EmHyTeC 2014, Taormina, Italy, 9-12 December 2014

Hydrogen production via ethanol decomposition in atmospheric pressure microwave plasma

Bartosz Hrycak, Dariusz Czylkowski, Robert Miotk,
Mirosław Dors, Mariusz Jasiński, Jerzy Mizeraczyk

Centre for Plasma and Laser Engineering
The Szewalski Institute of Fluid-Flow Machinery Polish Academy of Sciences
Gdańsk, Poland





Outline

- Introduction
- Microwave plasma source (MPSs) for hydrogen production from ethanol
- Experimental setup
- Results:
    - Visualization of the plasma flame
    - Spectroscopic diagnostics - plasma gas temperature
    - Hydrogen production via ethanol conversion
- Microwave plasma module for hydrogen production - prototype
- Summary and conclusions

Introduction

- Hydrogen is considered as a promising fuel of the future
- It is listed as a primary energy source in the energy development strategy in many developed countries
- Plasma technologies on hydrocarbon reforming to generate hydrogen has been gradually attracting attention (no expensive and impurity vulnerable catalysts)
- Hydrogen production reactions from ethanol:

$C_2H_5OH + {}^1/_2O_2 \rightarrow 3H_2 + 2CO$ (partial oxydation)
$C_2H_5OH + CO_2 \rightarrow 3H_2 + 3CO$ (dry reforming)
$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$ (steam reforming)
$C_2H_5OH + H_2O \rightarrow 4H_2 + 2CO$ (steam reforming)
$C_2H_5OH \rightarrow 3H_2 + CO + C$ (thermal decomposition)

- Investigation concerns microwave (915 MHz, 2.45 GHz) atmospheric pressure plasma source (MPS) for hydrogen production via ethanol conversion
- The main objective of this investigation is to obtain the knowledge about processes during microwave plasma conversion of liquids hydrocarbons (ethanol) as a hydrogen source

Selection of microwave plasma source

Microwave plasma sources (MPSs) for gas processing

- surface-wave-discharge MPSs:
  - coaxial-line-supplied, called surfatrons
  - waveguide-supplied, called surfaguides
- nozzle-type MPSs:
  - coaxial-line-supplied coaxial-line-based (low gas flow rate, several NL/min)
  - waveguide-supplied coaxial-line-based (low and high gas flow rate, several thousands NL/h)
- nozzleless MPSs:
  - waveguide-supplied coaxial-line-based (with or without an inner dielectric tube)
  - <u>waveguide-supplied metal-cylinder-based (with or without an inner dielectric tube)</u>
  - waveguide-supplied resonant-cavity-based
- plasma-sheet MPSs:
  - coaxial-line-supplied strip-line-based
  - waveguide-supplied
- microwave microplasma sources (MmPSs)
  - antenna type
  - coaxial-line-based

Mizeraczyk et al., *Studies of atmospheric-pressure microwave plasmas used for gas processing,* **Nukleonika** 2012 (57), 241−247

Waveguide-supplied metal-cylinder-based MPS

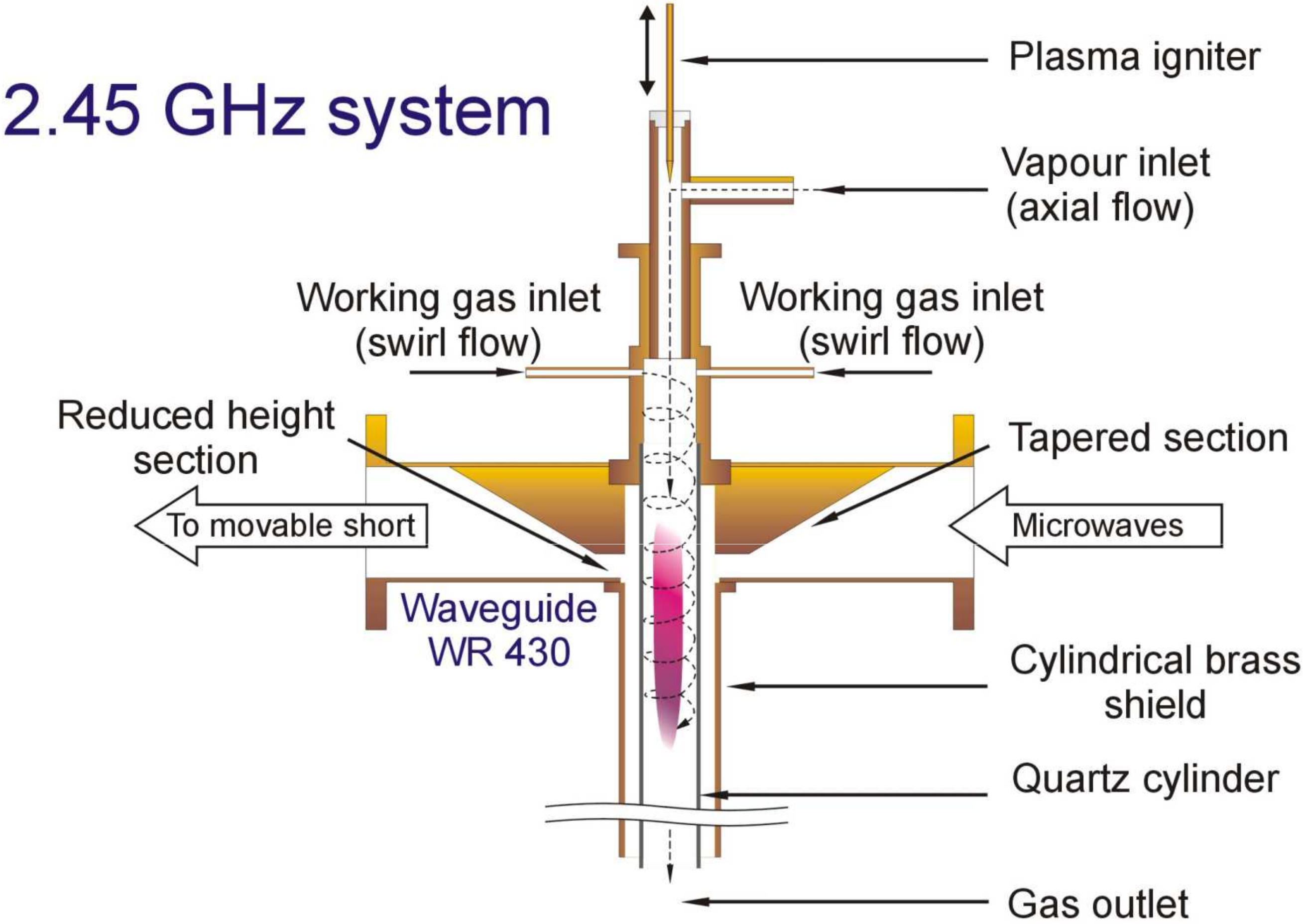
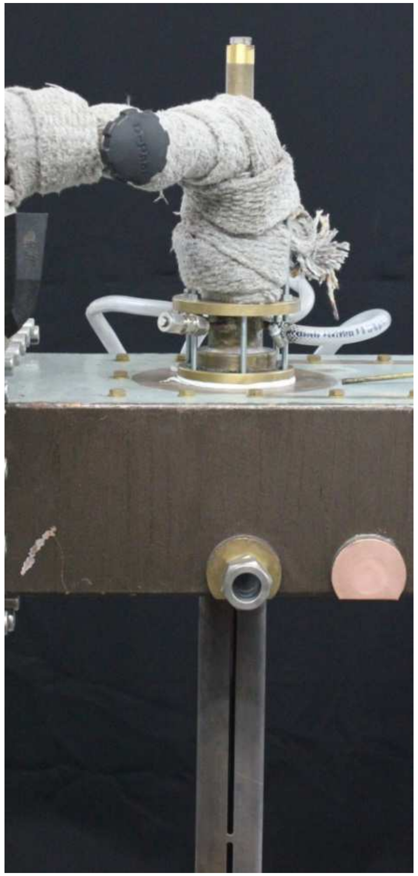


Photo and schematic view of the waveguide-supplied cylindrical type MPS

Waveguide-supplied metal-cylinder-based MPS



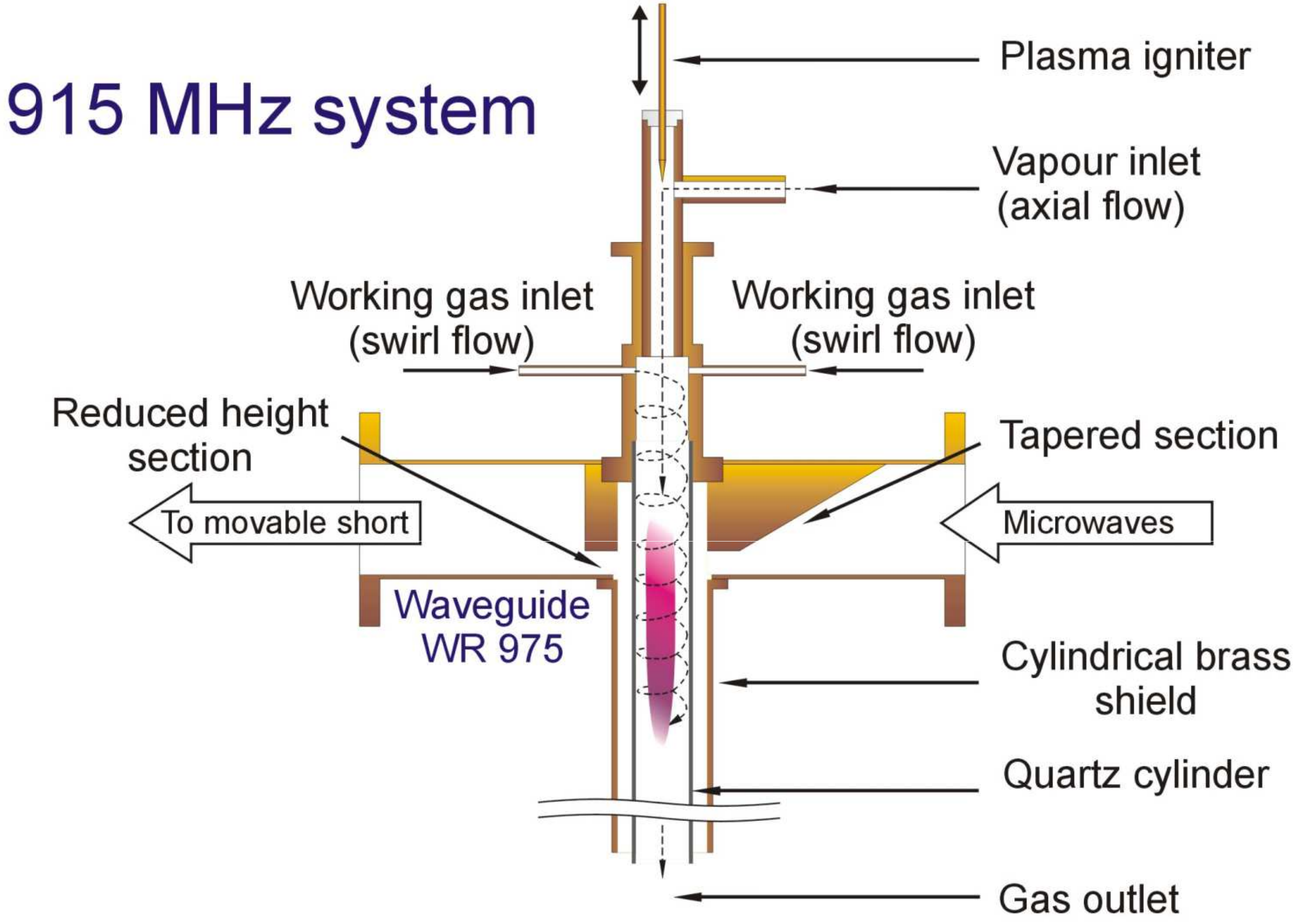
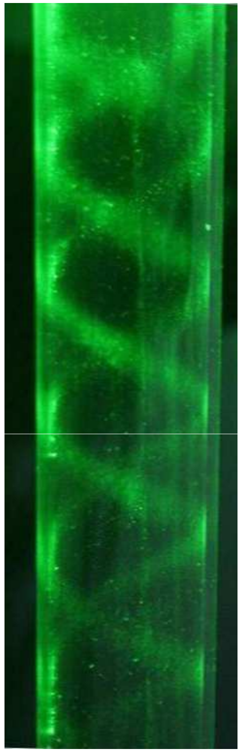
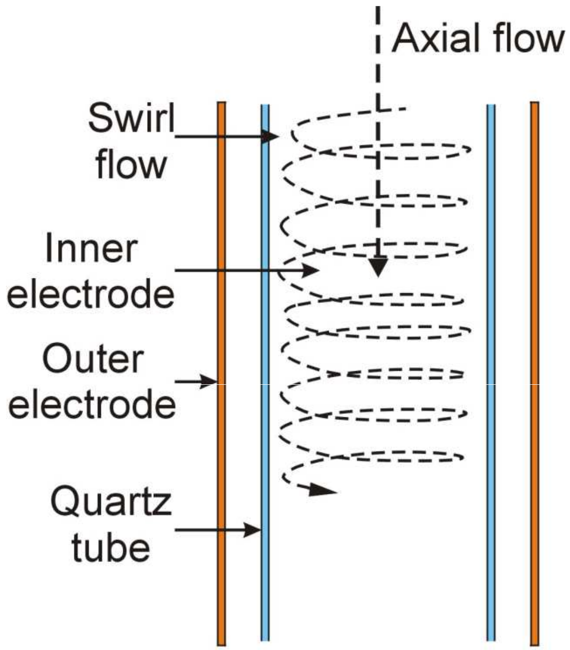
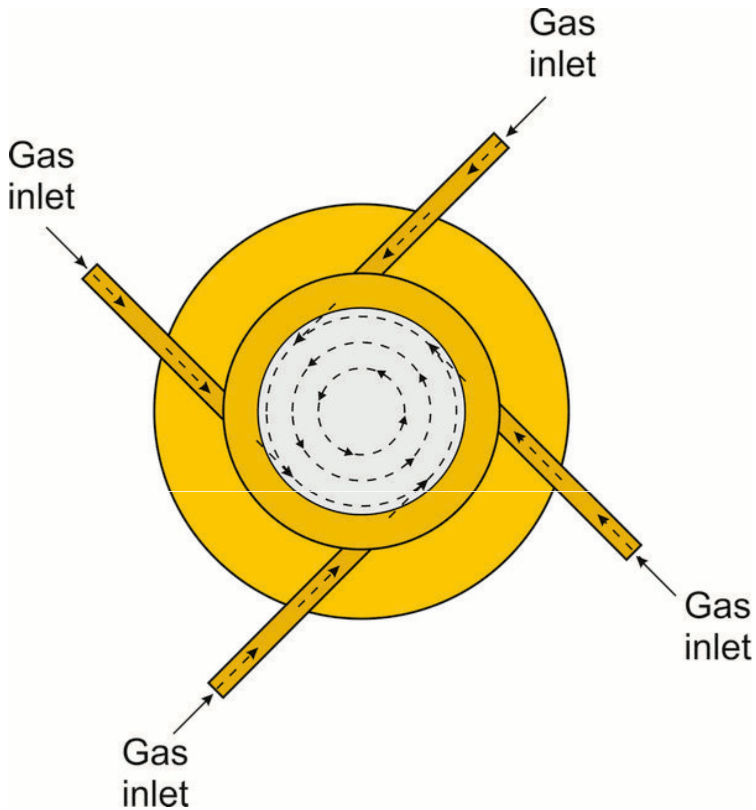


Photo and schematic view of the waveguide-supplied cylindrical type MPS

Waveguide-supplied metal-cylinder-based MPS







Laser visualization of the swirl flow without plasma

Illustrations of the gas swirl and axial flows.

Experimental setup

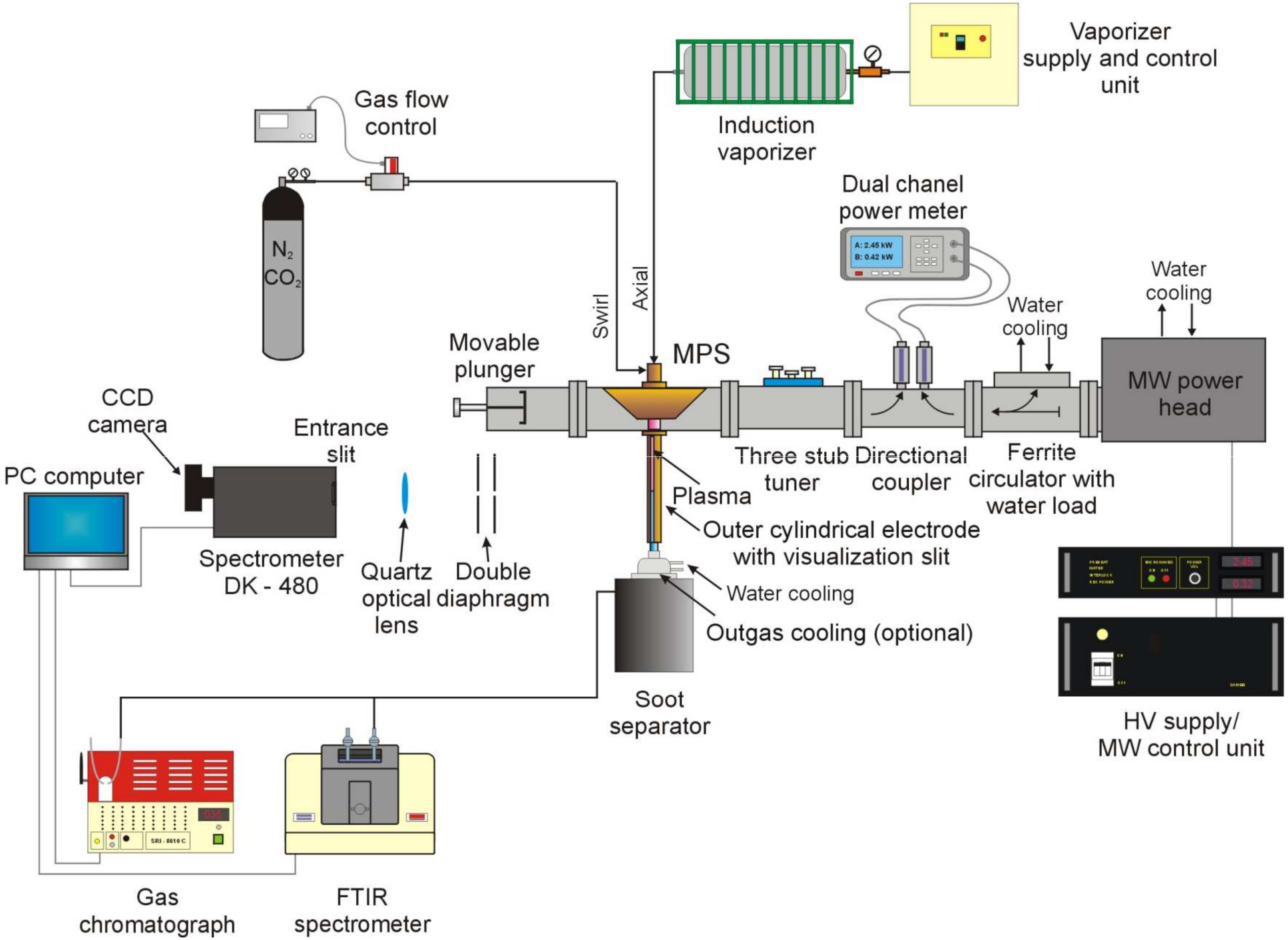
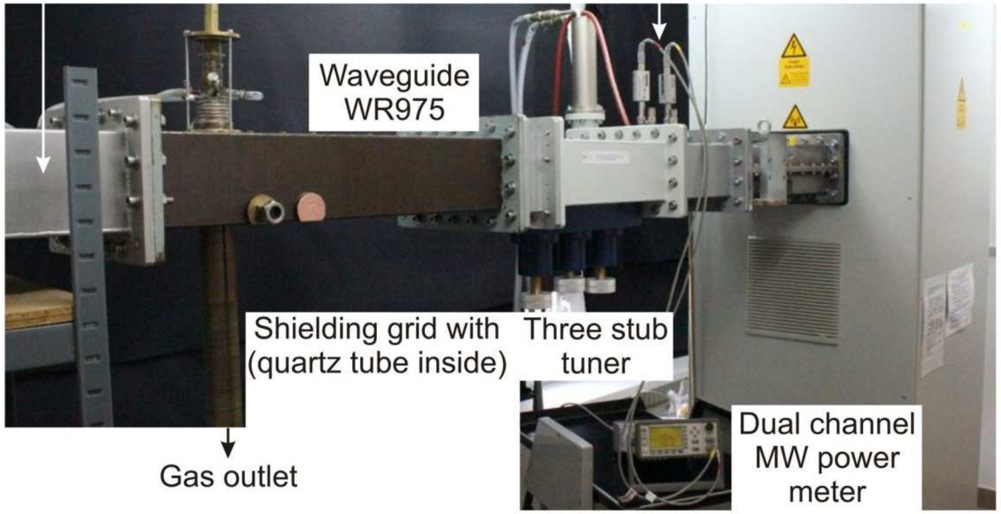


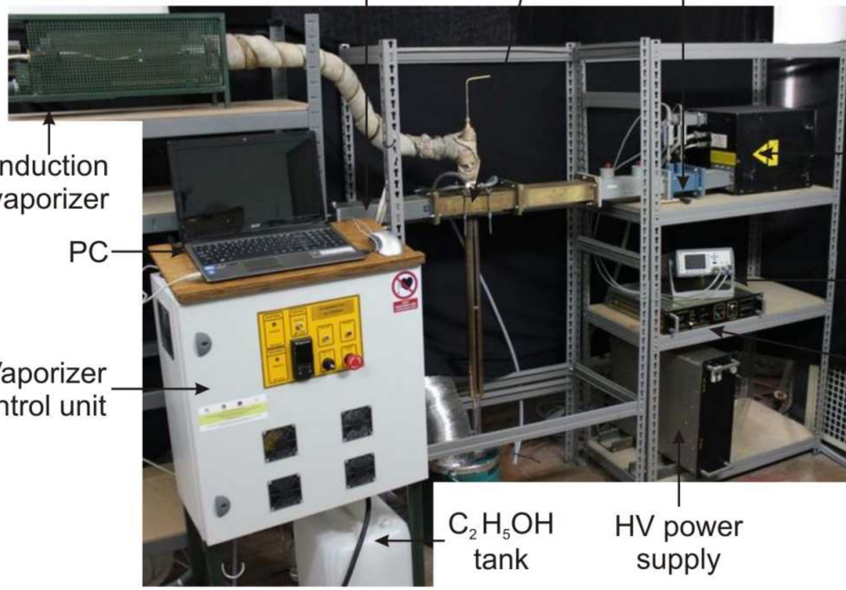
Diagram of the experimental setup for hydrogen production via ethanol conversion

Experimental setup



915 MHz microwave system up to 20 kW

2.45 GHz microwave system up to 6 kW



Experiment parameters

MPS type

- Waveguide-supplied metal-cylinder-based MPS

Processes

- Thermal decomposition of ethanol

$$C_2H_5OH \rightarrow 3H_2 + CO + C$$

- Dry reforming of ethanol

$$C_2H_5OH + CO_2 \rightarrow 3H_2 + 3CO$$

- Steam reforming of ethanol

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$$

$$C_2H_5OH + H_2O \rightarrow 4H_2 + 2CO$$

Constant parameters

- Pressure: atmospheric
- Catalyst: no catalyst

Variable parameters

- Microwave frequency: 915 MHz, 2.45 GHz
- Absorbed microwave power (2 – 5.5 kW)
- Working gases flow rate: up to 3900 NL/h
- C_2H_5OH addition

Measured parameters

- Emission spectra of plasma in range of 300 – 600 nm
- Percentage concentration of following components at the output of the MPS: H_2, Ar, O_2, N_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_2H_5OH

Calculated parameters

- Hydrogen production rate in NL(H_2)/h
- Energy yield of hydrogen production in NL(H_2)/kWh
- Total ethanol conversion
- Conversion into hydrogen

Hydrogen production effectiveness parameters

- Hydrogen production rate in $NL(H_2)/h$, shows how many litters of hydrogen is produced per unit of time (one hour).

- Energy yield of hydrogen production in $NL(H_2)/kWh$ is define as a ratio of the hydrogen production rate to absorbed microwave power in kW. Energy yield describes the amount of litters of hydrogen produced using 1 kWh of energy.

- Total 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 ethanol and $(C_2H_5OH)_{converted}$ is the converted mass of etanol.

- Conversion into hydrogen is given by

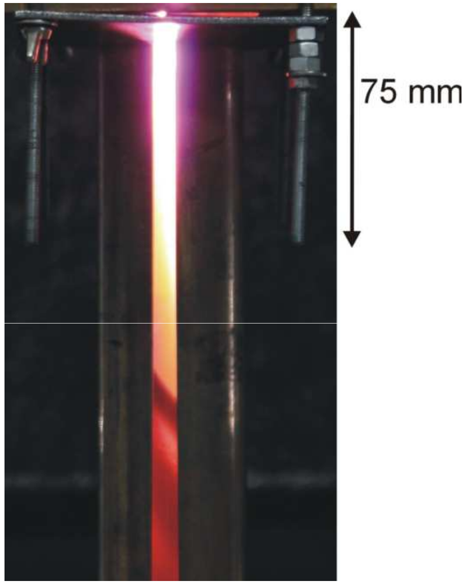
$$[\text{moles of } H_2 \,/\, 3^* \text{ moles of } C_2H_5OH \times 100\%] \text{ or}$$

$$[\text{moles of } H_2 \,/\, (3^* \text{ moles of } C_2H_5OH + \text{moles of } H_2O) \times 100\%] \text{ (for steam reforming)}$$

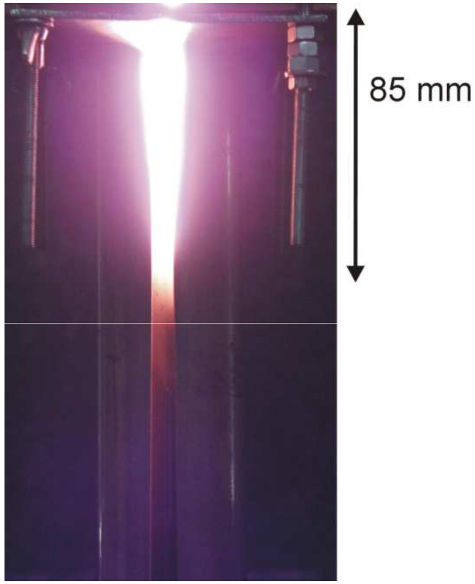
where H_2 is the produced hydrogen, C_2H_5OH is the ethanol and H_2O is the water used for hydrogen production.

Visualization of the plasma flame

without C_2H_5OH

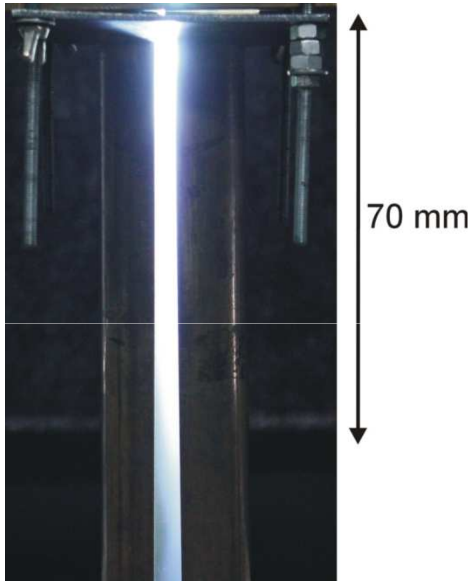


with C_2H_5OH

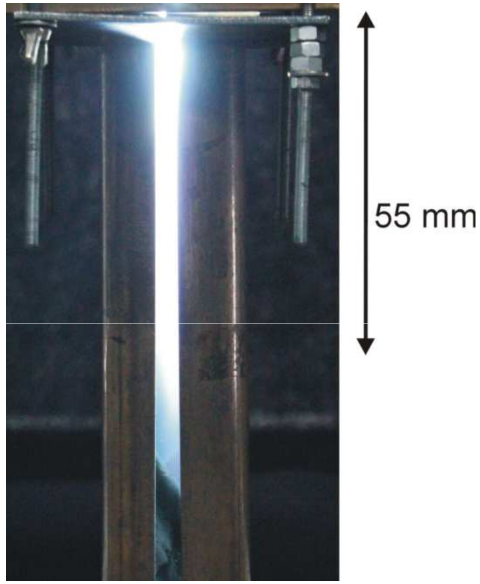


Front view of the of N_2 plasma with and without ethanol vapor addition. 2.45 GHz plasma system, absorbed microwave power P_A - 2 kW, working gas flow rate - 2700 NL/h.

without C_2H_5OH

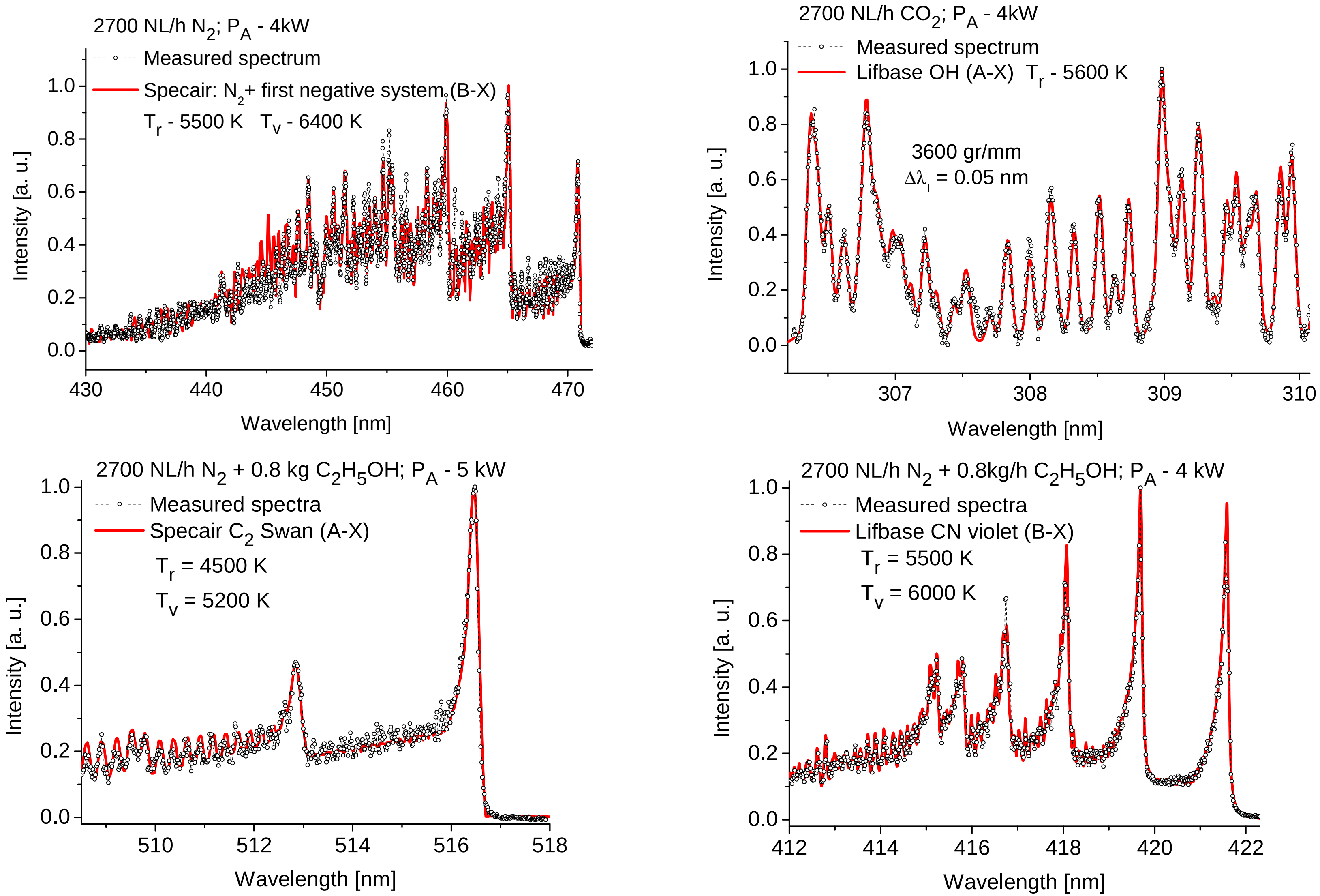


with C_2H_5OH



Front view of the CO_2 plasma with and without ethanol vapor addition. 2.45 GHz plasma system, absorbed microwave power P_A - 2 kW, working gas flow rate - 2700 NL/h.

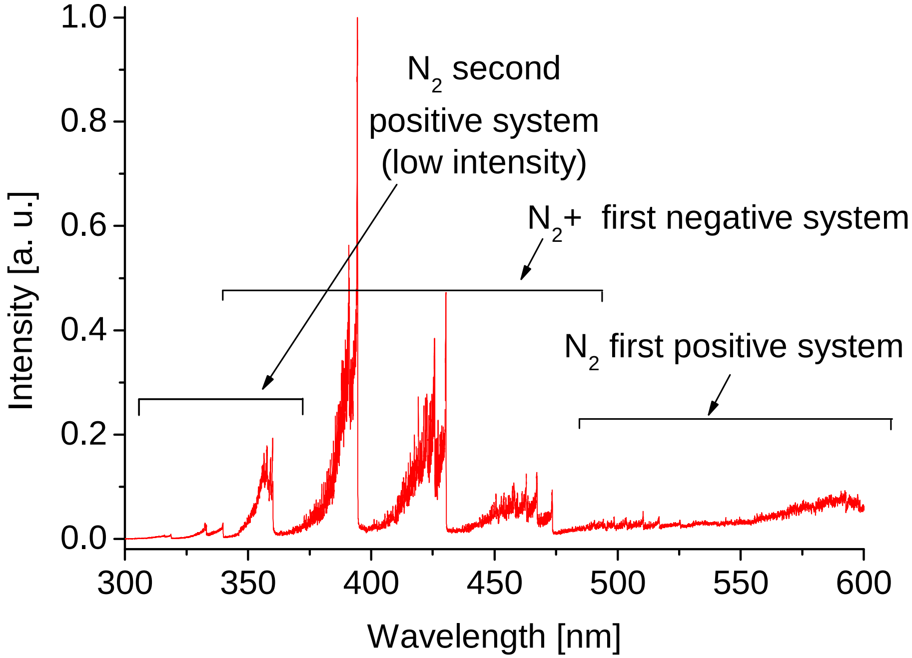
Spectroscopic diagnostics of plasma (rotational temperatures)



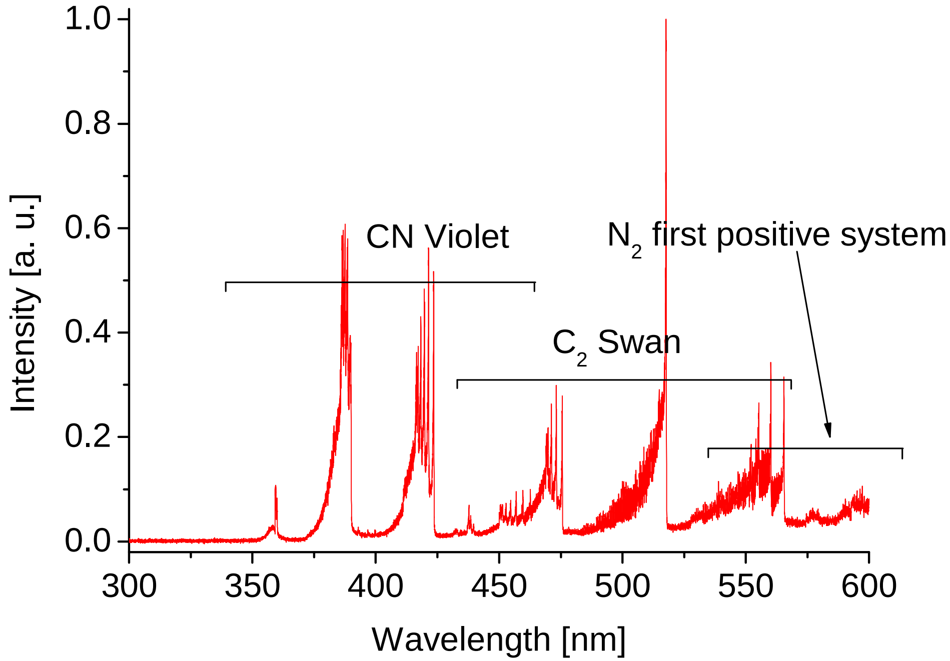
Comparison of the measured and simulated emission spectra of plasma. Absorbed microwave power P_A - 4 kW. 15 mm below the waveguide bottom.

Plasma spectroscopic diagnostics

without C_2H_5OH



with 0.8 kg C_2H_5OH



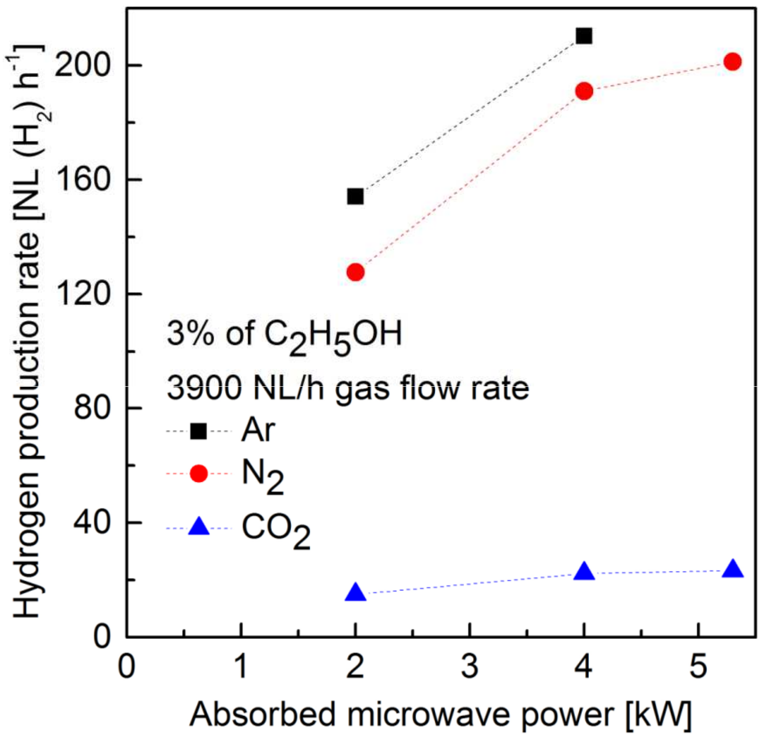
		at 15 mm and P_A – 2kW	ranged (dep. P_A & location)
T_r	N_2+	5500 K	4500 – 6000 K
	OH	5200 K	3300 - 5500 K

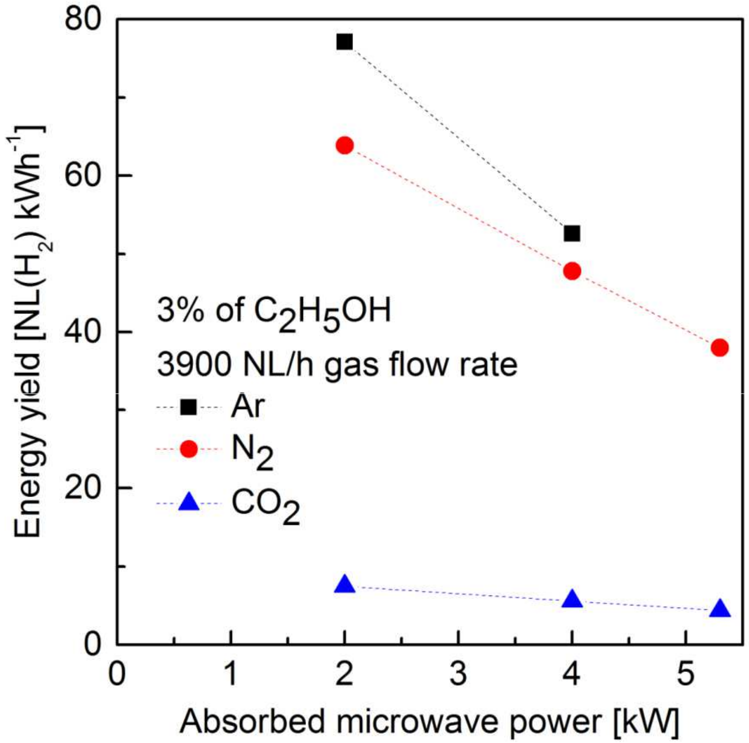
		at 15 mm and P_A – 2kW	ranged (dep. P_A & location)
T_r	CN	5400 K	4000 – 6000 K
	C_2	3600 K	3500 - 4600 K

Measured emission spectra of N_2 plasma and rotational temperatures with and without ethanol vapor addition. 2.45 GHz plasma system. Absorbed microwave power P_A - 4 kW. Working gas flow rate - 2700 NL/h.

Thermal decomposition of ethanol

2.45 GHz; C_2H_5OH added to swirl flow





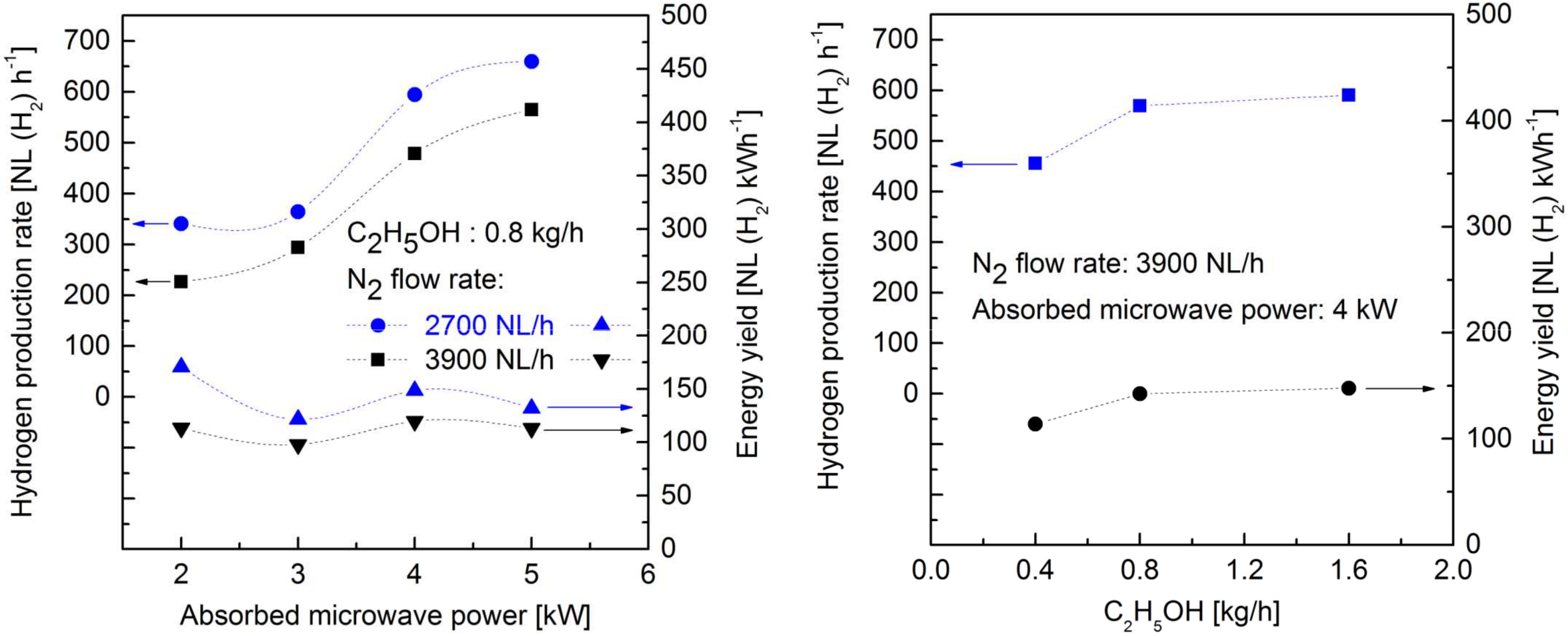
Best results: up to 210 NL(H_2)/h [17.5 g(H_2)/h] and up to 77 NL(H_2)/kWh [6.3 g(H_2)/kWh]
Ethanol conversion: 100%

Comparison of the hydrogen production rate and energy yield as a function of absorbed microwave power for Ar, N_2 and CO_2 plasmas in 2.45 GHz system.

Hrycak et al., *Application of atmospheric pressure microwave plasma source for hydrogen production from ethanol,* **Int J Hydrogen Energy** (2014) 39, 14184-14190

Thermal decomposition of ethanol

2.45 GHz; C_2H_5OH added to swirl flow



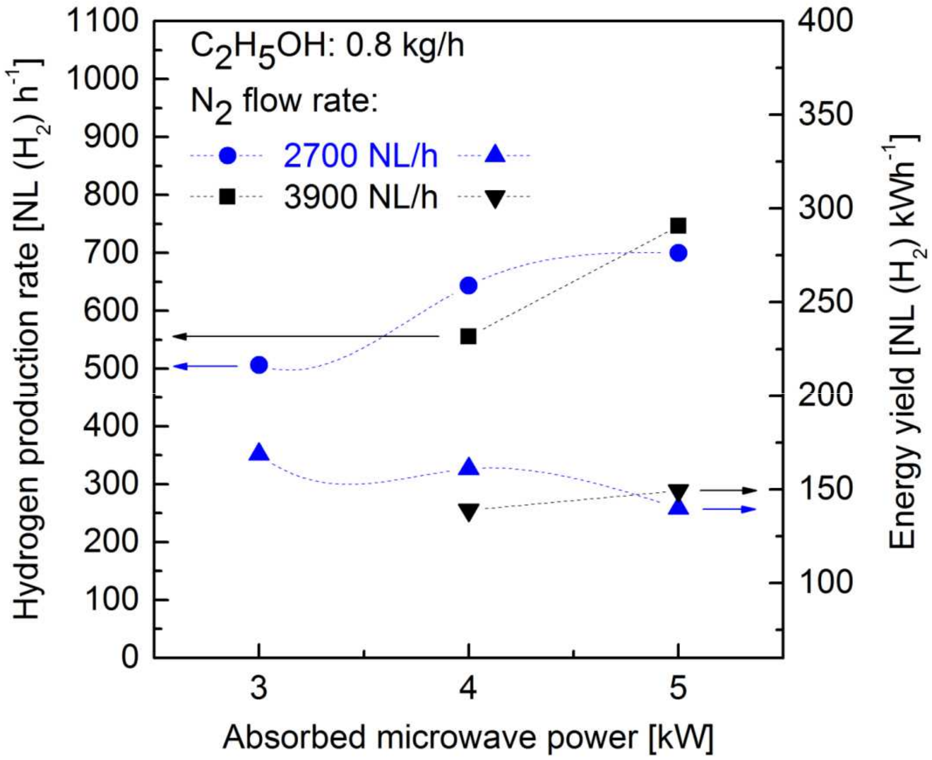
Best results: up to 660 NL(H_2)/h [54,8 g(H_2)/h] and up to 170 NL(H_2)/kWh [14.1 g(H_2)/kWh]
Ethanol conversion: up to 99.9%

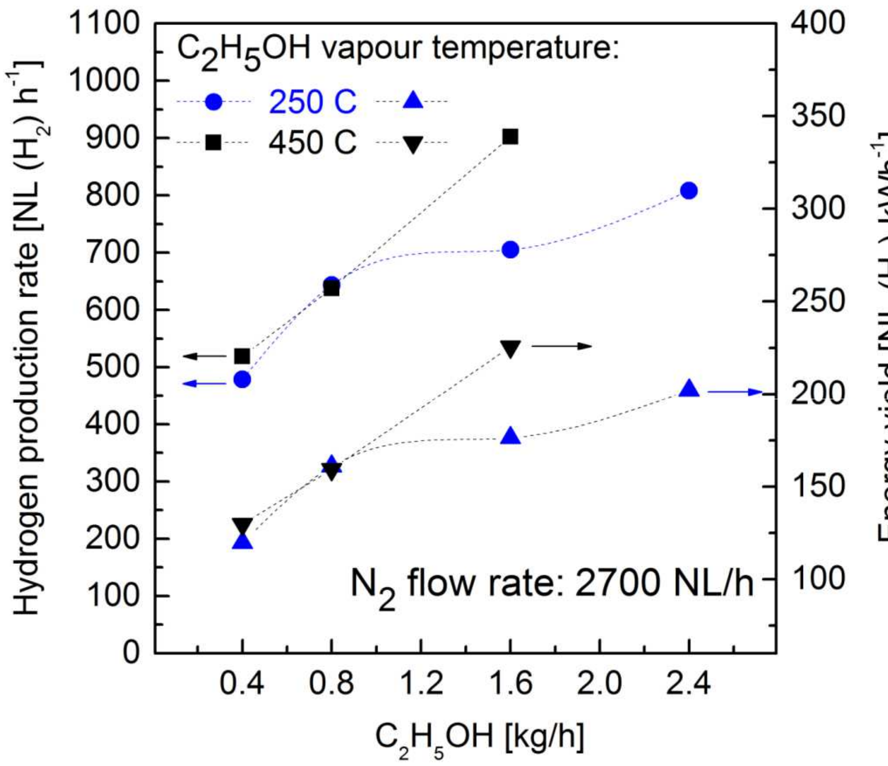
Hydrogen production rate and energy yield for N_2 plasma as a function of absorbed microwave power (on the left) and as a function of C_2H_5OH flow rate (on the right).

Hrycak et al., *Hydrogen production from ethanol in nitrogen microwave plasma at atmospheric pressure*, **Open Chem.** (2015) 13, 1–8

Thermal decomposition of ethanol

2.45 GHz; C_2H_5OH added to axial flow



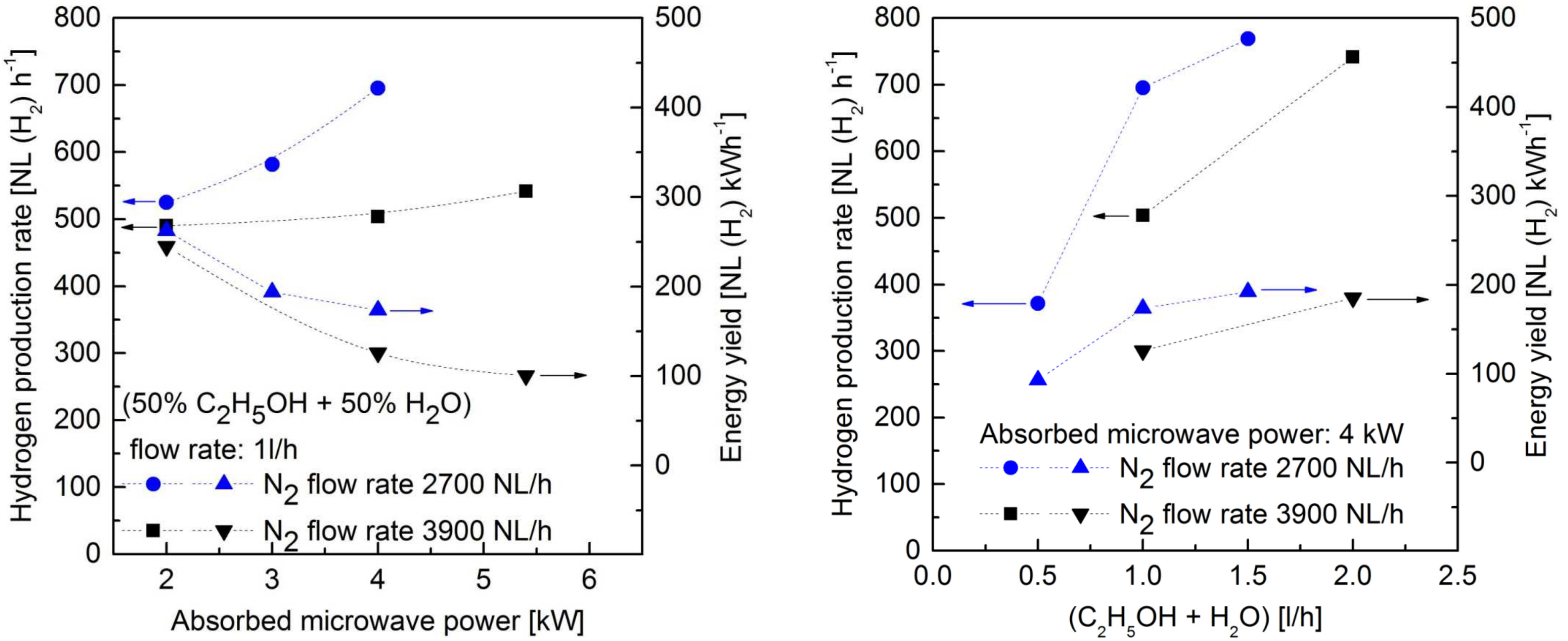


Best results: up to 902 NL(H_2)/h [75 g(H_2)/h] and up to 225 NL(H_2)/kWh [18.7 g(H_2)/kWh]
Ethanol conversion into hydrogen: up to 82%

Hydrogen production rate and energy yield for N_2 plasma as a function of absorbed microwave power (on the left) and as a function of C_2H_5OH flow rate (on the right).

Ethanol steam reforming

2.45 GHz; $C_2H_5OH + H_2O$ added to axial flow

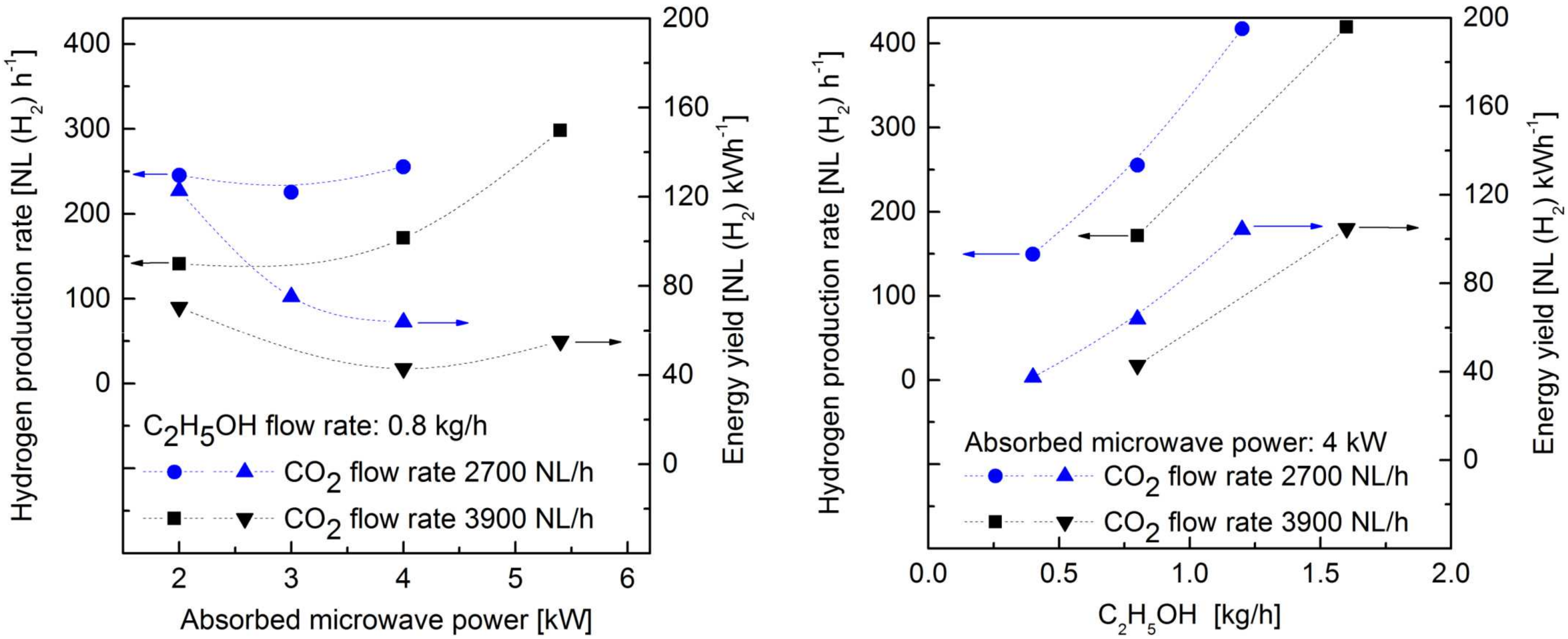


Best results: up to 768 NL(H_2)/h [63.9 g(H_2)/h] and up to 262 NL(H_2)/kWh [21.8 g(H_2)/h]
(50 % C_2H_5OH + 50% H_2O) conversion into hydrogen: up to 100%

Hydrogen production rate and energy yield for N_2 plasma as a function of absorbed microwave power (on the left) and as a function of ($C_2H_5OH+H_2O$) flow rate (on the right).

Ethanol dry reforming

2.45 GHz; C_2H_5OH added to axial flow

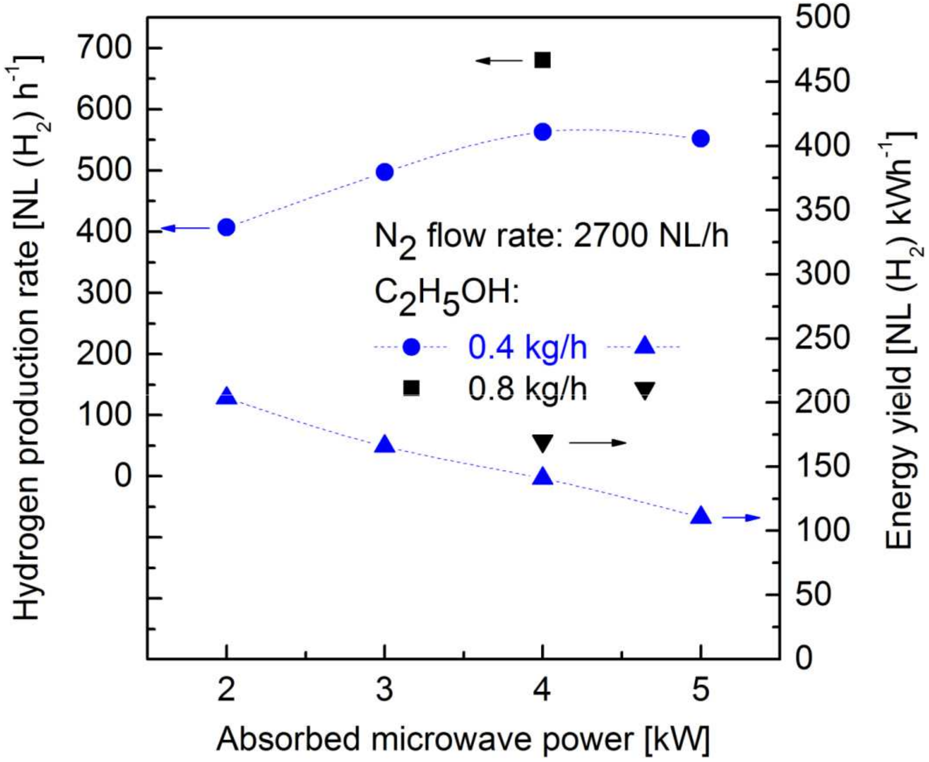


Best results: up to 419 NL(H_2)/h [34.8 g(H_2)/h] and up to 122 NL(H_2)/kWh [10.2 g(H_2)/kWh]
Ethanol conversion into hydrogen: up to 24 %

Hydrogen production rate and energy yield for N_2 plasma as a function of absorbed microwave power (on the left) and as a function of C_2H_5OH flow rate (on the right).

Thermal decomposition of ethanol

915 MHz; C_2H_5OH added to axial flow



Hydrogen production rate and energy yield as a function of absorbed microwave power for N_2 plasma.

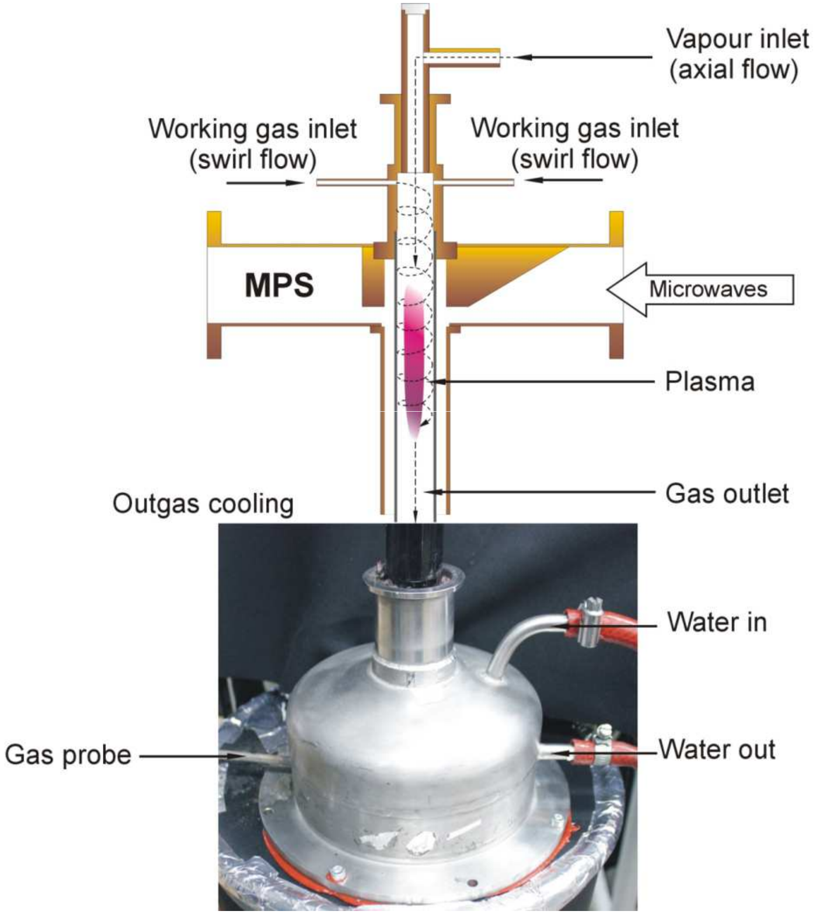
Comparison of the hydrogen production rate and energy yield for different microwave systems. N_2 flow rate: 2700 NL/h, C_2H_5OH: 0.8 kg/h, P_{abs}: 4kW:

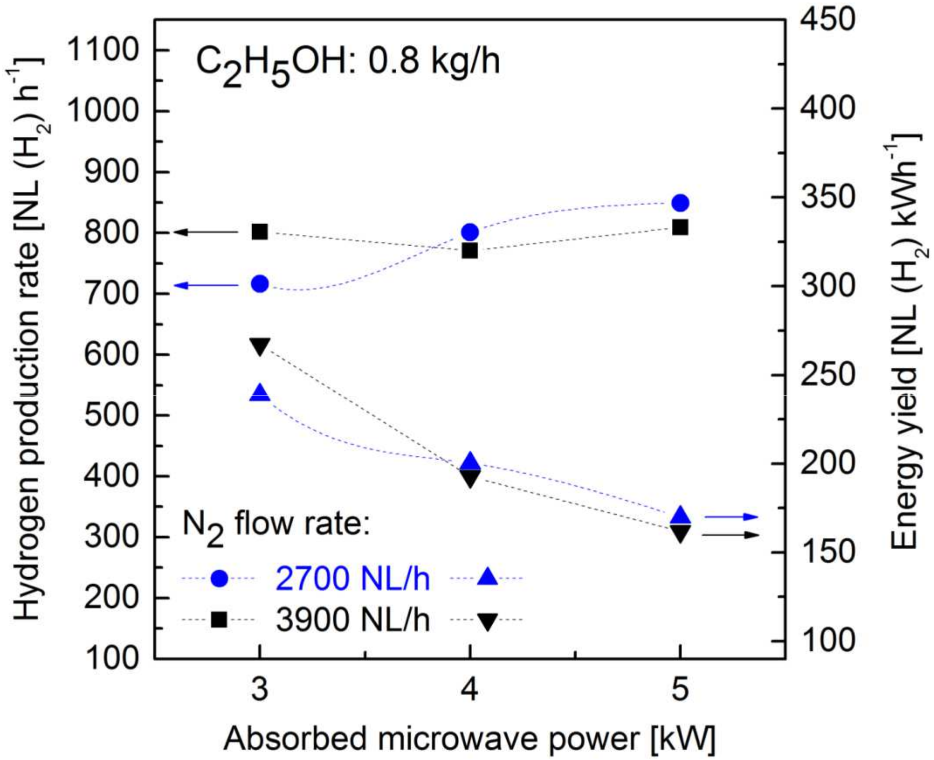
	Hydrogen production rate $NL(H_2)h^{-1}$ $[g(H_2)h^{-1}]$	Energy yield $NL(H_2)/kWh^{-1}$ $[g(H_2)/kWh^{-1}]$
2.45 GHz	643 [53.5]	160 [13.3]
915 MHz	680 [56.5]	170 [14.1]

Problem with soot separator overheating in 915 MHz system

Thermal decomposition of ethanol

915 MHz; C_2H_5OH added to axial flow





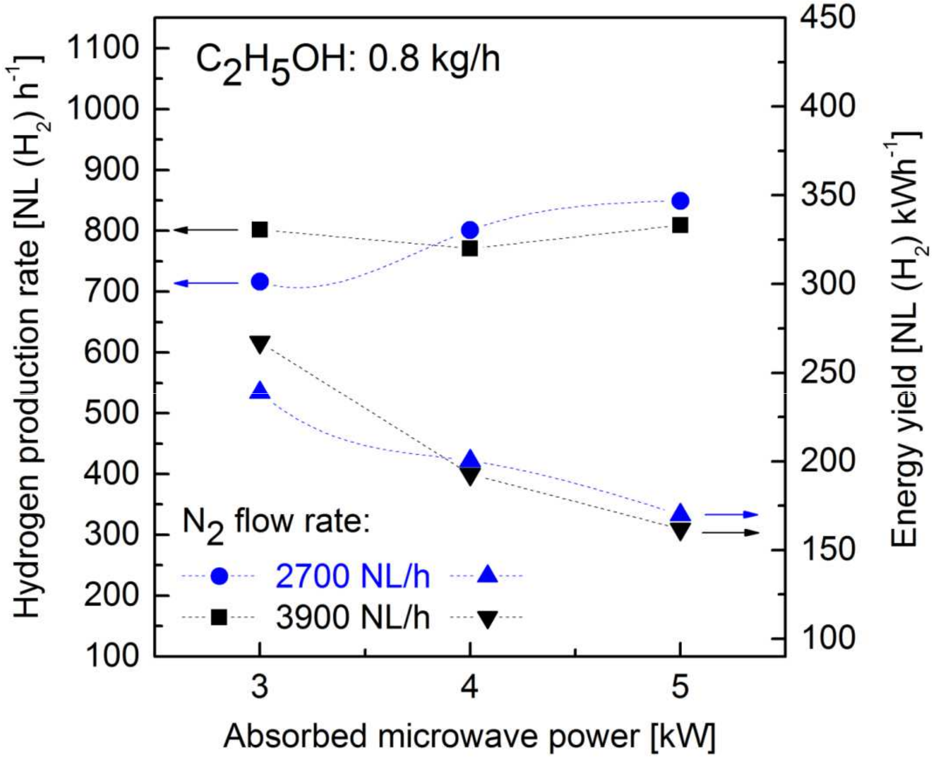
Hydrogen production rate and energy yield as a function of absorbed microwave power for N_2 plasma.

Thermal decomposition of ethanol

915 MHz; C_2H_5OH added to axial flow

Comparison of the hydrogen production rate and energy yield for systems without and with outgas cooling. N_2 flow rate: 2700 NL/h, C_2H_5OH: 0.8 kg/h, P_{abs}: 4kW:

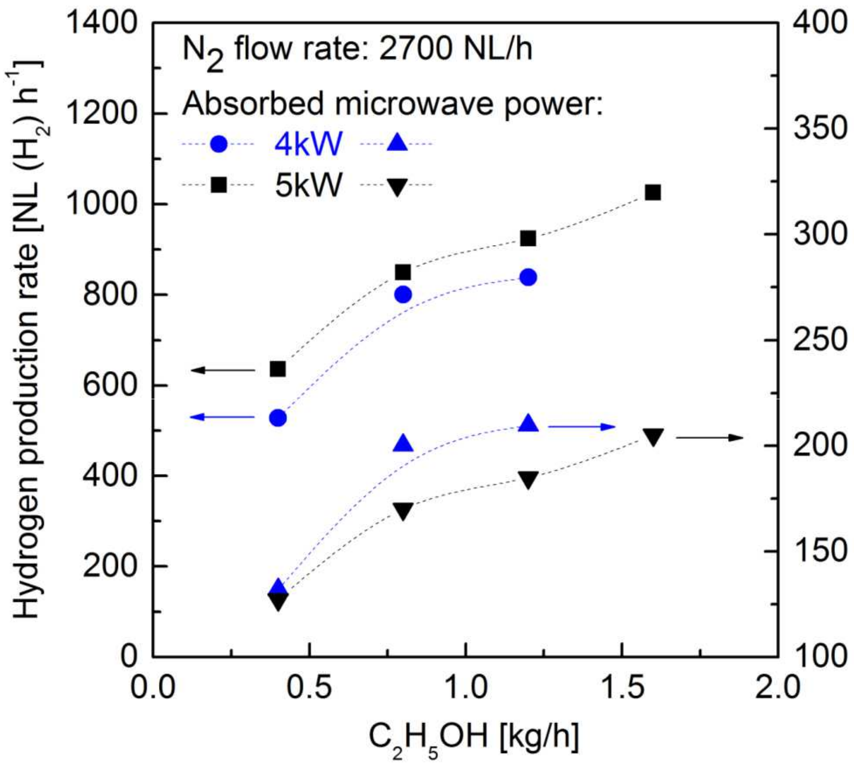
	Hydrogen production rate $NL(H_2)h^{-1}$ $[g(H_2)h^{-1}]$	Energy yield $NL(H_2)/kWh^{-1}$ $[g(H_2)/kWh^{-1}]$
915 MHz without outgas cooling	680 [56.5]	170 [14.1]
915 MHz with outgas cooling	800 [66.6]	200 [16.6]

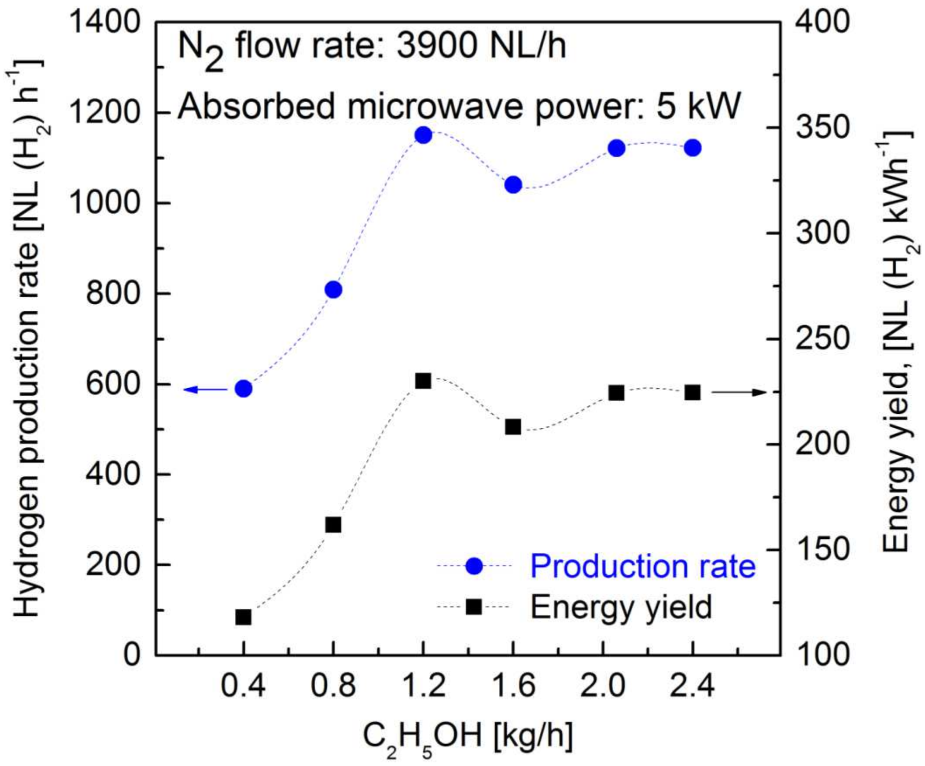


Hydrogen production rate and energy yield as a function of absorbed microwave power for N_2 plasma.

Thermal decomposition of ethanol

915 MHz; C_2H_5OH added to axial flow



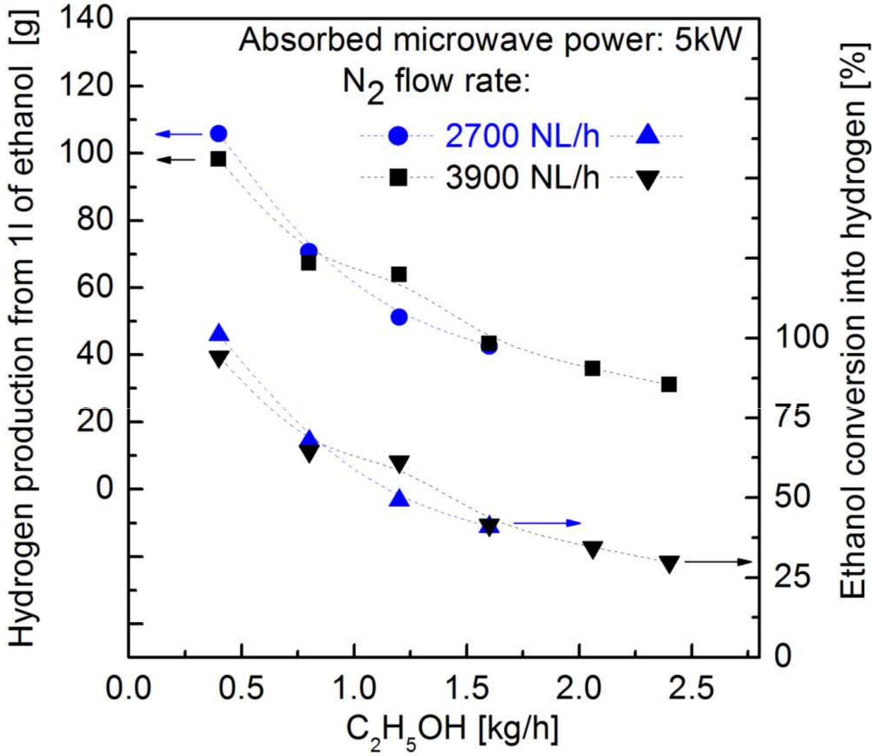


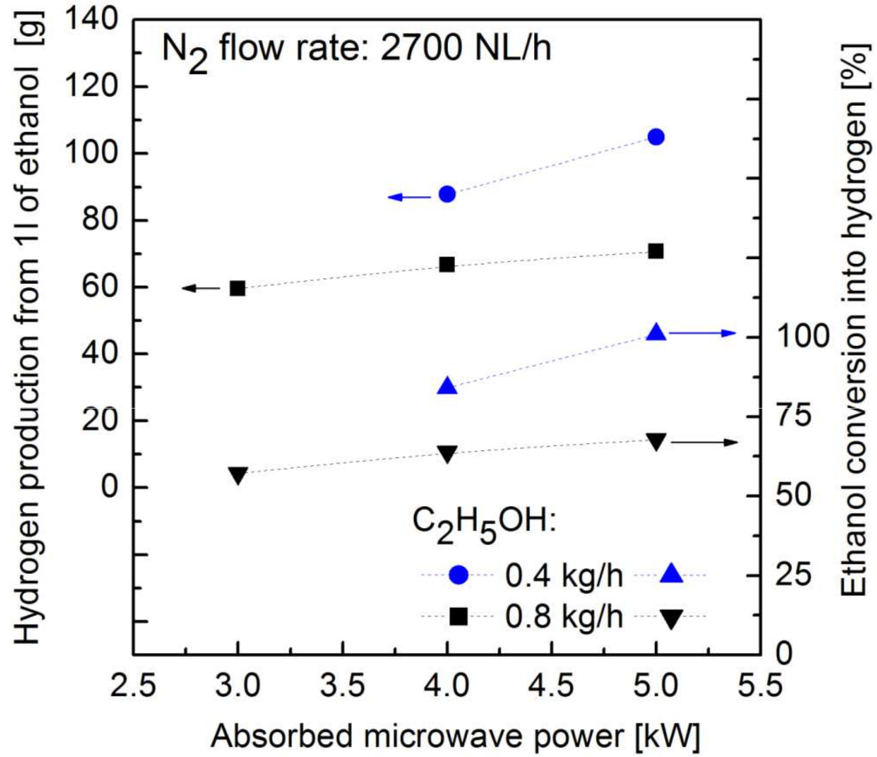
Best results: up to 1150 NL(H_2)/h [95.7 g(H_2)/h] and up to 267 NL(H_2)/kWh [22.2 g(H_2)/kWh]
Ethanol conversion into hydrogen: up to 100%

Hydrogen production rate and energy yield for N_2 plasma as a function of C_2H_5OH flow rate for N_2 flow rate 2700 NL/h (on the left) and 3900 NL/h (on the right).

Ethanol conversion into hydrogen

915 MHz; C_2H_5OH added to axial flow





Best results: up to 105 g(H_2)/lC_2H_5OH and up to 100% conversion into hydrogen

Hydrogen production from 1 l of ethanol and ethanol conversion into hydrogen for N_2 plasma as a function of C_2H_5OH flow rate (on the left) and as a function of absorbed microwave power (on the right).

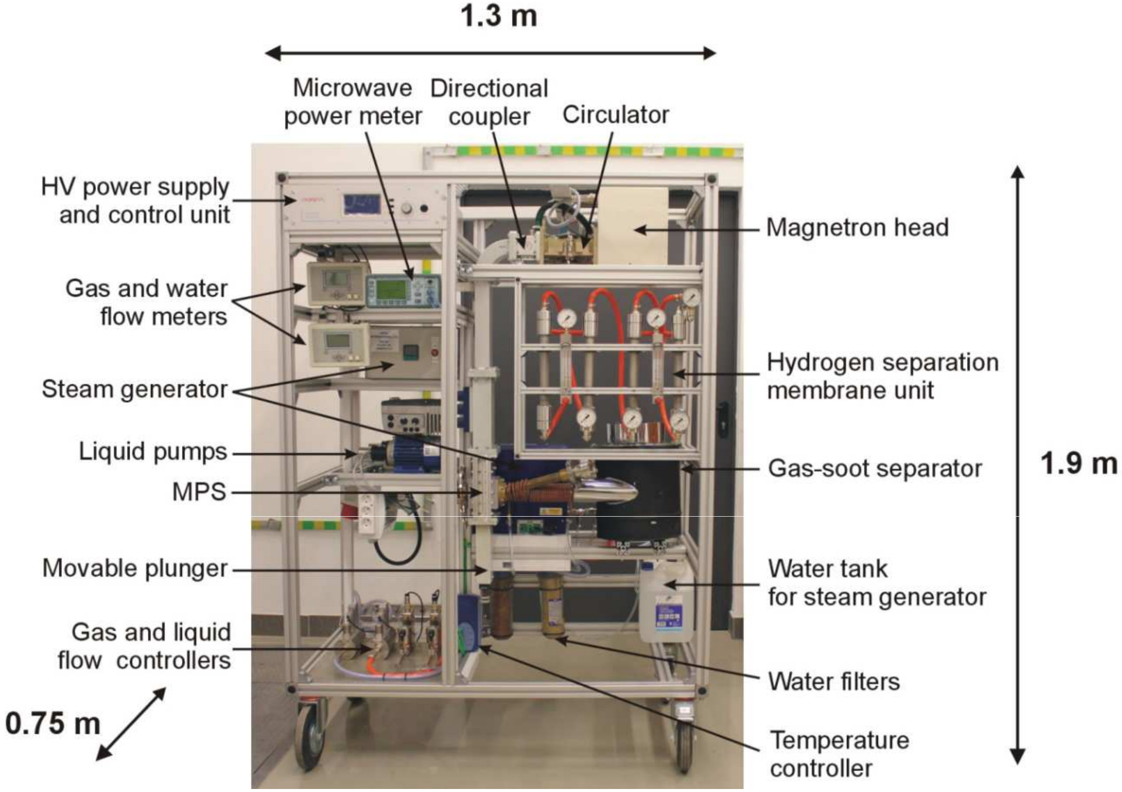
Hydrogen production - the best results

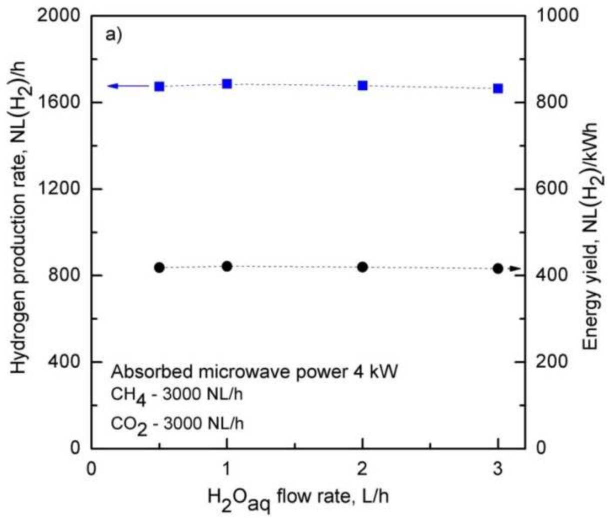
Absorbed microwave power kW	Working gas flow rate NL/h	C_2H_5OH flow rate kg/h	Hydrogen production rate $NL(H_2)/h$ $[g(H_2)/h]$	Energy yield $NL(H_2)/kWh$ $[g(H_2)/kWh]$	C_2H_5OH conversion into H_2 %	Products in the outgas %
5	N_2 – 3900	1.2	1150 [95.7]	230 [19.1]	61	N_2 – 67.5 H_2 – 23.4 CO_2 – 0.2 CO – 7.8 CH_4 – 1 C_2H_2 – 2.8 C_2H_4 – 0.25 C_2H_6 – 0.05
3	N_2 - 3900	0.8	801 [66.7]	267 [22.2]	64	N_2 – 71.7 H_2 – 17.5 CO_2 – 0.2 CO – 6.4 CH_4 – 1.8 C_2H_2 – 1.5 C_2H_4 – 0.8 C_2H_6 – 0.07
4	N_2 - 2700	0.4 + 0.5 kg/h H_2O	695 [57.8]	173 [14.4]	100	N_2 – 70,2 H_2 – 21 CO_2 – 0.9 CO – 7.2 CH_4 – 0.3 C_2H_2 – 0.2 C_2H_4 – 0.1 C_2H_6 – 0.05

Conventional and plasma methods of hydrogen production

Production method	Initial composition	Energy yield $g(H_2)/kWh$	Reference
Conventional steam reforming of methane (catalyst)	CH_4 +H_2O+ air	60 Established Industrial Process	Katie Randolph, U.S. DOE, Hydrogen Production, 2013 Annual Merit Review and Peer Evaluation Meeting, May 16, 2013
Water electrolysis	H_2O	20 - 40	Katie Randolph, U.S. DOE, Hydrogen Production, 2013 Annual Merit Review and Peer Evaluation Meeting, May 16, 2013
Electron beam radiolysis	CH_4+H_2O	3.6	T. Kappes et al., 8th Int. Symp. on High Pressure Low Temperature Plasma Chemistry, 196, 2002
Dielectric barrier discharge	CH_4+air	6.7	M. Heintze, B. Pietruszka Catal. Today 89, 21, 2004
Dielectric barrier discharge	CH_4 +CO_2 / H_2O CH_3OH+CO_2 / H_2O CH_3CH_2OH+CO_2 / H_2O	0.5 3.3 6.7	B. Sarmiento et al. Journal of Power Sources 169, 140, 2007
Dielectric barrier discharge	CH_4 +CO_2	5.2	M. Dors, T. Izdebski, A. Berendt, J. Mizeraczyk Int. J. Plasma Envir. Sci. Technol., 6, 93, 2012
Gliding arc	CH_4+H_2O+air	40	J.M. Cormie, I. Rusu J. Phys. D: Appl. Phys. 34, 2798, 2001
Glid arc spray	Ar+CH_3OH	176	R. Burlica, K.-Y. Shih, B. Hnatiuc, B. R. Locke Ind. Eng. Chem. Res., 50, 9466, 2011
Plasmatron with catalyst	CH_4+H_2O+air	225	L. Bromberg et al. Int. J. Hydrogen Energy 25, 1157, 2000
Coaxial-line-based MPS	CH_4+N_2	17	M. Jasiński, D. Czylkowski et al. Int. J. Hydrogen Energy 38, 11473, 2013
Metal-cylinder-based MPS	CH_4 +CO_2+H_2O	42.9	M. Jasiński, D. Czylkowski et al., to be published
Metal-cylinder-based MPS	N_2+C_2H_5OH+H_2O	22.2	present work

Microwave plasma module for hydrogen production - prototype





Hydrogen production rate and energy yield as a function of H_2O_{aq} flow rate. CH_4 i CO_2 flow rates 3000 NL/h and 3000 NL/h. Absorbed microwave power 4 kW.

Microwaves: up to 6kW
Gas flow rate : up to 12000 NL/h

Best results: up to 2300 NL(H_2)/h [192g(H_2)/h] and up to 515 NL(H_2)/kWh [42.9 g(H_2)/kWh]

Jasiński et al., *Atmospheric pressure microwave plasma source for hydrogen production*, **Int J Hydrogen Energy** (2013) 38, 11473-11483

Summary and conclusions

- The investigations showed advantages of using the metal-cylinder-based MPS in terms of the performance and hydrogen production rate and energy yield
- The metal-cylinder-based MPS can operate in different gases (nitrogen, argon, carbon dioxide, methane) and mixtures with high gas flow rates at atmospheric pressure and microwave power of a few Kw
- The spectroscopic measurements showed that 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) which makes the MPS an attractive tool for hydrogen production via gaseous and liquid hydrocarbon conversion
- The axial method of introduction of the ethanol into the plasma solved the problem with microwaves penetration and damages of the quartz tube (resulting from soot production) and allowed to improve the production of hydrogen efficiency parameters
- The best achieved results of hydrogen production rate and energy yield were 1150 NL(H_2)/h and 267 NL(H_2)/kWh, respectively
- Conversion into hydrogen can rich up to 100 %.
- The metal-cylinder-based MPS has a high potential for hydrogen production via other liquid hydrocarbons conversion

Thank you for your attention!

Authors:


Bartosz Hrycak


Dariusz Czylkowski


Robert Miotk


Mirosław Dors


Mariusz Jasiński


Jerzy Mizeraczyk

Acknowledgment :

We are grateful to The National Science Centre (programme no. 2012/05/B/ST8/02789) and The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences for financial support of this work

Centre for Plasma and Laser Engineering
The Szewalski Institute of Fluid-Flow Machinery Polish Academy of Sciences,
Gdańsk, Poland