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ポストハーベストにおける鮮度保持を目指した プラズマ殺菌技術の開発

Development of inactivation technology using plasma for freshness-keeping on post-harvest management

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1. Introduction

In agricultural fields and plant protection stations, pesticides are sprayed to protect crops from various insects and viruses. Fungi, such as *Aspergillus* or *Penicillium*, contaminate foods, such as cereals, fruits, vegetables, meats. However, residual agricultural chemicals (*e.g.*, thiabendazole, imazalil, and ortho-phenylphenol) are harmful to the human body and the environment. Moreover, methyl bromide, which is the one of effectively pesticides, is also sprayed to the crops. Methyl bromide is an ozone depletion material and had been forbidden to be used since 2005, based on "Montreal Protocol on Substances that Deplete the Ozone Layer". However, the useful substitute-technology has not been developed yet. Conventional inactivation techniques are autoclaves, ovens, and chemicals such as ethylene oxide, hydrogen peroxide, etc. However, their chemicals cause some harmful problems for the human body and environment due to its toxicity. In the cases of autoclaves and ovens, the heat damages to crops become a problem. The establishment of substitute-technology has been required.

Recently, non-equilibrium atmospheric pressure plasma (NEAPP) has been much attention for applications in biology, medicine, agriculture and so on. There are many reports that microorganisms such as fungi, yeast, bacteria, cancer cell, and so on, were inactivated using cold plasmas. The cold plasma simultaneously produces various factors, such as vacuum ultraviolet (VUV) and UV-C emissions, neutral and charged species, and electric fields, which may synergistically affect to inactivate microorganisms. Several studies suggested that reactive oxygen species (ROS) may be the dominant factor on the inactivation of the microorganisms by plasmas. The bactericidal effect of plasma differs depending on microorganisms owing to the resistance against the bactericidal factor. It is essential to study the resistance against the bactericidal factor produced by the plasma based on the quantitative diagnostics of the plasma.

We have focused on inactivating the spores of *Penicillium digitatum* in gas phase. [1-6] The green mold of citrus is caused by spores of *P. digitatum*. Spores of *P. digitatum*, which is fungus, are different from other microorganisms for medical applications because of the resistant structure, composition, and function of their cell wall.

In this study, in order to develop the inactivation technology using plasmas with high effectiveness for freshness-keeping on post-harvest management, we quantitatively elucidated the inactivation mechanism of *P. digitatum* spore based on the measurement of the number density of radicals such as ground-state atomic oxygen [$O(^3P_j=0,1,2)$], singlet oxygen molecule [$O_2(^1\Delta_g)$] , and ozone.

2. Experimental

Figure 1 shows a schematic diagram of the experimental setup containing an oxygen-radical source employing a non-equilibrium atmospheric pressure O_2/Ar plasma with a vacuum ultraviolet absorption spectroscopy optical system. The radical

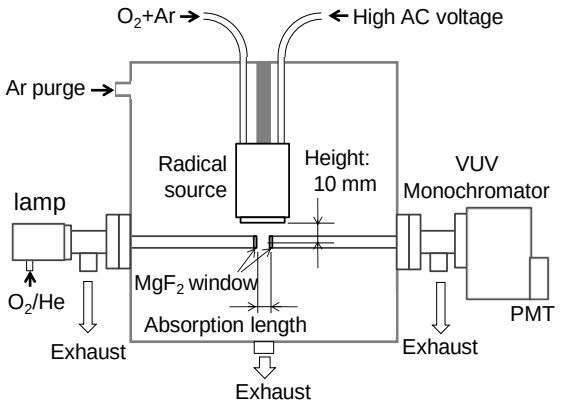

Figure 1. schematic diagram of the experimental setup containing an oxygen-radical source.

source was developed based on the high-density NEAPP, which generates high-density electrons of about 10^{16} cm^{-3}.[7, 8] The charged species and optical radiation from the plasma were blocked by the exit aperture of the radical source, so that samples are exposed to only neutral species. The chamber containing the radical source was purged with Ar gas to eliminate the influence of atmospheric gases. Measurements and exposures of radicals to spores were performed at 10 to 20 mm downstream from the radical head. Flow rate ratio $O_2/(O_2+Ar)$ was also varied from 0 to 1.2 % at total flow rate of 5 slm.

The absolute densities of $O(^3P_j)$ and $O_2(^1\Delta_g)$ were measured by VUVAS using a microdischarge hollow-cathode lamp (MHCL) and a deutrium lamp, respectively. VUV light from the light source passed though the MgF_2 window and was introduced into the chamber. VUV light passing through the absorption region was focused on the slit of a VUV monochromator with the MgF_2 lens and detected by a photomultiplier tube.

3. Results

Figure 2 shows the result of the inactivation of *P. digitatum* spores on *Citrus unshiu* with or without the oxygen radical treatment.

Figure 3 shows the relationship between D-value and the results of $O(^3P_j)$ and $O_2(^1\Delta_g)$ densities. $O_2(^1\Delta_g)$ density were constant from 10 mm to 20 mm of exposure distances, while $O(^3P_j)$ density decreased dependent on exposure distance. These results indicates that the inactivation efficiencies are related to $O(^3P_j)$ density rather than those of $O_2(^1\Delta_g)$. We suggested that $O(^3P_j)$ is the main factor in oxygen radicals to inactivate *P. digitatum* spores and that $O_2(^1\Delta_g)$ is less effective.

4. Summary

In order to investigate the effect of reactive oxygen species on inactivation of *P. digitatum* spores, we measured the radical densities of $O(^3P_j)$ and $O_2(^1\Delta_g)$, both of which have high oxidation reactivity, using VUV absorption spectroscopy. Considering that the inactivation rate of *P. digitatum* spores decreased as a function of exposure distance, we elucidated that $O(^3P_j)$ is the main factor responsible for inactivation of *P. digitatum* spores rather than $O_2(^1\Delta_g)$.

5. References

[1]S. Iseki, T. Ohta, A. Aomatsu, M. Ito, H. Kano, Y. Higashiyama and M. Hori: Appl. Phys. Lett., 96 (2010) 153704.

[2]S. Iseki, H. Hashizume, F. Jia, K. Takeda, K. Ishikawa, T. Ohta, M. Ito and M. Hori: Appl. Phys. Express, 4 (2011) 116201.

[3]M. Ito and T. Ohta M. Hori: J. the Korean Phys. Soc., 60, (2012) 937.

[4]H. Hashizume, T. Ohta, J. Fengdong, K. Takeda, K. Ishikawa, M. Hori, M. Ito: Appl. Phys. Lett., 103 (2013) 153708.

[5]H. Hashizume, T. Ohta, T. Mori, S. Iseki, M. Hori, and M. Ito: Jpn. J. Appl. Phys., 52 (2013) 056202.

[6]K. Ishikawa, H. Mizuno, H. Tanaka, K. Tamiya, H. Hashizume, T. Ohta, M. Ito, S. Iseki, K. Takeda, H. Kondo, M. Sekine, and M. Hori: Appl. Phys. Lett., 101, (2012) 013704.

[7]M. Iwasaki, H. Inui, Y. Matsudaira, H. Kano, N. Yoshida, M. Ito and M. Hori: Appl. Phys. Lett., 92 (2008) 081503.

[8]H. Inui, K. Takeda, H. Kondo, K. Ishikawa, M. Sekine, H. Kano, N. Yoshida and M. Hori: Appl. Phys. Express, 3 (2010) 126101.

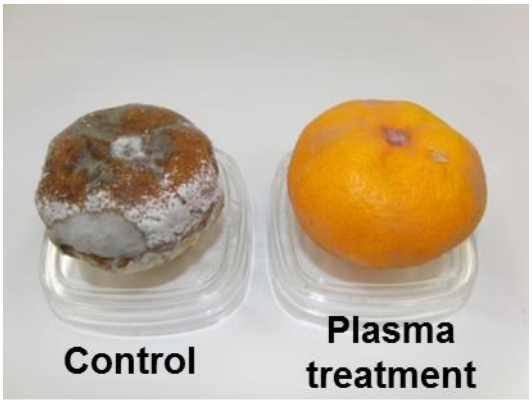

Figure 2 the result of the inactivation of *P. digitatum* spores on *Citrus unshiu* with or without the oxygen radical treatment.

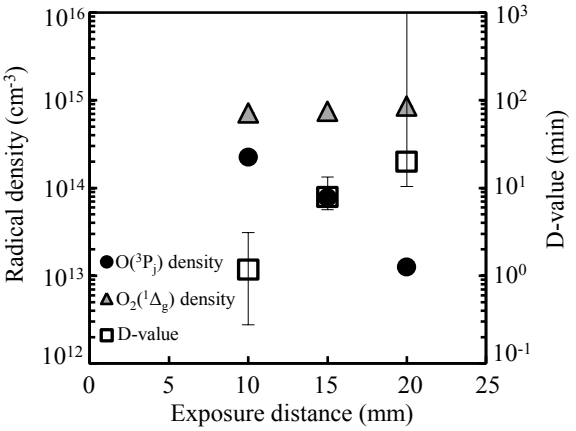

Figure 3 number densities of $O(^3P_j)$ and $O_2(^1\Delta_g)$, and D-value as a function of exposure distance.