Cold Plasma

Subjects: Agricultural Engineering

Contributor: Fabiano Fernandes

Plasma is referred to as the fourth state of matter. It is an ionized gas comprising several excited atomic, molecular, ionic, and radical species, co-existing with electrons, positive and negative ions, free radicals, gas atoms, molecules in the ground or excited state, and quanta of electromagnetic radiation (UV photons and visible light).

cold plasma   Plasma Reactive Species

1. Fundamentals, Cold Plasma Generation, and Technologies

Plasma is classified as thermal or nonthermal plasma. In thermal plasmas, the ionization and chemical processes are mainly governed by the temperature, which can reach more than 20,000 K. Thermal plasma systems are used for applications requiring enormous heat, such as coating technology, welding, cutting, and treatment of hazardous wastes [1].

In nonthermal plasmas, different temperatures can be achieved for different plasma species, mostly around room temperature. Nonthermal plasma uses energy more efficiently to gain better chemical selectivity. In nonthermal plasmas, the electron temperature governs ionization and chemical processes [1]. Plasma is in a metastable state with a roughly zero net electrical charge [2][3]. Only nonthermal plasma is applied to food products.

Cold plasma can be generated in gases like helium, argonium, oxygen, nitrogen, and a mixture of these. Most studies with fruits and fruits juices have applied air or modified atmospheres. Some early studies have used helium or argonium, but studies with these gases have diminished due to their high cost, which would impact the price of the treated product.

Nonthermal plasma can be formed by electrical, microwave, and radiofrequency power sources that generate a high electrical potential difference between two or more electrodes. Among all technologies used to form cold plasma, dielectric barrier discharge (DBD) plasma, jet plasma, and glow discharge plasma are the most studied technology concerning application with fruit and fruit juices.

There is high interest in atmospheric pressure cold plasma technologies in food applications because they do not require vacuum systems and enable continuous material processing [4]. Glow discharge plasma (also called vacuum plasma) has been used in food and materials processing; however, since its application requires a vacuum, this technology cannot be directly applied to volatile materials. Jet plasma has been widely studied, but this technology has been less used due to the small surface areas that can be treated [5].

Among all technologies available, atmospheric dielectric barrier discharge plasma seems adequate to treat fruits and fruit juices rather than vacuum plasma. Several sensory characteristics of fruits come from volatile chemical compounds that may readily volatize when a vacuum is applied, inducing changes in aroma and flavor. On the other hand, vacuum plasma showed increased vitamin C and phenolic content in fruits, improving the nutritional quality of the product. Thus, the best technology depends on the goals established for the product and the main chemical components that characterize the fruit.

2. Plasma Reactive Species

Plasma consists of an ionized gas comprising several excited atomic, molecular, ionic, and radical species, co-existing with electrons, positive and negative ions, free radicals, gas atoms, molecules in the ground or excited state, and quanta of electromagnetic radiation (UV photons and visible light). The reactive species generated during plasma application depend on the gas and operating conditions applied.

Helium and argonium plasma generate plasma species that do not react with many bioactive compounds and are mainly used for sanitization [6][7][8][9]. The first studies with cold plasma on food consisted primarily of applying jet plasma using helium and argonium, which produced reactive species that are mainly inert to the chemical compounds present in food. These first studies with inert gases, and therefore, inert plasma, induced minimal chemical changes on the main food constituents. The results attained by these studies helped to propagate the idea that cold plasma did not alter the food quality while being very efficient in sanitizing it.

As the application of cold plasma migrated to the use of nitrogen, air, and modified atmosphere, several studies began to report slight to significant changes in the chemical composition of fruit and fruit products. Air plasma is a potent source of reactive oxygen species (ROS) and reactive nitrogen species (RNS). These reactive species tend to react when in contact with living cells or with organic compounds. Normal metabolism may be disrupted when plasma reactive species contact living cells or organisms, and several chemical reactions may occur when these species encounter organic molecules.

Plasma reactive species can be in the form of atoms, molecules, or ions with unpaired electrons. Free radicals are very unstable and usually react very fast with other molecules. Knowing how to use these free radicals is extremely important in plasma treatment. Working efficiently with plasma technology allows us to explore several chemical reactions with these non-toxic, free radicals, opening opportunities to improve product quality.

Air plasma free radicals include hydroxyl (HO•), superoxide ($O_2•^-$), alkoxyl (RO•), peroxyl (ROO•), and nitric oxide (NO•). Air plasma nonradical species include ozone (O_3), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$). The concentration of these species in plasma depends on the plasma technology being used, the operating conditions used to generate plasma, and environmental conditions (such as temperature and relative humidity).

Among the reactive oxygen species (ROS), hydroxyl radical is the most potent oxidant, followed by ozone and alkoxyl radicals [10]. These species react very rapidly with nearby molecules when they are formed. Thus, the generation of high amounts of hydroxyl radical, ozone, and alkoxyl radical may significantly change the fruit and fruit juices. Plasma species such as superoxide, nitric oxide, and lipid hydroperoxides are less reactive, allowing a higher control of the chemical reactions induced by plasma application.

Singlet oxygen ($^1O_2$) is formed when the two unpaired electrons of the molecular oxygen pair up into two different orbitals. This species is very reactive and a powerful oxidant. The species has two electrons that react quickly with unsaturated molecules, such as unsaturated lipids, phenolics, amino acids, or anthocyanins [11].

Superoxide radical ($O_2{\bullet}^-$) is formed when a single electron reduces oxygen. This species is highly reactive and the precursor of several other plasma species due to its tendency to abstract hydrogen atoms. It reacts mainly with compounds on the product's surface because this species does not permeate through membranes due to its charge [12]. The superoxide radical, therefore, is an important species in sanitizing processes.

Hydrogen peroxide (H_2O_2) has a long half-life and easily diffuses between cells. Thus, this species will continue to induce chemical changes to the product for long periods after plasma treatment. In fruits and minimally processed fruits, hydrogen peroxide is controlled by peroxidase enzymes and may have a lower effect. The decay of hydrogen peroxide produces water or hydroxyl radical, which is one of the most reactive plasma species.

Hydroperoxyl radical ($HO_2{\bullet}$) will be formed at a low pH by the protonation of superoxide radicals. This species is more reactive than its precursor. Because of its lack of charge, hydroperoxyl radicals can permeate the membrane phospholipid bilayer and react with bioactive compounds present in this cell region.

Hydroxyl radical (HO•) is one of the most reactive plasma species. The decay of ozone generates it in the presence of water or water vapor, the cleavage of water, and the decay of hydrogen peroxide (H_2O_2). Plasma technologies that generate higher quantities of UV light may produce more hydroxyl radicals due to their capacity to cleave H_2O_2, yielding two hydroxyl radicals. Fruits have defense systems that control hydroxyl radical concentration, but fruit juices have lower or no ability to control hydroxyl radicals. This species reacts with several molecules, including amino acids and terpenoids [13].

Ozone (O_3) is generated by the bombardment of oxygen molecules by electrons in the plasma discharge [14]. The concentration of ozone in plasma depends on several factors. Still, it is very dependent on the concentration of oxygen in the environment and on the excitation frequency of the plasma system. Higher excitation frequencies (>800 Hz) tend to form higher concentrations of ozone. Ozone has high oxidizing power and reacts with several compounds, including vitamins, phenolics, proteins, lipids, and nucleic acids. Ozone molecules react with water at the product surface or microorganism surface, thus having high sanitization power [15]. The half-live of ozone can be as high as 6 h after plasma application [15].

The reaction of oxygen plasma species with carbon-based compounds, such as lipids, proteins, amino acids, and nucleic acid, generates alkoxy radical (RO•) and peroxyl radical (ROO•) [16]. Both radicals are good oxidizing agents. The peroxyl radical (ROO•) has a long half-life and can diffuse considerably in fruit cells. As such, this radical has a good penetration capability and can induce changes in the interior of large products.

Nitric oxide (NO•) is the main reacting nitrogen species formed in plasma treatment. This species is a natural cellular messenger involved in several physiological processes. Thus, the formation of this species can trigger several physiological responses in fruit and fruit juices. An excess of nitric oxide is cytotoxic and can induce the formation of other nitrogen plasma species, such as peroxynitrite anion ($ONOO^-$) and nitrite anion (NO_2^-). Nitric oxide and its anions react with oils, proteins, sulfhydryls, lipids, and nucleic acids [17].

Nitric oxide also scavenges peroxyl and alkoxyl radicals, reducing the adverse effects of plasma in fruit and fruit juices with high contents of oils and lipids [18][19].

Fruits are constantly exposed to reactive oxygen species produced as by-products of metabolism, respiration, stress, and oxidation. Their antioxidant defenses are responsible for regulating the concentration of reactive oxygen species at acceptable levels to the cells. Oxidative stress occurs when an imbalance between the reactive oxygen species and antioxidant defenses is observed. Plasma application forms high concentrations of reactive oxygen species quickly, resulting in oxidative stress that the fruit antioxidant defense system cannot control. Thus, chemical changes are likely to occur.

In processed fruit-based products, where cells are not alive anymore, the reactive oxygen species will probably cause higher chemical modifications since no defense system will be available to regulate the reacting oxygen species' concentration. However, enzymes may still be viable and activated by some reactive oxygen species in some processed fruit juices, participating in some chemical modifications. This means that the chemical changes induced by plasma treatment in a blueberry may not have the same outcome as the changes induced in blueberry juice, dried blueberry, or blueberry jam. Thus, the analysis of the changes caused by plasma should consider its defense system.

The detection of plasma-reacting species is usually done with optical emission spectroscopy. Most labs working with plasma still do not have an optical emission spectrometer, and complete characterization of reactive plasma species is rare and usually not reported in most studies. Thus, the characterization and quantification of reactive plasma species is a knowledge gap that needs to be filled.

Dielectric barrier discharge plasma applied in air generates reactive nitrogen species and reactive oxygen species, with nitrogen species dominating plasma composition. The presence of oxygen singlet and hydroxyl radical are detected in lesser quantities [20]. The production of ozone in dielectric barrier discharge plasma depends on the excitation frequency of the power source. Low frequencies (<200 Hz) produce low quantities of ozone, whereas higher frequencies (>800 Hz) produce higher amounts of ozone. In systems where water or moisture are present, DBD plasma tends to increase the generation of OH radicals and restrict ozone production [21].

The plasma environment generated in glow discharge plasma is very different from that of dielectric barrier discharge plasma. Although nitrogen species are still prominent in glow discharge plasma, OH radicals and nitric oxide concentration are much higher than DBD plasma. Due to the high concentration of nitric oxide, air glow discharge plasma efficiently fixates nitrogen in organic materials [22].

The gliding arc plasma environment is characterized by OH radicals, NO, and other nitrogen species, as it is the technology that produces the greatest amount of OH radicals. Despite the generation of OH radicals from the dissociation of water in the air, only small quantities of other hydrogen species are generated. The formation of OH radical is dependent on the electrical current applied. Increasing the current increases the formation of OH radicals and decreases the formation of nitrogen species [23].

Different plasma technologies and operating conditions generate different compositions of reactive plasma species. Thus, the chemical modification induced by plasma will depend on the technology and operating conditions that are applied. In a general analysis, dielectric barrier discharge plasma will tend to cause more oxidation and hydrogenation reactions. Glow discharge plasma can induce hydrolysis, nitrogen fixation, and the formation of alcohols. Gliding arc plasma will induce more reactions with OH radicals. In comparison, jet plasma will be less reactive with most organic compounds because it operates mainly with inert gases.

References

1. Ananthanarasimhan, J.; Lakshminarayana, R.; Anand, M.S.; Dasappa, S. Influence of gas dynamics on arc dynamics and the discharge power of a rotating gliding arc. Plasma Sources Sci. Technol. 2019, 28, 085012.
2. Misra, N.; Tiwari, B.K.; Raghavarao, K.S.M.S.; Cullen, P.J. Nonthermal Plasma Inactivation of Food-Borne Pathogens. Food Eng. Rev. 2011, 3, 159–170.
3. Misra, N.N.; Martynenko, A.; Chemat, F.; Paniwnyk, L.; Barba, F.J.; Jambrak, A.R. Thermodynamics, transport phenomena, and electrochemistry of external field-assisted nonthermal food technologies. Crit. Rev. Food Sci. Nutr. 2018, 58, 1832–1863.
4. Turner, M. Physics of Cold Plasma. In Cold Plasma in Food and Agriculture; Elsevier: Amsterdam, The Netherlands, 2016; pp. 17–51.
5. Nishime, T.M.C.; Borges, A.; Koga-Ito, C.Y.; Machida, M.; Hein, L.; Kostov, K. Non-thermal atmospheric pressure plasma jet applied to inactivation of different microorganisms. Surf. Coat. Technol. 2017, 312, 19–24.
6. Lackmann, J.-W.; Bandow, J.E. Inactivation of microbes and macromolecules by atmospheric-pressure plasma jets. Appl. Microbiol. Biotechnol. 2014, 98, 6205–6213.
7. Lee, H.; Kim, J.E.; Chung, M.-S.; Min, S.C. Cold plasma treatment for the microbiological safety of cabbage, lettuce, and dried figs. Food Microbiol. 2015, 51, 74–80.

8. Tang, Y.Z.; Lu, X.P.; Laroussi, M.; Dobbs, F.C. Sublethal and Killing Effects of Atmospheric-Pressure, Nonthermal Plasma on Eukaryotic Microalgae in Aqueous Media. Plasma Process. Polym. 2008, 5, 552–558.
9. Baier, M.; Foerster, J.; Schnabel, U.; Knorr, D.; Ehlbeck, J.; Herppich, W.; Schlüter, O. Direct non-thermal plasma treatment for the sanitation of fresh corn salad leaves: Evaluation of physical and physiological effects and antimicrobial efficacy. Postharvest Biol. Technol. 2013, 84, 81–87.
10. Segat, A.; Misra, N.; Fabbro, A.; Buchini, F.; Lippe, G.; Cullen, P.; Innocente, N. Effects of ozone processing on chemical, structural and functional properties of whey protein isolate. Food Res. Int. 2014, 66, 365–372.
11. Davies, M.J. Free radicals, oxidants and protein damage. Aust Biochem. 2012, 43, 8–12.
12. Papuc, C.; Goran, G.V.; Predescu, C.N.; Nicorescu, V. Mechanisms of Oxidative Processes in Meat and Toxicity Induced by Postprandial Degradation Products: A Review. Compr. Rev. Food Sci. Food Saf. 2016, 16, 96–123.
13. Davies, M.J.; Hawkins, C.; Pattison, D.I.; Rees, M. Mammalian Heme Peroxidases: From Molecular Mechanisms to Health Implications. Antioxid. Redox Signal. 2008, 10, 1199–1234.
14. Fang, Z.; Qiu, Y.; Sun, Y.; Wang, H.; Edmund, K. Experimental study on discharge characteristics and ozone generation of dielectric barrier discharge in a cylinder–cylinder reactor and a wire–cylinder reactor. J. Electrost. 2008, 66, 421–426.
15. Misra, N.; Patil, S.; Moiseev, T.; Bourke, P.; Mosnier, J.-P.; Keener, K.; Cullen, P. In-package atmospheric pressure cold plasma treatment of strawberries. J. Food Eng. 2014, 125, 131–138.
16. Augusto, O.; Miyamoto, S. Oxygen radicals and related species. In Principles of Free Radical Biomedicine; Pantopoulos, K., Schipeer, H.M., Eds.; Nova Science Publishers: New York, NY, USA, 2011; pp. 19–42.
17. Radi, R.; Beckman, J.S.; Bush, K.M.; Freeman, B.A. Peroxynitrite-induced membrane lipid peroxidation: The cytotoxic potential of superoxide and nitric oxide. Arch. Biochem. Biophys. 1991, 288, 481–487.
18. Hogg, N.; Kalyanaraman, B. Review. Nitric oxide and lipid peroxidation. BBA Bioenerg. 1999, 1411, 378–384.
19. Hogg, N.; Darley-Usmar, V.M.; Wilson, M.T.; Moncada, S. The oxidation of α-tocopherol in human low-density lipoprotein by the simultaneous generation of superoxide and nitric oxide. FEBS Lett. 1993, 326, 199–203.
20. Amirabadi, S.; Milani, J.M.; Sohbatzadeh, F. Application of dielectric barrier discharge plasma to hydrophobically modification of gum arabic with enhanced surface properties. Food Hydrocoll. 2020, 104, 105724.

21. Deng, J.; He, L.; Zhao, B.; Chen, Q. Effects of air relative humidity on spectral characteristics of dielectric barrier discharge plasma assisted combustion reactor. Vacuum 2020, 175, 109189.
22. Gamaleev, V.; Britun, N.; Hori, M. Control and Stabilization of Centimeter Scale Glow Discharge in Ambient Air Using Pulse-Width Modulation. IEEE Access 2020, 8, 201486–201497.
23. Gamaleev, V.; Tsutsumi, T.; Hiramatsu, M.; Ito, M.; Hori, M. Generation and Diagnostics of Ambient Air Glow Discharge in Centimeter-Order Gaps. IEEE Access 2020, 8, 72607–72619.