Atmospheric pressure water vapour plasma source and its application to produce hydrogen-rich gas

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Abstract: Atmospheric pressure non-equilibrium water vapour plasma technology was developed, tested and partly employed for fuel conversion and production of hydrogen-rich gas. The results of experimental investigation on plasma source characteristics dependent on the anode material and prevailing external factors are presented. The effect of plasma source anode material on the elemental composition of exhaust plasma jet was investigated. The relation between the yield of hydrogen in an exhaust gaseous product, anode material, arc current and water vapour flow rate in plasma source was determined.

Keywords: plasma, water vapor plasma, plasma torch, plasma jet, plasma jet reactor, plasma conversion of fuel

1. Introduction

The interest rate for fuel conversion and production of hydrogen as an alternative energy source has markedly increased in the recent decades. Many researchers have emphasized the role of plasma ambient in the possible production of hydrogen-rich gas [1,2,3, etc.]. It has been reported that the inevitable employment of plasma processes enables improving the traditional technology of industrial hydrogen production or creating novel high efficient technology [1,4].

The authors of the present paper and the author of [5] assume that the atmospheric pressure plasma devices are important tools for technological application and that the essential approach to find a new technical solution for production of hydrogen-rich gas: the development of a novel water vapour plasma technology is probably the most advanced and realistic. So, the present research is devoted to the development and study of a novel water vapor plasma source for fuel conversion and wide range of other applications.

2. Experimental equipment

A novel linear, sectional, atmospheric pressure DC arc plasma source with copper or stainless steel anode was developed, manufactured and employed for realization of fuel conversion process (Fig. 1.). The novel water vapour plasma generator (PG) is based on a linear scheme with hot button type tungsten cathode, step-formed anode and neutral electrode as described in [6].

Over-heated water vapour was used as plasma forming gas at the arc current intensity of 200 A.

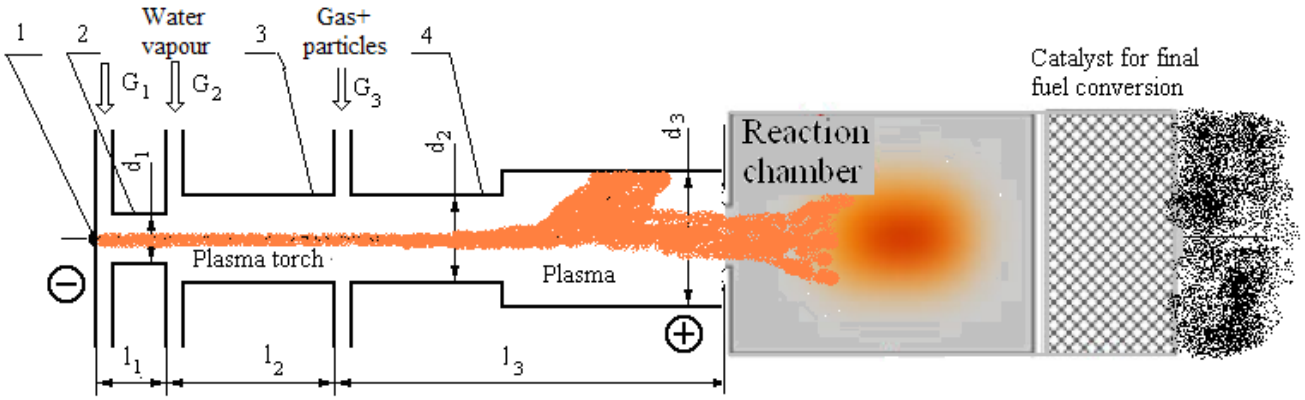

Fig. 1. The schematic presentation of water vapour plasma device for conversion of fuel and production of hydrogen rich gas. 1 – cathode junction, 2 – ignition section, 3 – neutrode, 4 – anode. G_1 is injection of initial ignition gas (argone), G_2 – injection of over-heated water vapour, G_3 – injection of additional gas mixed with *C* or *Cu* dispersed particles

By using a properly designed plasma jet reactor connected to the PG, heated by energy of electric discharge and keeping the fluid at 3600 K, it is possible to produce dissociated water vapor plasma, avoid the reverse fusion and extract hydrogen or hydrogen-rich gas. High purity copper and stainless steel AISI 304 were used as PG anode materials. Propane-butane gas, dispersed particles of copper and carbon were used as additional oxygen and ozone acceptors affected the specific conditions to reduce amount of oxygen molecules in the fluid gas. Substantial amounts of fluid gas could be converted into hydrogen and carbon monoxide with production of additional amounts of CuO or Cu_2O which could be used for further wide range applications. Voltage-current characteristics (VCC) of the PG were determined from the heat conservation calculations while measuring current strength in the circuit, voltage drop, and gas amounts. The generalized electric and thermal characteristics of the PG permit the determination of the operating regime needed for plasma technologies and selection of optimal operating modes.

The emission spectra of exhaust Ar/water vapour plasma jet at the exit nozzle of the PG was measured for the determination of elemental composition. This has been done by means of AOS4-1 spectrometer. The schematic presentation of the measurement set-up is shown in Fig. 2.

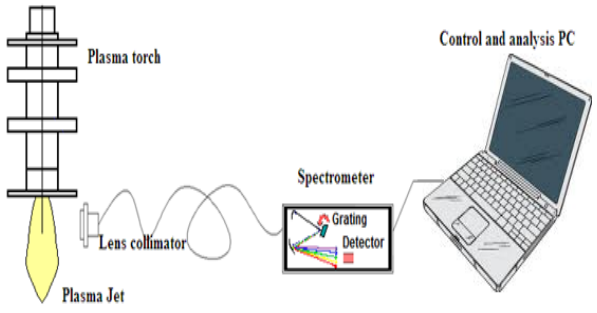

Fig. 2. A scheme of experimental set-up for optical emission spectroscopy

3. Results and discussion

Two constructions of linear DC plasma torch of analogical configurations were used for experimental investigation. They differed only in respect of the anode material. Firstly, a step-formed anode was made of copper. Overheated water vapour was injected in the anode side and was dissociated and ionisated in the arc channel. A large amount of ozone, which occurred as a very strong oxidizer, formed over the cooled anode surface. So, during the first operation of the system, a strong oxidation of anode surface was observed and the outflowing plasma jet assumed a green color. Therefore, a stainless steel anode was applied instead of copper to avoid oxidation. Thus, the influence of current, flow rate and discharge channel diameter on the VCC for such vortex PG with both copper and stainless steel anode is necessary to know.

The effect of the anode material is apparently visible in Fig. 3. The experimental dates are given for the same voltage, current and radial flow rate. It is important to notice that when G_2 increases by 10-12% of total flow rate, the intensity of electric field also increases. It is also visible that the generalized VCC are dropping. This means that the rising arc current leads to the decrease arc resistance. Hence, the increase of the electrical conductivity is achieved under the increase of arc column diameter and the arc voltage decreases due to the reduced resistance.

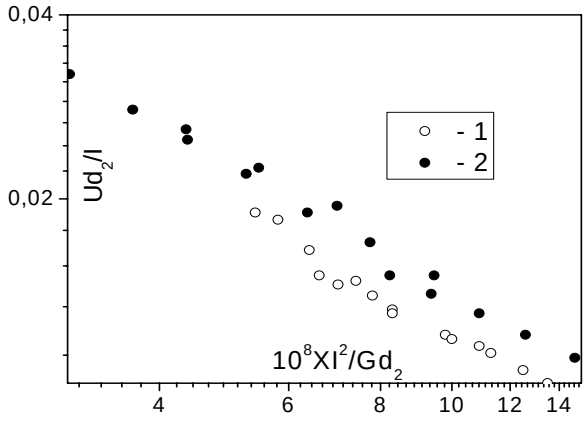

Fig. 3. Generalized characteristics of the PG with copper (1) and stainless steel (2) anode

After the analysis of the primary experimental results, VCC has been generalized on the basis of the principles of dynamic similarity theory [7].

The dependence in Fig. 3 suggests that VCC strongly depends on several factors which were established and showed in equations (1) and (2) for copper and stainless steel anode, respectively.

$$\frac{Ud_2}{I} = 8.6 \cdot 10^3 \left(\frac{I}{Gd_2}\right)^{-0.65}. \quad (1)$$

$$\frac{Ud_2}{I} = 2{,}9 \cdot 10^4 \left(\frac{I^2}{Gd_2}\right)^{-0.7}. \quad (2)$$

The relationships between the operating characteristics employing dimensionless equations describe physical phenomena in the PG. In the presented case when the plasma torch of 25 – 50 kW was used, the flow rate of vapour was (2.2 – 4.65) 10^{-3} kg s^{-1}, the arc current – 125 – 200 A, arc voltage – 180 – 260 V and the anode diameter d_2 – $8 \cdot 10^{-3}$ m. The investigation of chemical processes during the water vapour decomposition and conversion was performed using analytical equipment with optical spectrometer and gas chromatograph in a specific experimental setup (Fig.2.). It was found that copper anode effectively removes the oxygen and improves the output of hydrogen in the gasification products. The hydrogen conversion degree reaches up to 60%.

As a conclusion it can be stated that the employment of results of the present study enables constructing a specific device which allows a highly efficient production of synthetic gas containing an increased amount of hydrogen and its use in the production of second generation fuels. The injection of carbon or copper dispersed particles is considered for a better removal of dissociated oxygen.

The emission spectra of DC electric arc discharge in the argon-water vapour mixture were measured in the range of wavelength from 300 to 800 nm at 10 mm distance from the exit nozzle. Fig. 4 and Fig. 5 present the optical emission spectrum measured for the argon-water vapour (15% Ar/85% water vapour) plasma jet at the 5 mm distance from the exhaust nozzle of the anode. The experimental conditions in the emission spectra measuring (Fig. 4) were the following: the power of plasma torch – P=31.8 kW, argon flow rate – $5.2 \cdot 10^{-4}$ kg·s^{-1} and water vapor flow rate – $2 \cdot 10^{-3}$ kg·s^{-1}. In the second case (Fig. 5), the power of the torch and flow rate of water vapour were increased up to 36.2 kW and $2.63 \cdot 10^{-3}$ kg·s^{-1}, respectively, in order to examine the dependence of active species formation in the emission spectra. The main species observed in Ar/water vapour plasma were: Ar(I), Ar(II) OH, H, O(I), O(II), Cu(I), Cu(II).

The emission spectra also showed the peaks of H_α (656.2 nm), H_β (486.1 nm) and H_γ (434.1 nm), which belong to Balmer series of H_2. Visually, the H_α line tends not to be seen well due to the lack of sensitivity of the human eye in the deep red part of the spectrum, but the H_β line tends to come fairly intense. The emission intensities of the obtained peaks are quite low, because of the low energies of exited hydrogen atoms at the atmospheric pressure conditions. Consequently, the temperature of plasma jet at the nozzle exhaust of the plasma torch is high due to the intense collisions between molecules, but the energies of the exited species are low, because the mean free path is short.

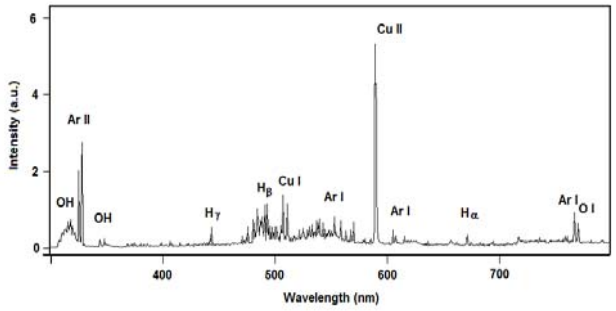

Fig. 4. Optical emission spectra of Ar/water vapour plasma jet at P=31.8 kW, flow rate of water vapour G_2=$2 \cdot 10^{-3}$ kg·s^{-1}

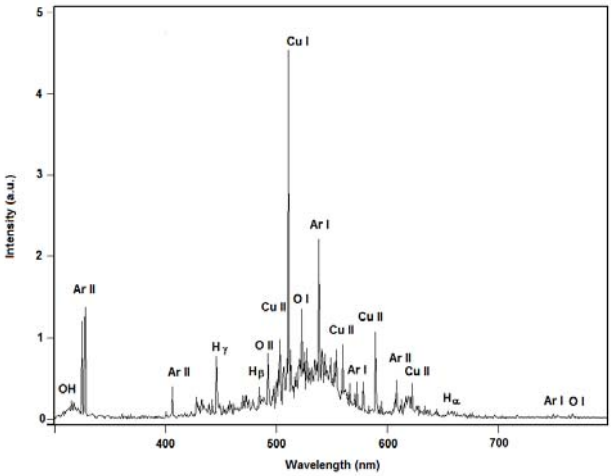

Fig. 5. Optical emission spectra of Ar/water vapour plasma jet at P=36.2 kW, flow rate of water vapour G_2=$2.63 \cdot 10^{-3}$ kg·s^{-1}

The experiments on the observation of plasma jet behaviour showed that the synthesis of hydrogen is occurring mainly on the wall of the PG anode and in the central region of plasma column inside the anode chamber. This hypothesis was tested by comparing the emission spectra of both copper and steel cases of anode compositions.

It was also observed that the intensity of copper (Cu) was much higher compared to the rest species detected. It is considered that copper anode emits Cu radicals in the plasma due to the erosion of the electrode, occurring in the discharge chamber where the electric arc spot burns. The presence of reactive atomic oxygen O(I), which forms during the ionization of water vapour, also amplifies the erosion process. This could be explained by the fact that oxygen molecule is much heavier compared to hydrogen and tries to settle down to the periphery of the anode, where it interacts with the inner wall forming the copper oxide (CuO). Hard metallic material, emitted from the outflow nozzle of the PG was collected and analyzed by X-Ray scattering technique and the results are presented in Fig. 6.

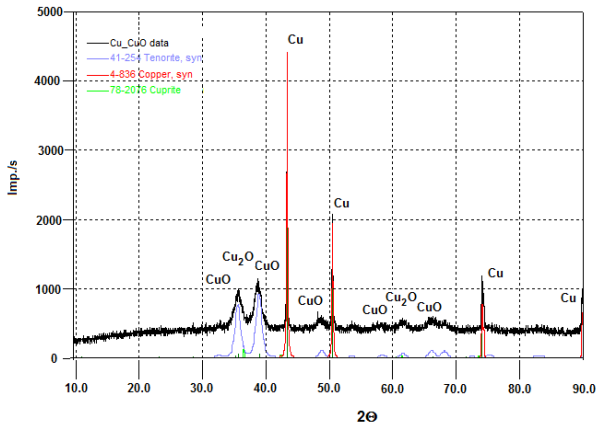

Fig. 6. Measured XRD pattern of Cu-CuO-Cu_2O mixture, emitted from the anode of the plasma torch

The main components that were found are the following: copper (Cu), cuprite (Cu_2O) and gray-to-black metallic mineral - tenorite (CuO). Naturally, tenorite occurs in addition to the hydrothermal oxidized environment, usually as a sublimation product on volcanic lavas.

Therefore, the performed spectral measurements confirmed that water vapour was decomposed into H, O and OH radicals by high voltage DC electric arc. Beside these important groups of spectral lines, the spectrum contains a large number of other lines with variable intensities, making the plasma emission spectrum rather complicated.

For further, more effective extraction of dissociated hydrogen without reversible recombination to water vapour, an original catalytic monolithic reactor was created on the basis of the catalytic coatings deposited using plasma spray technology at the atmospheric pressure (Fig.1). The coatings were deposited using catalytically active metals, metal oxides and their mixtures, such as Cu, CuO, Cr_2O_3, Ni, Al_2O_3 as described in [8]. The researchers demonstrated the low-temperature efficacy of a micro dispersed platinum-free catalyst, which could be suitable for the further purification of hydrogen.

Conclusions

The performed experimental investigation demonstrated that water vapour plasma is a potential raw material for the hydrogen-rich gas production. The regularities of the PG operating regimes influence the process of hydrogen synthesis and affect the yield of the product.

Plasma source anode material influences the elemental composition of exhaust gas and the emission spectrum of hydrogen rich gas. The copper anode enables increasing the amount of hydrogen in the exhaust gas. The synthesis of hydrogen is occurring mainly on the wall of the PG anode and in the central region of plasma column inside the anode chamber.

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References

[1] A. Fridman, *Plasma Chemistry*, Cambridge University Press, Cambridge, (2008).

[2] V. Givotov, et al, *Int. J. of Hydrogen Energy* 6 (5), 441–449 (1981).

[3] G. Petiptas, *28 ICPIG* Prague, Czech Republic, July 15-20, (2007).

[4] M. Deminsky et al, *Pure Appl. Chem.*, 74 (3), 413–418 (2002).

[5] M. Hrabovsky, *The Open Plasma Physics Journal*, 2, 99–104 (2009).

[6] V. Valinčius et al, Plasma Sources Sci. Technol., 13 (2), 199-206 (2004).

[7] M. F. Zhukov, V. Y. Smoliakov and B. A. Uriukov, *Electric Arc Gas Heaters (Plasma Generators)* (Moscow: Nauka) (1973).

[8] V. Valinčius, et al, *High Temperature Material Processes*, 10 (3), 365–378, (2006).