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# Application and Kinetics of Ozone in Food Preservation

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**ABSTRACT**
Ozone is activated oxygen and it is referred to as a triatomic form of oxygen. It is a natural agent and has a broad antimicrobial property, which together with an oxidation potential, make it an attractive option for the food industry. This article focuses on the use of ozone for preservation of vegetables, fruits and fruit juices, and highlights the inactivation mechanism of microorganisms. The application of ozone in grain storage and the quality of ozone treated grains is discussed, along with the reaction kinetics of ozone in grains.

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## Introduction

The current need of the food processing industries is innovative technologies to meet consumers demand for fresh and safe ready-to-eat products (Khadre, Yousef, and Kim 2001). Pulsed electric field, ohmic heating, cold plasma technique, high pressure processing, UV light treatment and pulsed light are some of these emerging technologies. Now the attention is focused on ozone as a powerful antimicrobial agent that may meet the requirements of the food industry, and achieve approval of food regulatory agencies and acceptance by the consumer.

Ozone is an unstable gas that is a natural part of the troposphere by the interaction of solar radiation with hydrocarbon (Steckel and Engdahl 1978). As an oxidizing agent in organic reaction, ozone is used in many fields such as pulp bleaching, water sanitation (drinking and bottled water treatment and swimming pool treatment), cooling tower treatment, disinfection of medical appliances, as well as odor control (Loeb 2011; Pandiselvam, Thirupathi, and Anandakumar 2015). Its application to the food preservation industry is attractive because ozone auto decomposes into oxygen leaving no toxic residues into environment (Tiwari et al. 2008). The advantage of ozone gas is that it is generated on-site using an oxygen cylinder or oxygen concentrator with an ozone generator at the time of use, which eliminates the need for storage (Kells et al. 2001; Pandiselvam et al. 2016a). This leads to much savings in the costs of transporting and storing antimicrobial agents or fumigants. Ozone treatment saves energy because it requires no thermal energy (Khadre, Yousef, and Kim 2001). The U.S. FDA approved its use as a direct additive for food (FDA 2001). An FDA Guidance manual in 2004 provided guidelines for processors of apple juice (cider) on the use of ozone for pathogen reduction purposes (FDA 2004).

## Properties of ozone

Ozone is a colorless gas with pungent odor that decomposes rapidly at room temperature. The high oxidation rate of ozone is due to the electron arrangement of the molecule (Beltran 2003). The molecular weight of ozone is 48, melting point −192.5 °C and boiling point −111.9 °C at 1 atm (Zhao and Cranston 1995). Density of ozone (2.14 kg $m^{-3}$) at standard temperature and pressure is 1.5 times greater than the density of air (1.43 kg $m^{-3}$). Oxidation potential of ozone is high (−2.07 V) as compared to that of chlorine (−1.36 V) (Brady and Humiston 1978). Consequently, it is capable of oxidizing organic and inorganic materials. In the stratosphere, UV radiation helps to degrade the ozone molecule. It absorbs the UV energy and converted to oxygen before it reaches the earth's surface. In addition to UV irradiation hydrogen peroxide, high pH and activated carbon enhance the decay rate of ozone (Jans and Hoigné 1998).

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The time required for a reduction in volume of ozone gas to decrease by half is shorter in an aqueous state than when compared with a gaseous state (Rice 1986). In distilled water the half-life of ozone ranges between 20 and 30 min at 20 °C. But in practical situations, the half-life of ozone can range from few seconds (dirty water) to an hour (clean water). The decay rate of ozone is mainly affected by temperature and pH; increases in both variables increases the decay rate. At high temperatures, decomposition of ozone into hydroxyl free radicals is faster than at atmospheric conditions(Graham 1997). The half-life of ozone decreases as the temperature increases, ranging between 8 to 10 min at 35 °C (Cullen et al. 2009). At pH below 6.5 and at cold temperature, the half-life of ozone is very high in aqueous solution. However, if the pH increases to 8 and as water temperature increases, the half-life of ozone decreases rapidly. No ozone is detected in buffers with pH 9.0; if the pH is 10 at any temperature, the ozone decay rate is instantaneous.

## Generation of ozone

Ozone is a blue gas at ordinary temperature when generated from dried air, but it is colorless when generated from high-purity oxygen. For food processing applications, the color is not noticeable (Greene, Guzel-Seydim, and Seydim 2012). Manley and Niegowski (1967) suggested that the energetic process that can produce ozone molecules can destroy ozone. The ratio of reaction heat decreases significantly with increasing inlet gas temperature and specific energy, which represents how much energy is utilized effectively to synthesize ozone (Wei, Xu, and Zhang 2016). Therefore, ozone concentration cannot be increased beyond the point where the rates of formation and destruction are equal. Maximum achievable ozone concentration is about 8–14% w/w of oxygen. Due to high oxidation potential, ozone gas cannot be stored as it degrades spontaneously.

Ozone is generated by the exposure of atmospheric air to a high-energy source, such as ultraviolet radiation or high voltage electrical discharge (Khadre, Yousef, and Kim 2001). Ozone production is predominantly achieved by one of three methods: ultraviolet (UV) radiation, corona discharge and the electrolysis method.

### *Ultraviolet radiation method*

In the stratosphere, ozone is generated by UV irradiation at 185 nm from the sun and during thunderstorms (lightning discharge). Commercially fresh air (20% $O_2$) passes across an ultraviolet (UV) light source, typically less than 210 nm. These systems comprised a lower cost but also have a more limited output (Mustafa 1990).

### *Corona discharge method*

Generation of the free oxygen radical take places by breakage of O-O bonds, requiring a significant energy input (Rice and Bollyky 1981). Corona discharge generators pass oxygen enriched air across a corona or high energy electric field (>5,000 V), similar to an automobile spark plug, which results in splitting the diatomic oxygen molecule into valent oxygen atoms. These oxygen atoms have a negative charge and will bond with another oxygen atom to produce ozone (Suslow 2004). Ozone production varies depending on oxygen concentration in feed gas, dielectric material property, discharge gap, current frequency and voltage. However, as the voltage increases, the dielectric materials and electrodes are subject to failure. Ozone generator operating at higher frequencies produces higher concentration of ozone but more cooling is required removing the heat and preventing ozone decomposition (EPA 1999).

### *Electrolysis method*

An electrolysis method has been introduced by Lynntech, Inc. (College Station, Tex.), in which water is split into oxygen and hydrogen atoms by an electrochemical or electrolysis process. Hydrogen atoms are separated from the water mixture and oxygen atoms combine to form ozone. The manufacturer states their system produces ozone that is three to four times (10 to 18% $O_3$) higher than the corona discharge method.

## Ozone measurement techniques

Ozone gas concentration is measured by a commercial UV meter. The ozone feed rate will define ozone concentration multiplied by the feed gas flow rate. Total ozone content of a small-scale system over a certain period can be measured by the wet chemistry method (Rakness et al. 1996). The applied ozone dosage is calculated by multiplying the exposure time of ozonation with concentration and divided by the sample volume.

## Application of ozone in food industry

In the application of ozone in the food industry, safety of use is an important issue. Ozone detection and destruction systems are needed for the safety of workers in the food preservation/processing industry. In addition, an efficient ozone treatment needs to be developed to avoid the excess use of ozone. Hazard analysis and critical control point systems (HACCP) and good manufacturing practice (GMP) are also needed to control the high ozone demand materials in food preservation (Kim, Yousef, and Dave 1999).

## Application of ozone in vegetable preservation

Ozone is known to be effective antimicrobial against in all types of micro-organisms even at room temperature (Clark 2004). It increases the shelf life of vegetables due to a reduction in surface microbial count. It could be seen as an alternative to refrigeration in order to enhance vegetables' shelf life (Zambre, Venkatesh, and Shah 2010). Various optimization studies were found in the literature (Table 1) about the ozone treatment of vegetables and fruits, considering the antimicrobial efficacy of the treatment.

Within the food processing industry, ozone has been used for washing of vegetables and fruits (Karaca and Velioglu 2007). Table 1 depicts that relatively short contact time and low concentration of ozone are sufficient to inactivate the bacteria. However, inactivation of bacteria in wastewater requires higher ozone concentration and longer contact time because of oxidizable materials. Ozone at a concentration of 0.04 ppm has the potential for extending the shelf life of seedless cucumbers and broccoli stored at 3 °C (Skog and Chu 2001). Zhang et al. (2005) found that treatment with 0.18 ppm ozonated water has the best preservation effect of fresh-cut celery maintained for 9 days of storage at 4 °C. The optimum ozone concentration for fresh-cut green leaf lettuce was 2 ppm at 2-min exposure time on *Listeria monocytogenes* counts. Sensory quality of the ozone-treated vegetable was better than the chlorine and organic acid treatments (Olmez and Akbas 2009). Mushrooms were subjected to ozone treatment prior to packaging, which caused a reduction of the internal browning rate (Esciche et al. 2001). Ozone treatment delayed the development of red color and rotting of tomatoes. Shelf life of ozonated tomato was enhanced by 12 days when stored at 15 °C (Zambre, Venkatesh, and Shah 2010).

## Application of ozone in fruit preservation

In the United States (US), legislation requires a 5-log reduction of harmful microbes for fruit juice processors (FDA 2001). As a result, a number of commercial food processors in the US started to employ ozone for fruit juice treatment and water pasteurization (Tiwari, Muthukumarappan, and Cullen 2009). Hence, the feasibility of using ozone in fruit juice processing has been the focus of several studies. Use of ozone has been reported for various fruit juice processing including; apple cider (Choi and Nielsen 2005) and orange juice (Tiwari et al. 2008a). Achen and Yousef (2001) reported that the ozone treatments resulted in lower the weight loss and spoilage of apples. Five ppm of ozone at 1-h treatment could be successfully used for reducing both *Staphlyococcus aureus* populations and coliform on date fruits (Najafi et al. 2009).

However, ozone treatment resulted in some negative effects on the fruit juices. Ozonation resulted in more than 90% degradation of anthocyanin and color in blackberry juice (Tiwari, Muthukumarappan, and Cullen 2009). But ozone treatment on strawberry fruit surfaces (Perez et al. 1999) and blackberries (Barth et al. 1995) were reported to have minor effects on anthocyanin content. Skog and Chu (2001) reported that ozone could effectively control the ethylene accumulation in apple and pear storage rooms at 0.4 ppm. If the

**Table 1.** Antimicrobial effects of ozone under different treatment conditions.

| Vegetable | Target bacteria/fungi | Reduction | Ozone concentration | Exposure time | Medium | Reference |
|---|---|---|---|---|---|---|
| Tomato | *B. cinerea* | Total population inactivated | 3.8 ppm | 10 min | ozonated water | Ogawa, Feliciano, and Manji (1990) |
| Garlic and ginger | Total bacterial population | 80–90% | 6 mg/L/s | 60 min | Gaseous ozone | Kim et al. (1993) |
| Carrot | *Botrytis cinerea Pers* and *Sclerotinia sclerotiorum* | 50% reduction | 60 mg/L at 0.5 L/min | 8 h/day for 28 days | Gas mixture | Liew and Prange (1994) |
| Carrot | *Fecal coliforms* | <3 log reduction | 5 g/L/h | 30 min | ozonated water | Williams et al. (1995) |
| Lettuce | Total bacterial population | 3.9–4.6 log reduction | 4.9% (vol/vol) at 0.5 L/min | 5 min | Gaseous ozone + ozone water | Kim, Yousef, and Dave (1999) |
| Lettuce | *E. coli* O157:H7 | *E. coli* Population reduced from 8.12 log CFU/g to 6.45 log CFU/g | 9.3 ppm | - | ozonated water | Singh et al. (2002) |
| Carrots | *E. coli* O157:H7 | *E. coli* Population reduced from 7.85 log CFU/g to 5.93 log CFU/g | 9.3 ppm | - | ozonated water | Singh et al. (2002) |
| Lettuce | Natural microflora | Reduction of microflora on the lettuce by 1.4 log CFU/g | 7.5 ppm | - | Combination of ozone and chlorine | Garcia, Mount, and Davidson (2003) |
| Celery | Total bacterial population | Initial population 6.78 log CFU/g and ozone treated 5.63 log CFU/g | 0.18 ppm | 5 min | ozonated water | Zhang et al. (2005) |

atmospheric air was dry (35% RH), a dose of 5 to 10 times higher was required. Fumigation with high concentration of ozone during pre-cooling of grapes controlled post harvest decay and reduced residues of commonly used fungicides. Ozone fumigation up to 10,000 μ L $L^{-1}$ of ozone up to 2 h to control post harvest gray mold of table grapes caused by *Botrytis cinerea* (Gabler et al. 2010). [PQ1]

The effectiveness of ozone can be affected by product surface characteristics (Han et al. 2002) and application mode, such as agitation and bubbling of ozone (Kim, Yousef, and Chism 1999a). The antimicrobial activity of ozone will be influenced by variations in these factors and microorganisms surrounded in product surfaces are more resistant to ozone (Cullen et al. 2010). Oxidation reactions are caused by either dissolved molecular ozone or by free radical species formed during auto decomposition of ozone (Hunt and Marinas 1997). The half-life of gaseous ozone in ambient atmosphere depends on atmospheric temperature and relative humidity, but in water the half-life of dissolved ozone depends on the amount of ozone-demanding material present.

In the food processing industry, it is important to keep the applied ozone levels as low as possible. Not limited by regulation, but according to Henry's law, theoretical limit of ozone in water is about 30 ppm (μg $L^{-1}$ at 20 °C). It is known that the corrosion potential of stainless steel increases at above 1 ppm ozone concentration. Most of the materials used for fabricating food processing equipments are well suited with ozone at reasonable concentrations of 1 to 3 ppm (Pascual, Llorca, and Canut 2007). It would be easier to maintain these low levels of ozone in the processing industries. Moreover, achieving high concentrations of ozone in water is costly and difficult to stabilize. Therefore, the use of the lowest concentration of ozone for the disinfection of fruits and vegetables through optimization of parameters is important and necessary (Tiwari, Muthukumarappan, and Cullen 2009).

## Inactivation mechanism

Ozone is a powerful sanitizer that is suitable for application in fruits and vegetables processing industries in gaseous or aqueous states. Ozone or its decomposition products (hydroxyl radical) inactivate the microorganisms rapidly by reacting with nucleic material including thymine and cytosine (Ishizaki et al. 1981) and components of their cell envelope (polyunsaturated fatty acids, polysaccharides), intracellular enzymes and viral capsids or spore coats (amino acids) (Khadre, Yousef, and Kim 2001). Oxidation of sulfhydryl groups by ozone may inactivate the microorganisms. Ozone reacts with polysaccharides resulting to breakage of glycosidic bonds and formation of aldehydes and aliphatic acids (Bablon et al. 1991). It may oxidize various components of cell envelope including membrane, bound enzymes, polyunsaturated fatty acids, glycoproteins and glycolipids causing to leakage of cell contents and ultimately causing oxidative burst (Scott and Lesher 1963).

## Application of ozone in grain storage

The insects of stored products are controlled by Malathion and Dichlorvos (organophosphate insecticide) or by applying phosphine or methyl bromide. To control the insects, fumigant gases are heavily relied on in many countries. Consequently, resistance to phosphine is an increasing problem in controlling stored-product insects throughout the world (Benhalima et al. 2004). The problem of resistance to phosphine is worrisome and demands for the development and optimization of new techniques to manage the stored grain pests (Sousa et al. 2008).

Ozone is a highly reactive and strong oxidizing agent with insecticidal activity. The feasibility of using ozone in grain storage has been the focus of several studies. The ozone fumigation setup consists of an oxygen concentrator, ozone generator, storage bin, ozone analyzer and ozone destructor (Figure 1). The storage bin connects with the ozone generator to distribute the gaseous ozone throughout a grain mass. It is generally developed using stainless steel (SS 304) (because of corrosion resistance) to carry out the ozone fumigation study (Pandiselvam et al. 2016a).

Laboratory and field studies reported as ozone as a fumigant has shown promise in controlling stored-grain insects such as *Sitophilus oryzae, Rhyzopertha dominica, Tribolium castaneum, Oryzaephilus surinamensis* and *Ephestia elutella*. Table 2 lists the applications of ozone for the control of stored grain insect pests. Ozone toxicity varies, depending on the insect life stage. For example, larval and pupal stages of *T. castaneum* are ozone sensitive and sensitivity decreasing with age (Erdman 1980). Most of the ozone exposed *T. castaneum* larvae on paddy grains did not advance to the pupal stage because they were developmentally arrested. Kells et al. (2001) reported that high mortality was achieved for the larval stage of the Indian meal moth and *P. interpunctella* exposed to 50 ppm ozone for 3 days.

The eggs of *P. interpunctella* were requiring 180 min exposure at 1800 ppm ozone (McDonough, Mason, and Woloshuk 2011). Among the insects, *R. dominica* species were most difficult to kill, because it

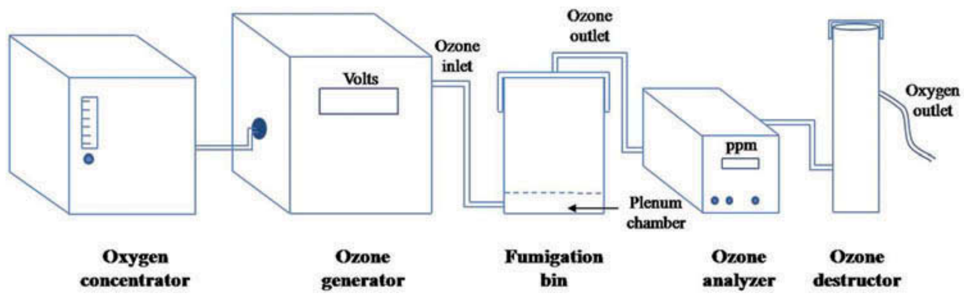


**Figure 1.** Schematic diagram of ozone fumigation setup.

**Table 2.** Effect of ozone treatment on major storage insects.

| Grain | Target insects | Ozone concentration | Exposure time | Mortality | Reference |
|---|---|---|---|---|---|
| Stored grain | Two Tribolium spp. (*Coleoptera: Tenebrionidae*) | 45 ppmv | ≥6.5 h | 100% | Erdman (1980) |
| Flour /corn meal mix | Saw-toothed grain beetle, *Oryzaephilus surinamensis* (L.) and confused flour beetle (Adult) | 5 ppm | 3 and 5 days | 100% | Mason, Woloshuk, and Maier (1997) |
| Stored grains | Adult confused flour beetles, Red flour beetles and Maize weevils | 10 ppm | 12, 9 and 4 days | 100% | Strait (1998) |
| Stored grains | *Tribolium confusum* *Tribolium castaneum* (Herbst), and *Sitophilus zeamais* (Adult) | 50 ppmv | 3 days | 100% | Mason et al. (1999) |
| Maize | *T. castaneum* (TC) *Sitophilus zeamais* (SZ) *P. interpunctella* (PI) | 25 ppm | 5 days | 91.4% (TC) 99.9% (SZ) 77.0% (PI) | Kells et al. (2001) |
| Corn | Adult *T. castaneum*, adult *S. zeamais*, and larval *P. interpuntella* | 50 ppmv | 3 days | 92–100% | Kells et al. (2001) |
| Maize | Adults of maize weevil, red flour beetle and larvae of Indianmeal moth | 50 ppmv | 3 days | 100% | Maier et al. (2006) |
| Corn | *Sitophilus zeamais* Mots. | 50 ppm ozone (8 L min-1) | 48 h | 100% | Faroni, Pereira, and Sousa (2007) |
| Wheat | *Sitophilus oryzae* (L.), adults | 25 and 50 ppmv | 4 and 2 days | 100% | Bonjour et al. (2008) |
| Maize | Adults of *S. zeamais* and *T. castaneum* | 50 mg $kg^{-1}$ | 23.76 and 64.19 h | 95% | Rozado et al. (2008) |
| Stored products mortality | *T. castaneum* *R. dominica* *O. surinamensis* | 50 ppm | 11.39–20.10 h (TC) 9.22–12.19 h (RD) 6.1–9.66 h (OS) | 50% | Sousa et al. (2008) |
| | *T. castaneum* (TC) *R. Dominica* (RD) *O. surinamensis* (OS) | | 22.17–37.9 h (TC) 21.85–35.17 h (RD) 11.03–18.72 h (OS) | 95% | |
| Wheat | *Tribolium castaneum* (Herbst) adults | 70 ppmv. | 4 days | 100% | Bonjour et al. (2011) |
| Wheat | Eggs of *P. interpunctella*, adult *S. zeamais* and adult *S. oryzae* | 1800 ppm | 180, 120 and 60 min | 100% | McDonough, Mason, and Woloshuk (2011) |
| Wheat | *Ephestia kuehniella* (EK) and *Tribolium confusum* du Val (TC) | 13.88 mg/L | 30-min interval ozone flush treatment for 5 h | 90–100% (L, P and A of EK) 72.6% (L) 1.3–22.7% (E, P and A of TC) | Isikber and Oztekin (2009) |

*Note*. *A-adults, L-larvae, P-pupae, E-eggs.

is more tolerant than *T. Castaneum* and *S. Oryzae* and because *R. dominica* have the ability to close spiracles for prolonged periods and account for failure of ozone to reach target tissue in effective concentrations. Similar results were found by Leesch (2003) treated *T. confusum* adults in a chamber with 300 ppm ozone at 18 h treatment to reach 100% mortality. Ozone gas was also reported to inactivate fungal spores on stored wheat by Wu, Doan, and Cuenca (2006) and on barley by Allen, Wu, and Doan (2003). Barley and wheat fumigated with ozone concentrations of 3000 and 6000 ppmv at 5-min exposure time resulted in 96% of fungal spores being inactivated.

Table 2 shows that, inside different media, the same concentration and fumigation time would not reach the same mortality. This difference was caused by the different structures of the grain and chemical composition on the surface of the materials. Difference in structures and chemical composition of the grains would influence the reaction of ozone on the surface of the materials (Jian, Jayas, and White 2013). After this reaction process, ozone will move freely and faster in the grain mass.

Completion of the ozone fumigation process also depends on the initial concentration, quantity of available ozone to react with insects, flow rate of the ozone and bed thickness and moisture content of grain mass. The initial saturation phase is until the target ozone concentration of 50 ppm is reached in the whole content of the grain mass. Once ozone reaches the desirable concentration (50 ppm), ozonated air must be moved through the grain mass and kept constant for the whole fumigation time to complete the ozonation sterilization (Kells et al. 2001). Pandiselvam et al. (2016a) observed a significant difference in ozone concentrations from 502 to 180 ppm between 0.2–0.6 m grain bed thicknesses.

Ozone at 47–106 ppm could damage the storage structure and rubber couplings in 2 months by corrosion. Most of the researchers used 50 ppm of ozone to control the insects. To kill the insects a higher concentration will be required but it might not be justified because the requirement of ozone-resistant materials would result in a cost challenge for the grain. Based on these facts, the researchers recommended that ≤ 50 ppm ozone should be used in the stored-grain industry (Jian, Jayas, and White 2013). Moisture-dependent engineering properties of grains were estimated to design an ozone-based storage bin (Pandiselvam, Thirupathi, and Mohan 2015a; Ravi and Venkatachalam 2014). A minimum air velocity of 0.03 m/s must move through the grain bed to achieve a desirable ozone concentration (Mendez et al. 2003). The research results confirmed that higher ozone concentration has the potential to affect the respiration rate of insects and increase fumigant toxicity(Lu et al. 2009). Also, surviving insects under an ozone atmosphere may have high metabolic rates due to induced cellular immune response (Bouwer, Nardini, and Duncan 2009).

## Mechanism of ozonation on pest control

Insects breathe discontinuously to reduce oxidative tissue damage due to ozone toxicity (Hetz and Bradley 2005). Toxic gases entered through the respiratory system of insects (Lu et al. 2009). Increased temperature leading to increase the respiration rate may result in more gas exchange due to an overall increase in metabolic and respiration rate (Rozado et al. 2008). Oxidative tissue damage caused by ozone (Pimental et al. 2007) resulted in alteration of pulmonary function, DNA strand breaks, bronchial responsiveness and membrane oxidation (Ballinger et al. 2005). Also, survivors of insects under ozone atmosphere may have high metabolic rates due to an energy–intensive induced cellular immune response (Bouwer, Nardini, and Duncan 2009).

Different modes of action were reported in the literature regarding the efficacy of ozone against insects in grains. Modified atmosphere can increase the action of low humidity, by prolonging opening of the spiracles, thereby permitting rapid loss of water. The maintaining water within certain limits (usually 50–90%) in insects is a vital aspect of their structure and physiology (Nayar, Ananthakrishnan, and David 1976). For exposure to high concentration atmospheres, death was the result of exhaustion of triglyceride energy reserves rather than by the prolonged narcotic effect of anaesthesia and desiccation, or the accumulation of toxic end products (Ofuya and Reichmuth 2002).

## Quality of ozone-treated samples

The ozone concentration level for sterilization or fumigation has to be optimized based on quality changes of samples (Pandiselvam, Sunoj, and Uma 2016c; Pandiselvam, Thirupathi, and Vennila 2016b). Kırıs et al. (2016) reported that ozonated water washes had no effect on fatty acid composition of olives. They washed the olives with ozonated water for 2 and 5 min, respectively, and pressed to olive oil. They recorded the maximum values after 2-min ozonated water washes were 9.58 meq$O_2$/kg and 0.73% for peroxide and free acid, respectively.

Prudente and King (2002) confirmed the absence of changes in saturated and unsaturated fatty acid levels of ozone-treated corn grains. The study of disinfected grain with 50 ppm ozone for 30 days showed no changes in fatty acid and amino acid composition of soybean, wheat and maize, popping volume of popcorn, baking characteristics of wheat, stickiness of rice and milling characteristics of wheat and maize (Mendez et al. 2003). But Desvignes et al. (2008) reported a significant reduction in milling energy ranging from 10–20% for ozonated wheat flour, yet total flour yield was unchanged.

Only at high concentration of $O_3$ (over 2 g $m^{-3}$) do total nitrogen and fat content of the grain reduce. However, short exposure with high concentration is more damaging to the biologically active substances (enzymes) of the treated product (Krivopishin and Pugin 2000). Ruan et al. (2004) confirmed that ozonated corn grains could efficiently replace $SO_2$ to isolate high starch yields. Furthermore, ozone processing facilitated the treatment of grains at lower temperature (20 °C and 50 °C) for short time (36 h and 48 h) compared to $SO_2$. However, it depends on the ozone exposure time, different results suggest that the observed effects depend on ozone dose and penetration.

Faroni, Pereira, and Sousa (2007) investigated the effect of ozone on corn grains quality at a concentration of 50 ppm with flow rate of 8 L per min with an ozone exposure of 24 to 48 h. The authors observed that, no change in lipids and concluded that the quality (fat acidity and peroxide values) of corn oil extracted from treated grains was the same as untreated grains. White et al. (2010) reported the effects of ozone on dry matter loss of high moisture maize (22%). They found that ozone treatment was decreasing the dry matter loss in maize grains at 32 ºC for 9 days.

## Reaction kinetics of ozone gas in stored grains

Different research results suggest that ozone fumigation is a possible alternative to conventional insecticides such as phosphine and methyl bromide for pest control treatments. But the reaction kinetics of ozone in the stored grains needs to be understood before it can be used as a fumigant (Pandiselvam, Thirupathi, and Anandakumar 2015). Hardin et al. (2010) confirmed that the rapid decay of ozone, as it passed through wheat grain, poses a significant design challenge. To maintain insecticidal ozone concentrations throughout the grain column, several engineering measures can be used. The velocity of gaseous ozone through the grain and initial concentration of ozone can be increased. Both of these measures, however, have practical limitations. There is a scarcity of information available in the published literature on the practical application of ozone as a fumigant in stored grains. An application method needs to be developed to distribute the fumigant evenly and quickly throughout the chamber (Ravi, Venkatachalam, and Rajamani 2015).

Reaction kinetics of ozone gas can be used to understand the effect of ozone on stored grains, and to find out the total fumigation time of farm-level storage bin and optimize the design parameters of ozone fumigation bin. It determines the concentrations of ozone gas at any time during the reaction on grains with the following three aspects: ozone penetration or saturation time, decomposition time and half-life of ozone gas.

### *Saturation time*

The saturation time is the residual ozone concentration inside the storage container as a function of time. At the start of the fumigation progress, ozone gas was consumed soon after it entered the storage structure due to the interaction with the grains and storage structure. The initial ozone gas flow through a grain mass takes more time to complete than subsequent treatments. This is because ozone reacts with the grain kernel surface, insects and cell structures of fungi or mold spores contained within the grain mass. After the saturation period (saturation of grain active sites), the rate of ozone consumption gradually decreased, resulting in ozone gas penetrating the grain column slowly (Hardin et al. 2010).

Similar results reported to maize (Santos et al. 2007), wheat (Hardin et al. 2010), peanut (Alencar et al. 2011) and green gram (Pandiselvam et al. 2016a; Pandiselvam

**Table 3.** Reaction kinetics of ozone gas in different grains at different moisture contents.

| Grain | Moisture content | Saturation time (min) | Decomposition time (min) | Half-life (min) | Reference |
|---|---|---|---|---|---|
| Maize | 12.8% (w.b) | 70 | 17 | 5.57 | Santos et al. (2007) |
| Peanut | 7.1% (w.b) | 173 | - | 7.7 | Alencar et al. (2011) |
| | 10.5% (w.b) | 230 | - | 7.4 | |
| Paddy | 11.2% (w.b) | 71 | 46 | 11.93 | Pandiselvam, Thirupathi, and Anandakumar |
| | 14.3% (w.b) | 103 | 38 | 9.24 | (2015) |
| Rice | 11.4% (w.b) | 119 | 61 | 13.80 | Ravi, Venkatachalam, and Rajamani (2015) |
| | 14.2% (w.b) | 144 | 47 | 11.61 | |

*Note*. w.b—wet basis.

and Thirupathi 2015). The effectiveness of ozone for grain disinfection depends on initial concentration, exposure time (Kells et al. 2001), bed thickness and moisture content of grain mount (Pandiselvam, Thirupathi, and Anandakumar 2015). Table 3 depicts that the saturation time increases as the moisture content increases. The efficacy of ozone increased in insect control on low moisture grains.

### *Decomposition time*

Decomposition time is residual ozone concentration as a function of time after the saturation period (Pandiselvam and Thirupathi 2015). The decay kinetics for the ozone decomposition in a presence of maize, peanuts, rice and paddy grains were performed by data fitting with models of several orders. The best fit was identified as first order (Equation [1]).

$$\ln(O_3) = \ln(O_3)_0 - kt \qquad [1]$$

The decomposition rate of ozone in air is directly correlated with grain moisture content (Table 3). This indicates that an increase in moisture content fastens the adsorption of ozone by the stored grains and thus increased the reactivity of the gas. Therefore, moisture content has to be considered as a significant variable in the ionization process when ozone used as a fumigant. The rate of decay is dependent on the surface characteristics of the materials with which it comes into contact (Hardin et al. 2010). Ozone movement through the grain layer is restricted by the highly reactive nature of ozone.

Initial movement of ozone through the grain is slow because the gas reacts with the chemical constituents present in the outer layer of grain (seed coat) (Mendez et al. 2003). Raila et al. (2006) observed slower ozone penetration between grain layers with higher mycological contamination. The diffusion process describing the self-dispersion and distribution of ozone particles in the grain layer also depends on the air infiltration velocity through the grain mound. The interaction between the ozone molecules results in a breakdown of ozone to oxygen, which results in a reduction in ozone concentration (McClurkin and Maier 2010).

### *Half-life of ozone in stored grains*

Half-life is defined as the time necessary to reach half of its initial ozone concentration (Ravi, Venkatachalam, and Rajamani 2015). The half-life of ozone against grains can be caused by surface area of grains, differences in moisture content, pore space between the grains, or ozone application methods. At ambient condition, the half-life of ozone is 20–40 min (Kells et al. 2001). But in the presence of grains the half-life time is 5.57–13.8 min. The half-life of ozone ranged from 2.03 min in grade-four wheat mixed with high foreign matter, to 4.03 min in grade-two wheat (Hardin et al. 2010). This is mainly due to the interaction between the ozone gas and the grains, even after the saturation phase. A higher half-life time could result in more effective during fumigation.

## Safety of ozone

Ozone is a highly toxic and corrosive compound, and all researchers must approach its use with caution. Ozone is detectable by human olfactory senses at concentrations of 0.02 to 0.05 ppm (by volume), which is below concentrations of health concern (EPA 1999). Occupational Safety and Health Administration (OSHA) limits of exposure of ozone in the working environment; the TLV (Threshold Limit Value) for short term (15 min) and long term (8 h) are 0.3 (0.6 mg $m^{-3}$) and 0.1 ppm, respectively. The time weighted average is determined to be 0.1 ppm for light work and 0.2 ppm for less than 2 h of work, according to the Threshold Limit Value (TLV) of the American Conference of Governmental Industrial Hygienists (ACGIH).

At 1 ppm ozone has a pungent disagreeable odor. It is irritating the eyes and throat. Ozone lethal to humans being with prolonged exposure at concentrations above 4 ppm (Suslow 2004). Ozone concentration that is immediately dangerous to health and life (IDHL) is 5 ppm. This is the upper limit for which there are approved respirators; higher rates than this are dangerous (Smilanick 2003). It is highly corrosive to equipment made of mild steel, galvanized iron as compared to stainless steel.

## Conclusion

Currently there is an increasing emphasis and trend toward the safe storage of fruits, vegetables and food grains in the food processing industry, while minimizing the quantitative and qualitative losses. Food laws and legislation to phase out conventional chemicals due to toxic and environmental effect and growing consumer demand for organic has forced the food processors and grain handlers to find alternatives. Ozone is a potential alternative for traditional sanitizer in fruits and vegetable preservation and phosphine resistance insect management in the stored products. The research described in this article confirmed that ozone is active against a range of micro-organisms, fungi, mycotoxins and insect pests at relatively low concentrations.

However, adaptation of ozone technology in the large-scale grain processing industry has some practical limitations including environmental factors (temperature, relative humidity, grain moisture, bed thickness), generation of high concentration ozone, diffusion of ozone gas into the grain column (depends upon the grain surface characteristics and shape) and half-life of ozone (reducing the efficacy to kill insects at deeper levels). This may be overcome by a combination of ozone with appropriate advanced technology results in advanced oxidation processes that are potentially effective against the microorganisms, fungi and pests. Ozone offers unique advantages for the food processing sector with desirable or minimal effects on the biochemical properties and leaving no residues. Therefore, ozone can be a potential alternative to conventional sanitizers and fumigants in food processing industries.

## References


American Conference of Governmental Industrial Hygienists (ACGIH). 2003. *Adopted Threshold Limit Values*. Cincinnati, OH: ACGIH.

Achen, M., and A. E. Yousef. 2001. “Efficacy of Ozone Against *Escherichia coli* O157: H7 on Apples.” *Journal Food Science* 66 (9):1380–4. doi:10.1111/j.1365-2621.2001.tb15218.x.

Alencar, E. R. D., L. R. D. Faroni, M. A. Martins, A. R. D. A. Costa, and P. R. Cecon. 2011. “Decomposition Kinetics of Gaseous Ozone in Peanuts.” *Engineering Agricultural Jaboticabal* 31 (5):930–9. doi:10.1590/S0100-69162011000500011.

Allen, B., J. N. Wu, and H. Doan. 2003. “Inactivation of Fungi Associated with Barley Grain by Gaseous Ozone.” *Journal of Environmental Science and Health Part B-Pesticides, Food Contaminants and Agricultural Wastes* 38:617–30. doi:10.1081/PFC-120023519.

Bablon, G., W. D. Belamy, M. M. Billen, G. Bourbigot, F. B. Daniel, C. Gomella, G. Gordon, P. Hartemann, J. C. Joret, W. R. Knocke, B. Langlais, A. Laplanche, B. Legube, J. B. Lykins, N. Martin, G. Martin, A. Montiel, M. F. Morin, R. S. Miltner, D. Perrine, M. Prevost, D. A. Reckhow, P. Servais, P. C. Singer, O. T. Sproul, and C. Ventresque. 1991. “Practical Applications of Ozone: Principles and Case Studies.” In *Ozone in Water Treatment: Application and Engineering*, edited by G. Langlais, D. A. Reckhow, and D. R. Brink, 133–316. Chelsea, MI: Lewis Publishers, Inc.

Ballinger, C. A., R. Cueto, G. Squadrito, J. F. Coffin, L. W. Velsor, W. A. Pryor, and E. M. Postlethwait. 2005. “Antioxidant-Mediated Augmentation of Ozone Induced Membrane Oxidation.” *Free Radical Biology and Medicine* 38:515–26.

Barth, M. M., C. Zhou, J. Mercier, and F. A. Payne. 1995. “Ozone Storage Effects on Anthocyanin Content and Fungal Growth in Blackberries.” *Journal of Food Science* 60(6):1286–8. doi:10.1111/jfds.1995.60.issue-6.

Beltran, F. J. 2003. *Ozone Reaction Kinetics for Water and Wastewater Systems*, 358. Boca Raton, FL: CRC Press.

Benhalima, H., M. Q. Chaudhry, K. A. Mills, and N. R. Price. 2004. “Phosphine Resistance in Stored-Product Insects Collected From Various Grain Storage Facilities in Morocco.” *Journal Stored Product Research* 40:241–9. doi:10.1016/S0022-474X(03)00012-2.

Bonjour, E. L., C. L. Jones, R. T. Noyes, J. A. Hardin, R. L. Beeby, D. A. Eltiste, and S. Decker. 2008. “Efficacy of Ozone Against Insect Pests in Wheat Stored in Steel Grain Bins.” In *Proceedings of the 8th International Conference on Controlled Atmosphere and Fumigation in Stored Products, 21-26 September 2008, Chengdu, China*, edited by G. Daolin, S. Navarro, Y. Jian, T. Chang, J. Zuxun, L. Yue, L. Yang, and W. Haipeng, 522–9. Chengdu, China: Sichuan Publishing Group.

Bonjour, E. L., G. P. Opit, J. Hardin, C. L. Jones, M. E. Payton, and R. L. Beeby. 2011. “Efficacy of Ozone Fumigation Against the Major Grain Pests in Stored Wheat.” *Journal of Economic Entomology* 104 (1):308–16. doi:10.1603/EC10200.

Bouwer, G., L. Nardini, and F. D. Duncan. 2009. “*Helicoverpa Armigera* (*Lepidoptera: Noctuidae*) Larvae that Survive Sub-Lethal Doses of Nucleopolyhedrovirus Exhibit High Metabolic Rates.” *Journal of Insect Physiology* 55:369–74. doi:10.1016/j.jinsphys.2009.01.003.

Brady, J. E., and G. E. Humiston. 1978. *General Chemistry Principles and Structure*, 2nd ed. New York, NY: John Wiley & Sons.

Choi, L. H., and S. S. Nielsen. 2005. “The Effects of Thermal and Non Thermal Processing Methods on Apple Cider Quality and Consumer Acceptability.” *Journal of Food Quality* 28:13–29. doi:10.1111/j.1745-4557.2005.00002.x.

Clark, P. J. 2004. “Ozone Cure for Some Sanitation Problems.” *Food Technology* 58(4):75–6.

Cullen, P. J., B. K. Tiwari, C. P. O’Donnell, and K. Muthukumarappan. 2009. “Modelling Approaches to Ozone Processing of Liquid Foods.” *Trends in Food Science and Technology* 20(3):125–36. doi:10.1016/j.tifs.2009.01.049.

Cullen, P. J., V. P. Valdramidis, B. K. Tiwari, S. Patil, P. Bourke, and C. P. O’Donnell. 2010. “Ozone Processing for Food Preservation: An Overview on Fruit Juice Treatments.” *Ozone: Science and Engineering* 32(3):166–79. doi:10.1080/01919511003785361.

Desvignes, C., M. Chaurand, M. Dubois, A. Sadoudi, J. Abecassis, and V. Lullien- Pellerin. 2008. “Changes in Common Wheat Grain Milling Behavior and Tissue Mechanical Properties Following Ozone Treatment.” *Journal of Cereal Science* 47:245–51. doi:10.1016/j.jcs.2007.04.004.

Environmental Protection Agency (EPA). 1999. *Alternative Disinfectants and Oxidants. EPA Guidance Manual*

Erdman, H. E. 1980. “Ozone Toxicity during Ontogeny of Two Species of Flour Beetles, *Tribolium Confusum* and *T. Canstaneum*.” *Environ. Entomol* 9:16–17. doi:10.1093/ee/9.1.16.

Esciche, I., J. A. Serra, M. Gomez, and M. J. Galotto. 2001. “Effect of Ozone Treatment and Storage Temperature on Physicochemical Properties of Mushrooms (Agaris Bisporus).” *Food Science and Technology International* 7 (3):251–8. doi:10.1106/6A9R-DKEV-ADV7-Y30X.

Faroni, L. R. D., A. M. Pereira, and A. D. Sousa. 2007. “Influence of Corn Grain Mass Temperature on Ozone Toxicity to Sitophilus Zeamais (Coleoptera: Curculionidae) and Quality of Oil Extracted from Ozonized Grains". IOA Conference and Exhibition, Valencia, Spain–October (29–31), 5.8, 1–6.

FDA, United States Food and Drug Administration. Rules and Regulations. 2001. "Part 173-Secondary Direct Food Additives Permitted in Food for Human Consumption (21 CFR Part 173 Authority: 21 USC. 321, 342, 348)." *Federal Register* 66:123.

Gabler, F. M., J. L. Smilanick, M. F. Mansour, and H. Karaca. 2010. "Influence of Fumigation with High Concentrations of Ozone Gas on Postharvest Gray Mold and Fungicide Residues on Table Grapes." *Postharvest Biology and Technology* 55 (2):85–90. doi:10.1016/j.postharvbio.2009.09.004.

Garcia, A., J. R. Mount, and P. M. Davidson. 2003. "Ozone and Chlorine Treatment of Minimally Processed Lettuce." *Journal of Food Science* 68(9):2747–51. doi:10.1111/jfds.2003.68.issue-9.

Graham, D. M. 1997. "Use of Ozone for Food Processing." *Food Technology* 51:72–5.

Greene, A. K., Z. B. Guzel-Seydim, and A. C. Seydim. 2012. "Properties of Ozone". In *Ozone in Food Processing*, edited by O. C. Donnell, B. K. Tiwari, P. J. Cullen, and R. G. Rice, 1st ed., 19–32. Oxford, UK: Blackwell Publishing Ltd.

Han, Y., J. D. Floros, R. H. Linton, S. S. Nielsen, and P. E. Nelson. 2002. "Response Surface Modeling for the Inactivation of *Escherichia Coli* O157: H7on Green Peppers (Capsicum Annuum) by Ozone Gas Treatment." *Journal of Food Science* 67 (3):1188–93. doi:10.1111/j.1365-2621.2002.tb09475.x.

Hardin, J. A., C. L. Jones, E. L. Bonjour, R. T. Noyes, R. L. Beeby, D. A. Eltiste, and S. Decker. 2010. "Ozone Fumigation of Stored Grain; Closed-Loop Recirculation and the Rate of Ozone Consumption." *Journal of Stored Products Research* 46 (3):149–54. doi:10.1016/j.jspr.2010.03.002.

Hetz, S. K., and T. J. Bradley. 2005. "Insects Breathe Discontinuously to Avoid Oxygen Toxicity." *Nature* 433 (7025):516–19. doi:10.1038/nature03106.

Hunt, N. K., and B. J. Marinas. 1997. "Kinetics of *Escherichia coli* Inactivation with Ozone." *Water Research* 31 (6):1355–62. doi:10.1016/S0043-1354(96)00394-6.

Ishizaki, K., N. Shinriki, A. Ikehata, and T. Ueda. 1981. "Degradation of Nucleic Acids with Ozone. I. Degradation of Nucleobases, Ribonucleosides, and Ribonucleoside- 5′-Monophosphates." *Chemical Pharmaceutical Bulletin* 29:868–72. doi:10.1248/cpb.29.868.

Isikber, A. A., and S. Oztekin. 2009. "Comparison of Susceptibility of Two Stored-Product Insects, *Ephestia Kuehniella* Zeller and *Tribolium Confusum* Du Val to Gaseous Ozone." *Journal of Stored Products Research* 45 (3):159–64. doi:10.1016/j.jspr.2008.12.003.

Jans, U., and J. Hoigné. 1998. "Activated Carbon and Carbon Black Catalyzed Transformation of Aqueous Solution into OH-Radicals." *Ozone Science & Engineering* 20:67–90. doi:10.1080/01919519808547291.

Jian, F., D. S. Jayas, and N. D. G. White. 2013. "Can Ozone Be a New Control Strategy for Pests of Stored Grain." *Agricultural Researcher* 2 (1):1–8. doi:10.1007/s40003-012-0046-2.

Karaca, H., and Y. S. Velioglu. 2007. "Ozone Applications in Fruit and Vegetable Processing." *Food Reviews International* 23(1):91–106. doi:10.1080/87559120600998221.

Kells, S. A., L. J. Mason, D. E. Maier, and C. P. Woloshuk. 2001. "Efficacy and Fumigation Characteristics of Ozone in Stored Maize." *Journal of Stored Products Research* 37:371–82. doi:10.1016/S0022-474X(00)00040-0.

Khadre, M. A., A. E. Yousef, and J. G. Kim. 2001. "Microbiological Aspects of Ozone Applications in Food: A Review." *Journal of Food Science* 66 (9):1242–52. doi:10.1111/j.1365-2621.2001.tb15196.x.

Kim, J. G., A. E. Yousef, and G. W. Chism. 1999a. "Use of Ozone to Inactivate Microorganisms on Lettuce." *Journal Food Safety* 19(1):17–34. doi:10.1111/j.1745-4565.1999.tb00231.x.

Kim, J. G., A. E. Yousef, and S. Dave. 1999. "Application of Ozone for Enhancing the Microbiological Safety and Quality of Foods: A Review." *Journal of Food Protection* 62(9):1071–87. doi:10.4315/0362-028X-62.9.1071.

Kim, M. J., Y. A. Oh, M. H. Kim, M. K. Kim, and S. D. Kim. 1993. "Fermentation of Chinese Cabbage Kimchi Inoculated with *Lactobacillus Acidophilus* and Containing Ozone Treated Ingredients." *Journal Korean Social Food Nutrition* 22:165–74.

Kırış, S., Y. S. Velioglu, and A. Tekin. 2016. "Effect of Ozonated Water Treatment on Fatty Acid Composition and Some Quality Parameters of Olive Oil." *Ozone: Science & Engineering*, just –accepted. doi:10.1080/01919512.2016.1257932

Krivopishin, I. P., and A. M. Pugin. 2000. "The Use of Ozone in Agriculture." *Selskokhoziajstvennaia Biologia* 6:11–20.

Leesch, J. G. 2003. "The Mortality of Stored-Product Insects following Exposure to Gaseous Ozone at High Concentrations." In *Advances in Stored Product Protection, Proceedings of the 8th International Working Conference on Stored-Product Protection, 22–26 July 2002*, edited by P. F. Credland, D. M. Armitage, C. H. Bell, P. M. Cogan, and E. Highley, 827–31. York, UK: CAB International.

Liew, C. L., and R. K. Prange. 1994. "Effect of Ozone and Storage Temperature on Postharvest Disease and Physiology of Carrots (*Caucus Carota L.*)." *Journal American Social Horti Sciences* 119:563–7.

Loeb, B. L. 2011. "Ozone: Science & Engineering: Thirty-Three Years and Growing." *Ozone: Science & Engineering* 33(4):329–42. doi:10.1080/01919512.2011.584302.

Lu, B., Y. Ren, Y. Z. Du, and J. Gu. 2009. "Effect of Ozone on Respiration of Adult *Sitophilus Oryzae (L.), Tribolium Castaneum (Herbst)* and *Rhyzopertha Dominica* (F)." *Journal of Insect Physiology* 55(10):885–9. doi:10.1016/j.jinsphys.2009.05.014.

Lynntech. 1998. *The Detox System: Applications Overview*. College Station, TX: Lynntech.

Maier, D. E., R. Hulasare, C. A. Campabadal, C. P. Woloshuk, and L. Mason. 2006. "Ozonation as a Non-Chemical Stored Product Protection Technology." In *Proceedings of the 9th International Working Conference on Stored Product Protection*, edited by Lorini, I., Bacaltchuk, B., Beckel, H., Deckers, D., Sundfeld, E., Santos, J. P. dos, Biagi, J. D., Celaro, J. C., Faroni, L. R. D., Bortolini, L. de O. F., Sartori, M. R., Elias, M. C., Guedes, R. N. C., Fonseca, R. G. da, and Scussel, V. M., 773–7. Canpinas, Brazil: Brazilian Post-harvest Association.

Manley, T. C., and S. J. Niegowski. 1967. "Ozone." *Encyclopedia of Chemical Technology* 14:410–32.

Mason, L. J., C. A. Strait, C. P. Woloshuk, and D. E. Maier. 1999. "Controlling Stored Grain Insects with Ozone

Fumigation." In *Proceedings of the 7th International Working Conference on Stored-Product Protection, 14–19 October 1998, Beijing, Peoples Republic of China*, edited by J. Zuxun, L. Quan, L. Yongsheng, T. Xianchang, and G. Lianghua, 536–47. Chengdu, Peoples Republic of China: Sichuan Publishing House of Science and Technology.

Mason, L. J., C. P. Woloshuk, and D. E. Maier. 1997. "Efficacy of Ozone to Control Insects, Molds and Mycotoxins." In *Proceedings of the International Conference on Controlled Atmosphere and Fumigation in Stored Products*, edited by E. J. Donahaye, S. Navarro, and A. Varnava, 665–70. Nicosia, Cyprus: Nicosia, Cyprus Printer Ltd.

McClurkin, J. D., and D. E. Maier. 2010. "Half-Life Time of Ozone as a Function of Air Conditions and Movement". 10th International Working Conference on Stored Product Protection, 27 June–2 July 2010, Estoril, Portugal, Estoril Congress Center, 381–5.

McDonough, M. X., L. J. Mason, and C. P. Woloshuk. 2011. "Susceptibility of Stored Product Insects to High Concentrations of Ozone at Different Exposure Intervals." *Journal of Stored Products Research* 47:306–10. doi:10.1016/j.jspr.2011.04.003.

Mendez, F., D. E. Maier, L. J. Mason, and C. P. Woloshuk. 2003. "Penetration of Ozone into Columns of Stored Grains and Effects on Chemical Composition and Processing Performance." *Journal of Stored Products Research* 39:33–44. doi:10.1016/S0022-474X(02)00015-2.

Mustafa, M. G. 1990. "Biochemical Basis of Ozone Toxicity." *Free Radical Biology and Medicine* 9(3):245–65. doi:10.1016/0891-5849(90)90035-H.

Najafi, M. B. H., and M. H. H. Khodaparast. 2009. "Efficacy of Ozone to Reduce Microbial Populations in Date Fruits." *Food Control* 20(1):27–30. doi:10.1016/j.foodcont.2008.01.010.

Nayar, K. K., T. N. Ananthakrishnan, and B. V. David. 1976. *General and Applied Entomology*, 589. New Delhi, India: Tata McGraw-Hill Publishing Company Ltd.

Ofuya, T. I., and C. Reichmuth. 2002. "Effect of Relative Humidity on the Susceptibility of *Callosobruchus Maculatus* (Fabricius)(Coleoptera: *Bruchidae*) to Two Modified Atmospheres." *Journal of Stored Products Research* 38(2):139–46. doi:10.1016/S0022-474X(01)00009-1.

Ogawa, J. M., A. J. Feliciano, and B. T. Manji. 1990. "Evaluation of Ozone as a Disinfectant in Postharvest Dump Tank Treatments for Tomato." *Phytopathology* 80:1020.

Olmez, H., and M. Y. Akbas. 2009. "Optimization of Ozone Treatment of Fresh-Cut Green Leaf Lettuce." *Journal of Food Engineering* 90:487–94. doi:10.1016/j.jfoodeng.2008.07.026.

Pandiselvam, R., A. Kothakota, V. Thirupathi, S. Anandakumar, and P. Krishnakumar. 2016a. "Numerical Simulation and Validation of Ozone Concentration Profile in Green Gram (*Vigna Radiate*) Bulks." *Ozone: Science & Engineering*, 39(1): 54–60. doi:10.1080/01919512.2016.1244641.

Pandiselvam, R., S. Sunoj, and D. Uma. 2016c. "Development of Multivariate Regression Model for Quantification of Proximate Content in *Vigna Radiata* Using Fourier Transform–Nir Spectroscopy." *Poljoprivredna Tehnika* 41 (2):61–70.

Pandiselvam, R., and V. Thirupathi. 2015. "Reaction Kinetics of Ozone Gas in Green Gram (*Vigna Radiata*)." *Ozone: Science & Engineering* 37:1–7. doi:10.1080/01919512.2014.984158.

Pandiselvam, R., V. Thirupathi, and S. Anandakumar. 2015. "Reaction Kinetics of Ozone Gas in Paddy Grains." *Journal of Food Process Engineering* 38:594–600. doi:10.1111/jfpe.12189.

Pandiselvam, R., V. Thirupathi, and S. Mohan. 2015a. "Engineering Properties of Rice." *Poljoprivredna Tehnika* 40:69–78.

Pandiselvam, R., V. Thirupathi, and P. Vennila. 2016b. "Fourier Transform–Near Infrared Spectroscopy for Rapid and Nondestructive Measurement of Amylose Content of Paddy." *Poljoprivredna Tehnika* 41 (2):93–100.

Pascual, A., I. Llorca, and A. Canut. 2007. "Use of Ozone in Food Industries for Reducing the Environmental Impact of Cleaning and Disinfection Activities." *Trends in Food Science and Technology* 18:529–35. doi:10.1016/j.tifs.2006.10.006.

Perez, A. G., C. Sanz, J. J. Rios, R. Olias, and J. M. Olias. 1999. "Effects of Ozone Treatment on Postharvest Strawberry Quality." *Journal of Agricultural and Food Chemistry* 47:1652–1656. doi:10.1021/jf980829l.

Pimentel, M. A. G., L. R. D. Faroni, and R. N. C. Guedes. 2007. "Phosphine Resistance, Respiration Rate and Fitness Consequences in Stored-Product Insects." *Pest Management Science* 63(9):876–81. doi:10.1002/ps.1416.

Prudente, A. D., Jr, and J. M. King. 2002. "Efficacy and Safety Evaluation of Ozonation to Degrade Aflatoxin in Corn." *Journal of Food Science* 67(8):2866–72. doi:10.1111/j.1365-2621.2002.tb08830.x.

Raila, A., A. Lugauskas, D. Steponavicius, M. Ralliene, A. Steponaviciene, and E. Zvicevicius. 2006. "Application of Ozone for Reduction of Mycological Infection in Wheat Grain." *Annals of Agricultural and Environmental Medicine (AAEM)* 13:287–94.

Rakness, K., G. Gordon, B. Langlais, W. Masschelein, N. Matsumoto, Y. Richard, C. M. Robson, and I. Somiya. 1996. "Guideline for Measurement of Ozone Concentration in the Process Gas from an Ozone Generator." *Ozone: Science and Engineering* 18(3):209–29. doi:10.1080/01919519608547327.

Ravi, P., and T. Venkatachalam. 2014. "Important Engineering Properties of Paddy." *Poljoprivredna Tehnika* 39:73–83.

Ravi, P., T. Venkatachalam, and M. Rajamani. 2015. "Decay Rate Kinetics of Ozone Gas in Rice Grains." *Ozone: Science and Engineering* 37:450–5. doi:10.1080/01919512.2015.1040912.

Rice, R. G. 1986. "Application of Ozone in Water and Waste Water Treatment." In *Analytical Aspects of Ozone Treatment of Water and Wastewater*, edited by R. G. Rice, and M. J. Browning, 7–26. Syracuse, NY: The Institute.

Rice, R. G., and L. J. Bollyky. 1981. "Fundamental Aspects of Ozone Technology." In *Ozone Treatment of Water for Cooling Applications*, edited by R. G. Rice, 1–19. Vienna, VA: *The International Ozone Association*.

Rozado, A. F., L. R. A. Faroni, W. M. I. Urruchi, R. N. C. Guedes, and J. L. Paes. 2008. "Ozone Application Against Sitophilus Zeamais and Tribolium Castaneum on Stored Maize." *Revista Brasileira de Engenharia Agrı´Cola E Ambiental* 12 (3):282–5.

Ruan, R., H. Lei, P. Chen, S. Deng, X. Lin, Y. Li, W. Wilcke, and G. Fulcher. 2004. “Ozone-Aided Corn Steeping Process.” *Cereal Chemistry* 81(2):182–7. doi:10.1094/CCHEM.2004.81.2.182.

Santos, J. E., M. A. Martins, L. R. A. Faroni, M. P. Andrade, and M. C. S. Carvalho. 2007. “Ozonization Process: Saturation Time, Decomposition Kinetics and Quality of Maize Grains (Zea Mays L.).” IOA Conference and Exhibition, Valencia, Spain, October 29–31.

Scott, D. B. M., and E. C. Lesher. 1963. “Effect of Ozone on Survival and Permeability of *Escherichia coli*.” *Journal Bacteriological* 85:367–76.

Singh, N., R. K. Singh, A. K. Bhunia, and R. L. Stroshine. 2002. “Efficacy of Chlorine Dioxide, Ozone, and Thyme Essential Oil or a Sequential Washing in Killing *Escherichia Coli* O157: H7on Lettuce and Baby Carrots.” *Lebensmittel Wissenschaft and Technologie* 35:720–9. doi:10.1006/fstl.2002.0933.

Skog, L. J., and C. L. Chu. 2001. “Effect of Ozone on Qualities of Fruits and Vegetables in Cold Storage.” *Canada Journal Plant Sciences* 81(4):773–8. doi:10.4141/P00-110.

Smilanick, J. L. 2003. “Use of Ozone in Storage and Packing Facilities”. Proceedings of Washington Tree Fruit Post Harvest Conference. Accessed January 21, 2016. http://postharvest.tfrec.wsu.edu/PC2003H.pdf.

Sousa, A. H., L. R. D. A. Faroni, R. N. C. Guedes, M. R. Totola, and W. I. Urruchi. 2008. “Ozone as a Management Alternative against Phosphine-Resistant Insect Pests of Stored Products.” *Journal of Stored Products Research* 44 (4):379–85. doi:10.1016/j.jspr.2008.06.003.

Steckel, P. R., and R. B. Engdahl. 1978. “Air Pollution”. In *Encyclopedia of Chemical Technology*, vol. 1, 3rd ed, 624–49. New York, NY: Wiley-Interscience.

Strait, C. A., 1998. “Efficacy of Ozone to Control Insects and Fungi in Stored Grain”. M. S. Thesis, Purdue University, W. Lafayette, IN, 59.

Suslow, T. V. 2004. “Ozone Applications for Postharvest Disinfection of Edible Horticultural Crops,” 8, Publication 8133:7–12. Oakland, CA: University of California - Division of Agriculture and Natural Resources.

Tiwari, B. K., K. Muthukumarappan, C. P. O’Donnell, and P. J. Cullen. 2008. “Modelling Colour Degradation of Orange Juice by Ozone Treatment Using Response Surface Methodology.” *Journal of Food Engineering* 88:553–560. doi:10.1016/j.jfoodeng.2008.03.021.

Tiwari, B. K., K. Muthukumarappan, C. P. O’Donnell, and P. J. Cullen. 2008a. “Effects of Sonication on the Kinetics of Orange Juice Quality Parameters.” *Journal of Agricultural and Food Chemistry* 56:2423–28. doi:10.1021/jf073503y.

Tiwari, B. K. C. P., O. K. Muthukumarappan, and P. J. Cullen. 2009. “Anthocyanin and Colour Degradation in Ozone Treated Blackberry Juice.” *Innovative Food Science and Emerging Technologies* 10:70–5. doi:10.1016/j.ifset.2008.08.002.

United States Food and Drug Administration. U.S. FDA. 2004. “FDA Guidance to Industry, 2004: Recommendations to Processors of Apple Juice or Cider on the Use of Ozone for Pathogen Reduction Purposes.” http://www.cfsan.fda.gov/~dms/juicgu13.html (accessed March 8, 2016).

Wei, L., M. Xu, and Y. Zhang. 2016. Energy Conversion and Temperature Dependence in Ozone Generator Using Pulsed Discharge in Oxygen. *Ozone: Science & Engineering*. just-accepted. doi:10.1080/01919512.2016.1230488

White, S. D., P. T. Murphy, C. J. Bern, and J. H. Van Leeuwen. 2010. “Controlling Deterioration of High-Moisture Maize with Ozone Treatment.” *Journal of Stored Products Research* 46:7–12. doi:10.1016/j.jspr.2009.07.002.

Williams, D. W., J. Montecalvo, E. Mueller, D. Earls, K. Swanson, and L. Petersen. 1995. “Ozonation as an Alternative Disinfectant for Carrot Washwater.” In *Institute of Food Technologists Annual Meeting*, 8. Book of abstracts.

Wu, J. N., H. Doan, and M. A. Cuenca. 2006. “Investigation of Gaseous Ozone as an Antifungal Fumigant for Stored Wheat.” *Journal of Chemical Technology and Biotechnology* 81:1288–93. doi:10.1002/jctb.1550.

Zambre, S. S., K. V. Venkatesh, and N. G. Shah. 2010. “Tomato Redness for Assessing Ozone Treatment to Extend the Shelf Life.” *Journal of Food Engineering* 96:463–8. doi:10.1016/j.jfoodeng.2009.08.027.

Zhang, L., Z. Lu, Z. Yu, and X. Gao. 2005. “Preservation of Fresh-Cut Celery by Treatment of Ozonated Water.” *Food Control* 16:279–83. doi:10.1016/j.foodcont.2004.03.007.

Zhao, J., and P. M. Cranston. 1995. “Microbial Decontamination of Black Pepper by Ozone and the Effect of the Treatment on Volatile Oil Constituents of the Spice.” *Journal of the Science of Food and Agriculture* 68:11–18. doi:10.1002/(ISSN)1097-0010.