



OZONE TECHNOLOGIES FOR FOOD INDUSTRIES

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ABSTRACT

This paper addresses the use of ozone in the food industry. The main limitation to ozone use by food processors remains the lack of applied industrial knowledge. Although ozone has been commercially available for more than a century, its uses in agri-foods and food processing proliferated after its approval by the USFDA (2001) as an antimicrobial agent for direct contact with foods of all types. Described herein are specific commercial applications of ozone in food processing plants, particularly in conjunction with other food processing techniques (ultrasound, electrolyzed water, UV radiation, modified atmosphere packaging, etc.).

Key words : Ozone, agri-foods, food processing, commercial food processing plants, future prospects.

Consumers worldwide, and more particularly in the United States, are increasingly demanding fresh or fresh-like foods. To accommodate this demand is a profound need for environmentally safe and non-toxic elimination of pathogenic microorganisms from foods in order to prevent spoilage during transport or storage, retain quality, and prevent harmful disease transmission to consumers. Ozone is one of the emerging technologies that can be used to treat food products without imparting thermal degradation effects. The following review will discuss some key elements that would contribute to the success of implementing ozone to food industry. Main topics will be covered are: biocidal efficacy of ozone (both in gaseous and aqueous phase); ozone safety (how to use ozone properly); and integrated system for food applications (Ewell, 1950).

Because ozone is a safe, powerful disinfectant, it can be used to control biological growth of unwanted organisms in products and equipment used in the food processing industries. Ozone is particularly suited to the food industry because of its ability to disinfect microorganisms without adding chemical by-products to the food being treated, or to the food processing water or atmosphere in which food is stored. In aqueous solutions, ozone can be used to disinfect equipment, process water and some foodstuff. In gaseous form, ozone can act as a preservative for certain food products and can also sanitize food packaging materials. Some products currently being preserved with ozone include eggs during cold storage, fresh fruits and vegetables, and fresh fish.

Until recently, the food processing industry limited its use of ozone mainly to the treatment of bottled water and wastewater because ozone was not approved by the FDA for food applications. Recent actions, however, have cleared away some major barriers to wider applications of ozone. In 1997, through efforts of the Electric Power Research Institute (EPRI), the FDA granted ozone with the status of "Generally Recognized As Safe" (GRAS) as a sanitizer and disinfectant for foods. EPRI accomplished these following guidelines set forth by the FDA. The process involved assembling a panel of experts on food, toxicology and ozone to evaluate scientific and historic information on the use of ozone in food processing. The panel affirmed GRAS classification for ozone "as a sanitizer or disinfectant for foods when used at levels and by methods of application consistent with Good Manufacturing Practices." The FDA does not have to reaffirm the GRAS classification and food processors are now free to use ozone for sanitation or disinfection (Graham, et al., 1997). The GRAS classification for ozone was announced within a few months of the passage of a new Federal law which, for the first time, limits the presence of E. coli and Salmonella on meat and poultry. The timing of the GRAS classification is advantageous because ozone is particularly effective in inactivating these infectious agents.

Food processors and beverage manufacturers consume billions of gallons of water daily for food handling, washing, processing, cooking and for

cleaning equipment. All of this water must be free of contaminants. Even before ozone received GRAS status, the food and beverage industry had begun to recognize its potential as a disinfectant and as an alternative to chlorine, which traditionally has been used to treat food processing water. This is because ozone eliminates a problem associated with chlorine disinfection - the potential for the build-up of toxic residues of chlorine and chlorinated by-products in water that has been treated more than once (Rice *et al.*, 1982).

The new ruling allows food industry in all commodity categories to use ozone in either gaseous or aqueous form without any concentration limit as long as food manufacturer follows the guidance of good manufacturing practice (GMP). This ruling has led to an increase in interest and use of ozone by various segments of the food industry, ranging from production agriculture, packing, and processing operations. These uses of ozone as a sanitizing agent and alternative germicide are largely in the developmental stages, however, many companies are using ozone and the number is growing. Ozone is used as a gaseous fumigant applied to store rooms, coolers, silos, or the inside of transport vehicles, and ozone dissolved in water is used as an aqueous germicide solution for sanitation. Additionally, ozone provides an environmentally sound alternative to the processor for water treatment enabling extended use of water or recyclability.

In the early days of investigating applications for ozone in food processing, most efforts were concentrated upon maximizing the effects of ozone either as a strong disinfectant or as a strong oxidant, or maximizing both attributes simultaneously. Several food processing applications for ozone in aqueous solution derived from the commercial use of ozone in treating drinking water. However, after approval of ozone as an antimicrobial agent by the USFDA in 2001, many efforts to apply ozone to raw or cooked foods solely for disinfection ran afoul of the strong oxidizing capabilities of ozone. Although conditions could be found whereby the food could be disinfected with ozone, in all too many cases the food also was altered either in appearance or in taste due to oxidation side effects (Margosan and Smilanick, 2000). In recent

years it has been recognized that the combination of ozone with other acceptable food processing technologies (electrolyzed water, ultrasound, modified air packaging, ultraviolet radiation) can overcome the deficiencies of employing ozone by itself to solve a particular food disinfection problem.

Applications of Ozone in Food Industries : Ozone was discovered and named by SchoËnbein in 1840, but its applications for food treatment did not develop until much later. Studies conducted by the German Imperial Ministry of Health on the microbiological effects of ozone led to German approval of ozone for meat storage lockers in 1909 (Heise, 1917) at an ozone concentration of $\sim 3 \text{ mg/m}^3$ (ppm) applied every 3-4 hours, an amount sufficient to destroy more than 95% of individual spores located on the surface of culture media. In other applications, Hartman (1924) discussed cold storage of eggs in ozone-containing atmospheres. Gane (1936) found that exposure of ripening bananas to 1.5 and 7 ppm of ozone caused no changes in the rate of banana respiration, and was effective in retarding the rate of banana ripening, but only if the fruit was not within a few days of its period of rapid ripening. Salmon and LeGall (1936a,b) found that the storage life of freshly caught fish could be nearly doubled (extended to 5 days) by storing them under ice made from ozonized seawater. Thanks to the pioneering scientific research studies of Dr Shigezo Naito and his colleagues (Naito and Takahara, 2006, and multiple references cited therein) at the Aichi Industrial Technology Institute,

Food Research Center in Nagoya, the introduction of ozone treatments to food manufacturing plants began in 1982. Japanese food processing industries were looking for feasible ways of eliminating or greatly reducing levels of microorganisms in or on food products and thus producing safer foods. Currently, a major reason for recent interest in applying ozone to food processing applications is the 2001 approval by the US Food and Drug Administration of ozone as an antimicrobial agent for direct contact with all foods (USFDA, 2001). The most recent examples utilize ozone in combination with other food processing technologies, e.g. ultraviolet radiation (both for producing and interacting with ozone), electrolyzed water, ultrasound, and modified atmosphere packaging (MAP).

Ozone is now an accepted commercial

technology in many aspects of the agri- foods industry, ranging from irrigation (Parmenter *et al.*, 2004) and soil treatment, to spraying crops (to avoid spraying noxious chemicals - Steffen and Rice, 2008a,b), odor control in animal housing (Parmenter *et al.*, 2004), and for uses in food processing plants (water and air treatment, food processing, packaging and storage). Commercial applications also exist in fish hatcheries (Blogoslawski *et al.*, 1993; Eugster and Stanley, 1995; EPRI, 2002; Brazil and Summerfelt, 2005), many beverage-producing plants, and wineries (Steffens, 2006). Clean-in-place (CIP) washing of plant processing equipment and drains with ozone- containing water is now commonplace (Parmenter *et al.*, 2004; Lowe, 2002).

Ozone is applied in either gaseous or aqueous form. Ozone is very effective against bacteria because even concentrations as low as 0.01 ppm are toxic to bacteria. Whereas disinfection of bacteria by chlorine involves the diffusion of HOCl through the cell membrane, disinfection by ozone occurs with lysing (i.e., oxidative rupture) of the cell wall. Disinfection rates by ozone, however, depend on the type of organism and are affected by ozone concentration, temperature, pH, turbidity, the presence of ozone-oxidizable materials, the tendency (or not) for the microorganisms to form clumps, and the type of ozone contact or employed (Margosan *et al.*, 1989). The presence of ozone oxidizable substances in water exerts an ozone demand, and this can retard disinfection until the initial ozone demand has been satisfied, at which point rapid disinfection is observed. Its efficacy against a wide range of microorganisms, including bacteria, fungi, viruses, protozoa and bacterial fungal spores, has been reported (Restaino *et al.*, 1995; Khadre *et al.*, 2001). Such advantages make ozone attractive to the food industry and consequently it has been affirmed as Generally Recognised as Safe (GRAS) for use in food processing (Graham, 1997) and was approved as an antimicrobial food additive in 2001 (FDA, 2001). Several incidents of food borne disease have been associated with fruit and vegetable products.

In raw product storage, ozone is used to reduce and control growth of mold and fungi. Ozone does not penetrate into the product, rather, acts on the product's

surface. The atmosphere in the cold storage room is fed with ozone, and shelf life is extended by this exposure of the product surfaces to a gaseous ozone atmosphere. The ozone in the room also acts to inhibit the growth of surface molds on the walls and other surfaces of the cold storage room.

Ozone would work as a good disinfectant as long as we recognize the importance of the safety, its biocidal efficacy, and be sure to integrate all necessary components into one system. In addition, we have to remember that each food product is unique, hence, we need to understand the nature of our product and process, and formulate the optimum ozone parameters into the processing line. Some of the ozone uses in food industries are as follows.

Removal of contaminants : Fungicides, pesticides and other chemicals used during farming practices can contaminate the surface of food. This can be potentially dangerous as simple washing cannot remove these accumulations. Ozone can be used to oxidize the chemicals and remove the contaminant safe for sale or for further processing.

Cleaning in process (CIP) : Ozone charged water is used for CIP for cleaning pipes, tanks floors, surface equipment etc. Use of ozone system to food processing is that it provides the opportunity to reuse the water that could bring about a lot of savings in terms of availability and water cost. CIP washing of plant processing equipment and drains with ozone-containing water is now common practice (Parmenter *et al.*, 2004; Lowe, 2002).

Sanitation : Food for consumption must be free from pathogenic microorganisms. Contamination can occur from harvesting stage, during transportation, from processing water, equipment or from human interventions or by cross contamination. Usually non-oxidative biocides such as chlorine were widely used for 2-log unit reduction of microorganisms. Chlorine, the most common used disinfecting agent, selectively destroys certain intracellular enzyme systems, whereas ozone causes widespread oxidation of internal cellular proteins causing rapid cell death. Chlorine, however, is not effective for virus. Also it takes more concentration and exposure time for microbial reduction as compared to ozone since the mechanism is by penetration through the membrane. Ozone is an oxidative biocide and is better than non-oxidative to avoid undesirable taste or carcinogenic

effects. Ozone is 3000 times powerful than chlorine and regarded as Generally Recognised as Safe (GRAS). Commercial processing applications of ozone expanded in processing water treatments in the near future especially in fish hatcheries (Brazil and Summerfelt, 2005), beverage producing plants, and wineries (Steffens, 2006). The use of ozone for the sanitation of equipment and surfaces in the beverage manufacturing industry has yielded impressive results in terms of controlling microorganisms and saving costs due to less chemical handling and less maintenance (Hampson et al., 1994; Kereluk, 1971).

Stop ripening and spoilage : Consideration of fresh food requirement standards for consumers should assure fresh and safe food products. Ethylene formation on the food surface is responsible for the food ripening and spoilage. By virtue of its chemical properties, ozone prevents ethylene formation and thereby retards ripening and spoilage by microorganisms. This property extends the shelf life of food. Ozone oxidises ethylene completely and leaves carbon dioxide, water and oxygen (Rice et al., 1982). The reaction is as follows.



Cold storage : Utilisation of the properties makes ozone eminently suitable for increasing the storage life of perishables foods in refrigerated premises. At the same time, it is economic as the investment and operational cost of the equipment are on an acceptable level in relation to the size of refrigeration rooms. Its application eliminates the risk of unpleasant odours or other traces of antiseptics used for preservation of food stuffs. During storage ozone exerts a threefold effects by destroying the microorganisms, oxidising odours and affecting the processes of metabolism. Its primary action is mold free surface and has only slight depth of penetration. Increasing the moisture content of the environment favourably influences the germicidal effect. This brought about by the swelling of microbes making them more susceptible to destruction. Experiments conducted with beef showed that ozone is most efficient if the surface has a definite moisture content of around 60% ((Rice et al., 1982).

Biocidal Efficacy of Ozone : Ozone was shown to be a highly reactive oxidant with many of bacterial cellular constituents including lipids. It reacted especially well with proteins containing sulfhydryl groups. Generally, spores are 10–15 times more resistant to ozone than vegetative cells resulting from several layers of protection including a thick cortex, a multilayered

protein spore coat, and an exosporium. It is believed that the bacterial spore coat is the primary protective barrier against ozone. However, the resistance of spores only prolongs the inevitable, resulting in effective kills, with increased durations of ozone application. Virus particles are extremely small and only visible using an electron microscope. In recent years, hepatitis has been spread from infected produce handlers to patrons of salad bars in restaurants. Fortunately, ozone is extremely effective against the single protein layer of protection afforded by most viruses. Damage to RNA rather than capsid protein has been shown to be the major cause of polio virus type 1 inactivation by ozone. In all instances, the effectiveness of ozone and its mode of action can be traced to the oxidation of organic compounds.

Microorganisms attached to food surfaces weaken the effectiveness of sanitizers, and ozone is no exception. When microorganisms are attached to surfaces, their disinfectant resistance can be increased by 10- to 100-fold. It is the weakly attached bacteria which rinse away and are attacked by ozone most effectively. The presence of additional organic matter (a.k.a. biofilm) protects the microorganisms. It has been concluded that organic loading and poor ozone penetrability are key factors affecting the ability of ozone to disinfect surfaces rapidly (Kim *et al.*, 1999).

Nevertheless, in light of the fact that ozone attacks any organic molecules, it will over time cause a reduction of biofilms, which in turn will result in a cleaner environment, while still acting as a germicide. Ozone was most effective against microorganisms suspended in water and this indicated ozone's appropriateness for use in industries recycling wash water. Bacterial spores were most resistant followed by fungal spores and vegetative cells. Logarithmically growing cells were more resistant than those in lag phase. Polio virus type 1 in water was the most sensitive to oxidation using ozone. Gaseous ozone was effective in reducing microbial numbers after long exposures and/or high concentrations treatment. Several arguments have been presented for ozone's use as a powerful disinfectant (Rice *et al.*, 1982).

However, ozone alone may not be able to completely solve every microbiological contamination problem. Ozone applications can only be as effective as the systems for which they were designed. Other

elements, such as filtration, agitation, dispersion, combination with surfactants, low pH, low temperature, and soluble organic load are as important as ozone generation.

Ozone Safety : Food processors should be aware that although ozone can be used safely, ozone is an acute toxin, i.e., extremely irritating to the eyes, mucous membranes, and respiratory tract. Exposure to ozone levels in the range of 0.1–1.0 ppm can cause irritation of the eyes, headache, dryness of the throat, and coughing. The Occupational Safety and Health Administration (OSHA) has established the permissible exposure limit (PEL) of workers to ozone at 0.1 ppm. This represents the time-weighted average concentration that must not be exceeded during any 8 hour work shift of a 40 hour workweek. The short-term exposure limit (STEL), set at 0.3 ppm over 15 minutes, should not occur more than twice in an 8 hour workday (Barth *et al.*, 1995).

Finally, a concentration of 5 ppm ozone in air is generally accepted as “immediately dangerous to life or health” (IDLH). While the Environmental Protection Agency has established the level of the national ambient air quality standard for ozone at 0.12 ppm, it is not uncommon for populations of large metropolitan areas to be exposed to pollution levels in excess of this standard.

CONCLUSION

Ozone application has given promising results for important problems of food industry, such as mycotoxin and pesticide residues. Degradation products, formed after ozonation of these residues, have not exactly been determined, and this seems to be the most crucial obstacle on this subject. In vivo and in vitro toxicological tests are needed to be conducted to screen the effects of degradation products on human and animal health. Through emerging new techniques, as well as improvements and innovations in ozone generating and application systems, the subject will be evaluated more effectively in future. Ozone is an effective sanitizer with great potential applications in the food industry. It decomposes into simple oxygen with no safety concerns about consumption of residual byproduct. Due to its high oxidation capacity and microbial inactivation potential, ozone has prevented various kinds of microbial spoilages usually encountered in fruits and vegetables. Decontamination of products by ozone depends on number and kind of

contaminating microorganisms, physiology of the product, ozone application system, temperature, pH, and other factors. If improperly used, ozone can cause some deleterious effects on physiology and quality of products such as losses in sensory quality. For effective and safe use in food processing, optimum ozone concentration, contact time and other treatment conditions should be defined for all products. Pilot trials must be conducted before starting commercial application, because every ozone application is unique.

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