

Short communication

Production of hydrogen via methane reforming using atmospheric pressure microwave plasma

Mariusz Jasiński^{a,*}, Mirosław Dors^a, Jerzy Mizeraczyk^{a,b}

^a Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, Fiszerza 14, 80-952 Gdańsk, Poland

^b Department of Marine Electronics, Gdynia Maritime University, Morska 83, 81-225 Gdynia, Poland

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Abstract

In this paper, results of hydrogen production via methane reforming in the atmospheric pressure microwave plasma are presented. A waveguide-based nozzleless cylinder-type microwave plasma source (MPS) was used to convert methane into hydrogen. Important advantages of the presented waveguide-based nozzleless cylinder-type MPS are: stable operation in various gases (including air) at high flow rates, no need for a cooling system, and impedance matching. The plasma generation was stabilized by an additional swirled nitrogen flow (50 or 100 l min⁻¹). The methane flow rate was up to 175 l min⁻¹. The absorbed microwave power could be changed from 3000 to 5000 W. The hydrogen production rate and the corresponding energy efficiency in the presented methane reforming by the waveguide-based nozzleless cylinder-type MPS were up to 255 g[H₂] h⁻¹ and 85 g[H₂] kWh⁻¹, respectively. These parameters are better than those typical of the conventional methods of hydrogen production (steam reforming of methane and water electrolysis).

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1. Introduction

Methane or natural gas reforming is widely applied in industry to obtain hydrogen or synthesis gas (H₂ + CO), which then are utilized, for example as source materials for the production of raw chemicals, like methanol and ammonia, and as hydrogenation agents in the oil refinery and reducing gases in the steel industry. In the last decade, hydrogen gains in importance as fuel in the fuel cell applications, combustion engines or gas turbines with the goal to achieve a more efficient exploitation of energy sources and to reduce noxious emissions.

Conventional technologies of hydrogen production, i.e. coal gasification, hydrocarbon reforming and water electrolysis, are too expensive or not applicable for specific applications due to technical reasons. Thus, new methods are under development, like water photolysis, biological and plasma methods. Recently developed microwave plasma sources (MPSS) operated at atmo-

spheric pressure [1–6] seem to have a high potential for hydrogen production via hydrocarbon reforming.

In this paper, a method for production of hydrogen via methane reforming by the use of an atmospheric-pressure waveguide-based nozzleless cylinder-type MPS operated at high gas flow rates is presented.

2. Experimental setup

The main parts of the experimental setup used in this investigation were a microwave generator (magnetron), microwave plasma source (MPS), microwave supplying and measuring system, and gas supplying system (Fig. 1). The microwave power (2.45 GHz, 6 kW) was supplied from the magnetron to the MPS via a rectangular waveguide (WR-430) having a reduced-height section.

The waveguide-based nozzleless cylinder-type MPS (Fig. 1) was used for hydrogen production via methane reforming both without and with a catalyst (Fig. 2). As the catalyst an alumina globules ($\phi \approx 0.5$ cm) covered with the nickel oxide were used. It was a commercial high temperature catalyst (made by

* Corresponding author. Tel.: +48 58 341 12 71; fax: +48 58 341 61 44.
E-mail address: mj@imp.gda.pl (M. Jasiński).

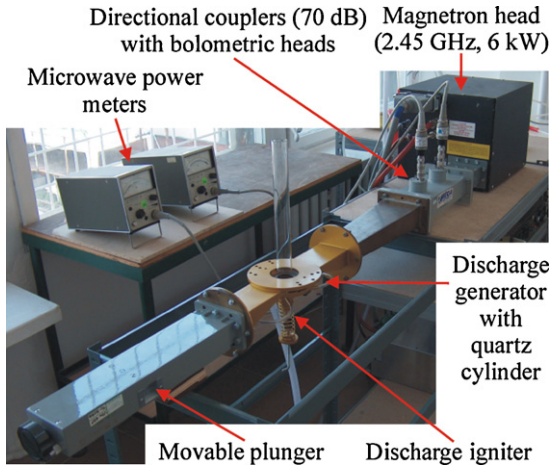


Fig. 1. Photo of the experimental setup with the waveguide-based nozzleless cylinder-type MPS.

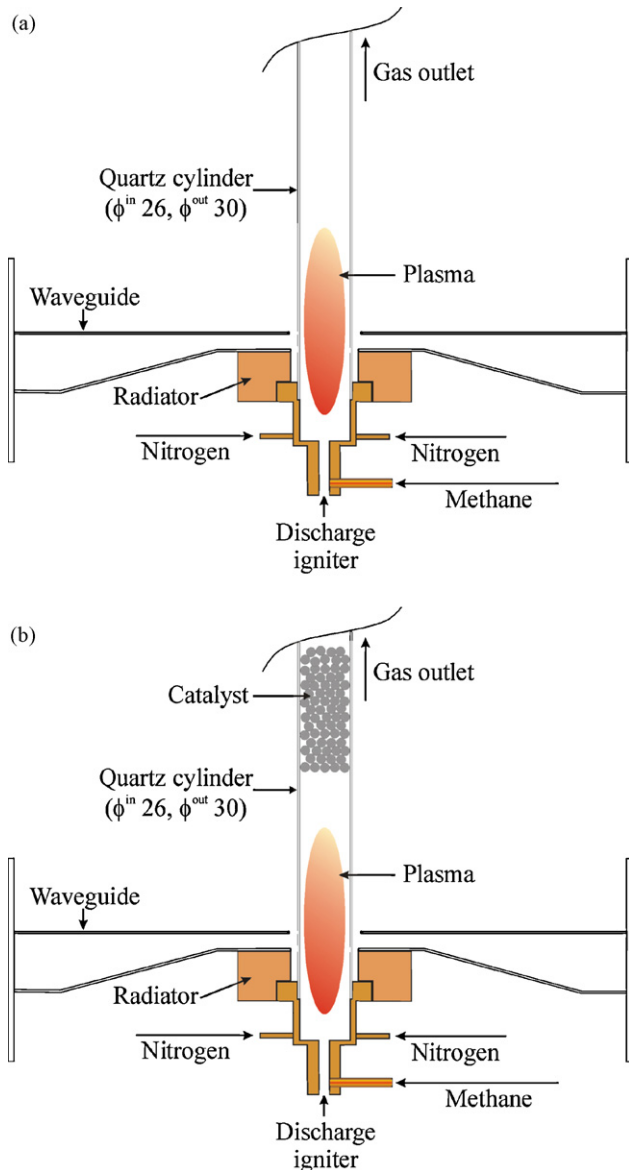


Fig. 2. Sketch of the waveguide-based nozzleless cylinder-type MPS without (a) and with a catalyst (b).

Katalizator Sp. z o.o., Kraków, Poland) used in industry for methane steam reforming, which is realized at temperature about $800\text{ }^{\circ}\text{C}$. Since our microwave plasma is of temperature even higher than $800\text{ }^{\circ}\text{C}$, we could not use catalysts based on noble metals, which are destroyed by such high temperature.

On the contrary to operating at atmospheric pressure [2,3], there was not any nozzle in our MPS. Instead, the plasma was generated straightforward inside a quartz cylinder, similarly as in [4,5]. The processed methane (up to 175 l min^{-1}) was introduced to the plasma by the central duct of MPS. The plasma generation was stabilized by forming an additional swirled nitrogen flow (50 or 100 l min^{-1}) in the quartz cylinder. The swirled gas held the discharge in the centre of the cylinder and thus protected the cylinder wall from overheating. As the swirl the nitrogen was used instead of air to avoid production of harmful oxides. When catalyst was used, then it was placed in the quartz tube as a pack of globules. The pack was fixed 15 cm from the waveguide and its length was about 15 cm .

Important advantages of the presented waveguide-based nozzleless cylinder-type MPS are: initiation of the discharge without any admixture of noble gases, stable operation in various gases (including nitrogen, air and methane) at high flow rates, no need for any special cooling system and for sophisticated impedance matching (e.g., no need for a three-stub tuner).

Diagnostics of the working gas composition before and after the microwave plasma processing of methane was carried out using hydrogen detector (Crowcon XGard), gas chromatograph (SRI 8610C) and Fourier Transform Infrared spectrophotometer (Perkin-Elmer 16 PC).

3. Results

A photo of the atmospheric pressure microwave discharge generated in methane–nitrogen mixture by the waveguide-based nozzleless cylinder-type MPS is shown in Fig. 3. The inner diameter of the used quartz discharge tube was 26 mm .

The dependence of the reflection coefficient P_R/P_I (P_R –reflected microwave power, P_I –incident microwave power) on incident microwave power P_I for different methane flow rates Q at the best microwave system matching (corresponding to the optimum position of the movable plunger shown in Fig. 1) is presented in Fig. 4. It seems that the better matching was obtained for lower microwave power (e.g., for $P_I < 4500\text{ W}$, $P_R/P_I \approx 5\%$).



Fig. 3. Photo of the atmospheric pressure microwave discharge in methane generated by the waveguide-based nozzleless cylinder-type MPS. The methane flow rate (central flow) and the nitrogen flow rate (swirl flow) were 175 and 100 l min^{-1} , respectively. The absorbed microwave power was 4000 W .

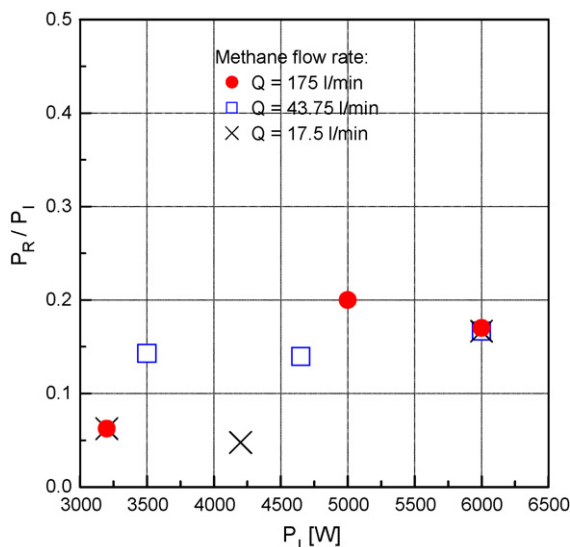


Fig. 4. The reflection coefficient P_R/P_I vs. incident microwave power P_I for different methane flow rates. The nitrogen swirl flow rate was 501 min^{-1} .

However, the methane plasma could not be sustained at the microwave power lower than about 3000 W. More research is needed to improve the presented MPS performance in terms of minimum reflected power.

The hydrogen was detected using hydrogen detector and calculated from the balance of exit products.

Fig. 5 shows FTIR spectrum (a) and chromatogram (b) of the working gas mixture after the microwave plasma processing at absorbed microwave power of 3000 W, methane flow rate of 1751 min^{-1} and swirl nitrogen flow rate of 501 min^{-1} . As it can be seen from the after-process spectrum and chromatogram, unprocessed methane CH_4 and acetylene C_2H_2 were found as by-product in the exit gas. The methane decomposed to hydrogen H_2 , acetylene C_2H_2 and carbon (soot). The soot deposit could be easily noticed on the reactor walls. The soot deposition started just after plasma ignition, however not all soot deposited on the reactor walls. Major part of the soot was blown off the reactor by the high gas flow. As a result, the thickness of the soot layer deposited on the reactor walls has not exceeded 2 mm and did not influence the reactor lifetime.

For example, at the methane flow rate of 1751 min^{-1} and swirl nitrogen flow rate of 501 min^{-1} , the production rate of the soot varied from 330 g h^{-1} (at an absorbed microwave power of 5000 W) up to 600 g h^{-1} (at an absorbed microwave power of 3000 W). At the same conditions, the production rate of acetylene C_2H_2 was in the range of $174\text{--}98 \text{ g h}^{-1}$.

As mentioned, the hydrogen production process was carried out for two cases: without and with catalyst.

The energetic parameters of the hydrogen production via the methane reforming, i.e., the production rate of hydrogen in $\text{g}[\text{H}_2]\text{h}^{-1}$ and energy efficiency of hydrogen production in $\text{g}[\text{H}_2]\text{kWh}^{-1}$ for the case when catalyst was not used can be inferred from Figs. 6 and 7.

Fig. 6a and b shows the production rate of hydrogen and the energy efficiency of hydrogen production as a function of absorbed microwave power for different conditions at methane

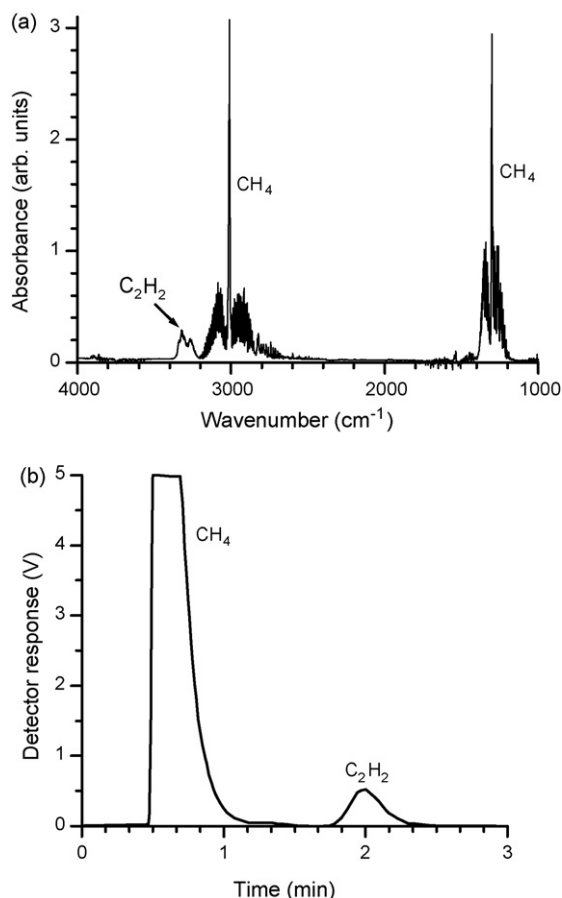


Fig. 5. FTIR spectra (a) and chromatogram (b) of the working gas mixture after the microwave plasma processing. Absorbed microwave power: 3000 W, methane flow rate: 1751 min^{-1} , nitrogen flow rate: 501 min^{-1} .

flow rate of 1751 min^{-1} . At the best condition, i.e., at the swirl nitrogen flow rate of 501 min^{-1} and absorbed microwave power of 3000 W, the production rate of hydrogen and the energy efficiency of hydrogen production reached about $222 \text{ g}[\text{H}_2]\text{h}^{-1}$ and $74 \text{ g}[\text{H}_2]\text{kWh}^{-1}$, respectively. Both process parameters decreased with increasing microwave power. It was caused by changes in the kinetics of the chemical reactions involved. It was observed that increasing absorbed microwave power, the length of plasma increased. Since a higher microwave power results in a higher resident time of the processed gas in the plasma region, the conversion of methane to acetylene exceeded that to hydrogen when increasing microwave power from 3000 to 5000 W.

At the swirl nitrogen flow rate of 1001 min^{-1} , the above energetic parameters were about 1.2 times lower than those obtained at the best condition. This was caused by lower working gas temperature. Addition of argon (201 min^{-1}) added to the methane flow decreased the energetic parameters about three times. This resulted from loss of the microwave energy in the excitation and ionisation processes of argon, which do not contribute in the methane conversion reactions.

The production rate of hydrogen and the energy efficiency of hydrogen production versus absorbed microwave power at a lower swirl nitrogen flow rate (501 min^{-1}) for different methane

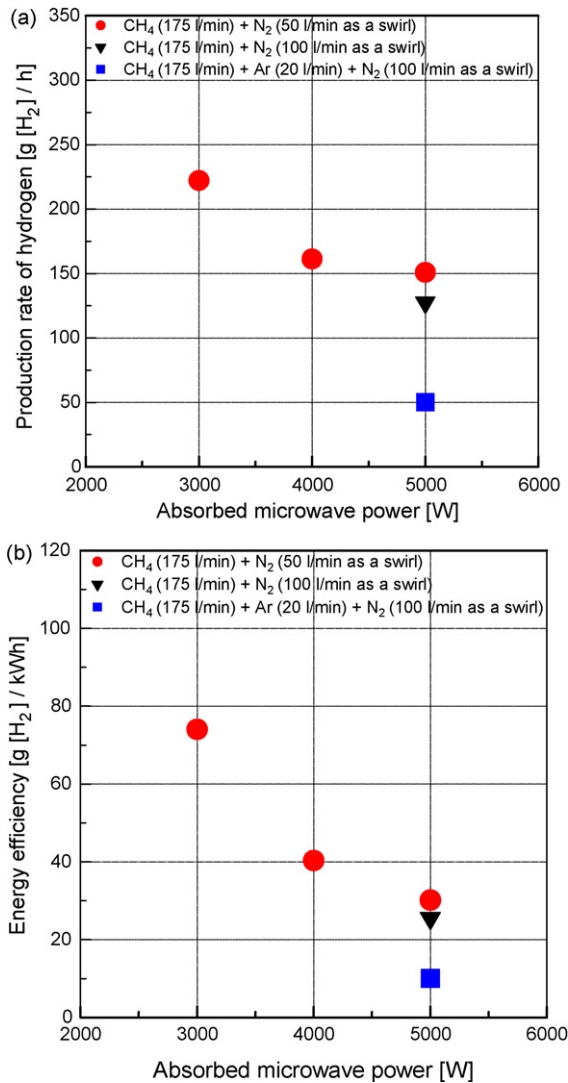


Fig. 6. The production rate of hydrogen (a) and the energy efficiency of hydrogen production (b) vs. absorbed microwave power for different conditions. The methane flow rate was 175 l min⁻¹.

flow rates are shown in Fig. 7a and b, respectively. As it is seen from these figures, the production rate of hydrogen and the energy efficiency of hydrogen production decrease with increasing absorbed microwave power at higher methane flow rates (175 l min⁻¹).

At the best condition, i.e. when the flow rates of methane and nitrogen were 175 l min⁻¹ of 50 l min⁻¹, respectively, and the absorbed microwave power was 3000 W, the methane reforming was carried out also using a catalyst [alumina globules ($\phi \approx 0.5$ cm) covered with the nickel oxide] as shown in Fig. 2b. The use of the catalyst increased both the production rate of hydrogen and the energy efficiency of hydrogen production by about 15%, i.e. up to 255 g[H₂] h⁻¹ and 85 g[H₂] kWh⁻¹, respectively. Since initial composition of gas processed in our experiment is far from that for which the catalyst was designed (i.e., lack of water vapour which is a key element in the methane steam reforming process with nickel-based catalysts), we could not expect higher increase.

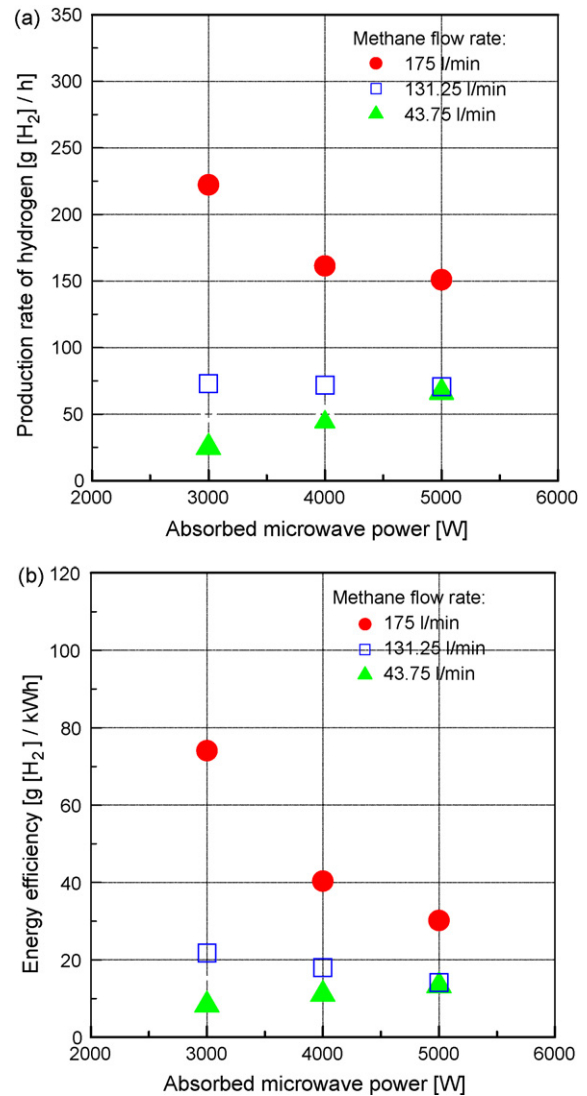


Fig. 7. The production rate of hydrogen (a) and the energy efficiency of hydrogen production (b) vs. the absorbed microwave power for different methane flow rates. The swirl nitrogen flow rate was 50 l min⁻¹.

Comparison of the energy efficiencies of hydrogen production for different conventional and plasma methods is given in Table 1. In general, the conventional methods (steam reforming [7] water electrolysis [8]) exhibit lower energy efficiency of hydrogen production than plasma methods, except for the dielectric barrier discharge [9]. As seen from Table 1, the energy efficiency of hydrogen production by the conventional methods is 3–4 times lower than that in the presented investigation. It is worth mentioning that the method presented by us is more efficient than in other plasma methods operated without a catalyst (dielectric barrier discharge [9] and gliding arc [10]).

At the methane flow rate of 175 l min⁻¹ and swirl nitrogen flow rate of 50 l min⁻¹, the total conversion efficiency of methane $[(CH_4)_{conv}/(CH_4)_{tot} \times 100\%]$ was from about 9.5% (at an absorbed microwave power of 5000 W) up to 13.2% (at 3000 W), where $(CH_4)_{tot}$ is the total (initial) mass of CH₄, and $(CH_4)_{conv}$ is the converted mass of CH₄.

Table 1

Comparison of the energy efficiency of hydrogen production via methane reforming for different methods (including our results)

Hydrogen production method	Initial gas composition	Energy efficiency [g[H ₂]/kWh ⁻¹]
Conventional methods		
Steam reforming of methane [7]	CH ₄ + H ₂ O + air	20
Water electrolysis [8]	–	21
Plasma methods		
Waveguide-based cylinder-type MPS (our results without catalyst)	CH ₄ + N ₂	74
Waveguide-based cylinder-type MPS (our results with catalyst)	CH ₄ + N ₂	85
Dielectric barrier discharge [9]	CH ₄ + air	6.7
Gliding arc [10]	CH ₄ + H ₂ O + air	40
Plasmatron with catalyst [11]	CH ₄ + H ₂ O + air	225

At the methane flow rate of 175 l min⁻¹ and swirl nitrogen flow rate of 50 l min⁻¹, the yield of hydrogen [H₂/(2CH₄)_{tot} × 100%] was from about 8.7% (at an absorbed microwave power of 5000 W) up to 12.8% (at 3000 W).

At the same conditions, the selectivity of hydrogen [H₂/(2CH₄)_{conv} × 100%] was from about 91.9% (at an absorbed microwave power – 5000 W) up to 96.8% (at 3000 W).

When air is used as an additive to methane, as for example in the methane steam reforming [7], the emission of oxide compounds, e.g., carbon oxides and nitrogen oxides, is expected. Our experiment was carried out without any admixture of air, thus we avoided emission of any oxygen compounds usually harmful.

4. Conclusions

The results of this investigations show that the production rate of hydrogen (up to 255 g[H₂]/h⁻¹) and the energy efficiency of hydrogen production (up to 85 g[H₂]/kWh⁻¹) by atmospheric pressure microwave plasma are attractive. The absence of oxygen compounds as by-products in the off-gas is highly beneficial. The proposed atmospheric pressure microwave plasma system for hydrogen production via methane reforming is expected to be of low cost and effective, and thus promising for applications.

Acknowledgements

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References

- [1] M. Moisan, G. Sauve, Z. Zakrzewski, J. Hubert, Plasma Sources Sci. Technol. 3 (1994) 584.
- [2] M. Moisan, Z. Zakrzewski, J.C. Rostaining, Plasma Sources Sci. Technol. 10 (2001) 387.
- [3] M. Jasiński, J. Mizeraczyk, Z. Zakrzewski, T. Ohkubo, J.S. Chang, J. Phys. D: Appl. Phys. 35 (2002) 2274.
- [4] K.M. Green, M.C. Borrás, P.P. Woskow, G.J. Flores, K. Hadidi, P. Thomas, IEEE Trans. Plasma Sci. 29 (2001) 399.
- [5] H.S. Uhm, Y.C. Hong, D.H. Shin, Plasma Sources Sci. Technol. 15 (2006) S26.
- [6] M. Jasiński, Z. Zakrzewski, J. Mizeraczyk, Proceedings of the 16th Symp. on Application of Plasma Processes “SAAP2007”, Podbanske, Slovakia, 2007, p. 165.
- [7] P.L. Spath, M.K. Mann, National Renewable Energy Laboratory Technical Report, 2001 (NREL/TP-570-27637).
- [8] <http://www.loim.vrn.ru/index.php?m=63&page=58&nm=74&p=.2.3.56.64.70.71.72.73.74>.
- [9] M. Heintze, B. Pietruszka, Catal. Today 89 (2004) 21.
- [10] J.M. Cormie, I. Rusu, J. Phys. D: Appl. Phys. 34 (2001) 2798.
- [11] L. Bromberg, D.R. Cohn, A. Rabinovich, N. Alexeev, A. Samokhin, R. Ramprasad, S. Tamhankar, Int. J. Hydrogen Energy 25 (2000) 1157.