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Research Article

Characterization of an Atmospheric-Pressure Argon Plasma Generated by 915 MHz Microwaves Using Optical Emission Spectroscopy

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The paper presents the investigations of an atmospheric-pressure argon plasma generated at 915 MHz microwaves using the optical emission spectroscopy (OES). The 915 MHz microwave plasma was inducted and sustained in a waveguide-supplied coaxial-line-based nozzleless microwave plasma source. The aim of presented investigations was to estimate parameters of the generated plasma, that is, excitation temperature of electrons T_{exc}, temperature of plasma gas T_g, and concentration of electrons n_e. Assuming that excited levels of argon atoms are in local thermodynamic equilibrium, Boltzmann method allowed in determining the T_{exc} temperature in the range of 8100–11000 K. The temperature of plasma gas T_g was estimated by comparing the simulated spectra of the OH radical to the measured one in LIFBASE program. The obtained T_g temperature ranged in 1200–2800 K. Using a method based on Stark broadening of the H_β line, the concentration of electrons n_e was determined in the range from 1.4×10^{15} to 1.7×10^{15} cm^{-3}, depending on the power absorbed by the microwave plasma.

1. Introduction

The atmospheric-pressure microwave plasma sources (MPSs) found many different physical and technical applications such as decomposition of gaseous pollutants [1–4], deposition thin layers in nanosensors [5, 6], medicine for bacteria inactivation [7], and production of hydrogen via conversion of hydrocarbons or other hydrogen carriers [8–12].

Since in process of the gas treatment by the plasma, the temperature of plasma gas and concentration of electrons play an important role; therefore, the knowledge of these basic parameters is crucial for understanding the chemical kinetics and its optimization.

In this work, an optical emission spectroscopy (OES) [13–17] method has been used for diagnosing the microwave argon plasma. The plasma was induced by microwaves at a frequency of 915 MHz in waveguide-supplied coaxial-line-based nozzleless MPS [1]. The presented device allows the generation of so-called cold plasma which is classified as a partial local thermodynamic equilibrium (PLTE) plasma [13, 14, 18–20].

2. Experiment

In Figure 1(a), a photo of the MPS is shown, whereas a draft of an experimental setup is presented in Figure 1(b). The MPS is supplied via a standard waveguide WR 975 and ended by a movable plunger which allows for an effective transfer of the microwave power from the electric field to the plasma.

Inside the used MPS, a quartz tube is placed. In the tube, two gas flows are formed. The first one is the axial flow (processed gas), and the second one is the swirl flow (cooling gas). In the axial flow, the processed gas is introduced into the quartz tube through the inner electrode. In the swirl flow, the cooling gas is delivered into the MPS by four inlets located tangentially to the quartz tube wall [1]. This resulted in a vortex (swirl) flow inside the quartz tube. In this type of the MPS, plasma in a form of flame occurs inside the quartz

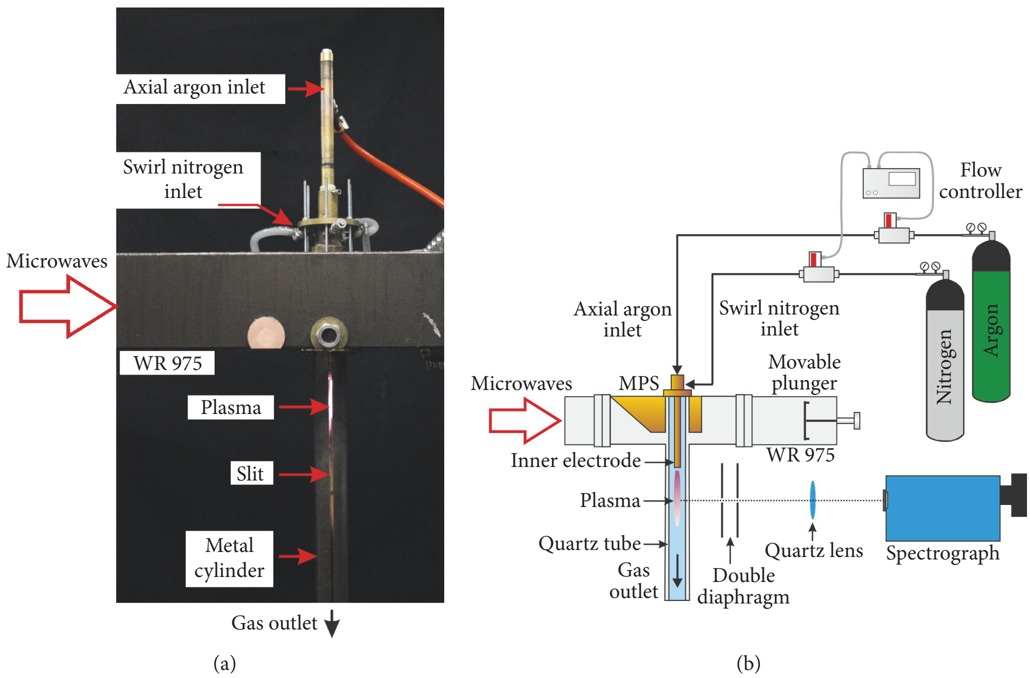

Figure 1: (a) Photo of the microwave plasma source and (b) the experimental setup used for the spectroscopic investigations.

tube at the tip of the inner electrode. The additional swirl flow stabilized the discharge in the center of the quartz tube and protects the quartz wall from overheating [1]. Below the MPS waveguide, the quartz tube is surrounded by a metal cylinder with a vertical slit for the observation of the generated discharge.

Symmetrical double convex quartz lens (50 mm in diameter, focal length 75 mm) was used to focus light emitted by the microwave plasma. Additionally to collimate the emitted light, two diaphragms with pinholes of 1 mm in diameter were placed. In these investigations, the spectrum of the microwave plasma was measured by McPherson model 209 spectrometer, equipped with double-pass scanning monochromator. The used spectrograph is equipped with sensitivity-calibrated iCCD camera and diffraction grating 1200 grooves/mm.

Using Hg I lines $\lambda = 365.02$ nm, 435.84 nm, and 546.07 nm emitted from low-pressure calibration Hg-Ne lamp, the instrumental line broadening $\Delta\lambda_I$ has been determined. The obtained values of $\Delta\lambda_I$ was about 0.07 nm.

3. Results

During the experiment, the nitrogen was used as a cooling gas with constant flow rate of 50 NL/min. The investigations were performed with argon as processed gas with flow rate equal to 50 NL/min. The power absorbed by the microwave plasma P_A was calculated as a difference between power incident P_I and power reflected P_R in the MPS [1]. The P_I and P_R were directly measured using a directional coupler. In these investigations, the power P_A was changed from 2 to 4 kW.

The spectra were recorded 15 mm below the tip of the inner electrode. In our measurements, we focused on the range of emission spectra from 300–600 nm. An example of the recorded spectra is shown in Figure 2. To detect emission spectral lines of the H or the OH radicals, a small addition of H_2O vapour (H_2O—0.1 kg/h, H_2O vapour temperature was equal to 400°C) was added to the process gas flow.

In performed investigations, we assumed that microwave plasma at atmospheric pressure is generally in partial local thermodynamic equilibrium [13, 14, 18–20]. This assumption allowed us to use the Boltzmann plot method to determine the T_{exc} [14, 15]. Five transition lines of argon (see Figure 2) were selected to determine the T_{exc}. Selected argon lines with the parameters for the Boltzmann plot method were presented in Table 1. An example of Boltzmann plot is shown in Figure 3. Conformity of a straight line with experimental points indicates balance in the excited states of argon atoms. The obtained T_{exc} was in the range of 8100–11000 K, as shown in Figure 4. The estimated T_{exc} temperature increased with increasing the absorbed microwave power P_A.

It is widely accepted that in the microwave discharges, the rotational temperature of the OH radical T_{rot} corresponds to the translational temperature of heavy particles in the plasma (temperature of plasma gas T_g) [16, 17]. To obtain the molecule rotational temperature, the OH band $A^2\Sigma^+ \rightarrow X^2\Pi$ was used. This band is very sensitive against the changes of the rotational temperature [16]. After measuring the OH spectrum, we simulated this band in the LIFBASE program [21]. This program allows calculating the emitted spectrum of plasma radiation of various gases at individually given rotational and vibrational temperatures. In this program, the simulated OH band was fitted to the experimental one (Figure 5). A good agreement has been found. Spectrum simulations were performed for Gaussian line shapes with a FWHM value equal to

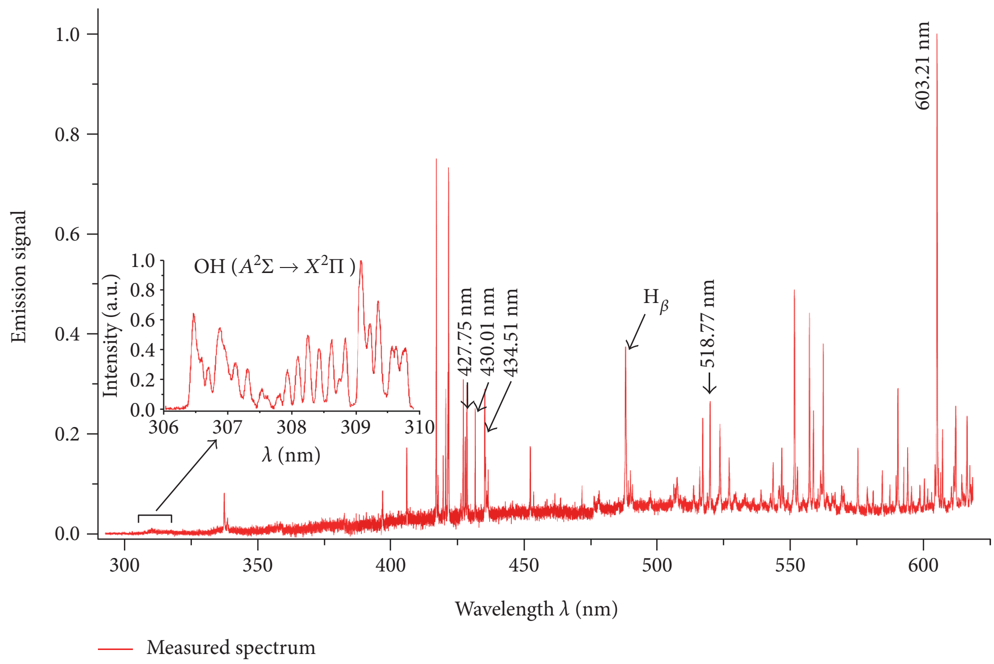

FIGURE 2: Measured emission spectra of argon plasma (with a small amount of H_2O vapour) with selected argon $4p$–$4s$ and $5p$–$4s$ transition lines for Boltzmann plot method. Absorbed microwave power $P_A = 3$ kW and argon flow rate $Q = 50$ l/min.

TABLE 1: Parameters of selected argon emission lines used to determine the excitation temperature of the electrons T_{exc}. n/m: energy levels upper/lower, respectively; λ_{nm}: wavelength of transition $n \rightarrow m$, A_{nm}: Einstein coefficient for transition $n \rightarrow m$, g_n: statistical weight of the upper level n. E_n is the energy of the upper level n.

l.p.	λ_{nm} (nm)	Transition	A_{nm} (10^7 s^{-1})	g_n	E_n (cm^{-1})
1	427.75		0.0797	3	117,151
2	430.01	$5p \rightarrow 4s$	0.0377	5	116,999
3	434.51		0.0297	5	118,407
4	518.77	$5d \rightarrow 4p$	0.1380	5	123,372
5	603.21		0.1400	9	122,036

0.07 nm. The obtained gas temperature T_g ranged from 1200 to 2800 K (Figure 6).

By using the method based on Stark broadening of the hydrogen H_β line, the concentrations of electrons n_e in the plasma were determined [13–15, 17]. The introduction of water vapour caused the emergence of emission lines of hydrogen H_β, H_δ, and H_γ. In our work, we focus only on the H_β (486.13 nm) line. The H_δ and H_γ lines were hardly noticeable or partially overlapped by the argon lines. Therefore, these two lines were not used to determine the concentration of electrons n_e.

The shape of the recorded H_β line is affected by several different mechanisms of broadening (instrumental $\Delta\lambda_I$, Van der Waals $\Delta\lambda_W$, Stark $\Delta\lambda_S$, resonance $\Delta\lambda_R$, Doppler $\Delta\lambda_D$, and natural $\Delta\lambda_N$) which result to a Voigt profile [13–15]. In order to obtain the FWHM of H_β line in investigations to the measured profile, the Voigt function was fitted. The fitting was performed using the Origin software [22].

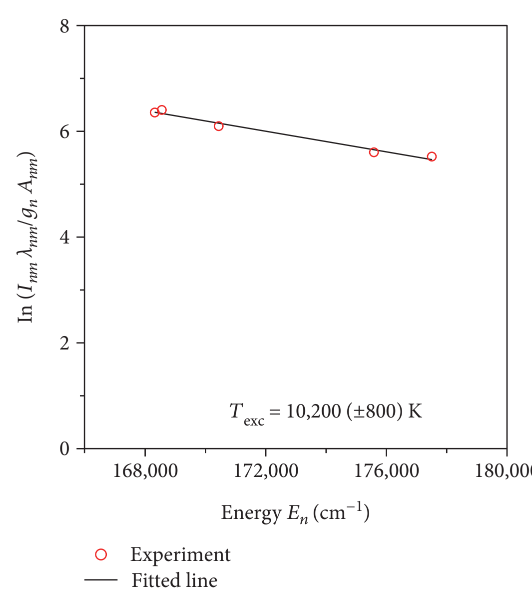

FIGURE 3: Example of Boltzmann plot for determination of the T_{exc}. I_{nm}—intensity of the recorded emission line from transition $n \rightarrow m$, microwave power absorbed $P_A = 3$ kW, and argon flow rate $Q = 50$ l/min.

The Doppler broadening $\Delta\lambda_D$ is a result of atoms' random motions in the plasma. This effect can be calculated from [15, 23]

$$\Delta\lambda_D = 7.17 \times 10^{-7} \lambda_0 \sqrt{\frac{T}{M}}, \quad (1)$$

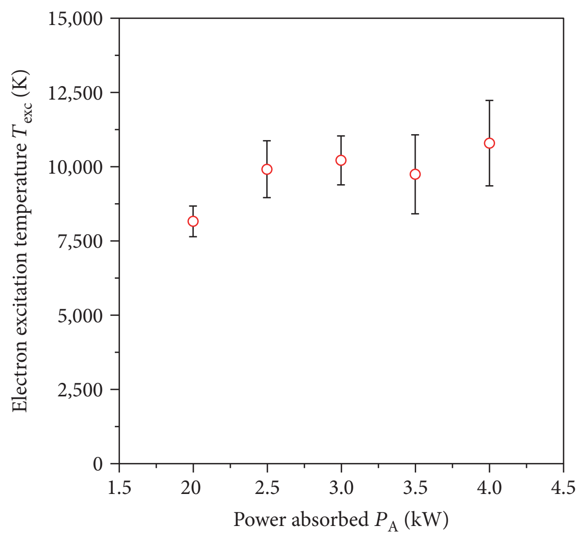

Figure 4: Electron excitation temperature as a function of absorbed microwave power P_A.

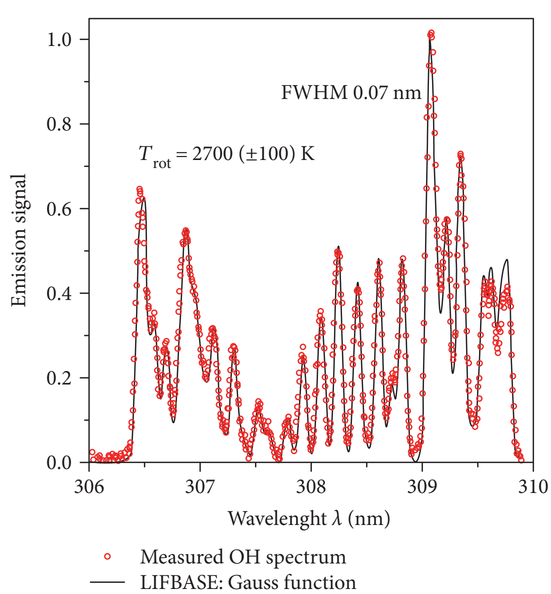

Figure 5: Comparison of the measured and simulated in LIFBASE emission spectra of OH band. Absorbed microwave power $P_A = 3$ kW and argon flow rate $Q = 50$ l/min.

where λ_0 is the wavelength, T is the temperature of the emitter in Kelvins, M is the mass of the emitter in a.m.u. In this work, T was assumed equal to the temperature of plasma gas T_g. The Van der Waals broadening $\Delta\lambda_W$ is the effects of dipolar interaction between excited the atoms and the neutral ground state atom [14]. The $\Delta\lambda_W$ broadening can be estimated from [23]

$$\Delta\lambda_W = 6.48 \times 10^{-22} \frac{p}{kT_g^{0.7}}, \tag{2}$$

where p is the pressure and k is the Boltzmann constant. Determination of plasma gas temperature T_g allows to

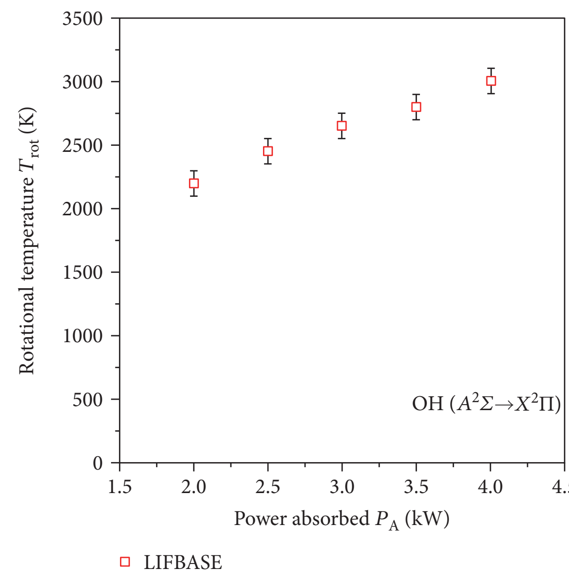

Figure 6: Measured rotational temperatures of the OH radical as a function of absorbed microwave power P_A.

estimate values of Van der Waals and Doppler broadening effect. Using the above formulas, the values of $\Delta\lambda_D$ and $\Delta\lambda_W$ broadening of the H_β line were calculated. The obtained value of $\Delta\lambda_D$ was equal to 0.003 nm while $\Delta\lambda_W = 0.02$ nm, respectively. In the tested range of the absorbed microwave power P_A, determined values were constant. In the presented work, resonance and natural broadening have been omitted due to low FWHM values in comparison to the other effects [13–15].

Taking into account the estimated values of $\Delta\lambda_I$, $\Delta\lambda_D$, and $\Delta\lambda_W$ and obtained value FWHM of H_β line, the Stark broadening $\Delta\lambda_S$ was calculated [15, 23]. In the experiment, we observed a linear relationship between the estimated value of Stark broadening $\Delta\lambda_S$ of H_β line and the absorbed microwave power P_A by the plasma. In calculation of the n_e, a Gig-Card theory [24] was used. The measured concentration of electrons n_e ranged from 1.4×10^{15} to 1.7×10^{15} cm^{-3} (Figure 7). The values of the electron concentration indicate that the balance between electrons and heavy particles as a result of collisions cannot be achieved. Thus, the plasma cannot be described by a single temperature.

Adopting a classical ideal gas model and using the measured concentration of electrons, we estimated that the ionization degree in plasma was about $\sim 10^{-4}$. This indicates that ionization degree is too low to thermalize the electron energy distribution function. Therefore, there may be a lack of balance between the basic state and the excited states of argon atoms in plasma. This cause that the measured temperatures could be overestimated. In measurements, we record the radiation from the excited states, which are the result of collisions, while the basic states remain neutral.

4. Conclusions

The investigations of an atmospheric-pressure argon plasma generated at 915 MHz microwaves using optical emission

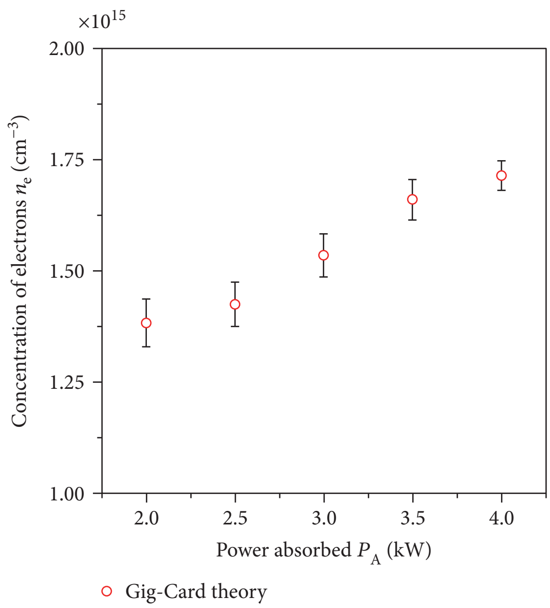

Figure 7: The concentration of electrons as a function of absorbed microwave power P_A.

spectroscopy (OES) are presented in this work. These investigations yielded the excitation temperature of electrons T_{exc}, the gas temperature T_g, and the concentration of electrons n_e in the generated argon plasma. In the tested range of the absorbed microwave power P_A by the plasma, we observed an increase in the excitation temperature T_{exc}, the gas temperature T_g, and the concentration of electrons n_e. These results indicate that appropriate selection of the gases and the operating parameters of the MPS (central and the additional flow rate, absorbed microwave power) enables in obtaining the plasma with desired parameters. It should also be mentioned that the investigated MPS works very stable with various processing gases (argon, nitrogen, air, and carbon dioxide) at high flow rates and absorbed microwave power by the plasma can be changed in a wide range. Thus, the above properties make the presented MPS an attractive tool for different gas processing at high flow rates.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

[1] J. Mizeraczyk, M. Jasiński, H. Nowakowska, and M. Dors, "Studies of atmospheric -pressure microwave plasmas used for gas processing," *Nukleonika*, vol. 57, no. 2, pp. 241–247, 2012.

[2] Y. C. Hong, H. S. Uhm, M. J. Kim, H. S. Han, S. C. Ko, and S. K. Park, "Decomposition of phosgene by microwave plasma-torch generated at atmospheric pressure," *IEEE Transactions on Plasma Science*, vol. 33, no. 2, pp. 958–963, 2005.

[3] H. S. Uhm, Y. C. Hong, and D. H. Shin, "A microwave plasma torch and its applications," *Plasma Sources Science and Technology*, vol. 15, pp. 26–34, 2006.

[4] Y. Ko, G. Yang, D. P. Y. Chang, and I. M. Kennedy, "Microwave plasma conversion of volatile organic compounds," *Journal of the Air & Waste Management Association*, vol. 53, no. 5, pp. 580–585, 2003.

[5] X. Landreau, B. Lanfant, T. Merle, C. Dublanche-Tixier, and P. Tristant, "A thorough FT-IR spectroscopy study on micrometric silicon oxide films deposited by atmospheric pressure microwave plasma torch," *The European Physical Journal D*, vol. 66, no. 160, p. 8, 2012.

[6] X. Landreau, B. Lanfant, T. Merle, E. Laborde, C. Dublanche-Tixier, and P. Tristant, "Ordering of $SiO_xH_yC_z$ islands deposited by atmospheric pressure microwave plasma torch on Si(100) substrates patterned by nanoindentation," *The European Physical Journal D*, vol. 65, pp. 421–428, 2011.

[7] J. Mizeraczyk, M. Dors, M. Jasiński, B. Hrycak, and D. Czylkowski, "Atmospheric pressure low-power microwave microplasma source for deactivation of microorganisms," *The European Physical Journal Applied Physics*, vol. 61, article 24309, 2013.

[8] J. Mizeraczyk and M. Jasiński, "Plasma processing methods for hydrogen production," *The European Physical Journal Applied Physics*, vol. 75, article 24702, 2016.

[9] Y. F. Wang, H. Tsai Ch, W. Y. Chang, and Y. M. Kuo, "Methane steam reforming for producing hydrogen in an atmospheric-pressure microwave plasma reactor," *International Journal of Hydrogen Energy*, vol. 35, pp. 135–140, 2010.

[10] M. Jasinski, D. Czylkowski, B. Hrycak, M. Dors, and J. Mizeraczyk, "Atmospheric pressure microwave plasma source for hydrogen production," *International Journal of Hydrogen Energy*, vol. 38, no. 26, pp. 11473–11483, 2013.

[11] R. Rincon, M. Jimenez, J. Munoz, M. Saez, and M. D. Calzada, "Hydrogen production from ethanol decomposition by two microwave atmospheric pressure plasma sources: surfatron and TIAGO torch," *Plasma Chemistry and Plasma Processing*, vol. 34, pp. 145–157, 2014.

[12] D. Czylkowski, B. Hrycak, R. Miotk, M. Jasinski, M. Dors, and J. Mizeraczyk, "Hydrogen production by conversion of ethanol using atmospheric pressure microwave plasmas," *International Journal of Hydrogen Energy*, vol. 40, pp. 14039–14044, 2015.

[13] B. N. Sismanoglu, K. G. Grigorov, R. A. Santos et al., "Spectroscopic diagnostics and electric field measurements in the near-cathode region of an atmospheric pressure microplasma jet," *The European Physical Journal D*, vol. 60, pp. 479–487, 2010.

[14] R. Miotk, B. Hrycak, M. Jasinski, and J. Mizeraczyk, "Spectroscopic study of atmospheric pressure 915 MHz microwave plasma at high argon flow rate," *Journal of Physics: Conference Series*, vol. 406, article 012033, 2012.

[15] B. N. Sismanoglu, K. G. Grigorov, R. Caetano, M. V. O. Rezende, and Y. D. Hoyer, "Spectroscopic measurements and electrical diagnostics of microhollow cathode discharges in argon flow at atmospheric pressure," *The European Physical Journal D*, vol. 60, pp. 505–516, 2010.

[16] C. Izarra, "UV OH spectrum used as a molecular pyrometer," *Journal of Physics D: Applied Physics*, vol. 33, no. 14, pp. 1697–1704, 2000.

[17] B. Hrycak, M. Jasinski, and J. Mizeraczyk, "Spectroscopic investigations of microwave microplasmas in various gases at atmospheric pressure," *The European Physical Journal D*, vol. 60, pp. 609–619, 2010.

[18] M. Capitelli, G. Colonna, and A. D'Angola, *Fundamental Aspects of Plasma Chemical Physics*, vol. 66 of Springer series on Atomic, Optical and Plasma Physics: Thermodynamics, Springer, New York, NY, USA, 2012, chapter 9.

[19] M. Capitelli, R. Celiberto, G. Colonna et al., *Fundamental Aspects of Plasma Chemical Physics*, vol. 85 of Springer series on atomic, Optical and Plasma Physics: Kinetis, Springer, New York, NY, USA, 2016, chapter 5.

[20] H. R. Griem, "Principles of plasma spectroscopy," in *Cambridge Monographs on Plasma Physics, chapter 7*, pp. 187–220, Cambridge University Press, Cambridge, 1997.

[21] J. Luque and D. R. Crosley, *LIFBASE: Database and Spectral Simulation Program (Version 1.5) [Computer Software]*, SRI International, Silicon Valley, CA, USA, 2015.

[22] Origin Lab, *Origin pro 9.1 [Computer Software]*, OriginLab Corporation, Northampton, MA, USA, 2015.

[23] C. Lazzaroni, P. Chabert, A. Rousseau, and N. Sadeghi, "Sheath and electron density dynamics in the normal and self-pulsing regime of a micro hollow cathode discharge in argon gas," *The European Physical Journal D*, vol. 60, pp. 555–563, 2010.

[24] M. A. Gigosos and V. J. Cardenosos, "New plasma diagnosis tables of hydrogen Stark broadening including ion dynamics," *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 29, no. 20, pp. 4795–4836, 1996.