Application of Response Surface Methodology for characterization of ozone production from Multi-Cylinder Reactor in non-thermal plasma device

Tan Lian See¹, Ahmad Zulazlan Shah Zulkifli², Lim Mook Tzeng²

¹Malaysia - Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia (UTM), 54100 Kuala Lumpur, Malaysia.
²TNB Research Sdn. Bhd., 43000 Kajang, Selangor, Malaysia.

E-mail: mook.tzeng@tnb.com.my; mooktzeng.lim@live.com

Abstract. Ozone is a reactant which can be applied for various environmental treatment processes. It can be generated via atmospheric air non-thermal plasmas when sufficient voltages are applied through a combination of electrodes and dielectric materials. In this study, the concentration of ozone generated via two different configurations of multi-cylinder dielectric barrier discharge (DBD) reactor (3 x 40 mm and 10 x 10 mm) was investigated. The influence of the voltage and the duty cycle to the concentration of ozone generated by each configuration was analysed using response surface methodology. Voltage was identified as significant factor to the ozone production process. However, the regressed model was biased towards one of the configuration, leaving the predicted results of another configuration to be out of range.

1. Introduction

Ozonation is gaining attention as an environmental remediation process due to its ability to decompose contaminants into safer compound compared to the conventional chemical treatments [1, 2]. Ozone (O₃) can be used for drinking water treatment as an alternative to chlorination [3-5]. It can be used to degrade antibiotics and organic compounds in water [6-11].

Ozone is also a powerful antimicrobial agent which can be applied in processing of food. It is capable of inactivating microorganisms rapidly by reacting with intracellular enzymes, nucleic material and components of their cell envelope, spore coats, or viral capsids [12]. This is an important aspect in preservation of food.

Non-thermal plasma discharge is one of the popular and cost effective method to generate ozone artificially [1, 13-16] and is synthesized from corona discharges [17]. Non-thermal plasma (NTP) reactor can be operated at ambient temperature and atmospheric pressure condition [3, 18]. It is also more energy saving compared to thermal plasma [19]. There are various types of NTP discharge and they are usually categorized based on their electrode geometry, breakdown mechanism, and the presence (or absence) of dielectric materials between the gas flow and the electrodes [13].
One of the common types of NTP reactor is based on dielectric barrier discharge (DBD) [13, 16]. The electrode configuration is characterized by the presence of at least one dielectric barrier (insulator) in the current path in addition to the gas gap used for discharge initiation [16]. It has a relatively quiet discharge operation when the narrow discharge gap of a few millimeters in the reactor is fed with low flow rate of oxygen or air for ozone synthesis [15].

The reactor is able to convert majority of the electrical energy into producing high temperature electrons, rather than directly into gas heating [14, 16]. The energetic electrons rarely collide directly with the pollutants. Rather, the electrons tend to collide with the dominant nitrogen (N₂) and O₂ molecules and produce radicals such as oxygen atom which subsequently lead to the generation of O₃ [14, 16]. O₃ has relatively longer lifetime than electrons. It is well-known for its strong oxidizing capability [15, 16]. It decays without residues that are harmful to the environment [12, 14]. Since the production of ozone requires only air/oxygen (O₂) and electricity, the need for material handling of hazardous chemicals (for decontamination) is eliminated [14]. Therefore, ozonation process can be considered as a treatment process which is benign to the environment.

Ozone generation is expected to increase with the increasing activities of a corona discharge on the surface of dielectric barrier. Specifically, the generated ozone concentration would increase with the increasing voltage applied to the system [14]. However, after optimum condition of the corona discharge, the generated ozone concentration could decrease with increasing applied voltage [14]. This is because the heat from the discharges in the small discharge gap promotes ozone disassociation [20]. Hence, it is important to identify the optimum voltage level to be applied to a NTP reactor. The ozone generation rate is also associated with the duty cycle, which controls the amount of current injected into the DBD. Higher duty cycles (and amperes) could cause localized heating at the location of the discharges, dissociating ozone.

In this work, a multi-cylinder in an enveloping cylinder was developed in order to minimize the possibility of fine particle clogging in the reactor. It is an alternative to the conventional plate-type reactor. A multipoint configuration electrode is also expected to present the advantage of low voltage operation [21]. In this paper, specifically, the ozone generation performance with respect to the voltage and the duty cycle for two configurations of multi-cylinder DBD was investigated using response surface methodology. This is important to get insight of influencing parameters for characterization of ozone production from the developed device.

2. Materials and methods

2.1 Experimental setup

A schematic flow of the experimental setup used in this study is shown in Figure 1. The NTP rig had an enveloping cylinder with inner diameter of 110 mm which acts as the ground electrode. The dielectric barrier was silica cylinders with a thickness of 2 mm and held in place by a Teflon holder. Two different configurations of dielectric barrier discharge (DBD) reactors were tested in this study. In the first configuration, the arrangement consisted of three silica cylinders with 40 mm outer diameter (3 x 40 mm). In the second configuration, the arrangement consisted of ten silica cylinders with 10 mm outer diameter (10 x 10 mm). The inner surface of the silica cylinders were lined with copper sheets that are connected to the high voltage supply. The smallest air gap formed between the silica cylinders and the outer enveloping shell was 1 mm.
The input power into the NTP rig was supplied by a high voltage (HV) power supply (PVM 2000). The HV source included a 2 kW VARIAC which controlled the total power to the system. The current was controlled by the duty cycle which provided the current pulses. A circuit breaker was placed before the NTP reactor as a safety device to protect the reactor from damage. It would cut off voltage supply if the voltage or current induced from the HVT was too high.

All the experiments were conducted at atmospheric pressure and room temperature. The concentration of ozone produced from the NTP reactor was measured using Aeroqual Series 500 Portable Ozone Analyzer.

2.2 Design of experiment
The variables in this experiment were voltage, duty cycle and configuration of the multi-cylinder in the reactor. The numerical variables are voltage and duty cycle while the categorical variable is the configuration of the cylinders. Experimental runs were conducted based on the combinations of the variables were generated using response surface methodology (RSM) provided by Design-Expert software 6.0.6 (Stat-Ease Inc., Minneapolis, USA). This is done to investigate the influence of variables selected to the amount of ozone synthesized.

Central Composite Design (CCD), with an alpha value of ±1.00 was applied to study the experimental variables. The range for voltage was 12 kV to 16 kV while the range for duty cycle was 10–30 based on the equipment specifications. The level of condition for the numerical and categorical variables are given in Table 1 and Table 2, respectively.

Table 3 shows the twenty-six sets of experimental condition generated by Design Expert software. Evaluation on the effect of voltage, duty cycle and electrode configuration to the ozone concentration synthesized from the multi-cylinder reactor was subsequently conducted using analysis of variance, ANOVA.
### Table 1. Levels of the condition for numerical variables.

| Numerical Factors | Coding | Unit | Levels |
|-------------------|--------|------|--------|
| Voltage           | A      | kV   | -1 12 14 16 |
| Duty cycle        | B      | -    | 10 20 30 |

### Table 2. Levels of the condition for categorical variables.

| Categorical Factor | Coding | Level 1 | Level 2 |
|--------------------|--------|---------|---------|
| Configuration      | C      | 3 x 40 mm | 10 x 10 mm |

### Table 3. Central composite experimental design matrix.

| Run | Voltage (kV) | Duty cycle | Configuration |
|-----|--------------|------------|---------------|
| 1   | 16           | 20         | 10x10 mm      |
| 2   | 16           | 10         | 3x40 mm       |
| 3   | 14           | 20         | 10x10 mm      |
| 4   | 12           | 10         | 3x40 mm       |
| 5   | 12           | 30         | 3x40 mm       |
| 6   | 16           | 30         | 10x10 mm      |
| 7   | 14           | 30         | 10x10 mm      |
| 8   | 12           | 30         | 10x10 mm      |
| 9   | 14           | 20         | 3x40 mm       |
| 10  | 14           | 20         | 3x40 mm       |
| 11  | 12           | 10         | 10x10 mm      |
| 12  | 16           | 20         | 3x40 mm       |
| 13  | 14           | 20         | 10x10 mm      |
| 14  | 12           | 20         | 10x10 mm      |
| 15  | 16           | 10         | 10x10 mm      |
| 16  | 14           | 10         | 3x40 mm       |
| 17  | 16           | 30         | 3x40 mm       |
| 18  | 14           | 20         | 3x40 mm       |
| 19  | 14           | 30         | 3x40 mm       |
| 20  | 14           | 10         | 10x10 mm      |
| 21  | 14           | 20         | 10x10 mm      |
| 22  | 14           | 20         | 10x10 mm      |
| 23  | 14           | 20         | 10x10 mm      |
| 24  | 14           | 20         | 3x40 mm       |
| 25  | 14           | 20         | 3x40 mm       |
| 26  | 12           | 20         | 3x40 mm       |
3. Results and Discussion

3.1 Ozone Production Model based on RSM

Based on the response (ozone concentration) obtained for the designated set of experiments in Table 3, linear model was analyzed by the Design Expert software as the suggested model. It was the best model with highest order polynomial whereby the additional terms were significant and the model was not aliased.

| Source   | Sum of Squares | Mean Square | F Value | Prob > F | Remarks |
|----------|----------------|-------------|---------|----------|---------|
| Mean     | 70.95          | 70.95       |         |          |         |
| Linear   | 2.39           | 0.80        | 5.50    | 0.0057   | Suggested |
| 2FI      | 0.27           | 0.091       | 0.59    | 0.6272   |         |
| Quadratic| 0.59           | 0.29        | 2.16    | 0.1460   |         |
| Cubic    | 1.13           | 0.23        | 2.28    | 0.1119   | Aliased |
| Residual | 1.19           | 0.099       |         |          |         |
| Total    | 76.52          | 2.94        |         |          |         |

The significance and the fitness of the model was also verified by using Analysis of Variance (ANOVA) in the Design Expert software. The results are presented in Table 5. The model F-value of 5.50 implies the model generated was significant. Based on the analysis by ANOVA, there is a 0.57% chance that a "Model F-Value" this large could occur due to noise. The model terms with "Prob > F" less than 0.0500 indicates that it contributed significantly to the model.

Based on statistical analysis, voltage was the only significant factor in influencing the amount of ozone generated. Duty cycle was deemed as not significant in influencing the model. The configuration of cylinders was also deemed as not significant in affecting the results of the ozone production, based on ANOVA results.

The increasing trend of ozone concentration with the increase of voltage was also observed by Chae et al. [13] and Fang et al. [7]. However, if it passed an optimum point, a drastic decrease of ozone concentration could occur with increased voltage applied to the NTP reactor [14]. Increasing voltage would lead to the increased activities of corona discharge. However, the temperature would also increase due to the heat coming from the intense discharges in the air gap. This would lead to the dissociation of the generated ozone, hence, it reduced the generated ozone concentration [14]. Therefore, careful consideration must be taken while increasing the voltage as total net ozone concentration would decrease once it passed the optimum condition.
Table 5. ANOVA for the significance of model and model terms

| Source          | Sum of Squares | DF | Mean Square | F Value | Prob > F | Remarks       |
|-----------------|----------------|----|-------------|---------|----------|---------------|
| Model           | 2.39           | 3  | 0.80        | 5.50    | 0.0057   | Significant   |
| Voltage         | 2.24           | 1  | 2.24        | 15.44   | 0.0007   | Significant   |
| Duty cycle      | 0.007          | 1  | 0.007       | 0.048   | 0.8534   | Not significant |
| Configuration   | 0.15           | 1  | 0.15        | 1.01    | 0.3258   | Not significant |
| Residual        | 3.19           | 22 | 0.14        |         |          |               |
| Lack of Fit     | 2.36           | 14 | 0.17        | 1.63    | 0.2477   | Not significant |
| Pure Error      | 0.83           | 8  | 0.10        |         |          |               |
| Cor Total       | 5.57           | 25 |             |         |          |               |

Since configuration of the electrodes was considered as categorical factor while the voltage and duty cycle was the numerical factors in this analysis, the correlations for each categorical factor could be generated by RSM accordingly. The corresponding coefficients of the model obtained by regression analysis of the experimental data are shown in Equation (1) and (2) for configuration of 3 x 40 mm and 10 x 10 mm, respectively.

Ozone concentration = -0.2464 + 0.2158*Voltage - 0.00242*Duty cycle         (1)

Ozone concentration = -1.3964 + 0.2158*Voltage - 0.00242*Duty cycle        (2)

where the units for ozone concentration, voltage, and duty cycle are ppm, kV and percentage respectively.

Based on the correlations generated by RSM, the predicted versus actual data for configuration of 3 x 40 mm and 10 x 10 mm were plotted and presented in Figure 2 and Figure 3 respectively. It is observed that the correlation generated for 3 x 40 mm, as in Figure 2, consistently over-predict the ozone concentration. Meanwhile, the ozone concentration was quite well predicted for configuration of 10 x 10 mm as almost all data fell within the 25% range of prediction target. Therefore, although the model generated by RSM was analysed to significant model based on ANOVA, it appeared that the model was biased toward cylinders configuration of 10 x 10 mm.

RSM is able to analyse the significance and conformation of both numerical and categorical factors based on statistical analysis. However, the resulting model from simultaneous numerical and categorical factor needs to be graphically verified based on set deviation target such as in Figure 2 and Figure 3. Otherwise, the biasness of the model towards a certain categorical factor might be undetected.

It should be noted here that the trend of ozone production depends on the parameter or combination of parameters varied and it is not always in polynomial form. Under this circumstance, an alternative method needs to be used to correlate the variables with the response. This method is under development and would be presented in an upcoming manuscript.
Figure 2. Predicted versus actual ozone concentration for 3 x 40 mm configuration based on correlation by RSM.

Figure 3. Predicted versus actual ozone concentration for 10 x 10 mm configuration based on correlation by RSM.
4. Conclusion
The effect of voltage and duty cycle for two different configuration of dielectric barrier on ozone concentration in multi-cylinders reactor in NTP was investigated using RSM. Based on analysis using RSM, voltage was identified as significant factor to the ozone production process. Duty cycle was found to be insignificant in influencing the concentration of ozone generated. However, the regressed model was biased towards one of the configuration, leaving the predicted results of another configuration to be out of range.

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