Non-thermal electron cyclotron resonance (ECR) air plasmas characteristics and preliminary results in tomato seeds germination

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Abstract: Non-equilibrium plasmas have been studied to be used in agricultural applications. Synthetic air plasmas were generated at 1 Pa in an 80 litres vacuum chamber by an ECR coaxial microwave source at 2.45 GHz. Plasma characteristics were determined by OES and Langmuir probe measurements. Tomato seeds adding showed no influence on plasma characterizations. A 12% increase in germination rate was measured after 14 days following a plasma treatment of 10 min at 50 W.

Keywords: ECR plasma source, OES, Langmuir probe, seed germination

1. Introduction

Non-thermal plasmas are emerging alternative treatments relative to seed conservation and improvement on their germination [1]. Nowadays, chemical products are used by industrial agriculture. They imply water and soil pollution which cause biodiversity and human health troubles. Non-thermal plasmas are advantageous because of their composition: heavy particles (ions and neutrals) induce a low-temperature preserving the seeds integrity; and energetic electrons produce reactive species and UV-photons impacting on germination and seed conservation. Different low-pressure and atmospheric pressure plasma sources have been tested on many seeds in this field [2].

In this work, an investigation into the low-pressure plasma action on seeds germination has been carried out with an electron cyclotron resonance microwave plasma source. The approach used to define the plasma treatment conditions and to better understand the mechanisms involved in these processes consisted in different steps. Firstly, a plasma parametric study without seeds was performed to determine the evolution of plasma temperatures (electron, vibration and rotation temperatures) and electronic densities. Secondly, seeds were placed inside the vacuum chamber to observe their influence on plasma characteristics. Finally, the source efficiency on modification of tomato seeds was highlighted with germination experiments.

2. Experimental setup

Air plasmas were generated at 1 Pa in an 80 litres vacuum chamber presented in Fig. 1 and Fig. 2 where vacuum pumping, gas monitoring and plasma diagnostics were set up through different vacuum passages.

The electron cyclotron resonance coaxial microwave source (ECR – see Fig. 1) powered by a 2.45 GHz solid-state generator was designed to sustain microwave plasmas over several decades of pressure varying from 10^{-2} Pa to a few Pa (Aura-wave – SAIREM SAS). This configuration ensures minimal power-losses and perfectly matched impedance from 0 W to 200 W injected power. The ECR source was positioned at the top centre of the reactor through a KF40 passage as shown in Fig. 1 and Fig. 2. At the bottom of the vacuum chamber, a radiofrequency capacitively coupled plasma electrode (CCP) could be added to the ECR plasma source to homogenize the discharge. This electrode is a 30 cm diameter disk feed by a 13.56 MHz generator. The impedance matching system is tunable with two position parameters.

Fig. 1. Aura-wave ECR plasma source (left) and the sustained discharge at 1 Pa in air plasma with 150 W power input (right).

Plasma diagnostics were conducted along the reactor central axis at three different height positions (Y = 6 cm, 14 cm and 22 cm from the top). For each height position, diagnostics were also performed radially where X = 0 cm correspond to the central position.

The experimental conditions for the plasma physical characterization are resumed in Table 1. All measurements were realized at 1 Pa with injected microwave power varied between 25 W to 150 W.

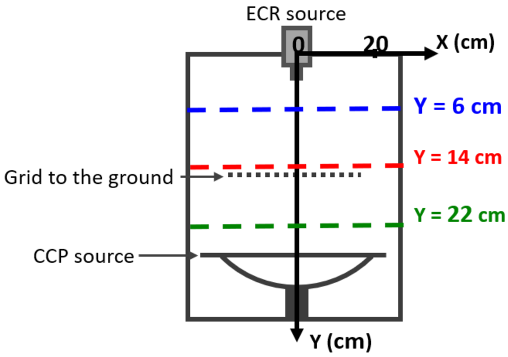

Fig. 2. Schematic diagram of the vacuum chamber and the plasma diagnostics positions.

Table 1. Plasma experimental conditions.

Plasma source	ECR
Gaz	Synthetic air 4.0
Flow	50 sccm
Pressure	1 Pa
Injected power	25 W to 150 W – step: 25 W
Diagnostic positions	Axial (Y): 6, 14, 22 cm from the top Radial (X): 0 to 20 cm from the centre

Species identification has been conducted on spectra obtained from Ocean Optics HR2000+ optical emission spectrometer measurements. Acquired spectra were calibrated on relative intensity in order to follow the evolution of band emitted intensities as a function of microwave power. Table 2 shows the nitrogen and oxygen compounds identified from all spectra conditions, N_2 emissions are predominant and will be used for vibrational and rotational temperature determination.

Table 2. Species identified in the ECR plasma.

Emitted species	Wavelength range (nm)
$N_2: C^3\Pi_u - B^3\Pi_g$ (SPS)	296.2 – 464.9
$N_2: B^3\Pi_g - A^3\Sigma_u^+$ (FPS)	559.2 – 891.2
$N_2^+: B^2\Sigma_u^+ - X^2\Sigma_g^+$ (FNS)	391.4 – 470.9
$NO_\gamma: A^2\Sigma^+ - X^2\Pi$	259.6
$NO_\beta: B^2\Pi - X^2\Pi$	267.2
$O\ I: 3s\ ^5S - 3p\ ^5P$	777.1
$O\ I: 3s\ ^3S - 3p\ ^3P$	844.6

In order to estimate the rotational and vibrational temperatures, a higher resolution spectrometer (Horiba Jobin Yvon iHR320) has been used. This spectrometer was equipped with an 1800 g/mm grating blazed at 400 nm and with a 0.3 nm resolution. Spectra from 365 nm to 385 nm were collected to measure the $N_2(C-B)$ emission bands at 370.9, 375.4 and 380.4 nm. Prior to measurements, intensity relative calibration has been done with a Deuterium-Halogen calibration light source (DH3-plus Ocean Optics). These spectra were fitted with Specair software to determine the vibration and rotation temperatures (resp. T_{VIB} and T_{ROT}). The baseline was adjusted, and the measurement data were normalized to be compared with the simulation theoretical spectra. The vibrational temperature was obtained through the 375.4 nm and 380.4 nm maximum intensities ratio. Once T_{VIB} was known, a focus on the 380.4 nm band slope allowed T_{ROT} estimation.

A linearly driven double Langmuir probe Impedans ALP system has been used to calculate electron temperatures and densities. The linear translation system permitted the collect of intensity-voltage characteristics from X = 0 cm to 20 cm every 5 cm (see Fig. 2). Electron temperatures and densities were calculated by IV-characteristics interpretation. Electron temperature T_e was determined by equation 1 and electron density n_e by equation 2 as following.

$$\frac{1}{k_B T_e} = \frac{I(V_p)}{\int_{V_f}^{V_p} I_e(V)dV} \quad (1)$$

$$n_e = \frac{I(V_p)}{A_p}\sqrt{\frac{2\pi m_e}{e^2 k_B T_e}} \quad (2)$$

k_B: Boltzmann constant
m_e and e: electron mass and charge
A_p: probe area (9.4 µm²)
I_e: electron current
(probe current subtracted by ion current)
V_p: plasma potential
(probe potential when the IV-first derivative is maximal)
V_f: floating potential
(probe potential when there is no probe current)

The diagnostics on plasma spectra, densities and different temperatures (T_{VIB}, T_{ROT} and T_e) were also replicated with about 500 tomato seeds on the grid inside the reactor to estimate eventual plasma parameters modification on plasma characteristics.

Evaluation on germination rate enhancement by plasma was performed on tomato (*Solanum lycopersicum*) seeds. Each sample consisted in about 50 seeds exposed to ECR plasmas at different power input and exposition time related in Table 3. After plasma treatment, seeds were stocked between two imbibed towel papers disposed in a 20°C dark chamber during germination experiments. The percentage of germinated seeds in a sample was estimated at 5 days and 14 days after treatment as indicated in the standard rules for germination assessment [3] and compared with the control sample (without plasma treatment).

Table 3. Plasma conditions for seed treatments.

Plasma source	ECR
Gaz	Synthetic air 4.0
Flow	50 sccm
Pressure	1 Pa
Injected power	50 W, 100 W, 150 W
Seeds position	Y = 15 cm from the top (onto the grid)
Seeds quantity	about 50 seeds (about 0.1 g)
Seeds treatment time	0 (control), 5, 10, 20 and 30 min

3. Plasma characterization results

Vibration and rotation temperatures as a function of microwave power are presented in Fig. 3. Measurements were taken at the three axial positions. The spectrometer resolution of 0.3 nm allows best-fitted spectra with standard deviations around ± 100 K for T_{VIB} and around ± 50 K for T_{ROT}. The closer the spectrometer is to the source, the higher is the vibration and rotation temperatures. T_{VIB} ranges from 5000 K to 8000 K and globally increase with power and T_{ROT} remained constant around 400 K.

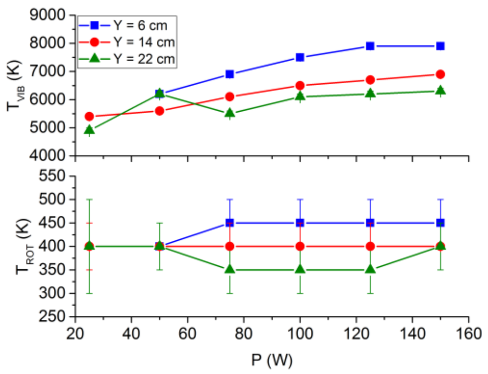

Fig. 3. T_{VIB} (top) and T_{ROT} (bottom) determined by the $N_2(C-B)$ emission bands fitted with Specair software.

Triangular interpolation has been performed on Langmuir probe measurements for all positions specified in Table 1 in order to issue cartographies of electron temperature and electronic density in the vacuum chamber. The obtained cartographies for electronic temperature are shown in Fig. 4 whereas Fig. 5 corresponds to electronic density cartographies.

Electron temperature globally increases with power between 0.7 to 1.7 eV (*i.e.* 8000 to 20000 K). The higher temperature zone is found around the source (see Fig. 4), in the principal ionisation area. Although the structure is slightly different, these values are consistent with the ones found in the literature [4].

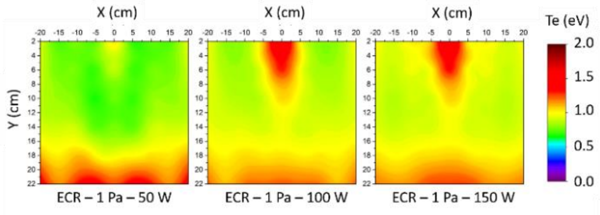

Fig. 4. Electron temperature cartographies with X, the radial position (0 to 20 cm from the centre) and Y, the axial one (6, 14, 22 cm from the top).

Electronic densities obtained inside the plasma generation zone are in the range of 10^{13} cm^{-3} exceeding by far the microwave critical density which is defined at 7.6×10^{10} cm^{-3} for 2.45 GHz excitation (see Fig. 5). It decreases however with distance and becomes radially uniform for Y = 15 cm (and further), corresponding to seeds position inside the reactor.

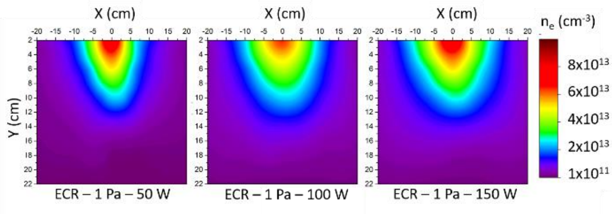

Fig. 5. Electron density cartographies with X, the radial position (0 to 20 cm from the centre) and Y, the axial position (6, 14, 22 cm from the top).

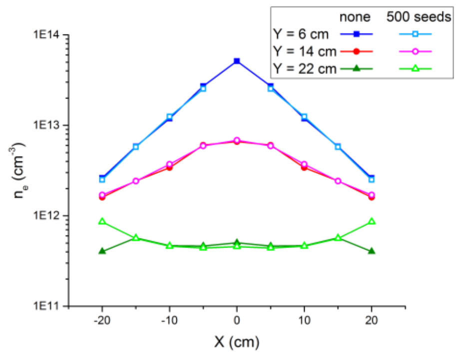

Fig. 6. Electron density radial distribution at 50 W without (full) and with (empty) seeds inside the reactor.

Fig. 6 is an example of the seeds influence on plasma characteristics. It represents electron density radial distribution at 50 W. Seeds sample introduction does not induce any significant changes within the reactor except at Y = 22 cm, X = ± 20 cm.

4. Preliminary results in seed germination

Germination rates evaluation at different treatment times was performed as presented on Fig. 7 for a 50 W ECR plasma treatment. The dark points correspond to control sample – seeds unexposed to plasma. On the 5^{th} and 14^{th} days after plasma treatments, control seeds' germination rates are lower than plasma-exposed seeds' germination rates. Furthermore, certain exposure durations are more favourable than others in order to improve germination rates. Compared to control sample, 10- and 20-minutes plasma treatment induce an increase about 12 % in germination rates against 4 % raise in the case of 5 and 30 min of plasma treatment at 50 W.

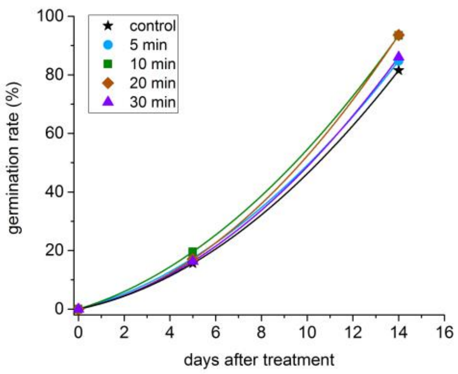

Fig. 7. Tomato seeds germination rates at 5 and 14 days after 50 W plasma treatments – treatment time varied as indicated in legend.

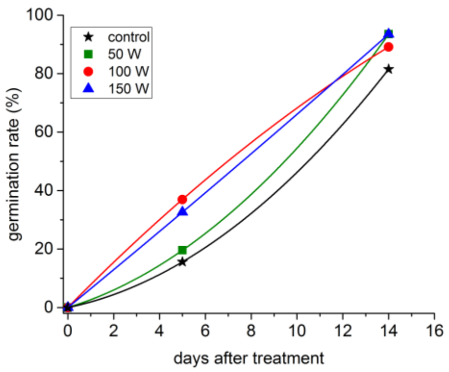

Fig. 8. Tomato seeds germination rates at 5 and 14 days after 10 min exposed to plasma – treatment power varied as indicated in legend.

In Fig. 8, 10-minutes treatment time was used as a benchmark in order to evaluate microwave power influence on germination rates. As in the case of Fig. 7, increases in germination rates thanks to plasma treatments should be noted. On the 14^{th} day after plasma treatment, 12 % increase in seed germination was obtained with 50 W and 150 W against 7 % with 100 W injected power. Moreover, the germination index [5] which takes into account germination relative to time, is higher on the 5^{th} day after plasma treatment with higher power input.

5. Conclusion

Air plasmas generated at 1 Pa by a microwave ECR source have been characterized in order to optimize plasma treatments for tomato seeds germination. A study of plasma temperatures as a function of microwave power has been conducted from 25 W to 150 W. Electron temperatures are between 0.7 and 1.7 eV (from 8000 to 20000 K). As expected on non-thermal plasmas, they are higher than the vibration temperatures (from 5000 K to 8000 K) and the rotation ones (around 400 K). Electron density cartographies show a maximum density in the range of 10^{13} cm^{-3} inside the plasma generation area and a decrease far from the source.

Tomato seeds presence inside the reactor does not modify plasma characteristics. First experiments on tomato seeds showed a promising 12% increase in germination rate after 14 days following a 50 W – 10 min plasma treatment.

The parametric studies undertaken indicated that this germination rate could be increased by choosing optimal microwave power-treatment time values.

6. Acknowledgements

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7. References

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