Synthesis and determination of ozone levels in the ozonated waste cooking oils by dielectric barrier discharge (DBD) plasma

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Abstract. Converting the waste cooking oil into the ozonated oil is one way to reduce environmental pollution. The synthesis of ozonized oil can be done with plasma technology using the dielectric barrier discharge (DBD) plasma method. This research aims to synthesize the ozonized waste cooking oil using DBD plasma and determine the ozone levels therein. Plasma was generated using argon and oxygen gas at a flow rate ratio of 0.6 L/min:0.4 L/min that connected to an AC voltage of 5 kV. The treatment was done with time variations of 15, 30, 45, and 60 min. The results of the treatment were investigated with UV-Vis spectrophotometer and ozonation titration. Furthermore, the reactive species present in plasma were analyzed with optical emission spectroscopy (OES). After the treatment, the waste cooking oil has a clearer color than before treatment. The absorption peaks of waste cooking oil and treatment oil were observed at 240 and 273 nm. Meanwhile, the highest ozone concentration of 0.197 ppm was achieved for 30 min plasma treatment. The results conclude that the waste cooking oil is able to be converted to the ozonated oil by DBD plasma generated in this study with high efficiency.

1. Introduction
Waste cooking oil is an oil produced from frying food several times or heating oil at high temperatures, which causes risks to the environment and human health. The use of waste cooking oil can cause the risk of triggering cancer [1, 2]. However, the disposal of untreated waste cooking oil into a landfill or river harms the environment. One of the main environmental issues arising is the eutrophication process that occurs when there is a barrier to sunlight to penetrate the surface of a river caused by the blocking of a thin layer of oil that can cause the oxygen supply in water disrupted [3].

On the other hand, ozone gas is generally generated from oxygen gas passed between two electrodes connected to a high voltage electrical power supply, resulting in a highly reactive gas. The ozone application was to sterilize microorganisms, treat open wounds and herpes because of its anti-microorganism effectiveness. Additionally, ozone has other advantages: improving wound healing, enhancing immune, not toxic, environmentally friendly, high efficacy, and no side effect [4].

The ozonated oils have been used in many disease treatments, such as joint and skin pathologies. Ozonated oil has been used topically for the treatment of chronic wounds [5]. The ozonated oil as monotherapy also shows a significant improvement in clinical parameters and microbiological parameters over time without any documented side effects. Ozonated oils are obtained from the
chemical reaction between ozone and unsaturated fatty acids of vegetable oils [6]. Ozone gas is able to react with molecules that have a carbon double bond, opening the bond to be further linked with oxygen atoms [7].

The ozone gas can be produced by plasma technology which is an environmentally friendly technology. Plasma is an ionized gas that consists of various reactive species, including positive ions, negative ions, electrons, free radicals, gas atoms, and or excited state molecules and photons [8]. Plasmas can be distinguished into two main groups, i.e., the high temperature or fusion plasmas (equilibrium plasma) and low temperatures plasma or gas discharges. High-temperature plasma implies that all species (electrons, ions, and neutral species) are in a thermal equilibrium state. Low-temperature plasma is further subdivided into thermal plasma, also called quasi-equilibrium plasma, which is in a local thermal equilibrium (LTE) state, and non-thermal plasma (NTP), also called nonequilibrium plasma or cold plasma [9]. DBD plasma is a type of non-thermal plasma that generally consists of two electrodes separated by a gap of a few millimeters and covered with a dielectric layer, where the electrodes are connected with high voltage AC. Dielectric functions as a current limiter that prevent spark formation and evenly distributes discharges throughout the electrode area [10]. In the textile industry, ozone generated by DBD plasma is used in wastewater treatment to reduce color parameters, COD, and TSS [11]. The efficiency of DBD plasma degradation highly depends on the composition of the atmospheric gas [12]. Therefore, this study aims to treat the waste cooking oil using ozone generated by DBD plasma, followed by determining the ozone levels therein. The research is potentially applied to reduce environmental pollution caused by waste cooking oil disposal. Moreover, the ozonated waste cooking oil also might be further studied in skin treatment applications.

2. Experimental

2.1. Equipment and materials

The equipment that used in this study includes AC 5 kV power supply, flow meters, regulators, Cu wire, Cu tape and mesh, dielectric, quartz tubes, oxygen gas, argon gas, sandpaper, vials, a set of glassware, and a UV-Vis spectrophotometer. The research materials used were waste cooking oil, fresh cooking oil, KI 2% solution, H2SO4 2 N solution, Na2S2O3 0.2 N solution, amylum 2%, and distilled water.

2.2. Synthesis of ozonated waste cooking oil with DBD plasma

The plasma used in this study is DBP plasma using two electrodes of Cu wire and stainless steel mesh separated by dielectric materials of glass. Before plasma was generated, 30 mL waste cooking oil was placed in a quartz tube. The plasma was generated using argon gas at 0.4 L/min mixed with oxygen gas 0.6 L/min. After that, the regulator alongside the AC power supply was turned on at 5 kV to release the plasma. The changes that occur are seen and recorded from the time of initial treatment. Treatment of waste cooking oil was done with time variations of 15, 30, 45, and 60 min.

2.3. UV-Vis spectrophotometer characterization

UV-Vis spectrophotometer instrument firstly scanned the distilled water as a blank sample. The fresh cooking oil, waste cooking oil after and before treatment were continuously measured. The characterization observed the absorbance and spectra of samples scanned between a wavelength of 200-800 nm.

2.4. Determination of ozone levels

The 3 mL ozonated waste cooking oil was mixed with 2 mL 2% KI solution producing a pale yellow color. The mixture was then added with 0.1 mL Na2S2O3 0.2 N solution and one drop of 2% starch, giving the changing of solution color turning into dark blue. The solution was then titrated with Na2S2O3 0.2 N solution until the color turns clear. The volume of Na2S2O3 0.2 N solution titration was
recorded. Titration was done in triple. The ozone concentration was then determined using equation (1).

\[ C_{\text{ozone}}(\text{ppm}) = \frac{24xV_{\text{thiosulfate}}(\text{mL}) \times C_{\text{thiosulfate}}(\text{N})}{V_{\text{gas}}(\text{l})} \]  

(1)

2.5. Plasma emission characterization
The plasma emission was characterized using optical emission spectroscopy (OES). When the plasma system was turned on, then the fiber-optics was directed to the plasma discharge that appeared. The active plasma species were analyzed from the spectra revealed.

3. Results and Discussions
During plasma discharging, the use of oxygen gas in the reactor system is purposed to produce more reactive oxygen species and ozone. Meanwhile, argon gas was used as an inert gas to stabilize the plasma discharge. The reactive species produced by DBD plasma was characterized using OES. Furthermore, the reactions of ozone formation from oxygen atoms are shown in reaction equations (2) and (3) [13, 14].

\[ e + O_2 \rightarrow O + O + e \]  

(2)

\[ O + O_2 \rightarrow O_3 \]  

(3)

Moreover, the ozone formation in DBD plasma begins with the formation of oxygen and free radicals, such as shown in the reaction equations (4-6).

\[ O_3 + OH^- \rightarrow O_3^- + OH^- \]  

(4)

\[ O_3^- \rightarrow O^- + O_2 \]  

(5)

\[ O^- + H^+ \rightarrow OH^- \]  

(6)

3.1. Degradation color of waste cooking oil
In this study, it is revealed that the longer the treatment time, the clearer the color of the samples. This phenomenon occurred more ozone was produced from the DBD plasma causing ozonation on waste cooking oil. The structure of waste cooking oil is shown in Fig. 1. Ozone is a strong oxidizing agent that highly plays a role in the degradation of pollutants, such as consistent with the literature in the treatment of the textile industry using DBD plasma to reduce color parameters, COD, and TSS [11]. In this study, the ozone directly degraded the color of waste cooking oil following reaction equation (7). Furthermore, the color degradation of ozonated cooking oil is shown in Fig. 2.

\[ O_3 + M \rightarrow M^+ + O_3^- \]  

(7)

M is waste cooking oil.
3.2. Optical Emission Spectroscopy (OES)
Optical Emission Spectroscopy (OES) was used to identify reactive plasma species generated in DBD plasma. The characterization of plasma ionization emitted in DBD plasma was carried out in closed and dark spaces to minimize external light that can interfere with the retrieval of plasma emission data generated. The collision of plasma particles with electrons will further excite plasma particles to a higher electronic state that is unstable. An unstable state will force plasma particles to relax. This relaxation will produce photons of emitted light and plasma emission. The emission spectrum was then recorded by OES. The energy of the photons released is the same as the difference between the excited energy state and the lower energy state. The OES absorption spectrum data are shown in Fig. 3. From the spectrum, the reactive species produced in DBD plasma includes O₃, OH*, N₂, N₂⁺, Ar⁺, and O. The absorption of O₃ is at 315.4 nm, while OH* at 335.3 and 401 nm, N₂ at 358 nm, N₂⁺ at 381 nm, Ar⁺ at 750 and 816 nm, and finally O at 777 and 843 nm.

Figure 2. Color degradation of waste cooking oils.

Figure 3. OES spectrum of DBD plasma. The inset is the image of DBD plasma generated in the quartz tube.
3.3. **UV-Vis spectrophotometry characterization**

UV-Vis spectrophotometry was used to determine the effect of ozonation in the waste cooking oil by looking at the shift in wavelength and absorbance of each sample. The UV-Vis spectra are shown in Fig. 4. The name of MT is the name for plasma-treated waste cooking oil.

![UV-Vis spectra of each sample.](image)

The maximum wavelength of fresh cooking oil is at 240 and 271 nm, while waste cooking oil is at 240 and 297 nm, showing a bathochromic shift. This shift is due to the presence of the oxide compounds formed after the repeated use of cooking oil. Ozonated waste cooking oil has a wavelength that is almost the same as in the waste cooking oil. The treatment oil in 15 min experienced a significant increase in absorbance or, in other words, called a hyperchromic effect. The plasma treatment at oils for 30 and 45 min also experience hyperchromic effects, but for oil treatment in 60 min, the absorbance value is almost the same as a waste cooking oil. This phenomenon indicates that the longer the treatment time of using DBD plasma will cause the oil absorbance to decrease. Among the sample with various treatment times of 15, 30, 45, and 60 min, the sample with treatment time in 15 and 30 min shows a positive effect of DBD plasma. This is because, at the treatment time of 15 and 30 min, the absorbance of the treatment oil was near the same as the absorbance of the fresh oil.

3.4. **Ozonation Titration**

Ozonation titration aims are to determine the amount of ozone contained in the ozonated waste cooking oil. The ozonation titration was applied by using KI solution to react with ozone and produce iodine. The amount of iodine is equivalent to the amount of ozone, which further analyzed in the titration using sodium thiosulfate. After the addition of starch, there was a solution color change into a dark blue color. The darker the blue, the more the ozone content therein. After titration with sodium thiosulfate solution, the color turns clear, which means the iodine content in the solution had reacted completely. The ozone concentrations of each sample are shown in Table 1.

| Sample               | Ozon Concentration (ppm) |
|----------------------|--------------------------|
| Fresh Oil            | 0                        |
| Waste Cooking Oil    | 0                        |
| MT 15                | 0.171                    |
| MT 30                | 0.197                    |
| MT 45                | 0.196                    |
| MT 60                | 0.133                    |
The highest ozone concentration of 0.197 ppm was revealed for the waste oil, treated for 30 min. Eventually, the reactions that occur during the titration are explained in reaction equations of (8) and (9), which are the reaction when adding KI and the reaction during titration with a standard solution of Na$_2$S$_2$O$_3$·5H$_2$O, respectively.

$$\text{O}_3(g) + 2 \text{KI}(_{\text{aq}}) + \text{H}_2\text{O}(_{\text{aq}}) \rightarrow \text{O}_2(g) + \text{I}_2(_{\text{aq}}) + 2 \text{KOH}(_{\text{aq}}) \quad (8)$$

$$\text{I}_2(_{\text{aq}}) + 2 \text{Na}_2\text{S}_2\text{O}_3(_{\text{aq}}) \rightarrow 2 \text{NaI}(_{\text{aq}}) + \text{Na}_2\text{S}_4\text{O}_6(_{\text{aq}}) \quad (9)$$

4. Conclusion
The DBD plasma method presented in this study efficiently degraded the waste cooking oil. The longer the treatment time, the clearer the color of the waste cooking oil. In addition, based on the OES spectra, the reactive plasma species generated in DBD plasma include O$_3$, OH*, N$_2$, N$_2^+$, Ar*, and O. The absorption peaks of waste cooking oil and treatment oil were observed at 240 and 273 nm. Moreover, the absorbance value significantly increased during the treatment time of 15 min, with the highest ozone concentration of 0.197 ppm revealed for the waste oil by 30 min treatment.

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