Proc. of the 8th International Conference NEET 2013, Zakopane, Poland, June 18–21, 2013

Optical Emission Spectroscopy of Microwave (915 MHz) Plasma in Atmospheric Pressure Nitrogen with Addition of Ethanol Vapour

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In this paper results of optical emission spectroscopic study of microwave 915 MHz plasma in atmospheric pressure nitrogen with an addition of ethanol vapour are presented. The plasma was generated in waveguide-supplied cylinder-type nozzleless microwave plasma source. The aim of research was to determine the rotational T_{rot} and vibrational T_{vib} temperatures of CN and C_2. A method called bubbling was employed to introduce alcohol (ethanol) into the plasma. The T_{rot} and T_{vib} were determined by comparing the measured and simulated spectra. Obtained rotational and vibrational temperatures of CN and C_2 were ranged from 4400 to 5400 K and from 2800 to 3400 K, respectively, depending on the location in the plasma and the microwave absorbed power P_{A}.

DOI: 10.12693/APhysPolA.125.1329

PACS: 52.50.Sw, 52.70.Kz

1. Introduction

Hydrogen is being considered as a strategic fuel for the future. This is because hydrogen can be considered as a renewable fuel which liberates a considerable quantity of energy per unit weight (120 kJ/g) without liberating CO_2 in its combustion [1–3]. Moreover, hydrogen is easily converted into electricity by fuel cells. Hence, the investigation of new hydrogen sources is of utmost importance. Microwave plasma sources (MPS) operated at atmospheric pressure seem to have a high potential for hydrogen production via hydrocarbon reforming [3–6]. Since thermal reactions play an important role in the production of hydrogen in MPS, the knowledge of the gas temperature in such plasmas is crucial for understanding the chemical kinetics of the production process and its optimization.

Optical emission spectroscopy (OES) based on plasma sources is a well-accepted technique for plasma characterization [3, 7–12]. OES is a well-used technique because it is simple, can be used *in situ* and is noninvasive. In this paper spectroscopic study of microwave (915 MHz) plasma in nitrogen with an addition of ethanol vapour is presented. The ethanol has been introduced in the nitrogen plasma environment by the *bubbling* method.

The study concerns determining the rotational and vibrational temperatures of CN (Violet system) and C_2 molecules (Swan system) emitted by microwave plasma. The CN Violet system ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) is frequently observed in plasma sources containing hydrocarbons and nitrogen mixture [12]. Taking into account the strong coupling between translational and rotational energy states, the temperature derived from experiments is, in a general case, close to the gas temperature [3].

2. Experimental

The microwave generator 915 MHz was connected to a waveguide WR 975 system, which includes: isolator, directional couplers, 3-stub tuner and MPS with movable plunger (Fig. 1). The microwave discharge in a form of flame takes place inside waveguide-supplied cylinder-type nozzleless MPS. The MPS was based on a standard WR 975 rectangular waveguide with a section of reduced-height, preceded by tapered section. The plasma flame was generated in a quartz tube with internal/external diameters of 26/30 mm. The quartz discharge tube were inserted vertically on the axis of the reduced-height waveguide wider wall and protruded below bottom waveguide wall. On the outside of the waveguide the quartz tube was surrounded by metallic tube shield with 5 mm slit for visualization.

A method called bubbling was employed to introduce alcohol (ethanol 99.8% purity) into the plasma at room

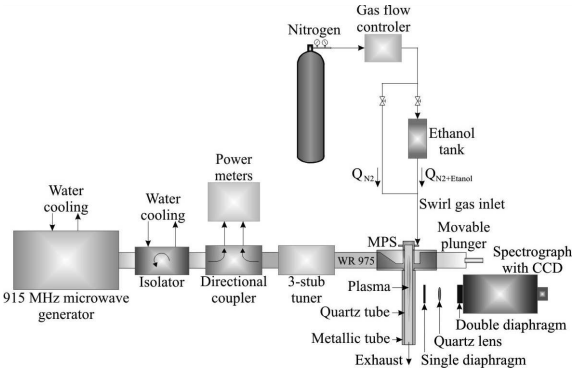

Fig. 1. Diagram of the experimental setup.

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temperature in order not to involve any additional energy in the process. The nitrogen gas flow was divided into two parts. First flow Q_{N2} were only used to initiated the microwave discharge. Then nitrogen used as the carrier gas, was bubbled into the recipient containing the alcohol (ethanol tank) to drag its molecules. The resulting nitrogen–ethanol mixture $Q_{N2+ethanol}$ (gas and alcohol vapour) was introduced into the quartz discharge tube. From the rate of alcohol loss in ethanol tank as a result of nitrogen flow, we estimated that the ethanol vapour was around 3% of $Q_{N2+ethanol}$.

The plasma generation was stabilized by injecting a swirl gas in the quartz tube. The swirled gas held the plasma in the center of the tube and thus protected the quartz wall from overheating [13]. The microwave discharge was initiated by the brass rod entered to the discharge area. The absorbed microwave power P_A by the discharge was calculated as $P_I - P_R$, where P_I and P_R were the incident and reflected microwave powers, respectively.

To measure the plasma spectrum we used the spectrograph (DK-480 CVI with 1200 grooves/mm) equipped with CCD sensitivity calibrated camera (SBIG ST-6 750*242). A PC computer was used to control the spectrograph and acquire the data. The light emitted by the plasma was focused with a quartz lens (50 mm in diameter, focal length 75 mm) onto a double diaphragm with pinholes of 1 mm diameter at the entrance slit of the spectrometer. The width of the spectrometer entrance slit was 40 μm (20 mm height). The double diaphragm was placed to collimate the light. One single diaphragm with a pinhole of 1 mm diameter was placed near the MPS. Using a Hg–Ne low-pressure calibration lamp we measured that the Gaussian instrumental line profile FWHM was about 0.15 nm.

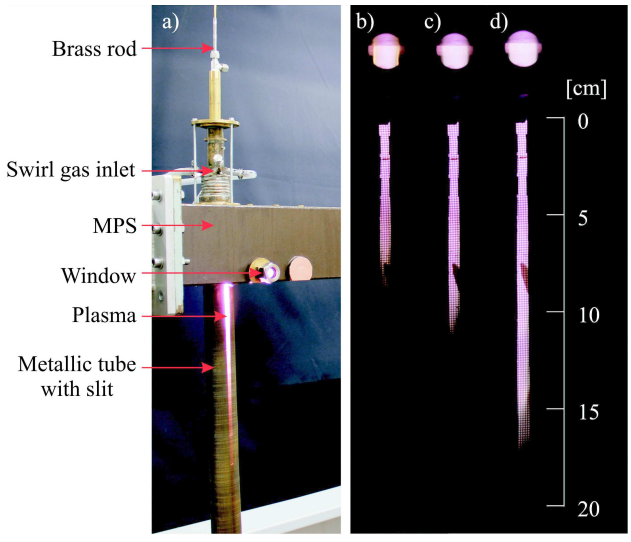

Fig. 2. (a) Photo of waveguide-supplied cylinder-type nozzleless MPS. Microwave nitrogen–ethanol mixture plasmas generated at different values of absorbed microwave power P_A: (b) 2 kW, (c) 4 kW, (d) 6 kW (nitrogen flow rate 45 l/min + 3% ethanol vapour).

Photos of presented MPS and nitrogen–ethanol mixture plasma generated at different values of absorbed microwave power are shown in Fig. 2. The figure shows that the plasma length increases with increase of the value of absorbed microwave power. Window in the wall of the generator allow for observation of the microwave plasma inside the MPS. The slit in the metallic tube allow for observation of the plasma outside the MPS below the underside of the waveguide (BUW).

3. Results and discussion

All experimental tests were performed with a nitrogen flow rate from 25 to 65 l/min (+3% ethanol vapour) and absorbed microwave power P_A from 2 to 6 kW. Figure 3a shows spectrum emitted by the nitrogen–ethanol mixture plasma. As seen, the dominant spectrum is CN Violet system. The spectrum contained also C_2 Swan system. The intensity of all measured systems increased linearly with increase of microwave absorbed power. The CN and C_2 systems only appear if the alcohol were introduced into the plasma, which indicates the existence of dissociation reactions of the ethanol molecules and, at the same time, recombination reactions which lead to the formation of these new species. Furthermore, carbon black deposit formation at the wall was observed during the operation of the nitrogen–ethanol mixture plasma. The rotational and vibrational temperatures of CN (Fig. 3b) and C_2 (Fig. 3c) were determined by comparing the measured and simulated spectra in Lifbase [14] and Specair [15] programs, respectively. In this experiment, for the temperatures determination we used wavelength ranges as follows: 412–422 nm for CN Violet system and 508–518 nm for C_2 Swan system, respectively.

The temperatures increased with increase of the microwave absorbed power (Fig. 4a). This increase was not

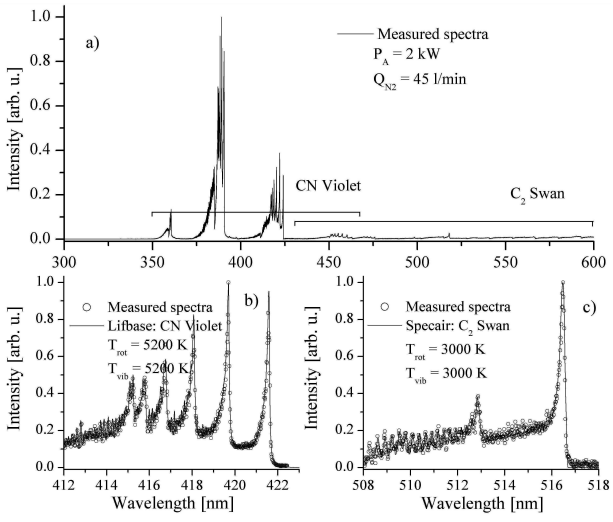

Fig. 3. (a) Measured emission spectrum of nitrogen–ethanol mixture plasma. Comparison of the measured and simulated emission spectra of (b) CN Violet system, (c) C_2 Swan system (P_A = 2 kW, nitrogen flow rate 45 l/min + 3% ethanol vapour, measured at the height of the MPS window).

significant as it could been seen in Fig. 2. The increase of the microwave power caused almost proportional increase of the plasma length and thus the plasma volume. It could be concluded that the microwave power influence the plasma volume and much less the plasma gas temperature. The influence of nitrogen flow rate through the ethanol tank is presented in Fig. 4b. The increase of the nitrogen flow from 25 to 65 l/min did not cause any significant changes of obtained temperatures. The rotational and vibrational temperatures of CN and C_2 molecules as a function of distance BUW in nitrogen–ethanol mixture plasma ($P_A = 4$ kW, nitrogen flow rate 45 l/min + 3% ethanol vapour) are presented in Fig. 4c. At this condition the plasma length was about 12 cm BUW (see Fig. 2c). Regardless the plasma length it was impossible to determine the temperature of CN and C_2 molecules at the further area of plasma. The reason of this was low intensities of band of CN Violet system and C_2 Swan system used for temperature determinations.

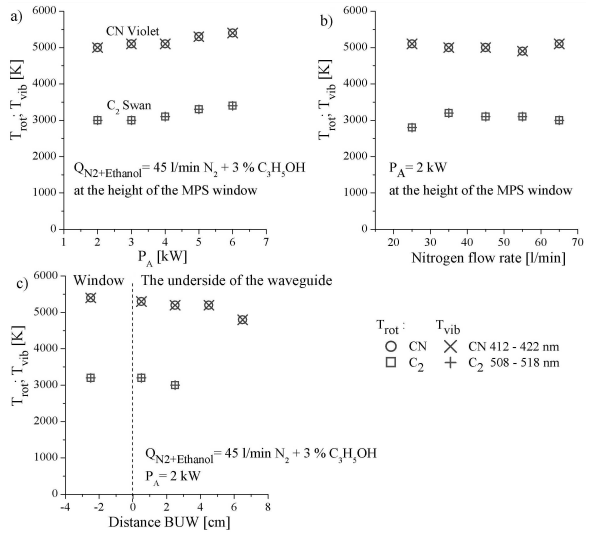

Fig. 4. Measured the rotational and vibrational temperatures of CN and C_2 molecules as a function of: (a) microwave absorbed power P_A, (b) nitrogen flow rate, (c) distance below the underside of the waveguide (distance BUW).

Obtained temperatures of CN and C_2 were ranged from 4400 to 5400 K and from 2800 to 3400 K, respectively, depending on location in the plasma and microwave absorbed power. In all conditions T_{vib} were equal to T_{rot} but the measured CN temperatures were not in agreement with the measured C_2 temperatures under conditions in this study. In all cases C_2 molecules provided lower temperatures than CN (about 2000 K). This suggests the non-equilibrium plasma, whose population density does not necessarily follow a Boltzmann distribution and obtained temperatures may not provide reliable information about the gas temperature. A possible explanation of these temperatures difference between CN and C_2 could be the mechanism of formation of these new species in the plasma. The best way to estimate the plasma gas temperature is to measure rotational spectrum of OH radical. However, in our study we have not registered spectrum of this particle.

4. Conclusions

Spectroscopic study of the microwave 915 MHz nitrogen–ethanol mixture plasma at atmospheric pressure was presented in this work. The comparison of measured and simulated spectra of CN and C_2 were performed and rotational T_{rot} and vibrational T_{vib} temperatures were determined. Obtained rotational and vibrational temperatures of CN and C_2 ranged from 4400 to 5400 K and from 2800 to 3400 K, respectively, depending on the location in the plasma, the microwave absorbed power and nitrogen flow rate.

The described MPS works very stable with various working gases at high flow rates. That makes it attractive tool for different gas processing, including conversion of liquid hydrocarbons into useful gaseous hydrocarbons and hydrogen.

Acknowledgments

This research was supported by the National Science Centre, under the programme no. 2012/05/B/ST8/02789.

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