



Hydrogen Production via Synthetic Biogas Reforming in Atmospheric-Pressure Microwave (915 MHz) Plasma at High Gas-Flow Output

B. Hrycak¹ · D. Czyłkowski¹ · M. Jasiński¹ · M. Dors¹ · J. Mizeraczyk²

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Abstract

This paper is a contribution to the development of microwave plasma-based technology for hydrogen (H_2) production from a so-called synthetic biogas, considered as a mixture of methane (CH_4) and carbon dioxide (CO_2). The efficiency of hydrogen production via reforming of CH_4 in the synthetic biogas flowing through a waveguide-supplied metal cylinder-based microwave plasma source (MPS) operating at atmospheric pressure was tested experimentally. The MPS operated at a frequency of 915 MHz. The working plasma-forming gas was a mixture of $CH_4:CO_2$ of volume ratios from 0 to 1. Its flow rate was varied from 3 to 12 m^3/h . The microwave power absorbed by the plasma was up to 7.5 kW. The experiment showed that using this kind of MPS, the plasma processing of the synthetic biogas can be run stably at high flow rates (up to 12 m^3/h). The optimal $CH_4:CO_2$ ratio in terms of high energy efficiency of the microwave plasma reforming of CH_4 was found to be 40:60. The maximum achieved hydrogen production rate was 156 $g(H_2)/h$ at a microwave absorbed power of 7.5 kW (at a flow rate of 6 m^3/h) with the energy efficiency of hydrogen production of 21 $g(H_2)/kWh$. The maximum energy yield of hydrogen production of 24 $g(H_2)/kWh$ was achieved at 4.5 kW of the microwave absorbed power (the hydrogen production rate was 108 $g(H_2)/h$ in this condition). The maximum methane conversion degree and maximum hydrogen selectivity were 86.5% and 73.3%, respectively at an absorbed microwave power of 6.5 kW (at 3 m^3/h).

Keywords Microwave reforming of biogas · Dry reforming · Microwave plasma · Hydrogen production · Microwave plasma reforming

✉ B. Hrycak
bhrycak@imp.gda.pl

¹ Institute of Fluid Flow Machinery, Polish Academy of Sciences, Fiszerka 14, 80-231 Gdańsk, Poland

² Department of Marine Electronics, Gdynia Maritime University, Morska 81-87, 81-225 Gdynia, Poland

Introduction

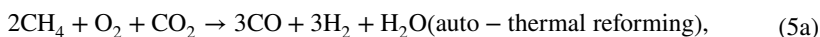
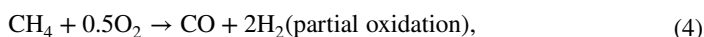
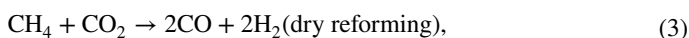
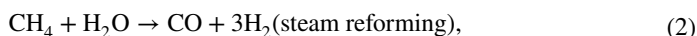
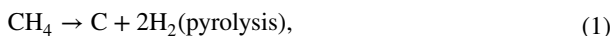
Effective energy sources alternative to fossil-based fuels become the main area of research for sustainable energy development. The declining reserves of fossil fuels and the thread of global warming impose that the newly developed energy source must simultaneously meet the requirements of being renewable and ecological. In this aspect hydrogen (H_2) is one of the most promising renewable and environmentally clean energy sources. The technologies related to H_2 production from fossil fuels and other resources have been described in many review papers, e.g. [1–4].

Although H_2 has a high combustion heat (142 kJ/g) [1], it is envisaged to be used in the future as an energy carrier for activating the fuel cells [5–8] rather than a fuel for heat production through the combustion [9]. The applicability of hydrogen for fuel cells boosts an interest in new sources and production methods of hydrogen. Biogas is regarded as a new ecological and renewable hydrogen source. It becomes an alternative for methane (CH_4), which has so far been a common hydrogen source [2].

Biogas is a gas formed during the breakdown of organic matter in the absence of oxygen. It can be produced from raw materials such as green waste, household waste, agricultural waste, municipal waste, sewage etc. [10]. Biogas is a hydrogen carrier similar to fossil natural gas. Methane (CH_4), carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), ammonia (NH_3), volatile organic compounds (VOCs), including organic silicon compounds, halogenated compounds and sulphur compounds (mainly hydrogen sulphide (H_2S)) are components of biogas from landfills, waste water treatment plants (WWTP) sludge digesters and biogas plants processing different materials [11, 12]. The content of CH_4 in the biogas from landfills, WWTPs and biogas plants usually ranges from 50 to 70%, CO_2 content—from 35 to 45% and N_2 content—from 1 to 3%. O_2 content is less than 1%. Biogas can also contain water vapour (H_2O), carbon oxide (CO) and particulate matter. Thus, the main components of typical biogas are: CH_4 and CO_2 . It should be pointed out that the origin of CO_2 in biogas produced from plants is ecologically neutral because it is absorbed by the plants from the atmosphere. The production-and-use cycle of biogas is continuous, and it does not generate any net CO_2 . These attributes make biogas a renewable and ecological hydrogen source [11, 13].

For many of the applications biogas has to be cleaned from some components and upgraded in terms of higher concentration of CH_4 in it [1, 14]. For example, the typical concentration of corrosive H_2S in raw biogas is enough to destroy the biogas installations and devices [15]. To have the same standards as fossil natural gas, biogas has to be cleaned and upgraded to natural gas standards to become bio-methane, which consisting of 98% of CH_4 is capable of being used in local natural gas networks. In particular, both cleaning and upgrading have most likely to be applied, if high-purity H_2 for activating the fuel cells is expected to be obtained from biogas.

Since the major component of biogas is CH_4 , several conventional CH_4 reforming processes can be adopted for producing hydrogen from biogas. They are pyrolysis, steam reforming, dry reforming, partial oxidation, auto-thermal reforming:





The conventional methods (1)–(5a and 5b) for producing hydrogen from biogas have been broadly discussed in many papers (e.g. [11–13, 16]). It is acknowledged that some of the conventional reforming technologies listed above are already or will be soon commercialized (steam reforming, partial oxidation reforming and auto-thermal reforming). In almost all conventional reforming technologies using biogas as raw material, high activity catalysts have to be employed to increase the efficiency of the reforming process and useful lifetime of the reforming devices. The main problems encountered in the biogas conventional reforming are related to coke formation on the catalyst surface and its poisoning by substances containing sulphur, which lead to deactivation of the catalyst and reduction of H_2 production.

In the recent two decades an alternative technology has been proposed and developed for hydrogen production. This technology uses thermal and non-thermal plasma for reforming gaseous and liquid compounds containing hydrogen (e.g. review papers: [17–28]). These compounds can originate from fossil fuels and biofuels.

Different types of plasma have been investigated for reforming biogas-like mixtures (containing CH_4 and CO_2) into syngas (H_2 and CO): corona discharges [29, 30], glow discharges [31], dielectric barrier discharges (DBDs) [15, 32–34], arc discharges [35–38] and microwave discharges [39–42].

In this paper, we present a microwave plasma-based technology for hydrogen production from methane-containing gases, in particular from biogas. Microwave plasma-based technology appears to create the most promising plasma environment for such thermal and chemical processing as coal/biomass/waste pyrolysis/gasification, waste gas treatment, plasma reforming and CO_2 conversion. Microwave plasma is a gas ionized by means of a high frequency electromagnetic field (0.3–300 GHz). The electric field energizes the electrons which become capable of exciting and ionizing the neutral atoms and molecules, creating the plasma and sustaining the so-called microwave discharge. The technologically important advantage of microwave discharge over other discharges is that it does not require internal electrodes, which need regular maintenance or replacement due to erosion caused by contaminants. Microwave discharges can operate over a wide pressure range (from a fraction of mbar to several bars). Furthermore, the energy efficiency transfer from microwaves to plasma efficiency is high (up to 90%). The microwave plasma parameters (mainly the electron concentration and energy) result in high concentrations of active species enhancing the chemical reactions in the working gas forming the plasma. These properties of microwave plasma make it attractive for many applications, including reforming the biogas for hydrogen production.

The microwave plasma-based technology for hydrogen production presented in this paper concerns the efficiency of hydrogen production via reforming of the so-called synthetic biogas flowing through a waveguide-supplied metal cylinder-based microwave plasma source (MPS). The synthetic biogas is a mixture of CH_4 and CO_2 , which are the main constituents of a raw biogas. In the experiment carried out in this work, the ratio of CH_4 : CO_2 in the synthetic gas was varied from 0 to 1. We will call the processes occurring in the MPS the microwave plasma dry (CO_2) reforming of CH_4 .

Experimental

The experimental setup used for hydrogen production via synthetic biogas reforming in atmospheric-pressure microwave plasma is presented in Fig. 1. The main parts of microwave system were: microwave (915 MHz, 20 kW) generator with an isolator, power

measuring system (directional coupler: Mega Industries, power meter: Agilent N1914A, power heads: Agilent E9301A), microwave plasma source (MPS) impedance matching elements (three stub tuner + movable plunger) and gas supply and flow control system (Bronkhorst EL-FLOW). The error of the measured gas flow rate and microwave power did not exceed $\pm 3\%$.

The microwave power P_A absorbed in the plasma was determined as the difference between incident (P_I) and reflected (P_R) powers, measured by the power measuring system. This is a reasonable approximation despite of the fact that in addition to the microwave absorption by the plasma other microwave energy losses (e.g. losses in the tapered section, microwave leakage) exist in the microwave duct around the microwave plasma. As a consequence of such an approximation, the microwave power P_A calculated as the difference ($P_I - P_R$) is overestimated. This results in the underestimation of energy efficiency of the biogas reforming presented in this work. The additional losses seem to be small, however, an estimation of these losses is difficult. The errors of measuring the incident and reflected microwave powers were $\pm 1\%$.

The microwave duct was formed by a standard rectangular waveguide WR 975, which also was a mount base for the elements of microwave system. The plasma was generated by the waveguide-supplied metal-cylinder-based type MPS with a section of reduced-height, preceded by tapered section (Fig. 2). The microwave plasma flame was generated inside a quartz cylindrical tube passing through the waveguide as shown in Fig. 2. A cylindrical brass shield surrounding the quartz tube had a 5 mm slit for plasma observation and monitoring. The working gas was introduced to the MPS by four gas inlets which formed a swirl flow inside the quartz tube. The matching of the microwave generator with the discharge section was set at a level of 75%, using three stub tuner and movable plunger (see Fig. 1). This means that 75% of the incident microwave power was absorbed by the plasma. The MPS was described in detail in [43].

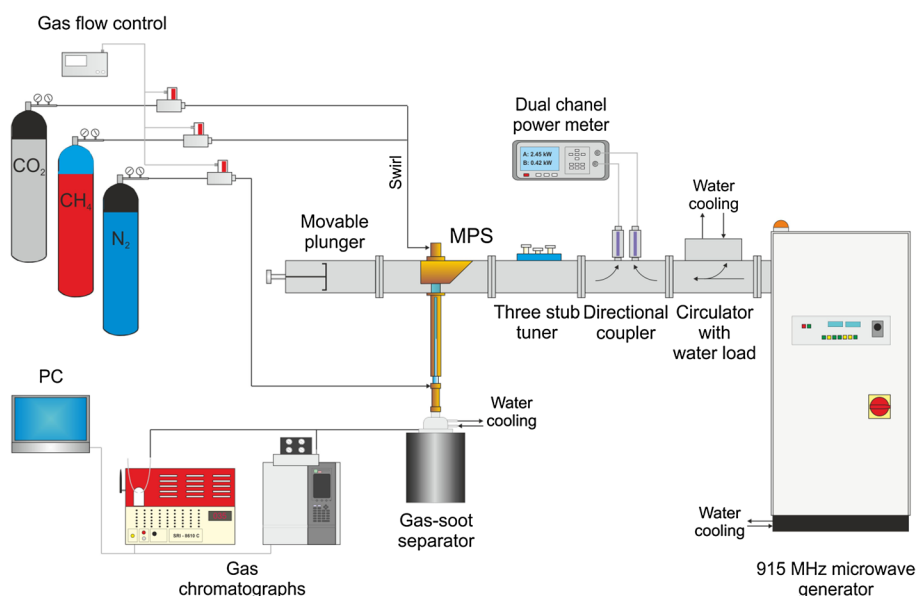


Fig. 1 Experimental setup

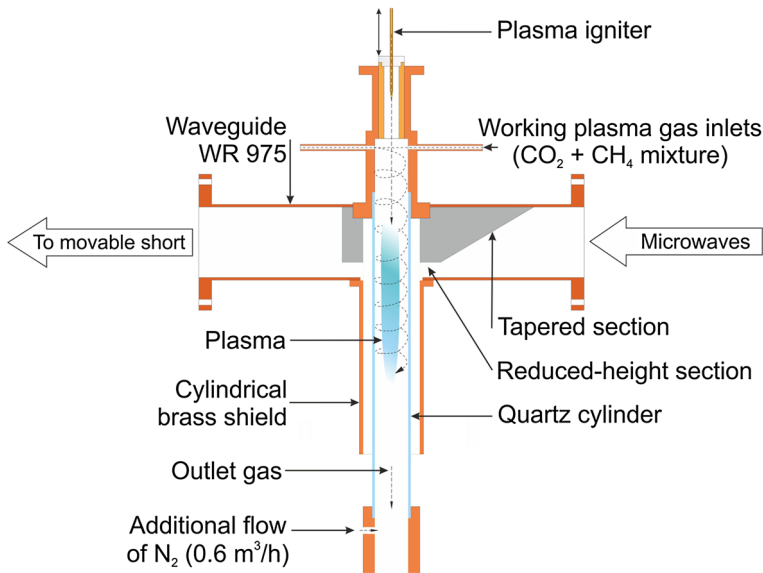


Fig. 2 Schematic view of the waveguide-supplied metal cylinder-based type MPS

The experimental tests were performed with the working gas simulating biogas (a mixture of CH_4 and CO_2). Its flow rate through the MPS was varied from $3 \text{ m}^3/\text{h}$ up to $12 \text{ m}^3/\text{h}$. The absorbed microwave power P_A ranged from 4.5 kW up to 7.5 kW . The $\text{CH}_4:\text{CO}_2$ ratio was varied from 0 (pure CO_2) to 1 (CH_4 –50 Vol.% and CO_2 –50 Vol.%).

The working gas composition after its processing by the MPS was measured using a gas chromatographs: Shimadzu GC-2014 and SRI 8610C. The presence of following components: H_2 , O_2 , N_2 , CO , CO_2 , CH_4 , C_2H_2 , C_2H_4 and C_2H_6 in the outlet gas was detected and their concentrations were measured. The average of 3 measuring trial runs was taken to determine the concentrations of each component in every gas sample. The error of measured concentration of each component did not exceed $\pm 5\%$.

The volumetric flow of the working gas changed when processed by the plasma due to reactions between its components. This influenced the individual volumetric flows of plasma processing components. To determine the individual component volumetric flows, an additional stream of N_2 with a flow rate of $0.6 \text{ m}^3/\text{h}$ was introduced as a flow marker into the outlet gas, as shown in (Figs. 1 and 2). Analyzing the concentrations of gas components in a gas sample taken at the MPS outlet (Fig. 1) enabled determining the individual volumetric flows of plasma processing components.

To determine the effectiveness of hydrogen production by the MPS the hydrogen production rate and the energy yield of hydrogen production were measured in this work. The hydrogen production rate in $\text{g}(\text{H}_2)/\text{h}$ shows how many grams of hydrogen is produced per unit of time. The energy yield of hydrogen production in $\text{g}(\text{H}_2)/\text{kWh}$ determines the amount of grams of hydrogen produced using 1 kWh of microwave energy. The other parameters determined in this work were: the methane conversion degree and the hydrogen selectivity. The methane conversion degree is a fraction (or percent) of the methane introduced into the microwave plasma, which was converted into plasma non-methane products. It is given by a ratio:

$$\frac{([\text{CH}_4]_{\text{inlet}} - [\text{CH}_4]_{\text{outlet}})}{[\text{CH}_4]_{\text{inlet}}} \times 100\%, \quad (6)$$

where $[\text{CH}_4]_{\text{inlet}}$ is the number of CH_4 mol at the MPS inlet, and $[\text{CH}_4]_{\text{outlet}}$ is the number of CH_4 mol at the MPS outlet. The hydrogen selectivity is defined as:

$$[\text{H}_2]_{\text{outlet}} / < 2 \times ([\text{CH}_4]_{\text{inlet}} - [\text{CH}_4]_{\text{outlet}}) > \times 100\%, \quad (7)$$

where $[\text{H}_2]_{\text{outlet}}$ is the number of moles of produced H_2 and $([\text{CH}_4]_{\text{inlet}} - [\text{CH}_4]_{\text{outlet}})$ is the number of moles of CH_4 converted in the plasma. This parameter describes a fraction of the methane introduced into plasma converted finally into hydrogen.

Results and Discussion

Figure 3 shows images of plasma flame generated in the waveguide-supplied metal-cylinder-based type MPS at different $\text{CH}_4:\text{CO}_2$ ratio at a working plasma gas flow rate of $6 \text{ m}^3/\text{h}$ and an microwave absorbed power of 6.5 kW. The images of plasma were taken through the slit along the outer cylindrical shield. The plasma flame length was about 20 cm measured from the bottom wall of the waveguide for pure CO_2 plasma ($\text{CH}_4:\text{CO}_2$ ratio = 0) and decreased with increasing $\text{CH}_4:\text{CO}_2$ ratio, i.e. with increasing CH_4 content in the working gas. As it can be seen from the images, the microwave plasma changed significantly when a $\text{CH}_4:\text{CO}_2$ ratio was higher than 40:60 (about 0.7). It changed not only colour but became clearly shorter and brighter (note that the camera exposure time at $\text{CH}_4:\text{CO}_2 = 50:50$ had to be shortened to avoid overexposure). For a $\text{CH}_4:\text{CO}_2$ ratio of 50:50 the microwave discharge became unstable and intense soot production could be observed. Further increasing $\text{CH}_4:\text{CO}_2$ ratio (above 1) resulted in extinguishing the discharge. The soot deposited on the quartz tube inner surface and in the plasma zone, similarly as we observed earlier in the decomposition of ethanol in nitrogen plasma [44]. The images of $\text{CH}_4:\text{CO}_2$ plasma shown in Fig. 3 suggest that the parameters of the plasma change substantially with increasing

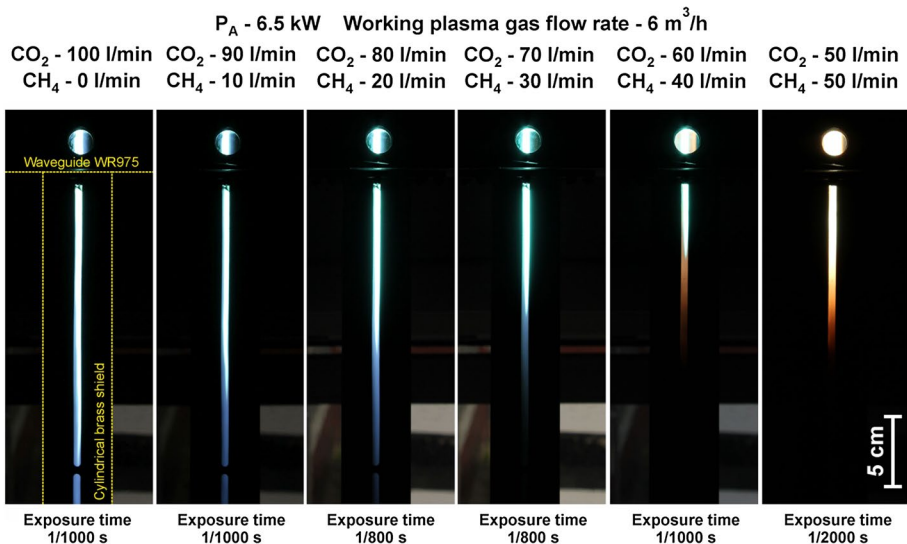


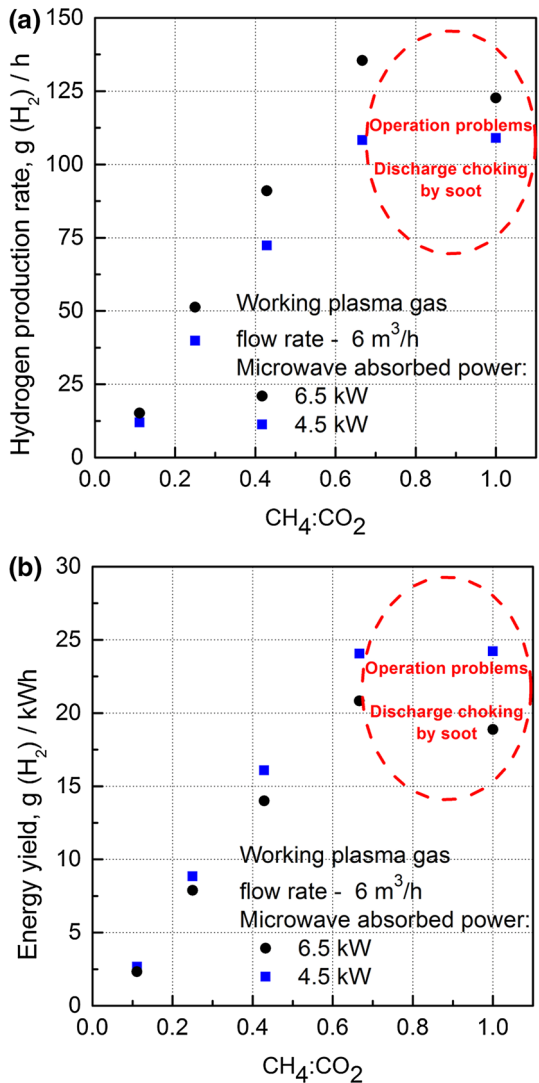
Fig. 3 Images of microwave plasma at various ratios of $\text{CH}_4:\text{CO}_2$ (working plasma gas flow rate— $6 \text{ m}^3/\text{h}$, absorbed microwave power—6.5 kW)

content of CH_4 . This undoubtedly influences the plasm-chemical processes in the plasma, and, eventually, the hydrogen production efficiency.

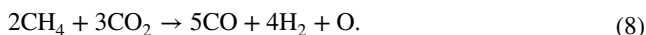
Figure 4 presents the hydrogen production rate and energy yield of hydrogen production as a function of $\text{CH}_4:\text{CO}_2$ ratio in the MPS. As it could be expected the hydrogen production rate increased with the increasing CH_4 content in the working gas. The MPS operated very stably up to a $\text{CH}_4:\text{CO}_2$ ratio of 40:60 (about 0.7). The hydrogen production parameters, the hydrogen production rate and the energy yield were highest at $\text{CH}_4:\text{CO}_2 = 40:60$. As mentioned above, the plasma started to change significantly at $\text{CH}_4:\text{CO}_2 > 40$, and the discharge became unstable even for an absorbed microwave power higher than 7.5 kW.

Such a behaviour of the microwave discharge can be explained by changes in the chemical processes caused by the higher content of CH_4 in the $\text{CH}_4:\text{CO}_2$ mixture. For the

Fig. 4 Hydrogen production rate (a) and energy yield of hydrogen production (b) as a function of $\text{CH}_4:\text{CO}_2$ ratio (working plasma gas flow rate— $6 \text{ m}^3/\text{h}$, absorbed microwave power—4.5 and 6.5 kW)

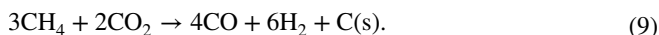


CH₄:CO₂ of 40:60, an overall reaction occurring in such a plasma can be formulated as follows:



According to reaction (8) there should not be any solid carbon (soot) in the MPS. This was confirmed in our experiment (manifested by no soot in the MPS and stable operation of the microwave discharge).

On the other hand, for the CH₄:CO₂ ratio higher than 50:50 (or 1) the chemical processes in the MPS can be described by an overall reaction:



The production of solid carbon predicted in reaction (9) resulted in soot presence and deposition in the MPS, which caused instability of the microwave discharge.

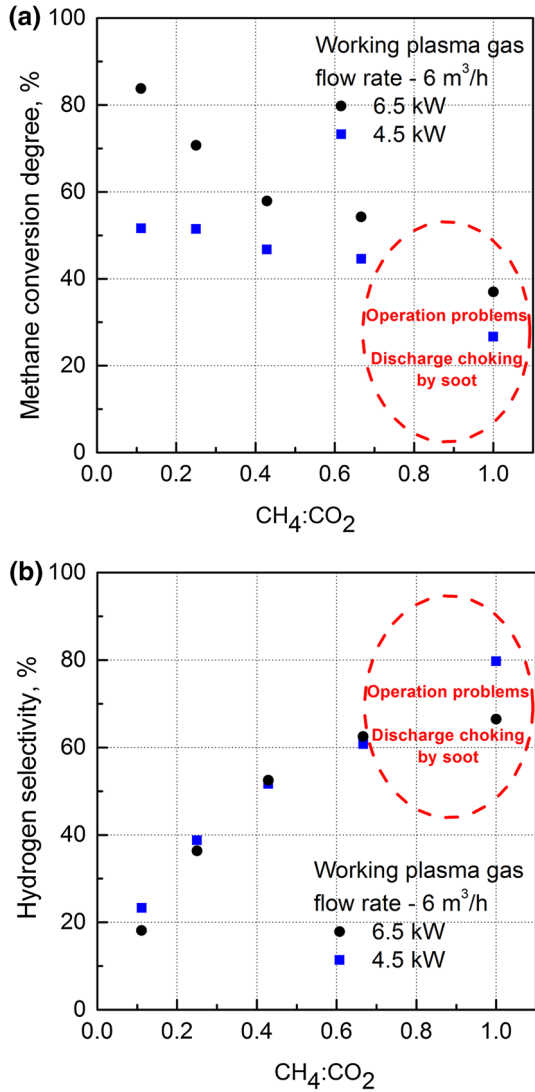
For the CH₄:CO₂ ratio equal to about 50:50 (or 1), the so-called dry (or CO₂) reforming of CH₄, described by reaction (3) should occur in the MPS, and soot should not be produced there. This is true in the thermodynamic equilibrium conditions. The experimental results showed, however, that soot was produced at the CH₄:CO₂ ratio equal to about 50:50 (or 1) and it choked the microwave discharge (Figs. 4 and 5). The above discrepancy can be explained by axial and radial temperature inhomogeneity inside the working gas stream, in which hot plasma regions and colder swirl flow regions exist. It means that the working gas stream is far from being in the thermodynamical equilibrium. In the colder plasma regions the temperature cannot be high enough to run the dry reforming (3) but sufficient to run pyrolysis of CH₄ instead. Pyrolysis of CH₄ (reaction (1)) results in soot presence in the MPS.

Figure 5a shows that the methane conversion degree decreased with increasing CH₄:CO₂ ratio. This means that the high ability of microwave CH₄:CO₂ plasma for converting CH₄ weakens when the content of CH₄ in the CH₄:CO₂ increases. In contrast, the hydrogen selectivity increased with increasing CH₄:CO₂ ratio (Fig. 5b). This can be attributed to the decreasing presence of oxygen in the microwave CH₄:CO₂ plasma when the content of CH₄ in the CH₄:CO₂ increases (see Eqs. (8), (9), and (10)). At lower contents of CH₄, a significant amounts of the produced H₂ as well as the introduced CH₄ can be combusted due to the presence of oxygen.

The hydrogen production rate increased with increasing microwave absorbed power (see Fig. 6a). The maximum achieved hydrogen production rate was 156 g(H₂)/h at a microwave absorbed power of 7.5 kW and CH₄:CO₂ ratio of 40:60 with an energy yield of hydrogen production of 21 g(h₂)/kWh. On the other hand, the maximum energy yield of hydrogen production [24 g(H₂)/kWh] was achieved at an microwave absorbed power of 4.5 kW (Fig. 6b) with a hydrogen production rate of 108 g(H₂)/h. Thus the highest hydrogen production rate can be achieved at a loss of the energy yield (also see Table 1).

Figure 7a, b show the hydrogen production rate and the energy yield do not depend on working plasma gas flow rate in a range from 3 m³/h to 12 m³/h. This proves that the MPS can operate with at high gas-flow output, which can be attractive for various plasm-chemical processing purposes and technologies. However, in the case of the biogas simulator having different CH₄:CO₂ ratios, the optimal working gas flow rate is about 3 m³/h or a bit less (a lower flow rate can result in overheating the MPS). As it is seen in Fig. 8a, b, the methane conversion degree and the hydrogen selectivity are highest when the working gas flow rate is about 3 m³/h, and they decrease significantly with increasing working gas flow rate. This means that operating at flow rates higher than 3 m³/h would not give any positive effects in term of the hydrogen production

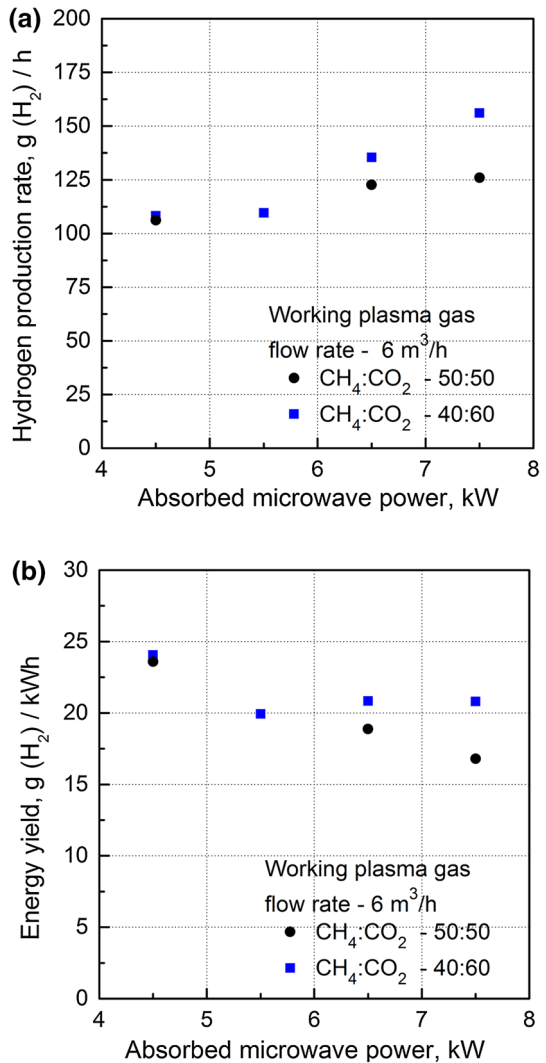
Fig. 5 Methane conversion degree (a) and hydrogen selectivity (b) as a function of CH₄:CO₂ ratio (working plasma gas flow rate–6 m³/h, absorbed microwave power–4.5 and 6.5 kW)



efficiency. On the contrary, the microwave processing of the biogas simulator at the flow rates higher than 3 m³/h would lead to a loss of the unprocessed biogas (a significant fraction of the biogas would just pass the MPS unprocessed).

The major components of outlet gas are listed in Table 1. They are H₂, CO₂, CO, CH₄, C₂H₂, C₂H₄, and C₂H₆. At the optimal conditions, H₂ content in the outlet gas was 22.4% and 30.3% for 4.5 kW and 7.5 kW of the microwave absorbed power, respectively. The content of the other components were: CO₂ (34.3% and 24.7%, respectively), CH₄ (22.9% and 15%, respectively), CO (19% and 28%, respectively), C₂H₂ (1.1% and 1.4%, respectively), C₂H₄ (0.1% and 0.16%, respectively) and C₂H₆ (0.06%).

Fig. 6 Hydrogen production rate (a) and energy yield of hydrogen production (b) as a function of absorbed microwave power (working plasma gas flow rate–6 m³/h, CH₄:CO₂ ratio–40:60 and 50:50)



Conclusions

The experiment showed that the microwave plasma reforming of synthetic biogas (a mixture of CH₄:CO₂) can be run stably at high gas flow rates (up to 12 m³/h) in the waveguide-supplied metal cylinder-based microwave plasma source (MPS) operating at atmospheric pressure. This makes the MPS attractive for different plasm-chemical processing purposes and technologies. The CH₄:CO₂ ratio optimal in terms of hydrogen production from the synthetic biogas was found to be 40:60. The working gas flow rate optimal from the view point of hydrogen production efficiency was found to be about 3 m³/h. The highest hydrogen production rate of 156 g(H₂)/h [1.8 m³(H₂)/h] was obtained at a microwave absorbed power of 7.5 kW. The highest energy yield of hydrogen production of 24 g(H₂)/kWh [0.3 m³(H₂)/kWh] was achieved at 4.5 kW of a microwave absorbed power.

Table 1 Hydrogen production via microwave plasma reforming of synthetic biogas—the best results

Absorbed microwave power [kW]	Working gas flow rates and composition	Hydrogen production rate [g(H ₂)/h]	Energy yield [g(H ₂)/kWh]	Methane conversion degree (Hydrogen selectivity) [%]	Outlet gas components [vol.%]
7.5	CH ₄ –2.4 m ³ /h CO ₂ –3.6 m ³ /h CH ₄ :CO ₂ 40:60	Maximum 156	21	61.4 (63.7)	H ₂ –30.3 CO ₂ –24.7 CO–28.0 CH ₄ –15.0 C ₂ H ₂ –1.4 C ₂ H ₄ –0.16 C ₂ H ₆ –0.06
4.5	CH ₄ –2.4 m ³ /h CO ₂ –3.6 m ³ /h CH ₄ :CO ₂ 40:60	108	Maximum 24	44.6 (60.8)	H ₂ –22.4 CO ₂ –34.3 CO–19 CH ₄ –22.9 C ₂ H ₂ –1.1 C ₂ H ₄ –0.1 C ₂ H ₆ –0.06
6.5	CH ₄ –1.2 m ³ /h CO ₂ –1.8 m ³ /h CH ₄ :CO ₂ 40:60	130	20	Maximum 86.5 (73.3)	H ₂ –41.0 CO ₂ –8.6 CO–44.6 CH ₄ –3.6 C ₂ H ₂ –1.9 C ₂ H ₄ –0.3 C ₂ H ₆ –0.07

Fig. 7 Hydrogen production rate (a) and energy yield of hydrogen production (b) as a function of working plasma gas flow rate ($\text{CH}_4:\text{CO}_2$ ratio—40:60, absorbed microwave power—4.5 and 6.5 kW)

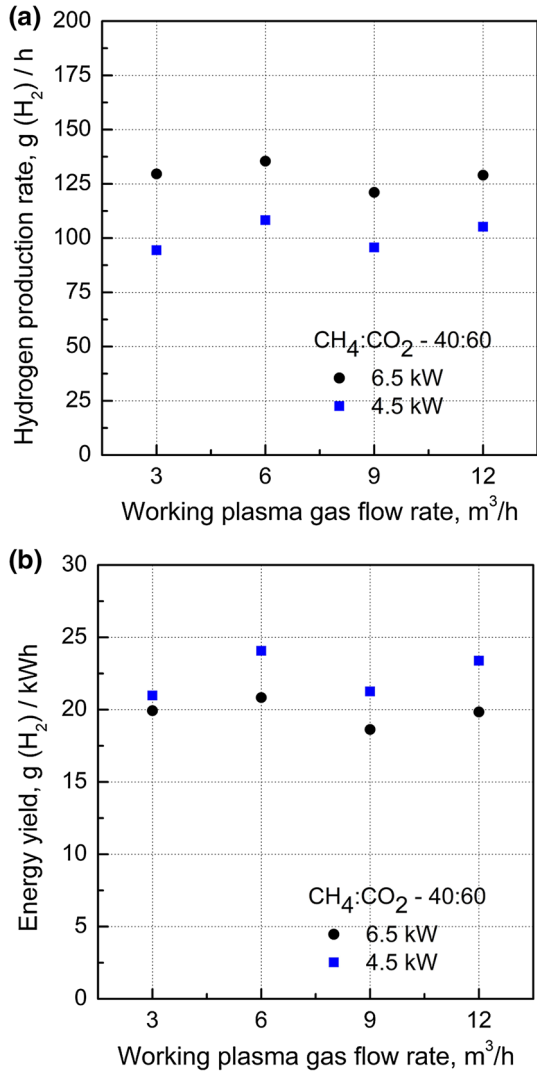
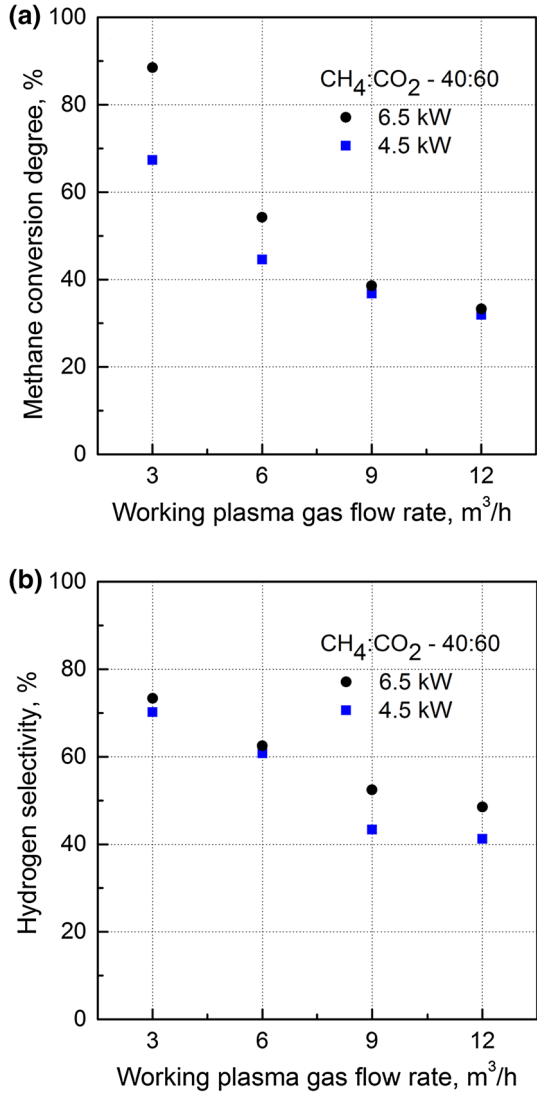


Table 2 summarizes to some extent the plasma technologies, along with their energy efficiencies, tested for hydrogen production from (CH_4 and CO_2) mixtures, which are the main components of typical biogases. As a reference, parameters of the large-scale conventional steam reforming of methane is also given in Table 2. The large-scale conventional steam reforming of methane is an established industrial process, which exhibits an energy yield of hydrogen production at 60 g(H_2)/kWh. This value is recognized by the U.S. Department of Energy (DOE) as a 2020 target for large-scale emerging technologies to be able to compete with the well-established technologies for hydrogen production [9, 24, 25]. An accepted 2020 target for small-scale plasma technologies intended for the distributed hydrogen production is expected to be lower than 60 g(H_2)/kWh.

In the plasma processing of (CH_4 and CO_2) mixtures shown in Table 2 several conventional CH_4 reforming processes were adopted: pyrolysis (Eq. 1), steam reforming (Eq. 2),

Fig. 8 Methane conversion degree (a) and hydrogen selectivity (b) as a function of working plasma gas flow rate ($\text{CH}_4:\text{CO}_2$ ratio—40:60, absorbed microwave power—4.5 and 6.5 kW)



dry reforming (Eq. 3), and auto-thermal reforming (Eqs. 5a and 5b). From the thermodynamic point of view (considering the standard reaction enthalpy and the thermodynamic limit of hydrogen production energy yield) the most effective processing is the auto-thermal reforming, then the pyrolysis, the steam reforming, and finally the dry reforming [25]. As seen from Table 2, regardless of the reforming processing adopted, only the arc and microwave plasmas have a potential for hydrogen production with a high energy yield, closed to the DOE's 2020 target. A very high energy yield of hydrogen production was actually achieved in the auto-thermal reforming of (CH_4 and CO_2) mixture by an AC-pulse arc plasma [35]. However, this result has to be taken with cautiousness because the energy from the CH_4 combustion has not been included in the energy consumed for the hydrogen production. Applying the classic pyrolysis of methane for hydrogen production from (CH_4 and CO_2) mixtures requires costly removal of CO_2 from them prior to the processing.

Table 2 Plasma methods of hydrogen production. Comparison of the hydrogen production rates and energy yields

Production method	Initial composition (volume ratio)	Hydrogen production rate [g(H ₂)/h]	Energy yield [g(H ₂)/kWh]	Methane conversion degree (Hydrogen selectivity) [%]	Reference
Conventional steam reforming of methane (catalyst)	CH ₄ + H ₂ O + Air	large scale	60 Established industrial process		[9]
Corona discharge	CH ₄ + CO ₂ (1:1)	0.46	12.6	27.8 (55.1)	[30]
Glow discharge	CH ₄ + CO ₂ (1:1)	0.28	12.2	61 (77)	[31]
DBD	CH ₄ + CO ₂ (7:3)	0.25	5.5	11 (98)	[15]
DBD	CH ₄ + CO ₂ (1:1)	0.06	0.42	62 (75)	[32]
AC-pulsed arc plasma	CH ₄ + CO ₂ + Air (3:2:10)	13.1	394*	80 (54)	[35]
Rotating gliding arc + catalyst	CH ₄ + CO ₂ (3:7)	12.4	25.2	58.5 (35.3)	[36]
Coaxial-line-based microwave plasma (2.45 GHz)	CH ₄ + N ₂ (2:1)	50	14.6	40.1 (30)	[40]
Metal-cylinder-based microwave plasma (2.45 GHz)	CH ₄ + CO ₂ (1:1)	66	19	32.5 (40.9)	[40]
Metal-cylinder-based microwave plasma (2.45 GHz)	CH ₄ + CO ₂ + H ₂ O (30:12:25)	192	43	22 (unknown due to H ₂ O presence)	[41]
Quartz-cylinder-based microwave plasma (2.45 GHz)	CH ₄ + CO ₂ (1:1)	112	19	96.8 (77.2)	[42]
Metal-cylinder-based microwave plasma (915 MHz)	CH ₄ + CO ₂ (2:3)	156	21	61.4 (63.7)	This work

*The energy from CH₄ combustion not taken into account when calculating the energy yield

As shown in [40], the microwave plasma pyrolysis of methane is characterized by a relatively high hydrogen production rate and energy yield, however, severe soot production makes the microwave plasma malfunction, limiting the hydrogen production rate and energy yield. To avoid or at least reduce the soot production, the microwave plasma steam reforming can be used. However, in this case first CO_2 has to be removed from (CH_4 and CO_2) mixtures and then H_2O vapour has to be introduced to form stable and efficient (CH_4 and H_2O) microwave plasma. To avoid costly removal of CO_2 , the so-called combined dry and steam reforming ($\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O}$) for microwave plasma processing of (CH_4 and CO_2) mixtures has been tested in [41]. As found, the combined dry and steam reforming allowed stable plasma processing of ($\text{CH}_4 + \text{CO}_2$) mixtures of a higher content of methane without the soot problems, whereby the hydrogen production rate and energy yield higher than in the classic dry reforming could be achieved. Although the thermodynamic limit of hydrogen production energy yield for the classic dry reforming is lower than that of the DOE's 2020 target of hydrogen production yield [25], the classic dry reforming processing has been tested employing the rotating gliding arc plasma [36] and the microwave plasmas ([40, 42] and the present work). This is justified because the dry reforming is attractive from the technological point of view. It offers almost direct introducing the biogas (considered as a CH_4 and CO_2 mixture) into the plasma source, without its costly modification, when, for example adding H_2O vapour is considered. As the present work showed, using the classic dry reforming in the 915 MHz microwave system resulted in a relatively high (156 [g(H_2)/h]) hydrogen production rate compared to the other plasma methods (at the similar value of the energy yield). The promising results achieved when using the 915 MHz microwave system may suggest that attractive results can be obtained if such a system is employed for processing (CH_4 and CO_2) mixtures according to the combined dry and steam reforming and auto-thermal reforming schemes. Such tests are planned in the near future. We believe that they will give results which may meet the DOE's 2020 requirements, taking into account that the reforming of renewable and ecological biogas is considered.

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