

Research Article

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Hydrogen production from ethanol in nitrogen microwave plasma at atmospheric pressure

Abstract: Hydrogen seems to be one of the most promising alternative energy sources. It is a renewable fuel as it could be produced from *e.g.* waste or bio-ethanol. Furthermore hydrogen is compatible with fuel cells and is environmentally clean. In contrast to conventional methods of hydrogen production such as water electrolysis or coal gasification we propose a method based on atmospheric pressure microwave plasma. In this paper we present results of the experimental investigations of hydrogen production from ethanol in the atmospheric pressure plasma generated in waveguide-supplied cylindrical type nozzleless microwave (2.45 GHz) plasma source (MPS). Nitrogen was used as a working gas. All experimental tests were performed with the nitrogen flow rate Q ranged from 1500 to 3900 NL h⁻¹ and absorbed microwave power P_A up to 5 kW. Ethanol was introduced into the plasma using the induction heating vaporizer. The process resulted in an ethanol conversion rate greater than 99%. The hydrogen production rate was up to 728 NL[H₂] h⁻¹ and the energy efficiency was 178 NL[H₂] per kWh of absorbed microwave energy.

Keywords: hydrogen production; microwave plasma; atmospheric pressure; liquid hydrocarbons; ethanol reforming

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1 Introduction

Decrease of natural reserves of fossil fuels and the greenhouse effect from CO₂ emissions generated by currently-used processes of energy production incites searching of new energy sources. The newly developed energy sources must meet the requirements of being environment-friendly and renewable simultaneously. Hydrogen seems to be one of the most promising alternative energy sources. The heat released during the combustion of hydrogen is 142 kJ g⁻¹, compared with 47 kJ g⁻¹ for gasoline, 29.7 kJ g⁻¹ for ethanol and 54 kJ g⁻¹ for natural gas [1]. Hydrogen rich gas can be produced from different kinds of feedstock such as fossil fuels [2,3], water [4], alcohols [5-10], biomass [11,12] or carbon [13,14]. Hydrogen is also considered to be a renewable fuel as it could be produced from *e.g.* waste [15, 16] or bio-ethanol [17]. Furthermore hydrogen is compatible with fuel cells and is environmentally clean. The importance of hydrogen for future energy can be easily understood taking into account the fact that it is listed as a primary energy source in the energy development strategy of many developed countries [18,19].

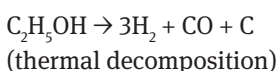
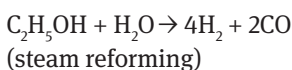
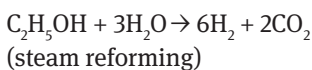
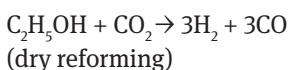
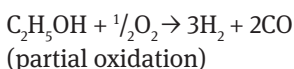
A variety of methods can be used for hydrogen production. The more developed are conventional methods of hydrogen production such as coal gasification, hydrocarbon reforming and water electrolysis. Currently, catalytic hydrocarbon reforming process is the most well-developed and economical technique for hydrogen production. In addition to the hydrocarbon, the other reactant for the reforming process could be either steam or oxygen, which is known as the steam reforming or partial oxidation.

Application of plasma technologies to hydrocarbon reforming to generate hydrogen has been gradually attracting attention. The plasma is composed of reactive radicals, ions and high-energetic electrons. High reactivity of these species enhances the chemical reaction rates allowing to avoid the use of expensive and impurity vulnerable catalysts. These advantages as well as its high energy density can be used to design a compact plasma

reformer. Besides, the plasma system can be modified in order to reform various liquid hydrocarbons.

The plasma could be operated at low pressure or atmospheric pressure. Although the low pressure plasma, such as radio frequency (RF) plasma or microwave (MW) plasma, could achieve high hydrocarbon conversion and good hydrogen selectivity, the low hydrogen production rate and extra energy requirement for the vacuum device restrict its practical use. Different kinds of atmospheric pressure plasma was tested experimentally in hydrogen production investigations: gliding arc plasma [20], dielectric barrier discharge [21,22], corona discharge [23] and microwave plasma [10,24,25].

There are a few different ethanol based methods of hydrogen production including: steam reforming, dry reforming, partial oxidation, thermal decomposition. They process through the following reactions:



All these processes can be performed in plasma reactors [26,27].

At present, methane is the most common hydrocarbon used for hydrogen production [2]. Recently, interest in efficient plasma methods of hydrogen production from liquids, such as water or alcohols, is increasing. The use of a liquid source of hydrogen can decrease the cost of hydrogen production due to much easier handling and greater availability than gaseous sources.

Microwave plasma at atmospheric pressure has found applications in the processing of various gases. Decomposition of volatile organic compounds (VOCs) [28] and reforming of methane [29] into hydrogen were reported by us recently.

In this paper we present results of the experimental investigations of the hydrogen production from ethanol in the atmospheric pressure microwave plasma. The main objective of this investigation is to obtain knowledge

about processes during microwave plasma conversion of ethanol as a hydrogen source.

2 Experimental procedure

In this investigation we used a 2.45 GHz plasma system based on a standard WR 430 waveguide. The diagram of the experimental setup is shown in Fig. 1. It consisted of a magnetron generator, microwave power supplying and measuring system, microwave plasma source (MPS), impedance matching elements, gas supply and flow control system, gas analysis system and optical emission spectroscopy (OES) system.

The microwave generator is composed of a high voltage power supply, a control unit and a magnetron head. The magnetron head is equipped with a water cooled circulator which protects it against damages caused by the reflected microwave power. The microwave power measuring system includes a directional coupler, two power meter heads and a digital dual-channel power meter. This system enables direct measurements of an incident P_I microwave power entering into the MPS and reflected P_R microwave power outgoing from the MPS, regardless of the losses in the microwave launcher. An absorbed power P_A was obtained from the subtraction of $P_I - P_R$.

The plasma was generated by waveguide-supplied nozzleless cylindrical type MPS based on a standard rectangular waveguide WR 430 with a section of reduced-height, preceded and followed by tapered sections. The plasma flame was generated inside a quartz tube which penetrated MPS through circular gaps on the axis of the waveguide wide wall and protruded below bottom waveguide wall. On the outside of the waveguide the quartz tube was surrounded by a cylindrical metal electrode with a slit for visualization. Working gas was introduced to the plasma by four gas ducts which formed a swirl flow inside the quartz tube. The MPS was described in detail in [30].

The plasma generator was followed by a movable plunger. It played a role of impedance matching circuits between the plasma generator and the waveguide. Matching the impedance in the waveguide system improves efficiency of microwave power transfer from the microwave generator to the plasma generator.

For optical emission spectroscopy a spectrometer CVI DK-480 (1200 gr mm⁻¹ and 3600 gr mm⁻¹ grating) equipped with CCD (sensitivity calibrated) camera was used. In this experiment the light emitted by the plasma was focused with a quartz lens (50 mm in diameter, focal length – 75 mm) onto the entrance slit of the spectrometer.



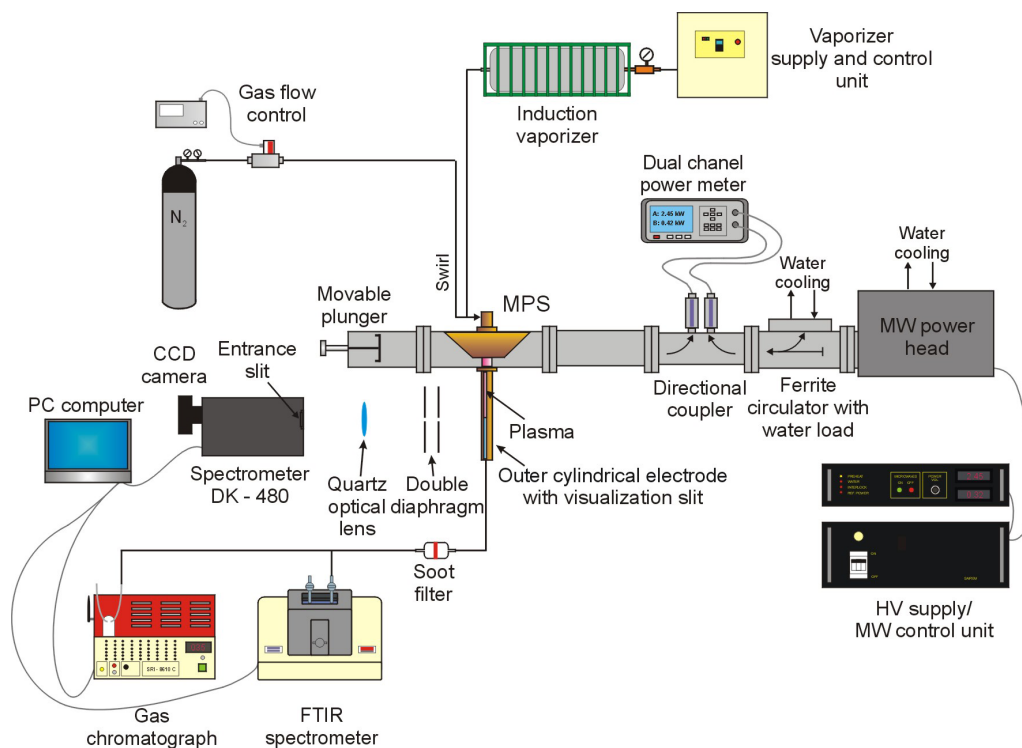


Figure 1: The experimental setup.

A double diaphragm of a 1 mm diameter was placed near the plasma. The diameter of the measured area was about 8 mm. The spectra in range 300 – 600 nm were recorded. Gas temperature in the plasma was estimated using Specair [31] and Lifbase [32] programs with reference to recorded spectra following a procedure described elsewhere [33-37].

Diagnostic of the working gas composition before and after the microwave plasma generator was carried out using a gas chromatograph (Shimadzu GC-2014 and SRI 8610C) and Fourier Transform Infrared Spectrophotometer FTIR (Thermo Nicolet 380) operating in the range of 1000-4000 cm^{-1} . Concentration of the following components: H_2 , O_2 , N_2 , CO , CO_2 , CH_4 , C_2H_2 , C_2H_4 and C_2H_6 in investigated gas samples were defined. The experimental results of gas composition were also compared with theoretical calculations based on a model proposed by Marinov [38].

Nitrogen (N_2) was used as a working gas. Nitrogen is one of the less expensive gases. Furthermore, the results with nitrogen were comparable with the results when argon was used [39]. All experimental tests were performed with the working gas flow rate Q ranged from 1500 to 3900 NL h^{-1} and absorbed microwave power P_A up to 5 kW. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) was introduced into the plasma using induction heating vaporizer. The $\text{C}_2\text{H}_5\text{OH}$ vapors were introduced to the plasma by one of four gas ducts of the MPS. The amount of $\text{C}_2\text{H}_5\text{OH}$ ranged from 0.4 to

1.6 kg h^{-1} . The purity of $\text{C}_2\text{H}_5\text{OH}$ used in these investigations was 96%. Assuming that 4% of the impurities is mainly water, two types of reactions are expected in this experiment: thermal decomposition and steam reforming.

3 Results and discussion

3.1 Spectroscopic diagnostics

Figure 2 shows spectra of N_2 plasma measured 15 mm below the waveguide bottom in the cylindrical type MPS (2.45 GHz plasma system) at working gas flow rate of 2700 NL h^{-1} and absorbed microwave power of 3 kW without and with the addition of 0.8 kg h^{-1} of $\text{C}_2\text{H}_5\text{OH}$. Measured spectra of N_2 plasma without addition of $\text{C}_2\text{H}_5\text{OH}$ vapor (Fig 2a) contained bands of N_2^+ first negative system ($\text{B}^2\Sigma \rightarrow \text{X}^2\Sigma$), N_2 first positive ($\text{B}^3\Pi \rightarrow \text{A}^3\Sigma$) and weak N_2 second positive system ($\text{C}^3\Pi \rightarrow \text{B}^3\Pi$). The intensity of the emitted N_2^+ first negative system was dominant. After measuring the experimental spectra they were compared with simulated ones in order to determine the rotational temperature of heavy species in plasma. This temperature is used to estimate gas temperature in plasma [35-37]. Obtained rotational temperatures of N_2^+ ranged from

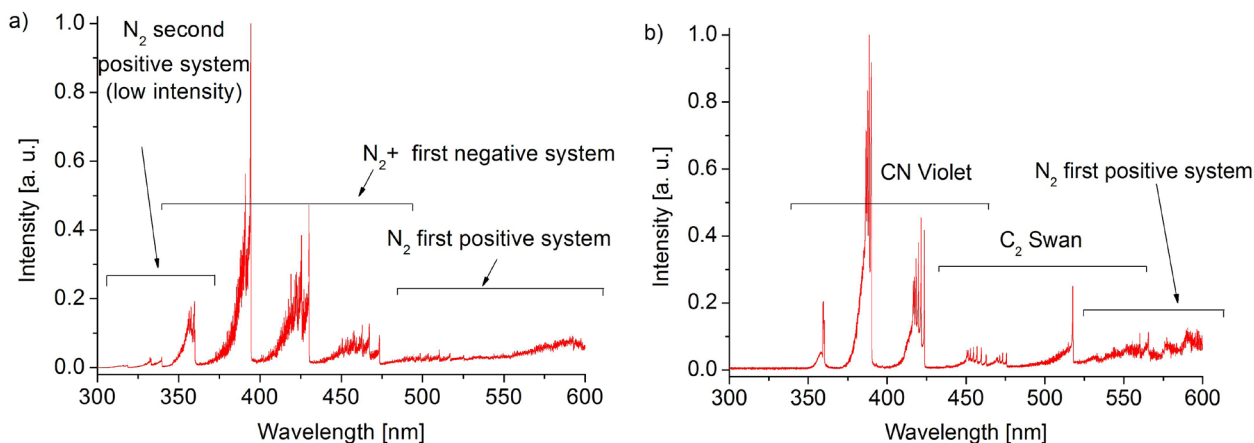


Figure 2: Photos and measured emission spectra of N_2 plasma without (a) and with (b) ethanol vapor addition (absorbed microwave power $P_a = 3$ kW, N_2 flow rate - 2700 NL h^{-1} , C_2H_5OH flow rate - 0.8 kg h^{-1} , 15 mm below the waveguide bottom).

4500 to 6000 K depending on location in plasma and N_2 flow rate [37]. Similar temperatures were obtained for OH radicals (when a small amount of water vapour was added to swirl gas flow in order to achieve detectable intensity of OH ($A^2\Sigma \rightarrow X^2\Pi$) spectra). In the case of N_2 plasma with the addition of 0.8 kg h^{-1} of C_2H_5OH (Fig. 2b) the dominant spectrum was C_2 Swan system ($A^3\Pi \rightarrow X^3\Pi$). The spectrum contained also a CN Violet system ($B^2\Sigma \rightarrow X^2\Sigma$). The obtained rotational temperature of CN molecules was 4000 K at N_2 flow rate of 2700 NL h^{-1} and absorbed microwave power of 3 kW. The lower rotational temperature was measured in case of C_2 molecules - 3700 K.

3.2 Ethanol conversion

The ethanol conversion degree is given by $[(C_2H_5OH)_{converted} / (C_2H_5OH)_{initial} \times 100\%]$, where $(C_2H_5OH)_{initial}$ is the total mass of C_2H_5OH and $(C_2H_5OH)_{converted}$ is the converted mass of C_2H_5OH . In the case of the experiment carried out in the cylindrical type MPS, the C_2H_5OH conversion degree was above 99%.

Analysis of the output gas composition showed that apart from soot the main products of C_2H_5OH plasma conversion were: hydrogen (H_2), carbon monoxide (CO), acetylene (C_2H_2) and methane (CH_4). A small amount of ethylene (C_2H_4) and ethane (C_2H_6) as well as carbon dioxide (CO_2) was also detected in the output gas samples (see Table 1).

The C_2H_5OH conversion was evidenced by production of carbon observed on the wall of the quartz tube inside the MPS. The problem we faced during the experiments with the increased amount of C_2H_5OH was the intense soot production. The soot was forming on the quartz tube inner

Table 1: The best achieved results of hydrogen production via ethanol conversion in microwave nitrogen plasma (N_2 flow rate - 2700 NL h^{-1} , C_2H_5OH flow rate - 0.8 kg h^{-1}).

Absorbed microwave power kW	Hydrogen production rate NL(H) h^{-1} [g(H_2) h^{-1}]	Energy yield NL(H) kWh^{-1} [g(H_2) kWh^{-1}]	Ethanol conversion degree %	Products in the outgas %
5	728 [60.6]	145 [12.1]	99.99	N_2 - 67.1 H_2 - 19.85 CO_2 - 0.18 CO - 7.59 CH_4 - 2.45 C_2H_2 - 2.59 C_2H_4 - 1.17 C_2H_6 - 0.07
2	357 [29.7]	178 [14.8]	99.99	N_2 - 82 H_2 - 11.3 CO_2 - 0.18 CO - 3.98 CH_4 - 0.83 C_2H_2 - 1.03 C_2H_4 - 0.58 C_2H_6 - 0.07

surface as well as in the plasma zone. This caused the problem with microwave penetration and consequently damage the quartz tube. To solve this problem another method of introducing C_2H_5OH into the plasma must be developed. We believe that introducing the C_2H_5OH axially and introducing the working gas plasma by four gas ducts, which formed a swirl flow, allowed this problem to be avoided and protected the quartz tube.



3.3 Hydrogen production

The effectiveness of hydrogen production in our experiment was described by the following parameters: hydrogen production rate and energy yield of hydrogen production. The hydrogen production rate in NL(H₂)/h describes how many litres of hydrogen are produced per unit of time (one hour). Energy yield of hydrogen production in NL(H₂)/kWh is defined to describe the amount of litres of hydrogen produced using 1 kWh of energy.

Fig. 3 presents the hydrogen production rate and energy efficiency of hydrogen production as a function of absorbed microwave power in the atmospheric pressure N₂ plasma. Table 1 presents a summary of the best achieved results of hydrogen production, together with the detailed output gas composition. As it can be seen, the best achieved results of hydrogen production rate and energy efficiency of hydrogen production were 728 NL[H₂]/h and 178 NL[H₂] per kWh of microwave energy used, respectively. It should be noted that decrease of working gas flow rate to 1500 NL h⁻¹ did not improved the obtained results. It also should be noticed that the best result of hydrogen production rate was achieved for 5 kW of microwave absorbed power while the best result of energy yield of hydrogen production was achieved for 2kW of microwave absorbed power. Thus the faster production of hydrogen is less effective in terms of energy.

As it could be observed in Fig. 4 increasing the C₂H₅OH vapour flow caused an increase of hydrogen production parameters. However the increase is not linear. Taking into account that the conversion of ethanol was above 99% in all cases this phenomena is caused by decrease of conversion selectivity into hydrogen. The increase of C₂H₅OH vapour flow over 0.8 kg h⁻¹ was performed only for N₂ flow rate of 3900 NL h⁻¹ because of the intense soot production mentioned before. We believe that applying the axial C₂H₅OH introducing method allowed for an increased C₂H₅OH vapour flow over 0.8 kg h⁻¹, also for lower N₂ flow rate. Naturally this could improve the production of hydrogen efficiency parameters.

3.4 Theoretical modelling

The presence of four hydrocarbons in the gas leaving the microwave plasma shows that the mechanism of ethanol decomposition is not as simple as observed by Tsyganov *et al.* [40]. In their experiment they found no acetylene or other hydrocarbons. So, they could describe the ethanol decomposition by one reaction:

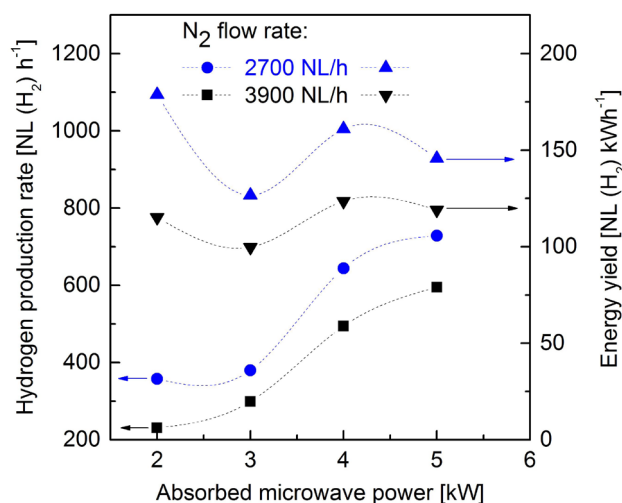
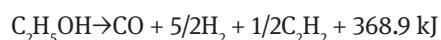


Figure 3: Hydrogen production rate and energy efficiency of hydrogen production as a function of absorbed microwave power (C₂H₅OH flow rate – 0.8 kg h⁻¹).

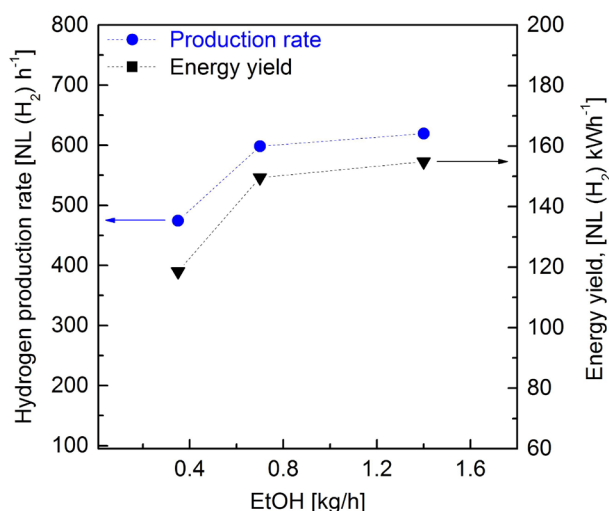


Figure 4: Hydrogen production rate and energy efficiency of hydrogen production as a function of ethanol mass introduced into the plasma. (absorbed microwave power P_a = 4 kW, N₂ flow rate - 3900 NL h⁻¹).

In our case we should employ a much more complex mechanism such as that proposed by Marinov [38]. In fact we did that using the model and the software successfully used when studying methane processing in the same experimental system [41]. The result of the calculation as a function of temperature is presented in Fig. 5. In the same figure we incorporated the experimental results by matching hydrogen concentrations to the gas temperature. The matching procedure does not give an accurate temperature but shows how closely the experimental results are to the calculation ones.

As can be seen, after matching hydrogen concentrations the other compounds do not follow the calculated values. The concentrations of acetylene are 3 times lower than predicted by the model. In the case of other hydrocarbons their concentrations increase in the experiment whereas according to the model they should decrease. The discrepancy between experimental and calculated results cannot be explained by post-plasma quenching reactions because they were included in the model. At the moment

the most plausible reason is a formation of several regions of different properties in axial and radial directions in the quartz tube which can be modeled with a sophisticated fluid dynamics model.

4 Conclusions

The previous results showed that the investigated nozzleless waveguide-supplied cylindrical type MPSs for hydrogen production can be operated with a good power efficiency and stability. It can be operated in different gases such as argon, nitrogen and carbon dioxide with microwave power of a few kW with gas flow rates of thousands $l\ h^{-1}$ [30]. The temperature of heavy species (assumed to be close to gas temperature) was up to 6000 K (for N_2 plasma without C_2H_5OH) [37]. This encouraged us for performing tests of the hydrogen production via liquid hydrocarbons conversion. In this work we presented the results of thermal conversion of ethanol in microwave plasma.

Addition of C_2H_5OH vapor in N_2 plasma caused a slight decrease of rotational temperatures of selected molecules. However these temperatures are still at the level of 4000 K. The ethanol conversion rate in all cases was greater than 99%. The hydrogen production rate and energy efficiency of hydrogen production were up to 728 NL(H_2) per h (60.5 g[H_2] per h) and up to 178 NL(H_2) per kWh (14.8 g[H_2] per kWh) of microwave energy used, respectively. It should be noticed that purity of ethanol was 96% with the water as a main impurity. The presence of water could improve achieved results [42]. Table 2 presents a comparison of selected plasma methods of hydrogen production

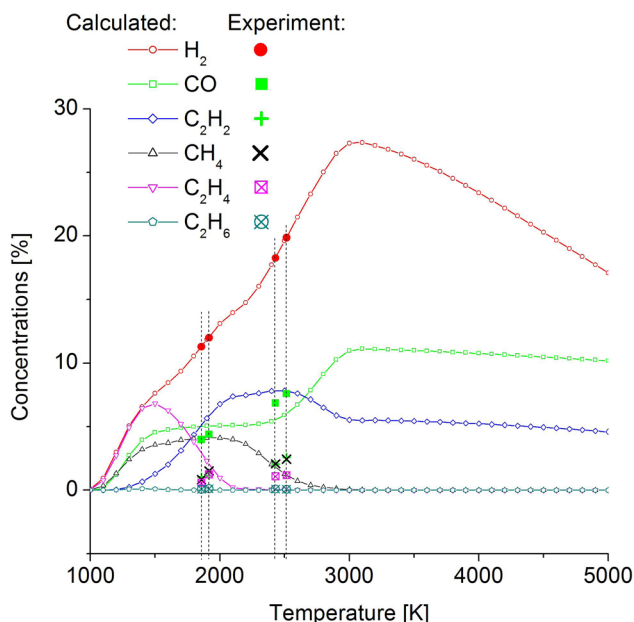


Figure 5: Calculated and experimental concentration of selected species in plasma as a function of the temperature (the experimental results are matched by hydrogen concentrations to the gas temperature).

Table 2: Comparison of selected plasma methods of hydrogen production *via* alcohols decomposition.

Production method	Initial composition	Conversion degree, %	Energy yield, g(H_2) kWh ⁻¹	Reference
Microwave (2.45 GHz) plasma	Ar + C_2H_5OH	almost 100	0.37	[10]
Laval nozzle arc discharge	C_2H_5OH + H_2O	50-90	100	[17]
Glid arc spray	Ar + CH_3OH	up to 33	176	[20]
Dielectric barrier discharge	CH_3OH + CO_2/H_2O	up to 100	3.3	[21]
	C_2H_5OH + CO_2/H_2O		6.7	
Microwave (2.45 GHz) plasma	Ar + C_2H_5OH	98.4*	0.55	[40]
Microwave (2.45 GHz) plasma	Ar + CH_3OH	almost 100	1.4	[43]
	Ar + C_2H_5OH + H_2O		0.5	
Microwave (2.45 GHz) plasma	Ar + CH_3OH	100	0.29	[44]
	Ar + CH_3OH + H_2O		0.41	
Microwave (2.45 GHz) plasma	N_2 + C_2H_5OH	99.9	14.8	present work

*conversion into H_2 , total alcohol conversion up to 100%



via alcohol decomposition. As it can be observed our results are competitive compared to DBD discharge previously presented and also very competitive with other microwave discharges. It should be noted that in contrast to arc plasmas which demonstrate higher hydrogen mass yield and higher energy yield the conversion rate in all microwave plasmas are almost 100% and the selectivity of conversion into hydrogen can be above 98% [40].

A problem with intense soot production occurred for the ethanol vapour flow rate 0.8 kg h⁻¹ and higher. This caused the problem with microwave penetration and consequently damaged the quartz tube. However we believe that the axial method of introduction of the ethanol into the plasma will solve this problem and allow further improvements to the production of hydrogen efficiency parameters. Such studies are in the progress and results will be presented soon.

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