Development of Ozone Technology Rice Storage Systems (OTRISS) for Quality Improvement of Rice Production

M. Nur¹, E. Kusdiyantini², W. Wuryanti³, T.A. Winarni⁴, S.A. Widyanto⁵, and H. Muharam⁶

¹Department of Physics, ²Department of Biology, ³Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Semarang, Indonesia
⁴Department of Fishery Product Technology, Faculty of Fisheries and Marine Science, Diponegoro University, Semarang, Indonesia
⁵Department of Mechanical Engineering, Faculty of Engineering, Diponegoro University, Semarang, Indonesia
⁶Department of Management, Faculty of Business and Economics, Diponegoro University, Semarang, Indonesia
E-mail: m.nur@undip.ac.id

Abstract. This research has been carried out by using ozone to address the rapidly declining quality of rice in storage. In the first year, research has focused on the rice storage with ozone technology for small capacity (e.g., household) and the medium capacity (e.g., dormitories, hospitals). Ozone was produced by an ozone generator with Dielectric Barrier Discharge Plasma (DBDP). Ozone technology rice storage system (OTRISS) is using ozone characteristic which is a strong oxidizer. Ozone have a short endurance of existence and then decompose, as a result produce oxygen and radicals of oxygen. These characteristics could kill microorganisms and pests, reduce air humidity and enrich oxygen. All components used in SPBTO assembled using raw materials available in the big cities in Indonesia. Provider of high voltage (High Voltage Power Supply, 40-70 kV, 23 KH, AC) is one of components that have been assembled and tested. Ozone generator is assembled with 7 reactors of Dielectric Barrier Discharge Plasma (DBDP). Rice container that have been prepared for OTRISS have adjusted so can be integrated with generator, power supply and blower to blow air. OTRISS with a capacity of 75 kg and 100 kg have been made and tested. The ability of ozone to eliminate bacteria and fungi have been tested and resulted in a decrease of microorganisms at 3 log CFU/g. Testing in food chemistry showed that ozone treatment of rice had not changed the chemical content that still meet the standard of chemical content and nutritional applicable to ISO standard milled rice. The results of this study are very likely to be used as an alternative to rice storage systems in warehouse. Test and scale-up is being carried out in a mini warehouse whose condition is mimicked to rice in National Rice Storage of Indonesia (Bulog) to ensure quality. Next adaptations would be installed in the rice storage system in the Bulog.

1. Introduction
Technology of rice storage in Indonesia has not been able to keep the quality of rice in a long time. Often, distribution of rice in large quantities had to be canceled by the damage of rice, due to the quality of the rice that was not fit for consumption. It is very worrying the government in this case Bulog can not replace the rice in a large amount in a short time. On the other side the needs of the
community may not be delayed. In remote regions that are not producing rice this problem may be more fatal, such as famine. The rapid of decay of rice occurs due to high water levels and breeding of microorganisms contained in the rice storage container. Rice that has been reduced quality is also easily become breeding places of which often called mite pests of rice.

So far, in rice storehouses owned Bulog, fumigation and spraying insecticides have been done as efforts for maintaining the quality of rice. Fumigation is a method of insect pest control with specific gases generated by the fumigant. With this method, pest insects that were in or at surface of a sack of rice can be eradicated. To improve the effectiveness of the insect pests eradication on rice and sacks, fumigation collaborated with insecticide spraying method. Insecticides was sprayed on surface of the sack, sack piles sidelines, warehouse floors, and the surrounding environment that serves to eradicate insects that exist in the area. So the insect pest population can be reduced and also can prevent the insects return to the rice barn.

Technology of rice storage has not been able to keep the quality of rice. The new technology is needed to resolve the issue. The alternative is ozone technology. Based on research, this technology proved can maintain and even increase the quality of cereals (especially wheat). Utilization of appropriate ozone generating technology and proper dosage of ozone is believed to be used for rice storage technology.

Ozone can also be generated by using a plasma reactor for a particular purpose. Ozone consists of three oxygen atoms and has chemical formula \( \text{O}_3 \). Ozone is an unstable molecule with a very short life span (20-30 minutes) before return to be oxygen, therefore ozone will always seek 'target' to able release one oxygen atom by means of oxidation, so it can be turned into oxygen molecules stable (\( \text{O}_2 \)).

The precise dose of ozone is determined by configuration of the ozone reactor and the generator. [1]. Ozone as an oxidant has many potential applications in food industry due to the advantages of ozone technology compared to traditional food preservation techniques. Ozone has been known to be extensive utilization for microbial inactivation. Ozone has been reported to eliminate micro-organisms including bacteria, fungi, viruses, protozoa, fungi and bacteria spores. Another advantage of the use of ozone for food is that ozone compounds rapidly decompose and produce oxygen so it does not leave residues in food [2]. Ozone treatments for wheat and corn with ozone concentration of 50 ppm for (3-5) days treatment can kill insect pests reach 70% - 100% [2]. The factors that determine the ability of ozone to kill insects, eliminate fungus and decontamination of toxins, depends on: ozone concentration, exposure time, pH and moisture content of the grains (e.g., wheat, and corn) [3] [4] [5].

In recent years, Diponegoro University has developed research of applications of plasma technology including ozone produced by the plasma technology [6] [7]. Utilization of ozone to maintain the shelf life of rice [8]. In 1995, ozone expressed by Generalize Recognized as Safe (GRAS) or is generally recognized as safe by FDA (U.S. Food and Drug Administration) for the treatment of drinking water bottles. These applications are then developed as "GRAS" for processing food by some experts in last few years [9].

Disinfectant properties of ozone have been tested by several researchers. For example Tiwari et al. [2], which examined the effectiveness of ozone against grain pests such as Tribolium castaneum and Ephestia elutella and the coliform bacteria, Micrococcus, Bacillus spores, fungi and the like. In his journal Tiwari et al. [2] write that the respiratory system be the entrance of ozone to the inside the body of the insect. Ozone causes oxidative tissue damage (even at low concentrations), causing DNA damage, changes in pulmonary system, bronchial sensitivity, membrane oxidation or mutation in vivo. Increased respiratory system with an increase in temperature can result excessive gas exchange due to the increase in metabolism and respiration rate. [10].

In a different study, Ran et al. [11] examined the effectiveness of ozone against Cryptosporidium (intestinal protozoa, one of the causes of diarrhea) and protozoan parasite Giardia. In addition, Ran also investigated the mechanism of cell destruction Cryptosporidium by ozone using scanning electron microscopy (SEM) at treatment of time 0, 60, 120, and 480 seconds. As a result, the cell Cryptosporidium suffered the greatest damage in 480 seconds.
Research on microbial inactivation of bacteria and molds (fungi) using ozone has been done by several researchers. For example, Zorlugenc et al. [12] who observed the effectiveness of ozone gas and liquid against the bacteria E. coli and coliform bacteria as well as fungi. The tests proved, disinfectant properties (against E. coli and coliform bacteria) ozone gas is lower than the liquid ozone. Similarly, when testing against molds (fungi), which perfectly reduced the mold in 15 minutes using liquid ozone while in ozone gas still leaving approximately 1 log CFU/g. Types of mold that identified having degraded populations include Aspergillus flavus, Aspergillus niger, Aspergillus parasiticus [12]. Test effectiveness of ozone against E. coli was also conducted by Patil et al. [13], where they use ozone to sterilize orange juice from bacterial contamination.

The bacteria can be symbiotic mutualism and/or parasitism. In many ways, the bacteria associated with causing disease (parasites and pathogens), accelerating the decay and the like. Overcome the things that adverse caused by bacteria, it is used various types of disinfecting agents. Disinfectant agent that is quite popular in use today is chlorine. Chlorine can kill bacteria with a low concentration, in quick time, and little risk. Chlorine kills bacteria in a way, destabilize cell membranes and inhibit biochemical reactions. Besides chlorine, ozone and ultraviolet is also used. Disinfecting ability of ozone has been studied by several experts in recent years. Ozone, in some cases can kill the bacteria in which chlorine is quite difficult to use. Effectiveness of the disinfectant agent is different, depending on the type of microbes, concentration, and the like [14].

The ability of ozone to kill bacteria, fungi, and insects used as basis for utilizing ozone in rice storage system. In addition, due to ozone within 40 minutes will decompose and possible to bind water molecules, the water content in rice will also be reduced. This paper discusses the use of ozone for rice storage. The discussion is about ozone generation systems, the ability to hold the growth of microorganisms and the quality of rice that has undergone ozonized. In this paper also discussed adaptation of ozonized system into the storage system in Bulog warehouse.

2. Method
Ozone generators are made in the laboratory can be adapted for rice storage system which is based on techniques Dielectric Barrier Discharge Plasma (DBDP) and raised with an AC voltage source; 40-70 kV, frequency of 23 kHz.
Active electrode is made of spiral wire copper and passive electrodes made from tube-shaped copper plate. Between the two electrodes is given dielectric made of pyrex glass with varying diameter (2 cm, 3 cm and 5 cm). Air pump (Amara AA-250) was used to deliver the air into the reactor, and ozone from recombination process, into treatment media. Probe (Ser. No. 20048737) was used to divide the power supply voltage to 1000 times smaller before being connected to an oscilloscope. Oscilloscope (Instek, GOS-620 20Mhz) was used to monitor the voltage, and operating frequency of the power supply. Ozone detector (Model OS-4, serial # 1208) was used to test the generated ozone levels for treatment (figure 1). Ozone generator was integrated of DBDP reactor with a spiral configuration of copper and copper-dielectric cylindrical pyrex pipes (diameter 3 cm and length 15 cm for research on rice with small and medium capacity). Adjustments to the requirements of adaptation to SPBTO containers, using one generator unit with 7 reactor DBDP. Rice samples were placed in a cylindrical media. Ozone is supplied using an air pipe through the bottom of rice samples. Variation of ozone exposure time was 30, 60, 90, 120, 150 and 180 minutes. Each treatment was performed 4 times, so to be obtained at least 20 data from each object, where the objects of this study are bacteria and mold or fungi which contaminate rice. Testing of samples for chemical analysis (proximate), biological analysis (bacteria and mold/fungi), physical analysis (amilografi, hardness, viscosity and whiteness) and SEM analysis (SEM morphology and SEM EDS).

3. Results and Discussion

3.1. Characterization of Current-Voltage and Ozone concentration

The influence of voltage to electrical current average is presented in Figure 2 for the integrated generator which consists of 7 pieces reactor Spiral Cylinder (SC) with 3 cm of diameter pyrex tube. Total electric current has two components: capacitive electric current from the capacitor barrier and capacitive electrical current from the capacitor gas. Therefore, the electric current that actually being measured is the average capacitive electrical current. Influence of electric voltage to ozone concentrations are presented in figure 3 for spiral cylinder reactor of pyrex tube with a diameter of 3 cm.

![Figure 2. Electric current as a function of applied voltage for DBDP spiral-cylinder reactor, to 3 cm diameter pyrex tube.](image)

![Figure 3. Ozone concentration as function of applied voltage, for DBDP reactor spiral-cylinder, for diameter of Pyrex tube of 3 cm](image)
3.2. Inactivation of Bacteria and Fungi

In Figure 4, we find that the effect of ozone on the amount of bacteria that contaminate rice showed a negative correlation. Bacterial growth is inversely related to ozone exposure time. The average number of bacteria decreased 0.41 log CFU / g every 30 minutes during treatment lasts beyond. This condition is caused by the amount of contaminating bacteria do not survive to breeding process. Resulting slower in population growth of bacteria. The curve above shows, the optimum point decline in bacteria occurs on treatment for 180 minutes.

The number of bacteria decreased to 2.48 log CFU / g from the initial state (5.39 log CFU/g). Bacterial growth at 180 minutes, only reached 2.91 log CFU/g indicate that the highest number of bacteria which died before the proliferation (in vitro incubator) done. Remaining bacteria after treatment for 180 minutes is 54.02% of the total number of bacteria before treatment, or can be said to be 45.98% of the bacteria died before breeding. The most significant decrease in the yield curve occurs in treatment between 0 to 30 minutes, in which the number of bacteria decreased 1.44 log CFU/g compared to the transition time of 30-60 minutes. The influence of ozone to the number of fungi is presented in Figure 5. Research of ozone treatment for inactivation of fungi indicate decline from an average of 3.44 log CFU/g to an average of 1.88 log CFU/g. The curve above shows the optimal reduction in the number of fungi occurred at 180 minutes. Where the number of fungi population decreased 1.56 log CFU/g compared with no treatment. The number of fungi surviving 180 minutes after treatment was 1.88 log CFU/g (approximately 54.56% than without treatment). The most significant decrease in the curve occurs at the transition 0 to 30 minutes, in which the number of fungi fell 0.52 log CFU/g. The curve is a significant decrease in the number of fungi in the first 30 minutes also occur in bacteria. This decrease may be due to some fungi can not survive environmental changes abruptly.
3.3. Content of Carbohydrate, Amylose and Amylopectin

Chemical content in rice are being subjected to ozone should be studied seriously. Application of ozone at sufficient doses for effective decontamination of rice can affect various quality parameters. Utilization of ozone are not all beneficial and in some cases can lead to oxidative degradation of the chemicals present in rice. Surface oxidation, discoloration or change unwanted odors can be occur from excessive use of ozone [5]. The main part of rice is carbohydrate, then the rice used to meet nutritional needs as a source of carbohydrate. Carbohydrate content in rice, corn, and potatoes are 78.9; 72.4; 19.1% respectively [16]. In different exposure time tends to decrease carbohydrate content, but in relatively small amounts. Carbohydrate in rice consists of amylose and amylopectin. The content both of the compounds is commonly used as a standard of rice quality (figure 6, figure 7).

The results shows that there is no change in significant chemical content in rice for conditions in this study. Table 1 shows chemical composition Nutritional value per 100 grams rice.

| No | Chemical composition | Great contains          |
|----|----------------------|-------------------------|
| 1  | Carbohydrate         | 79 g                    |
| 2  | Glucose              | 0.12 g                  |
| 3  | Dietary fiber        | 1.3 g                   |
| 4  | Fat                  | 0.66 g                  |
| 5  | Protein              | 7.13 g                  |
| 6  | Water content        | 14 g                    |
| 7  | Thiamine (Vit.B1)    | 0.070 mg (5 % AKG)      |
| 8  | Riboflavin (Vit B2)  | 0.049 mg (3 % AKG)      |
| 9  | Niacin (Vit B3)      | 1.6 mg mg (11 % AKG)    |
| 10 | Pantotenik acid (B5) | 1.014 mg (20 % AKG)     |
| 11 | Vitamin B6           | 0.164 mg (13 % AKG)     |
| 12 | Folik Acid Vit B9    | 8 μg (2 % AKG)          |
| 13 | Forum                | 0.8 mg (6 % AKG)        |
| 14 | Phosphorus           | 115 mg (16 % AKG)       |
| 15 | Potassium            | 115 mg (2 % AKG)        |
| 16 | Calcium              | 28 mg (3 % AKG)         |
| 17 | Magnesium            | 25 mg (7 % AKG)         |
| 18 | Zinc                 | 1.09 mg (11 % AKG)      |
| 19 | Calories             | 354 kcal                |

There are 4 classes of rice [17], the first class is rice with high amylose content about 25-33%, the second class is rice with intermediate amylose content about 20-25%, the third class is rice with low amylose content about 9-20%; the fourth class is rice with very low amylose content about < 9%.
The analysis result of amylose and amylopectin content in rice known that generally, amylose content increased with increasing of exposure time by ozone. The treated rice by ozone content 16.26 % of amylose. As previously described, based on the amylose content, the quality of rice is classified into 4 classes [17], the first class is rice with high amylose content about 25-33%, the second class is rice with intermediate amylose content about 20-25%, the third class is rice with low amylose content about 9-20%; the fourth class is rice with very low amylose content about < 9%.

The samples that used in this research are rice with low amylose and high amylopectin. Therefore, when it cooked into cooked rice, it has high adhesion level. Content of amylose and amylopectin in rice are one one of the factors that determine the quality of rice. Glutinous rice has a low amylose content of less than 2%, it caused the glutinous rice more sticky than rice.

### 3.4 Content of Fat and Protein

From the data of test result known that the fat content tended to decrease after treat by ozone irradiation. Changes in fat content in rice were being treatment by ozone are still in a very small amount such that there is no significant change after rice being treat by ozone (Figure 8). Fat content is generally below the analytical results of the fat content of milled rice [16]. This is not being problem because the rice used as a source of carbohydrate.

Raw white rice contains about 6.7% protein, while if it is cooked, it contain about 2%. Rice contains glutelin protein group that is orizenin and in the protein contained 24.1% of glutamate amino acid and slightly lysine. Physical properties of protein of cereal grains is very important, although the protein content is not so high. The size of protein content depends on: species, type of soil, fertilizers, and climate. In general, changes in protein content is very small due to the irradiation is done at room temperature about 29 °C, less than 50 °C. While the character of protein is easy to denatured at temperatures about 50 °C and having surface denaturation in range of pH of 4.5 to 6.0. In the Figure 9 shown that there is an
slightly increase of protein on 60 minutes exposure by ozone. The increase can not provide conclusion, as to the provision of higher ozone, protein levels return as in the control

![Figure 8. The test result of fat content on rice with variation of time of treatment by ozone, compared to control, for the same rice condition.](image1)

![Figure 9. The test result of protein contain on rice with variation of time of treatment by ozone, compared to control, for the same rice condition](image2)

3.5 **Content of Ash and Water**

The analysis result of ash content on treated rice by ozone is shown in figure 10. It shows that there is no significant change of ash content, and still in the range of milled rice standard. From the data analysis it appears that the water content before and after irradiation are not much different (figure 11). Rice with minimum water contain will be more resistant to microbial attack due to the properties of microbial that tend to live in high humid condition. In addition, rice with minimum water contain is also will be more resistant to insect attack. The level of water contain reduced by 12.4%, and according to the experience on Bulog, it can be stored for more than 3 years.
Figure 10. The test result of ash content on rice with variation of time of treatment by ozone, compared to control, for the same rice condition

Figure 11. The test result of water content on rice with variation of time of treatment by ozone, compared to control, for the same rice condition

4. Conclusion

In this study has successfully developed ozone technology rice storage system (SPBTO). Ozone was generated with application of plasma technology by Dielectric Barrier Discharge Plasma (DBDP) reactor. Development of the product begins with the electro mechanical testing of DBDP plasma reactor and ozone generator. The results indicate that the DBDP reactor can produce ozone properly and can be adjusted to the desired concentration to maintain the quality of rice. The test results on treated rice by ozone indicate that the bacteria in rice greatly reduced over a period time, and the most effective decrease is in 180 minutes.

Utilization of ozone have also been able to reduce the growth of fungi, it also obtained that the optimal reduction in the number of fungi occurred at 180 minutes. This time will be used for each repetition period of ozonation on rice. There are no insects on treated rice by ozone although it has been stored for 12 months. The analysis of fat, water, and protein, ash, and carbohydrate that content in rice before and after treatment by ozone results that there is no significant change.

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