**Regular** Article

# Application of atmospheric pressure microwave plasma source for production of hydrogen via methane reforming

M. Jasiński<sup>1</sup>, M. Dors<sup>1,a</sup>, and J. Mizeraczyk<sup>1,2</sup>

 $^2\,$ Dept. of Marine Electronics, Gdynia Maritime University, Morska 83, 81-225 Gdynia, Poland

Received 5 September 2008 / Received in final form 8 October 2008 Published online 28 November 2008 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2008

**Abstract.** In this paper, results of hydrogen production via methane pyrolysis in the atmospheric pressure microwave plasma with  $CH_4$  swirl are presented. A waveguide-based nozzleless cylinder-type microwave plasma source (MPS) was used to convert methane into hydrogen. The plasma generation was stabilized by a  $CH_4$  swirl having a flow rate of 87.5 L min<sup>-1</sup>. The absorbed microwave power was 1.5-5 kW. The hydrogen production rate and the corresponding energy efficiency were 866 g  $(H_2)$  h<sup>-1</sup> and 577 g  $(H_2)$  kWh<sup>-1</sup> of microwave energy absorbed by the plasma, respectively. These parameters are better than our previous results when nitrogen was used as a swirl gas and much better than those typical for other plasma methods of hydrogen production (electron beam, gliding arc, plasmatron).

**PACS.** 52.50.Dg Plasma sources – 52.50.Sw Plasma heating by microwaves; ECR, LH, collisional heating – 82.30.Lp Decomposition reactions – 84.40.Dc Microwave circuits

### **1** Introduction

Methane or natural gas reforming is widely used in industry to obtain hydrogen or synthesis gas (H<sub>2</sub>+CO), which are utilized in industry, for example as source materials for the production of raw chemicals (e.g. methanol and ammonia), as well as hydrogenation agents in oil refinery and reducing gases in steel industry. Recently hydrogen gains in importance as fuel in fuel cell applications, combustion engines or gas turbines with the goal to achieve more efficient exploitation of energy sources and to reduce noxious emissions [1].

Usual reforming of methane is carried out thermally with steam and oxygen where oxidation of methane takes place to provide reaction heat because the methane reforming reaction using steam is endothermic. The main reaction in the steam reforming of methane is the oxidation with steam, yielding a mixture of hydrogen and carbon monoxide:

$$CH_4 + H_2O \leftrightarrow CO + 3 H_2, \Delta H_{298} = 206 \text{ kJ mol}^{-1}.$$
 (1)

Since that process is highly endothermic, to decrease activation energy, it requires catalyst, which is usually  $Ni/Al_2O_3$  working at temperature 1100–1150 K. Hence the reforming system is sensible to impurities in substrates which deactivates catalysts.

Conventional technologies of hydrogen production, i.e. coal gasification, hydrocarbon reforming and water electrolysis, are too expensive or not applicable for specific applications (e.g. for fuel cells) due to technical reasons. Thus, new methods are under development, like water photolysis, biological and plasma methods.

One of the attractive methods for reforming hydrocarbons to produce hydrogen is the use of plasmas [1-19]. The plasma contains reactive radicals, ions and highlyenergetic electrons. High reactivity shown by these species enhances the chemical reaction rates whereby expensive and impurity vulnerable catalysts can be avoided. These advantages as well as its high energy density ensure the compactness of the plasma reformer. Besides, the plasma system can be adapted for reforming various hydrocarbons, like natural gas, gasoline, heavy oils and biofuels. Fast response time can be also achieved because the plasma is operated by electricity. When steam is used as the plasma supporting gas, reductive and oxidative radicals such as H, OH, and O, are produced in the plasma, enabling the plasma to be effective for reforming different hydrocarbons.

Recently developed microwave plasma sources (MPSs) operated at atmospheric pressure [7,8,18–27] seem to have a high potential for hydrogen production via hydrocarbon reforming. The microwave plasma at atmospheric pressure is one of the plasma techniques providing the electron

<sup>&</sup>lt;sup>1</sup> Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, Fiszera 14, 80-952 Gdañsk, Poland

<sup>&</sup>lt;sup>a</sup> e-mail: mdors@imp.gda.pl

temperature of 4000-10000 K, and the heavy particle temperature of 2000-6000 K [22-27].

Our previous investigations in methane conversion to hydrogen [19] were carried out using methane  $(17.5-175 \text{ Lmin}^{-1})$  and nitrogen swirl  $(50-100 \text{ Lmin}^{-1})$  at relatively high absorbed microwave powers (3000-5000 W). The best conditions corresponded to the absorbed microwave power of 3000 W and methane flow rate of 175 Lmin<sup>-1</sup>. Since the hydrogen production presented in [19] was carried out in the presence of nitrogen without any oxygen carriers, the main chemical reaction producing hydrogen was methane pyrolysis.

Presence of nitrogen as well as methane conversion byproducts, i.e. acetylene and unconverted methane, necessitate to separate hydrogen from other gaseous components using a pressure swing adsorbent (PSA) unit or membrane filter unit. In order to avoid separation process we propose to use methane as the only gas entering the plasma generator. Results of methane conversion to hydrogen without any other gaseous admixture are presented in this paper.

## 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. Below the reduced-high section a radiator conducting heat from the microwave plasma source was placed.

The absorbed microwave power  $P_A$ , i.e. microwave power delivered to the discharge was calculated as  $P_I - P_R$ , where  $P_I$  and  $P_R$  are the incident and reflected microwave powers, respectively. The incident and reflected microwave powers  $P_I$  and  $P_R$  were directly measured using directional coupler equipped with bolometric heads and HP power meters (Fig. 1).

For hydrogen production via methane conversion we used similar waveguide-based nozzleless cylinder-type MPS as in our previous work (Fig. 2, [19]). In contrary to the previous work, the processed methane (87.5 L min<sup>-1</sup>) was introduced to the plasma not by the central duct of MPS but in the form of a swirl. The swirl concentrated near the quartz cylinder wall and stabilized plasma generation. The swirl held the discharge in the centre of the cylinder and thus protected the cylinder wall from overheating. The inner diameter of the quartz discharge tube was 26 mm.

Moreover, we added external and internal cylindrical electrodes to the MPS. The external electrode was a copper cylinder shielding the quartz one. The diameter of the external cylindrical electrode was 46 mm, so microwave at frequency of 2.45 GHz cannot be guided along it (operation below the cut-off frequency). This causes lower losses of microwave energy, i.e., the higher microwave power is delivered to the unit volume of the plasma. The internal cylindrical electrode was a bras tube of outer diameter



**Fig. 1.** (Color online) Photo of the experimental setup with the waveguide-based nozzleless cylinder-type MPS.



**Fig. 2.** (Color online) Sketch of the waveguide-based nozzleless cylinder-type MPS.



Fig. 3. FTIR spectra of the working gas mixture after the microwave plasma processing. Absorbed microwave power: 5000 W, methane flow rate:  $87.5 \text{ Lmin}^{-1}$ .

20 mm. This inner electrode forms a section of microwave coaxial line, which causes that maximum of the electric field corresponds to the down position of the plasma. We observed that the inner electrode improved the stability of plasma generation.

Important advantages of the presented waveguidebased nozzleless cylinder-type MPS are: stable operation in various gases (including  $CO_2$ , air and methane) at high flow rates, easy initiation of the discharge in various gases without any admixture of noble gases, 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 gas chromatograph (SRI 8610C) and Fourier transform infrared spectrophotometer (Perkin Elmer 16 PC). Production of hydrogen was calculated from methane and its conversion products mass balance.

#### 3 Results

Diagnostics of the exit gas composition showed that unprocessed methane was found as the only gaseous byproducts resulting from methane conversion in microwave plasma (Fig. 3). The methane decomposed to hydrogen  $H_2$  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.

Concentrations of  $H_2$  and  $CH_4$  in the exit gas depend on the absorbed microwave power (Fig. 4). At the power of 1.5 kW concentrations of hydrogen and methane were 99.88% and 0.12%, respectively, whereas at the power of 5 kW they were 99.94% and 0.06%, respectively. Thus, the total methane decomposition degree



Fig. 4. (Color online) Concentrations of methane and hydrogen resulting from methane conversion using the waveguidebased nozzleless cylinder-type MPS. Methane flow rate  $87.5 \text{ Lmin}^{-1}$ .

 $((CH_4)_{conv}/(CH_4)_{tot} \times 100\%)$  was 99.76–99.88%, where  $(CH_4)_{tot}$  is the total (initial) mass of  $CH_4$ , and  $(CH_4)_{conv}$  is the converted mass of  $CH_4$ . The selectivity of methane conversion to hydrogen  $(H_2/(2CH_4)_{conv} \times 100\%)$  was 100%. Such a high selectivity as well as lack of other gaseous by-products and significant production of soot show that reaction of methane pyrolysis was the main path of methane conversion into hydrogen.

The energetic parameters of the hydrogen production via the methane pyrolysis, i.e. the hydrogen production rate and energy efficiency were up to 866 g (H<sub>2</sub>) h<sup>-1</sup> and 577 g (H<sub>2</sub>) kWh<sup>-1</sup> of microwave energy absorbed by the plasma, respectively. In our experiment, the plug efficiency of the microwave magnetron generator was higher than 66%, so taking into account this efficiency, the energy efficiency of hydrogen production is 381 g (H<sub>2</sub>) kWh<sup>-1</sup> of electrical energy used.

Comparison of the energy efficiency of hydrogen production for different methods in which electric energy is directly used for methane conversion into hydrogen, is given in Table 1.

It must be pointed out that the energy efficiency of hydrogen production shown in Table 1 take into account only the electrical energy used in the reforming (in some cases it is not clear either the total electric energy used or absorbed by the plasma is considered). In the plasma methods presented in Table 1, the energy equivalent of methane used in the reforming was not considered.

It is seen from Table 1 that the plasma methods (except the electron beam [9] and dielectric barrier discharge [13]) exhibit higher energy efficiency of hydrogen production than the conventional water electrolysis [29]. However, when the energy equivalent of methane used in the conversion is taken into account, the energy efficiency of hydrogen production for the plasmatron with catalyst [2] and our method presented in this paper, which exhibit the highest yields, are comparable with that of the conventional water electrolysis.

**Table 1.** Comparison of the energy efficiency of hydrogen production for different methods in which electric energy is directly used for methane conversion into hydrogen.

Hydrogen	Initial	Energetic
production method	$\operatorname{composition}$	mass yield
		$(g~(H_2)~kWh^{-1})$
Conventional methods		
Water electrolysis [29]	$\mathrm{H}_{2}\mathrm{O}$	21
Plasma methods		
Waveguide-based cylinder-type MPS (this paper)	$\mathrm{CH}_4$	381*
Waveguide-based cylinder-type MPS [19]	$\mathrm{CH}_4 + \mathrm{N}_2$	85
Electron beam $[9]$	$\mathrm{CH}_4 + \mathrm{H}_2\mathrm{O}$	3.6
Dielectric barrier discharge [13]	$\mathrm{CH}_4 + \mathrm{air}$	6.7
Gliding arc [4]	$CH_4 + H_2O + air$	40
Plasmatron with catalyst [2]	$CH_4 + H_2O + air$	225

\* total electric energy used.

Comparing results presented in this paper with those obtained by us when using nitrogen swirl with methane introduced to plasma by the central duct (Tab. 1, [19]) one can see that we improved much the energy efficiency of hydrogen production. The total methane decomposition degree, reaching 99.88%, was also much higher than 13.2% presented in [19]. We suppose that residence time of methane in high temperature region is the reason of such different results. When nitrogen swirl was used then it cooled space in the plasma vicinity causing that high temperature region was limited to plasma only. However, when only methane was introduced into the reactor there was no cooling gas and high temperature region expands beyond plasma. As a result methane residence time in high temperature region was much longer comparing to that in the experiment with nitrogen swirl.

Considering both the cost of methane and the total energy consumption (including losses in power supplies), nowadays, among the hydrogen production methods, it seems that the conventional steam reforming of methane [28] ensures the lowest cost of hydrogen production. However, the conventional steam reforming of methane is a large volume hydrogen production method. When the distributed hydrogen production method are considered, the microwave plasma method presented in this paper seems to be attractive.

#### 4 Conclusions

The results of this investigations show that the energetic parameters of the hydrogen production, i.e. the hydrogen production rate (866 g (H<sub>2</sub>) h<sup>-1</sup>) and the energy efficiency (577 g (H<sub>2</sub>) kWh<sup>-1</sup>), via methane pyrolysis in the atmospheric pressure microwave plasma are attractive.

Taking into account the energy losses in the microwave power supply ( $\sim$ 33%), the energy efficiency of hydrogen production reaches about 381 g (H<sub>2</sub>) kWh<sup>-1</sup> of the total electric energy used.

The proposed atmospheric pressure microwave plasma system for hydrogen production via methane pyrolysis is expected to be of low cost and effective, and thus promising for applications in the distributed hydrogen production.

This research was supported by the Ministry of Science and Higher Education (MNiSW) under the programme 3020/T02/2006/31.

## References

- G. Petitpas, J.-D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Metkemeijer, L. Fulcheri, Int. J. Hydrogen Energy **32**, 2848 (2007)
- L. Bromberg, D.R. Cohn, A. Rabinovich, N. Alexeev, A. Samokhin, R. Ramprasad, S. Tamhankar, Int. J. Hydrogen Energy 25, 1157 (2000)
- L. Bromberg, D.R. Cohn, A. Rabinovich, N. Alexeev, Int. J. Hydrogen Energy 24, 1131 (1999)
- J.M. Cormie, I. Rusu, J. Phys. D: Appl. Phys. 34, 2798 (2001)
- N. Reveau, M. Nikravech, O. Martinie, P. Lefaucheux, J.M. Cormier, in *Proc. HAKONE VII*, Greifswald, Germany, 2000, pp. 252–256
- A. Czernichowski, M. Czernichowski, P. Czernichowski, in Proc. 16th Int. Symp. on Plasma Chemistry, Taormina, Italy, 2003, p. 578
- 7. H. Sekiguchi, Y. Mori, Thin Solid Films 435, 44 (2003)
- H. Sekiguchi, S. Nakanishi, K. Fukuda, H. Inagaki, in Proc. 16th Int. Symp. on Plasma Chemistry, Taormina, Italy, 2003, p. 598
- T. Kappes, W. Schiene, T. Hammer, in Proc. 8th Int. Symp. on High Pressure Low Temperature Plasma Chemistry, Puhajarve, Estonia, 2002, pp. 196–200
- H. Kabashima, H. Einaga, S. Futamura, IEEE Trans. Ind. Appl. 39, 340 (2003)
- S. Futamura, H. Kabashima, L. Ma, in Proc. 4th Int. Symp. on Non-thermal Plasma Technology for Pollution Control and Sustainable Energy Development, Panama City Beach, Florida, USA, 2004, pp. 211–215
- B. Pietruszka, K. Anklam, M. Heintze, Appl. Catal. A 261, 19 (2004)
- 13. M. Heintze, B. Pietruszka, Catal. Today 89, 21 (2004)
- B. Pietruszka, K. Anklam, M. Heintze, in 16th Int. Symp. on Plasma Chemistry, Taormina, Italy, 2003, p. 582
- O. Mutaf-Yardimci, A.V. Saveliev, A.A. Fridman, L.A. Kennedy, Int. J. Hydrogen Energy 23, 1109 (1998)

- J.S. Chang, Y. Uchida, M. Ara, J.T. Kim, K. Urashima, J.F. Kelly, M. Stanciulescu, R. Burisch, J.P. Charland, in Proc. 4th Int. Symp. on Non-thermal Plasma Technology for Pollution Control and Sustainable Energy Development, Panama City Beach, Florida, USA, 2004, pp. 216–220
- T. Kappes, T. Hammer, in Proc. 4th Int. Symp. on Non-thermal Plasma Technology for Pollution Control and Sustainable Energy Development, Panama City Beach, Florida, USA, 2004, pp. 206–210
- M. Deminsky, V. Jivotov, B. Potapkin, V. Rusanov, Pure Appl. Chem. 74, 413 (2002)
- M. Jasiński, M. Dors, J. Mizeraczyk, J. Power Sources 181, 41 (2008)
- M. Moisan, G. Sauve, Z. Zakrzewski, J. Hubert, Plasma Sources Sci. Technol. 3, 584 (1994)
- M. Moisan, Z. Zakrzewski, J.C. Rostaining, Plasma Sources Sci. Technol. 10, 387 (2001)

- M. Jasiński, J. Mizeraczyk, Z. Zakrzewski, Czech. J. Phys. 52, 421 (2002)
- M. Jasiński, J. Mizeraczyk, Z. Zakrzewski, T. Ohkubo, J.S. Chang, J. Phys. D: Appl. Phys. 35, 2274 (2002)
- M. Jasiński, J. Mizeraczyk, Z. Zakrzewski, J. Adv. Oxid. Technol. 7, 51 (2004)
- J. Mizeraczyk, M. Jasiński, Z. Zakrzewski, Plasma Phys. Contr. Fusion 47, 589 (2005)
- K.M. Green, M.C. Borras, P.P. Woskow, G.J. Flores, K. Hadidi, P. Thomas, IEEE Trans. Plasma Sci. 29, 399 (2001)
- H.S. Uhm, Y.C. Hong, D.H. Shin, Plasma Sources Sci. Technol. 15, S26 (2006)
- P.L. Spath, M.K. Mann, National Renewable Energy Laboratory Technical, Report, 2001, NREL/TP-570-27637
- 29. http://www.loim.vrn.ru/index.php?m=63& page=58\&nm=74&p=.2.3.56.64.70.71.72.73.74