

## ATMOSPHERIC COLD PLASMA AS NEW STRATEGY FOR FOODS PROCESSING - AN OVERVIEW

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**Abstract:** The atmospheric cold plasma is a non-thermal processing method. This technique becomes a subject of high interest for a wide variety of technologies including the food industry. The atmospheric cold plasma is proposed for decontamination of fruits and vegetables, especially, without changes in sensory attributes. This paper summarizes some relevant aspects of atmospheric cold plasma including generation, microbial inactivation mechanism and plasma applications in food industry. Although some aspects of antimicrobial mechanisms were presented here, more research should be done to clarify the antimicrobial mechanisms, in addition to confirm that no harmful by-products are generated by this technology.

**Keywords:** food, microbial inactivation, non-thermal processing.

### Introduction

The foods may be contaminated by different microorganisms or can undergo deterioration from natural food enzymes. The pathogenic and spoilage microorganisms are problematic in the food industry due to their significant public health risks and economic impact (Stoica *et al.*, 2011; Afshari and Hosseini, 2014). Therefore, in the food industry, the control of undesirable microorganisms is essential and decisive (Stoica *et al.*, 2011). There are a lot of methods to destroy these microorganisms, such as: thermal technologies, *e.g.* sterilization, pasteurization, ohmic heating, *etc.* (Afshari and Hosseini, 2014) and non-thermal technologies, *e.g.* high hydrostatic pressure, pulsed electric fields, high voltage arc discharge (Stoica *et al.*, 2011; Stoica *et al.*, 2013; Afshari and Hosseini, 2014). On the other hand, the thermal technologies lead to unwanted changes in the foods' sensory attributes (by

overheating) or to low nutritional value of the food products (Fernández *et al.*, 2012; Stoica *et al.*, 2013; Afshari and Hosseini, 2014), while the non-thermal technologies are often technically difficult to apply into production, expensive and require specialized equipment and trained personnel (Garcia-Gonzalez *et al.*, 2007; Afshari and Hosseini, 2014; Misra *et al.*, 2014b). ACP: atmospheric cold plasma, a non-thermal plasma technology, is proposed as a potential alternative to traditional methods for decontamination of foods (Bárdos and Baránková, 2010; Naïtali *et al.*, 2010; Niemira, 2012; Afshari and Hosseini, 2014; Ziuzina *et al.*, 2014). This technology does not require extreme process conditions and offers great opportunities for food product preservation (Fernández *et al.*, 2012; Rod *et al.*, 2012; Stoica *et al.*, 2013), where the heat is not desirable for it (Afshari and Hosseini, 2014) in conjunction with maintenance of sensory attributes

of the treated foods (Ziuzina *et al.*, 2014). This article briefly summarizes relevant aspects of ACP including plasma generation, microbial inactivation mechanism and plasma applications in food processing.

### **Generation of plasma**

The plasma is considered to be the fourth state of matter (Tendero *et al.*, 2006; Shakila Banu *et al.*, 2012; Suhem *et al.*, 2013; Surowsky *et al.*, 2013; Afshari and Hosseini, 2014; Mai-Prochnow *et al.*, 2014). The plasma (or more correctly, the gas discharge plasma) is a mixture of partially ionized gas (Bárdos and Baránková, 2010; Niemira, 2012; Ryu *et al.*, 2013; Pankaj *et al.*, 2014) that contains reactive species, such as: electrons, positive and negative ions, free radicals, gas atoms and photons (Bárdos and Baránková, 2010; Fernández *et al.*, 2012; Stoica *et al.*, 2013; Afshari and Hosseini, 2014; Pankaj *et al.*, 2014). The reactive species generated by electron collision play a key role in the microbial plasma inactivation process (Mai-Prochnow *et al.*, 2014). The ACP is dominated by reactive neutral species, such as: oxygen atoms, singlet oxygen and ozone rather than ions (Shibata *et al.*, 1996; Schutze *et al.*, 1998). In gas discharges at atmospheric pressure in air, the main reactive species are ozone, atomic oxygen, superoxide, peroxide, hydroxyl radicals (Afshari and Hosseini, 2014) with dominating role (Deng *et al.*, 2006) and nitric oxide and nitrogen dioxide (Afshari and Hosseini, 2014). The reactive species can cause damages in proteins, lipids and nucleic acids (Cabiscol and Ros, 2000; Afshari and Hosseini, 2014; Mai-Prochnow *et al.*, 2014). There are several means for artificial plasmas generation. The plasma is generated when the energy (Niemira, 2012; Shakila Banu *et al.*, 2012) is applied across a dielectric gas or fluid (Shakila Banu *et al.*, 2012). Any kind of energy can be used for gas ionization: microwave, radio frequency, electric or electromagnetic field, thermal, optical, radioactive and X-rays (Bárdos and Baránková, 2010; Afshari and Hosseini, 2014; Pankaj *et al.*, 2014). The most useful ionization tools are electric or electromagnetic fields. When it is applied a voltage of about 30 kV/cm between electrodes (cathode and anode) separated by 1 cm in ambient air, electric breakdown and ignition of atmospheric air plasma

can occur. Such electric breakdown can have the form of discrete sparks, but under certain conditions it is also possible to create a uniform-looking steady glow-type air discharge. The properties of plasma generally depend on the power, type of power (alternating current, direct current, pulsed, frequency) and type of gas (Bárdos and Baránková, 2010). The plasmas can be generated at low and high gas pressures (Bárdos and Baránková, 2010; Afshari and Hosseini, 2014). In plasmas generated at low gas pressures, where the density of gas particles available for ionization is low and the collision frequency is low, electron energies remain high compared to ion energies (is the case of the cold plasma, non-equilibrium plasma) (Bárdos and Baránková, 2010). The ACP, which is the most common plasma (Moisan *et al.*, 2001; Bárdos and Baránková, 2010), it is said “cold” because the temperature in plasma reactor stays the near room temperature (Shakila Banu *et al.*, 2012). Conversely, the high gas pressures with correspondingly high collision frequencies lead to equilibrium in the plasma (is the case of the hot plasma). The most feasible way to create non-equilibrium plasmas is “pumping” of power selectively to electrons (Bárdos and Baránková, 2010). The gas breakdown in a stationary electric field between electrodes it is the same of the production of electrons in a simple diode system. An electron emitted from the cathode collides along a unit length with a neutral gas particle and forms an ion and an additional (initial) electron (Bárdos and Baránková, 2010). The positive ions are attracted to the cathode and upon impact form secondary electrons which take part in subsequent ionizations in an avalanche type process. The secondary electron emission depends on a number of factors, such as: the material and the temperature of the cathode, the pretreatment of the cathode surface, gas and the effects of energetic ultraviolet radiation. In a stationary electric field, due to high collision frequencies at high gas pressure, it is nearly impossible to generate non-equilibrium cold plasma. The electric breakdown usually starts as a transient discharge in the form of a spark and at higher powers it easily turns into a high-current hot arc. The gases can also be ionized by electromagnetic (oscillating) field having amplitude of the electric component high enough for breakdown. Due to the immensely different

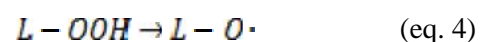
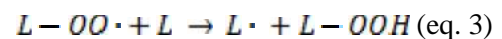
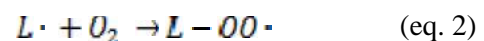
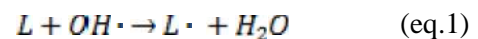
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mobility's of ions and electrons at high frequencies, the alternating current fields enable pumping of the power selectively to electrons, thus enabling non-equilibrium cold plasma at high gas pressures (Bárdos and Baránková, 2010). The alternating current power can be radiated into the plasma with electrodeless discharges (without electrodes), or with electrodes according to similar principles for direct current breakdown. The breakdown voltage depends on the gas, decreases with alternating current frequency due to a change in the electron loss mechanism. At high gas pressures, the electrons make many collisions per oscillation, and the production of secondary electrons at electrode surfaces is also less important. The magnitude of the electric field and the phase of the electron motion have a governing effect (Bárdos and Baránková, 2010). Often the noble gases are employed for inducing plasmas, but this can increase the cost of treatments. Thus, for inducing plasma should be the use of ambient air (Misra *et al.*, 2014a).

**Microbial inactivation mechanism of plasma**

The plasma treatment can effectively inactivate a wide range of microorganisms (De Geyter and Morent, 2012; Fernández *et al.*, 2012; Ryu *et al.*, 2013; Wolf, 2013; Afshari and Hosseini, 2014) (prokaryotic and eukaryotic), (Li *et al.*, 2013; Ryu *et al.*, 2013; Mai-Prochnow *et al.*, 2014) including spores and viruses (Li *et al.*, 2013; Afshari and Hosseini, 2014; Mai-Prochnow *et al.*, 2014). In many cases, the prokaryotic microorganisms (bacteria) are more vulnerable to plasma (Park *et al.*, 2004; Lee *et al.*, 2006; Muranyi *et al.*, 2007; Tang *et al.*, 2008; Kamgang-Youbi *et al.*, 2009; Xiong *et al.*, 2010). Bacteria from biotic and abiotic surfaces are effectively killed by plasma (Baik *et al.*, 2013; Pavlovich *et al.*, 2013) at different rates and that the different death rates are probably caused by differential changes in components and ions in the solutions (Baik *et al.*, 2013). The plasma generates different level of lethal effects on microorganisms through interaction with microbial surrounding environments (water, pH, nutrients, osmotic stability and temperature) (Ryu *et al.*, 2013). The use of plasma as a sterilization method was first patented in 1968 and the plasma made from oxygen was first applied in 1989 (Afshari and Hosseini, 2014). After

1990s, considerable researches have been done on mechanisms of microbial inactivation by plasma (Noriega *et al.*, 2011; Shakila Banu *et al.*, 2012; Ryu *et al.*, 2013; Afshari and Hosseini, 2014), however, these researches are remained very limited (Ryu *et al.*, 2013) and the exact mechanisms of this process remain unclear (Mai-Prochnow *et al.*, 2014). The bacterial killing occurs via three different mechanisms: (a) direct permeabilization of the cell membrane or wall, leading to leakage of cellular components, including potassium, nucleic acids and proteins; (b) critical damage of intracellular proteins from oxidative or nitrosative species and (c) direct chemical nucleic acids damage (Mai-Prochnow *et al.*, 2014). The reactive species can cause serious damages of the cells (Cabisco and Ros, 2000; Afshari and Hosseini, 2014; Mai-Prochnow *et al.*, 2014). Hydrogen peroxide was found to be the causative antibacterial agent that damages iron-sulphur and mononuclear iron enzymes (Mai-Prochnow *et al.*, 2014). The hydroxyl radicals (OH) in plasma have toxic effects (Kang *et al.*, 2011), being involved in membrane lipid peroxidation with the increase of membrane permeability (Ryu *et al.*, 2013; Mai-Prochnow *et al.*, 2014), through a destructive oxidation reactions (Gaunt *et al.*, 2006) (equations 1 - 4) leading to unsaturated lipids disintegrating into lipid peroxides (Surowsky *et al.*, 2013).



The ozone can accelerate the chain reaction by oxidation and leads to a reduction of membrane fluidity (Gaunt *et al.*, 2006) and the functions of the membrane lipids are compromised. The lipid peroxidation generates the stable aldehydes which can travel long distance to attack targets (Gaunt *et al.*, 2006). The aldehydes are very reactive and can damage the proteins (Singh and Singh, 1982). In case of proteins, the reactive species react with the amino-acid chains and cause proteins structure

changes (Stadtman, 1992; Berlett and Stadtman, 1997; Cabiscol and Ros, 2000; Surowsky *et al.*, 2013) and damage the cells (Afshari and Hosseini, 2014) and the spores (Laroussi, 2005; Afshari and Hosseini, 2014). Nucleic acids can be damaged, also (Farr and Kogoma, 1991; Afshari and Hosseini, 2014). In ACP, the reactive species are thought to be the major components that have antimicrobial effects (Shintani *et al.*, 2010; Afshari and Hosseini, 2014), while the effect of ultraviolet irradiation is minor (Afshari and Hosseini, 2014). The inactivation microorganism mechanisms depend on: type of food product, ACP design, type of microorganisms, voltage, gas pressure, gas composition, water content in the gas, and distance of the microorganism from the discharge glow (Afshari and Hosseini, 2014; Ziuzina *et al.*, 2014). The microbial response also depends on the bacterial mode of growth, with bacteria growing in biofilms requiring a longer exposure time before becoming inactivated (Mai-Prochnow *et al.*, 2014).

### ***Atmospheric cold plasma applications***

Due to their design simplicity and low operating cost, this form of discharge plays an important role for many technological applications. Several ACP applications have been identified in literature (Law *et al.*, 2012), such as: food industry (Fernández *et al.*, 2012; Shakila Banu *et al.*, 2012; Surowsky *et al.*, 2013; Pankaj *et al.*, 2014; Ziuzina *et al.*, 2014), medical and clinical (Terrier *et al.*, 2009; Isbary *et al.*, 2013; Hoffmann *et al.*, 2013; Arora *et al.*, 2014; Mai-Prochnow *et al.*, 2014), materials processing (Law *et al.*, 2012; Callard Preedy *et al.*, 2014; Sato *et al.*, 2014), material analysis (Sato *et al.*, 2014), surface modification (Law *et al.*, 2012; Sato *et al.*, 2014; Pankaj *et al.*, 2014), light source (Law *et al.*, 2012; Sato *et al.*, 2014) and microplasma chip (Sato *et al.*, 2014). ACP technology offers distinct advantages for decontamination of foods (Misra *et al.*, 2014b). ACP is increasingly under research for decontamination of fresh produce (Kabir Jahid *et al.*, 2014; Ziuzina *et al.*, 2014) fruits and vegetables, especially (Klockow *et al.*, 2009; Fan *et al.*, 2012; Fernández *et al.*, 2012; Baier *et al.*, 2014; Misra *et al.*, 2014a; Ziuzina *et al.*, 2014). ACP technology can be used to treat a variety of vegetables: fresh tomatoes (Bermúdez-Aguirre *et al.*, 2013; Misra *et al.*

*et al.*, 2014a; Pankaj *et al.*, 2014), cherry tomatoes (Misra *et al.*, 2014a), lettuce (Shakila Banu *et al.*, 2012; Bermúdez-Aguirre *et al.*, 2013; Kabir Jahid *et al.*, 2014; Misra *et al.*, 2014a), carrots (Bermúdez-Aguirre *et al.*, 2013; Misra *et al.*, 2014a), cucumbers and broccoli. The tomatoes and the lettuce were easier to decontaminate than the carrots, probably because of the surface structure (Bermúdez-Aguirre *et al.*, 2013). Also, ACP is used to reduce the microorganisms on strawberries (Misra *et al.*, 2014a), apples (Shakila Banu *et al.*, 2012), melons and mangos (Shakila Banu *et al.*, 2012), pears, spice *e.g.* red pepper (Kim *et al.*, 2014), nuts (Shakila Banu *et al.*, 2012). ACP can successfully decontaminate of the fresh meat and poultry (Shakila Banu *et al.*, 2012) and meat products (Noriega *et al.*, 2011; Frohling *et al.*, 2012; Rod *et al.*, 2012), *e.g.* bacon (Kim *et al.*, 2011), ham (Shakila Banu *et al.*, 2012) and ready to eat meat (Rod *et al.*, 2012) and cheese (Shakila Banu *et al.*, 2012). ACP it is able to control the microorganisms in the cereal industry (Shakila Banu *et al.*, 2012; Suhem *et al.*, 2013) because it doesn't generate too much heat which means it may damage food nutrition less (Suhem *et al.*, 2013). Recently, some researches show that ACP is suitable for inactivate enzymes from fruit or vegetable sources (Pankaj *et al.*, 2014). ACP is a powerful tool for surface decontamination of not only foods but also food packaging materials (Pankaj *et al.*, 2014; Surowsky *et al.*, 2014) (plastic bottles, lids and films) without adversely affecting their bulk properties, and does not result in any liquid effluents (residues) (Pankaj *et al.*, 2014). Newer, ACP technology can be combined with the essential oil (*e.g.* clove oil) to decontaminate the cellulose-based food packaging (Matan *et al.*, 2014).

### **Conclusions**

The atmospheric cold plasma, by far, is one of the newest technologies used in food industry for microbial inactivation. In the microbial inactivation plasma process, a key role is attributed to reactive species (atomic oxygen, singlet oxygen, ozone, superoxide, hydrogen peroxide, hydroxyl radicals, nitric oxide and nitrogen dioxide) generated by electron collision. The atmospheric cold plasma treatment can effectively inactivate a wide range of microorganisms including spores and viruses,

through permeabilization of the cell membrane, damage of the intracellular proteins and the nucleic acids and the inactivate of some enzymes. This technology is considered to be very promising alternative to thermal new processing technologies and it has many interesting applications in the food industry: decontamination especially of fruits and vegetables, spice, nuts, raw and meat products, cheese, or decontamination of the food packaging materials and newer can be combined with some antimicrobial agents such as essential oils. However, more information's are needed to clarify the microbial inactivation mechanisms and to confirm that no harmful by-products are generated by atmospheric cold plasma treatment.

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