Half-life time of ozone as a function of air conditions and movement

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Abstract

Stored grain products, such as corn, can harbor multiple microorganisms, including fungi such as *Aspergillus* species that produce toxins harmful to both humans and animals. In previous studies, we have demonstrated that ozone-treatment can significantly reduce the level of viable microorganisms on the surface of corn kernels. Ozone is a strong oxidizing agent, which is used in a growing number of industrial applications to control harmful microbes and volatiles. To achieve this goal, a better understanding of the properties of ozone is needed, especially with respect to the half-life of ozone and time/concentration criteria to reduce microbes on corn. The focus of this project was to determine the half-life time of ozone in air as a function of air speed (0 to 370 m^3/h), temperature (4 to 40°C) and relative humidity (0 to 80%) inside the cylinder. Half-Life Time (HLT) averaged ~1500 minutes in still air at room temperature (24°C) and zero humidity, which was substantially longer than previously published data (i.e., 30-40 minutes). As air speed, temperature and humidity increased, HLT decreased to ~40, 800 and 450 minutes, respectively. The results suggest that ozonation will be more effective in still air at low temperature and humidity (e.g., headspace ozonation of rail cars in the early spring) than at high flow rates of ozonated air at high temperature and humidity (e.g., grain storage silo in the middle of summer).

Keywords: Ozone, Ozone concentration, Half-life time, Treatment

1. Introduction

Ozone is a highly reactive gas that makes it useful in sterilizing surfaces, as it will react with many compounds. Due to the highly reactive nature of ozone, it is necessary to better understand key parameters about the gas before further investigation into its sterilizing abilities is undertaken. Methods for generating and analyzing ozone that will be used in this research must also be evaluated. Also, chemical reactions need to be explored as the ozone used will come in contact with various surfaces and compounds. These key parameters also involve evaluating ozone half-life at different airflow rates, temperatures and relative humidities. The half-life time (HLT) of ozone is the amount of time it takes to reduce the initial concentration by half. A lower HLT of ozone could result in less effective treatments during exposure. Once the HLT of ozone under varying conditions of airflow, temperature and relative humidity (r.h.) is determined, its effects on grain can be explored further. Ozone has been used for its sterilizing abilities in many types of containers. Grain bins as well as rail cars, which transport grains, have been treated with ozone before filling in order to sterilize container surfaces. At times these containers can be exposed to different air conditions and movement. Therefore, the objective of this study was to develop an equation that will quantify the HLT of ozone as a function of air conditions and movement. This equation can then be used to predict the HLT of ozone in containers that will be treated under varying air conditions and movement.

2. Materials and methods

2.1. Experimental set-up

Experiments were set up to determine the half-life time (HLT) of ozone produced by a lab-scale generator as a function of varying air movement, temperature and relative humidity inside a plexiglass cylinder. Air movement inside the cylinder was regulated with fans. Temperature was regulated by exposing the cylinder to different external environments. Relative humidity in the cylinder was controlled with salt solutions. Ozone was pumped into a 40L cylinder (r_i=5.5”, r_o=6”, h=24”) until it was filled to a pre-determined O_3 concentration. Two to three replications were performed for each test. To calculate HLT, the results from the tests were analyzed using SAS (version 9.3.1).

2.2 Ozone generation

The generator used in this work was provided by O_3Co Inc. (Idaho Falls, ID, USA) and utilized the corona discharge to produce ozone. The unit contains four electrodes where the oxygen-to-ozone transformation takes place. The system was placed in a fume hood and tap water flowed from the top of the system to the bottom, along the length of the electrode tubes, to keep the system cool. Ozone concentration was varied by adjusting the input voltage and air supply. The generator produces about 2.75 g/h of ozone at 115 V with dry air as the feed gas. The input voltage was varied from about 50 V to produce 0.5 g/h to 140 V to produce 3.5 g/h.

2.3. Ozone analyzer

The ozone analyzer used to monitor the ozone concentration from the generator was an IN2000LC unit from IN USA, Incorporated (Norwood,MA, USA). According to the analyzer’s manual, the unit has a measuring range from 0 to 2000 ppm, and is calibrated according to US NIST traceable standards (+/-1%). The ozonated air mixture is pumped into the analyzer at 1.0 L/min.

2.4. Data collection and analysis

Concentration measurements were taken through a valve at the top of the cylinder using a Kitagawa® Gas Sampling Tube. Over a period of time, samples were taken intermittently and recorded with a date and time stamp. Standard test conditions were all room temperature (about 24°C), ~0% humidity, and 0 m^3/h air movement. The other tests included an increased and decreased air temperature (40°C and 4°C), increased humidity (45% and 87%) and increased air movement (102 m^3/h, 187 m^3/h, 374 m^3/h).

3. Results

The results from the tests show that the HLT of ozone is affected by changes in temperature, air speed and humidity. For example, the addition of mixing fans into the cylinder allowed for the ozone inside of the cylinder to be moved around. As the fan speed increased, the HLT decreased exponentially. Incorporation of mixing fans showed a marked reduction of HLTs.

The average difference in HLT between the test with 0 m^3/h fan speed and 100 m^3/h fan speed was 1314 minutes. Table 1 shows that as temperature increased the half-life time of ozone decreased by about 38% from 4 to 24°C and 48% for 24 to 40°C. As humidity increased from 0 to 45%, HLT decreased by ~54%; and by ~35% from 45% to 87% r.h.

Table 1 Half Life Time results for tests on temperature, air speed, and humidity variations.

Temp (°C)	Fan Speed (m^3/h)	r.h. (%)	Reps	HLT (min)
24	0	0	3	1524
24	0	45	1	705
24	0	87	2	451
4	0	0	2	2439
40	0	0	2	796
24	100	0	1	210
24	185	0	2	49
24	370	0	2	39

3.1. Half-life time equation

By combining the results from the previous tests, stepwise regression could be performed in SAS. The SAS analysis yielded the following equation:

$$Y = 2274.4 + 0.483 * x_1 - 8.49 * x_2 - 51.64 * x_3 - 12.01 * x_4 \qquad \textbf{Eqn. 1}$$

Where y is the half-life time (min), x_1 is the initial ozone concentration (ppm), x_2 is the value for air flow rate (m^3/h), x_3 is the temperature (C), and x_4 is the relative humidity (%). Figures 1, 2 and 3 compare three variables at once using Eqn. 1. Figure 1 shows the relationship of air speed and temperature for HLT at ~24°C. For dry air at 0% r.h., the sterilization limit at which HLT = 0 is predicted to be an airflow rate of 290 m^3/h (170 CFM).

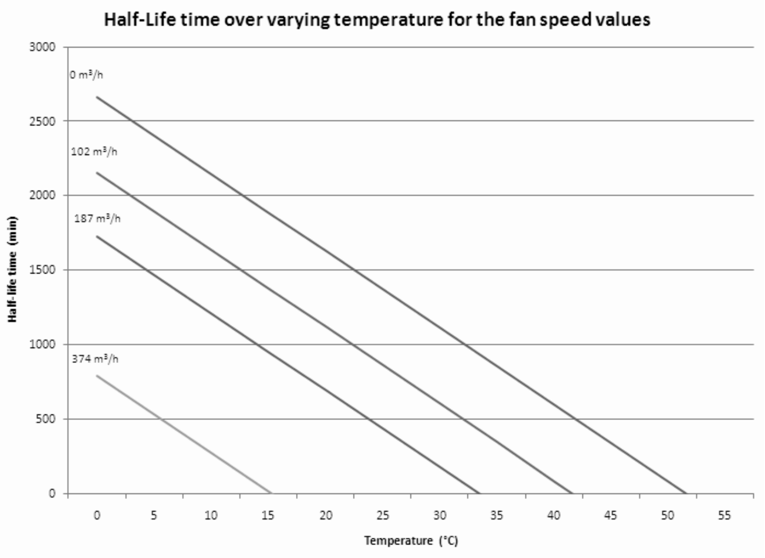

Figure 1 Comparison of HLT against temperature for four air flow values and 0% relative humidity air.

Figure 2 shows the relationship of relative humidity and temperature on HLT in still air. For the higher temperature (40°C) the HLT reaches zero at 50% r.h. This implies that a sterilization effect will unlikely be achieved in the treatment container above that level.

Interpolation was performed to find the temperature that would give an HLT of zero at 100% r.h., which was 28°C. This means that temperature lower than 28°C can sustain HLTs greater than zero at 100% r.h. An HLT of 1524 min was achieved at a temperature of 24°C and 0%r.h., and 2439 min was achieved at a temperature of 4°C. This implies that the equation does a good job of predicting the observed values.

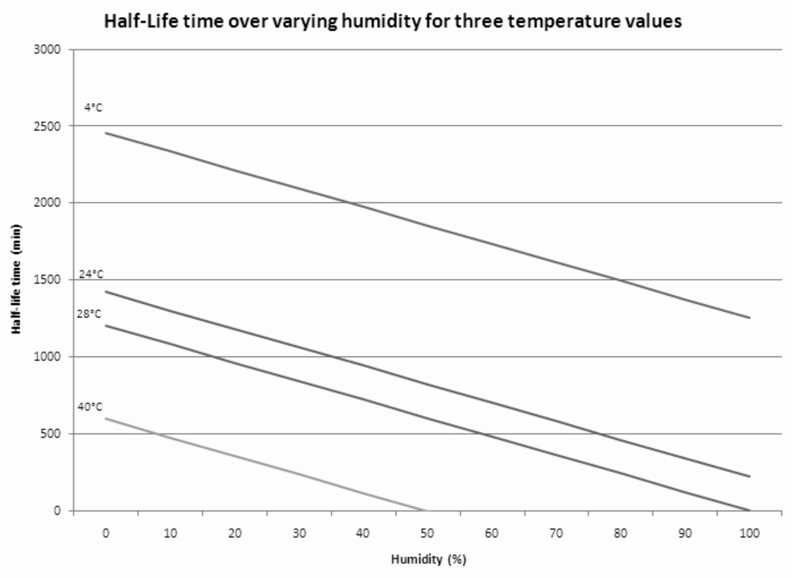

Figure 2 Comparison of HLT against humidity for four temperatures in still air.

Figure 3 shows the relationship of air speed and relative humidity for HLT at ~24°C. The equation both over and under predicts the true values. The 80% r.h. line predicts well, as the HLT for 80% r.h. is 451 minutes at 0 m^3/h.

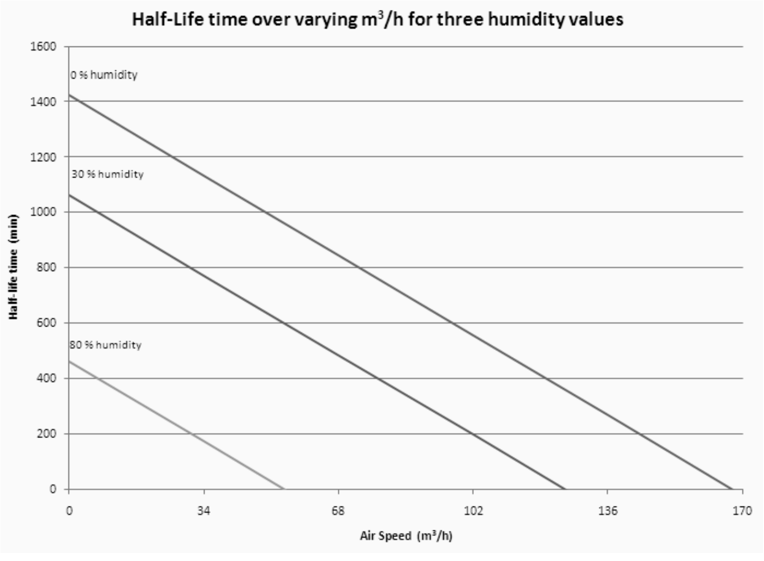

Figure 3 Comparison of HLT against air speed for three relative humidity value at ~24°C temperature.

4. Discussion

Ozone follows the common gas law. Therefore, as the air speed inside the cylinder increased the HLT of ozone decreased. The gas molecules inside the cylinder interact more rapidly when the air speed increases. This interaction of ozone molecules bouncing into other ozone molecules results in a breakdown of ozone to oxygen and, thus, a reduction in ozone concentration. Treating the plenum of grain bins before or after filling with grain has shown to sterilize the metal surfaces and kill mice when exposed to high enough ozone concentrations for sufficient time given the HLT in still air. Therefore, filling any container or chamber with ozone to a sufficiently high concentration and avoiding subsequent air agitation (mixing) for extended time periods has great potential as an alternative, non-chemical treatment. Strait (1998) showed that temperature affects ozone concentration. Gas half-life values ideally follow this linear trend concerning varying temperature. At lower temperatures gas molecules do not move quickly and therefore collide less frequently. At higher temperatures ozone molecules move faster and collide more frequently. The effect of relative humidity on ozone HLT was also tested. From Table 1 it can be noted that as humidity increased ozone HLT decreased. These results agree with Strait (1998) which stated that as humidity increases the HLT of ozone will decrease.

Applying these results to the headspace of a rail car and the plenum of a grain bin suggests that treatment with ozonated air would be more efficacious in drier western U.S. locations than more humid Eastern U.S. locations. Combined with the temperature results, these findings suggest that the efficacy of ozone treatment will be affected by the initial temperature and relative humidity of the air in the storage container or transport vehicle. Therefore, the initial ozone concentration will need to be adjusted upward under warmer and more humid weather conditions to achieve the same results as under cooler and drier weather conditions.

Acknowledgment

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Reference

Strait, C.A., 1998. Efficacy of ozone to control insects and fungi in stored grain. M.S. thesis, Purdue University, West Lafayette, IN, USA.