Comparison of Argon/CO2 and Helium/CO2 plasma jets for carbon monoxide (CO) production in plasma medicine

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Abstract: This abstract present a study of CO production for plasma medicine provided by an external rings DBD jet fed with He/CO_2 or Ar/CO_2 admixture. The two discharges were capable to produce a controlled amount of CO in the range used in clinical application. In log-log scale, CO concentration produced by plasma is linearly dependent on the specific energy input. The type of the feed gas does not have an impact on the CO_2 dissociation, but the addition of higher dose of CO_2 reduced significantly its dissociation efficacy.

Keywords: Plasma jet, carbone monoxyde, carbone dioxyde conversion, plasma medicine

1. General

Nonequilibrium 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] Nonequilibrium atmospheric-pressure plasmas are typically generated using different gases: air, helium, argon, O_2, N_2, or a mix of these gases. Their ability to create a large range of reactive species combined with electric field and radiation, while keeping the gas temperature near the room temperature allow their use in the medicine field.

In contact with living tissues, nonequilibrium atmospheric-pressure plasmas have various beneficial effects, including antibacterial, vasodilatory, anti-apoptotic, anti-cancerous, and antiproliferative effects. Although nonequilibrium atmospheric-pressure plasmas showed great results in wound healing process, their role on inflammation remains unclear. Several studies on animals and humans show that plasma can have sometimes no effect in the inflammation stage, and sometime have a pro-inflammatory or an anti-inflammatory effect. [2]

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, anti-apoptotic, and anti-proliferative effects. [3] CO can be produce by plasma via CO_2 dissociation.[4]

In order to combine the beneficial biological effects of CO and plasma in the same device, we present you a study of a plasma jet capable to produce locally small amount of CO to better control inflammation in wound healing application.

This abstract lay out a study of an external rings DBD jet fed with helium/CO_2 or argon/CO_2 admixture to produce CO at low doses for medical application. Breakdown voltage and energy consumed by the discharge were measured by means of electrical characterization. The concentration of CO produced by plasma was evaluated by IR absorption spectrometry with a gas analyzer. The aim of the study was to compare two feed gases: helium and argon, in term of electrical characteristic and CO_2 conversion efficiency to find the most suitable configuration for medical use.

2. Experimental setup

The external rings DBD jet represented Fig 1 is composed of a glass (borosilicate) tube with an outer diameter of a = 4mm and an inner diameter of b = 2mm. Two copper tapes (c = 5mm wide, d = 14mm apart) are wrapped around the tube. The upper tape is connected to a homemade high voltage power supply, which delivers a positive microsecond-duration voltage pulse with a kHz repetition rate, shown in Fig 2**Erreur ! Source du renvoi introuvable.**. From 2 kV up to 15 kV, the voltage rise time (defined here between 10% and 90% of the maximum values) and the full-width at half-maximum are almost constant, and rise (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 arc in the air between the two electrodes, the electrodes are separated by three glass beads and covered by an epoxy glue.

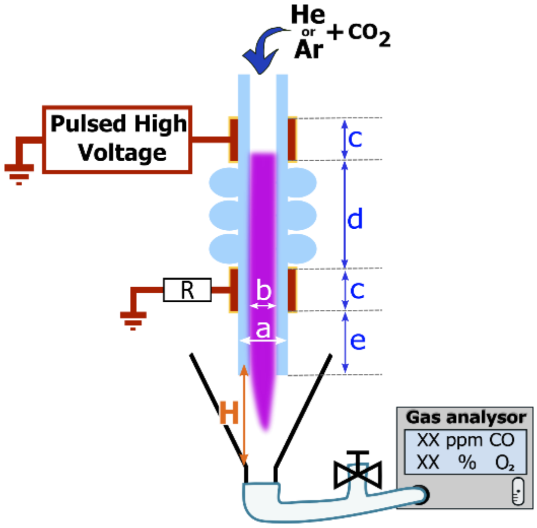

Fig 1. Schematic of the external rings DBD jet and the experimental setu

Helium (99.999% purity) or Argon (99.999% purity) gas was mixed with 0 to 1.2% CO2 ((99.999% purity) and flowing through the glass tube in a 100-2000 standard cubic centimeter per minute (sccm) range, regulated by calibrated mass flow controllers.

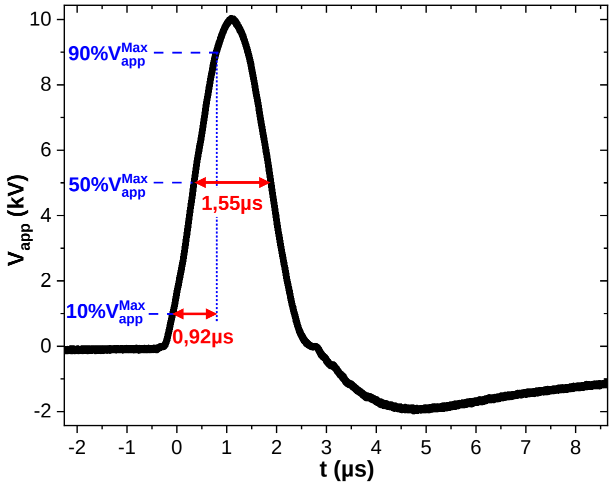

Fig 2. Temporal representation of one pulse delivered by the high voltage power supply to the jet

The applied voltage (V_{app}) and the cathode current ($I_c=V_c/R$) were respectively measured between the anode (upper tape) and the ground with a high voltage probe and across the resistor at the cathode (lower tape) with a voltage probe. The signals were recorded using a 500MHz bandwidth digital oscilloscope (Tektronix MDO 3054).

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

$$I_d = I_{tot}^{ON} - I_{tot}^{OFF} = I_{tot}^{ON} - I_{capa} \quad (1)$$

To measure the capacitive current, CO_2 gas was flowing through the discharge. As the breakdown voltage is higher in molecular gases than in noble gases, no plasma was ignited.

I_d allowed the determination of the energy consumed by the plasma E_p. E_p is calculated by integrating the instantaneous power (voltage-current product) over one pulse:

$$E_p = \int_0^{\Delta t_{pulse}} V(t).I_d(t)\,dt \quad (2)$$

In order to measure the carbon monoxide (CO) concentration produced by the discharge, a gas analyzer (SIEMENS Ultramat23) was used. As depicted in **Erreur ! Source du renvoi introuvable.** , a funnel was underneath the plasma reactor and connected to the gas analyzer thank a Teflon pipe. The distance between the funnels bottleneck and the nozzle of the reactor was H=30mm.

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, $[O_2]_{measured}$ was measured and can 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 % range produced by the plasma.

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

$$[CO]_{plasma}(ppm) = \frac{[CO]_{meas}(ppm)}{[O_2]_{air}(\%) - [O_2]_{meas}(\%)} \times [O_2]_{air}(\%) \quad (3)$$

The error of $[CO]_{plasma}$ was established from a 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.

3. Results and discussion

3.1- Influence of the specific energy input on CO production in argon and helium discharges

The specific energy input (SEI) is an intensive parameter depicting the average energy given to each atom (or molecule) of the gas during one discharge. It is defined as:

$$SEI\left(\frac{J}{l}\right) = \frac{P_{avg}(W)}{\varphi\left(\frac{l}{s}\right)} = \frac{E_p(J) * freq(Hz)}{\varphi\left(\frac{l}{s}\right)} \quad (4)$$

Where P_{avg} is the average power input in one discharge, E_p the average energy consumed by one discharge and φ the total gas flow rate in standard conditions (T0 =273.15K, p0= 1.013 bar).

The behavior of the SEI with respect to the discharge parameters (frequency, total gas flow rate, and applied voltage) is directly linked to their impact on energy consumed by the plasma E_p.

The influence of the SEI on CO production in the discharge of Ar/CO_2 (full blue-ish symbols) and of He/CO_2 (empty red-ish symbols) is shown in log-log scale in Fig. 3. The shape of the symbols (square, sphere of triangle) is related to the parameter modulating the SEI (square for the modulation by the applied voltage, etc.). The concentration of CO in the plasma can be seen on the right scale (ppm) and the conversion rate on the left scale (%). All the data were recorded for an admixture of CO_2 of 0.3% inside the discharge.

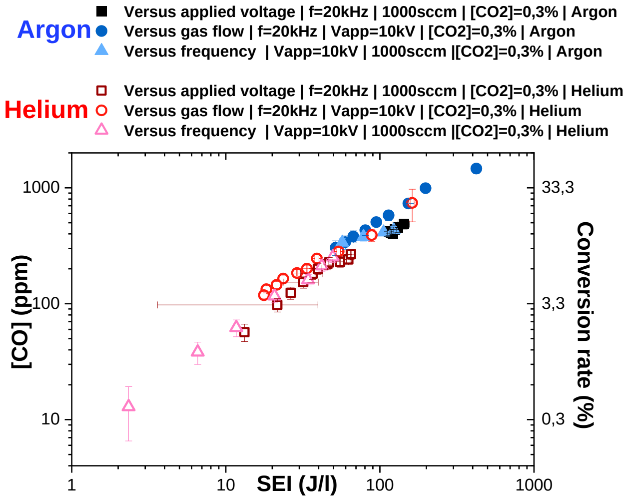

Fig. 3. Carbon monoxide (CO) concentration (left) and conversion rate of CO_2 into CO (right) in He/CO_2 ({99.7/0.3} %) or in Ar/CO_2 ({99.7/0.3} %) plasma for different specific energy input inside the discharges (SEI).

Fig. 3 shows that the reactor is capable to produce from a couple of ppm 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 follows a linear trend. Surprisingly, the type of the feed gas does not have an impact on the CO_2 dissociation, even though plasma exhibits different features in helium and argon. We can also noticed that for the conditions taken for our experiment, the Ar/CO_2 discharge can reach a higher SEI than He/CO_2 discharge but the first one do not ignite for a SEI below 50J/l. In between, it is worth noticing that the data taken in Ar/CO_2 discharge and in He/CO_2 discharge overlap.

This important result first redemonstrate that the scaling parameter for CO production in plasma is SEI, and secondly that the discharge (atomic) gas has no effect on the CO production for the same SEI. Whatever the chosen atomic carrier gas, the CO output for one [CO_2] will be determined by the SEI.

3.2- Influence of the CO2 concentration on CO production in argon and helium discharges

As the atomic carrier gas does not determined the formation of CO in the plasma, we may ask if the addition of a molecular gas will change the efficiency of CO_2 conversion. For a fixe SEI, does the addition of more CO_2 in the discharge change the efficacy of its own dissociation and are helium and argon plasma still comparable?

Fig. 4 evaluate CO concentration and CO_2 conversion rate for different admixture of CO_2 in discharges of argon and helium, at a SEI of (172±3)J/l, total gas flow rate of 500sccm and frequency of 20kHz. During the experiment, the addition of different concentration of CO_2 modified the SEI. The applied voltage was thus constantly modulated to keep SEI = (172±3)J/l.

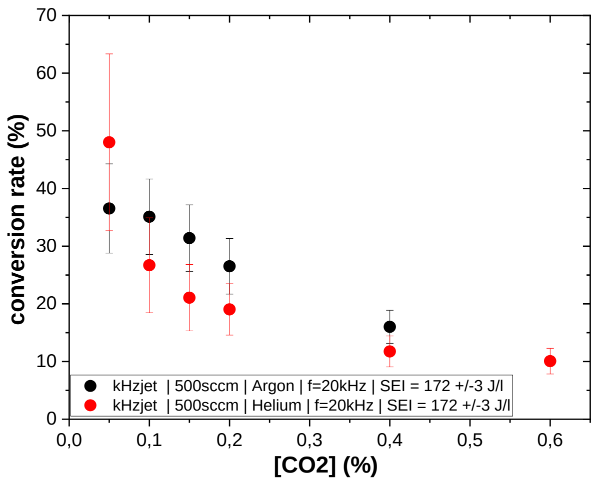

Fig. 4. Conversion rate of CO2 into Co in Helium/CO2 or Argon/CO2 plasma as a function of CO2 concentration. The data were recorded at 20kHz with a total gas flow rate of 1000sccm., for a fixe specific energy input (SEI) of 172J/l

It is immediately plain that the dissociation of CO_2 occur in the same rate in both argon and helium plasmas. An increase of CO_2 admixture in the discharges significantly decrease the efficiency of CO_2 conversion.

4-Conclusion

This abstract laid out a study of a external rings DBD jet fed with helium/CO_2 or argon/CO_2 admixture. Its aim was to compare two feed gases: helium and argon, in terms of electrical characteristic and CO_2 conversion efficiency to find the most suitable configuration for medical use.

An electrical characterization of the discharges allowed the measurement of the breakdown voltage and the energy consumed by the plasma. This characterization highlighted the differences between helium and argon: breakdown voltage and energy consumption in argon gas were twice than in helium.

The concentration of CO produced by plasma was measured by means of absorption spectrometry via a gas analyzer. In our conditions, we showed that the production of CO was from couple of ppm to thousands of ppm of CO, which is typically the range used in clinical application with CO inhalation. Thereby, this device is safe in terms of CO production for medical application.

In log-log scale, the concentration of CO produced by plasma as a function of the SEI with 0.3% of CO_2 followed a linear trend. Surprisingly, the nature of the feed gas had no impact on the CO_2 dissociation, even though plasma exhibited different features in helium and argon. Moreover, amount the potential dissociation paths for CO_2, direct impact dissociation with energetic particles (electrons or noble gas metastable atoms) must be one of the main dissociation path. In order to evaluate the role of metastable atoms on the dissociation, a deeper investigation will be carry in future.

We showed that an increase of CO_2 concentration in the discharge increased CO concentration but significantly decreased its production output. The main reason of this observation was due to the energy loss of electrons in the rotational-vibrational states of CO_2.

Finally, this study showed that this external rings DBD jet is able to produce a controlled amount of CO suitable for medical use, in both argon/CO_2 and helium/CO_2 mixture. The production of CO can be controlled by only two parameters: the SEI and the CO_2 concentration no matter of the nature of the feed gas used (helium or argon), simplifying the biological treatments.

5- Acknowledgements

The authors would like to thank the French Research Agency (ANR) for funding this research (MediCO-Plasma ANR-21-CE19-0005). EM would like to thanks the MESRI for founding her PhD thesis.

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