Development of DDBD and plasma jet reactors for production reactive species plasma chemistry

Muhammad Nur\textsuperscript{1,2*}, Eko Yuliyanto\textsuperscript{1}, Andi Wibowo Kinandana\textsuperscript{1}, Maryam Resti Wijaya\textsuperscript{1}, Fajar Arianto\textsuperscript{1}

\textsuperscript{1} Center for Plasma Research, Faculty of Science and Mathematics, Diponegoro University, Semarang, Indonesia
\textsuperscript{2} Physics Department, Faculty of Science and Mathematics, Diponegoro University, Semarang, Indonesia
* Corresponding author: m.nur@undip.ac.id

Abstract. A novel Double Dielectric Barrier Discharge (DDBD) and an atmospheric pressure plasma jet (APPJ) was generated with a dielectric barrier discharge (DBD) column by AC high voltage have been developed. This reactor can produce cold atmospheric plasmas (CAP) that formed in air reactive oxygen species (ROS). These species among others are O\textsubscript{3}, H\textsubscript{2}O\textsubscript{2}, was quantified in the outlet of reactors. The analysis for ROS has been conducted by using medium that we call Plasma-Activated Medium (PAM). Some analysis conducted including variation of exposure times by ROS to the plasma-activated medium. In addition, concentration-voltage characteristics of ozone production, Peroxide Value, Acid Value and Viscosity of virgin coconut oil (VCO, as PAM) increased with increasing exposure time of O\textsubscript{3}. The concentration of hydrogen peroxide in water (as PAM) has been measured. The concentration of H\textsubscript{2}O\textsubscript{2} 179 \textmu M with exposure time for 1 minute. The concentration of H\textsubscript{2}O\textsubscript{2} in the study is quite high when compared with some other research results. The results showed that increased exposure time resulted in increased concentrations of ozone and hydrogen peroxide.

Keywords: DDBD, RONS, PAM, hydrogen peroxide, peroxide value, acid value

1. Introduction
Non thermal plasmas in oxygen, argon gas and air present considerable interest for a wide range for industrial applications, such as air pollution control, waste water cleaning, bio-decontamination and sterilization, material and surface treatment, electromagnetic wave shielding, carbon beneficiation and nanotube growth, and element analysis [1]. Capabilities of plasma produces very high concentration of energetic chemically active species can be used for an attractive application in chemistry and related disciplines [1]. Non thermal plasmas can be developed by dielectric barrier discharge [2, 3], plasma jet [4]. Double DBD is used in this study because the decay of discharge is faster so that the discharge voltage is lowered. In double DBD, the external electric field is reduced additionally by the accumulated surface charges on the barrier at the cathode [5, 6] and this reactor is safer because there is no direct contact between the input gas and the active electrode. Dielectric barrier discharge (DBD) can be used for various applications such as deodorization, decolorization, disinfection, bleaching processes, gas/air treatment, chemical synthesis and recently in medical applications. Dielectric barrier discharge reactor can produce cold atmospheric plasmas (CAP) that formed in air reactive oxygen species (ROS). Electrical discharges in liquids and in gas phase over liquids generate a diversity of reactive oxygen species (ROS) and reactive nitrogen species (RNS) such as radicals, ions, excited atoms and molecules.
(O*, *OH, H₂O₂, O₃, N₂*, O²⁻, etc.) [7]. The most significant factor, produced by plasma that influence plasma chemistry is reactive oxygen and nitrogen species (RONS). RONS react with the surrounding air, aqueous media and with cells themselves. Plasma can be applied both directly on cell or tissues or indirectly by plasma-activated medium (PAM). A plasma-activated medium (PAM) is a medium that is irradiated with plasma. It is a cellular medium, which was treated by plasma and then applied onto the cells, so the cells interact only with RONS produced in PAM [8, 9]. On the other hand, species generated by the plasma may pass through the liquid and penetrate into the cells and join the similar species that are produced inside the cells. These processes are inter-dependent making it very difficult to identify the specific channels of the species production in the liquid medium and inside the cells. Indeed, species generated by the plasma and delivered to the liquid media affect the species production inside and nearby the cells, while the species released by the cells into the medium, interact with the plasma-generated species and modify the kinetics of chemical reactions in the medium [10]. In this research has been development of DBD reactor into DDBD reactor, the development includes the addition of dielectric layer on the reactor that serves to prevent direct contamination of the gas species with the electrodes. DDBD reactor is constructed by a double pyrex cylinder as dielectric material. The present of double dielectric inside the reactor during discharge makes this chamber is known as double dielectric barrier discharge (DDBD) and an atmospheric pressure plasma jet (APPJ) was generated with a dielectric barrier discharge (DBD) column and it was operated at atmospheric pressure and ambient temperature.

2. Methods

2.1. Double Dielectric Barrier Discharge Reactor

The AC voltage was applied in the range of 200-500 Volts and the frequency of 50 Hz. Gas sources; i.e. free air and pure oxygen; flowed into the reactor with several variations in flow rate, i.e. 2 to 24 L/min.

![Figure 1. Scheme series of experiment for DBDP reactor.](image-url)

The gas flow rate is measured using a flowmeter (WIEBROCK). Ozone concentration is measured using Iodometric titration method [11]. Measurement of ozone concentration begins by making a solution of KI (kalium iodide) 33 gr with a concentration of 0,2 M into 1 litre distilled water. Then prepare a solution of Na₂S₂O₃ (sodium thiosulphate) 6.32 gr with a concentration of 0.4 M to 100 mL of distilled water. Ozone streamed into the tube the Erlenmeyer flask containing 50 mL solution have KI. Ozonation time 2 minutes. Aqueous KI originally nodes because of the capture of ozone will change
colour to yellow. Then titrated with Na$_2$S$_2$O$_3$ using a micropipette (10-100 thoroughness) until the solution is clear coloured back.

2.2. Plasma Jet Reactor
This research was conducted by Analysis of Plasma-activated medium in Aqueous Solution by an Atmospheric Pressure Plasma Jet (APPJ) as shown in Fig. 2. This Atmospheric Pressure Plasma Jet was generated by AC high voltage. The plasma jet system that we used here is similar to the device developed by Nur et al. [12]. The research equipment scheme can be seen in figure 1. The ROS has been exposed to the medium that we call Plasma-Activated Medium (PAM) by Double Dielectric Barrier Discharge (DDBD) reactor. It is to be operated at atmospheric pressure and ambient temperature condition. The geometrical configuration is a double cylinder shape with a pyrex cylinder as dielectric material. The double cylinder inner diameter is 20 mm and an outer diameter is 40 mm, distance between pyrex is 5 mm and with a length is 150 mm. This DDBD was generated by AC high voltage. Electrical parameters of DDBD determined through a voltage divider (HV Probe DC Voltage DC Max 40 kV; 28 kV AC EC code number 1010, En G1010). The electrical signal from the probe detected by an Oscilloscope GOS-653, 50 MHz. The electric current, that was generated in the reactor was measured by using a multimeter (Sunwa TRXn 360) and ammeters (Kyoritsu, AC/DC Digital Clamp Meter). Argon gas as the industrial gas (Ar, 99.95%) was inserted into the reactor by regulating the gas flow rate in the range of 1-10 L/min.

![Figure 2. Scheme series of experiment for plasma jet reactor.](image)

3. Results and Discussion
3.1. Ozone Production with Oxygen as Source
Fig. 3 shows the current dependence on the voltage in the DDBDP reactor. From a voltage of 1 kV to 2.5 kV there is an increase in voltage following the law of I–V$^2$. For DHF and DDBD reactors in accordance with the Robinson formula that has undergone modification by Nur et al. [13]. This formula was originally only for corona discharge and can now be used on a dielectric barrier discharge. Nonlinear phenomena have occurred. The surge in currents has occurred on a regular basis. With the addition of a very small voltage (0.1kV), the discharge current is doubled. The current tendency is proportional to the square of the voltage not followed, this applies to all air flow rates. At the same time, with a sharp increase in current, the ozone starts to be detected and enlarges with the increase in discharge current.
Fig. 4 shows the ozone concentration as a function of voltage for with flowrate of 2 L/min, 4 L/min, 6 L/min. Ozone concentration rises following 3rd order polynomials. For lower flow rates, concentration is always greater than the larger flow rate. This can be explained based on the rest time of gas in the reactor. The longer it is in the reactor, the more dissociation of O₂ molecules and ozone form more concentrated.

Figure 3. The characteristic of electric current in oxygen gas as a function of voltage, with flowrate of 2 L/min.

Figure 4. Graphic of ozone concentration (at the flowrate of 2 L/min, 4 L/min, 6 L/min) in oxygen gas as the function of Voltage, with flowrate of 2 L/min, 4 L/min, 6 L/min.

3.2. **Ozone Production with Air as Source**

Fig. 5 shows the current dependence on the voltage in the DDBDP reactor with air as source. From a voltage of 1 kV to 2.5 kV there is an increase in voltage following the law of I–V². The phenomenon of decreasing ozone concentration with rising voltage (power input) can be explained by energetic concepts. Large input power will result in greater electric field in the reactor. Electrons and neutral molecules, charged molecules collide with each other. At high input power charged particles and electrons have high kinetic energy. This energy can be used to ionize, dissociate nitrogen (78%) and oxygen (20%) as the main component of air. So it is not just oxygen molecules that dissociate, but nitrogen molecules are also dissociated. The formation of ozone begins with dissociation (R-1), dissociation of electron binding (R-2) and dissociation ionization (R-3) like the reactions below [3].

\[
\text{Dissociation } e^- + O_2 \rightarrow 2O + e^- \quad (R-1)
\]

\[
\text{Dissociation of electron binding } e^- + O_2 \rightarrow O + O^- \quad (R-2)
\]

\[
\text{Dissociation ionization } e^- + O_2 \rightarrow O + O + 2e^- \quad (R-3)
\]

Then oxygen radicals will react with oxygen to produce ozone (R-4) with the help of neutral molecules as catalysts (R-5) [13].

\[
O_2 + e^- \rightarrow 2O + 2e^- \quad (R-4)
\]

\[
O + O_2 + M \rightarrow O_3 + M \quad (R-5)
\]

The dissociation energy of nitrogen molecules is 10 eV [14] while the dissociation energy of oxygen molecules is 5.2 eV [15].
With the difference in dissociation energy energetically the electron energy generated in the DBD reactor must be adjusted to the dissociation energy of the oxygen molecule. So for the higher input power in this DDBD Plasma reactor, the ozone concentration decreases.

3.3. Physico-chemical characterization of VCO before and after ozonation

The ozone as one of RONS that produced by DDBD has been exposed to the plasma activated medium (PAM). In this ozone study we use virgin coconut oil (VCO) as PAM. The change physico-chemical properties of VCO are shown by change the values of peroxide value (PV), acid value (AV) and viscosity. Table 1 shows the AV PV value and Viscosity for VCO without ozone exposure (VCO0) with an ozone exposure for 7 hours (VCO7) and exposure for 14 hours (VCO14). The graph showing change of PV and viscosity due to RONS exposure in this case O3 in VCO can be seen in Fig. 7 for PV and Fig. 8 for viscosity.

| Sample | Ozone Dose (milligrams) | Exposure Time (hours) | PV (mEq/1000 g) | AV (mg NaOH/g fat) | Viscosity (mPa s) |
|--------|------------------------|-----------------------|-----------------|-------------------|------------------|
| VCO 0  | 0                      | 0                     | 45.5 ±1.37      | 0.20±0.01         | 39.6±0.60        |
| VCO 7  | 341472.60              | 7                     | 301.7±9.55      | 0.22±0.00         | 41.7±0.76        |
| VCO 14 | 682367.28              | 14                    | 560.4±38.49     | 0.21±0.01         | 63.1±3.70        |
3.4. Hydrogen Peroxide in Distilled Water by Plasma Jet

This paper also reports on the results of Plasma Jet exposure to distilled water. Distilled water will become PAM by obtaining a certain concentration of H$_2$O$_2$ after getting exposure from Plasma Jet. The sample of PAM used was H$_2$O$_2$ 30% dissolved by distilled water. H$_2$O$_2$ 30% was dissolved by using distilled water to concentration of 1000 ppm with 25 mL volume. The sample is placed on a petri dish under the reactor. This treatment was performed with exposure time of 5 to 30 minutes with interval for 5 minutes with a distance (d) between electrode to plasma-activated medium at 1, 2 and 3 cm.

Table 2. Concentration of H$_2$O$_2$ generated by 1 minute plasma compared with other plasma sources results [16].

| Plasma sources                             | Medium            | Concentration H$_2$O$_2$ (μM) | Refs |
|--------------------------------------------|-------------------|--------------------------------|------|
| Plasma jet Ar 7 kV (2 L/m) d=3 mm          | DMEM              | 227                            | [15] |
| Plasma jet Ar 7 kV (2 L/m) d=13 mm         | DMEM              | 18                             | [16] |
| Plasma jet 7 kV (5 L/m) d=22 mm            | MEM               | 60                             | [17] |
| Plasma jet Ar 1 MHz 6 kV d=3 L/m           | RPMI + FBS 8%     | 33                             | [18] |
| Plasma jet Ar 1.1 MHz d=3 L/m              | RPMI + FBS 10%    | 60                             | [19] |
| RF Plasma Jet                              | distilled water   | 14.5                           | [20] |
| DC 27 kV d=12 mm                           | distilled water   | 3.6                            | [21] |
| DC Gas-Liquid 6.5 kV d=20 mm               | distilled water   | 147                            | [22] |
| Plasma Jet Ar 12 kV (2 L/m) d=20 mm        | H$_2$O$_2$ 30% + distilled water | 179 | This research |

The H$_2$O$_2$ measurements in the sample were performed using a Spectrophotometer UV-Vis (Shimadzu UV Mini 1240). This treatment to determine concentrations of H$_2$O$_2$ in PAM after treatment using plasma jet. This research resulted the highest concentration of H$_2$O$_2$ that is 215 ppm (6056 μM) with exposure time for 30 minutes at d=2 cm. The result of Hydrogen peroxide concentration increases with time of exposure. In this study, the concentration of H$_2$O$_2$ 179 μM with exposure time for 1 minute. The concentration of H$_2$O$_2$ in the study is quite high when compared with some other research results.
Some measurements of H$_2$O$_2$ concentrations with different plasma and media sources resulted in very different concentrations. The results of measurement of H$_2$O$_2$ concentrations from various references are shown in table 2. The highest concentration of H$_2$O$_2$ that can be produced on DMEM media is 227 μM with 1-minute exposure time, treatment using Ar 7 kV jet plasma source with 2 L/min gas flow discharge at reactor and PAM distance of 3 mm. The lowest concentration of H$_2$O$_2$ was generated on distilled water medium of 3.6 μM with exposure time of 1 min, treatment using a 27 kV DC plasma source at a distance between the reactor and a 12 mm PAM surface. Increasing concentrations of H$_2$O$_2$ in PAM which is due to the increasing jet plasma exposure time was also produced by Mohades et al. [17], by using medium SCaBER MEM (Minimum Essential Media) and MDCK EMEM (Eagle's Minimum Essential Media) [17]. This medium is used to grow cancer cells. Increased concentration of H$_2$O$_2$ is shown in Fig. 8. The H$_2$O$_2$ concentration was measured in MEM PAM immediately after plasma exposure and after 1, 8, and 12 hours aging. To evaluate the effect of serum on H$_2$O$_2$ concentration, a serum-free PAM made by MEM and 1% antibiotics was used and the H$_2$O$_2$ concentration was measured after 8 hours aging.

4. Conclusion
Ozone production in a DDBD Plasma reactor at exactly the same time as the discharge current is very high. This happens to both oxygen and air in the reactor. The resulting ozone concentration continues to increase in the reactor with oxygen as an ozone source. The increase occurs exponentially. DDBD Plasma with air as a source, at a voltage of 3 kV the ozone concentration decreases due to nitrogen in the air also undergoing dissociation, so that the energy is divided for nitrogen and oxygen. Peroxide value (PV), acid value (AV) and viscosity of virgin coconut oil (VCO, as PAM) increased with increasing exposure time of O$_3$. The highest concentration of H$_2$O$_2$ that is 215 ppm (6056 μM) with exposure time for 30 minutes at d=2 cm. The result of Hydrogen peroxide concentration increases with time of exposure. In this study, the concentration of H$_2$O$_2$ 179 μM with exposure time for 1 minute

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