

# Hydrogen Production from Gaseous Fuels by Plasmas - A Review

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**Abstract**—Nowadays development of systems for hydrogen production are of high importance. Hydrogen is more and more attractive as an efficient and environmentally friendly carrier of energy. It is considered as a promising fuel of the future hydrogen-oriented economy. There are several conventional methods of hydrogen production, e.g. methane or natural gas reforming, coal gasification, higher hydrocarbons reforming and water electrolysis. In a mass-scale (central) production these methods are well developed and their cost of hydrogen production is acceptable. However, due to the hydrogen transport and storage problems small-scale (distributed) technologies for hydrogen production are needed. In the small-scale case the objective is to develop technologies to produce hydrogen from clean, domestic resources at a production cost of \$(1-2)/kg [H<sub>2</sub>] (or about 60 g (H<sub>2</sub>)/kWh) by 2020.

Recently several plasma methods have been proposed for the small-scale hydrogen production. The plasmas proposed for hydrogen production are generated by: electron beam, dielectric-barrier discharge, gliding arc, plasmatron arc and microwave discharge. Methane, natural gas and other gaseous hydrocarbons have widely been tested to obtain hydrogen (or synthesis gas). Recently vaporized liquid alcohols and hydrocarbons (e.g., methanol, ethanol or gasoline) have been tested as hydrogen precursors. Several processes are employed when gaseous or liquid hydrocarbons are used for the plasma production of hydrogen. They are: pyrolysis, dry reforming, steam reforming, partial oxidation and auto-thermal reforming. Each of these processes has its advantages and disadvantages.

This paper is a short review of the plasma methods proposed for hydrogen production mainly from gaseous fuels. The plasma methods for gaseous fuels processing to produce hydrogen are described and critically evaluated from the view point of hydrogen production efficiency defined by such parameters as the hydrogen production rate (g(H<sub>2</sub>)/h) and energy yield (g(H<sub>2</sub>)/(kWh)), precursor conversion degree (%) and volume hydrogen concentration in the outgas (%).

The review conclusion is aiming at answering a question: Can any plasma method for the small-scale hydrogen production approach such challenges as the production energy yield of 60 g(H<sub>2</sub>)/kWh, high production rate, high reliability and low investment cost.

**Keywords**—Hydrogen production, plasma, methane reforming

## I. INTRODUCTION

Currently more than 80% of the world energy supply comes from fossil fuels, resulting in strong ecological and environmental impacts. Such factors as the exhaustion of reserves and resources, air pollution and modification of the atmospheric composition, impacts on climate and on human health, are now of primary importance. It is a wide opinion that hydrogen has a great role to play as an energy carrier in the future energy sector.

The most important reasons to transfer from the fossil fuel-based economy to hydrogen-based economy are as follows. The first one is the diversification of the energy sources and the reduction of dependency on fossil fuels, since hydrogen can be produced from any primary energy source. The second reason is the reduction of the environmental impact of the energy system. Most of the anthropogenic impacts on the environment come from the combustion of fossil fuels in the industrial, domestic and transport sectors. Hydrogen as a carbon-free energy carrier would reduce most of the related environmental

problems. The third reason is the control of acceptable costs and the hope of stable prices over time. At present the supply of energy at reasonable and stable prices is not ensured at all by the producers of crude oil or natural gas. Hydrogen facilitates the diversification of the sources and would contribute to the reliability, stability and security of the energy supplies.

At present the most important energy carriers are fossil-originated solids (coal), liquids (gasoline, diesel oil, jet fuel, ethanol, methanol, liquefied gases), gases (natural gas, synthetic gas), and electricity. Hydrogen is very seldom used as an energy carrier, except as pure liquid for rocket propulsion in the space industry. However, for decades hydrogen has been important for the chemical industry as a source material for the production of raw chemicals (e.g. methanol and ammonia), hydrogenation agents in oil refinery industry and reducing gases in steel industry.

Several processes have been developed for producing hydrogen mainly from fossil fuels and to some extent from water. Hydrogen can be produced from fossil fuels (or biomass and biomass-derived fuels) using such processes as steam reforming (mainly of natural gas), partial oxidation, auto-thermal reforming, and coal gasification. From any primary energy source (nuclear, wind, solar) converted into electricity hydrogen can be produced by the electrolysis of water. Hydrogen can also

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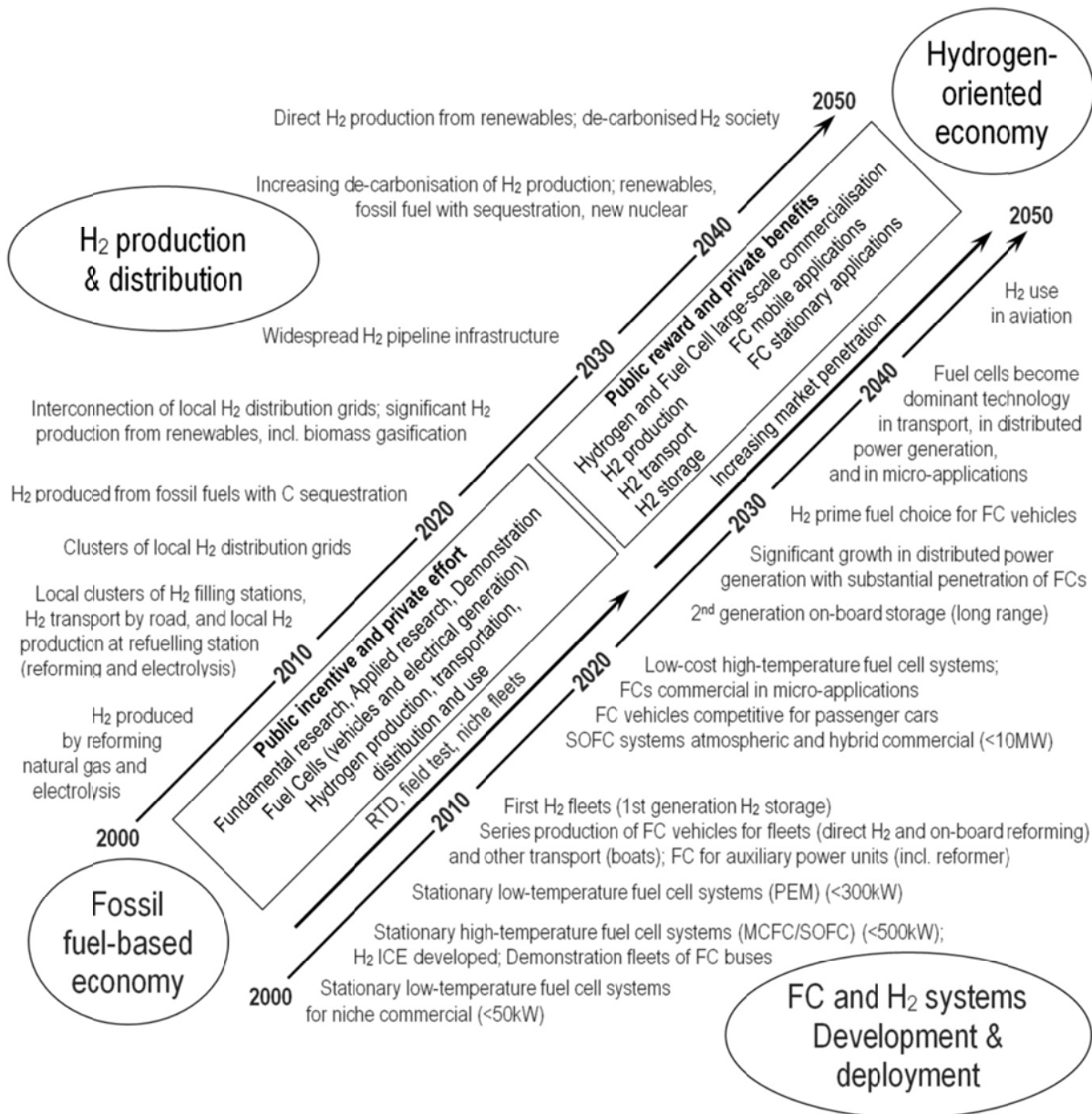
be produced using photochemical energy (photo-catalysis, bioconversion). At a large-scale in the chemical industry hydrogen has been produced as a by-product of sodium or potassium chloride electrolysis that gives chlorine and caustic soda or potash. Also hydrogen is a by-product of catalytic reforming of petroleum naphtha, made to improve the octane number, and of steam cracking of hydrocarbons for the production of ethylene. Smaller volumes of hydrogen are by-products in coke-ovens. In all the last cases hydrogen is mainly kept for internal use. More on various technologies related to hydrogen production by so-called conventional methods can be found in a review of [1].

Currently the USA and Japan are investing in R&D programs on hydrogen technology and fuel cells. The

European Union is lagging behind the USA and Japan in these areas. Being aware that the European industry can be excluded from the hydrogen economy, the European Commission has presented a European roadmap for the production and distribution of hydrogen, as well as fuel cells and hydrogen systems [2]. According to the European Commission vision of 2005 the transition to the hydrogen economy should have proceeded along the following steps (Table I).

In the first term to 2010, which has already passed, hydrogen and fuel cells should have been applied in several niche markets. Also research efforts in several fields related to hydrogen production, storage, distribution and safety, as well as to fuel cells have been envisaged together with the demonstration projects.

TABLE I  
EUROPEAN HYDROGEN-ORIENTED ECONOMY VISION. EUROPEAN ROADMAP FOR THE PRODUCTION AND DISTRIBUTION OF HYDROGEN, FUEL CELLS AND HYDROGEN SYSTEMS [2]



In the second term from 2011 to 2020, currently running, an increased production of hydrogen, still from fossil fuels, should be obtained. However, an increased production of hydrogen from renewable energy sources will be fostered. Owing to the increased availability of hydrogen the use of hydrogen as a fuel in modified conventional combustion engines and (or) fuel-cell systems in cars and trucks is expected. Since the majority of hydrogen is to be produced from fossil fuel, large demonstration projects for the capture and storage of CO<sub>2</sub>, which is a by-product of hydrogen production from fossil fuel are foreseen.

In the next term, beyond 2020 a growing production of hydrogen will accompany an increasing demand of consumers for clean energy supply. Both electricity and hydrogen will progressively replace the outdated carbon energy system. Renewable and nuclear energy sources will gradually substitute fossil fuels. In parallel at that time the hydrogen network will expand and become interconnected with the electricity grid.

One of the most advanced assessments of the present hydrogen policy needs has been made by the U.S. Department of Energy (DOE) [3]. The aim of this policy is to identify research pathways leading to hydrogen production technologies that produce near-zero net greenhouse gas emissions and use renewable energy sources, nuclear energy, and coal (with carbon dioxide capture and storage).

To analyze the future of hydrogen technology development it is convenient to divide the facilities for hydrogen production in 3 scales: small, medium and large. Small-scale facilities, called also distributed would produce from 100 to 1500 kilograms (kg) of hydrogen per day at fueling stations. Medium-scale (also known as semi-central or city-gate) facilities would produce from 1500 to 50000 kg per day on the outskirts of cities. The largest (central) facilities would produce more than 50000 kg of hydrogen per day.

According to DOE the current hydrogen production cost targets are \$3.00 per kilogram of hydrogen at fueling stations and \$2.00 per kg of hydrogen at a central facility (also known as the “plant” gate). (A kilogram of

hydrogen is approximately equal to a gallon (3.79 litres) of gasoline equivalent (gge) on an energy content basis. At present the cost of production of a gallon of gasoline is about \$2 in the USA (excluding delivery, storage and tax).

Centralized natural gas reforming is not being pursued because it is already an established commercial technology with a cost of \$2.00 per kg of hydrogen (currently most of the worldwide hydrogen production, more than 90%, originates from the large-scale steam reforming of natural gas). However, due to growing hydrogen demand the large scale (centralized) hydrogen production facilities will be needed. DOE is pursuing central production of hydrogen from a wide diversity of feedstocks, including nuclear energy and renewable sources. Hydrogen production technologies will be directed towards coal gasification with carbon sequestration to reduce or eliminate greenhouse gas emissions, biomass gasification, next generation nuclear energy high temperature sulphur-iodine thermochemical process, next generation nuclear energy high temperature steam electrolysis, current nuclear energy using standard electrolysis, and wind electrolysis.

Distributed hydrogen production (i.e., production of hydrogen at the point of use) may be the most viable approach for introducing hydrogen as an energy carrier because it does not require a substantial transport and delivery infrastructure or large capital investments as high as those needed for large central production plants. In this case such technologies as natural gas reforming, electrolysis, reforming of ethanol and methanol (both from biomass) are pursued.

Table II shows DOE’s envisage of hydrogen production targets in the distributed and central scales for the period 2011 - 2020. According to it the ultimate hydrogen production cost target is \$1 - \$2 per kilogram of hydrogen. DOE predicts that such a cost target will be difficult to achieve for technologies based on solar thermochemical, photoelectrochemical and biological processes.

Recently another technology has been proposed for distributed hydrogen production [4, 5]. This technology

TABLE II  
DOE’S ENVISAGE OF HYDROGEN PRODUCTION TARGETS IN DISTRIBUTED AND CENTRAL SCALES FOR THE PERIOD 2011 – 2020 [3]

	\$/kg (production costs only)	2011 Status Target	2015 Target	2020 Target	Ultimate Production Target
Distributed	Electrolysis from grid electricity	\$4.20	\$3.90	\$2.30	\$1-\$2
	Bio-derived Liquids (based on ethanol reforming case)	\$6.60	\$5.90	\$2.30	
Central	Electrolysis from renewable electricity	\$4.10	\$3.00	\$2.00	
	Biomass gasification	\$2.20	\$2.10	\$2.00	
	Solar thermochemical	NA	\$14.80	\$3.70	
	Photoelectrochemical	NA	\$17.30	\$5.70	
	Biological	NA	NA	\$9.20	

uses thermal and non-thermal plasmas for reforming gaseous and liquid compounds containing hydrogen. They can originate from fossil fuels and biomass. Unfortunately, DOE's scenario does not predict any role for the plasma technology in the future roadmap towards the hydrogen-oriented world economy.

This paper is a short review of the plasma methods proposed for hydrogen production mainly from gaseous fuels. In this review the plasma methods of gaseous fuels processing for hydrogen production are described and critically evaluated from the view point of hydrogen production efficiency defined by such parameters as the hydrogen production rate ( $\text{g}(\text{H}_2)/\text{h}$ ), and energy yield ( $\text{g}(\text{H}_2)/(\text{kWh})$ ), precursor conversion degree (%) and volume hydrogen concentration in the outgas (%).

As mentioned, plasmas are of increasing interest for the small-scale energy efficient production of hydrogen also from liquid fuels [5]. Alcohols, for example, can provide significant advantages when used as a liquid fuel for hydrogen generation due to a high hydrogen to carbon ratio, low boiling point, low temperature for conversion to hydrogen, no sulphur content, high water solubility and biodegradability [6]. The reforming of alcohols for producing hydrogen has been investigated in a wide variety of plasmas produced in dielectric barrier discharges [7], surface wave discharges [8], AC discharges [9-11], microwave discharges [12, 13], glow discharges [14], silent discharges [15, 16], corona discharges [17, 18], gliding arcs [19, 20], plasmatron arc [20], and discharges in liquids [19]. The major advantage of using these plasmas is that most of them have sufficiently high temperatures to vaporize the alcohols inside the plasma or to vaporize them prior to feeding them into the plasma. The cost of generating such high temperature plasmas seems to be competitive to that of creating the high operating temperatures for hydrogen production in thermal/catalytic steam reforming processing [21]. The growing interest in using liquid fuels for the hydrogen production by plasmas has resulted in numerous articles. This subject has become so broad that it demands a separate comprehensive

discussion.

The majority of plasmas proposed for hydrogen production from gaseous fuels are generated by: electron beam, dielectric-barrier discharge, gliding arc, plasmatron arc and microwave discharge. Table III shows the energy yields of hydrogen production from methane for different plasma methods. Methane is the most popular gaseous fuel used in the plasma production of hydrogen. For comparison, information on the energy yield of hydrogen production by the conventional steam reforming of methane (with a catalyst), water electrolysis, as well as dielectric barrier discharge and gliding arc, both employing alcohols as fuels, is given in Table III.

The conventional steam reforming method of producing hydrogen from natural gas (consisting mainly of methane) are well developed industrial technology and account for over 95% of all hydrogen produced in the USA and about 50% globally [22]. According to the U.S. Department of Energy (2013, [3], Table III) the energy yield of hydrogen production using this technology is  $60 \text{ g}(\text{H}_2)/\text{kWh}$ , which is equivalent to a cost of \$2 per kg of hydrogen (assuming that pricing of 1 kWh electric energy is \$0.12). The energy yield of hydrogen production of  $60 \text{ g}(\text{H}_2)/\text{kWh}$  is a target set by U.S. DOE at 2020 for other competitive methods. It is worthy of note that the thermodynamic limit of the energy yields in methane reforming, wet methane reforming and dry methane reforming are  $192 \text{ g}(\text{H}_2)/\text{kWh}$ ,  $105 \text{ g}(\text{H}_2)/\text{kWh}$  and  $58 \text{ g}(\text{H}_2)/\text{kWh}$ , respectively. As Table III shows water electrolysis does not reach the target of  $60 \text{ g}(\text{H}_2)/\text{kWh}$  at present [3]. From the plasma methods listed in Table III the plasma generated by a plasmatron arc and supported by a catalyst [23] is most advanced technology of hydrogen production from methane on an energy yield basis ( $225 \text{ g}(\text{H}_2)/\text{kWh}$  versus the 2020 target of  $60 \text{ g}(\text{H}_2)/\text{kWh}$ ). The gliding arc processing methane [24] offers yield similar to that of water electrolysis ( $40 \text{ g}(\text{H}_2)/\text{kWh}$ ). However, when gliding arc was used for producing hydrogen from liquid fuel (alcohol) the energy yield was impressive ( $176 \text{ g}(\text{H}_2)/\text{kWh}$ , [25]). This clearly shows that plasma reforming of liquid fuels is attractive

TABLE III  
CONVENTIONAL AND PLASMA METHODS OF  $\text{H}_2$  PRODUCTION. COMPARISON OF THE ENERGY YIELDS OF HYDROGEN PRODUCTION.

Production method	Initial composition	Energy yield		Reference
		NL( $\text{H}_2$ )/kWh	$\text{g}(\text{H}_2)/\text{kWh}$	
Conventional steam reforming of methane (catalyst)	$\text{CH}_4 + \text{H}_2\text{O} + \text{air}$	672	60 Established industrial process	K. Randolph, U.S. DOE, 2013, [3]
Water electrolysis	$\text{H}_2\text{O}$	224 - 448	20 - 40	K. Randolph, U.S. DOE, 2013, [3]
Electron beam radiolysis	$\text{CH}_4 + \text{H}_2\text{O}$	40	3.6	T. Kappes <i>et al.</i> , 2002, [26]
Dielectric barrier discharge	$\text{CH}_4 + \text{air}$	75	6.7	M. Heintze, B. Pietruszka, 2004, [27]
Dielectric barrier discharge	$\text{CH}_4 + \text{CO}_2 / \text{H}_2\text{O}$	5.6	0.5	B. Sarmiento <i>et al.</i> , 2007, [7]
	$\text{CH}_3\text{OH} + \text{CO}_2 / \text{H}_2\text{O}$	37	3.3	
	$\text{CH}_3\text{CH}_2\text{OH} + \text{CO}_2 / \text{H}_2\text{O}$	75	6.7	
Dielectric barrier discharge	$\text{CH}_4 + \text{CO}_2$	58	5.2	M. Dors <i>et al.</i> , 2012, [28]
Gliding arc	$\text{CH}_4 + \text{H}_2\text{O} + \text{air}$	448	40	J.M. Cormie, I. Rusu, 2001, [24]
Gliding arc (alcohol spray)	Alcohols + Ar	2100	176	R. Burlica <i>et al.</i> , 2011, [25]
Plasmatron with catalyst	$\text{CH}_4 + \text{H}_2\text{O} + \text{air}$	2520	225	L. Bromberg <i>et al.</i> , 2000, [23]
Metal-cylinder-based MPS	$\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O}$	480	42.9	M. Jasiński <i>et al.</i> , 2013, 4.5 kW, [29]
Waveguide supplied resonant-cavity-based MPS with catalyst	$\text{CH}_4 + \text{H}_2\text{O}$	703	62.8	M. Jasiński <i>et al.</i> , 2014, 2.5 kW, [30]

from the point of view of the energy efficiency. Both electron beam radiolysis [26] and dielectric barrier discharge [7, 27, 28] are much less energy efficient. Promising technology for hydrogen production seems to be microwave plasma. It was shown [29] that the use of the so-called waveguide-supplied metal-cylinder-based microwave plasma source resulted in a hydrogen production energy yield of 42.9 g(H<sub>2</sub>)/kWh. A higher energy yield of 62.8 g(H<sub>2</sub>)/kWh, i.e. above the DOE's 2020 target was obtained in a waveguide supplied resonant-cavity-based microwave plasma source (MPS) with a support of catalyst [30].

Recently developed microwave plasma sources (MPSs) operated at atmospheric pressure exhibit a high potential for hydrogen production via pyrolysis, wet and dry reforming of various gaseous (natural gas, methane) and liquid fuels (gasoline, heavy oils and biofuels). They provide a plasma environment in which the heavy particles (atoms and molecules) have temperatures of 2000–6000K while the electron temperature reaches 10000K. Besides, the plasma contains ions and reactive radicals (H, OH, and O) which enhance conversion of hydrocarbon containing compounds into hydrogen. The wide range of the offered gas plasma temperatures enables choosing the temperature optimum for a given reforming path. This results in higher selectivity of hydrogen production. The other advantages of the use of plasma for hydrogen production are the compactness of the plasma system due to high energy density of the

plasma and fast response time achieved by being powered by electricity.

The microwave plasmas operating at atmospheric pressure can be induced by several types of microwave field applicators, which may be classified as follows [31]:

- (A) Surface-wave-discharge MPSs:
  - a. coaxial-line-supplied, called surfatrons,
  - b. waveguide-supplied, called surfaguides.
- (B) Nozzle-type MPSs:
  - a. coaxial-line-supplied coaxial-line-based (low gas flow rate, several NL/min),
  - b. waveguide-supplied coaxial-line-based (low and high flow rates (gas swirl, several hundred NL/min)).
- (C) Nozzleless MPSs:
  - a. waveguide-supplied coaxial-line-based (with or without an inner dielectric tube),
  - b. waveguide-supplied metal-cylinder-based (with or without an inner dielectric tube),
  - c. waveguide-supplied resonant-cavity-based.
- (D) Plasma-sheet MPSs:
  - a. coaxial-line-supplied strip-line-based,
  - b. waveguide-supplied.
- (E) Microwave microplasma sources (MmPSs):
  - a. antenna-based,
  - b. coaxial-line-based.
- (F) Inductively coupled MPSs.

## Microwave plasma system for hydrogen production

- Microwave plasma sources (MPSs)**
- **surface-wave-discharge MPSs:**  
coaxial-line-supplied (surfatron)  
waveguide-supplied (surfaguide)
  - **nozzle-type MPSs:**  
coaxial-line-supplied coaxial-line-based  
waveguide-supplied coaxial-line-based
  - **nozzleless MPSs:**  
waveguide-supplied coaxial-line-based  
waveguide-supplied metal-cylinder-based  
waveguide-supplied resonant-cavity-based
  - **plasma-sheet MPSs:**  
coaxial-line-supplied strip-line-based  
waveguide-supplied
  - **MPSs for microdischarges**  
(antenna- and coaxial-line-based)

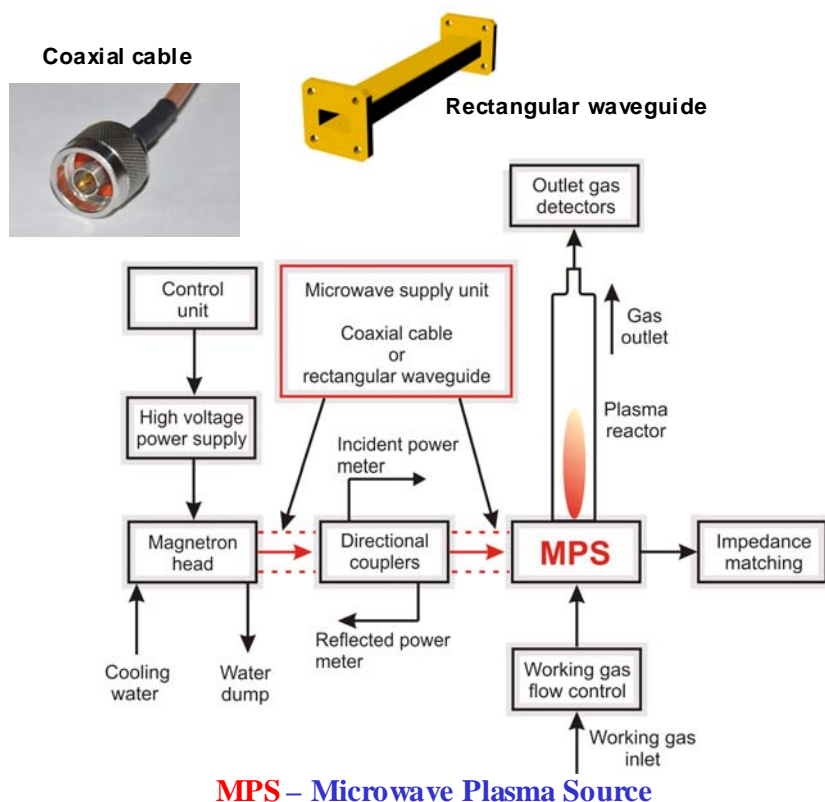


Fig. 1. Scheme of a microwave plasma system for hydrogen production.

The above listed MPSs are known under different names, usually given by their inventors. The classification introduced by us is mainly based on the way of supplying the microwave energy (e.g., waveguide-supplied - the microwave energy is supplied through a waveguide) and on the microwave principle of operation of the MPS (e.g., coaxial-line-based - the operation is based on the coaxial transmission line structure). In the name of MPS also its specific feature is included, e.g., nozzle-type (when a nozzle is an essential part of the MPS).

Atmospheric pressure microwave plasmas generated in MPSs are often demanded to be sustained within a dielectric (e.g., fused silica) tube due to the chemical reactivity of processed gases. This can cause some problems when large power densities are deposited into the plasma, resulting in deterioration of the tube due to plasma-tube interactions. A solution to these problems is a high flow of the operating gas through the dielectric tube, which can convey the produced heat. Another solution is using an additional gas flow, called a gas swirl, together with the main gas stream to protect the walls from heat deterioration. Using either the high working gas flow rate or additional gas swirl weakens the microwave power limitations imposed on the MPSs used for the gas treatment.

Depending on the kind of MPS, the microwave power is supplied from a microwave generator (magnetron) to the MPS through either a coaxial cable or a rectangular waveguide (Fig. 1).

We found that the most promising design of microwave plasma source for hydrogen production from gaseous fuels is the waveguide-supplied metal-cylinder-

based system which at present exhibited a hydrogen production yield from methane above 40 g(H<sub>2</sub>)/kWh ([29], Table III). The design of the waveguide-supplied metal-cylinder-based MPS is shown in Fig. 2.

When the waveguide-supplied metal-cylinder-based MPS is properly optimized and a swirling gas is injected into the operation region, the plasma is generated inside a metal cylinder or in the quartz cylinder inserted in it. The gas swirl stabilizes the plasma and also protects the cylinder wall (metal or quartz) from the discharge heat. The presented MPS showed stable operation at power levels from about 600 W up to 6000 W, provided that the total gas flow is sufficiently large (from 30 up to several hundred l/min).

The presented MPS was based on a standard WR 340 rectangular waveguide of internal dimensions 86.4 mm × 43.2 mm. The discharge cylindrical tube, made of quartz, with the inner and outer diameters of 26 mm and 30 mm, respectively, passed perpendicularly through the center of wide walls of the waveguide, as shown in Fig. 2. The quartz tube was enveloped by an outer cylindrical metal electrode (with an observation window). The outer cylindrical metal electrode was a part of the waveguiding structure of the MPS. The working gas (CH<sub>4</sub>, CO<sub>2</sub> and water vapor) was introduced to the plasma by four inlets, which formed a swirl flow inside the quartz tube. There was also another viewing window, enabling plasma observation in the axial direction of the flow. A metal igniter was used for making the microwave breakdown and initiating the plasma generation.

The overall diagram of the experimental setup for hydrogen production via methane conversion using the waveguide-supplied metal-cylinder-based MPS is shown

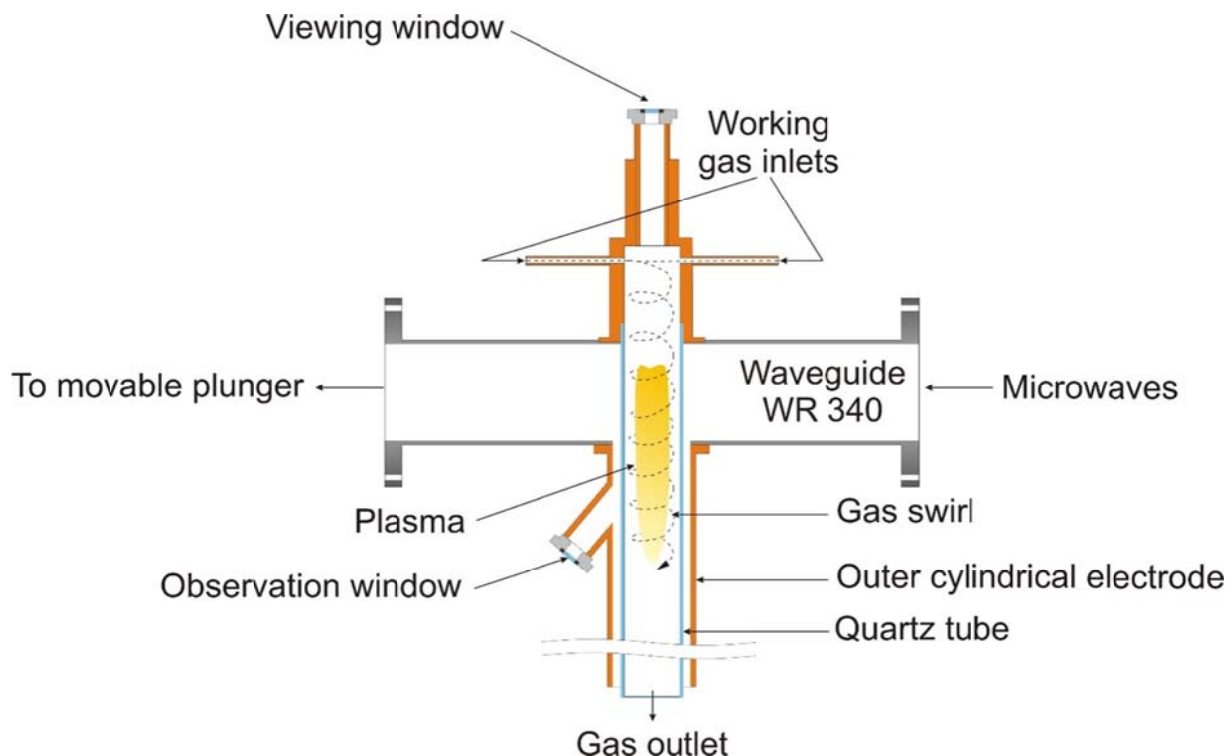


Fig. 2. Waveguide-supplied metal-cylinder-based (with or without an inner electric tube) microwave plasma source for hydrogen production.



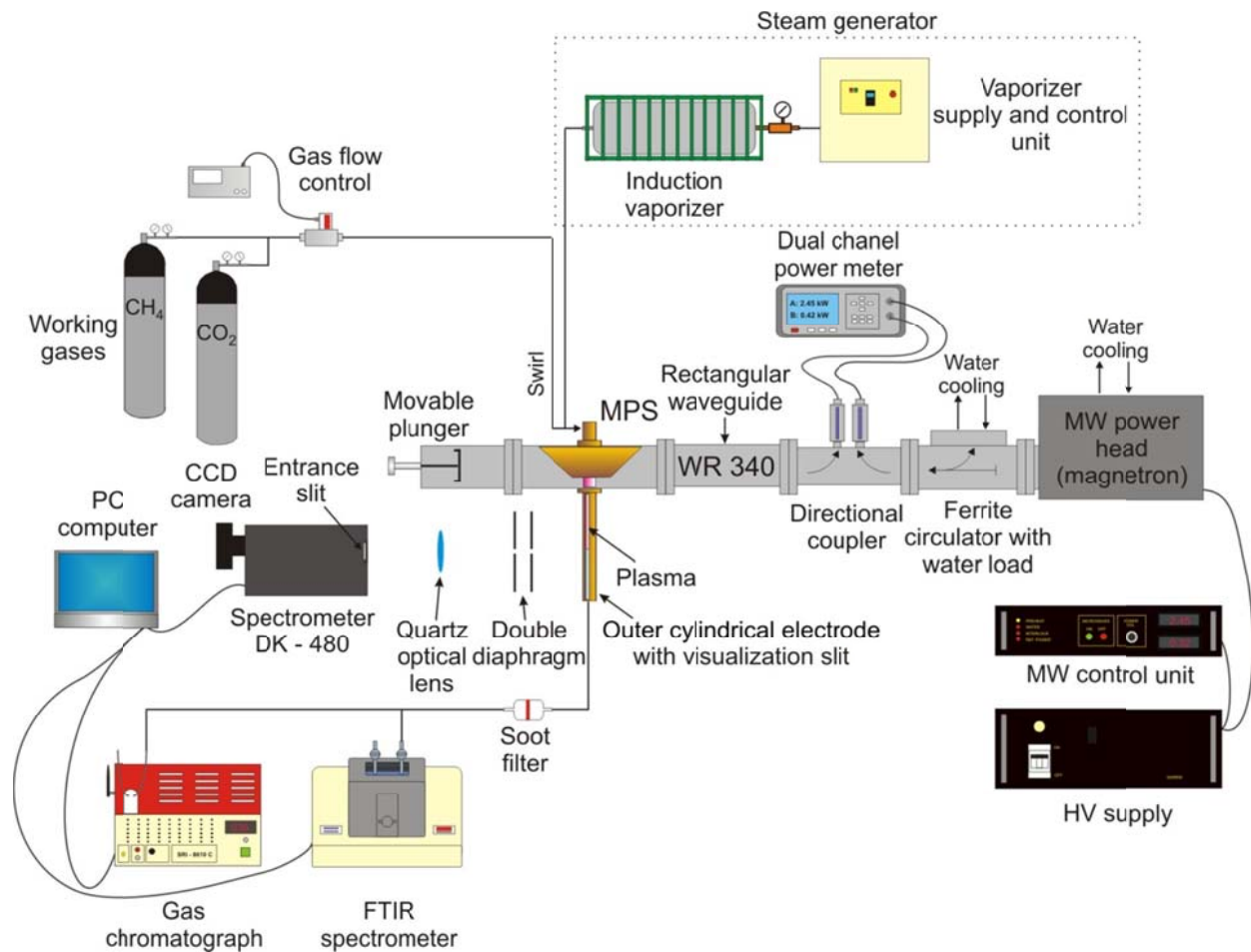


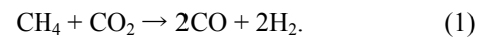
Fig. 3. Microwave plasma system for hydrogen production using a waveguide-supplied metal-cylinder-based microwave plasma source (MPS).

in Fig. 3. The microwaves were produced by a generator consisted of a magnetron head operating at a frequency of 2.45 GHz, high voltage supply and control unit. The maximum mean power of the microwave generator was 6 kW.

The microwave generator was equipped with a ferrite circulator which protected the magnetron head against the reflected microwave wave. A calibrated directional coupler, equipped with a digital dual-channel microwave powermeter was used to measure the incident  $P_I$  and reflected  $P_R$  microwave powers at the MPS input. The absorbed microwave power  $P_A$  was determined by deducting  $P_R$  from  $P_I$ . The MPS was preceded by a three-stub tuner and followed by a movable plunger. Both of them were used to minimize the reflected microwave wave at the MPS input. This helped in improving the efficiency of the microwave energy transfer to the microwave plasma. The working gases flow rates were controlled by a mass flow controller (MFC) placed before the MPS gas inlet. A steam generator, consisting of a water induction vaporizer and a supply and control unit (controlling the gas temperature and flow rate) was used to produce steam. The inlet and outlet gas compositions were determined using SRI 8010C Gas Chromatograph and Thermo Nicolet 380 Fourier transform infrared spectrophotometer (FTIR). The outlet

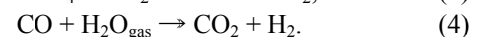
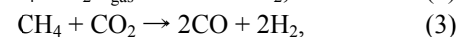
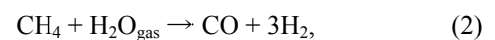
gas passed through a gas-soot separator to capture the soot if produced during the methane conversion. For the microwave plasma diagnostics an optical emission spectrometer (DK-480 CVI) equipped with a CCD camera (SBIG ST 6) was employed.

The dry and combined steam processing of methane were studied using the presented MPS. The dry reforming proceeds according to the following reaction:



In our experiment,  $\text{CH}_4$  and  $\text{CO}_2$  were mixed before entering the four inlets of MPS to form a gaseous mixture ( $\text{CH}_4 + \text{CO}_2$ ).

Methane combined steam processing is based on the following reactions:



To perform this process a mixture of  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}_{\text{gas}}$  was delivered to the MPS through the swirl forming ducts.

Table IV summarizes results of the reforming of methane in these two processes. It is seen from Table IV

TABLE III

COMPARISON OF THE EFFICIENCY OF DRY AND COMBINED STEAM REFORMING PROCESSING OF METHANE IN THE WAVEGUIDE-SUPPLIED METAL-CYLINDER-BASED MPS. ABSORBED MICROWAVE POWER - 3.5 KW.

MPS type	Hydrogen production method	Flow rate, NL/min	Hydrogen production rate NL(H <sub>2</sub> )/h	Energy yield		Reference
				NL(H <sub>2</sub> )/kWh	g(H <sub>2</sub> )/kWh	
Metal-cylinder-based	Dry reforming	CH <sub>4</sub> – 50, Swirl CO <sub>2</sub> – 50, Swirl	790	230	20	M. Jasiński <i>et al.</i> , 2013, [32]
		CH <sub>4</sub> – 100, Swirl CO <sub>2</sub> – 100, Swirl	1000	295	26	M. Jasiński <i>et al.</i> , 2013, [32]
	Combined steam reforming	CH <sub>4</sub> – 50, Swirl CO <sub>2</sub> – 50, Swirl H <sub>2</sub> O <sub>gas</sub> – 62, Swirl	1520	466	42	M. Jasiński <i>et al.</i> , 2013, [30]

that the energy yield of hydrogen production is higher for the combined steam reforming and it equals 42 g(H<sub>2</sub>)/kWh at 3.5 kW of absorbed microwave power. Although this value is lower than the DOE's target of 60 g(H<sub>2</sub>)/kWh, some improvements of the microwave source and technology to increase the energetic parameters are still possible. One possibility is using a catalyst which, as it was proven in [23, 30] resulted in substantial increase of the hydrogen production yield.

## II. CONCLUSION

As shown, the economic analysis of the U.S. Department of Energy has determined tough conditions for hydrogen production technologies to be accepted in the distributed and central scales by the market in 2020. The most important requirement which has to be met by the hydrogen producers in the distributed scale is the energy yield of 60 g(H<sub>2</sub>)/kWh (or 2US\$ per kg of hydrogen) in 2020. The DOE expects that such technologies as natural gas reforming, electrolysis from grid electricity, reforming of ethanol and methanol (both from biomass) are capable of targeting 60 g(H<sub>2</sub>)/kWh in 2020. Plasma technologies have not been mentioned by the DOE' report as an economically competitive technology for hydrogen production.

At present some plasma technologies have met the DOE's energy yield requirement foreseen for 2020. In the case of distributed hydrogen production from gaseous fuels they are: gliding arc, plasmatron arc with catalyst and microwave discharges (Table III). However, higher expectations are placed on these technologies when liquid fuels are used as a source of hydrogen.

Although the use of catalyst resulted in substantial increase of the hydrogen production yield (Table III), opinions on catalyst potential to be commercially attractive in supporting the plasma production of hydrogen are divided. Some claim unpracticality of using catalysts which are expensive and impurity vulnerable.

Other matters which have to be considered when assessing the usefulness of plasma technology for the commercial production of hydrogen are the investment and running costs. Generally there is lack of such information. A relatively well-developed cost model of

hydrogen production was presented for the plasmatron technology in [23]. The conclusion from this cost assessment is that although the plasmatron method is very efficient in hydrogen production, the investment and running costs are relatively high.

Finally, our investigation showed that the microwave plasma method (using either the metal-cylinder-based or resonant-cavity-based MPS) has a potential to become attractive in terms of the performance and hydrogen production rate and energy yield. At present the achieved energy yield of hydrogen production from methane is close to the DOE's 2020 target of 60 g(H<sub>2</sub>)/kWh. Our preliminary experiment on hydrogen generation from a mixture of nitrogen and ethanol by the metal-cylinder-based MPS showed potential of the microwave discharges for hydrogen production from liquid fuels (the energy yield was several tens g(H<sub>2</sub>)/kWh at a relatively low ethanol concentration).

Summarizing, at present, i.e. about 5 years before a milestone year 2020 determined by the U.S. DOE, some plasma methods for small-scale (distributed) hydrogen production from gaseous fuels seem to cross the energy yield target of 60 g(H<sub>2</sub>)/kWh. However these methods have to meet the challenge of the high hydrogen production rate, high reliability and low investment cost.

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