Characteristics of Low-temperature atmospheric pressure plasma for the treatment of natural products

Se Hoon Ki[1],Seungil Park[1], Sunghoon Jee[1], Seong Bong Kim[1]

[1] *Institute of Plasma Technology, Korea Institute of Fusion Energy, Gunsan, Rep. of Korea.*

Abstract: Low-temperature atmospheric pressure plasma is an effective green technologies available for chemical processes. Structural transformation of organic compounds using plasma is one of the technologies that can improve the low yield and environmental pollution problems of existing technologies. However, studies on controlling the structure of natural products using plasma are insufficient. In this study, plasma characteristics and new compound synthesis results were confirmed according to plasma treatment conditions.

Keywords: low-temperature atmospheric pressure plasma, reactive species, natural products

1. Introduction

Low-thermal atmospheric pressure plasma, capable of producing a variety of reactive species including ozone and nitrogen oxides, is one of the effective green technologies available for chemical processes. Plasma technology has been widely used in various fields, such as surface treatment, surface modification, sterilization, material synthesis, and decomposition [1-3]. Various plasma sources have been developed over the past century for these applied studies, but dielectric barrier discharge (DBD) is one of the most valuable. DBD is a widely used low-temperature atmospheric plasma with variable effects on the target depending on operating parameters. In plasma treatment, samples can be affected by one or a synergistic combination of reactive species, UV radiation, heat, electric fields, and charged particles.

Natural products have volatile properties under oxidizing conditions. Studies on the structural modification and biological function enhancement of natural products by plasma have been conducted by previous works [4-6]. In particular, it has been demonstrated that new compounds are created when natural product samples are directly irradiated with DBD plasma. These results show that plasma treatment can effectively cause the structural transformation of natural products.

In this study, plasma characteristics such as plasma energy, reactive species concentration, and electron temperature were measured according to plasma treatment conditions. Here, we confirmed the synthesis results of novel compounds according to plasma treatment conditions.

2. Method and materials

2.1 Plasma apparatus and experimental setup

Figure 1 shows a schematic diagram for the experiment. The treatment device comprises a DBD electrode, a treatment chamber, and a power supply. A DBD electrode were configured to change the number of surface dielectric barrier discharge (sDBD) from one to four, and a processing chamber made of Teflon were used for low chemical reactivity. Plasma was generated using an arbitrary waveform generator (Tektronix AFG3021C) and a high-voltage power amplifier (Trek 5/80) and was applied parallel to the SDBD electrodes. Current and voltage profiles during the plasma discharge were acquired by a current probe and a 1000X voltage probe (P6015A and P6021A Tektronix) using an oscilloscope (Tektronix MDO 4024C). A spectrophotometer (HR4000, Ocean Optics, Dunedin, FL, USA) measured optical emission spectra (OES) before the electrodes. The intensity of light emitted from the device was recorded according to the wavelength. Reactive species generated by the plasma were measured using the following method. To measure gaseous ozone and nitrogen oxide concentrations O_3 and NO_X gas analyzers (Anseros GM-PRO, EcoPhysics CLD 60) were used. The concentration of liquid phase reactive species was confirmed using reagents such as KI-starch, terephthalic acid(TA) , and DIOX-250 Quantichrom Peroxide assay kit.

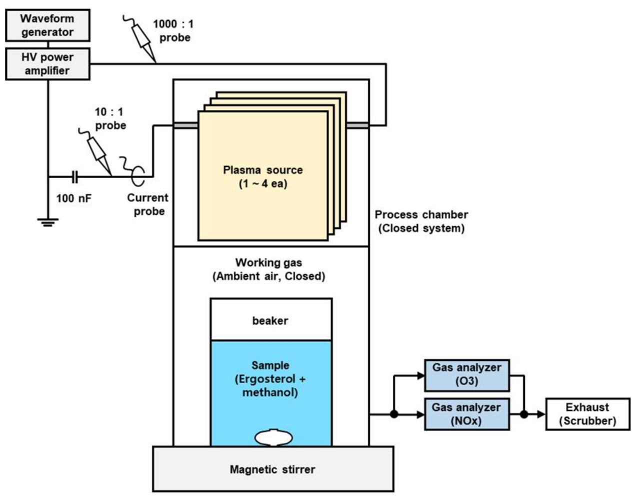

Fig. 1. Schematic diagram of the experimental setup for the natural products treatment by DBD plasma.

2.2 Sample preparation and operating conditions

Samples were prepared by dissolving 200 ppm of ergosterol in a methanol solution. Plasma treatment was performed at 20 to 25 °C and 40 to 60% humidity.

To confirm the newly formed compounds, the plasma-treated samples were analyzed by high-performance liquid chromatography (HPLC). HPLC analysis was performed using a YMC-Pack ODS A-302 column (4.6 mm i.d. x 150 mm) at a 1.0 ml/min flow rate in an oven temperature of 40 °C.

3. Results and discussion

Figure 2-a shows the DBD plasma shows sinusoidal voltage and current. Under the 2.5 kHz frequency, the electric discharge power is 5.7 J/sec for V_{rms} ~ 2.5 kV and I_{rms} ~ 12.19 mA. As the frequency and number of plasma sources increased, the discharge energy increased (Figure 2-b,c). Although the change in the applied voltage was insignificant according to the difference in the above conditions, the discharge energy increased as the current value increased.

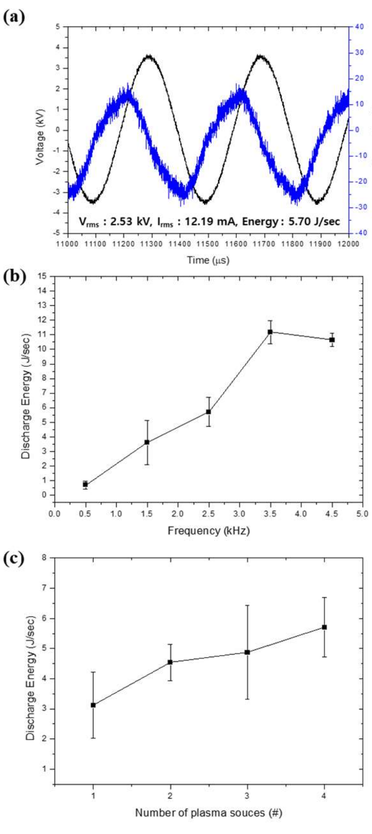

Fig. 2. Electrical characteristics of the surface DBD. (a) Voltage and current waveforms plasma source. (b), (c) Plasma discharge power according to frequency and number of sources.

The OES of the DBD plasma is shown in Figure 3-a. The N_2 SPS (Second Positive System) peaks were detected as major peaks in the near-ultraviolet region (300-440 nm). As the frequency increased, the intensity detected by the spectrometer increased. The measured OES results were used to calculate the electron temperature based on the CR model. The electron temperature increased from 0.625 eV (0.5 kHz condition) to 0.8 eV (4.5 kHz condition) with increasing frequency.

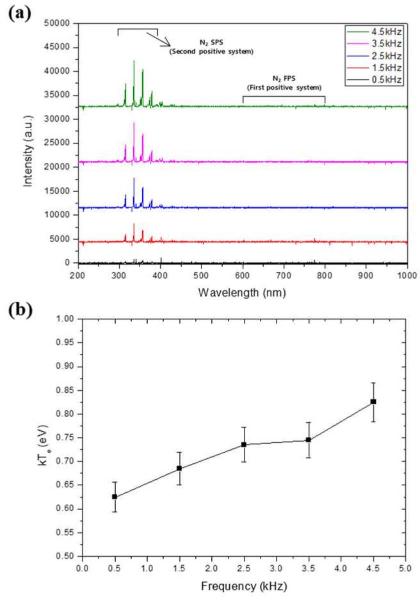

Fig. 3. Optical characteristics of the surface DBD. (a) Optical emission spectra (b) electron temperature.

The gas phase reactive species of O_3, NO, and NO_2 generated in the plasma were confirmed through a gas analyzer. The plasma generated ozone, but NO and NO_2 were hardly detected. As shown in Figure 4, the plasma driving frequency increased the initial ozone generation. However, in the case of high frequencies, the amount of ozone decreased as the plasma treatment time increased. As a result, the average ozone concentration during the driving time of one hour was the highest at 129.6 ppm under the 2.5 kHz condition. An increase in the number of plasma sources also affected the ozone generation amount, and an increase in the number of sources increased the ozone concentration. In the case of using four sources, a decrease in ozone concentration according to treatment time was confirmed, but the average ozone concentration was measured as the highest.

An experiment was conducted using a KI-starch solution to detect reactive species in the liquid phase. It is a reagent suitable for measuring reactive oxygen species in the solution and is a method that can indirectly check OH radicals, dissolved ozone, H_2O_2, etc., that may exist in the solution. The absorbance of the KI-starch solution increased as the plasma treatment time increased. In addition, increasing the plasma driving frequency and the number of sources increased the absorbance of the solution. OH radical also showed a similar tendency and was verified using TA solution.

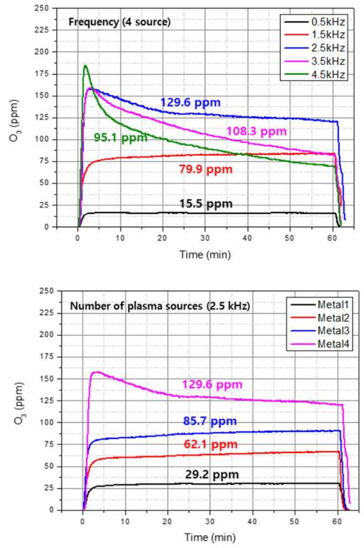

Fig.4. Metal sticker type electrode reactive species (ozone) concentration according to frequency and number of sources.

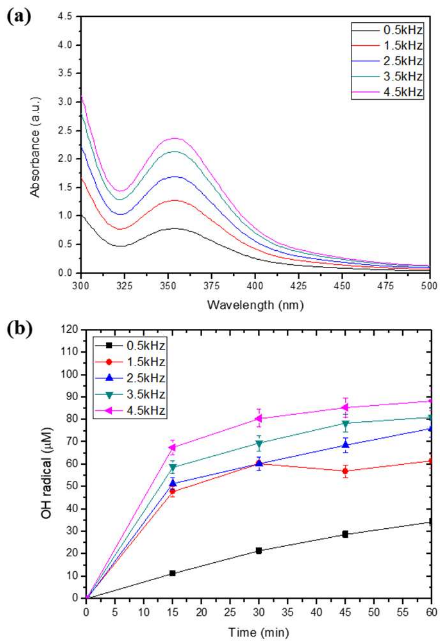

Fig. 5. (a) KI-starch reaction and (b) OH radical generation according to plasma treatment time, frequency, and number of sources.

ESP1 ((22E,24R)-5α, 6α-Epoxy-3β-hydroxyergosta-8,22-dien-7-one) and ESP2 (5,6-Epoxyergosterol) synthesized from ergosterol using plasma treatment were confirmed by HPLC analysis. As the plasma treatment time increased, the peak of ergosterol decreased, whereas the peaks of ESP1 and ESP2 increased. These results show that reactive species generated by plasma effectively cause the structural transformation of natural products.

4. Summary

Through this study, we developed a plasma device for synthesizing natural products and studied the characteristics of the plasma source. Plasma characteristics were measured according to electrode structure, frequency, and the number of plasma sources. The increase in the number and frequency of plasma sources contributed to the increase in plasma discharge energy and electron temperature. During plasma treatment, reactive oxygen was generated. In particular, gaseous ozone was detected as the primary reactive species by plasma. In the liquid phase, some OH radicals and H_2O_2 were measured. ESP1 and ESP2 synthesized from ergosterol using plasma treatment were confirmed through HPLC analysis. It was confirmed that effective treatment of natural products occurs in a specific range of reactive species by plasma treatment.

5. References

[1] Vu, Phat T., Jackson P. Conroy, and Amy M. Yousefi. *Biomimetics* **7.4**, 218 (2022).

[2] J. He, M. Waring, A. Fridman, A. Rabinovich, C. Bailey, G. Fridman, and C. M. Sales, *Scientific Reports*, **12(1)**, 19944 (2022).

[3] S. Li, Z. Lu, B. Yuan, R. Hu, and M. Zhu, *ACS Applied Materials & Interfaces*, **13(12)**, 13909-13919 (2021).

[4] G. H. Jeong, D. H. Kim, C. Jo, S. Park, S. B. Kim, and T. H. Kim, *Journal of Physics D: Applied Physics*, **53(27)**, 274005 (2020).

[5] S. Park, G. H. Jeong, S. H. Jee, T. H. Kim, and S. B Kim, *Scientific Reports*, **12(1)**, 1-9 (2022).

[6] G. H. Jeong, S. Park, S. B. Kim, C. Jo, and T. H. Kim, *Bioscience, Biotechnology, and Biochemistry*, **85(5)**, 1069-1076 (2021).

6. Acknowledgements

This work was supported by the R&D Program entitled "R&D of Plasma Advanced Technology for Agriculture and Food (code No. EN2225-9)" through the Korea Institute of Fusion Energy (KFE) funded by the government of the Republic of Korea and the National Research Council of Science & Technology (NST) grant by the Korea government (MSIT) (No. CRC-21021-300).