Study of Simulated Odor Treatment for a Factory Farm by Using Microplasma

Marius Blajan, Masaki Kanamori, Tatsuya Ishii, and Kazuo Shimizu, *Member, IEEE*

***Abstract*—Microplasma could be obtained at relatively low discharge voltages (about 1 kV) and small discharge gaps (0~100µm). Treatment of bad odors from factory farms has carried out by using microplasma. Odors which contain butyric acid and valeric acid could be removed by generation of ozone and radical species in microplasma. Removal efficiencies of 27 % for butyric acid and 12% for valeric acid were observed.**

The smell analysis show considerably changes in the smell similarity chart after the microplasma treatment of simulated odors.

***Index Terms*—Microplasma, dielectric barrier discharge, ozone, butyric acid, valeric acid.**

I. Introduction

THE quality of the air can be affected by various pollutants such as NOx, SOx, VOC etc. Also the pollution of air by bad odors produced by the factory farms imposes a solution. The factory farms or intensive livestock operations involve collection, storage, transport and disposal of animal manures which are the source of bad odors that lowers the air quality for the surrounding communities. Nonthermal plasma is an efficient method for removing pollutants [1]–[5].The dielectric barrier discharge microplasma which is atmospheric nonthermal plasma can be easily applied for air purification because of its reduced size of the reactor and power supply.

The factory farm smell is due to the various acids that give the sensation of bad odor. Among the major components are valeric acid $C_5H_{10}O_2$ and butyric acid $C_4H_8O_2$ [6]–[13].

This paper presents the microplasma treatment for the simulated air of a factory farm which contains low concentration of valeric acid and butyric acid in air.

The bad odors from the factory farms' livestock manure could be removed by using chemical methods such as Fenton's reagent [14]. These kind of chemical methods are relatively expensive and the chemical processes are relatively slow.

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Nonthermal plasma is a good source of highly reactive species and high energy electrons that efficiently couples electrical energy into favorable chemistry. Furthermore Kitayama and Kuzumoto concluded that nonthermal plasma generated at small discharge gaps is a effective way of generating ozone [15]. The highly reactive species, energetic electrons and the presence of ozone generated by microplasma could be expected to decompose the source of bad odors such as butyric acid and valeric acid to transform them in simpler compounds.

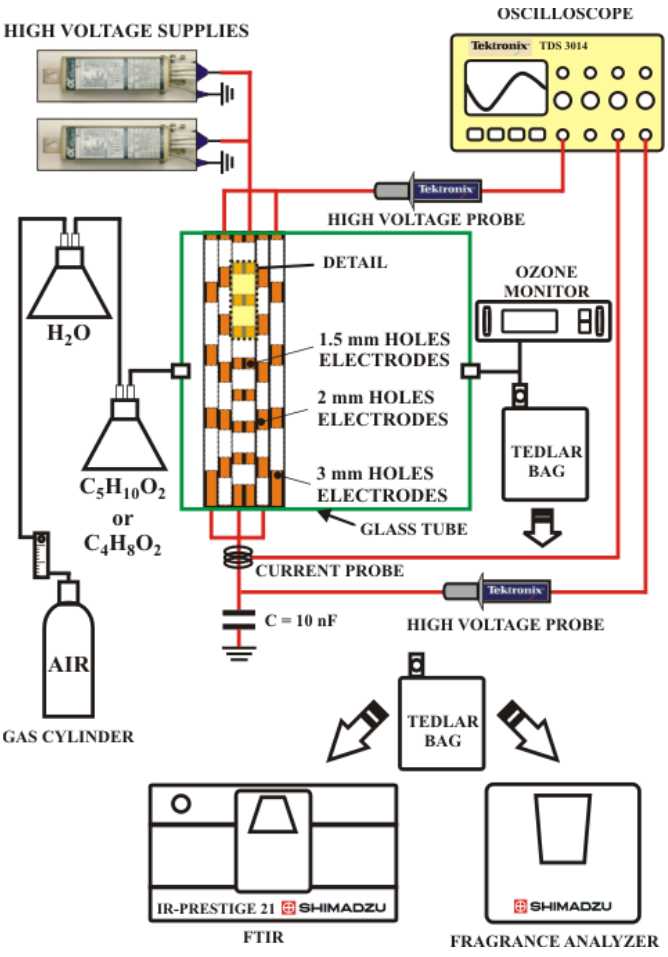

Fig. 1. An experimental setup. Air is flown from a gas cylinder trough a bottle containing distilled water and butyric acid or valeric acid. The treated gas is analyzed by a Ozone Monitor, a Forier Transform Infrared Spectrometer (FTIR) and a Fragrance Analyzer. Microplasma electrodes are powered by two small high voltage power supplies. Two high voltage probes, a current probe and a oscilloscope are measuring the discharge voltage and the corresponding discharge current.

II. Experimental Setup

A. Experimental Setup

The experimental setup is shown in Fig. 1. Air is flown from a gas cylinder at various gas flow rates (2~10L/min) through a bottle of water and valeric acid or butyric acid. Simulated odor gas containing water and valeric acid or butyric acid is treated in the microplasma reactor. The microplasma reactor consists in 6 microplasma electrodes with Ø 41mm faced together inside a glass tube. After the microplasma treatment, gas components are analyzed by a Fourier Transform Infrared Spectrometer (FTIR, Shimadzu, IR-Prestige 21), a Fragrance Analyzer (Shimadzu, FF-2A) and an Ozone Monitor (Seki Electronics, SOZ-3300).

The microplasma electrodes are powered by two small sizes high voltage supply with output voltages up to 1.2 kV, frequency of 25 kHz. The power supplies are neon transformers and their retail price is low.

Discharge voltage is measured by two high voltage probes (Tektronix, P6015A), corresponding discharge currents by a current probe (Tektronix, P6022) and an oscilloscope (Tektronix, TDS 3014).

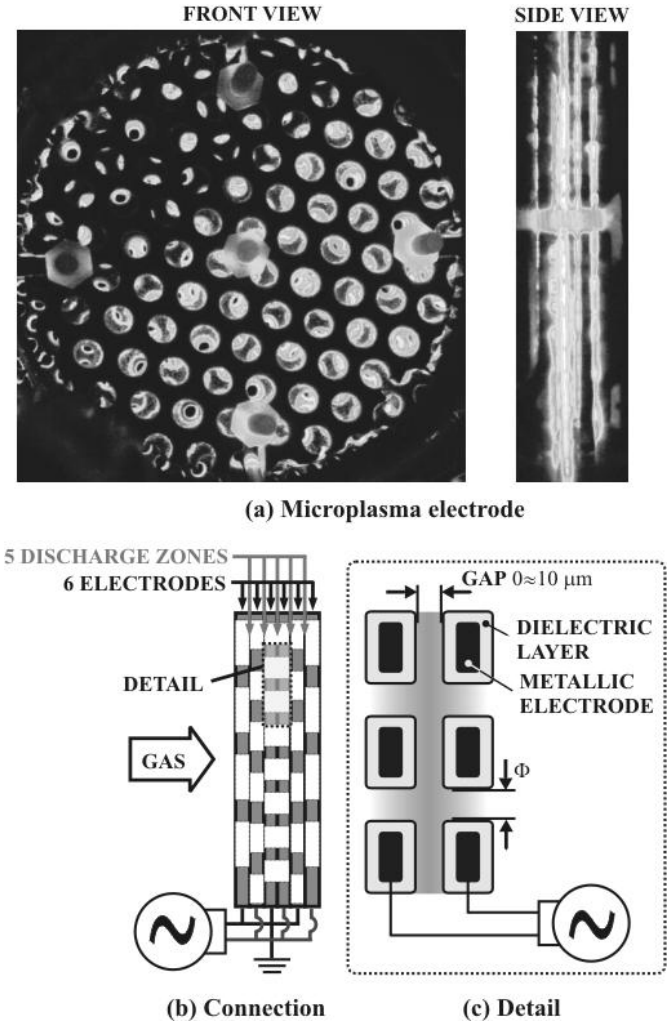

Fig. 2. Microplasma electrode. Photo of the microplasma electrode during discharge (1.1 kV) (a). Connection of electrodes: a honeycomb like structure is obtained by facing togheter 6 electrodes thus resulting 5 discharge zones (b). Detail of electode (c).

A 10 nF capacitor is linked in series with the electrodes for power measurements using the Lissajous method.

B. Microplasma Electrodes

The microplasma electrodes are perforated metal plates covered with a dielectric layer. The electrodes are faced together wit a discharge gap 0~10 μm. Due to the very small discharge gap and the assumed specific dielectric constant of $\varepsilon_r=10^4$ high intensity electric fields (10^7 ~ 10^8 V/m) are obtained.

Experiments presented in this paper were performed with an electrode arrangement consisted in 6 electrodes with Ø 41mm faced together thus resulting 5 discharge zones. An interior electrode pair has 1.5 mm holes, an intermediate has 2 mm holes and an exterior one has 3 mm holes. Electrode arrangement and various size of holes size make a honeycomb like structure of the electrodes.

Discharge voltage waveform and corresponding discharge current waveform are shown in Fig. 3. Discharge current is observed at the steepest slope of discharge voltage. Spike currents convoluted in the discharge current appeared due to streamers [16].

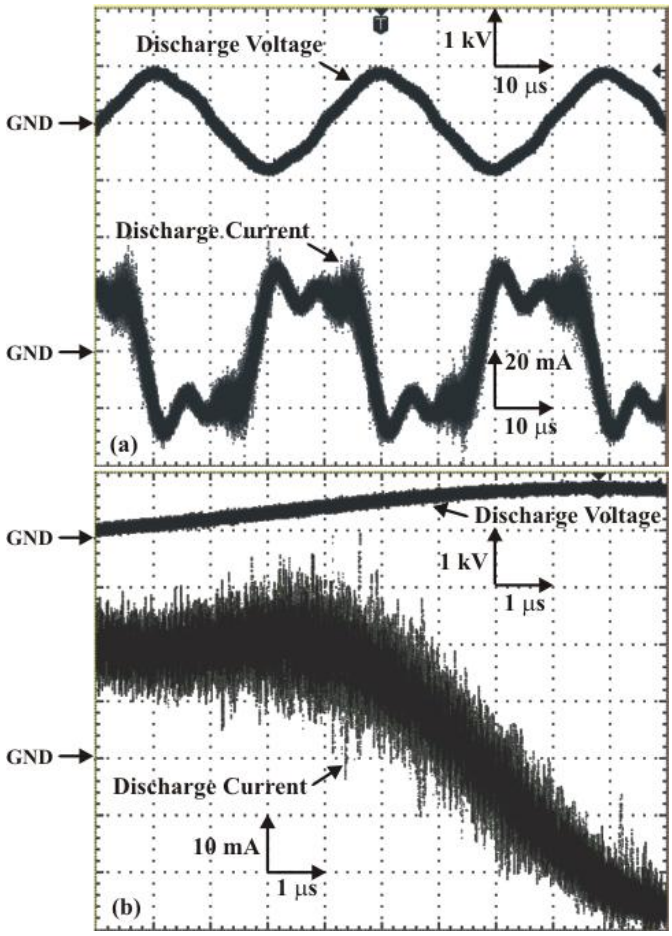

Fig. 3. Waveforms of discharge voltage and corresponding discharge current. Discharge current appeared at steepest slope of discharge voltage (a). Spike currents convoluted in discharge current appeared due to streamers (b).

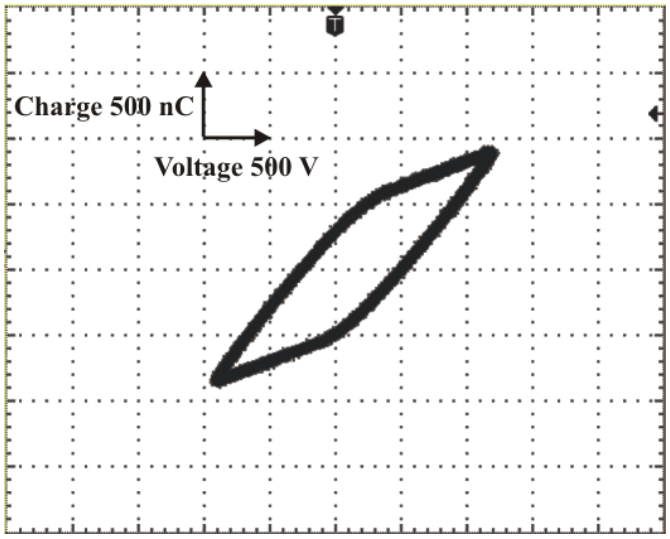

Fig. 4. Lissajous figure represents discharge power of microplasma for electrode arrangement with 6 electrodes faced togheter at 1.1 kV.

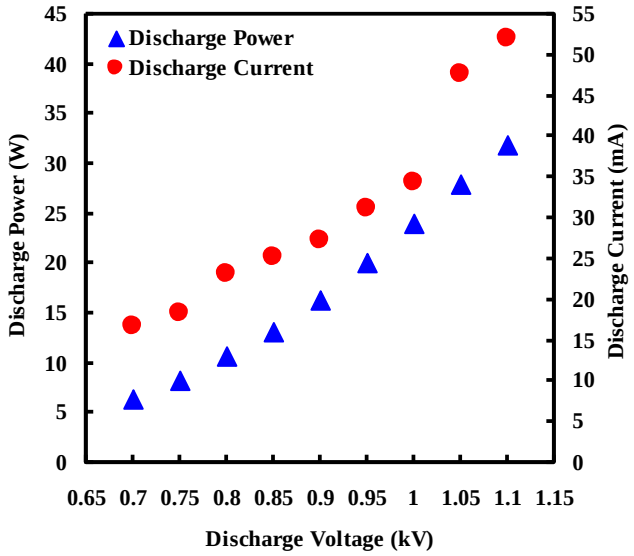

Fig. 5. Characteristic of the microplasma discharge power and discharge current versus discharge voltage for air at 2 L/min.

Discharge power was measured using Lissajous method. Fig. 4 shows a typical Lissajous figure for discharge voltage of 1.1 kV.

Characteristics between discharge voltage and corresponding discharge current and power are shown in Fig. 5. With increase of discharge voltage, discharge current and discharge power are increasing. The maximal discharge current and discharge power ware 52 mA and 32 W respectively.

Due to the 5 discharge zones, discharge power and discharge current are relatively high, comparing to that of 1 discharge electrode [5].

III. Odor Treatment

A. *Odor Treatment of Butyric Acid*

An experimental setup shown in Fig. 1 was used for the removal of butyric acid by microplasma.

Gas flow rate was set at 2 L/min. 50 ppm of butyric acid was obtained with a bottle that contains liquid phase of butyric acid and a gas cylinder. Simulated odor gas was flown trough the microplasma reactor. A tedlar bag was filled with the treated gas and analyzed by the FTIR.

The other experiments with a bottle of distilled water and liquid phase of butyric acid were performed at gas flow rates of 2~10 L/min.

Concentration of butyric acid before and after microplasma treatment was estimated by comparing height of peaks around 3000 cm^{-1} from measured spectra with FTIR.

The difference of butyric acid with and without microplasma treatment at 1.1 kV is shown in Fig. 6.

The removal efficiencies versus discharge voltage for dry air containing butyric acid and for butyric acidwith relative humidity of 58% are presented in Fig. 7. With increase of discharge voltage, removal efficiency increases. In the absence of humidity, the highest removal efficiency of 25% was obtained at 1.05 kV. Higher removal efficiencies were obtained for the gas containing humidity. It was obtained the highest removal efficiency of 27% at 1.1 kV.

Generation of active species and ozone by the microplasma lead to a removal of butyric acid without presence of humidity [15]:

$$e + O_2 \rightarrow e + O(^3P) + O(^1D) \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (2)$$

Electron impact dissociation of H_2O leads to the production of H and OH radicals [17]:

$$e + H_2O \rightarrow e + H + OH \quad (3)$$

O_2 is also present and additional dissociation of H_2O come from reaction with the excited state $O(^1D)$ [17]:

$$O(^1D) + H_2O \rightarrow 2\ OH \quad (4)$$

That could be explained higher removal efficiency in the presence of humidity due to the interaction of OH radicals with butyric acid [18]:

$$H_3C–CH_2-CH_2-COOH + OH° \rightarrow H_3C–CH_2-CH°-COOH + H_3C–CH_2-CH°-COOH + °H_2C–CH_2-CH_2-COOH \quad (5)$$

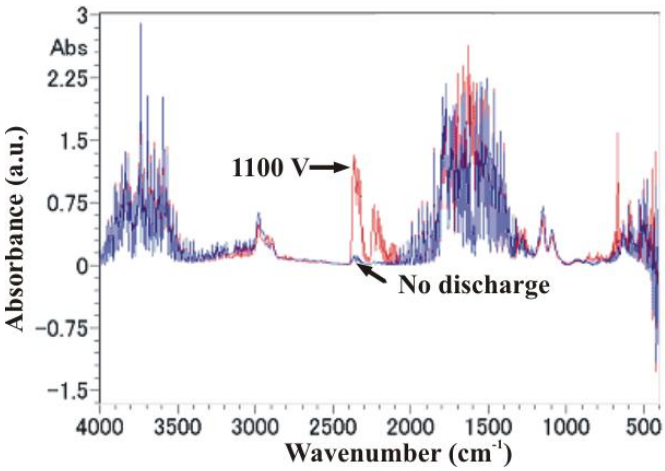

Fig. 6. FTIR spectra of air containing butyric acid and relative humidity of 58% before and after microplasma treatment at 1.1 kV.

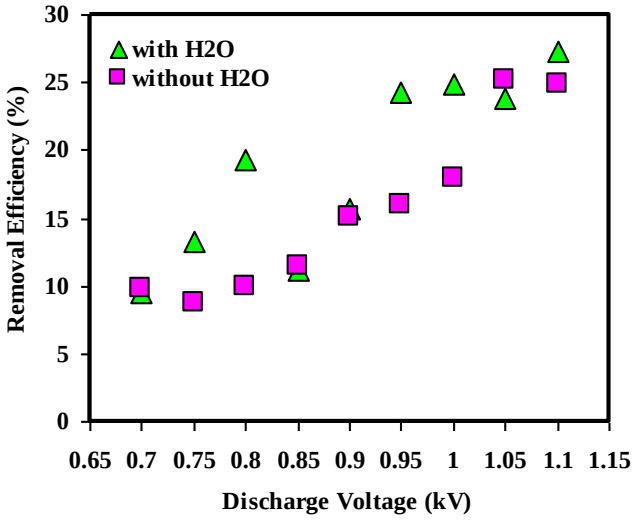

Fig. 7. Removal efficiency of butyric acid versus discharge voltage at a gas flow rate of 2 L/min for dry air and for air with relative humidity of 58%.

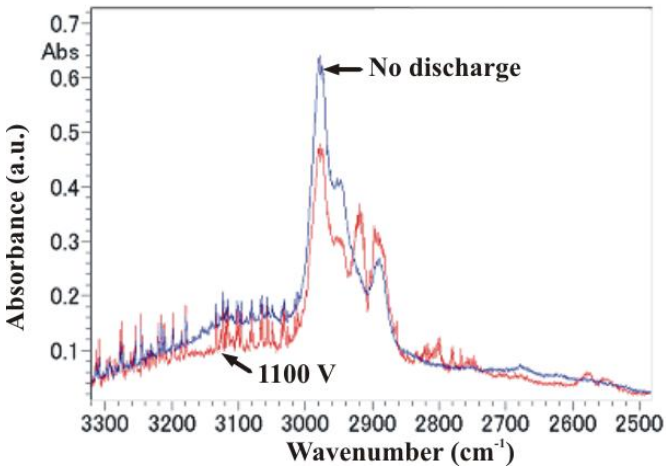

Fig. 9. Spectra of dry air containing butyric acid before and after microplasma treatment at 1.1 kV. Initial concentration of butyric acid is set at 50 ppm. Gas flow rate is set at 2 L/min.

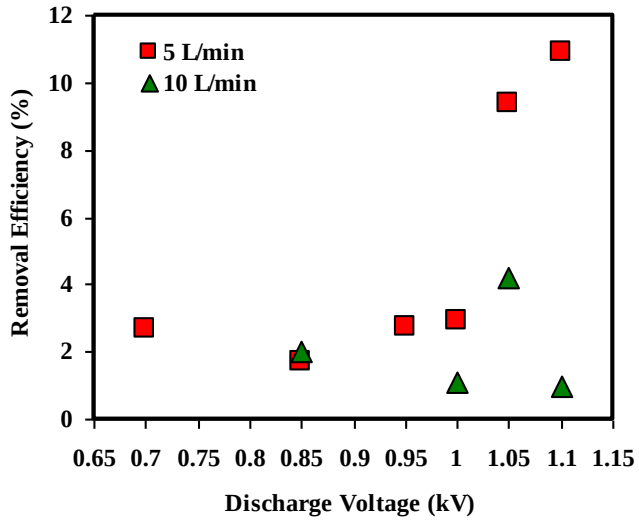

Fig. 8. Removal efficiency of butyric acid versus discharge voltage for air with 58% relative humidity at 5 L/min and 10 L/min.

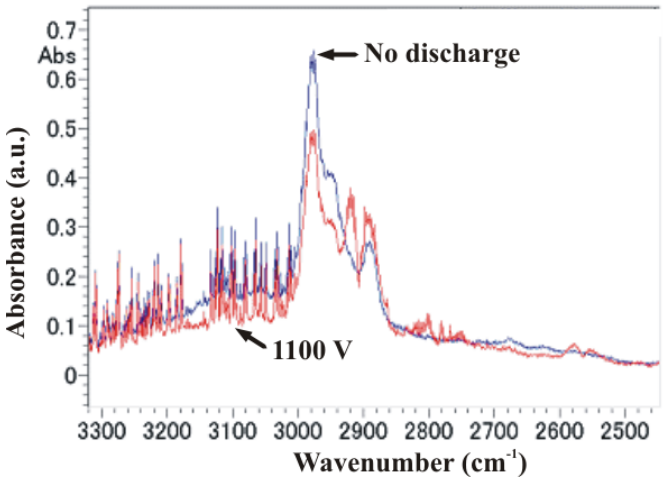

Fig. 10. Spectra of air with relative humidity of 58% containing butyric before and after microplasma treatment at 1.1 kV. Initial concentration of butyric acid is set at 50 ppm. Gas flow rate is set at 2 L/min.

Removal efficiency of butyric acid for various gas flow rates (5 L/min, 38% relative humidity and 10 L/min, 36% relative humidity) is presented in Fig. 8. Decrease of removal efficiency was observed with increase of gas flow rate.

The highest removal efficiency of 11% was obtained at 1.1 kV (5 L/min). When the gas flow rate was raised at 10 L/min, removal efficiency decreased to 1~4%.

FTIR spectra of butyric acid with or without microplasma treatment is presented in Fig.9. It is clearly show that after microplasma treatment, the peak height of butyric acid decreased.

Fig.10 shows the peaks of butyric acid with relative humidity of 58% in air. In this case, decrease of peaks are also observed after microplasma treatment (Vd = 1.1 kV).

B. Odor Treatment of Valeric Acid

The experimental setup presented in Fig. 1 was used to perform valeric acid removal experiments. Air was flown from a gas cylinder trough a bottle of distilled water and a liquid phase valeric acid.

50 ppm of valeric acid in air with relative humidity of 58% was flown to the microplasma reactor. Removal efficiency versus discharge voltage is presented in Fig. 11. It is observed a significant removal of 12% at 1.1 kV. The mechanism of removal could be explained by interaction with ozone and also with OH radical.

Due to the molecular structure of the valeric acid, it could be considered to hard to decompose than butyric acid.

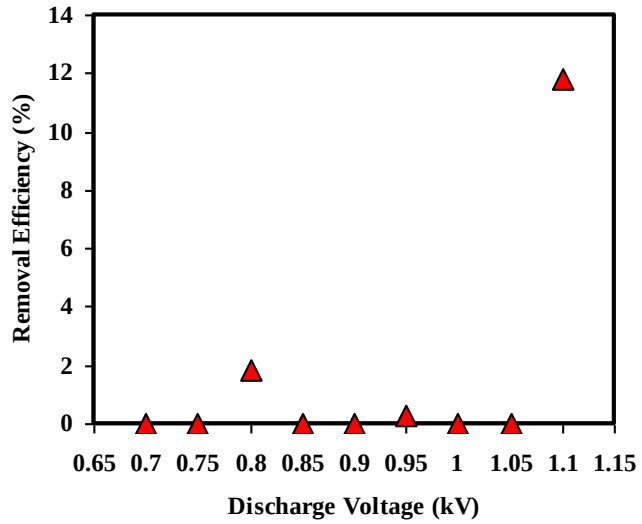

Fig. 11. Removal efficiency of valeric acid versus discharge voltage for air with relative humidity of 58% at a gas flow rate of 2 L/min.

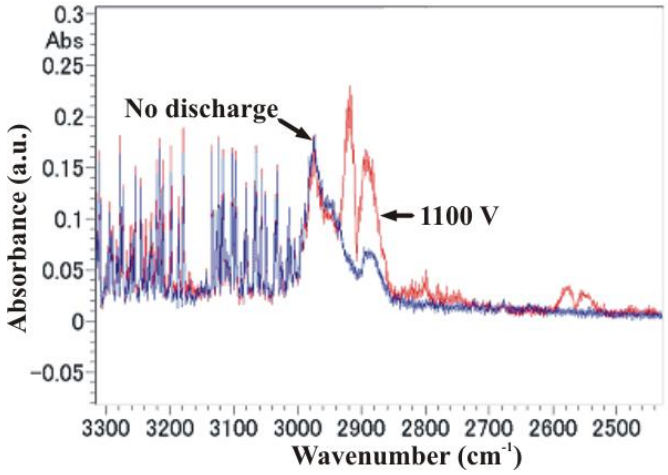

Fig. 12. FTIR spectra of air containing valric acid and relative humidity of 58% before and after microplasma treatment. Discharge voltage is 1.1 kV. Gas flow rate is set at 2 L/min.

Fig. 12 shows the FTIR spectra of the air containing valeric acid and 58% humidity before and after microplasma treatment at 1.1 kV. After the microplasma treatment only a small decrease in the peak height was measured.

IV. Ozone Generation

Ozone generation values for the complex electrode are presented in Fig.13. With increase of discharge voltage, ozone concentration increases. At lower discharge voltages, generated ozone are low and as well as removal efficiencies of butyric and valeric acid. The maximal value of 129 ppm was obtained at 1.05 kV. Ozone concentration at 1.1 kV is lower due to destruction of ozone at intense electric AC fields, and thermal effect.

Ozone generation plays a role in the reaction with the butyric acid and valeric acid.

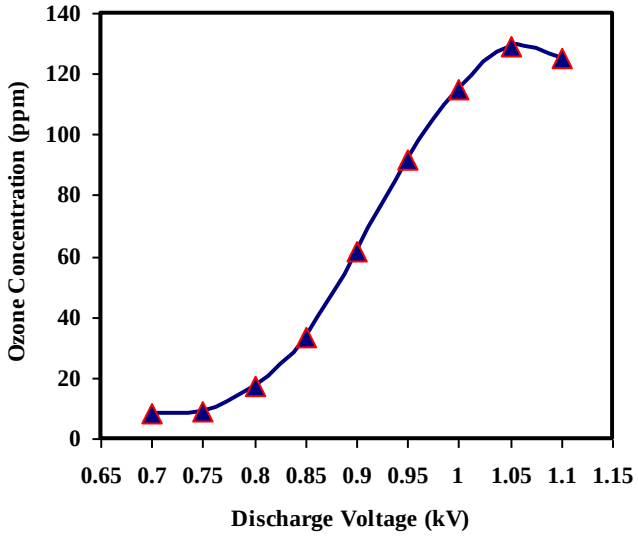

Fig. 13. Ozone generation characteristic versus discharge voltage for air with relative humidity of 58% humidity at 2 L/min.

V. Smell Analysis

Butyric acid and valeric acid are known for their unpleasant odors. Odor detection threshold for butyric acid is 10 ppm and for valeric acid 0.03 ppm [19].

A smell analysis was carried out to confirm difference before and after microplasma treatment. Sample gas was collected and analyzed by a Fragrance Analyzer, which has ten different semiconductor sensors with different sensitivities. Nine standard gases, each with different kind of smell are imputed in this device and analyzed sample gas is compared with them, outputting similarity against each standard gas.

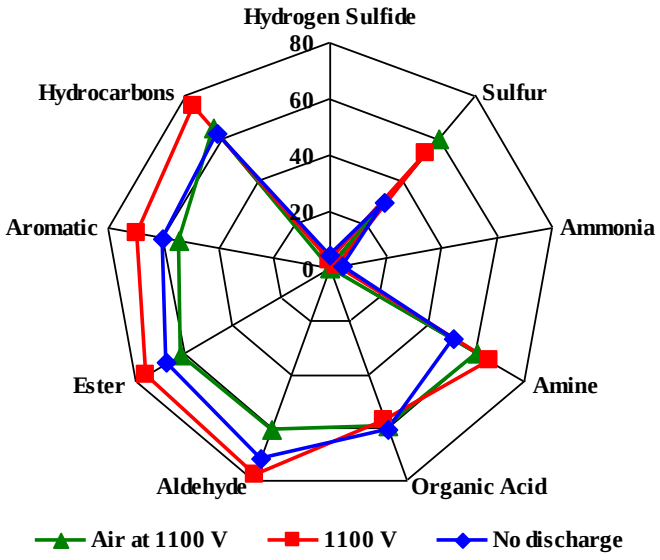

Fig. 14. Smell similarity analysis for the air containing butyric acid and 58% relative humidity before and after microplasma treatment. Discharge voltage is set at 1.1 kV. Gas flow rate is set at 2 L/min.

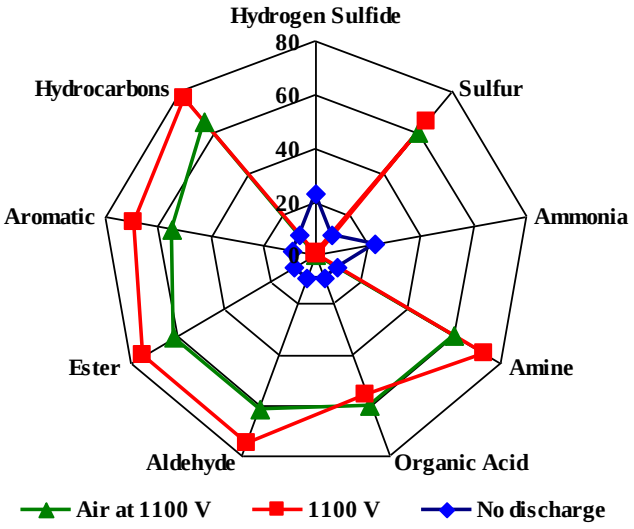

Fig. 15. Smell similarity analysis for the air containing valeric acid and 58% relative humidity before and after microplasma treatment. Discharge voltage is set at 1.1 kV. Gas flow rate is set at 2 L/min.

The smell similarity of air with humidity and butyric acid with and without microplasma treatment (Vd = 1.1 kV), and treated air at 1.1 kV is presented in Fig.14. After the treatment, similarities with organic acid decreased while the similarities with other standard gases increased. That could be explained by generation of ozone as characteristic of air treated at 1.1 kV shows.

Smell similarity of the air containing humidity with and without microplasma treatment (Vd = 1.1 kV) and air at 1.1 kV with relative humidity of 58% is presented in Fig. 15.

After the microplasma treatment, smell has a similar characteristic with smell of air without valeric acid and treated at 1.1 kV. This could be explained by generation of ozone.

VI. Conclusion

The microplasma treatment of simulated farm house odors could increase the quality of the air. A removal of butyric acid and valeric acid cwas measured:

1) With the increase of discharge voltage, removal efficiency of butyric acid increases up to 27% for air containing 58% relative humidity. Without humidity removal efficiency of 25% was observed at 1.05 kV.

2) With the increase of gas flow rate, butyric acid removal efficiency decreases at 11% for 5 L/min and 1.1 kV.

3) The smell analysis shows a change of air containing valeric acid after the microplasma treatment. The smell of butyric acid has change, and it could be resulted by generation of ozone.

References

[1] J. S. Clements, A. Mizuno, W. C. Finney, and R. H. Davis, "Combined removal of SO2 and NOx and fly ash from flue gas using pulsed streamer corona," *IEEE Trans. Ind. Appl.*, vol. 25, pp. 62-69, 1989.

[2] S. Masuda, and. H. Nakao, "Control of NOx by positive and negative pulsed corona discharges," *IEEE Trans. Ind. Appl.*, vol. 26, pp. 374-383, 1990.

[3] A. Mizuno, A. Chakrabarti, and K. Okazaki, "Application of corona technology in the reduction of greenhouse gases and other gaseous pollutants", *Non-Thermal Plasma Techniques for Pollution Control*, NATO ASI Ser. 34, Part B, Springer-Verlag Pub., Oxford, pp. 165-185, 1993.

[4] L.A. Rosocha, G. K. Anderson, L. A. Becthold, J. J. Coogan, H. G. Heck, M. Kang, W. H. McCulla, R. A. Tennant, and P. J. Wantuck, "Treatment of hazardous organic wastes using silent discharge plasmas," *Non-Thermal Plasma Techniques for Pollution Control*, NATO ASI Ser. 34, Part B, Springer-Verlag Pub., Oxford, pp. 281-308, 1993.

[5] K. Shimizu, T. Sugiyama, and Nishamani Liyanage Samaratunge Manisha, "Study of air pollution control by using micro plasma filter," *IEEE Trans. Ind. Appl.*, vol. 44, no. 2, pp. 68-73, March/April 2008.

[6] J. Zhu, "A review of microbiology in swine manure odor control," *Agriculture Ecosytems & Environment*, vol. 78, pp. 93-106, 2000.

[7] S. S. Schiffman, J. L. Bennett, and J. H. Raymer, "Quantification of odors and odorants from swine operations in North Carolina," *Agricultural and Forest Meteorology*, vol. 108, pp. 213-240, 2001.

[8] S. Willig, M. Lacorn, and R. Claus, "Development of a rapid and accurate method for the determination of key compounds of pig odor," *Journal of Chromatography A*, vol. 1038, pp. 11-18, 2004.

[9] S. Rappert, and R. Muller, "Odor compounds in waste gas emissions from agricultural operations and food industries," *Waste Management*, vol. 25, pp. 887-907, 2005.

[10] B. Van der Stelt, E. J. M. Temminghoff, P. C. J. Van Vliet, and W. H. Van Riemsdijk, "Volatilization of ammonia from manure as affected by manure additives, temperature and mixing," *Bioresource Technology*, vol. 98, pp. 3449-3455, 2007.

[11] M. B. Lynch. T. Sweeney, J. J. Callan, and J. V. O'Doherty, "The effect of dietary barley level on volatile fatty acid concentration and manure ammonia emissions in finishing pigs," *Livestock Science*, vol. 109, pp. 236-239, 2007.

[12] N. Hudson, and G. A. Ayoko, "Odour sampling. 1: Physical chemistry considerations," *Bioresource Technology*, vol. 99, pp. 3982-3992, 2008.

[13] N. Hudson, and G. A. Ayoko, "Odour sampling. 2. Comparison of physical and aerodynamic characteristics of sampling devices: A review," *Bioresource Technology*, vol. 99, pp. 3993-4007, 2008.

[14] J. Dec, M. A. Bruns, L. Cai, J. A. Koziel, M. Snyder, K. B. Kephart, and J. E. Watson, "Removal of odorants from animal waste using Fenton's reaction," *International Symposium Air Quality and Waste Management for Agriculture*, CD-ROM proceedings of the 16-19 September 2007 Conference, Broomfield, Colorado, Publication, 16 September, 2007, ASABE Publication Number 701P0907cd.

[15] J. Kitayama and M. Kuzumoto, "Analysis of ozone generation from air in silent dischaghe," *J. Phys. D: Appl. Phys.*, vol. 32, pp. 3032-3040, 1999.

[16] 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, no. 1, pp. 14-20, March 2007.

[17] C. R. McLarnon, and B.M. Penetrante, "Effect of gas composition on the NOx conversion chemistry in plasma," *Society of Automotive Engineers, Fall Fuels and Lubricants Meeting*, San Francisco, CA, 1998.

[18] C. Guillard, "Photocatalytic degradation of butanoic acid. Influence of its ionization state on the degradation pathway: comparison with O_3/UV process," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 135, pp. 65-75, 2000.

[19] M. T. Yokoyama, S. Park, K. C. Chou, and S. J. Bursian, "Comprehensive review on human health effects of pork production emissions – NPB# 00-173, Research Report," *Michigan State University*, 2003.

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