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In-package atmospheric pressure cold plasma treatment of cherry tomatoes

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Cold plasma is increasingly under research for decontamination of foods, especially fresh fruits and vegetables. The effect of cold plasma on food quality, however, remains under researched. This study investigates the effects of cold plasma generated within a sealed package from a dielectric barrier discharge on the physical quality parameters and respiration rates of cherry tomatoes. Respiration rates and weight loss were monitored continuously, while other parameters are reported at the end of storage period. Differences among weight loss, pH and firmness for control and treated cherry tomatoes were insignificant towards the end of storage life. Changes in respiration rates and colour of tomatoes were recorded as a function of treatment, which were not drastic. The results implicate that cold plasma could be employed as a means for decontamination of cherry tomatoes while retaining product quality. © 2014, The Society for Biotechnology, Japan. All rights reserved.

[Key words: Cold plasma; Spectroscopy; Tomato; Respiration rate; Quality; Nonthermal; Barrier discharge]

Raw agricultural produce has frequently been associated with foodborne outbreaks. Microorganisms can grow on raw and minimally processed produce at populations ranging from 10^3 to 10^9 CFU/g (1). Sanitizing with chemicals, often chlorine based, is the most common intervention aimed at providing produce safety and preservation. However, in a number of European countries, such as the Netherlands, Sweden, Germany and Belgium, the use of chlorine on minimally processed vegetable products is prohibited due to the association of chlorine with the possible formation of carcinogenic chlorinated compounds in water (2,3). Considering this, there is a need to provide the fresh produce industry with intervention technologies to effectively eliminate pathogenic microorganisms associated with fresh produce (4).

Recently, cold plasma has been added to the list of nonthermal processes offering potential for the decontamination of fresh produce. A gas energised to such degree whereby the constituent molecules of the gas split to yield free electrons, radicals, positive and negative ions, quanta of electromagnetic radiation, while some molecules may still remain neutral is known as plasma. The term cold plasma refers to the fact that the temperature of electrons (T_e) is much higher than that of the ions, neutrals and global gas (T_g) temperature ($T_e >> T_g$). Thus, the overall temperature of cold plasma is limited to ambient temperatures, even at atmospheric pressures. The various aspects of application of cold plasma technology for inactivation of foodborne pathogens were reviewed by Misra et al. (5).

Several research works have identified the potential of cold plasma technology in decontaminating fresh produce and other foods. Majority of studies, to this end report the use of plasma jets for treatment of foods. Recently, Baier et al. (6) reported the use of a plasma jet operated with Ar gas for treatment of corn salad leaves, while Bermúdez-Aguirre et al. (7) employed a plasma jet array operating in Ar for decontamination of lettuce, carrots and tomatoes. In order for food industries to adopt the cold plasma technology, the operating cost of the gas would play an important role. Often noble gases are employed for inducing and sustaining plasmas, which increase the cost of treatments. An ideal gas for such treatments would be the use of ambient air.

An alternative plasma source for treatment of foods is the use of a dielectric barrier discharge (DBD) set-up, which allows treatment over large volumes in air and discharge gaps, when sufficiently high potential difference is maintained across the gas gap. In particular, a DBD set-up offers further advantage in that it allows treatment of produce inside sealed packages, which eliminates the risk of postprocess contamination. The use of in-package plasma technology for treatment of foods is now well-established (8–10). We have recently demonstrated the in-package cold plasma decontamination of strawberries, without compromise in their quality (2), and also inactivation of peroxidase enzymes in tomatoes (11).

In the present work we investigated the use of a DBD set-up to generate cold plasma in ambient humid atmospheric air inside a package containing cherry tomatoes. The package itself served as the dielectric material and helped to limit the charge transported, thereby permitting the generation of a stable discharge. This also eliminated the need for additional charge barriers. The effects of cold plasma treatment on the respiration rates and quality parameters are reported.

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MATERIALS AND METHODS

Produce characteristics Whole fresh cherry tomatoes (class I, origin – Egypt) were used for respiration rate and storage experiments. The required amount was bought from a whole-sale agricultural produce market (Smithfield, Dublin) and chosen based on bright red colour, indicating ripeness. Tomatoes were divided into two groups – one group was used as control, while the other for in-package plasma treatment.

To estimate the volume filled by the tomatoes inside the package, their density was determined. For this, the mass of the cherry tomatoes was obtained using a precision balance (Sartorius, Germany) and the volume by the method based on Archimedes principle. The tomatoes were fixed with a thin, straight and hard copper wire and introduced into beaker filled with a known mass (kg) of water. The temperature of water was recorded using a thermometer to be $15 \pm 0.2^{\circ}$ C. The resulting force measured as weight with the balance corresponds to buoyancy of the cherry tomatoes and equals the volume of the water displaced by the tomatoes. The apparent density was determined using the following equation:

$$d = \frac{W_{\text{Tomato}}}{W_{\text{Water}}} \tag{1}$$

where *d* is the density, W_{Tomato} is the mass of the tomato and W_{Water} is the mass of volume of water displaced by the tomato (equal to mass of the tomato). The apparent density of the tomatoes was estimated to be 1.026 ± 0.003 based on water displacement measurements for 10 samples. This value is in agreement with that reported by Stertz et al. (12) for organically grown Brazilian cherry tomato variety.

Package design Flexible packages made from high barrier Cryovac B2630 film of size 34 cm \times 33 cm were used to pack 107 \pm 3 g of tomatoes (10 tomatoes in each package). The average thickness of the film was 48 µm. The oxygen and carbon dioxide transmission rates for this film were 4.5 cm³ (STP)/(m²-24 h-atm) and 66 cm³ (STP)/(m²-24 h-atm) at 0% RH, 4°C. The water vapour transmission rates of the film were 0.45 g/(100 in²-24 h) at 100% relative humidity and 37°C. The bags were filled to approximately 3.5 l with air using a laboratory electric pump. It may be noted that the thickness of the packaging film employed in this study is higher than those used in actual practice. However, the high barrier nature of the packaging film allows retention of the active plasma species without leakage and also serves as a stable dielectric material preventing a transition of the discharge to arc regime (13). Studies in our laboratory have revealed that nature and thickness of packaging material plays an important role in preventing sparks. The atmospheric conditions at the time of treatment were 22 \pm $1^\circ C$ and 45 \pm 4% relative humidity, as measured using a humidity-temperature probe connected to a data logger (Testo 176 T2, Testo Ltd., UK).

Nonthermal plasma treatment The cold plasma was generated in air inside the bag using a dielectric barrier set-up, as shown in Fig. 1. The electrode separation was fixed at 2.2 cm and powered using a high-voltage (60 kV) source, pulsed at 50 Hz from a step-up transformer operated at 60% of the input voltage (120 V) using a variac. The electrodes had a contact surface area of 249.64 cm². A single value of 30 kV RMS voltage and four different treatment times, 30 s, 60 s, 180 s and 300 s were selected for the experiments, while each experiment was performed in duplicate. This voltage is much higher than those commonly employed in most studies, thereby allowing drastic reduction in treatment times, and use of large packages. Treatments were carried out by indirect mode,

meaning that the tomatoes were placed away from the inter-electrode zone thereby ensuring homogeneous discharge. When indirectly treated, the charged particles and short-lived transient-state species do not affect the sample under treatment, as they recombine before reaching it (10). This leaves only stable reactive species to act on the samples. The control and treated packages were stored at $20 \pm 2^{\circ}$ C temperature and $60 \pm 5\%$ relative humidity conditions in an environmental incubator (MLR-350HT, Sanyo Electric Biomedical Co. Ltd., Japan). These storage conditions were selected to simulate room temperature storage conditions.

Optical emission spectroscopy The energy transferred to the plasma produces various gaseous species in excited states. Some of these species can be identified based on the characteristic optical emission spectra of the plasma. Therefore, a computer controlled Stellarnet EPP 2000C-25 spectrometer was employed for optical emission spectroscopy (OES). The light emission from the plasma generated inside an empty package was captured via an optical fibre, directed towards the centre of the inter-electrode space where the species density is likely to be highest. Empty packages were employed since the presence of produce posed difficulties in maintaining a consistent alignment of the optical fibre. The diffraction grating of the spectrometer had a radius of curvature of 40 mm, 590 grooves per mm and an entrance slit width of 25 µm. The spectrometer had a resolution of 1.5 nm and operated in the spectrum of 190-850 nm. The fibre had a numerical aperture of 0.22 and was suitable for use in the ultraviolet and visible portion of the spectrum. The integration time was 5000 ms and 5 samples were averaged for the collection of spectra. The spectra were noise cancelled, averaged and analysed using National Institute of Standards and Technology (NIST) atomic spectra database and published works (14,15) for identification of active chemical species.

Gas concentration analysis The change in gas composition (O_2 and CO_2) inside each package was monitored over time using gas analyser (Systech Instruments, UK). Gas extractions were performed with a hypodermic needle inserted through an adhesive septum previously fixed to the bags, at a flow rate of 150 mL/ min for 10 s. The instrument is based on electrochemical sensor to record O_2 concentration, and uses a mini-IR spectrophotometer to record CO_2 concentrations (accuracy: $0.1\% v/v O_2$; $2\% v/v CO_2$). Initial experiments showed that sampling had no significant influence on gas concentration in the bag, as the bag volume was much greater than the total volume sampled by the instrument during the experiment.

A two parameter, non-exponential equation was fitted to average O_2 and CO_2 concentrations of control and treated packages at different storage periods (16,17) as shown in Eqs. 2 and 3 to determine the values of the coefficients:

$$G_{0_2} = 0.209 - \left[\frac{t}{K_1 t + K_2}\right]$$
(2)

$$G_{\rm CO_2} = \frac{t}{K_1 t + K_2} \tag{3}$$

where K_1 and K_2 (h) are the regression coefficients, *t* is the time of storage in hour, G_{O_2} is the oxygen concentration in decimal and G_{CO_2} is the carbon dioxide concentration in decimal. The rate of change of gas concentration was determined from the first derivative of the regression functions. Thus, at each sampling time, the respiration rates in terms of CO₂ evolution and O₂ consumption were calculated using Eqs. 4 and 5:



FIG. 1. The experimental set-up for indirect DBD plasma treatments of cherry tomatoes. The cold plasma is generated inside the bag. The tomatoes are placed outside the interelectrode space.

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