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Plasma Technology in Food Industry: mini-review

Plazmové technologie v potravinářském průmyslu: mini-review

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Plasma treatment is an interesting technology with many potential applications in industry. At present, more and more often we encounter papers that deal with utilization of plasma technology in food industry. This mini-review provides an overview of the latest developments in this area. At the beginning the principles of plasma interaction with solid surfaces are shortly discussed. The next chapters are focused on sterilization of food from bacteria and fungi. The influence of plasma treatment on the food quality and nutritional parameters is discussed in last section.

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Ošetření plazmatem je zajímavá technologie s možností mnoha potenciálních aplikací v průmyslu. V současnosti se setkáváme stále častěji s články, které se zabývají využitím technologie plazmatu v potravinářském průmyslu. Tato mini-review uvádí přehled nejnovějšího vývoje v této oblasti. Úvodem jsou krátce diskutovány principy interakce plazmatu s pevným povrchem. Další část je věnována sterilizaci potravin od bakterií a hub. V poslední části jsou diskutovány otázky spojené s vlivem ošetření plazmatem na kvalitu potravin a jejich nutriční vlastnosti.

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Die Behandlung unter Anwendung der Plasma Technologie in der Industrie stellt eine interessante Technologie mit einer Möglichkeit von vielen potenziellen Möglichkeiten dar. Im Gegenwart man findet immer mehr Artikel mit der Applikation der Plasma Technologie Anwendung in der Lebensmittelindustrie. Der Artikel (Mini Review) bringt eine Übersicht der neuesten Entwicklung in diesem Bereich bei. In der Einleitung werden im kurz die Prinzipen der Interaktion Plasma mit der festen Oberfläche diskutiert. Ein anderer Teil wird dem Thema der Sterilisation von Lebensmitteln von Bakterien und Pilzen gewidmet. Im letzten Teil werden die mit dem Einfluss der Plasma Behandlung verbundene Fragen auf die Lebensmittelqualität und ihre Ernährungseigenschaften diskutiert.

Keywords: *plasma technology, sterilization, decontamination, food industry, bacteria, fungi, mycotoxins*

Klíčová slova: *plazmové technologie, sterilizace, dekontaminace, potravinářský průmysl, bakterie, plísně, mykotoxiny*

1 INTRODUCTION

High quality and safe foodstuffs are one of the fundamental achievements of our time. The quality of foodstuffs gain considerable attention and the hygiene limits are exceeded in Europe only in exceptional circumstances. Regardless, the Food and Agriculture Organization (FAO) estimated that nearly 25 percent of food is contaminated by undesirable chemicals, like pesticides or mycotoxins, or undesirable microorganisms, like fungi and bacteria (Köppen et al., 2010). These unwholesome substances get into the food due to pre-harvest or post-harvest contamination. Contamination of animal-origin foodstuffs, such as milk, meat or eggs, occurs mainly due to the feeding of contaminated feedstuffs.

The amount of undesirable microorganisms and chemicals in food and feed can be reduced by keeping appropriate measures during the primary agricultural production. Special technological procedures were developed, which can be used in order to reduce the quantity of these undesirable substances in raw materials for food production - for example, methods of physical separation, biological detoxification or suitable chemical procedures.

In this short mini-review we would like to introduce some potential applications of plasma technology in food industry, such as sterilization and preservation of raw materials by plasma discharge or undesirable chemical substances elimination from the foodstuffs.

2 THE MECHANISM OF LOW TEMPERATURE PLASMA ACTION ON MICROORGANISMS

Low temperature plasma is partially ionized gas, where the energy of almost all particles except electrons is the same or insignificantly higher than the room temperature. It is a source of many highly reactive particles, such as reactive oxygen, atomic oxygen (O), ozone (O_3), hydroxyl radicals (OH·) and nitrogen species (N_2, NO, NO_2, nitric oxide radical NO·) (Bußler et al., 2015). The concentration of these reactive particles in working gas can be customized according to the process needs by adding of gas admixtures into the working gas. Because of these features, low temperature discharges are still well utilized in many applications, such as material surface modification (Penkov et al., 2015), plasma etching or plasma chemistry.

The presence of highly reactive particles in plasma discharge is not the only mechanism, which is utilized in technical applications. Plasma is also a source of ultraviolet radiation in UV-A and UV-B spectrum (Laroussi and Leipold, 2004) which has been successfully used for a long time for sterilization of medical devices (V. Scholtz et al., 2015).

Last but not least, plasma discharge can be also used as a source of heat or as a source of intensive electrically charged particles flux (Bermúdez-Aguirre et al., 2013). In this point of view, plasma is a very complex system that offers wide scale of potential applications. Sterilization of cutting tools (Leipold et al., 2010), biomedical applications (Yang et al., 2011), decontamination of objects in sealed containers (Leipold et al., 2011), or inactivation of bacteria on disposable food containers (Yun et al., 2010) are examples of several applications developed recently.

Many systems were developed for generation of plasma discharges, which work in various working regimes. Unfortunately, the diversity of the devices and complexity of plasmas made the comparison of them almost impossible (Moreau et al., 2008), which also partially complicates further development. Although low pressure plasma systems are widely used in many applications, the development of equipments working at atmospheric pressure are strongly preferred because of easier utilization in commercial applications (Ziuzina et al., 2014; 2015; Baier et al., 2013; Schutze et al., 1998).

2.1 Effect of plasma discharges on bacteria

In food industry, the biggest progress has been achieved in plasma utilization for bacteria devitalization. Even so the research and development in this area are still in intensive progress.

A major issue of plasma sterilization is the respective role of UV radiation and highly reactive particles, such as atoms, molecules and radicals (Moisan et al., 2001). The concentration of these particles depends significantly on working gas composition. Experiments suggest that a significant role in the elimination of pathogens represent mainly oxygen and nitrogen molecules. It is a good combination in respect to the fact that the Earth atmosphere is formed mainly by these two gases. Cui, H. et al. (2016) refers low antimicrobial efficiency of pure cold nitrogen plasma against bacteria *Salmonella Enteritidis* and also *Salmonella Typhimurium* inoculated on eggshell surface. On contrary, Ragni, L. et al. (2010) showed significant reduction in the number of these bacteria, if discharge generated in air was used.

Fernández, and Thompson (2012) published the review surveying the main factors affecting the sensitivity and resistance of *Salmonella* to cold atmospheric gas plasma treatment as one of the methods for low-temperature innovative processes for food preservation. Fernández et al. (2012; 2013) proved that nitrogen plasma jet treatment of *Salmonella enterica* serovar Typhimurium on filter discs as well as inoculated on various fresh food (lettuce, strawberry or potato) leads to inactivation of the bacteria, but the inactivation rate depends strongly on the food surface features.

Maeda et al. (2015) tested inactivation of *Salmonella* cells by nitrogen gas plasma generated by a static induction as a pulsed power supply. No viable cell count was detected after plasma treatment for 5 min or longer, which confirmed that *Salmonella* was inactivated to a level below the detectable limit within 5 min. As shown, cell surface and genomic DNA of bacteria was damaged by plasma.

Inactivation of *Listeria monocytogenes* on agar and processed meat surfaces was also proved by Lee et al. (2011). The number of bacteria was reduced up by to 7.59 log unit, when treatment for 2 minutes by atmospheric pressure plasma jets of various gas mixtures was used. In the case of bacteria inoculated on sliced chicken meat and ham the reduction was 6.52. Moreover the maximal reduction was achieved in the case of nitrogen and oxygen mixture.

Highly positive effect of the plasma treatment by plasma processed air on different bacteria (*Bacillus atrophaeus, Escherichia coli, Listeria innocua, Pectobacterium carotovorum, Pseudomonas marginalis and Staphylococcus aureus*) was presented by Ehlbeck et al. (2015). The number of surviving bacteria in all monitored types decreased below the detection limit, when treated for 15 minutes.

Moreau et al. (2005) showed that cold plasma treatment by Gliding Arc has also highly positive effect on surviving bacteria of *Erwinia* spp. For treatments longer than 10 minutes, the level of the apparent bacterial population reached zero values for all tested strains.

The dependence of plasma treatment efficiency on the surface topography was studied also by Noriega et al. (2011). It was reported that reduction of *Listeria innocua* inoculated on membrane filters is more than 3 log after 10 s of plasma treatment whereas in the case of bacteria inoculated on chicken muscle the same reduction was achieved after 4 minutes of plasma treatment. Furthermore, the number of bacteria inoculated on chicken skin decreased even just 1 log after 8 minutes plasma treatment.

Naïtali et al. (2012) experimentally proved, that the humidity of the air also influences the oxidizing power of plasma discharge because of the generation of hydrogen peroxide and peroxynitrous acid/peroxynitrite - species involving quite similar mechanism of treatment as oxygen reactive particles.

Discharges burning in other gases than various mixtures of oxygen and nitrogen are tested in laboratory conditions, but their utilizations in practice seems to be rather hypothetical. Song et al. (2009) reported that the inactivation effects of RF discharge of 150 W, for 120 s burning in Helium at atmospheric pressure on *Listeria monocytogenes* are also strongly dependent on the type of inoculated food. More than 8 log reductions can be achieved in the case of sliced cheese, but in contrast, reductions ranged from 0.25 to 1.73 log CFU/g in the case of sliced ham.

The importance of the oxygen presence in the working gas also follows from the work of Kim et al. (2011), who conducted experiments with bacteria *Listeria monocytogenes*, *Escherichia coli*, and *Salmonella Typhimurium* inoculated on bacon. The effect of two different feeding gases (pure helium and mixture of helium and small amount of oxygen) was compared, whereas oxygen significantly increased the efficiency of overall process.

2.2 Plasma and Food Packaging Industry

The ability of plasma to kill bacteria can find use in food packaging industry. The technology can be used for sterilization of both the packaged product and the packaging material itself. Overview of low temperature plasma applications in food packaging can be found for example in the review of Pankaj et al. (2014). Some quite intensive research is still ongoing in this area as it can be clear from a literature review.

For instance the reduction in bacterial counts of *Bacillus cereus*, *Bacillus subtilis*, and *Escherichia coli* by approximately 2.30 log CFU/g inoculated on brown rice was presented by Lee et al. (2016), where cold low frequency plasma generated in ambient air in a plastic container with the samples was used. Also Wang et al. (2016) presented that in-package cold plasma treatment with packaging in modified atmosphere resulted in more than 4-log reduction of microbial populations compared with the air control during storage.

Also Rød et al. (2012) confirmed that indirect cold atmospheric pressure plasma treatment by dielectric barrier discharge can reduce *Listeria innocua,* namely on the surface of a ready-to-eat meat product (bresaola) inside sealed polyethylene bags. In addition such plasma treatment increased lipid oxidation, however, it was below the detectable threshold. Also concentrations of thiobarbituric acid reactive substances was increased after 14 days of storage at refrigerated temperature.

2.3 Plasma and foodstuffs quality

According to the results of laboratory experiments, plasma treatment can lead to significant reduction of the bacteria count on the food surface. Use of plasma technology in food industry will only be meaningful, when the food quality (foodstuff taste, aroma, and colour or undesirably affect foodstuff composition or its nutrition value) will not be affected by plasma treatment. Effective methods were developed for estimation of the quality of treated samples, for example Hlaváč et al. (2012), Božiková et al. (2014).

The ability of plasma utilization for improvement quality and safety of the fresh fruit and vegetables was well reviewed by Ramos et al. (2013). Minimal changes in the monitored parameters were confirmed in the case of application of atmospheric pressure cold plasma generated by dielectric barrier discharge to strawberries (Misra, N. N., Patil S. et al., 2014) or cherry tomatoes (Misra, N. N., Keener, K. M. et al., 2014). Minimal impact of plasma on the nutritional value of nuts was also demonstrated in the work of Amini and Ghoranneviss (2016). Kříž et al. (2014; 2015) reported minimal changes in nutrition values of the wheat and triticale seeds treated by Gliding Arc plasma for up to 4 minutes.

Ragni et al. (2010) applied a resistive barrier discharge for treatment of shell eggs contaminated by *Salmonela Enteritidis* and *Salmonella Typhimurium* and no significant negative effects on the eggs quality traits were observed, despite the long treatment times (up to 90 minutes). Wang et al. (2016) found that DBD plasma treatment does not cause any significant changes in surface lightness and therefore in the appearance of fresh chicken breast fillets with contemporary significant enhancement of microbial shelf life.

The study of Pasquali et al. (2016) proved the positive effect on *Listeria monocytogenes* and *Escherichia coli* bacteria decontamination of red chicory leaves, but significant changes in quality were observed. The quality remained relatively intact immediately after the cold plasma treatments whereas significant impact even in terms of visual quality was already observed after 1 day of storage with respect to the control untreated sample. On the other hand Baier et al. (2014) performed tests on corn salad, cucumber, apple, and tomato, and showed that the use of DBD does not maintain an adequate quality of the treated vegetable and fruit products.

Plasma treatment sometimes resulted into the foodstuff color changes. For example Bursać Kovačević et al. (2016) observed the change of the color of orange juice, when it was treated by plasma discharge. Simultaneously the increase of Anthocyanin content from 21% to 35% was observed. Ramazzina et al. (2015) referred the immediate loss of pigment on kiwifruit, when treated by plasma.

Besides color changes some articles referring to changes of the physical parameters of the plasma treated foodstuffs were published. For example Lee et al. (2016) observed significant hardness decrease of brown rice. Oh et al. (2016) used cold plasma treatment to investigate physical properties of defatted soybean meal based edible film used for the storage stability of smoked salmon. They achieved the changes in the tensile strength, elongation, and moisture barrier property of the film which increased by 6.8%, 13.4%, and 24.4%, respectively. The DBD gas plasma effect on fresh-cut apple quality was studied by Tappi et al. (2014).

The influence of plasma treatment on the antioxidant activity of the foodstuffs is next problem investigated by many researchers. For instance Chen et al. (2016) observed higher antioxidant activity of brown rice treated by cold plasma discharge, which can increase the nutrition value for consumers. Similar results were achieved by Lee et al. (2016), who also found slight pH decrease. On the other hand, Ramazzina et al. (2015) did not observed significant changes in antioxidants content and antioxidant activity of kiwifruit. Tappi et al. (2014) referred that influence of plasma on the reduction of polyphenol oxidase activity on the apple slices was found.

Cold plasma treatment did have a significant effect on the free fatty acid and phospholipid complement of the wheat flour. Both of these species, known to be highly oxidatively labile, were significantly reduced by the higher voltage treatment (20 V) for 60 s or 120 s (Bahrami et al., 2016).

2.4 Effect of plasma on fungi and mycotoxins

As follows from the previous chapters, plasma can be successfully used for surface sterilization of the bacteria infected food. Recently, the plasma application research has been intensively focused also on fungi elimination. These fungi generally produce undesirable chemical compounds, secondary metabolites – mycotoxins. They represent the adverse load with possible health risks for living organism (Iheshiulor et al., 2011; Devreese et al., 2014; Bryden, 2012; Bullerman and Bianchini, 2007; Malíř et al., 2013; Nagl and Schatzmayr, 2015). Currently, there are over three hundred known mycotoxins, of which about twenty are significant from a toxicological point of view. Certain types of mycotoxins can possess additional combined toxic effect (Speijers and Speijers, 2004).

Aflatoxin, deoxynivalenol, vomitoxin, ochratoxin, zearaleone and T-2 toxins are mycotoxins, which are most commonly considered due to their toxicity and frequency of occurrence in foods. The detailed summary of mycotoxins presence in the food and feedstuff is described for example by Bhat et al. (2010) or Kostelanska et al. (2009).

Mycotoxins are present in almost all of harvested grains, however, their concentrations can be affected by the agrotechnical procedures (Konvalina et al., 2016). Influence of the growing conditions on distribution of zearalenone in malted barley was also studied by Habschied et al. (2011). The results indicate the importance of storage conditions on zearaleone levels in commercially relevant grain fractions of malted barley.

Mycotoxins are thermally and chemically stable and the fungicidal treatment cannot change the levels of mycotoxins in barley (Malachová et al., 2010). Kottapalli and Wolf-Hall (2008) tried to decrease the mycotoxin concentration in infected barley by hot water treatment. Chemical and biological approaches for detoxification of trichothecene mycotoxins, such as alkalization, oxidation, reduction, hydrolysis, hydration and conjugation, were well reviewed by He et al. (2010). These approaches can decrease the concentration of mycotoxins, but the toxicity of products may remain the same.

Mycotoxins in beer are a specific issue, because these undesirable chemical compounds can be easily, and in high concentrations, wash out into the final product – beer. Experimental determination of the concentration of mycotoxins is quite complicated. Moreover, it is influenced by processes occurring inside the seed and varies with time (Pazderů et al., 2016; Maul et al., 2012; Wolf-Hall, 2007). Detailed analysis of the transfer of five Fusarium toxins – deoxynivalenol (DON), HT-2 toxin (HT-2), zearalenone (ZON) and sum of 15- and 3-acetyl-deoxynivalenol (ADONs) – from field barley through malt to beer was investigated in detail by K. Lancova and co-workers (Lancova et al., 2008). The content of monitored mycotoxins was higher in the malt compared with the original barley and the concentration tends to increase during the brewing process.

The occurrence of major mycotoxins in brewing barley was observed in detail between years 2008 and 2011 by Běláková et. al. (2014) and Bolechová et al. (2015). The concentrations were estimated by methods of high-performance liquid chromatography coupled with mass spectroscopy. DON occurred more frequently in tested samples, although only one sample exceeded the maximum allowable limit (MAL). The authors highly recommend to monitor the quality of input raw materials in order to ensure consumers' health protection. The concentration of DON and fumonisins was measured also by Piacentini at al. (2015).

Some works were focused on various plasma system application for reduction of fungi that often produce mycotoxins at high concentrations. The first significant work dealing with plasma degradation of mycotoxins was probably published by Park et al. (2007). For this issue microwave-induced argon plasma at atmospheric pressure was used. Unfortunately this work was solitary and research in this field has been switched into another direction in recent time. Amini and Ghoranneviss (2016) tested the effect of plasma on the fungus *Aspergillus flavus*, which are responsible for producing the mycotoxin aflatoxin during storage. Plasma jet treatment of dried walnuts for 10 minutes eliminated the fungi *Aspergillus flavus* from walnut surface. Plasma treatment of walnuts may be an effective way, how to reduce the production of mycotoxins during the storage.

Dasan et al. (2016) confirmed efficiency of a nonthermal atmospheric pressure fluidized bed plasma (APFBP) system used for decontamination of maize. The microbial flora of the maize grains contaminated with *Aspergillus flavus* and *Aspergillus parasiticus* spores decreased to less than 3 logs after 3 min APFBP treatment, and no viable cells were counted. Furthermore during the storage of plasma treated maize samples at 25 °C for 30 days, the *Aspergillus spp.* spores log reduction was maintained with no occurrence of regrowth.

Also Zahoranová et al. (2016) reported that plasma treatment by barrier discharge leads to a significant reduction of the toxigenic filamentous fungi, namely *Fusarium nivale, Fusarium culmorum, Trichothecium roseum, Aspergillus flavus,* and *Aspergillus clavatus* from artificially infected wheat seeds surface.

3 CONCLUSIONS

Treatment of foodstuff by cold plasma discharges leads to reduction of the number of microorganisms (bacteria, fungi) on it's surface. Plasma could be also used for decomposition of many undesirable chemical compounds, which are frequently present in foodstuff, for example pesticides or mycotoxins. Plasma discharge is capable to change slightly some properties of treated raw materials, like their color or consistency. Unfortunately, the promising results were obtained in laboratory conditions so far and expansion of plasma technologies in food-industry is not yet so large, as it could be expected due to mentioned results.

Many problems still require satisfying explanation. For example, an important question is, which intermediates are formed during decomposition of mycotoxins and other chemical compounds. They can be dangerous or even more dangerous than original mycotoxins.

It will be also necessary to explain, whether some undesirable mycotoxins are released into the foodstuff, when fungi are treated (killed) by plasma. Significant milestone will be upscaling of the whole process into industrial area, nevertheless it will be complicated due to wide variety of used devices and process parameters.

It is clear that the research in this field will intensively continue and it will gain on importance due to our increasing expectations on the foodstuff quality.

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