

Production of Hydrogen via Methane Reforming using Atmospheric Pressure Microwave Plasma Source with CO₂ swirl

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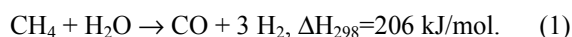
Abstract— In this paper, results of hydrogen production via methane reforming in the atmospheric pressure microwave plasma with CO₂ swirl are presented. A waveguide-based nozzleless cylinder-type microwave plasma source (MPS) with CO₂ swirl was used to convert methane into hydrogen. The plasma generation was stabilized by an additional CO₂ swirl having a flow rate of 50 l/min. The methane flow rate was 175 l/min. The absorbed microwave power was 1000-5000 W. The hydrogen mass yield rate and the corresponding energetic hydrogen mass yield were 950 g[H₂]/h and 940 g [H₂] per kWh 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).

Keywords— hydrogen production, methane reforming, microwave plasma

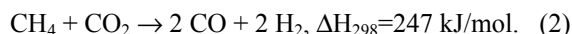
I. INTRODUCTION

Methane or natural gas reforming is widely used in industry to obtain hydrogen or synthesis gas (H₂+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:



Similar process, named partial oxidation, occurs when CO₂ is used instead of H₂O:



Since both processes are highly endothermic, to decrease activation energy, they require catalyst, which is usually Ni/Al₂O₃ working at temperature 1100-1150 K. Hence the reforming system is sensible to impurities in substrates which deactivates catalysts.

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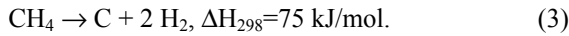
Conventional technologies of hydrogen production, i.e. coal gasification, hydrocarbon reforming and water electrolysis, are too expensive or not applicable for specific applications (e.g. for fuel cells) due to technical reasons. Thus, new methods are under development, like water photolysis, biomass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

One of attracting methods for reforming hydrocarbons to produce hydrogen is the use of plasmas [1-13]. The plasma contains reactive radicals, ions and high-energetic 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. Such a reformer is ready for operation instantaneously and does not need a start time typical for conventional reformers. Besides, the plasma system can be adapted for reforming various hydrocarbons, like natural gas, gasoline, heavy oils and biofuels. 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 [5, 12-18] 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 temperature of 4000-10000 K, and the heavy particle temperature of 2000-6000 K [16-18].

Our previous investigations in methane reforming to hydrogen [13] were carried out using methane (17.5-175 l/min) and nitrogen swirl (50-100 l/min) 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 l/min. Since the hydrogen production presented in [13] was carried out in the presence of nitrogen without any oxygen carriers, the main chemical reaction producing hydrogen was methane pyrolysis:



Due to the fact that the methane plasma could not be sustained at an absorbed microwave power lower than 3000 W, the energy consumed for the methane conversion in the presence of nitrogen only, calculated from electrical energy delivered to the plasma and methane mass flow rate, was 190 kJ/mol. Thus, comparing to energy of reaction (3) most of energy delivered to the plasma was lost.

In order to use more of the energy delivered to the MPS for methane conversion we propose to replace nitrogen with CO_2 , which reacts with methane consuming energy of 247 kJ/mol (reaction 2). Thus, we assume that all energy delivered to the plasma will be consumed for methane conversion to hydrogen. Results of methane reforming to hydrogen using CO_2 swirl with relatively low absorbed microwave power (1000 W) are presented in this paper.

II. 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 (Figure 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. Length of the experimental setup measured from the end of magnetron to the end of movable plunger was about 2 m.

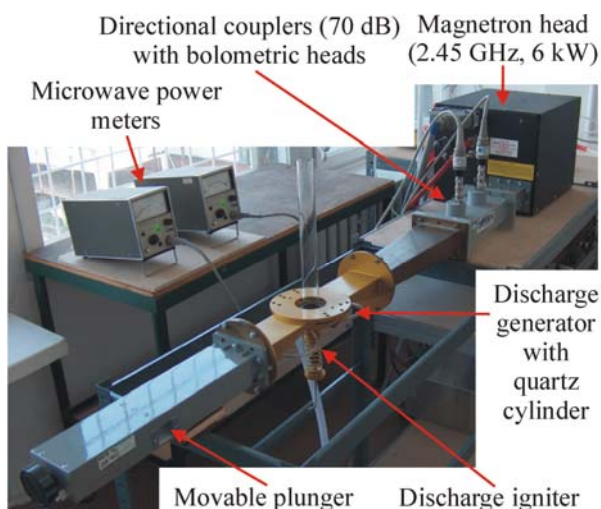


Fig. 1. Photo of the experimental setup with the waveguide-based nozzleless cylinder-type MPS.

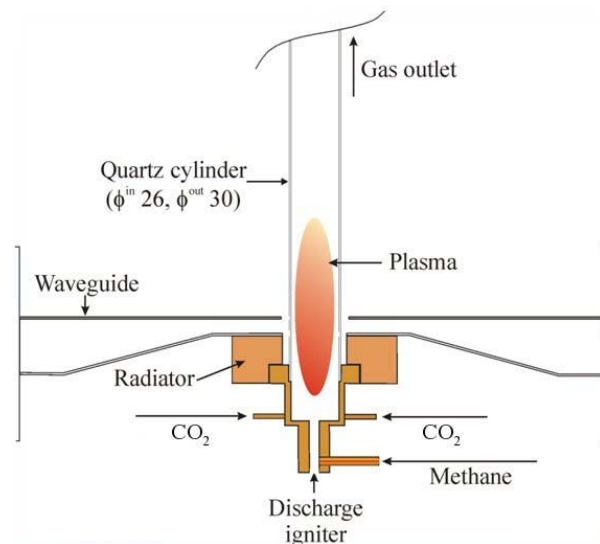


Fig. 2. Simplified sketch of the waveguide-based nozzleless cylinder-type MPS.

The absorbed microwave power P_A (1000-5000 W), 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 power meters (Figure 1).

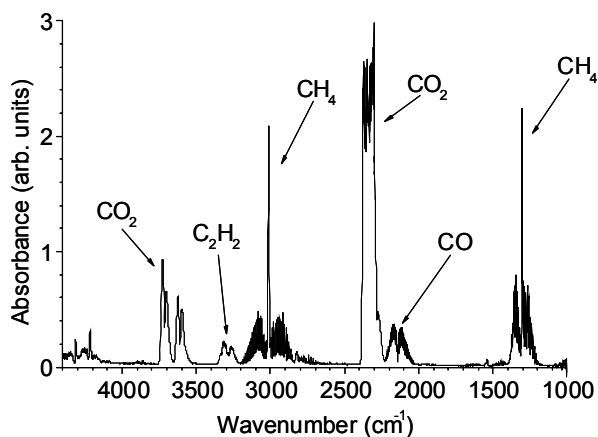
For hydrogen production via methane reforming we used the same waveguide-based nozzleless cylinder-type MPS as in our previous work (Figure 2, [13]). The processed methane (175 l/min) was introduced to the plasma by the central duct of MPS. The plasma generation was stabilized by an additional flow of CO_2 (50 l/min) in the form of a swirl that concentrated near the quartz cylinder wall. The CO_2 swirl held the discharge in the centre of the cylinder and thus protected the cylinder wall from overheating. The inner diameter of the used quartz discharge tube was 26 mm.

Important advantages of the presented waveguide-based 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).

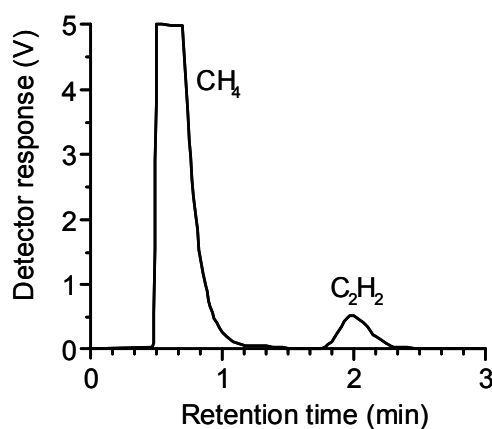
Diagnostics of composition of the gas exiting the quartz cylinder before and after the microwave plasma processing of methane was carried out using gas chromatograph (SRI 8610C) and Fourier Transform Infrared spectrophotometer (Perkin Elmer 16 PC).

III. RESULTS

Before plasma inception the gas exiting the quartz cylinder was a mixture of CH_4 (78%) and CO_2 (22%). This composition changed when plasma was generated in the cylinder. Figure 3 shows FTIR spectra (a) and



(a)



(b)

Fig. 3. FTIR spectra (a) and chromatogram (b) of the gas mixture after the microwave plasma processing. Absorbed microwave power – 3000 W, CH₄ flow rate – 175 l/min, CO₂ swirl flow rate – 50 l/min. Chromatogram obtained from gas chromatograph equipped with silica packed column 1m long and FID detector; column oven temperature 150°C.

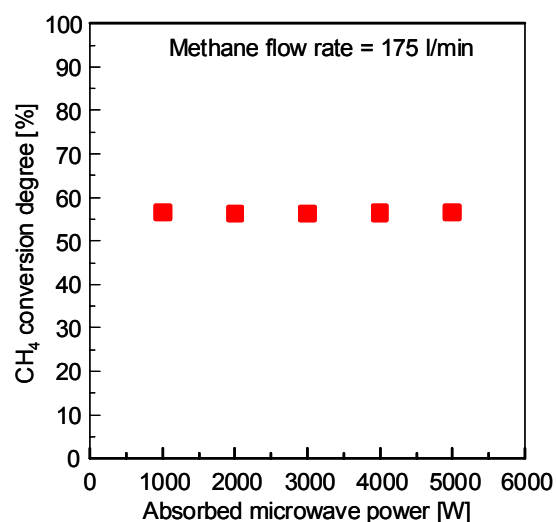
chromatogram (b) of the gas mixture after the microwave plasma processing at absorbed microwave power of 3000 W, methane flow rate of 175 l/min and CO₂ swirl flow rate of 50 l/min. As it can be seen from the after-process spectra and chromatogram, unprocessed methane CH₄, CO₂, CO and acetylene C₂H₂ were found as by-products in the exit gas. The methane decomposed to hydrogen H₂, acetylene C₂H₂ 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.

Concentration of H₂, C₂H₂ and CO in the exit gas were about 60%, 0.8% and 0.9%, respectively.

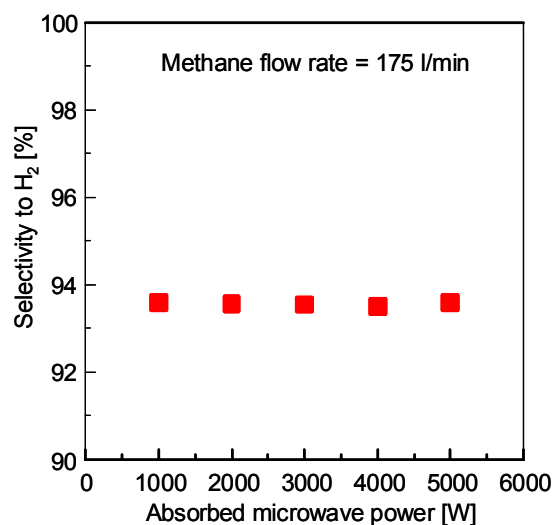
The total methane decomposition degree $[(CH_4)_{conv} / (CH_4)_{tot} \times 100 \text{ \%}]$ was about $58.5 \pm 0.4\%$ (Figure 4a), where $(CH_4)_{tot}$ is the total (initial) mass of CH₄, and

$(CH_4)_{conv}$ is the converted mass of CH₄. The hydrogen conversion selectivity $[H_2 / (2CH_4)_{conv} \times 100 \text{ \%}]$ was about $93.7 \pm 0.1\%$ (Figure 4b). Constant conversion degree and selectivity when increasing microwave power results probably from no change in gas temperature in the plasma region. After igniting plasma at 1000 W further increase in power causes heating of plasma generator metal parts. Thus, all power exceeding 1000 W is lost.

Such a high selectivity as well as low concentration of CO show that reaction of methane partial oxidation (reaction 3) was not the main path of methane conversion into hydrogen. From the significant production of soot one may conclude that methane pyrolysis (reaction 2) was the main process of hydrogen production. Small contribution of reaction (3) in the total methane conversion, proven by low CO concentration (0.9%),



(a)

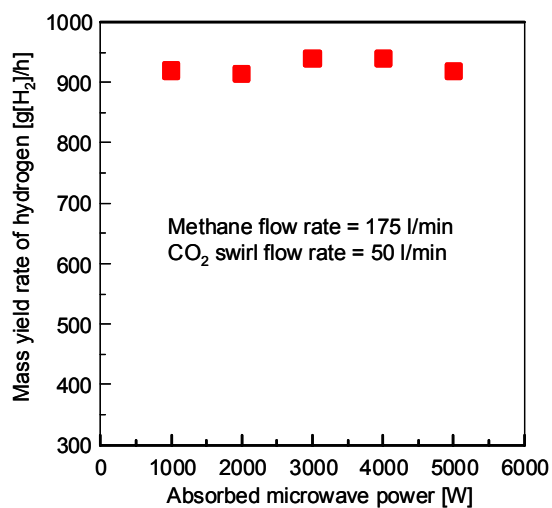


(b)

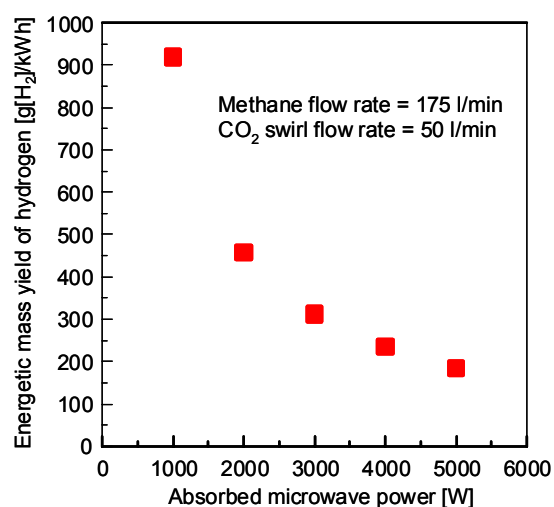
Fig. 4. CH₄ conversion degree (a) and hydrogen conversion selectivity (b) vs absorbed microwave power. Methane flow rate - 175 l/min. CO₂ swirl flow rate – 50 l/min).

suggests that there is no mixing of CO_2 from the swirl with methane introduced to the plasma by the central duct of MPS. It means that plasma is formed in the stream of methane only, whereas CO_2 swirl flows outside plasma. Small amounts of CO are formed probably at plasma- CO_2 boundary. Such a hypothesis requires experimental verification by flow visualization and/or measurements of flow velocity fields.

The energetic parameters of the hydrogen production via the methane reforming, i.e. the hydrogen mass yield rate and energetic hydrogen mass yield were about $950 \text{ g}[\text{H}_2]/\text{h}$ and $940 \text{ g}[\text{H}_2]$ per 1 kWh of microwave energy absorbed by the plasma, respectively (Figures 5a and 5b). Due to constant methane conversion degree when increasing microwave power, also hydrogen mass yield almost did not change. Small variations seen



(a)



(b)

Fig. 5. Mass yield rate (a) and energetic mass yield of hydrogen (b) vs absorbed microwave power. Methane flow rate - 175 l/min. CO_2 swirl flow rate - 50 l/min.

in Figure 5a resulted from instabilities in the gas flow near the plasma region caused by soot detaching from cylinder walls. On the other hand, since all power exceeding 1000 W is lost, the energetic hydrogen mass yield decrease with microwave power. Thus, the highest value of this parameter, i.e. $940 \text{ g}[\text{H}_2]$ per 1 kWh, was obtained at 1000 W. In our experiment, the plug efficiency of the microwave magnetron generator was higher than 66 %, so taking into account this efficiency, the energetic hydrogen mass yield was about $620 \text{ g}[\text{H}_2]$ per 1 kWh of electrical energy used.

Comparison of the energetic hydrogen mass yields for different low-scale methods in which electric energy is directly used for methane conversion into hydrogen, is given in Table 1. Production of hydrogen via methane steam reforming is not considered in the comparison since it is a large-scale method and its investment and exploitation costs involve many elements which are not present in low-scale methods of hydrogen production.

It must be pointed out that the energetic hydrogen mass yields 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 [6] and dielectric barrier discharge [9]) exhibit higher energetic hydrogen mass yield than the conventional water electrolysis [20]. However, when the energy equivalent of methane used in the conversion is taken into account, the energetic hydrogen mass yields for the plasmatron with catalyst [2] and our method, which exhibit the highest yields, are comparable with that of the conventional water electrolysis.

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 [19] 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.

Comparison of energetic parameters of hydrogen production by microwave plasma, which is a laboratory scale at the moment, with industrial scale conventional steam methane reforming is difficult. Only comparison with water electrolysis, where the only kind of energy used is electricity similarly as in our method, is possible. The best available commercial electrolyzers produce hydrogen with energetic hydrogen mass yield up to $21 \text{ g}[\text{H}_2]/\text{kWh}$ [20]. This value is much lower than that obtained using plasma methane reforming. However, energetic hydrogen mass yield is not good parameter for comparing plasma reforming with electrolysis since both methods use different substrates. One of the way for comparing those both methods is calculating of costs of

TABLE I
COMPARISON OF THE ENERGETIC HYDROGEN MASS YIELDS FOR DIFFERENT METHODS IN WHICH ELECTRIC ENERGY IS DIRECTLY USED FOR METHANE CONVERSION INTO HYDROGEN.

Hydrogen production method	Initial composition	Energetic mass yield [g [H ₂]/kWh]
CONVENTIONAL METHODS		
Water electrolysis [29]	H ₂ O	21
PLASMA METHODS		
Waveguide-based cylinder-type MPS (our result)	CH₄ + CO₂	620*
Electron beam [9]	CH ₄ + H ₂ O	3.6
Dielectric barrier discharge [13]	CH ₄ + air	6.7
Gliding arc [4]	CH ₄ + H ₂ O + air	40
Plasmatron with catalyst [2]	CH ₄ + H ₂ O + air	225

* total electric energy used (the plug efficiency of the microwave magnetron generator was higher than 66 %)

methane and electricity. Assuming that water cost in electrolysis is negligible the cost of 1 kg of hydrogen produced by plasma method is about 2 times lower than that obtained via electrolysis.

We propose a hybrid system for hydrogen production consisting of an atmospheric pressure microwave plasma source and a device for separation of the exit gases [e.g. a pressure swing adsorbent (PSA) unit or membrane filter unit]. The role of the gas separation device is to produce pure hydrogen from the exit gas from the microwave plasma. The PSA unit can produce the hydrogen with purity of 99.999 %, whereas the membrane filter unit can produce the hydrogen with purity of 99.9999 %. The methane unprocessed in the plasma is to be turned back to the plasma. The acetylene (C₂H₂) and soot can be recovered for industry purposes, while the recovered nitrogen can be used once more as the swirl gas in the MPS.

IV. CONCLUSION

The results of this investigations show that the energetic parameters of the hydrogen production, i.e. the hydrogen mass yield rate (950 g[H₂]/h) and the energetic hydrogen mass yield (940 g[H₂]/kWh), via methane reforming in the atmospheric pressure microwave plasma are attractive.

Taking into account the energy losses in the microwave power supply (~33 %), the energetic hydrogen mass yield reaches about 620 g[H₂] per kWh of the total electric energy used.

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 in the distributed hydrogen production.

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