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Semi-Continuous Ozonation System for Pest Control

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Abstract: Previous trials of ozone treatment for post-harvest food grains have proved ozonation as a potential non-chemical, non-residual and environmentally-friendly alternative for methyl bromide fumigation for treatment of stored food grains. Ozone is a strong oxidizing agent, which is used to control harmful microbes and volatiles. Stored grain products can harbor multiple microorganisms including molds that produce harmful toxins. To examine the effect of ozone on surface microbes, samples of stored maize were treated for a maximum of 60 minutes at a maximum ozone concentration of 1900 ppm. The data showed that the amount of microorganisms significantly decreased or were completely absent after the maize samples were treated with ozone. In order to improve the treatment effect, a counter-flow semi-continuous ozonation treatment system was designed in order to ozonate grain at a faster rate, based on the concentration-time product (CTP) of ozone required to eliminate microbial growth on grain kernels and achieve insect mortality. The ozonation treatment system can be installed in typical grain silos. Ozone is generated at a constant rate and introduced into the plenum of the silo with a variable speed fan to control treatment effect. The bottom grain layer is removed with a specially designed unloading conveyor after it has reached the desired ozone CTP. Air velocity was quantified for each grain layer to determine the theoretical ozone concentration. Ozone concentration was allowed to build up for 60 to 120 minutes in the bottom grain layer. As the layers of grain were removed, the ozone concentration in each layer increased until the maximum value was reached. A counter-flow semi-continuous ozonation system was successfully tested and proved to be a technically feasible non-chemical tool for pest control.

Introduction

Ozone (O_3) is a gas made up of three bonded oxygen molecules; it is highly unstable and reacts with many elements. O_3 reacts with microorganisms quickly by degrading them. Theories suggest that O_3 attacks the lipid double bonds in the cell membrane and results in a change in cell permeability to lyses[1]. Ozone has the ability to oxidize (i. e., cause the loss of electrons) the chains and break down the enteroviruses. Such strong oxidative abilities make O_3 a very reactive element.

Insects and molds cause a significant amount of damage to grain each year producing economic losses that affect farmers, elevators managers and processors throughout the world[2]. Stored grain protection relies heavily on the use of chemicals like phosphine and methyl bromide to control pests. Due to the increased concern over the use of post-harvest chemicals worldwide, there is much interest in the development and use of non-chemical treatments such as temperature, moisture management, modified atmospheres, heat treatment of empty structures, physical exclusion, non-chemical protectants, biological controls and ozonation to control stored product pests. Ozonation is a powerful oxidant that reduces or inhibits mold spore development and kills stored product insects, therefore serving as a non-chemical alternative for stored grain protection[3,4].

Fungi and bacteria contribute to quality deterioration of stored grains; they can cause nutrient loss (changes in vitamins, lipids, proteins and carbohydrates), functional property losses (germination), and aesthetic changes (discoloration, caking and odors). Given that ozone inhibits or eliminates fungal spores, it reduces the potential production of mycotoxins that can be toxic to humans and mammals when ingested. Ozone has the tendency to transform or decay into two molecules of oxygen within 20 to 50 minutes[5]. Therefore, a properly designed ozonated airflow system is important for the effective movement and distribution of ozone through the grain mass in a storage structure. A

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recirculation or exhausting system is needed so ozone is replenished once the leading front exits the grain mass and is exhausted to the air.

The ozone generator needs to be capable of producing ozone at a constant rate and at the capacity needed for the grain mass to be treated. Among the advantages of ozonation compared to traditional phosphine fumigation for pest control are that it can be generated on the treatment site and no residue remains on the treated product[4]. The initial ozonation treatment of a grain mass takes more time to complete than subsequent treatments on the same grain mass (as long as it is not moved and recontaminated with dust, etc.) because ozone reacts with the cell structures of mold spores, insects, bacteria and other biological matter attached to the grain kernel surface and contained within the grain mass. Completion of the sterilizing ozonation effect depends on the quantity of biological matter to be reacted with, the quantity of ozone available to react, and the supply of ozone to complete the reaction process throughout the grain mass within a timely manner. After this reaction process, ozone will move faster and more freely in the grain mass increasing in concentration.

Given ozone's tendency to decay into oxygen within a short time period, and to fully understand its behavior in any environment, it is necessary to determine its half-life (HLT). HLT is the time when the initial concentration of a chemical is reduced by half; it is most commonly denoted by $t_{1/2}$. The primary objective of this study was to determine the engineering parameters and half-life of ozone to design a counter-flow, semi-continuous ozonation treatment system in a grain bin in order to ozonate the grain mass at a faster rate based on the known concentration-time product (CTP) of ozone required to eliminate microbial growth on grain kernels and to achieve insect mortality.

Materials and Methods

The counter-flow, semi-continuous ozonation system was set up in metal silo of 9.1m diameter with a sidewall height of 4.9m and a capacity of 178t. The silo was equipped with grain drying system consisting of a 0.71m diameter axial-flow fan powered by a 9.7kW motor, a propane burner, and a sweep unloading auger system (Shivvers Blue Fame Corydon, IA) to remove a layer of maize from inside the silo after it was dried to the appropriate moisture content. The sweep auger consisted of a 4.5m radius tapered screw conveyor, which rotated around the silo diameter removing 0.10 to 0.15m of grain for each full rotation. The removed grain was transferred by a vertical screw conveyor to the top of the bin where it was transported by a roof-mounted screw conveyor into a nearby bin.

The ozone was produced by a four quad generator manufactured by O_3Co. (Aberdeen, ID) that has a capacity of producing 250g/h. It was powered by a 40kW diesel generator. The four ozone supply lines were positioned to empty into the plenum of the silo through to a fan plenum in order to achieve a uniform distribution of ozone below the perforated drying floor.

Ozone was quantified and controlled with a monitoring system that measured the ozone concentration in different layers of the grain mass using multiple monitoring lines. The ozone concentration was quantified using an ozone analyzer model IN-2000 made by INUSA (Boston, MA) and recorded using a data acquisition system. Ozone monitoring lines were placed in the silo at the following depths: 0.076, 0.17, 0.23, 0.30, 0.61 and 0.89m above the floor and in the headspace and at the grain surface. Each monitoring line was connected to a valve control manifold so only one monitoring line was sampled at a time.

The air velocity was measured using the procedure described by Bartosik[6] that uses a custom-built funnel and a vane-wheel anemometer (Omega HHF91, Omega Engineering Inc., Stanford, Connecticut). The funnel is placed with its larger diameter end on the grain surface and the anemometer is placed on the smaller diameter end to measure air velocity, which then is converted into volumetric airflow through the grain mass.

The ozone half-life was measured using a 40L cylinder which was filled with ozone and sealed off. Ozone was produced from a lab-scale ozone generator manufactured by O_3Co. (Aberdeen, ID) and pumped into the cylinder until it was completely filled with O_3. Once this occurred the chamber was sealed and measurements of O_3 concentration were taken using gas detection tubes. Concentration measurements were taken through a valve at the top of the cylinder using a Kitagawa Gas Sampling Tube.

Results and Discussion

The procedure for the counter-flow, semi-continuous ozonation treatment system involved removing the bottom grain layer with the tapered unloading auger after the layer reached the desired ozone concentration to achieve insect mortality, mold reduction, and/or odor removal. The treated grain was subsequently transported to a storage or shipping silo. Mendez *et al.* [4] reported that in order to have optimal ozone concentration in the plenum, a minimum air velocity of 0.03 m/s is needed. Therefore, air velocity was quantified for each grain layer to determine the theoretical ozone concentration. Air velocity was measured at several locations along the grain surface after the grain surface was levelled. For each airflow measurement at the surface, the airflow was calculated for each grain depth, which was then used to determine the theoretical ozone concentrations using the following formula that relates ozone production of the 250g/hr generator with airflow (Table 1).

$$O_3 = \frac{O_3\text{Flow} \times R \times T}{P \times Q \times 1000 \times 60} \qquad (1)$$

Where, O_3 = ozone concentration (ppm); O_3Flow = ozone flow (250g/h); R = 8314.4 J/kmol. K; T = Air temperature (K); P = Pressure (Pa)

Table 1. Calculated ozone concentration and airflow at various grain depths.

Grain Depth (m)	Airflow (m^3/s)	Ozone Concentration (ppm)
1.55	0.525	67
1.40	0.580	60
1.32	0.600	58
1.25	0.620	56
1.17	0.640	55
1.02	0.706	50
0.94	0.701	50
0.86	0.721	49
0.79	0.741	47
0.64	0.782	45
0.56	0.801	44
0.48	0.822	43
0.41	0.841	42
0.23	0.889	39
0.15	0.909	39
0.076	0.929	38
0	0.949	37

During the treatment process, the ozone concentration was allowed to build up for 60 to 120 minutes in the bottom grain layer. As the layers of grain were removed, no ozone concentration in the headspace was measured until only 0.90m of grain was left in the silo. After additional layers were then removed, ozone concentration was detected in the headspace and increased with time. This occurred because ozone moved through the shallower grain too quickly for it all to react with the grain kernels before reaching the surface and exiting into the headspace where it could be detected.

The comparison of the theoretical and measured values for ozone concentration showed a larger than expected difference at each grain depth. Two possible causes were identified. Firstly, the actual ozone producing capacity of the generator was likely lower than the rated capacity, and secondly there was likely ozone measurement error in the monitoring system as some monitoring lines were longer than they should have been.

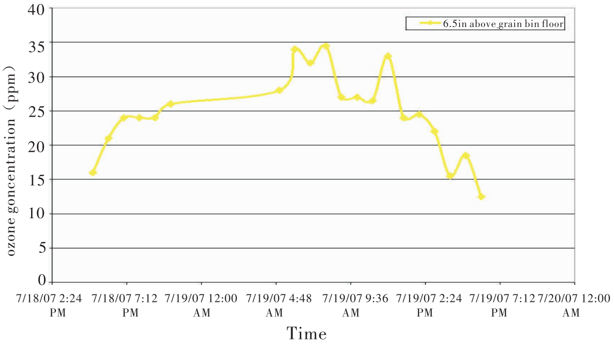

Fig. 1 Ozone concentration at the 0.165 m (6.5 inch) grain depth.

Design Parameters

In order to effectively control and design the semi – continuous counterflow system, the variables of airflow, ozone mass flow and exposure time were controlled. The airflow was controlled by sizing up the appropriate fan that can deliver at least the minimum air velocity of 0.03 m/s and the maximum airflow that will not cause a dilution effect with the initial amount of grain that will be ozonated.

The exposure time of the grain to ozone was controlled and determined by the amount of ozone concentration that was allowed to build up in each grain layer. Once the desired ozone concentration was achieved, the unloading sweep auger removed the bottom grain layer, allowing the ozone concentration to build up again. Based on the previous trial, the exposure time for each layer was between 60 to 120 minutes. Due to the lack of ozone producing capacity by the ozone generator, the CTP was not properly calculated. Therefore, a maximum ozone concentration of 25 ppm for 60 to 120 minutes was used.

The results of the half-life ozone experiments gave insight into how long the ozone was staying active under varying air conditions. Each of the experiments calculated the half-life of ozone, or the time at which half of the initial concentration was reached, under that particular condition. To examine the effect of ozone on surface microbes, samples of freshly-harvested and stored corn were treated with ozone for 60 minutes and 180 minutes at ozone concentrations of 1 600 – 1 700 ppm and 800 ppm. To determine the effect of ozone treatment on resistance to ozone flow, grain from each ozone concentration/time treatment was placed in a one-meter column and ozone was applied to the inlet of the treatment system. The time it took for the ozone concentration to exit the column and equal the intake concentration was measured. Although these values were not always an exact match, the output concentration generally approached the inlet concentration over time.

Concentration values from the ozone analyzer were continually recorded. The concentration value is important in understanding what concentration it will take to destroy all microbial growth over the shortest period of time. Data retrieved from the ozone analyzer were graphed and used as the basis of the research results.

Half – Life Time Calculation

The first tests performed were to determine the HLT of ozone. In this experiment, ozone was produced in the lab through dielectric excitation of oxygen. This excitation transforms the oxygen (O_2) molecules found in air to ozone (O_3). As the airflow increased within the cylinder, the HLT for O_3 decreased (Table 2). The first two tests were all with zero airflow for which the average HLT was approximately 26 hours. This value was much greater than the previously assumed 37 minutes for O_3 HLT. Weilandics *et al.* [7] determined that the chemical decay constant of ozone was 3.1e – 4 (s^{-1}). This value yields $t^{1/2}$ = 2235.97 sec = 37.26 min using Wolberg's equation of HLT = 0.69315/(Decay Constant).

Airflow Rate HLT Tests

In the next tests, mixing fans were incorporated to compare ozone HLT as a function of airflow rate. As the fan speed increased, the HLT decreased (Table 2). Incorporation of mixing fans showed marked reduction of HLTs. The greatest difference in HLT was noted with the 0.0283 m^3/s fan. Table 3 shows HLT results from tests when two different initial ozone concentrations were used. The HLTs for the two initial concentrations were consistent; there was no significant change in HLT when the initial concentration was reduced by half.

Table 2. Summary of ozone HLT values as a function of four airflow rates.

Exp. #	Fan Airflow (m^3/s)	HLT(min)
1	0	1590
7	0.0283	112
4	0.0519	57.7
5	0.104	47.5

Table 3. Summary of ozone HLT values as a function of two different initial concentrations at zero airflow.

Exp. #	Initial O_3 Conc.	HLT(min)
1	1300	1590
2	700	1553

Conclusions

A counterflow semi – continuous ozonation system was successfully tested and proved to be a technically feasible tool for properly ozonating grain at a faster rate than with a batch ozonation system. The half-life time of ozone was significantly decreased upon the incorporation of a mixing fan. This reduction can be explained by the fact that when ozone molecules are agitated they break down to oxygen more quickly.

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