

Article

Hybrid Dielectric Barrier Discharge Reactor: Characterization for Ozone Production

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Abstract: The generation of ozone by dielectric barrier discharge (DBD) is widely used for water and wastewater treatment, the control of catalytic reactions, and surface treatment. Recently, a need for compact, effective, and economical ozone and reactive oxygen–nitrogen species (RONS) generators for medical, biological, and agricultural applications has been observed. In this study, a novel hybrid DBD (HDBD) reactor fulfilling such requirements is presented. Its structured high-voltage (HV) electrode allows for the ignition of both the surface and volume microdischarges contributing to plasma generation. A Peltier module cooling of the dielectric barrier, made of alumina, allows for the efficient control of plasma chemistry. The typical electrical power consumption of this device is below 30 W. The operation frequency of the DBD driver oscillating in the auto-resonance mode is from 20 to 40 kHz. The specific energy input (SEI) of the reactor was controlled by the DBD driver input voltage in the range from 10.5 to 18.0 V, the Peltier current from 0 to 4.5 A, the duty cycle of the pulse-width modulated (PWM) power varied from 0 to 100%, and the gas flow from 0.5 to 10 SLM. The operation with oxygen, synthetic air, and compressed dry air (CDA) was characterized. The ultraviolet light (UV) absorption technique was implemented for the measurement of the ozone concentration. The higher harmonics of the discharge current observed in the frequency range of 5 to 50 MHz were used for monitoring the discharge net power.

Keywords: cold atmospheric pressure plasma (CAPP); dielectric barrier discharge (DBD); ozone; reactive oxygen–nitrogen species (RONS); Peltier cooling; pulse-width modulation (PWM)



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1. Introduction

Ozone owes its widespread applicability [1] to its high oxidation potential of 2.07 V. The second strong advantage of ozone is its ability to decay spontaneously, with the half-life time (HLT) dependent on environmental conditions [2,3], reaching tens of hours. This decay process can be strongly accelerated by decomposition [4] using activated carbon [5] or catalytic filters [6]. The classical application of ozone represents the treatment of water and wastewater [7]. Recently, the bio-active properties of ozone are used in numerous applications, like improving the safety and preserving the quality of foods [8,9], healthcare [10], therapeutic ozone-induced cell death [11], bactericidal disinfection [12], the removal of odors [13], or high-grade disinfection using high-concentration ozone-containing gas [14], for example, in bio-clean rooms [15].

Ozone can be generated photochemically [16] by UV radiation, produced for example by an antimony vapor lamp at the wavelength 214 nm or by an Xe₂⁺ excimer lamp at 172 nm [17,18], electrochemically [19,20], and by electrical discharges [21]. Examples of atmospheric discharges used for this purpose are corona discharge in air [22] and carbon dioxide [23], and piezoelectric direct discharge in air (PDD) [24–26], and oxygen [27,28]. However, the most popular method is by the use of dielectric barrier discharge (DBD) in both oxygen [29] and air [30].

The application of DBD for ozone generation is one of the oldest applications of atmospheric pressure gaseous discharge [31]. Despite this, it remains a focus of contemporary

research [32–34]. Two main types of DBD are widely used: the volume DBD (VDBD) and the surface DBD (SDBD) [35,36]. The main difference between them is the way the microdischarges develop. In VDBD, they spread vertically between the dielectric barrier and the electrode (an asymmetric VDBD or DBD with a floating barrier) or the second barrier (symmetric VDBD) [37]. In SDBD, they spread over the surface of the dielectric barrier. They start either from the discharge electrode in the standard SDBD [38] or spread between two regions of the dielectric barrier in the co-planar version of SDBD [39–41]. Further differences between VDBD and SDBD are the subject of newer research. SDBD shows a much lower voltage needed for ignition [42,43]. The direct comparison of VDBD and SDBD with similar sizes and structures shows that the SDBD reactor performs better in ozone production. Nassour et al. [44] have shown that the energy efficiency of the SDBD reactor is higher compared to the VDBD by a factor of 2.5–3.5. Recently, it was shown that further improvement in energy efficiency can be achieved by hybrid surface-volume-DBD (HDBD) [45,46]. This type of discharge was implemented in the HDBD reactor described in Section 2.2. The operation in the HDBD mode is documented through visualization in Section 3.1. For this purpose, the ITO-coated plates described in Section 2.3 were used.

Different DBD electrode designs have been reported to improve O₃ outcomes and chemistry control. Chang et al. [47] investigated the influence of aluminum oxide inside the discharge gap of a packed bed reactor. For a similar purpose, the packed bed reactor, made of a ferroelectric material such as barium titanate, (BaTiO₃) was used [48]. The multi-point electrodes [49] or needle arrays [50] were investigated, showing the reduction in the operation voltage. Zhao et al. [51] used the SDBD, ignited along the wire touching the cylindrical surface of the dielectric barrier, instead of technologically complex metal coatings. Jodzis et al. [52] have shown that by using a metal mesh adhered to the dielectric barrier, a high ozone concentration, and the yield and energy efficiency of the ozone generator operated with pure oxygen can be achieved. Mercado-Cabrera et al. [53] reached the improvement of the discharge efficiency by using a structured electrode. In an SDBD variant called surface microdischarge (SMD), a coating with round holes with a diameter of 5 mm [54], or a stainless-steel wire mesh with a separation of 5 mm [55] or 10 mm [56], is used as an electrode. It was shown that the convex shape of the SDBD electrode results in higher microdischarge currents than the concave ones [57]. Tański et al. [58] used the serrated electrode to reduce the ignition voltage of SDBD. In this paper, a novel HDBD reactor is presented. The hybrid operation mode is achieved by the use of an innovative structure of the electrode. The important features of this design are the conductive posts attached to the electrode (see Section 2.2), and the direct contact between the faces of these posts and the dielectric barrier surface. Around the area of contact between the post and the dielectric barrier, the convex SDBD can be ignited. Further advantages of the posts (spacers) are an improved gas convection, the heat flow from the electrode to the actively cooled dielectric barrier, and hence, the increased efficiency of the device.

The influence of DBD conditions on ozone production was the focus of numerous research studies [59]. Especially critical is the influence of temperature. The cooling is crucial for the chemistry of the DBD discharge [33]. It is known that the power efficiency of ozone production increases with decreasing temperature [60]. The increase in ozone production in the air is supported by the removal of residual humidity. A significant improvement is observed for the temperature down to −60°C. To obtain the highest values of ozone production per unit of electric energy, cryogenic technology was applied [24,61]. To achieve the high efficiency and controllability of the discharge chemistry in the presented HDBD reactor, a Peltier cooling is implemented [62] (see Section 2.2).

The decrease in the ozone concentration with the increasing humidity of air is confirmed in many experimental studies, e.g., in Chang et al. [63]. Zhang et al. [64] used the global model numerical simulation to show that hydroperoxyl HO₂ and OH radicals from water vapor significantly consume O atoms, resulting in a reduction in ozone generation [64]. Even though the humidity is detrimental to the production of ozone, the humid air in DBD has been used recently for many purposes, e.g., in medicine [65–68]. For a better

understanding of the chemical mechanisms of ozone generation, experiments with three gases were conducted (see Section 2.6). The results for pure oxygen (Section 3.5), synthetic air (Section 3.6), and compressed dry air (CDA) with residual humidity (Section 3.7) are compared and discussed.

Kimura et al. [69] have shown that the application of a time-modulated power supply to the DBD results in a better energy efficiency than a continuous-wave supply. The independent adjustment of the excitation voltage and duty cycle of the PWM, as described in detail in [70], enables control over the power coupled into the discharge, regardless of the density of the microdischarges. To utilize these advantages, the DBD driver used in this study for the generation of the high-voltage is designed for the operation in both the continuous-wave and pulse-width modulation (PWM) mode (see Section 2.4). A typical modulated HV signal, measured during plasma operation, is shown in Section 3.2.

The influence of four basic parameters: the DBD driver voltage, gas flow, Peltier module current, and the duty cycle on ozone production is investigated. The main method of reactor characterization is the UV absorption technique [71,72], used for the determination of the ozone concentration (Section 2.5).

The known methods of estimation of the net discharge power are indirect and based on the electric discharge power measured on electrode terminals. The different methods of estimation of the DBD power are summarized in the work of Ashpis et al. [73]. The oldest one is the measurement of the voltage drop on a shunt connecting the passive electrode of the DBD and the ground [74]. The most frequently cited is the method based on charge measurement using a monitor (probe) capacitor. The instantaneous capacitor charge Q_m and the instantaneous actuator voltage V_a , plotted against each other, generate a Lissajous curve in the Q_m – V_a plane, performing accurate power measurements [73]. In this study, for characterizing the DBD driver, the high voltage (HV) and the discharge current are measured concurrently on the model load and multiplied to obtain the apparent power (see Section 3.3). A novel method of estimation of the net power deposited in the microdischarges is proposed. It is based on the MHz harmonics occurring in the discharge current during plasma generation, as documented in Section 3.4. These high-frequency current components are measured as (MDIR) signals, (see Section 2.1) used to discuss the influence of the HDBD reactor settings on ozone production.

2. Materials and Methods

2.1. Setup

The experimental setup for the characterization of the HDBD reactor is shown schematically in Figure 1. The HDBD reactor described in Section 2.2 is supplied with high voltage from the DBD driver (see Section 2.4). The second task of the DBD driver is generating the MDIR signal to monitor the net discharge power. The Peltier module, part of the reactor, is supplied by a DC power unit with an adjustable current or voltage level. The working gas flow is controlled using a flow meter and dosing valve. The gas processed in the HDBD reactor is directed for UV absorption O_3 measurements. Subsequently, the plasma gas is extracted, and ozone and other oxidizing species are neutralized. The voltage between the HV electrode and ground was measured using the Tektronix P6015A voltage probe, with an input resistance of 100 M Ω and an input capacitance of less than 3 pF. The current that drained to the ground was measured using a Tektronix TCP312 100 MHz current probe. Both probes are connected to the Tektronix DPO3034 phosphor oscilloscope, operated with 5,000,000 samples per measurement and a sampling time of 0.4 ns. The temperature sensor of type K is used for the temperature measurement of the Peltier module heat sink, thus allowing the temperature of the dielectric barrier to be controlled.

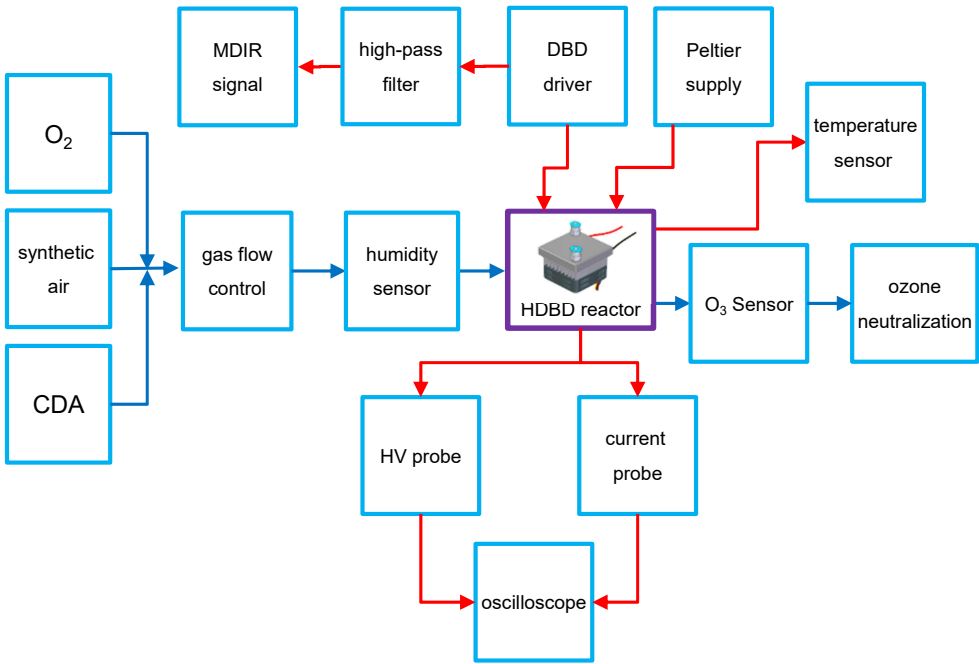


Figure 1. Setup for HDBD reactor characterization.

2.2. HDBD Reactor

The HDBD reactor used for performance characterization in this study is based on a modified rectangular, parallel-plate, single dielectric barrier architecture [33] and is shown schematically in a cross-sectional view in Figure 2. The novelty of this device is its structured stainless-steel HV electrode (see Section 3.1), allowing for hybrid volume-surface DBD, and the Peltier module for the cooling of the dielectric barrier. The application of Peltier cooling instead of air or water cooling allows for a much better controllability of the heat removed from the discharge and the reproducibility of the reactor temperature.

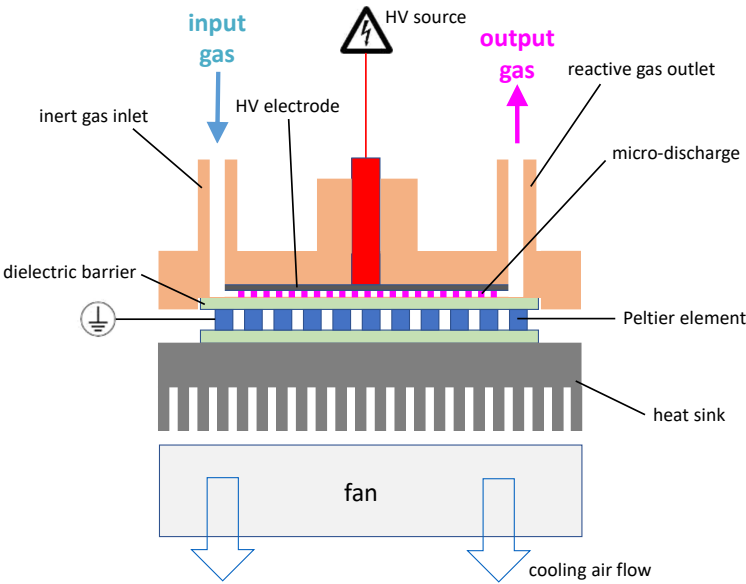


Figure 2. The schematic cross-sectional view of the HDBD reactor used for ozone generation.

The microdischarges are ignited between the HV electrode and the aluminum oxide cover of the Peltier module. The HV is guided from the DBD driver described in Section 2.4 over the HV cable attached to the back side of the electrode. The series of Peltier semiconductor elements has a low resistance and plays the role of grounded electrode for the kHz excitation. The Peltier module is supplied with a DC of up to 5 A.

The size of the electrode is 35 mm × 36.8 mm × 1 mm. The discharge side of the electrode is structured with posts distributed over the entire electrode surface (see Figure 3a). They fulfil four important tasks:

- They act as spacers between the electrode bulk and the dielectric barrier, defining the length of the volume DBD microdischarges and the cross-section area for the gas flow.
- The circular face surface of the spacer touches the dielectric barrier, resulting in the generation of the convex SDBD.
- The heat deposited on the electrode surface is conducted to the Peltier cooler via the posts and the alumina plate, promoting a lower discharge temperature. To optimize this effect, the position of each post is aligned with the center of each Peltier element.
- The posts obstruct the gas flow, causing better mixing, resulting in better convective cooling, and hence, better ozone production performance of the HDBD reactor.

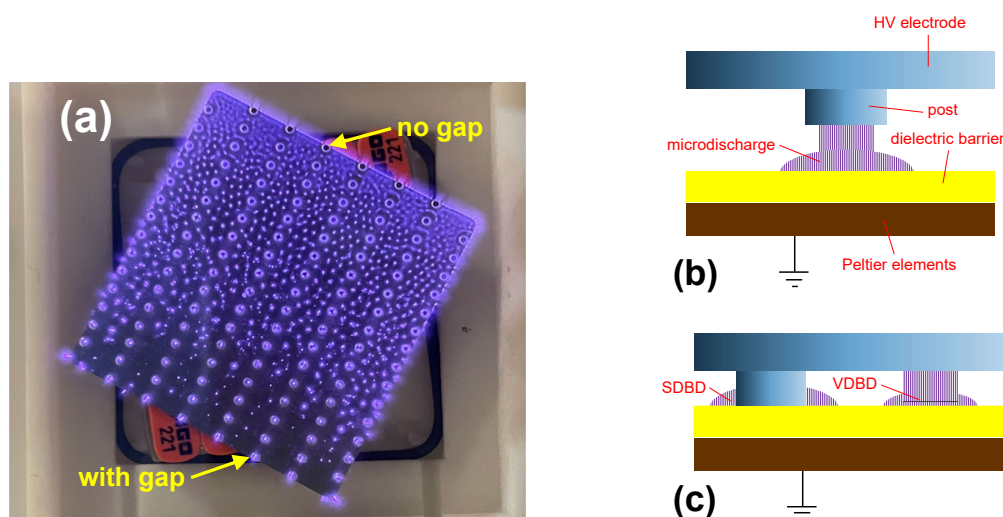


Figure 3. The hybrid SDBD-VDBD discharge operation principle. (a) Visualization by use of a glass plate coated with ITO, placed at a tilt on the HV electrode surface. (b) The volume microdischarge in the gap between the post surface and the dielectric barrier. (c) The hybrid DBD with surface and volume microdischarges at the post touching the dielectric barrier surface.

The heat transferred by the Peltier module from the dielectric plate on its discharge side to the opposite surface (see Figure 2) must be dissipated in the ambient air. For this purpose, the Peltier module is fixed on an aluminum heat sink cooled by a silent fan.

Further technical data of the commercial version of the HDBD reactor are published in the datasheet [75].

2.3. ITO-Coated Plate

For better insight into the HDBD discharge with the HV electrode touching the dielectric barrier, the microdischarge distribution is visualized. The soda-lime glass plate with a size of 100 mm × 100 mm and a thickness of 1.1 mm, coated on one side with 1850 ± 200 nm of indium tin oxide (ITO), is positioned in place of the Peltier module (see Figure 2). The ITO coating shows away from the discharge [76]. The ITO film is grounded and plays the role of the DBD passive electrode, but is not obstructing the view of the discharge. The glass plate is the dielectric barrier in this setup. The visualization experiment was conducted in ambient air without gas flow.

2.4. DBD Driver

The basic technical data of the DBD driver are summarized in the datasheet [77]. The core component of the DBD driver is a transformer converting the small to high voltage signal in the range of 2 to 6 kV. The output circuit works under resonant conditions. The output impedance is adjusted to the HDBD reactor load by swiping the frequency from 20 to 40 kHz (auto resonant). The resonant conditions can be established for a capacitive load from 2 to 90 pF. The maximum continuous power of the device is 30 W. The acceptable load resistance range is 0.3 to 1 M Ω . The AC output HV root mean square (RMS) is linearly proportional to the DC input voltage (see Section 3.3). An additional control voltage input allows for the switching between the power pulse-width modulation (PWM) mode (see the example in Section 3.2) and the continuous AC mode. The PWM pulse frequency can be up to 100 Hz and the duty cycle from 0 to 100%.

The discharge power determination by oscilloscope requires expensive measurement equipment and cannot be integrated into a simple DBD driver. For this reason, a simplified net discharge power estimation method is proposed. It involves the higher harmonic frequencies of the load signal. The voltage is measured on an inductive shunt to determine the current flowing to the ground. The obtained signal is passed through an inductive high-pass filter [78] and rectified. Its inductance $L_f = 12 \mu\text{H}$ is connected as a shunt to the ground, in series with the secondary winding of the HV transformer. The signal from the inductance is rectified using fast Schottky diodes, and the DC voltage in a high mV range is obtained and used as an MDIR signal. The cut-off frequency of the filter, computed under consideration of the rectifying circuitry as a load, is $\omega_f = 5 \text{ MHz}$. This value is sufficient to filter out the resonant frequency of the HDBD reactor in the range of 50 to 100 kHz, and at the same time pass the frequencies resulting from the impulse responses of microdischarges in the range of 20 to 50 MHz. The resulting MDIR signal correlates with the net power coupled into the microdischarges (see Section 3.4). The use of the MDIR signal for the estimation of the net discharge power is justified by the role played by microdischarges for ozone generation. Since the mean charge transferred per microdischarge remains constant in the nC range [79], and the number of microdischarges in a half-period is increasing proportionally to the AC voltage applied to the HV electrode [80], the net discharge power can be considered as proportional to the number of microdischarges per AC period.

2.5. UV Absorption Measurement

For the measurement of ozone concentration, the Ozone Analyzer BMT 965 ST was used. It is equipped with a dual-beam 253.7 nm UV photometer, a low-pressure mercury lamp for UV light generation, and a built-in sample gas filter. It allows for the determination of ozone concentration in the ranges between 500 ppm to 280,000 ppm. The subtraction of the reference spectrum measured in gas with filtered ozone allows for the determination of the ozone concentration in air with relative humidity up to $50\% \pm 5\%$.

2.6. Gases

The HDBD reactor was fed with three gases: oxygen, synthetic air, and CDA. Oxygen 5.0 in pressurized bottles was used. It contains less than 2 ppm humidity, 0.2 ppm carbon dioxide, and 0.2 ppm hydrocarbons. The results obtained with the gas referred to as synthetic air are conducted with the hydrocarbon-free gas mixture of Linde GmbH, with certified conformity according to ISO/IEC 17050-1:2004 [81]. It consists nominally of 20% oxygen and 80% nitrogen. The residual amount of water vapor is less than 2 ppm. The residual CO and CO₂ are less than 1 ppm each. The hydrocarbons are less than 0.5 ppm. The contents of each of the nitrogen oxides NO, NO₂, and N₂O are below 0.02 ppm. All ppm specifications are based on ideal gas volumes (mole/mole). The relative humidity of the CDA was 7%.

3. Results and Discussion

3.1. Discharge Morphology

The reactor configuration described in Section 2.3 was used to visualize its hybrid DBD operation mode. In Figure 3a, the DBD discharge, ignited between the slightly tilted ITO-coated plate and the structured stainless-steel electrode, is shown. At the place with a gap between the post and the glass surface, the densest discharge can be observed between the post faces' center and the glass surface. They can be recognized as the volume microdischarges, as shown in the explanatory drawing in Figure 3b. Only a few microdischarges are present in the space between the posts. Since the distance between the electrode surface and the dielectric barrier is at this position larger than that between the post face and the dielectric barrier, a higher voltage is needed to ignite a volume microdischarge at this position, or in other words, the probability of microdischarge at this position is lower.

The closer to the zone without the gap, the more apparent the discharges around the edges of the post faces. However, more microdischarges also develop in the space between the posts. If the posts of the electrode structure touch the glass surface, the discharges between the post face and the glass surface disappear, and the discharges around the post edges get more intense. They can be interpreted as the SDBD. The coexistence of the volume and surface microdischarges is shown schematically in Figure 3c. The hybrid operation mode (HDBD) ensures the efficient production of chemically active species.

3.2. High Voltage Signal

Figure 4 shows the high voltage measured on the HDBD electrode during PWM operation. Figure 4a depicts the times required to define the duty cycle. These are the on-time t_{ON} , off-time t_{OFF} , and PWM period T_{PWM} . The PWM duty cycle is defined as follows:

$$\tau = \frac{t_{ON}}{T_{PWM}} \quad (1)$$

This definition is related to the control voltage of the DBD driver input. The alternative definition of the duty cycle can take into account switching delays. The increase in the high voltage after switching on and off the input PWM pulse was delayed by the rise time t_r and the decay time t_d , respectively. Such a definition would not be ideal for determining the effective duty cycle, because the discharge is present only during parts of the rise and decay times when a high voltage is sufficient for the onset of the microdischarges. The onset voltage depends on the HV voltage amplitude, the excitation frequency, and the gas type. This makes the precise determination of the effective duty cycle difficult. The DBD driver input signals were used for the duty cycle definition to avoid this difficulty and additional sources of error.

The kHz excitation period is not recognizable on the time scale of Hz, as shown in Figure 4a. An excerpt of this diagram, representing two periods T_{kHz} of kHz excitation, is shown in Figure 4b. The plasma load caused a nonideal sinusoidal shape of the voltage signal. The deformation of the HV signal increases with the voltage amplitude.

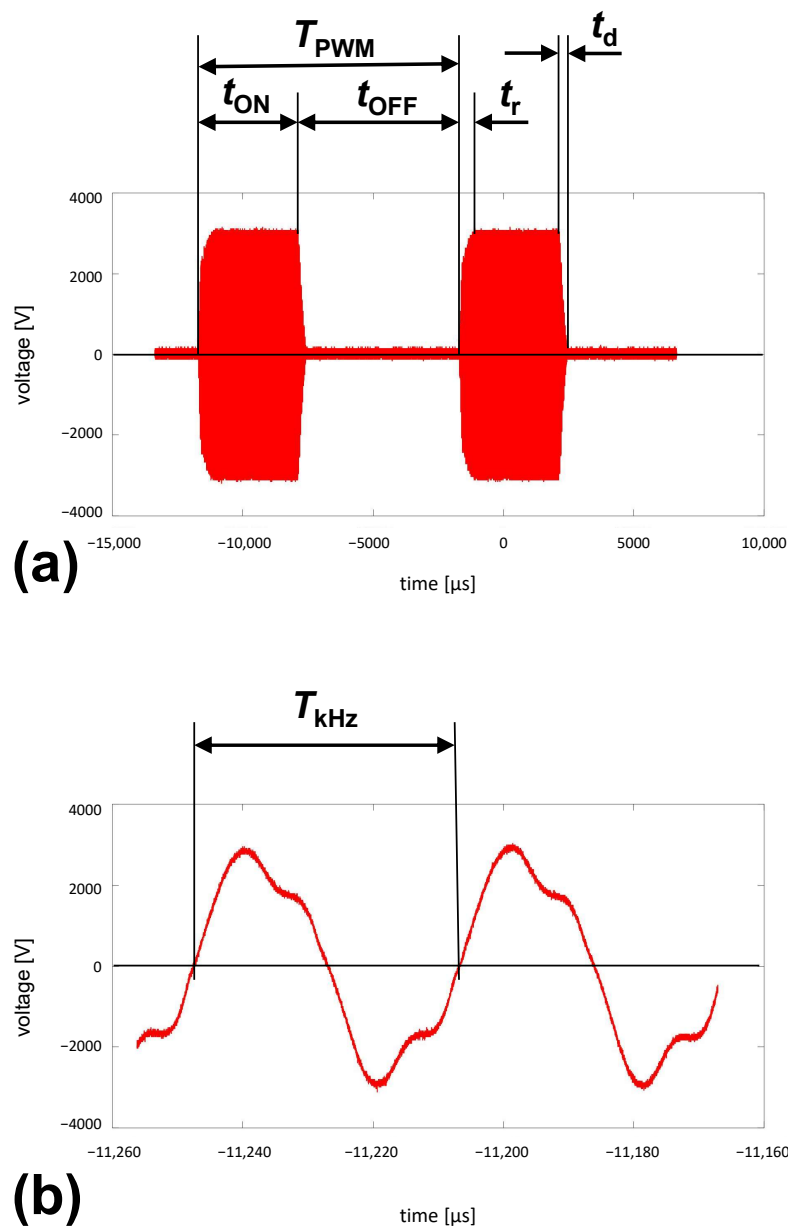


Figure 4. (a) Two PWM cycles of PWM, and (b) two cycles of kHz excitation of the high voltage measured between the HDBD electrodes as a function of time for the driver input voltage of 12 V, PWM frequency of 100 Hz, PWM duty cycle of 40%, CDA flow of 1 SLM, and Peltier module current of 2 A.

3.3. Discharge Power Estimation

The high voltage applied to the DBD electrodes is controlled by the DC input voltage of the DBD driver (control voltage). Figure 5 shows the linear dependence of the RMS output voltage on the control voltage in the range of 12–27 V. This dependence is valid only for a linear load on the DBD driver output, because sinusoidal time dependence can be assumed only in such a case. For an RMS voltage below 1800 V, which corresponds to a control voltage of 10.5 V, no stable discharge ignition in air was observed. Control voltages greater than 18 V can cause the overheating of the HDBD reactor under certain conditions.

As shown in Figure 4b, the shape of the time-dependent curve of the high voltage between the HDBD reactor electrodes, measured during the plasma generation, is far from sinusoidal. The simple sinus-based formulae for power determination cannot be

applied. Therefore, the apparent power, P_{app} , defined for arbitrary voltage and current, was used. In the case of a non-modulated voltage signal, the apparent power coupled into the plasma can be calculated for a single period of kHz excitation T_{kHz} as a product of the time-dependent voltage $V(t)$ and current $I(t)$ using the general integral Formula (2):

$$P_{app}(t_1) = \int_{t_1}^{t_1+T_{kHz}} V(t) \cdot I(t) dt \quad (2)$$

where t_1 is the start time of the calculation.

The direct determination of the electric power consumed in the HDBD reactor on the base of the control voltage is not possible, because its load impedance strongly varies. The load component related to the HDBD electrode geometry depends on the resonant frequency. The resistance of the microdischarges depends on many factors, such as gas composition, discharge voltage, gas temperature, and deposited power. The apparent power, measured on three different load impedance models on the DBD driver output, is shown in Figure 5 as a function of the DC input voltage. These three curves demonstrate that the power coupled into the HDBD reactor varies strongly with the output impedance. Consequently, the changes in the plasma properties strongly influence the coupled power. On the other hand, this power influences the resistance of the plasma. The electric measurement of the HDBD power does not allow for discrimination between different kinds of resistive power losses in the system and the power coupled into the microdischarges. The MDIR signal used in this study does not allow for the determination of absolute values of the microdischarge power. Still, it refers to their number and strength, giving valuable information about variations of the power dissipated in microdischarges.

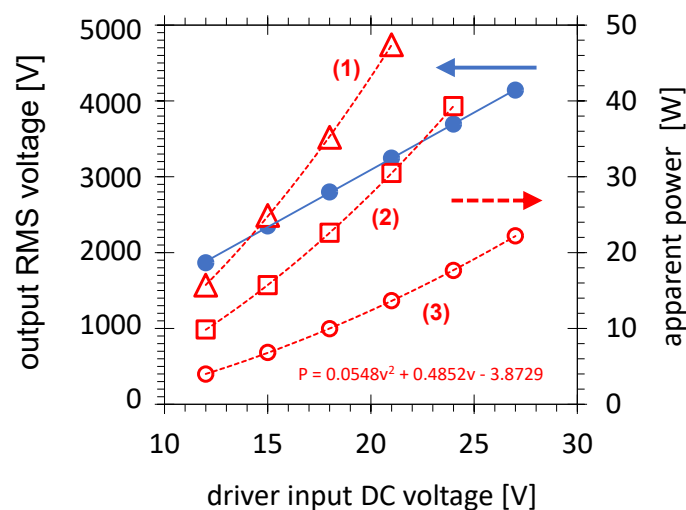


Figure 5. The output RMS high voltage and apparent power for load capacity and resistance of (1) 2 pF and 1 MΩ (triangle), (2) 40 pF and 150 kΩ (square), and (3) 80 pF and 300 kΩ (circle), respectively, as a function of the input DC voltage of the DBD driver.

3.4. Current Spectrum

The higher harmonics are detected in the FFT spectrum [82] of the alternated DBD current. Figure 6 shows such spectra collected in the air DBD for power densities from 0.01 W cm^{-2} to 0.75 W cm^{-2} . The strongest increase in the spectrum magnitude with power density can be observed in a frequency range from 10 MHz to 40 MHz. It corresponds to the time constants from 25 to 100 μs. Our previous work [83] shows that the integral area under the spectral lines of the harmonics increases with the number density of the microdischarges. However, the duration of microdischarges in dry air is about 10 ns [84], three orders of magnitude shorter than the time constants of the MHz harmonics. The dependence of the MHz frequency spectrum on the number of microdischarges is indirect. The current spikes are observed in the DBD current [73] with a duration of orders of magnitude longer than the

microdischarge lifetime. These spikes represent the electric oscillation in the measurement circuit [85] and cause the current signal deformations manifested in the presence of signal harmonics in the middle MHz range. From their oscillatory pattern, the electric charge shifted during the single microdischarge between the DBD electrodes can be calculated [86]. The spike current amplitude is influenced by breakdown voltage, which depends on the initial gas composition [87], pressure, temperature, and the actual ozone concentration [88]. The proportionality of the net discharge power to the number of microdischarges [64] allows for the use of the MDIR signal for its estimation.

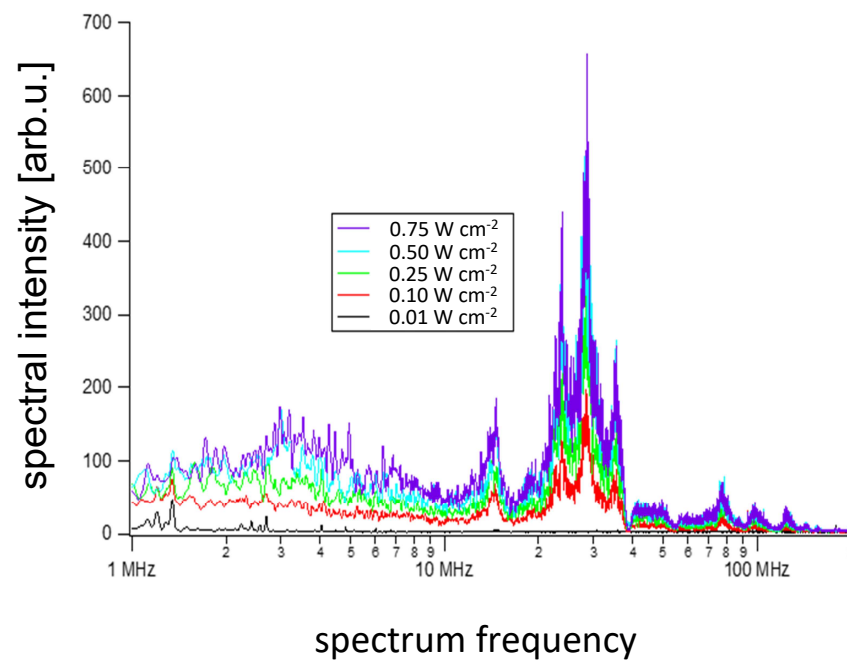


Figure 6. The current spectrum measured for the DBD operating in air at different power densities.

3.5. Ozone Production in Oxygen

Some threshold values of the ozone concentration N_{O_3} defined in molar percent units, ppm of the gas, or g/m^3 must be reached to destroy some specific microorganisms efficiently. Such thresholds depend on the exposure time of the microorganisms and increase with shorter exposure. Sterilization, decontamination, or disinfection processes can be accomplished faster when higher ozone concentrations are applied. For these types of tasks, the ozone concentration should be maximized [14].

The direct functional dependence exists between ozone concentration N_{O_3} in the gas flowing through the DBD reactor with the speed f_{gas} given in this study in standard liter per minute (SLM), and the production rate R_{prod} given typically in g or mg per hour.

$$N_{O_3} = \frac{V_A \cdot R_{prod}}{M_{O_3} \cdot f_{gas}}, \quad (3)$$

where V_A is the molar volume for a given temperature and pressure and M_{O_3} is the molar mass of ozone (48 g/mol). In Sections 3.5, 3.6, and 3.7, the subscript gas means molecular oxygen, synthetic air, and CDA, respectively. The two parameters, ozone concentration and ozone production rate, are used for the characterization of the HDBD reactor presented in this work.

3.5.1. Specific Energy Input

The ozone concentration is frequently presented in the literature as a function of the energy density, [89] alternatively called specific energy input (SEI) [90] or beta parameter β [91], expressed in J/cm^3 or $eV/molecule$.

$$\beta = \frac{P}{f_{\text{gas}}}, \quad (4)$$

where P is the electric power coupled to the discharge. The dependence of ozone concentration on SEI is not monotonous. For low SEI, the ozone concentration increases with SEI. At a certain value of SEI, the ozone concentration reaches saturation, and then, it decreases for higher SEI values [92].

The ozone production rate is mainly determined by the energy coupled to the discharge. Since the DBD microdischarge duration, with a range of a few ns, is much shorter than the residence time in the reactor, ranging from 25.2 to 1.5 ms for a gas flow of 0.6 to 10 SLM, respectively, the ozone production rate should not change in a broad gas flow range [83]. Consequently, the observed dependence of ozone concentration on gas flow [27], expressed by Equation (3), could be explained by the increasing dilution of the microdischarge products with increasing amounts of oxygen.

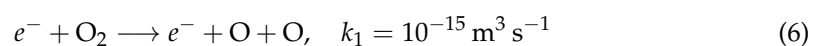
If ozone concentration N_{O_3} is known from measurement, Equation (3) can be reformulated to express the ozone production rate as a function of ozone concentration:

$$R_{\text{prod}} = \frac{M_{\text{O}_3}}{V_A} \cdot f_{\text{gas}} \cdot N_{\text{O}_3}. \quad (5)$$

For precise calculation, the reduction in the molar amount due to the conversion of O_2 in O_3 should be considered. Further corrections are needed for the actual gas temperature and pressure.

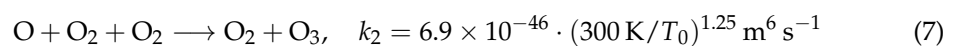
3.5.2. Mechanisms of Ozone Production and Destruction in Oxygen

The simplest chemistry is involved in ozone production in the low-temperature atmospheric pressure discharge, fed by pure oxygen. The majority of the reaction channels available in ambient air are disabled in the absence of nitrogen and water molecules. Despite this, a comprehensive list of possible reactions is quite long [93]. The main production mechanisms are described in [94]. The ozone is generated in a two-step process, where the first step is the production of atomic oxygen by the collision of the electron with molecular oxygen, as follows:



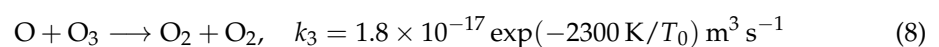
The production rate for this equation and other equations involving the electron impact dissociation in Sections 3.6.1 and 3.7.1 increases with the electron temperature, assuming a Maxwellian electron energy distribution function (EEDF) [95]. The rate coefficient k_1 value given in Equation (6) is a typical value for DBD microdischarge at atmospheric pressure in oxygen.

The second step is the three-body collision:

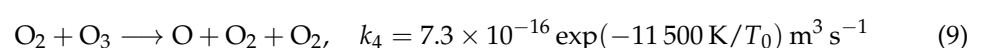


where k_2 is the gas temperature T_0 dependent rate coefficient for this reaction.

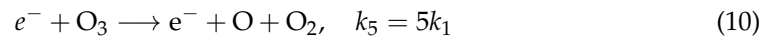
From these reactions, the only limit of the ozone concentration produced in closed volume would be the availability of the diatomic oxygen. However, the practically measured concentrations are much lower than that. The main reason for this is ozone destruction, which remains balanced with ozone production. The main destruction mechanisms are the two body collisions between neutral particles [94]:



and



and two-body collisions of ozone with electrons:



characterized with destruction rate coefficients k_3 , k_4 , and k_5 , respectively. The efficiency of these destruction mechanisms increases with increasing ozone concentration, causing the saturation of ozone production at some level of ozone concentration.

The discharge parameters influence the maximum reachable ozone concentration. On the one hand, the fixed parameters related to the construction of the DBD reactor, such as the size of the electrode, the thickness and material of the dielectric barrier, and the size of the discharge gap, [94] typically optimized empirically or by use of numerical simulations, have a strong influence on device efficiency. On the other hand, the ozone concentration and production rate are influenced by operational parameters, such as HV frequency and amplitude, the duty cycle, the Peltier module current, and the kind and flow of gas used.

In further sections, the influence of these parameters on the performance of the HDBD reactor at the given construction is analyzed.

3.5.3. Influence of Oxygen Flow

Figure 7 shows the influence of the oxygen flow on ozone concentration, ozone production rate, and MDIR signal. The duty cycle and the Peltier current for these measurements were 100% and 0 A, respectively. As Equation (3) predicted, the ozone concentration decreases, roughly inversely proportional to the oxygen flow for all three input voltages (see Figure 7a). Figure 7b shows that the production rate of HDBD does not remain constant but varies strongly with oxygen flow. For all three curves, the production rate increases monotonously by more than 50% for oxygen flow, rising from 1.2 to 5.0 SLM. What is striking is the close correlation between the ozone production rate and the MDIR signal, shown as red curves in Figure 7b. It suggests that the production rate is proportional to the power coupled into the microdischarges.

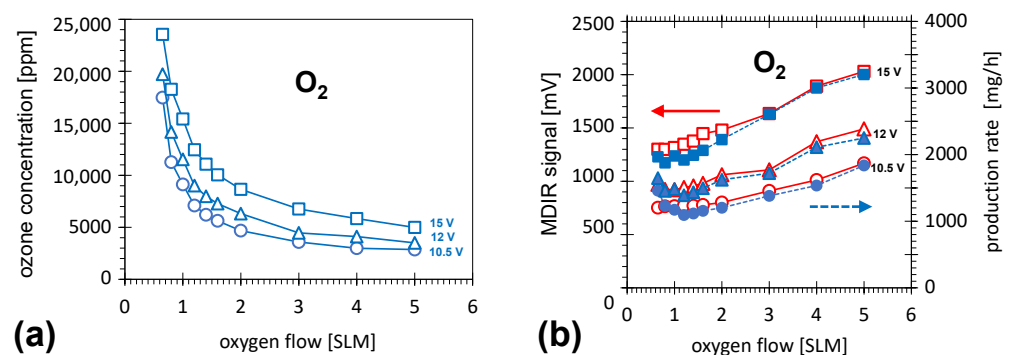


Figure 7. Influence of the oxygen gas flow on the ozone concentration expressed in ppm (a) and MDIR signal compared with ozone production rate (b) for the duty cycle of 100%, the Peltier current of 0 A, and with three DBD driver input voltages, as depicted at the curves.

Several reasons for the increase in power coupling with gas flow speed can be considered. First, the residence time of the gas, and hence the amount of heat transferred from the discharge to the unit of gas volume, is decreasing. The resulting gas temperature is decreasing as well. A lower temperature results in a higher gas particle concentration, collision frequency, and consequently, higher ozone production.

The pressure increase is another possible reason for higher gas particle concentration. The pressure difference across the HDBD reactor, and consequently, the mean pressure in the discharge space, increases with the gas flow. The resulting increase in particle concentration causes, like the temperature drop, more electronic collisions, and consequently, higher energy coupling. Additionally, the increased gas particle concentration causes a decrease in electron diffusivity, resulting in a reduced diameter of the microdischarge, the following increase in the microdischarge resistance, and consequently, more power coupling.

The production rate increase could be interpreted as an artifact caused by increasing the transfer time from the reactor to the UV measurement system. The ozone, once produced in the reactor, remains quite stable in the range of magnitude of hours [3]. The selected materials, such as the tubing made of silicone, support the long lifetime of ozone. Consequently, other reasons for this effect can be found.

The ozone production rate curves show a slight increase in the production rate for oxygen flow below 1 SLM, which is not observed in the behavior of the MDIR signal curves. This effect is stronger for lower DBD driver input voltage.

3.5.4. Influence of Voltage

In Figure 7b, the production rate and MDIR signal curves shift to higher values with increasing DBD driver input voltage. This result can be expected, since the number of microdischarges igniting per cycle of HV applied between the HDBD electrodes increases with HV amplitude. However, the increase in the number of microdischarges causes an increase in the oxygen production rate only for as long as the loss mechanisms described in Equations (8)–(10), playing a minor role in comparison with the ozone production. The strong influence of these loss mechanisms can already be observed for the DBD driver input voltage of 18 V.

The influence of increasing the DBD driver input voltage up to 18 V, representing the increase in the electric power coupled into the HDBD reactor on the ozone concentration and the ozone production rate, is visualized for four oxygen flows in Figure 8. For low oxygen flows (0.65 SLM and 0.8 SLM) the maximum ozone concentration is reached for the DBD driver input voltage of 15 V. With higher voltage at these flows, the ozone concentration decreases.

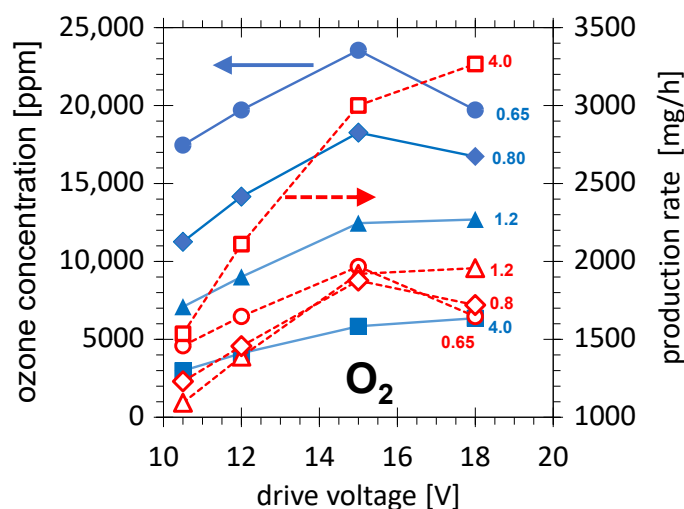


Figure 8. The ozone concentration and ozone production rate in pure oxygen, shown as a function of drive voltage for the duty cycle of 100%, the Peltier current of 0 A, and with four oxygen flows in SLM, as depicted at the curves.

As mentioned in Section 3.5.1, the maximum ozone concentration is reached for some SEI values, shifting with increasing flow to higher power (drive voltage) values. Starting with 1.2 SLM, no maximum is observed in the measured voltage range, which is to be expected for driver voltages over 18 V. As for ozone concentration, the maximum vs. applied input drive voltage is observed for the ozone production rate.

The DBD driver input voltage of 15 V corresponds to the power load of 25 W. Assuming this value and the ozone production rate of 3.2 g/h is reached for this voltage, the HDBD reactor produces 128 g per kWh of electric energy. This result is comparable to the best-reported values [24] of about 8 kWh/kg. This is better than conventional generators, as they require about 15–20 kWh/kg if ozone is synthesized from oxygen [96]. The

efficiencies closer to the thermodynamic minimum of the energy cost for the O_3 production of 0.8 kWh/kg can be reached by decreasing the discharge temperature.

3.5.5. Influence of Duty Cycle

The duty cycle variation has a strong influence on the ozone concentration reached in the HDBD reactor operated with pure oxygen. Figure 9a shows the ozone concentration as a function of the duty cycle of 70 Hz power pulses for three DBD driver input voltages. For the low voltage of 10.5 V, this increase is almost linearly proportional to the duty cycle, up to its value of 80%. For higher voltages, the ozone concentration only increases monotonously with the duty cycle for the low duty cycles. The curve for 15 V shows the saturation tendency for the duty cycle over 40%.

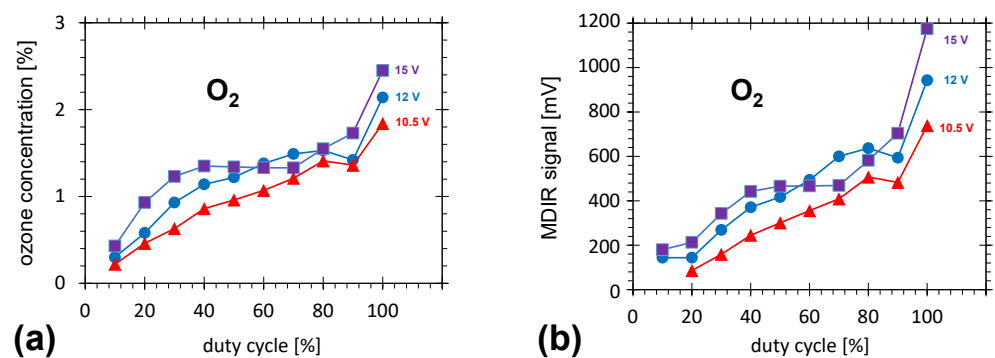


Figure 9. The ozone concentration expressed in volume percentage (a) and MDIR signal (b) shown as a function of the duty cycle of PWM for HDBD reactor operated with pure oxygen, switched off Peltier cooling, 0.6 SLM oxygen flow, and three driver input voltages, as depicted at the curves.

This behavior correlates very well with the MDIR signal shown in Figure 9b. The DBD driver input voltage and the duty cycle contribute to the SEI. On the one hand, it is known that the number of microdischarges contributing to SEI and ozone production increases with increasing voltage. On the other hand, it increases linearly proportional to the discharge time to total time ratio, defined as the duty cycle.

As mentioned in Section 3.5, the power coupled to the microdischarges and the related MDIR signal is not directly proportional to the HV or control voltage, because of the complex influence of the plasma impedance. This influence is stronger for higher voltages, which is manifested by the shape of the curves for 12 and 15 V. The higher the voltage, the lower the duty cycle, which is sufficient to cause the transition of the curve to saturation.

In all the ozone concentration and MDIR signal curves shown in Figure 9a and Figure 9b, respectively, an abrupt increase, with the duty cycle switching from 90 to 100%, is observed. A short break in the power supply, in the time range of ms, causes an effect that cannot be explained with the proportionality to the energy coupling time. A possible explanation is the influence of the surface charge accumulating and dissipating at the surface of the dielectric barrier. The shortest period of switching off the power supply during the pulse-width modulation (PWM) mode operation for the duty cycle of 90% is $0.1 \times 1/70 \text{ Hz} = 1.43 \text{ ms}$. A significant part of the charge accumulated during the microdischarges, sustained for a few ns at the surface of the dielectric barrier, remains there for a long time—seconds [97], or even minutes [98]. However, the time in ms is sufficient for a large part of this charge to diffuse away [99]. This charge can be built up again, using the capacitively coupled HV electric power for each new power-on pulse. In contrast to PWM conditions, during the continuous operation, the time between bursts of ignitions of the microdischarge in the range of 25 μs , half of the HV excitation cycle, is much shorter than the diffusion process at the dielectric barrier surface. Consequently, the charge accumulated at the dielectric barrier surface contributes to the effective voltage available for microdischarge ignition in the gap between the dielectric barrier and the electrode. For the same voltage between the electrodes of the HDBD reactor, more net power is coupled

into the discharge. This fundamental difference between the discharge operated in PWM and CW mode explains the abrupt change in the MDIR signal, and consequently, ozone production and ozone concentration when switching between modes.

3.5.6. Influence of Peltier Cooling

The Peltier cooling can increase the ozone concentration in oxygen HDBD. Figure 10a shows the dependence of the ozone concentration on the Peltier module current, increasing from 0 to 4 A. The three curves are for the driver voltage of 10.5, 12.0, and 15 V, respectively. The measurements are conducted with an oxygen flow of 0.6 SLM and without pulse-width modulation (duty cycle of 100%).

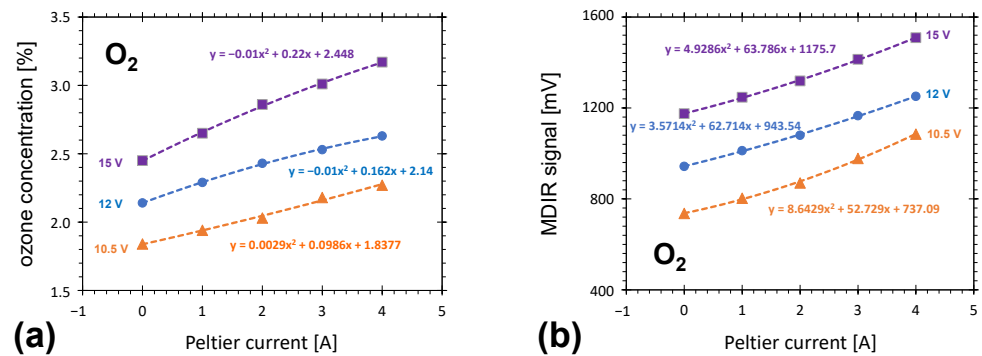


Figure 10. The ozone concentration in pure oxygen expressed in volume percentage (a) and MDIR signal (b), shown as a function of the Peltier module current for the HDBD reactor operated without pulse-width modulation, with 0.6 SLM oxygen flow, and with three driver input voltages as labeled at the curves. The fitting functions used for the sensitivity calculation in Equation (11) are included.

The curves of the ozone concentration correlate well with the MDIR signal curves collected for the same set of parameters and conditions and presented in Figure 10b. Two possible reasons for the increase in the number of microdischarges per HV period, and consequently, the net power deposited in the discharge, can be considered, both related to the temperature drop due to the Peltier cooling.

The first one is related to the temperature drop in the discharge gas. The concentration of oxygen molecules in the discharge space increases with decreasing gas temperature, resulting in a higher electronic collision frequency and a related increase in the energy coupled into the discharge, manifested in the rise of the MDIR signal. As shown in the simulations of a single microdischarge evolution, the diameter of the microdischarge in air is about 0.4 mm, and shrinks slightly with increasing gas density (lower temperature or higher pressure) [100], resulting in the increase in its resistance and consequently the amount of energy coupled into the discharge.

The second one is related to the temperature of the dielectric barrier cooled directly by the Peltier elements. The decreasing temperature of the dielectric barrier reduces the surface charge diffusivity. Consequently, the residence time of the charge accumulated during a microdischarge increases. Less external voltage is needed to ignite the subsequent microdischarge in the next half-period of HV. More microdischarges can be ignited in the same HV half-period, resulting in more energy coupled into the discharge and an increased MDIR signal.

To characterize the efficiency of the Peltier cooling, the sensitivity of the ozone concentration to the Peltier module current I_{Peltier} is used, defined as:

$$S_{\text{Peltier}} = \left. \frac{\partial N_{\text{O}_3}}{\partial I_{\text{Peltier}}} \cdot \frac{1}{N_{\text{O}_3}} \cdot 100\% \right|_{I_{\text{Peltier}}=0} \quad (11)$$

For the fit line, defined as $y = ax^2 + bx + c$, as specified in Figure 10, the sensitivity is given as $S_{\text{Peltier}} = b/c \cdot 100\%$. For the DBD driver input voltages of 10.5, 12.0, and

15.0 V, the sensitivity defined by Equation (11) is 5.37, 7.57, and 9.0%/A, respectively. The higher the specific energy, the stronger the effect of the Peltier cooling. Due to the slight non-linearity of the ozone concentration function on the Peltier current, the parabolic fit is chosen to allow for compatibility with the more non-linear results for air, as shown in Sections 3.6.4 and 3.7.4.

The main difference between the curves for ozone concentration and the MDIR signal at 12 and 15 V is that they are convex and concave parabolas, respectively. This discrepancy can be explained by the contribution of chemical processes to the temperature dependence of ozone concentration. Such a direct contribution is absent in the MDIR signal. The main chemical channels of ozone production and destruction are presented in Section 3.5.2. Since the ozone production rate determined in Equation (7) increases with decreasing temperature, and at the same time the destruction rate determined by Equations (8) and (9) decreases [94], the balance between ozone production and destruction bends the curves in the direction of lower ozone concentration.

The maximum ozone concentration shown in Figure 10, reaching 3.17%, can be increased to 5.5% using so-called dynamic cooling. For this purpose, the HDBD reactor is pre-cooled for 2 min, using the Peltier module operated with 4 A without driver power, and subsequently briefly generating the discharge in oxygen. The temperature reached for a short time after such a pre-cooling process can be much lower than that for continuous (stable) operation.

3.6. Ozone Produced in Synthetic Air

The common understanding of the definition of dry air refers to its dew point. No significant amount of water chemistry is involved in gaseous discharge if the air dew point is lower than -60 °C. However, even at this low temperature, 10 ppm of water vapor is present in the air. The lower concentration specified, of less than 2 ppm of water vapor, can be reached by the application of bottles with pressurized synthetic air or medical air (see Section 2.6). This low-humidity synthetic air was used in this study to investigate the influence of humidity on ozone production.

3.6.1. Reaction Channels Due to Nitrogen

The main reaction channels for ozone production are the same as in pure oxygen, as described by Equations (6) and (7), but in the initiating reaction involving nitrogen, the electron impact dissociation of N_2 is as follows:

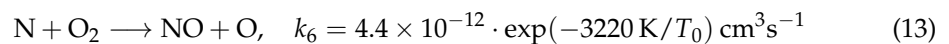


This allows for many additional reactions involving oxygen and nitrogen. They are summarized, e.g., in [101,102]. The most important reactions are responsible for the production of different nitrogen oxides. The existing nitrogen oxides can be ordered with increasing oxidation state [103], as shown in Table 1:

Table 1. The existing nitrogen oxides ordered with increasing oxidation state.

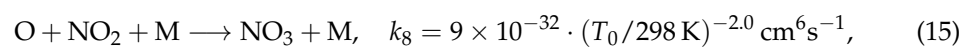
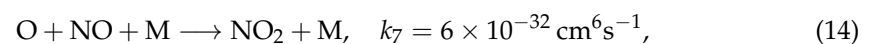
Molecule	Name	Equation
N_2O	nitrous oxide	(19)
NO	nitric oxide	(13)
N_2O_2	dinitrogen dioxide	
N_2O_3	dinitrogen trioxide	
NO_2	nitrogen dioxide	(14)
N_2O_4	dinitrogen tetraoxide	
N_2O_5	dinitrogen pentoxide	(20)
NO_3	nitrogen trioxide	(15)
N_2O_6	dinitrogen hexaoxide	

The simplest oxidizing reaction is the production of NO [104]:

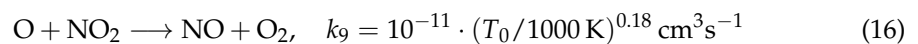


where atomic oxygen is a byproduct supporting ozone production.

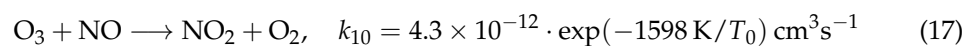
Due to the addition of nitrogen to the gas mixture with oxygen, the ozone destruction mechanism, stronger than the one described by Equations (8) and (10) [96], plays an important role. For lower gas flows or higher power, equivalent to higher specific energy, the presence of nitrogen initiates chemical mechanisms, suppressing ozone production and promoting its destruction. The nitrogen oxides are consuming the atomic oxygen needed for ozone production (discharge poisoning effect) [105] according to the following equations:



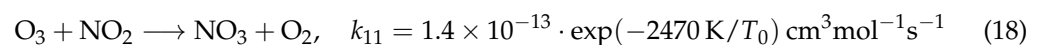
and



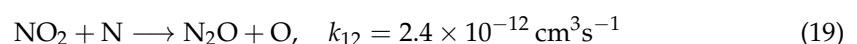
but also, the already existing ozone is converted back to oxygen according to the equations [104]:



or [102,106]

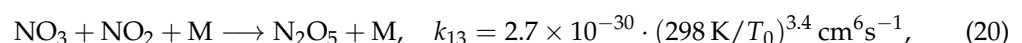


The reactions with atomic nitrogen produce oxides with a lower oxidation state. An example is the generation of nitrous oxide from nitrogen dioxide (N_2O) according to the following reaction [104]:



Nitrous oxide is the unstable intermediate of nitrogen oxidation, but its decomposition is kinetically inhibited [107]. Instead of being decomposed at room and higher temperatures, it remains present thanks to its passivity. Even for higher temperatures, the catalyst is needed to decompose the nitrous oxide. Consequently, its presence can be expected in ozone generators operated in the air.

The dinitrogen pentoxide is produced mainly by the following reaction [104]:



where M represents any other species.

3.6.2. Influence of Synthetic Air Flow

The results in Section 3.5.3 show that the ozone concentration and production rate for the duty cycle of 100% are strongly different compared to the values for the lower duty cycle. To make the comparison between dry synthetic air and humid CDA more plausible, the duty cycle of 80% was used for the analysis of the influence of airflow on the production rate and ozone concentration in Figure 11. The general appearance of the plots in this figure is like those for oxygen (Figure 7). The ozone concentration decreases inversely

proportional to the synthetic air flow when the ozone production rate increases. The explanations in Section 3.5.3 for oxygen are valid here for synthetic air at low SEI operation. The ozone concentration for the voltage of 15 V, the duty cycle of 80%, and synthetic air flow of 0.6 SLM is 3500 ppm. For the same conditions, but for oxygen flow (see the curve for 15.0 V at the duty cycle of 80% in Figure 9), the ozone concentration is 15,500 ppm, which is 4.4 times higher than for synthetic air. The main explanation is the molar concentration of oxygen in synthetic air, which is five times lower than in pure oxygen. The value 4.4 is lower than the one resulting from the stoichiometric consideration. The additional mechanism of atomic oxygen production, described in Equation (13), contributes to the increase in the ozone concentration.

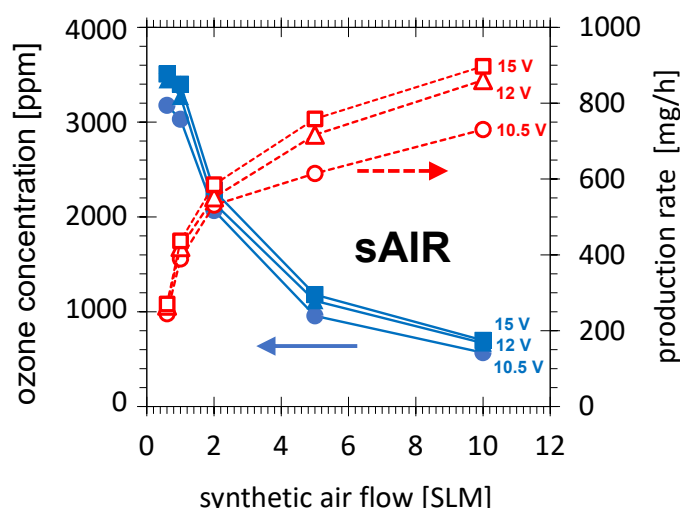


Figure 11. The ozone concentration and ozone production rate are shown as a function of synthetic air flow for the duty cycle of 80%, the Peltier current of 0 A, and three DBD driver input voltages, as depicted in the diagram.

The typical value of energy efficiency of ozone production calculated for 12 V, 10 SLM, an 80% duty cycle, and no Peltier cooling is 87 g/kWh. It is better than in the optimized DBD reactors described in the literature [108].

3.6.3. Influence of Duty Cycle

Figure 12 shows the dependence of the ozone production rate and MDIR signal on the duty cycle for four DBD driver voltages and two synthetic air flows. Consistent with the observation in Section 3.6.2, the ozone production rate is higher for higher synthetic air flow. The four production rate curves for the gas of 10 SLM, shown in Figure 12b, follow the corresponding MDIR curves shown in Figure 12d quite well. At the same time, the production rate and MDIR curves for 10.5, 12, and 15 V have shapes like the curves for oxygen in Figure 9a and Figure 9b, respectively. The production rate and the MDIR signal for 10.5 V grow almost linearly proportional to the duty cycle. The curves for 15.0 V reach the saturation for the duty cycle of about 50%. This similarity of the curves for oxygen and the high flow of synthetic air can be interpreted as resulting from the operation of the HDBD reactor in the range of low SEI in both cases. The physical explanation of the jump of the MDIR signal, and consequently, the ozone production rate for the duty cycle switching from 80 to 100% given in Section 3.5.5 for oxygen is valid for synthetic air.

A distinct difference in shape between the ozone production rate curves (Figure 12a) and the MDIR signal curves Figure 12c can be observed for the gas flow of 0.6 SLM, corresponding to a much higher SEI. The MDIR signal increases monotonously with the duty cycle and shows a strong increase between 80% and 100%. The ozone production rate curves show a maximum shift from the duty cycle of 70% for 10.5 V to 30% for 18 V, respectively. The variation in the MDIR signal has a physical nature, and follows the

increase in the SEI with the duty cycle. In contrast, the variation in the production rate is influenced by changes in the chemical processes as a function of SEI.

Also, the collapse of the ozone production rate for the duty cycle changing from 80% to 100% at high SEI cannot be explained by the shape of the MDIR signal curves following the power coupled into the discharge. The chemical processes described by Equations (17) and (18), causing a decrease in ozone production at high SEI in the presence of nitrogen, must be considered. These processes also explain why the collapse of the ozone production rate is stronger for higher voltages, related to an even higher SEI. In this case, the release of an additional amount of energy due to reduced energy losses of dielectric surface recharging causes a decrease in the ozone production rate, with increasing power coupled into the discharge.

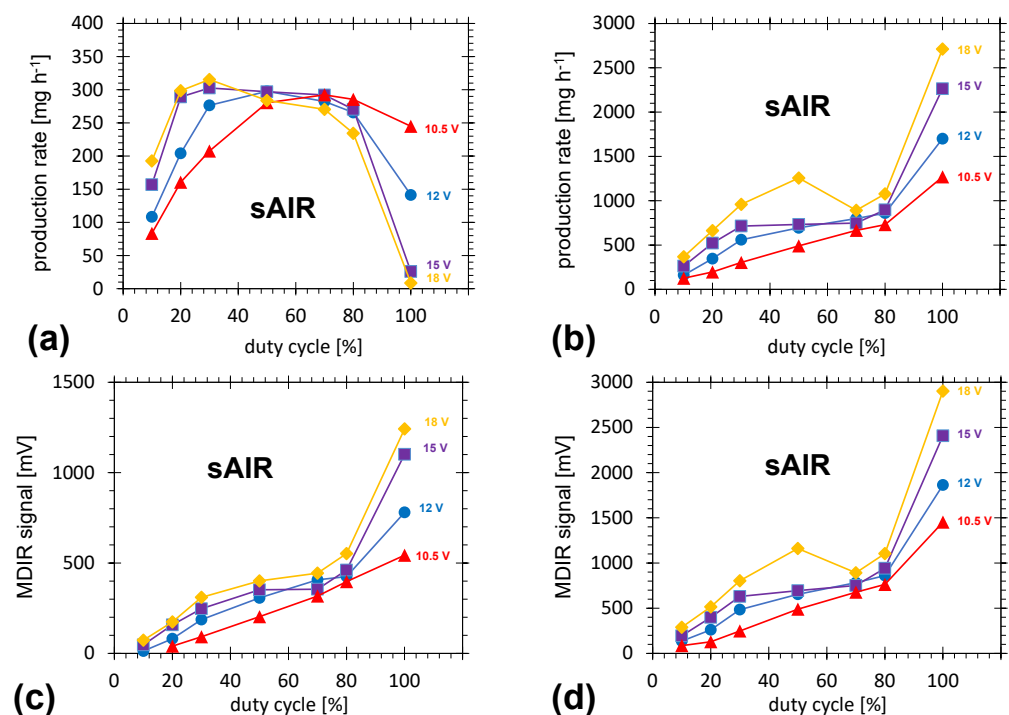


Figure 12. Influence of the duty cycle on ozone production rate at the synthetic air flow of (a) 0.6 SLM, and (b) 10 SLM and on MDIR signal voltage at synthetic air flow of (c) 0.6 SLM, and (d) 10 SLM with DBD driver input voltage as a parameter, and Peltier current of 0 A.

3.6.4. Effectivity of the Peltier Cooling

Figure 13 shows the influence of the Peltier module current on the ozone concentration and the MDIR signal for two DBD driver input voltages and synthetic air flow from 0.6 to 10 SLM. The duty cycle of 80% was used, to avoid the untypical results for 100%. The MDIR signal increases almost linearly with the Peltier current for all air flows and two voltages. This behavior is consistent with results for oxygen, and the explanation of the reason given in Section 3.5.5 is valid here. The mechanisms of increase in the MDIR signal with gas flow are the same as those discussed in Section 3.6.2.

The ozone concentration follows the variations in the MDIR signal for low airflow. It is almost linearly proportional to the Peltier module current. However, with increasing air flow, this dependence is getting weaker. For 5 and 10 SLM, no significant influence of the Peltier cooling on the ozone concentration can be observed.

The curvature of the curves for 0.6 SLM is stronger than for oxygen (compared with Figure 10). Comparing the two 0.6 SLM curves for 10.5 V and 15 V, as shown in Figure 13a and Figure 13b, respectively, the influence of cooling on the ozone concentration is stronger for the higher voltage, like for oxygen. The same sensitivity definition as in Equation (11) is used to evaluate this influence. The sensitivity for 10.5 V and 15 V is 12.3%/A and 17.0%/A,

respectively. These values are about twice as high as for oxygen (see Section 3.5.6). The main reason for this discrepancy can be the ozone loss mechanism described by Equation (17), which is a much stronger temperature-dependent factor than the loss mechanisms in pure oxygen.

For both driver input voltages, the influence of the Peltier current on the ozone concentration gets weaker with increasing synthetic air flow, even though the coupled power increases monotonically, as documented by the MDIR signal. For 10 SLM, it vanishes completely. The very short residence time of the gas in the discharge zone is suggested as the reason for this effect, which reduces the heat exchange between the electrodes and the discharge gas. Assuming a not-changing thermal energy, subtracted from the gas in the discharge volume by the Peltier module, the energy subtracted from the constant volume decreases with the increasing flow, inversely proportional to the gas flow.

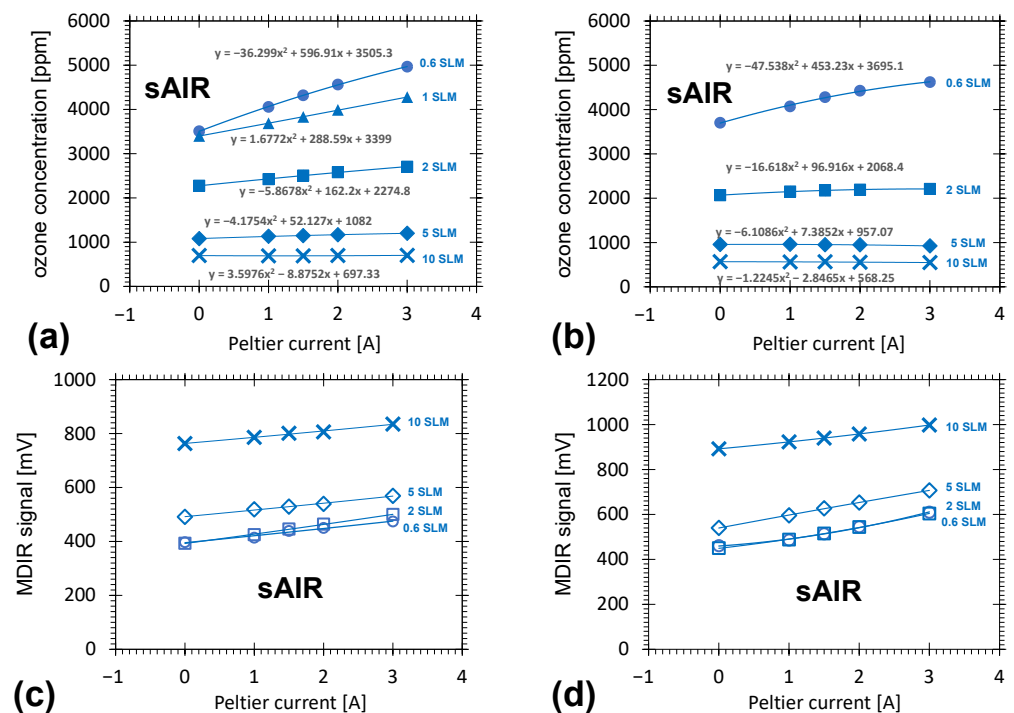
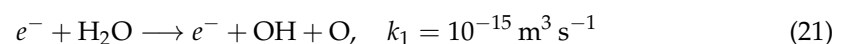


Figure 13. The ozone concentration for the DBD driver input voltage of (a) 10.5 V, and (b) 15 V, and the MDIR signal for the DBD driver input voltage of (c) 10.5 V, and (d) 15 V, shown as a function of the Peltier module current for the HDBD reactor operated with the duty cycle of 80%, for synthetic air flow varying from 0.6 to 10 SLM, as depicted at the curves.

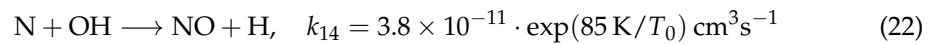
3.7. Ozone Produced in Compressed Dry Air

3.7.1. Reaction Channels Due to Humidity

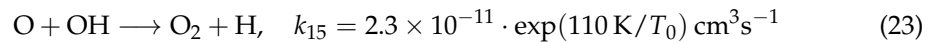
The main difference in the chemistry of compressed dry air (CDA) and synthetic air is caused by water vapor. A comprehensive list of chemical reactions and rate coefficients in the DBD discharge in humid air is compiled in [109]. The additional initiating reaction is the electron impact dissociation of H_2O :



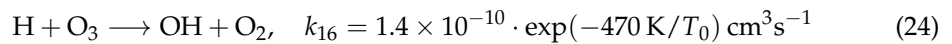
The production coefficient given in Equation (21), is a typical value, like that for Equations (6) and (12). The precise calculation requires knowledge about the EEDF. It is known that the efficiency of ozone production decreases with relative humidity [64]. The OH groups produced this way can contribute to NO production [104]:



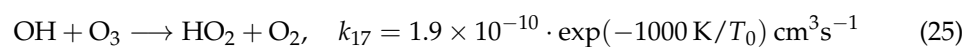
and atomic oxygen consumption



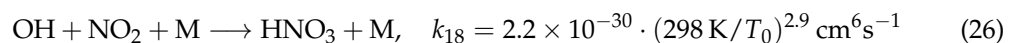
both intensifying with decreasing temperature and contributing to the reduction in ozone production. The hydrogen produced in Equations (22) and (23) contributes to the destruction of ozone by reacting with hydrogen [104]:



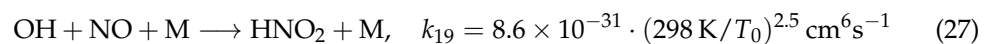
But also, the OH groups contribute to its destruction, which intensifies with increasing temperature:



In the humid air discharge, the nitrogen acids are present. The nitric acid and nitrous acid can be produced [104] from nitrogen dioxide and nitric oxide according to the following reactions:



and



respectively, and their production will increase with the amount of water and with decreasing temperature.

3.7.2. Influence of Compressed Air Flow

Figure 14 shows the ozone concentration and production rate as functions of CDA flow for three DBD driver input voltages and the zero current of the Peltier module. The duty cycle of 80% is chosen for compatibility with synthetic air results. The general tendencies of the curves for CDA and synthetic air (see Figure 11) are similar. The main difference between them is the absolute values. For example, for the DBD driver input voltage of 12 V, the ozone concentration at 0.6 SLM CDA flow is 8.5% lower than for the same synthetic air flow. At a gas flow of 10 SLM, the difference in production rate between CDA and synthetic air is 12%. The additional chemical reactions involving water are responsible for these differences. Equations (24) and (25) contribute to ozone destruction, especially at higher temperatures. Different from the destruction mechanism by NO in dry air, the destruction of ozone in humid air is primarily carried out by OH radicals generated mainly according to Equation (21), and consuming the atomic oxygen [110] as described in Equation (23). These loss reaction channels are growing with increasing humidity, resulting in a reduction in the ozone concentration and the production rate.

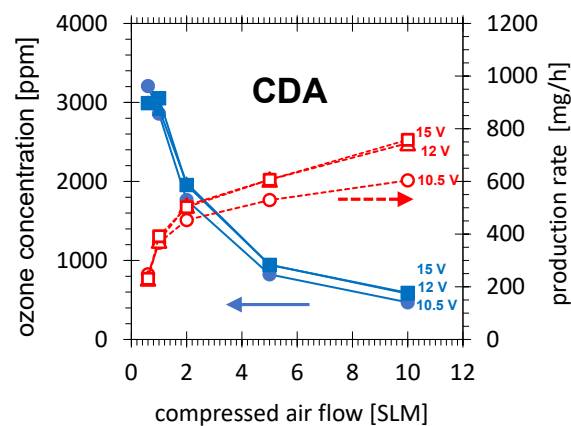


Figure 14. The ozone concentration and ozone production rate, shown as a function of CDA flow for the duty cycle of 80%, the Peltier current of 0 A, and with three DBD driver input voltages, as depicted in the curves.

3.7.3. Influence of Duty Cycle

Figure 15 shows the dependence of the production rate on the duty cycle for three DBD driver voltages and four CDA flows. The curve sets for the airflow of 0.6 and 10.0 SLM are very similar to those shown for synthetic air in Figure 12a and Figure 12b, respectively. Most of the observations and conclusions made in Section 3.6.3 for synthetic air are valid for CDA. However, distinctive differences can be observed.

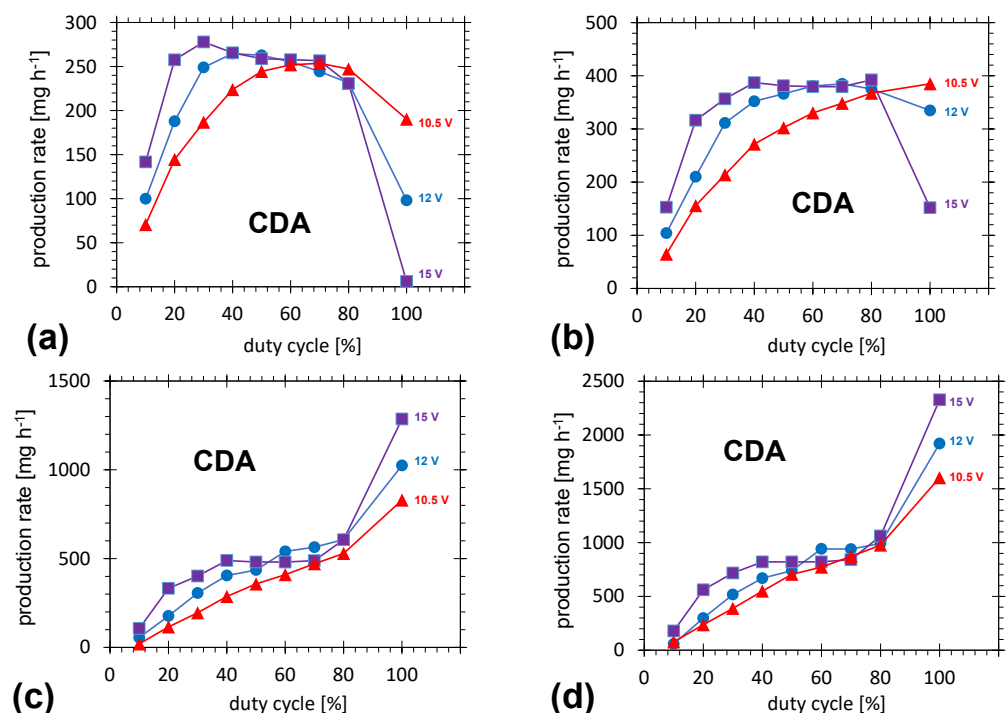


Figure 15. The ozone production rate as a function of duty cycle with DBD driver input voltage as a parameter; Peltier current of 0 A, compared for four CDA flows: (a) 0.6 SLM, (b) 1.0 SLM, (c) 5.0 SLM, (d) 10.0 SLM.

First, the maximum production rates reached as a function of the duty cycle are lower for CDA than for synthetic air. This is consistent with the observation from Section 3.7.2. For example, in Figure 15a, the maximum value for the driver input voltage of 15 V is 8% lower than for synthetic air.

But also, the lowest production rate of 6 mg/h reached in CDA is much smaller than the corresponding value of 26 mg/h for synthetic air. It shows that the ozone production rate reacts more sensitively to the additional energy increase due to the charging effect. A strong influence of the relative humidity on the dissipation speed of the surface charge at the dielectric surface is known. The higher the humidity, the faster the dissipation [111]. This explains the difference between synthetic air and CDA discharges when switching the duty cycle from 80% to 100%.

The set of curves valid for CDA flow of 1 SLM, shown in Figure 15b exhibit a transitional behavior. There is almost no 80% to 100% jump in production rate. This can be explained with the position of the working point on the curve, representing the dependence of the production rate on the SEI close to maximum. In such cases, the additional energy provided to the discharge causes neither an additional increase nor a decrease in the production rate. It shows that this effect results from combined power coupling from the HV excitation due to charge accumulation and chemical processes, forcing the decrease in production rate with increasing SEI.

3.7.4. Influence of Peltier Cooling

The influence of the Peltier module current on the ozone concentration for two driver voltages, 10.5 and 15 V, are shown in Figure 16a and Figure 16b, respectively. The parameter of the curve sets is the CDA flow. Here, the values for the duty cycle of 80% are also visualized for better comparability with synthetic air results. For a DBD driver input voltage of 15 V, the effect of Peltier cooling can be observed in the entire investigated CDA flow range from 0.6 to 10 SLM, but it is quite weak for flows higher than 2 SLM. The strongest effect for the CDA flow of 0.6 SLM, and the driver input voltage of 15 V, expressed with the sensitivity of ozone concentration to the Peltier module current of 19.8%/A, is significantly higher than 17.0%/A, determined for the same conditions in synthetic air. No such difference is observed for the DBD driver input voltage of 10.5 V.

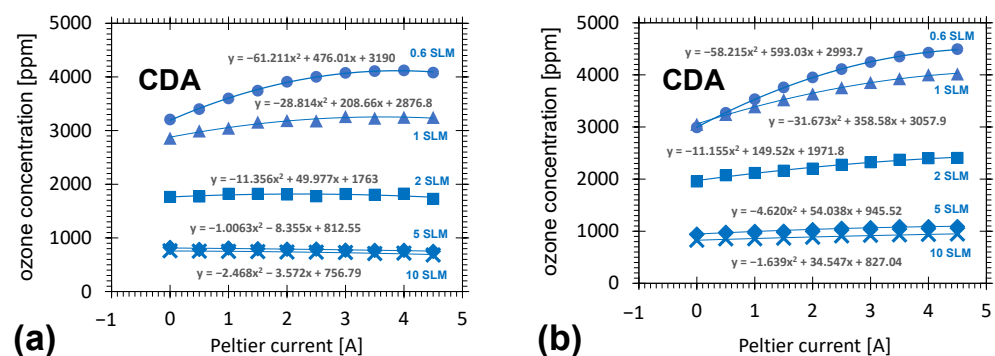


Figure 16. The ozone concentration is shown as a function of the Peltier module current for the HDBD reactor operated with the duty cycle of 80%, the DBD driver input voltage of (a) 10.5 V, and (b) 15 V, for CDA flow varying from 0.6 to 10 SLM, as depicted at the curves.

The results for CDA are presented in the range of the applied Peltier module current, reaching up to 4.5 A, which is a little higher than for synthetic air. It can be observed that the linear fit is not sufficient to approximate the low flow curves. Consequently, the parabolic curves approximate the ozone concentration results for all dependencies on the Peltier module current. It is known that the cooling effect of the Peltier module is saturating for higher currents, because the resistive losses of the device itself start to be comparable with the heat transferred from the dielectric barrier to the aluminum heat sink. However, this effect cannot be the reason for ozone concentration saturation, because it occurs in the Peltier module applied in this study for a much higher current. Such an effect is not apparent for the oxygen curves ranging to 4 A (Figure 10). This allows us to assume that the decreasing temperature due to the Peltier cooling causes the strong saturation of the low

CDA flow curves. The stronger destruction of atomic oxygen with decreasing temperature would be possible according to Equation (23), contributing to lower ozone production.

The influence of the duty cycle on the effectivity of the Peltier cooling is illustrated in Figure 17. The ozone concentration and the MDIR signal are shown as a function of a duty cycle for the two CDA flows, 0.6 and 2.0 SLM, and for the Peltier module current in the range of 0 to 4 A. A distinct difference in the character of the curves representing the ozone concentration and MDIR signal can be stated, which can be explained analogical to the low and high synthetic air flow in Section 3.6.3.

For both CDA flows, the MDIR signal curves shift toward the higher voltages with increasing Peltier module current. The explanation for the increase in the MDIR signal with the Peltier current, given in Section 3.5.6 for oxygen, is valid for CDA.

The ozone concentration monotonously increases with SEI for high gas flow. Consequently, the MDIR signal and the ozone concentration increase rapidly for the duty cycle step, from 90 to 100% at a CDA flow of 2.0 SLM.

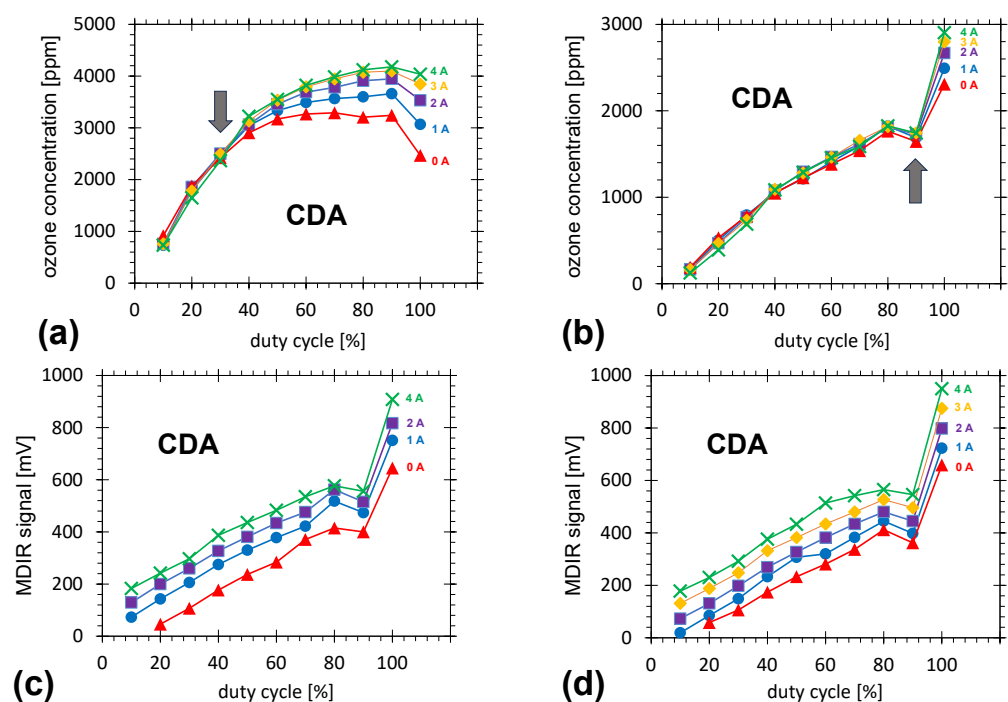


Figure 17. Influence of the Peltier module current on the ozone concentration at the CDA flow (a) 0.6 SLM and (b) 2.0 SLM, and on the MDIR signal at the CDA flow of (c) 0.6 SLM and (d) 2.0 SLM as a function of duty cycle for the DBD driver input voltage of 10.5 V.

With a gray arrow, the maximum duty cycle value is indicated, at which the ozone concentration does not react to the increase of the Peltier module current. In Figure 17a and b, the CDA flow is 0.6 and 2 SLM, respectively. For higher CDA flow, a much higher duty cycle is needed to achieve the sensitivity of the ozone concentration on the Peltier module current. The gray arrow shifts from the duty cycle of 30% for 0.6 SLM to 90% for 2 SLM.

As was observed before, the ozone concentration does not react on the Peltier module current for high gas flows. It changes more as a result of the Peltier module current increase when the gas flow is low.

It can also be observed that the ozone concentration increase, caused by the Peltier cooling, grows with the duty cycle and drive input voltage. The limiting values shown with the gray arrows in Figure 17 were evaluated for all available flows, duty cycles, and driver voltages, and summarized in Figure 18. It shows the limiting lines in the coordinate system, with CDA flow at the x-axis and duty cycle at the y-axis, separating the regions of the effective and ineffective Peltier cooling. The three limiting lines correspond to the driver voltages: 10.5, 12, and 15 V, respectively.

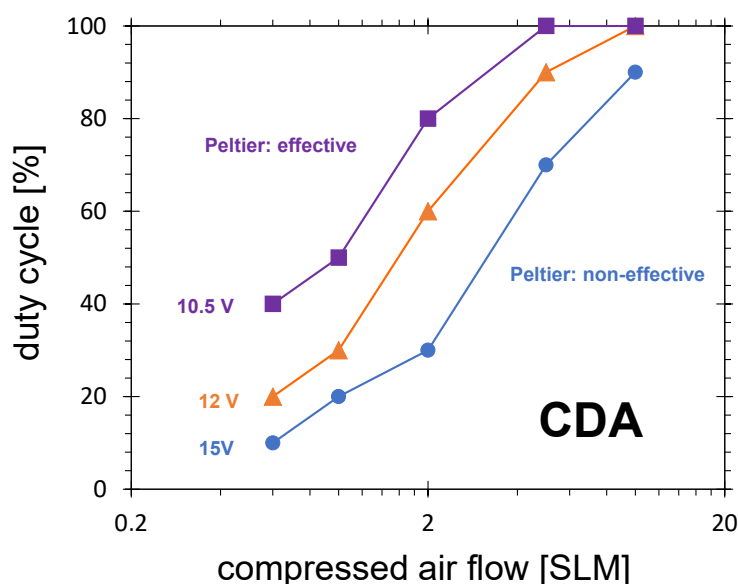


Figure 18. The limiting lines, separating the regions of the effective and ineffective Peltier cooling, in the CDA flow vs. duty cycle coordinate system for three driver voltages.

For the driver input voltage of 15 V, the influence of the Peltier cooling can already be observed, starting from the duty cycle of 10% at 0.6 SLM. For the decreasing drive voltage, the range of the Peltier cooling influence is narrower. For 10.5 V, it starts from 40% for 0.6 SLM and 80% for 2.0 SLM. For 5.0 SLM and more, the influence of Peltier cooling at 10.5 V cannot be observed, even at 100%. The limiting line shifts to lower duty cycle values with increasing driver power.

The general conclusion is that the system is more responsive to the Peltier cooling for conditions with higher SEI (lower flow, higher driver voltage, higher duty cycle).

4. Conclusions

A novel compact HDBD reactor with a novel electrode design is presented. Its performance for ozone generation was investigated for a wide range of parameters influencing the SEI: the DBD drive input voltage, gas flow, PWM duty cycle, and Peltier module current for three gases: oxygen, synthetic air, and CDA with a residual humidity of 7%.

The highest ozone concentrations reached without Peltier cooling are 23 500, 3500, and 3200 ppm for pure oxygen, synthetic air, and CDA, respectively. The maximum production rates for the three gases are 3.2, 0.897, and 0.785 g/h, respectively.

The sensitivity of ozone concentration to the Peltier module current is used to evaluate the influence of the Peltier cooling effect. The maximum sensitivity values are reached for the lowest gas flow and highest driver input voltage. It was observed that this sensitivity increases in the following gas sequence: oxygen, dry (synthetic) air, and humid air (CDA), and reaches values of 9.0%/A, 17.0%/A, and 19.8%/A, respectively, for the gas flow of 0.6 SLM, and the driver input voltage of 15 V. However, the increase in oxygen concentration vs. Peltier module current saturates faster for humid air than for dry air. Generally, the influence of the Peltier cooling on the ozone concentration increases with SEI (an increasing driver voltage or duty cycle or a decreasing gas flow).

A high-pass filter filters the current flowing through the shunt of the HDBD reactor. The resulting MDIR signal can be considered a relative measure of the net discharge power, because the higher harmonics generated in the discharge voltage increase with the number of microdischarges per voltage cycle. The comparison of the MDIR signal with ozone concentration allows for better discrimination between the effects resulting from the rise of SEI coupled into the discharge and the chemically based effects. For low SEI, the ozone production rate follows the MDIR signal. The influence of the duty cycle on ozone production can be incorporated into the global SEI influenced by the discharge power and

the gas flow. The duty cycle increase from 90 to 100% results in irregularly strong changes in the ozone concentration and the production rate for all three gases. The behavior of the surface charge during an interruption in plasma generation explains this effect.

The influence of the Peltier cooling can be included in the SEI indirectly by considering the increase in the gas density with decreasing temperature.

The results of HDBD operation shown in this work are just the beginning of the research on this type of discharge. The simple, compact, efficient, and cost-effective construction allows for many novel applications. To use the MDIR signal as a measure of the net discharge power for different gases, further research for calibration and absolute validation is needed.

5. Patents

There is the following patent pending resulting from the work reported in this manuscript: US 2023/0276561 A1.

Author Contributions: Conceptualization, S.N., F.F. and D.K.; methodology, F.F.; software, C.B.; validation, F.F., C.B. and D.K.; formal analysis, D.K.; investigation, C.B.; resources, P.P.; data curation, F.F.; writing—original draft preparation, D.K.; writing—review and editing, D.K.; visualization, D.K.; supervision, S.N.; project administration, F.F.; funding acquisition, S.N. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: Authors Dariusz Korzec, Florian Freund, Christian Bäuml, Patrik Penzkofer and Stefan Nettesheim were employed by the company Relyon Plasma GmbH. The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

APP	Atmospheric pressure plasma
APPJ	Atmospheric pressure plasma jet
CAPP	Cold atmospheric pressure plasma
CDA	Compressed dry air
DBD	Dielectric barrier discharge
EEDF	Electron energy distribution function
FFT	Fast Fourier-transform [112]
HDBD	Hybrid surface-volume-DBD
HLT	Half-life time
HV	High voltage
ICP	Inductively coupled plasma
ITO	Indium tin oxide
MDIR	microdischarges impulses response
MFC	Mass flow controller
PAA	Pulsed atmospheric arc
PWM	Pulse-width modulation
RMS	Root mean square
ROS	Reactive oxidized species

RONs	Reactive oxygen-nitrogen species
SDBD	Surface dielectric barrier discharge
SEI	specific energy input
SLM	Standard liter per minute
UV	Ultraviolet light
VDDB	Volume dielectric barrier discharge

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