

Review Article

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## Recent Development of Non-Thermal Cold Plasma Technology for Safe and Sustainable Seafood Processing: A Review

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### ABSTRACT

Seafood is one of the major protein sources in the world. Seafood products are praised worldwide for their high nutritional value and are increasingly popular among consumers. Consumer preferences range from fresh products, eaten raw or minimally processed seafood. So quality, safe and nutritionally rich processed seafood is high in demand. Cold Plasma (CP) is a novel non-thermal technology, potentially useful in the agriculture and food processing settings. Heat treatment can cause undesirable protein denaturation, non-enzymatic browning, loss of vitamins and volatile flavor compounds, freezing point depression, and flavor changes. CP has gained attention in recent years as a potential alternative method for chemical and thermal disinfection in foods using ambient or moderate temperatures and short treatment times in seafood sector. This review provides a critical summary of the studies to decontamination of seafood products using cold plasma technology along with a summary of the mechanisms involved. In addition, the review also discusses the effects of cold plasma on quality of seafood products, highlights some emerging applications of plasma technology in the seafood industry.

#### Keywords

Non-thermal, Cold Plasma technology, Seafood processing

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### Introduction

Seafood is high in nutritional value, containing high-quality proteins, omega-3 fatty acids, essential micronutrients, minerals and vitamins (Murray and Burt, 2001). Globally, seafood consumption has grown

exponentially over the past few decades. Abreast this increase in demand and consumption, food safety has become a vital public-health concern. Pathogens such as *Listeria monocytogenes*, *Escherichia coli* O157: H7, *Campylobacter jejuni* and *Salmonella* spp. can easily thrive on seafood,

causing severe foodborne illness in consumers.

Traditional thermal-based food-processing methods such as appertization, pasteurization, and canning have been dependent on high temperature, to ensure prolonged shelf life and seafood safety. Heating has a lethal effect on both vegetative cells and spores of any microbes. Thermal treatment also results in concurrent consequences, such as a decrease in nutritional properties such as vitamins or denaturation of proteins, and sometimes the undesirable alteration in the fresh flavour in food (Birwal, 2019). Additionally, lipid oxidation is a significant cause of rancidity and off-flavours during subsequent storage. This is particularly the case for seafood that contains substantial amounts of polyunsaturated fatty acids.

As human evolution progressed, the way food is consumed, and their priorities have also been evolved. The consumption of processed foods is on the rise due to change in lifestyle, particularly in urban and semi-urban areas. Today's consumer is also extremely aware of the requirement of nutritionally superior shelf-stable processed products whose sensory attributes are as close to the fresh product as possible. This has prompted food processing professionals to investigate novel and alternate technologies that have the potential to inactivate microorganisms in the seafood matrix with minimal change to preserve the seafood constituents. The novel approach has been to eliminate the use of heat treatment while targeting the set objective of improved safety and shelf life of the beverage leading to a category of non-thermal treatment technologies. Several such non-thermal high hydrostatic pressure (HPP), pulsed electric field (PEF), oscillating magnetic field, ionizing irradiation, ultrasound (US) pulsed light (PL), cold plasma (CP) and ozone (Zhao *et al.*, 2019). These technologies retain

nutritional and sensory properties quality of foods such as fruit and vegetables (Ramazzina *et al.*, 2015; Gomez-Lopez *et al.*, 2005), fish (Erkan *et al.*, 2011; Rode and Hovda, 2016; Okpala, 2014), or fresh and ready-to-eat meat products (Ganan *et al.*, 2013; McDonnell *et al.*, 2014) by inactivating of spoilage and pathogenic microorganism better than conventional or traditional methods.

Plasma is a mixture of charged ions, radicals, electrons and neutrals in gaseous form. Cold plasma technology is emerging, green processes have evolved in recent times in food industries, and its application on seafood industries has been encouraging. In this paper, we have reviewed the important aspects of nonthermal processing for seafood.

### **What is cold plasma?**

Cold plasma (CP) is an emerging non-thermal technology that could potentially decontaminate the surfaces of fresh produce. This antimicrobial intervention offers the advantage of being chemical and water-free, in addition to being able to operate openly and continuously at atmospheric pressure (Niemira, 2012).

Plasma is a quasi-neutral gas. Matter on earth exists mostly in three distinct phases (gas, liquid and solid) but when the universe is considered as the fourth state of matter which abundantly exists. So, Plasma is hence referred to as the fourth state of matter, next to solids, liquids and gases. It containing free electrons, ions and neutral particles and more than 99% of the visible matter in the universe are in the plasma state. It is a mixture of an electrified gas with chemically reactive compounds that consists of ions, free electron, activated and metastable species (NO<sub>x</sub> -), free radicals like reactive oxygen species (ROS), reactive nitrogen species (RNS) neutral particles (excited atoms and molecules), and

quanta of electromagnetic photons (visible, UV-A, and UV-B) (Tendero *et al.*, 2006; Mir *et al.*, 2016; Ekezie *et al.*, 2017; Misra *et al.*, 2011; Afshari and Hosseini, 2012; Mir *et al.*, 2016; Simoncicova *et al.*, 2018). Use of electrical discharges and low temperature make this process practical, cost-effective and suitable for decontamination of various food products where heat treatment is not adequate (Afshari and Hosseini, 2012).

### **Plasma Chemistry: History and Process**

Plasma was first discovered by Irving Langmuir (1881– 1957) in 1928. Plasma technology is based on a physical principle. Matter changes its state when power is supplied to it: solids become liquid, and liquids become gaseous. If even more power is provided to a gas, it is ionized and goes into the energy-rich plasma state, the final state of matter which exists over a vast range of temperature and pressure.

Plasma (at low-pressure or atmospheric pressure) produced by coupling energy to a gaseous medium by several means such as mechanical, thermal, chemical, radiation, nuclear, or by voltage application, or electromagnetic waves injection and also by a combination of these to dissociate the gaseous component molecules into a collection of ions, electrons, charge-neutral gas molecules, and other species (Mudgil and Mudgil, 2019)

Within nonthermal plasmas, plasma state can be attained by the application of energy in several forms including; thermal, electric or magnetic fields and radio or microwave frequencies, which increases the electrons kinetic energy resulting in increased number of collisions in the gas-forming plasma products like electrons, ions, radicals and radiation of varying wavelengths including that in the UV ranges (Thirumdas *et al.*, 2017). In the generation of cold plasma, most

of the coupled electrical energy is channelled to electron component instead of heating the entire gas stream, so the temperature of massive particle remains near the room temperature, these characteristics make it suitable to be used in processes in which high temperature is not desirable (Nehra *et al.*, 2008). In contrast, conventional devices generated plasma do not ionize all of the atoms in a gas, even for hot (i.e., thermal) plasmas, such as welding arcs and spark plugs (Fridman *et al.*, 2005). Within these hot plasmas, all species are incredibly reactive. Determining factor for the production of cold plasma by various types of reaction can be estimated by the chemical composition of gases used in it (Lieberman and Lichtenberg, 2005; Niemira and Gutsol, 2011).

### **Types of Plasma**

Type of energy supplied and amount of energy transferred to plasma initiate a change into the temperature of the electron which leads to the classification of plasma into two groups high-temperature plasma and low-temperature plasma (Nehra *et al.*, 2008). High-temperature plasma implies that neutral species of an electron, ions and neutral species are in a thermal equilibrium state. Low-temperature plasma can be further subdivided into thermal plasma (quasi-equilibrium plasma), also called local thermodynamic equilibrium (LTE) plasmas where species are in balance or near equality between electrons, ions and neutrals and nonthermal plasma(NTP) (non-equilibrium plasma), and also called non-local thermodynamic equilibrium plasmas (non-LTP) (Tendero *et al.*, 2006).

Plasma can also be distinguished into two classes depending on the pressure conditions, as high-pressure and low-pressure plasma. Another type of plasma which is generated at normal atmospheric pressure, known as atmospheric pressure plasma.

This type of plasma production is cost effective because it does not require reaction chambers to maintain pressure (Pankaj *et al.*, 2018). The nonthermal plasma, where electrons and more massive species are in thermal non-equilibrium, is referred to as cold plasma (CP). Cold atmospheric plasma (CP) is a novel nonthermal process with great antimicrobial potential.

The antimicrobial efficacy of CP is beneficial to food retailers and producers for extending shelf-life and ensuring food safety of fresh commodities along the food chain (Smeu and Nicolau, 2014).

### **Generation of cold plasma**

#### **Power Sources**

Power sources used for the generation of atmospheric pressure plasma are microwave, RF (radio frequency), pulsed, AC (alternating current), DC (direct current) or pulsed high voltages applied with repetition rates in the kilohertz range and mechanical, thermal, nuclear, electricity, radiation, extremely rapid compression and laser light energy sources are used for ionization of the gas.

#### **Devices used for plasma generation**

Devices for the production of cold plasma at or near atmospheric pressure are corona discharge, dielectric barrier discharges (DBD) or plasma jet and microwave plasma (Figure 1). Although other devices such as micro hollow cathode discharge, radio frequency plasma (RFP), gliding arc discharge, one atmospheric uniform glow discharge, dielectric plasma needle have been used for plasma production. Among all, dielectric barrier discharges (DBD) and Atmospheric Pressure Plasma Jet (APPJ) are most commonly used in the food industry (Ragni *et al.*, 2010; Nehra *et al.*, 2008).

### **Dielectric Barrier Discharge (DBD)**

Two flat metal electrodes, where at least one of these electrodes is covered with a dielectric material constitute DBD. Dielectric barriers (a stabilizing material) avoid arc transition, and help in creating a large number of micro-discharges for homogeneous treatments.

Plasma is created after ionization of a carrier gas by alternative current high voltages in kHz range (power 10-100 W) which moves between high voltage and grounded electrode.

There are variations in the configuration of the electrodes, but the concept behind them all remains the same (Hoffmann *et al.*, 2013). It can be applied for sterilization of living tissue, bacteria inactivation, angiogenesis, surface treatment and excimer formation.

### **Atmospheric pressure plasma jet**

#### **Radiofrequency plasma jets**

It is type of plasma jet, which is used for bacterial inactivation at atmospheric pressure, is called the Atmospheric Pressure Plasma Jet (APPJ) (Schutze *et al.*, 1998). The APPJ consists of two coaxial electrodes between which a gas (mixtures of helium, oxygen, and other gases) is transmitted at a high speed. The outermost electrode is grounded while Radio Frequency (RF) power (50- 100W) at 13.56 MHz is applied to the central electrode that creates a plasma discharge. The reactive species produced exits the nozzle at high velocity and arrives at the area that is to be treated.

APPJ has been used for the inactivation of several food born and harmful micro-organisms (Herrmann *et al.*, 1999; Abramson *et al.*, 2006; Hong *et al.*, 2009; Fricke *et al.*, 2012; Niemira., 2012; Tseng *et al.*, 2012; Alkawareek *et al.*, 2012; Jiang *et al.*, 2012; Matthes *et al.*, 2012; Hoffmann *et al.*, 2013).

### **Pulsed direct current-driven plasma jets**

Laroussi *et al.*, (2006) developed a miniature jet which he named as plasma pencil (Barekzi *et al.*, 2012).

It consists of a dielectric cylindrical tube where two disk electrodes of the same width as the tube are inserted.

The two electrodes are separated by a space (the distance can vary from 0.3 to 1 cm) and consist of a thin ring of copper attached to a dielectric disk. To generate the plasma, gases are injected through the holes of the electrodes for sub-microsecond with high voltage pulses.

A plasma plume (up to 5cm in length at temperature 290K) is launched through the shaft of the outer electrode into the air at the time of discharge.

The supply of electrical power through high voltage is provided by pulse generator. The plasma pencil has been used in the treatment of *E. coli*, Leukemia cells, and *P. gingivalis* (Foster *et al.*, 2010; Mahesh *et al.*, 2011).

### **Cold plasma for the safety and sustainability in the fish processing industry**

The natural composition of fish and the contaminations they encounter during the processing are the leading causes for the onset and subsequent undesirable quality changes in these commodities (Mahmud *et al.*, 2018). The spoilage mechanisms associated with microbial metabolic activities, endogenous enzymatic activities and chemical oxidation of lipids, all of shortening the shelf life of seafood. So the processing of seafood in a proper way is significant to make it suitable for the consumption for the final consumer.

Application of cold plasma on food which is at low temperatures, short processing times have been made in several processing stages such as treatment to raw material, intermediate or finished products, processing water, processing types of equipment and environment. Bourke *et al.*, (2018) showed the therapy to be energy efficient with a high antimicrobial effect on food quality and environment (Milosavljevic *et al.*, 2007; Bourke *et al.*, 2018).

Zouelm *et al.*, (2019) estimated the effects of cold plasma on chemical spoilage of pacific white shrimp (*Litopenaeus vannamei*) during frozen storage. Cold plasma (CP) was applied for different periods, i.e. 45, 90, and 150second as T1, T2, and T3, respectively, to freshly harvested shrimp. Post-mortem changes during cold storage reduce shelf life. The biochemical parameters and melanosis were analysed in comparison to metabisulphite treated (TM) and control sample during 12 days of frozen storage. The results showed that increase in pH, total volatile base nitrogen (TVB-N) content, thiobarbituric acid reactive substances (TBARS), free fatty acid (FFA), and peroxide value (PV) in shrimp exposed to CP and metabisulphite compared to control. Albertos *et al.*, (2017) estimated the significant effect of atmospheric cold plasma generated by a novel in-package dielectric barrier discharge (DBD) on lipid. However, effects on lipid oxidation parameters (PV, Dienes) were observed for the oxidation of the treated sample.

Nevertheless, no changes in pH or colour (except for L\*) were observed. These results suggest atmospheric cold plasma generated by DBD could be implemented as a technology for fish processing, retaining product quality over its shelf life.

### **Plasma-Activated Water (PAW) for chilling**

Plasma-treated water (PTW) an aqueous solution which is processed with plasma and the treatment results produces a wide range of chemically active species that can be retained within the water. Plasma treatment can be applied to liquid waste from various foods processing industry for decontamination or sterilization purposes. The term plasma-activated water is widely used for plasma medicine applications.

Liao *et al.*, (2018) uses plasma-activated water (PAW) ice for the preservation of fresh shrimps. The changes in microbiological, physical, chemical and protein properties were investigated during storage with conventional tap water (TW) ice and PAW ice. Compared with TW ice, PAW ice showed a significant advantage for inhibition of microbial growth, extending the storage time by 4–8 days. The pH of shrimps treated with PAW ice remained below 7.7 during storage. The PAW ice treatment delayed the deteriorating changes in colour characteristics and hardness. The production of volatile basic nitrogen (TVBN) was reduced to below 20 mg/100 g during PAW ice storage, significantly lower ( $p < 0.05$ ) than that of the samples treated with TW ice. Besides, PAW ice did not result in adverse changes in shrimp proteins. Therefore, the study showed that PAW ice might be used in the preservation of fresh seafood.

### **Antimicrobial effect of plasma on sea food**

A minimal attempt has been made at the use of plasma technology to enhance the quality and safety of seafood. Lee *et al.*, (2011) showed that CP treatment for 2 min with helium gas (5 L/min) mixed with oxygen (100 mL/min) at 60 Hz and 30 kV/cm retarded the growth of *L. monocytogenes* in smoked salmon by 1 log CFU/g.

Chiper *et al.*, (2011) reported that the population of *Photobacterium phosphoreum*, a bacterium associated with seafood spoilage in cold-smoked salmon, was significantly reduced ( $<3$  log CFU/g) by CP (air and air + 7% CO<sub>2</sub> mixture) treatments operated at an applied voltage: 13 kV at 15 kHz frequency for in 60 to 120 sec.

Park and Ha (2015) reported a significant decrease in the counts of *Cladosporium cladosporioides* and *Penicillium citrinum* on dried filefish fillets with increasing cold oxygen plasma (air subjected to high-energy deep-ultraviolet (UV) light with an effective radiation spectrum between 180 and 270 nm) with treatment times of 3 to 20 min.

Bacterial spores are most resistant form of life. Non-thermal atmospheric gas discharge plasma is effective sterilization methods that have very fewer disadvantages on the food quality and leaves no chemical residue. In this study, they used a helium radio-frequency cold plasma jet to examine its sporicidal effect on selected strains of gram-positive bacteria (*Bacillus* and *Clostridium spp*). The species tested included *B. subtilis*, *B. stearothermophilus*, *Cl. sporogenes*, *Cl. perfringens*, *Cl. difficile*, and *Cl. botulinum* type A and E. The plasmas were useful in inactivating spores of *Bacillus* and *Clostridium spp* with D values ranging from 2 to 8 min. Among all spores, *C. botulinum* type A and *C. sporogenes* were more resistant to plasma inactivation than other species.

Choi *et al.*, (2016) studied, microbial decontamination of dried Alaska pollock shreds using corona discharge plasma jet (CDPJ). Corona plasma jet was generated at a current strength of 1.5 A, and a span length of 25 mm was maintained between the electrode tip and fish sample. Upon the CDPJ treatment (0 to 3 min) of dried shreds, microbial

contaminants namely aerobic and marine bacteria, and *Staphylococcus aureus* were inactivated by 2.5, 1.5, and >1.0 log units, respectively. Also, a one-log reduction in molds and yeasts contaminants was observed.

The treatment of cold-smoked salmon packed in a sealed package, using a Dielectric-barrier discharge (DBD) plasma (operated at an applied voltage: 13 kV at 15 kHz frequency) in Ar and Ar + 7% CO<sub>2</sub> mixture has been reported (Chiper *et al.*, 2011). Up to a 3 log CFU/g decrease in the population of *Photobacterium phosphoreum* was observed from fish samples within 60–120 s of cold plasma treatment.

Park and Ha (2015) examine the effects of cold oxygen plasma on dried filefish fillets (*Stephanole piscirrhifer*) of the reductions of *Cladosporium cladosporioides* and *Penicillium citrinum*. Their plasma source employed relied on the use of high-energy ultraviolet radiation between 180 and 270 nm for the ionisation. They were able to estimate the reduction in both bacteria on the treated fillets after >10 min by >1 log CFU/g

Albertos *et al.*, (2017) estimated the effect of atmospheric cold plasma on microbial and quality parameters of mackerel fillets. Dielectric Barrier Discharge treatment, with 70 kV and 80 kV voltage and different treatment time (1, 3 and 5 min) reduced total aerobic psychrotrophic, *Pseudomonas* and lactic acid bacteria) were significantly reduced.

### **Mechanism of bacterial inactivation by cold plasma**

Inactivation of food-related microorganisms by plasma treatment is commonly conducted using model systems. An overview of microbial inactivation in model systems using nonthermal plasma published during the last

three years is given by Wan *et al.*, (2009). The antimicrobial activity of nonthermal plasma against Gram-negative and Gram-positive bacteria, yeast and fungi, biofilm formers, and endospores was shown in various studies (Brandenburg *et al.*, 2007, Kelly-Wintenberg *et al.*, 1999, Laroussi, 2005; Montie *et al.*, 2000; Vleugels *et al.*, 2005). Although several reviews focus on the inactivation mechanisms of plasma (Boudam *et al.*, 2006; Gaunt *et al.*, 2006; Moisan *et al.*, 2001; Moreau *et al.*, 2008), it is not yet fully understood. Microbial contamination has a significant economic impact in the seafood industry as it leads to product contamination, equipment damage, production downtime, energy losses, and investigations (Eissa *et al.*, 2014). Owing to their high-level heat resistance by spores produced by certain bacteria such as *Bacillus* and *Clostridium* under unfavourable environmental conditions, various sterilization processes are designed in such a way as to include the bacterial spores in the inactivating process (Hugo and Russell, 1998; Setlow, 2013). On the other hand, the existence of fungi or molds, especially mycotoxin and antibiotics producers, in manufacturing environments causes more concern since these types of organisms spread very rapidly by forming spores that are easily transferred from one site to another (Eissa *et al.*, 2014). Ordinarily, thermal processing is used to produce microbiologically, safe and stable food products. However, it is not a preferred method due to the loss of nutritional and sensorial qualities. This has led to the emergence of mild nonthermal decontamination technologies such as nonthermal plasma (Ekezie *et al.*, 2017).

Moisan *et al.*, (2001) stated that three primary mechanisms are involved in plasma inactivation to microbes: (a) ultraviolet (UV) irradiation of genetic material, i.e. damage to membranes and internal cellular components by UV radiation (b) intrinsic photodesorption,

means chemical interaction of radicals, reactive species, or charged particles with cell membranes. (c) etching means DNA strands may be broken by UV generated during recombination of the plasma species (Moisan *et al.*, 2002) (Figure 2).

Moreau *et al.*, (2008) compared plasma inactivation effects to the effects of micropulse. Similar to the impact of micro pulses, the cell membranes of microorganisms are perforated after plasma treatment. Besides the perforation of the cell membrane, the inactivation effect of plasma is induced by the bombardment of the cell membrane by radicals (OH or NO). These radicals are absorbed onto the bacteria surface, and volatile components are formed and eliminated from the cells (etching).

Two mechanisms of plasma inactivation, also described by Gaunt *et al.*, (2006) are the electrostatic disruption of cell membranes and lethal oxidation of cellular components.

While on a given commodity, one mode of action may be more significant than another, the most excellent sanitizing efficacy results from plasma with multiple antimicrobial mechanisms (Moisan *et al.*, 2002; Laroussi, 2002; Niemira, 2012). Lee *et al.*, (2011) estimated the effects of nonthermal plasma treatments against *Salmonella typhimurium*, *Escherichia coli* O157: H7, and *Listeria monocytogenes* living on polystyrene (PS), sausage casings, and smoked salmon were investigated. Inoculated PS, casings, and salmon were treated with nonthermal plasma generated with helium (5 L/min) or with both helium (5 L/min) and oxygen (100 mL/min) at 60 Hz and 30 kV/cm for 2, 5, or 10 min. *S. typhimurium* exhibited the highest sensitivity to the helium-used treatment. The most considerable reduction ( $3.9 \pm 0.8$  log CFU/cm<sup>2</sup>) was observed with *L. monocytogenes* on PS after the treatment with the mixed gas for 5

min. The treatment with the mixed gas inhibited *L. monocytogenes* on casings and salmon by  $0.5 \pm 0.3$  log CFU/cm<sup>2</sup> and  $1.0 \pm 0.3$  log CFU/g, respectively. Different treatment times did not result in different reductions of *L. monocytogenes* on both casings and salmon. The types of treatment gas and material of contamination need to be considered for evaluating the antimicrobial effects of nonthermal plasma treatments.

## **Plasma effect on the nutritional quality of seafood**

### **Effect on protein**

Protein can be denatured by the activity of cold plasma reactive species with amino acids and loss in the secondary structure due to injury of  $\alpha$ -helix and  $\beta$ -sheet (Li *et al.*, 2014; Segat *et al.*, 2016)

The effects of CP were studied on the muscle of raw mackerel, where it resulted in a decrease in immobilized water located in the protein-dense myofibrillar network (Albertos *et al.*, 2017).

Chen *et al.*, (2019) analyses effect of cold plasma on the microstructure of chub mackerel (*Scomber japonicus*) fillets. He was able to find that microstructure of the fillet of the Atmospheric cold plasma (ACP) treated and untreated chub mackerel was observed through a scanning electron microscope (SEM). The myofibrils and intramuscular connective tissues in the microstructures of the untreated samples differed from those of the treated samples. The muscle of the fresh fish displayed a bright and dense myofibril structure. No evident cracks appeared in the intramuscular connective tissues of the raw samples. Similarly, the ACP-pretreated samples maintained their regular and dense myofibril structure after six days of storage. The connective tissues were tightly connected.

On the contrary, the batch without the ACP pretreatment was characterized by loose myofibril structure and marked ruptures after six days of storage, indicating microstructure deterioration. The occurrence of breakdowns was probably due to the degradation of myofibrillar protein, which constitutes intramuscular connective tissues.

### **Impact on enzymes**

Enzymes as biocatalysts are widely applied to the food industry to improve the biochemistry reaction rates. Endogenous enzymes are naturally present in foods display either desirable or undesirable impacts on texture, colour and flavour of foods during food processing or preservation (Pasquali *et al.*, 2016; Zhang *et al.*, 2018). The sufficient inactivation of enzymes in foods is also necessary to advance our quest to develop cold plasma technology which could genuinely compete with thermal processing methods. The studies reported in the literature point to changes in the protein structure at multiple scales ranging from amino acids, specific linkages and the secondary structures. The plasma-induced changes in enzyme's activity depend on the environment, i.e. whether it is a simple buffered medium or a complex food extract, in addition to the parameters of the plasma process itself.

Dudak *et al.*, (2007) found a decrease of enzyme activity after treatment with plasma generated in Radio frequency driven glow discharge with the highest decline in operation within the first 10 minutes of treatment. They showed plasma-chemical oxidation as well as fragmentation of the proteins. Additionally, changes in the secondary protein structure due to the plasma treatment were detected. A fragmentation of proteins was also found by Deng *et al.*, (2007) after DBD treatment. In this process, atomic oxygen was shown to play a dominant role in destruction and degradation reactions. Oxygen plasma generated by RF

discharge led to a reduction of C-H and N-H bonds in casein protein and a modification of the secondary protein structure (Hayashi *et al.*, 2009).

Cold plasma has been reported to inactivate a range of enzymes such as lysozyme (Takai *et al.*, 2012), polyphenol oxidase and peroxidase (Pankaj *et al.*, 2013; Surowsky *et al.*, 2013; Tappi *et al.*, 2014).

Peroxidase (POD) and polyphenol oxidase (PPO) are essential enzymes which are responsible for melanosis in shellfishes, especially in shrimp. Peroxidases are often associated with reactions which could adversely influence food quality such as lipid and phenolic oxidations with consequent deterioration of flavour and colour. Mishra *et al.*, (2016) found that these enzymes are also important in vegetables and PPO catalyzes the hydroxylation of monophenols to o-diphenols and the oxidation of o-diphenols to the o-quinones.

The study by Surowsky *et al.*, (2013) shows that: non-thermal atmospheric pressure plasma is capable of reducing the activity of polyphenol oxidase and peroxidase. The inactivation efficiency depends on the plasma exposure time and gas composition; which leads to losses of the enzymes helical structure; and the active components inherent to the plasma are solely responsible for enzyme inactivation.

Zouelm *et al.*, (2019) estimated the effects of cold plasma on quality of endogenous enzymes polyphenol oxidase (PPO) enzyme, of pacific white shrimp (*Litopenaeus vannamei*) during refrigerated storage. Cold plasma was applied for 45, 90, and 150s as T1, T2, and T3, respectively, to freshly harvested shrimp. Results demonstrate that CP exposure effectively decreases the activity of polyphenol oxidase (PPO) enzyme, and prolonging the exposure to CP for 150 s

resulted in a 50% reduction in enzyme activity. They concluded that the application of CP for 90 s was the most efficient circumstance to extend the shelf life of white shrimp during cold storage.

A recent study was done by Ali *et al.*, (2016) on inactivation of tyrosinase by giving an exposure to plasma-treated eugenol derivatives. The plasma treatment was hypothesized to increase the functional groups in eugenol derivatives, which increase the interactions between the new compounds and tyrosinase. The authors also observed a change in the secondary structure of the enzyme by circular dichroism spectroscopy, on exposure to the derivatives. Plasma treatments have been shown to enhance the antibacterial activity of plant essential oils in food systems (Matan *et al.*, 2014a; Matan *et al.*, 2014b). However, the synergistic action on food enzymes remains unreported and is likely to have a positive impact.

Cold plasma is a promising, economic and environmentally friendly technology that exhibits the ability to inactivate endogenous enzymes activities such as PPO, POD and LOX in liquid or solid food systems, while the actions of  $\alpha$ -amylase and some antioxidase including SOD, CAT in an organism can be increased by applying cold plasma (Han *et al.*, 2019).

### **Effect on carbohydrates**

Carbohydrates play an essential role in defining and maintaining the quality of different food products. Seafood consists of a meagre amount of carbohydrate

Rodríguez *et al.*, (2017) reported an increase in sucrose content after prolonged exposure to CP, due to degradation of the oligosaccharides with a high degree of polymerization. A similar decrease in the fructose was also reported after CP treatment of prebiotic orange

juice (Almeida *et al.*, 2015). The studies suggest ozonolysis degradation causing the breakdown of glycoside bonds, leading to depolymerization of the macromolecule and the oxidation of functional groups to form carbonyl and carboxyl compounds, lactones, hydroperoxides and CO<sub>2</sub> (Ben'ko *et al.*, 2013; Almeida *et al.*, 2015).

CP alter the configuration of starch molecules, leading to transformation in swelling power, pasting characteristics, water absorption, enzyme susceptibility, solubility and changes in compositional, structural and thermal properties (Thirumdas *et al.*, 2017; Wu *et al.*, 2018).

Typically, these modifications are initiated via an increase in surface energy, incorporation of functional groups, cross-linking, depolymerization and change in hydrophilic nature (Thirumdas *et al.*, 2017).

### **Application of cold plasma in packaging**

Cold plasma technology is one of the advanced food processing technologies which find widespread potential as surface modification technique in the field of food packaging (Pahwa and Kumar, 2018). Cold plasma (CP) induces several chemical and physical processes in the plasma volume and on the plasma polymer interface, which modify the surface properties. This phenomenon is exploited in surface functionalisation to impart selective and tunable surface energies to the packaging polymers for promoting adhesion or sometimes anti-adhesion (Poncin-Epaillard *et al.*, 1999), improved printability, sealability, imparting antimicrobial properties and improving the polymer's resistance to mechanical failure. Packaging materials barrier properties towards gases (oxygen, carbon dioxide) and chemical solvents can be enhanced by using plasma deposition of barrier layers (Schneider *et al.*, 2009). A gas plasma reaction efficiently

inactivates polymer surface adhered-microorganisms (bacterial cells, spores, yeasts and moulds) within short treatment times. Muranyi *et al.*, (2007) established that packaging materials such as plastic bottles, lids and films can be rapidly sterilised using cold plasma, without adversely affecting their bulk properties or leaving any residues.

The plasma process is a simultaneous deposition/ removing process in which loosely deposited species over planar or topographical surfaces are sputtered off by reactive ions and radicals during deposition. However, it was shown that in some cases, UV photons could play a role in the inactivation process of microorganisms at atmospheric pressure (Boudam *et al.*, 2006).

**Atmospheric plasma: Characteristics and classification**

Properties	Local thermodynamic equilibrium plasmas (LTE)/ (Quasi-equilibrium plasma)	Non Local thermodynamic equilibrium plasmas (non- LTE)	References
<b>Current name</b>	Thermal plasma	Cold plasma	Tendero <i>et al.</i> , 2006
<b>Temperature</b>	$T_e=T_h$ 10,000 K	$T_e=10,000 - 100,000$ K $T_h=300 - 1000$ K	Tendero <i>et al.</i> , 2006; Misra <i>et al.</i> , 2016
<b>Pressure</b>	High pressure, 105 pa	Low pressure, 10pa	Scholtz <i>et al.</i> , 2015
<b>Density</b>	High electron density	Lower electron density	Tendero <i>et al.</i> , 2006
<b>Energy of Electrons</b>	Consumed by heavy particles ( $T_e=T_h$ )	Very High( $T_e \gg T_h$ )	Tendero <i>et al.</i> , 2006
<b>Constituents</b>	electrons, positive and negative ions, free radicals, and gas atoms, molecules	electrons, positive and negative ions, free radicals, and gas atoms, molecules	Tendero <i>et al.</i> , 2006
<b>State</b>	Excited/ionized	Excited	Tendero <i>et al.</i> , 2006
<b>Example</b>	Arc plasma	Glow discharges	Afshari and Hosseini., 2012

Whereas  $T_e$  - Temperature of electron and  $T_h$ - Temperature of heavy particles

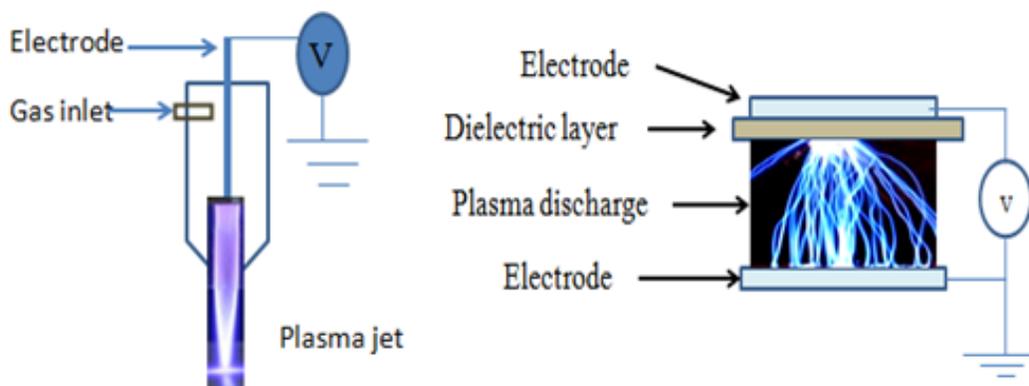


Figure 1. Devices used for production of atmospheric plasma: a) Plasma jet system; b) Dielectric barrier discharge

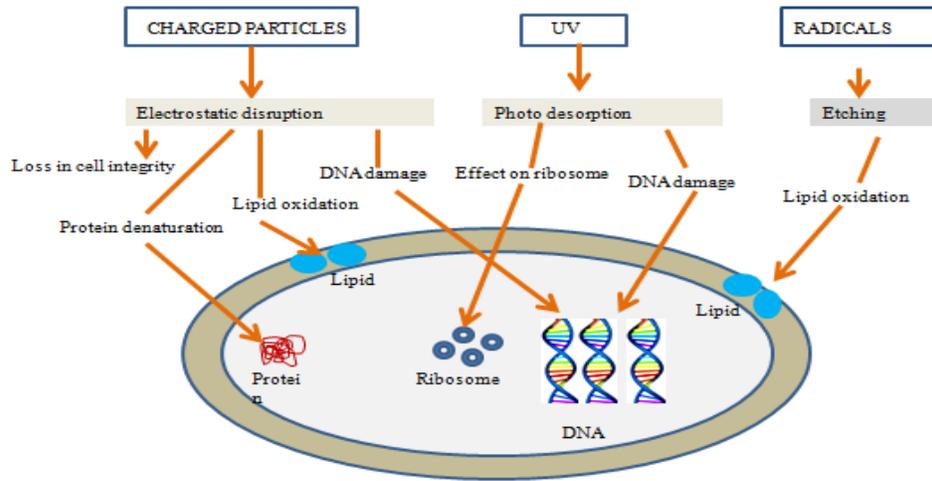


Figure 2. Schematic overview of cold atmospheric pressure plasma (CAPP) on inactivation mechanisms of bacterial cell

### Antioxidant activity of cold plasma

Antioxidants are considered as the first line of defence against free radicals. It is therefore of particular interest to elucidate and understand the fundamental interactions of plasma species with bioactive compounds, to avoid nutritional degradation or any other undesired effects in future applications. Antioxidants protect cells against the damaging effects of ROS (Reactive oxygen species), such as singlet oxygen, superoxide, peroxy radicals, hydroxyl ions and peroxynitrite etc. (Percival, 1996). There are only a few literatures available on the effect of plasma treatment on the phenolic compounds. Harborne and Williams (2000), reported that several plant species are tolerant to UV radiations accumulating flavonoid metabolites in epidermal cells. During plasma generation, the UV radiations formed may be responsible for the formation of phenolic compounds which are extracted from the cells of upper epidermis of leaves.

Ozone, atomic oxygen, UV radiations, photons, chemically reactive species, and charged particles generated in plasma are the active oxidising agents which are responsible

to affect the stability of microbial cell membranes and spawn the antimicrobial effect (Kelly-Wintenberg *et al.*, 1999; Brandenburg *et al.*, 2007; Perni *et al.*, 2008; Frohling *et al.*, 2012)

Seafood are rich in both polyunsaturated and saturated fats, which are much prone to oxidation during various processing methods. CP can decontaminate agricultural food products, Dairy products, meat products and poultry products in the food processing industry (Deng *et al.*, 2007).

Depending on the plasma sources, type of gases used, processing methods, and the concentrations of reactive species have different effect vary with various microbes.

Also, the different plasma devices have different inactivation kinetics regarding microbial cell (Frohling *et al.*, 2012). Atomic oxygen-reactive species can attach the bacterial cell wall, which makes them more prone to attack and lead to cell destruction (Critzler *et al.*, 2007). Oxidation of nucleic acids and amino acids also can cause changes in its fundamental properties, which can lead

damage to microorganism (Smeu and Nicolau, 2014).

### **Limitation of cold plasma technology**

Treatment with CP can induce lipid oxidation in fatty foods and other food products susceptible to oxidation. This may lead to the creation of short-chain fatty acids, aldehydes, hydroxyl acids, and keto acids, thus causing off-flavours and off-odours during storage (Ekezie *et al.*, 2017). Undesirable textural properties, acidity, and discolouration of treated food can occur. Also, surface topography can be influenced by plasma treatment (Fernandez-Gutierrez *et al.*, 2010). The high cost of installation is also a major drawback.

Currently, available data reveals that cold plasma technology could be utilised as a novel antimicrobial intervention for the inactivation of pathogens and improvement of the safety of foods of animal origin. However, studies performed to date also show certain limitations of cold plasma treatment in foods of animal origin, such as the acceleration of lipid oxidation and a negative impact on sensory characteristics. Further research is required to find out the effects of cold plasma on a broad range of quality aspects, including the sensory characteristics of various foods of animal origin, and the retention of these aspects during storage. Furthermore, the impact of cold plasma on the nutritional value of meat, eggs, fish, and their products requires comprehensive investigations. Additionally, the analysis of the marketability/consumer acceptance of cold plasma treated foods of animal origin is crucial, because the potential value of novel food technologies can only be realised if their application does not negatively affect the consumers' purchase decision making. In the past decade, CP treatment of food products has experienced increased popularity due to its potential contribution to non-thermal food processing. Several

experimental investigations have been conducted thus far on known applications while others explored new pathways for the exploitation of non-thermal plasma for the food industry.

Therefore, this review is a collation of recent studies focused on the applications of cold plasma in the food industry including microbial decontamination of food products, packaging material processing, modification of food components, seed germination performance and degradation of agrochemical residues. The review also highlights other trajectories for CP employment in the food industry such as hydrogenation of oils, mitigation of food allergens and anti-nutritional factors and effluent management. In consideration of the preceding, it should be safe to conclude that CP technology holds potential significance for the food industry.

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