Comparison of a kHz Helium/CO_2 plasma jet and a MHz Helium/CO_2 plasma jet for carbon monoxide (CO) production and bacterial disinfection in plasma medicine

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Abstract: This work presents a comparative study of the CO production and bactericidal effect of two discharges: a MHz He/CO_2 plasma jet generated by the COST jet and a kHz He/CO_2 plasma jet generated by DBD reactor. Experiments showed that the two discharges were capable of producing CO in a controlled amount from couple of ppm to respectively hundreds and thousands of ppm. It also demonstrates that for the same parameters, CO_2 conversion was more efficient in the kHz-jet than in the COST jet.

Keywords: Plasma jet, carbon monoxide (CO), CO_2 conversion, plasma medicine, bacterial disinfection

1. Introduction

Non-equilibrium atmospheric-pressure plasmas have drawn a growing interest in low-temperature plasma research over the last two decades, which has led to the development of a large variety of plasma sources. [1] Their ability to create a large range of reactive species combined with electric field and radiation, while keeping the gas near room temperature, allows their use in the fields of food preservation, agriculture and plasma medicine.

In contact with living tissues, non-equilibrium atmospheric-pressure plasmas have various beneficial effects, including antibacterial, vasodilatory, antiapoptotic, anticancerous, and antiproliferative effects making them interesting for the fields of cancerology, dermatology and wound healing. Although non-equilibrium atmospheric-pressure plasmas showed great results in wound healing process, their role on inflammation remains unclear.

Carbon monoxide (CO) has a bad reputation due to the potentially lethal consequences when inhaled at high concentrations. However, at low doses, it has a broad spectrum of biological activities such as anti-inflammatory, vasodilatory, antiapoptotic, and antiproliferative effects [2]. CO can be produce by plasma via CO_2 dissociation [3]. CO is a stable molecule, simplifying the control of its delivery by the plasma generator.

The aim of this study is to compare the CO production and bactericide effect of two different kinds of discharges with He/CO_2 as feed gas: a sinusoidal MHz discharge provided by the European Cooperation for Science and Technology (COST) plasma jet, and a kHz pulsed discharge provided by a coplanar-coaxial DBD plasma jet (kHz-jet).

2. Experimental setup

a. The kHz-jet and COSTjet reactors

The COST jet represented in Fig. 1 is composed of two parallel electrodes glued between two quartz glass plates. The electrodes are 1 mm thick, 30 mm long and 1 mm apart from each other. A homemade power supply was connected to one electrode via a RLC circuit and delivers a sinusoidal voltage at 13.56 MHz with a typical RMS value in the range of a hundred volts. More details about the COST jet can be found in J.Golda *et al*. article [4].

The kHz-jet represented in Fig. 2 is composed of a borosilicate glass tube with an outer diameter of a = 4mm and an inner diameter of b = 2mm. Two copper tapes (c = 5mm wide, d = 14mm apart) were wrapped around the tube.

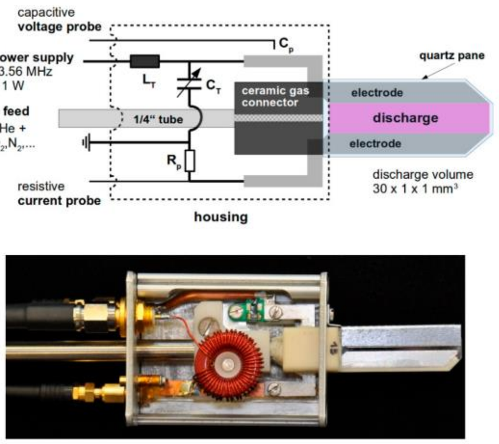

Fig. 1. Schematics (top) and a photograph (bottom) of the European Cooperation for Science and Technology (COST) plasma jet [5].

The upper tape is connected to a homemade high voltage power supply, which delivers a positive microsecondduration voltage pulse with a kHz repetition rate, shown in Fig. 3. From 2 kV up to 15 kV, the voltage rise time (defined here between 10% and 90% of the maximum value) and the full-width at half-maximum are (0.92±0.03) µs and (1.55±0.01) µs respectively. The lower tape is wrapped e = 14 mm away from the reactor nozzle and connected to a grounded resistor (R = 100 Ω). To avoid the formation of an arc in the air between the two electrodes, the electrodes are separated by three glass beads and covered by an epoxy glue.

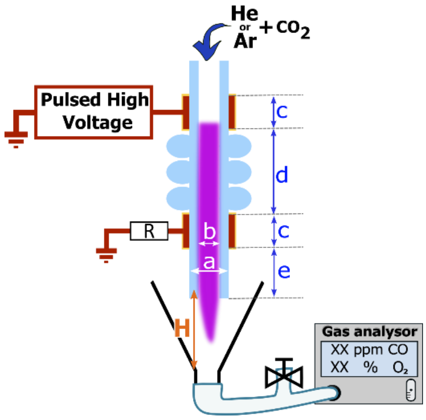

Fig. 2. Schematic of the kHz-jet and the experimental setup.

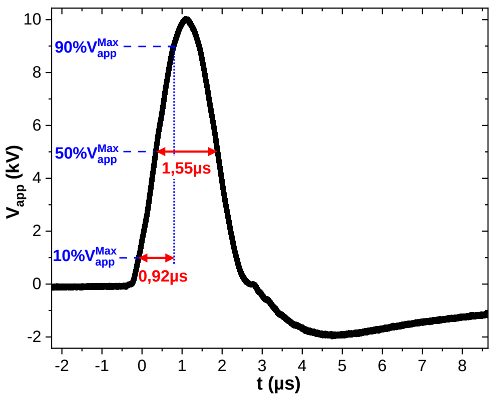

Fig. 3. Temporal representation of one pulse delivered by the high voltage power supply to the kHz-jet.

Both plasma reactors were fed with Helium (99.999% purity) gas mixed with 0 to 1.2% CO_2 (99.999% purity) flowing in a 100-2000 standard cubic centimeter per minute (sccm) range, regulated by calibrated mass flow controllers.

b. Electrical diagnostic: energy consumed by the plasma

The COST-jet incorporates miniaturized electrical probes inside its housing allowing a precise measurement of the voltage applied to the anode and the current leaving the cathode. A 500 MHz bandwidth digital oscilloscope (Tektronix MDO 3054) recorded both signals and the data were sent to a computer where the energy consumed by the plasma per excitation cycle was calculated:

$$E_p = \frac{V_{RMS} * I_{RMS} * cos(\varphi - \varphi_{ref})}{freq} \qquad (1)$$

with *freq* the frequency equal to 13.56 MHz, V_{RMS} and I_{RMS} the effective values of voltage and current, φ the phase shift between voltage and current, and φ_{ref} the instrumental reference phase shift. φ_{ref} is determined from measurements of the phase shift when voltage is applied but no plasma is ignited.

The described measurement technique for sinusoidal waveforms is valid as long as the COST jet is operated in stable homogeneous α-glow mode, which does not exhibit any constricted nanosecond sparks or streamers [4].

For the kHz-jet, the applied voltage (V_{app}) was measured between the anode (upper tape) and the ground with a high voltage probe. The cathode current ($I_c = V_c/R$) was measured across the resistor at the cathode (lower tape) with a voltage probe. The signals were recorded using the same oscilloscope as used with the COST jet.

When the plasma is OFF, the reactor is similar to a capacitor. Thus, when the plasma was ON measuring the discharge current, I_d, requires to subtract the capacitive current, I_{capa}, from the total current I_{tot}:

$$I_d = I_{tot}^{ON} - I_{tot}^{OFF} = I_{tot}^{ON} - I_{capa} \qquad (2)$$

To make sure that only the capacitive current was measured, CO_2 gas was flushed through the discharge. As the breakdown voltage is higher in molecular gases than in noble gases, no plasma was ignited.

The energy consumed by the plasma during one pulse (E_p) was calculated by integrating the instantaneous power (voltage-current product) over one pulse:

$$E_p = \int_0^{\Delta t_{pulse}} V_{app}(t).I_d(t)\,dt \qquad (3)$$

c. Measurement of CO production

The medical application of the plasma discharge requires to take into account the chemistry of the plasma with the surrounding air in the vicinity of the jet. The carbon monoxide (CO) produced by the discharge was collected from this area. A funnel was positioned underneath the plasma reactor and connected to a gas analyzer (SIEMENS Ultramat23) with a Teflon tubing. As shown in Fig. *2*, the distance between the funnel's bottleneck and the nozzle of the reactor was H = 30mm.

The measuring range of the gas analyzer was [0-500] ppm with an accuracy of 2 ppm for CO and [0-25] percentage with an accuracy of 0.25% for O_2.

The analyzer requires pumping to analyze a gas sample (gas flow rate between 1000-1500 sccm). The concentration of CO measured ($[CO]_{measured}$) in the sample was provided by the post-discharge and the surrounding air. The proportion of air in the sample has to be determined in order to obtain only the concentration of CO in the plasma ($[CO]_{plasma}$).

For that, the O_2 concentration, $[O_2]_{meas}$ was measured to represent in first approximation the proportion of air in the sample. Although the plasma can produce a very small amount of O_2 from the CO_2 dissociation, in the experimental conditions, this amount was not higher than 0.1%, since the maximum CO concentration measured in our conditions was 2000 ppm. In a first approximation, we assume that there was no O_2 in the percentage range produced by the plasma.

Finally, $[CO]_{plasma}$ was expressed as:

$$[CO]_{plasma}(ppm) = \frac{[CO]_{meas}(ppm)}{[O_2]_{air}(\%) - [O_2]_{meas}(\%)} \times [O_2]_{air}(\%) \quad (4)$$

The error of $[CO]_{plasma}$ was established from an uncertainty propagation calculation, knowing the accuracy of $[CO]_{meas}$ and $[O_2]_{meas}$. CO is a stable molecule and its concentration was not influenced by the time of flight of the gas. Considering that loss processes are negligible, we can assume that $[CO]_{plasma}$ represents the concentration of CO produced in the plasma.

d. Bacterial treatment

K-12 strain of *Escherichia coli* was used for *in vitro* plasma treatment on semi-solid medium. Petri dishes with uniform bacterial layer were prepared by inundation method, then treated immediately and left overnight for incubation at 37 °C. The photos of treated samples were taken the next day and surface of disinfected area was measured. During treatment, a plasma source was placed vertically above Petri dish at a height *h* varied within a range of few centimeters. Electrical parameters such as applied voltage and discharge current were registered simultaneously.

3. Results and discussion

a. Influence of the specific energy on CO production

The specific energy input (SEI) is a parameter commonly used to quantify the CO_2 dissociation. It is an intensive parameter depicting the average energy given to each atom or molecule of the gas during one cycle (or pulse). It is defined as:

$$SEI\left(\frac{J}{l}\right) = \frac{P_{avg}(W)}{\Phi\left(\frac{l}{s}\right)} = \frac{E_p(J) * freq(Hz)}{\Phi\left(\frac{l}{s}\right)} \quad (5)$$

where P_{avg} is the average power input in plasma, E_p the energy consumed during one pulse and Φ the total gas flow rate in standard conditions (T_0 =273.15K, p_0= 1.013 bar). One can notice that the SEI increases with the frequency and the consumed energy, and decreases with the total gas flow rate.

The influence of the SEI on CO production by the kHz-jet (blueish symbols) and by the COST jet (full red circle symbols) with 0.3% of CO_2 are shown in log-log scale in Fig. 4. For the kHz-jet, the shape of the symbols is related to the parameter modulating the SEI (square symbol for applied voltage, triangle for flow and open circle for frequency). The concentration of CO in the plasma is plotted in parts-per-million (ppm) (left axis) and the conversion efficiency in percentage (right axis).

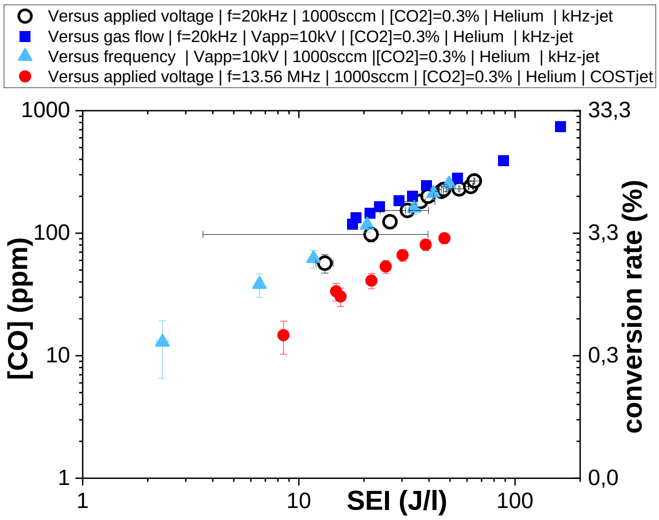

Fig. 4. Carbon monoxide (CO) concentration (left) and conversion rate of CO_2 into CO (right) in the COST jet and in the kHz-jet for different specific energy input into the discharges (SEI) with 0.3% of CO_2.

Fig. 4 shows that the COST jet and the kHz-jet were capable to produce from a couple of ppm to respectively hundreds and thousands of ppm of CO, which is typically the range used in clinical application with CO inhalation. The two reactors are safe in terms of CO production.

In log-log scale, the concentration of CO produced by plasma as a function of the SEI follows a linear trend. This result lead to the conclusion that the SEI is a scaling parameter for CO_2 conversion. For the same SEI, the COST jet is less efficient than the kHz-jet for CO_2 conversion at 0.3% CO_2.

Three main channels can lead to the dissociation of CO_2 into CO: 1) the dissociation via vibrational up-pumping along the asymmetric mode, 2) direct energetic particle impact (electrons and excited noble gas species) leading to the excitation transfer to CO_2 followed by direct dissociation or 3) dissociative recombination [6]. While the dissociation via vibrational up-pumping channel is the most efficient in term of energy, it does not play a significant role in kHz pulsed DBD as the molecules have time to relax between two pulses. However, in a MHz jet, the discharge never extinguishes and the vibrational up-pumping could play a role. Contrary to expectations based on high energy efficiency of vibrational up-pumping channel, the COST jet was less effective in CO_2 conversion than the kHz-jet.

b. Influence of the CO_2 ratio

To evaluate the role of the CO_2 ratio in the feed gas, we measured the CO concentration as a function of the CO_2 admixture at a SEI near 52 J/l at total gas flow rate of 500sccm.

Fig 5 presents the conversion rate as a function of the CO_2 admixture. By taking into account the error bars, up to 0.6% of CO_2 in the discharge, the two reactors were comparable. Below 0.6% of CO_2, the kHz-jet was a lot more efficient than the COST jet for the dissociation of CO_2. It can be noticed that the conversion rate decreased with CO_2 concentration. It is considered to be due to the energy loss of electrons in the rotational-vibrational states of CO_2.

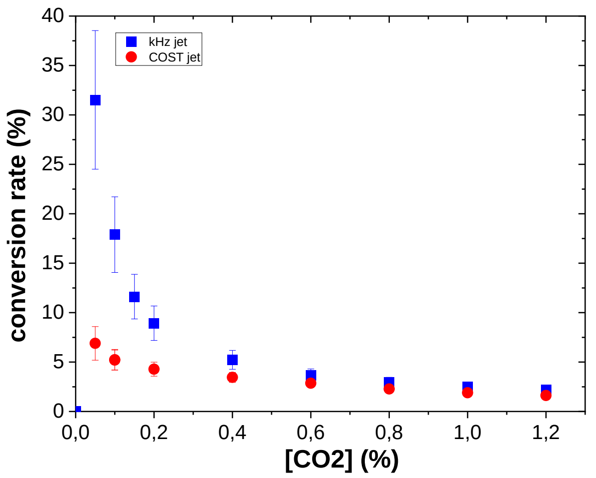

Fig 5. Conversion rate of CO_2 into CO in Helium/CO_2 plasma generated by the kHz-jet (blue square) and by the COST jet (red circle) as a function of CO_2 concentration. The data were recorded using a total gas flow rate of 500sccm, for a specific energy input (SEI) at (52±5) J/l.

c. Comparison of bactericidal effect of two plasma sources

The data on bacterial disinfection by both plasma sources would be presented as a function of SEI, produced CO and height *h* together with corresponding CO gas control.

4. Conclusion

The completion of this investigation raised the fact that a controlled amount of CO can be produced for both plasma reactors allowing their use in the field of plasma medicine. Both COST jet and kHz-jet were capable to produce from a couple of ppm to respectively hundreds and thousands of ppm of CO, which is typically the range used in clinical application with CO inhalation.

In log-log scale, the concentration of CO produced by plasma as a function of the SEI (fixed CO_2 concentration) followed a linear trend. Surprisingly, for the same SEI, the COST jet is less efficient than the kHz-jet for CO_2 conversion at 0.3% CO_2.

We showed furthermore that an increase of CO_2 concentration in the discharge significantly decreases its production output. It is considered to be due to the energy loss of electrons in the rotational-vibrational states of CO_2.

Thus, for both discharges, only SEI and CO_2 concentration allows the conrol of CO formation.

5. Acknowledgements

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6. References

[1] P. J. Bruggeman, F. Iza, and R. Brandenburg, *Plasma Sources Sci. Technol.*, vol. 26, nº 12 (2017)

[2] E. Carbone and C. Douat, *Plasma Med*, vol. 8, nº 1 (2018)

[3] C. Douat, P. Escot Bocanegra, S. Dozias, É. Robert, and R. Motterlini, *Plasma Process Polym* (2021)

[4] J. Golda *et al.*, *J. Phys. D: Appl. Phys.*, vol. 49, nº 8, (2016)

[5] Gorbanev, Golda, Gathen, and Bogaerts, *Plasma*, vol. 2, nº 3 (2019)

[6] A. Fridman, « Plasma Chemistry, p260-270 » (2008)