these methods, seeding discharge is generated at one end of the capillary and expanded toward the other end of the capillary by electric field along the capillary. We have demonstrated that NOx was successfully removed using the capillary discharge and honeycomb catalyst[6-10]. This is the only way to generate discharge on the honeycomb catalyst so far but simpler electrical configuration (smaller and lower cost) is required from a practical application viewpoint because two high voltage power supplies are necessary for the honeycomb discharge. It is also important to evaluate the influence of temperature and humidity on the honeycomb discharge because they vary significantly depending on operating condition of the engine.

In this study, we examined the method to generate the capillary discharge using a single high voltage power supply.

A new electrode configuration was investigated to make it serve as both a seeding discharge generator and its expander. The characteristics of the newly proposed honeycomb discharge were evaluated in terms of NO oxidation and NOx removal efficiency. In addition, stability, uniformity, onset voltage, flashover voltage and power consumption of the capillary discharge were observed against various humidity and temperature.

II. EXPERIMENTAL

A. Honeycomb discharge generation using a single high voltage power supply

First of all, generation of honeycomb discharge was investigated using a setup employing a bundle of glass capillaries simulating a honeycomb catalyst so that luminosity of the honeycomb discharge can be observed. Figure 1 shows a schematic illustration of the honeycomb discharge reactor. It consists of a bundle of glass capillaries (30mm in apparent diameter) and two surface discharge generators placed on the both ends of the capillaries. Length and outer / inner diameter of the capillary are 25mm and 3.0mm / 1.8mm respectively. Schematic illustration of the surface discharge generator is shown in figure 2. There is a pair of electrode by a through-hole. One electrode is embedded in ceramic base and the other is flush-mounted on the surface. The embedded electrode is grounded and the sinusoidal high voltage was applied to the flush-mounted electrode. AC high voltage application generates surface discharge inside the through-holes. A set of glass capillaries and two surface discharge generators is placed in a glass tube to feed the reactor with gas. Applied voltage was changed by $1kV_{p\text{-}p}$ from $8kV_{p\text{-}p}$ to 13 $kV_{p\text{-}p}$ at a fixed frequency of 1kHz.

NOx removal experiment was carried out using a reactor similar to the one described above but honeycomb catalyst was used in place of a bundle of glass capillaries. The catalyst is made of zeolite supporting iron (Fe) or copper (Cu), which should catalyze reduction of NOx in the presence of NH_3. Length, diameter and capillary size of the honeycomb catalyst are 30mm, 30mm and 1mm, respectively. Dry air consisting of 200ppm NO was used as simulated diesel exhaust. 200ppm NH_3 was supplemented to the simulated diesel exhaust as a reducing agent. Total gas flow rate was 5L/min. Experiment was carried out in a 130ºC convection oven to keep the ambient temperature of the reactor. NOx concentration in the gas sampled at downstream the reactor was continuously monitored by a FT-IR spectrometer. Sinusoidal wave was applied to the reactor and the applied voltage was changed by 1 $kV_{p\text{-}p}$ from $7kV_{p\text{-}p}$ to 13 $kV_{p\text{-}p}$ at a fixed frequency of 1kHz.

B. Influence of humidity and temperature on honeycomb discharge generation

Fundamental characteristics of the capillary discharge was measured using a capillary discharge reactor in an original configuration[5-6] consisting of a seeding discharge generator, glass capillaries and a counter electrode. Figure 3 shows a schematic illustration of the original type capillary discharge reactor. A packed bed type dielectric barrier discharge (DBD)

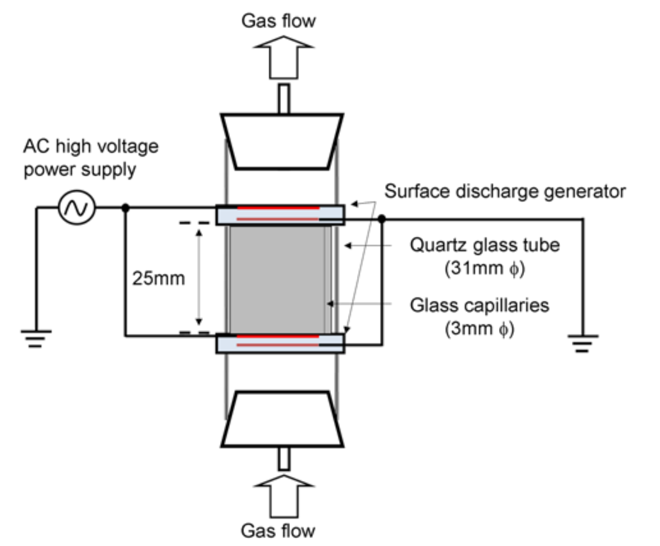


Fig. 1. Schematic illustration of a honeycomb discharge reactor.

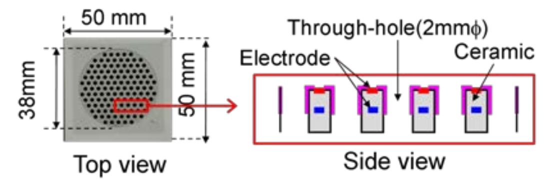


Fig. 2. Schematic illustration of a surface discharge generator.

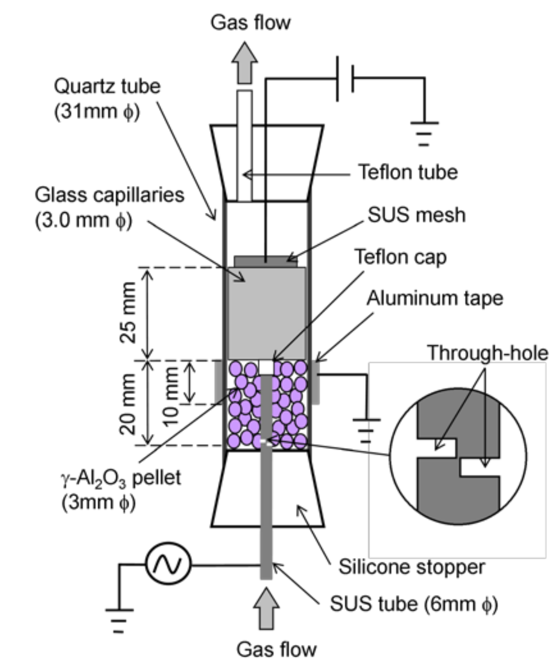


Fig. 3. Schematic illustration of a original honeycomb discharge reactor.

generator and the same surface discharge generator described above subsection were employed to generate seeding discharge in this experiment.

The packed bed type seeding discharge generator was illustrated in the figure. 3mm-diameter γ-Al_2O_3 pellets were packed in a 20mm-thick layer in a 31mm-diameter glass tube. A 6mm-diameter stainless steel tube serving as a high voltage electrode was coaxially placed in the glass tube. A 10mm-width grounded electrode was placed on the outer surface of the glass tube aligned on the upper end of the γ-Al_2O_3 pellet layer. AC high voltage application generates intense DBD at contact points between the pellets.

Glass capillaries were placed on the Al_2O_3 pellet layer. Length and outer / inner diameter of the capillary are 25mm and 3.0mm / 1.8mm respectively. A counter electrode made of a stainless steel mesh was placed on the upper end of the capillaries. A DC high voltage power supply was connected to the counter electrode. Homogeneous discharge was generated in the capillaries by applying DC high voltage in the presence of the seeding discharge. Test gas was introduced into the seeding discharge area and flowed through the capillaries to a gas outlet.

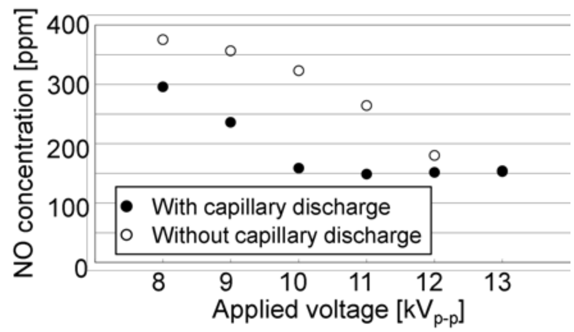
Humidity influence experiment was carried out at room temperature (24ºC) with humidity-controlled air of which relative humidity was changed by 10% from 10% to 90%. Temperature influence experiment was carried out with dry air under high temperatures. The reactor was placed in a convection oven whose temperature was changed by 30ºC from 80ºC to 170ºC. Dry air was preheated to the oven temperature before feeding to the reactor. Luminescence of the plasma, discharge current - applied voltage characteristics, and plasma onset / flashover voltage were measured.

III. Results

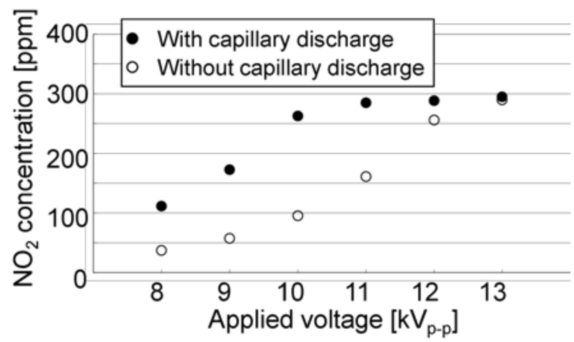
A. Honeycomb discharge generation using a single high voltage power supply

From preliminary experiment using glass capillaries, fundamental characteristics of the capillary discharge were obtained and stable operation voltage range, in which capillary discharge was generated without sparking, was determined (data not shown). NO removal performance was measured to estimate oxidation capability of the capillary discharge itself. Sample gas consisted of 400ppm NO in dry air. Figure 4 shows NO and NOx concentration as a function of applied voltage. Results when the capillaries were removed, i.e., only two surface discharge generators were operated were also shown for comparison. NO and NO_2 concentration decreased and increased with applied voltage respectively and saturated at voltages high enough in each case suggesting that NO was oxidized into NO_2 by discharge plasma. From the comparison of the cases with and without capillaries, capillary discharge resulted in lower NO and higher NO_2 concentration at the same applied voltage because of the generation of additional discharge inside capillaries. It means that the capillary discharge has higher NO oxidation capability.

Figure 5 shows comparison of the amount of oxidized NO and energy efficiencies for NO oxidation. At any applied voltages, capillary discharge showed higher energy efficiency. It should be noted that the capillary discharge resulted in significantly higher efficiency at low applied voltages whereas the difference was small when the applied voltage was high enough. It is also interesting that energy efficiency of the capillary discharge is highly dependent on applied



(a) NO concentration



(b) NO_2 concentration

Fig. 4. Schematic illustration of a honeycomb discharge reactor.

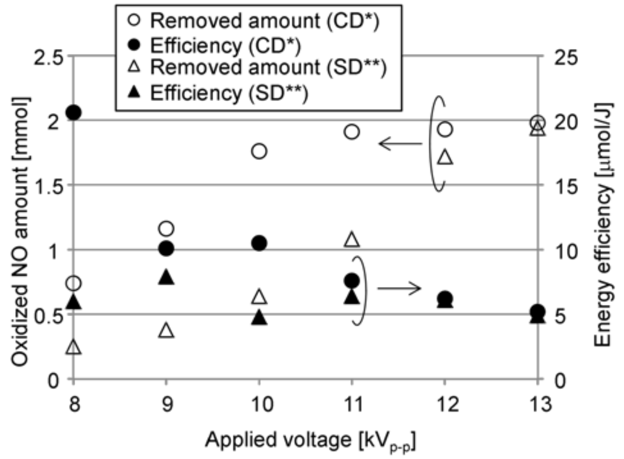
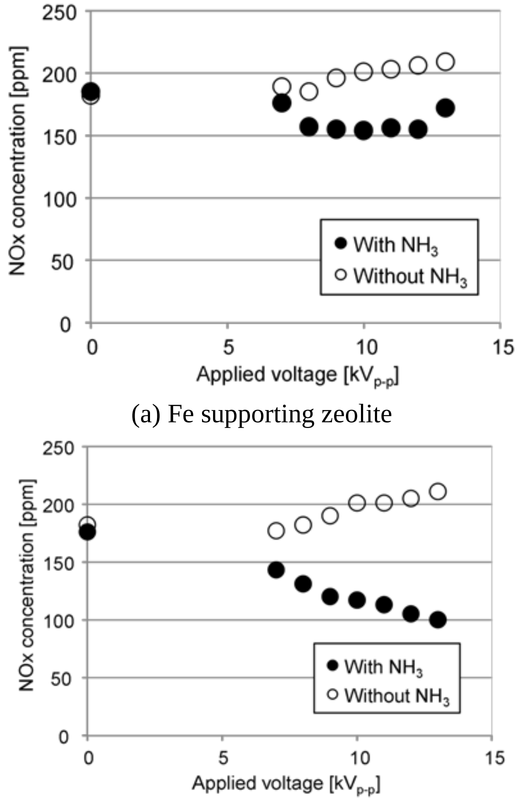


Fig. 5. Comparison of oxidized NO amount and energy efficiency for NO oxidation. CD*: Capillary discharge, SD**: Seeding discharge



(a) Fe supporting zeolite

(b) Cu supporting zeolite

Fig. 6. NOx removal using Fe-supporting zeolite and Cu-supporting zeolite activated by honeycomb discharge.

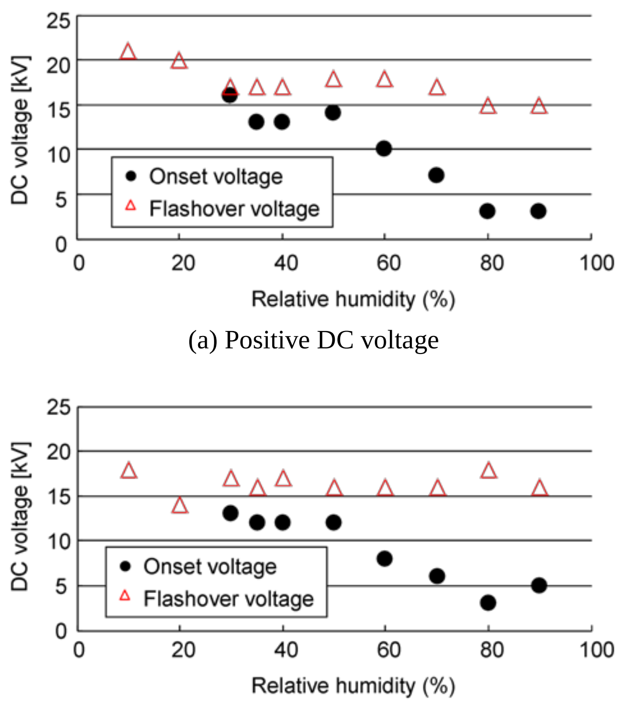
voltage but that of the surface discharge was nearly constant. These results suggest that discharge plasma in capillaries efficiently induces chemical reaction probably because it generates large area plasma for power consumption.

NOx removal experiment was carried out with honeycomb catalyst and capillary discharge at 130ºC where normally NOx cannot be catalytically removed. Simulated diesel exhaust consisting of 200ppm NO in dry air was used for the experiment. Figure 6 shows the results using Fe-supporting zeolite and Cu-supporting zeolite. NOx concentration decreased monotonously with applied voltage when Cu-supporting zeolite was used and 200ppm of NH_3 was added to the gas stream as reducing agent. When Fe-supporting zeolite was used, NOx concentration decreased with applied voltage upto 10kV but increased with further increase in applied voltage. NOx removal was very small without NH_3 addition for both catalysts. These results suggest that NOx was removed via NH_3-SCR process. It is notable that the capillary discharge on the catalyst surface successfully activates the catalyst at low temperatures where no catalytic activity is seen without plasma. It is possible that the catalyst was activated by the exposure to plasma or via interaction with the species generated by plasma. The mechanisms of plasma enhanced NH_3-SCR is not fully understood but from a viewpoint of practical application, it is very important that simple setup like this can be used to enhance the catalytic activity.

B. Influence of humidity on honeycomb discharge generation

Fundamental characteristics of the capillary discharge and seeding discharge in humid gas were studied in terms of plasma luminescence and discharge current. When packed bed type seeding discharge generator was used, capillary discharge was generated in any humidity condition examined in this study. When test gas contains humidity of 40% or higher, stable capillary discharge was generated and discharge current, power consumption and luminescence of both capillary discharge and seeding discharge increased with increasing applied voltage. On the other hand, the capillary discharge was not stable when the humidity was 30% or lower.

Figure 7 shows DC voltage values at which capillary discharge turned on (onset voltage) and flashover took place (flashover voltage) as a function of humidity. Seeding discharge was generated by AC high voltage at a fixed amplitude and frequency of 20kV$_{p\text{-}p}$ and 1kHz respectively. When positive DC high voltage was employed, both onset voltage and flashover voltage decreased with humidity. It is interesting to point out that the flashover voltage decreased with monotonously with humidity but the onset voltage has



(a) Positive DC voltage

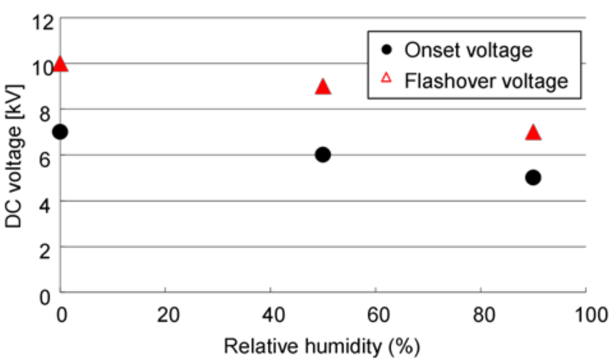
(b) Negative DC voltage

Fig. 7. Onset voltage and flashover voltage of a capillary discharge when packed-bed type discharge was used as a seeding discharge.

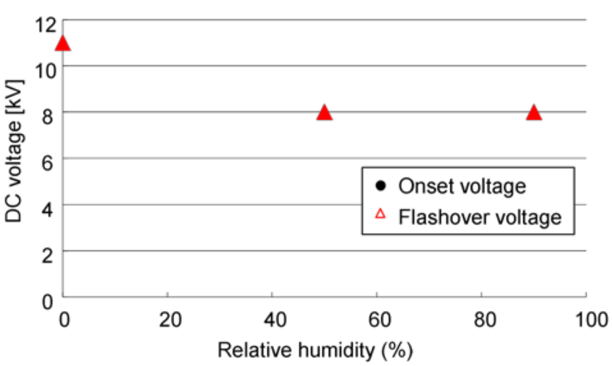
complicated dependency as follows. The onset voltage was strongly influenced by humidity when the humidity was 50% or higher while it was less dependent when the humidity was lower than 50%. This can be interpreted that stability of the capillary discharge increased with humidity because stable DC voltage region (margin between onset and flashover) increased with humidity. When negative DC high voltage was used, onset voltage monotonously decreased with humidity while flashover voltage was not influenced by humidity.

It is also interesting that corona discharge was observed at the counter electrode when humidity was high not depending on the polarity of the DC high voltage. This corona discharge can be accounted for increased conductivity due to water absorption to the capillary surface. When the humidity was 90%, no capillary discharge was generated but corona discharge was observed at the counter electrode even without DC high voltage application (only seeding discharge was on). This could be a collateral evidence for the above hypothesis on the corona discharge generation.

When surface discharge was employed for generating seeding discharge, characteristics of the capillary discharge was quite different. From the observation of luminescence of plasma, seeding discharge was suppressed when humidity increased. Figure 8 shows onset voltage and flashover voltage as a function of humidity. Seeding discharge was generated by AC high voltage at a fixed amplitude and frequency of 20kVp-p and 1kHz respectively. When positive DC voltage was used, onset and flashover voltages decreased with humidity denoting the same dependency. Onset-flashover margin was nearly constant not depending on the humidity showing that stability of the capillary discharge was not influenced by humidity. With negative DC voltage, no capillary discharge was generated but flashover took place when the DC voltage exceeded a threshold. The flashover voltage decreased with humidity. Corona discharge at the counter electrode was observed even the counter electrode was grounded, which was also seen when packed bed type seeding discharge was used. The fact that this interesting phenomenon was observed not depending on type of seeding discharge supports the above hypothesis.



(a) Positive DC voltage



(b) Negative DC voltage

Fig. 8. Onset voltage and flashover voltage of a capillary discharge when surface discharge was used as a seeding discharge.

C. Influence of temperature on honeycomb discharge generation

Influence of temperature on honeycomb discharge was investigated employing surface discharge as seeding discharge. Amplitude and frequency of the AC voltage applied to generate surface discharge was fixed at $12kV_{p\text{-}p}$ and 1kHz respectively. Figure 9 shows onset and flashover voltages as a function of humidity. Only positive DC voltage was examined in this experiment. Predictably both onset and flashover voltages decreased with temperature in the same tendency. Onset-flashover margin was about 5kV regardless of gas temperature.

Discharge current measurement indicated that surface discharge was not affected by temperature change. Luminescence of the seeding discharge and capillary discharge were observed to evaluate the influence of temperature. Luminescence of capillary discharge and corona discharge at the counter electrode increased with temperature while that of surface discharge was not changed significantly. Especially the corona discharge with DC voltage slightly lower than flashover voltage was remarkably enhanced with

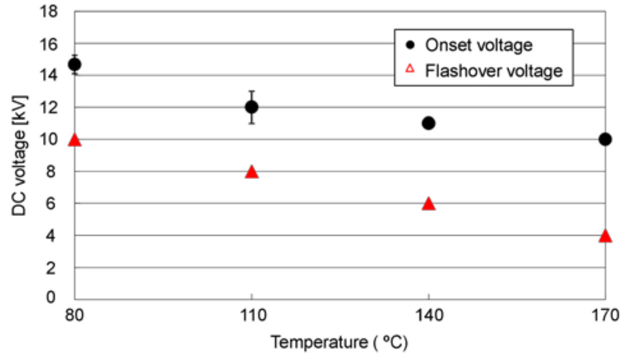


Fig. 9. Influence of temperature on onset and flashover voltage of a capillary discharge when surface discharge was used as a seeding discharge.

increasing temperature. Influence of temperature on power consumption showed the similar tendency as above. Power consumption by seeding discharge was nearly constant. Total power consumption at onset voltage was not affected significantly by temperature change. However, total power consumption at flashover voltage increased by 2 times by increasing the temperature from 80ºC to 170ºC possibly due to high power consumption by the corona discharge.

IV. Conclusion

Experimental study on capillary discharge generation was carried out mainly from a practical application viewpoint. Capillary discharge was successfully generated by a single AC high voltage power supply, of which configuration is much simpler and smaller than that used before. Capillary discharge under high temperatures and in humid gas was characterized. The capillary discharge was enhanced by increasing humidity and temperature suggesting that the capillary discharge can be promisingly applied to diesel exhaust cleaning.

Acknowledgment

The authors gratefully acknowledge the contributions of T. Yagi of KYOCERA Corporation, Japan for their co-work on the surface discharge generator used in this study.

References

Periodicals:

[1] K. Takashima, N. Zouzou, E. Moreau, A. Mizuno and , G. Touchard, "Generation of Extended Surface Barrier Discharge on Dielectric Surface -electrical properties-," International Journal of Plasma Environmental Science & Technology, vol. 1, pp. 14-20, Mar 2007.

[2] N. Benard, A. Mizuno, and E. Moreau, "A large-scale multiple dielectric barrier discharge actuator based on an innovative three-electrode design," Journal of Physics D: Applied Physics, vol. 42, 235204 (12 pp.), Dec 2009.

[3] J. Jolibois, K. Takashima, and A. Mizuno, "Influence of Coil and Capacitor on the Three-electrode Discharge Behavior," International Journal of Plasma Environmental Science and Technology, vol. 5, pp. 93-98, Mar 2011.

[4] J. Jolibois, K. Takashima, and A. Mizuno, "Effects of a transmission line on the properties of a surface discharge based on a segmented ground electrode design," Journal of Physics: Conference Series, vol. 301, 012021 (4 pp.), June 2011.

[5] K. Hensel, S. Sato, and A. Mizuno, "Sliding Discharge Inside Glass Capillaries," IEEE Transactions on Plasma Science, vol. 36, pp. 1282-1283, Aug 2008.

[6] S. Sato, K. Hensel, H. Hayashi, K. Takashima, and A. Mizuno, "Honeycomb discharge for diesel exhaust cleaning," Journal of Electrostatics, vol. 67, pp. 77-83, May 2009.

[7] S. Sato and A. Mizuno, "NOx Removal of Simulated Diesel Exhaust with Honeycomb Discharge" *International Journal of Plasma Environmental Science and Technology*, vol. 4, pp. 18-23, Mar. 2010.

[8] J. Jolibois, K. Takashima, and A. Mizuno, "NOx removal using a wet type plasma reactor based on a three-electrode device," Journal of Physics: Conference Series, vol. 301, 012011 (4 pp.), June 2011.

[9] J. Jolibois, K. Takashima, G. Touchard, and A. Mizuno, "NOx Removal Using a Non-thermal Surface Plasma Discharge Powered by a Modulated Voltage," International Journal of Plasma Environmental Science and Technology, vol. 6, pp. 74-80, Mar 2012.

[10] J. Jolibois, K. Takashima, and A. Mizuno, "Application of a non-thermal surface plasma discharge in wet condition for gas exhaust treatment: NOx removal," Journal of Electrostatics, vol. 70, pp. 300-308. June 2012.