Application of atmospheric pressure microwave plasma source for hydrogen production from ethanol

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 for N_2, CO_2, Ar plasma:
    - Visualization of the plasma flame
    - Spectroscopic diagnostics of the plasma flame
    - Hydrogen production via ethanol conversion
- 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 (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

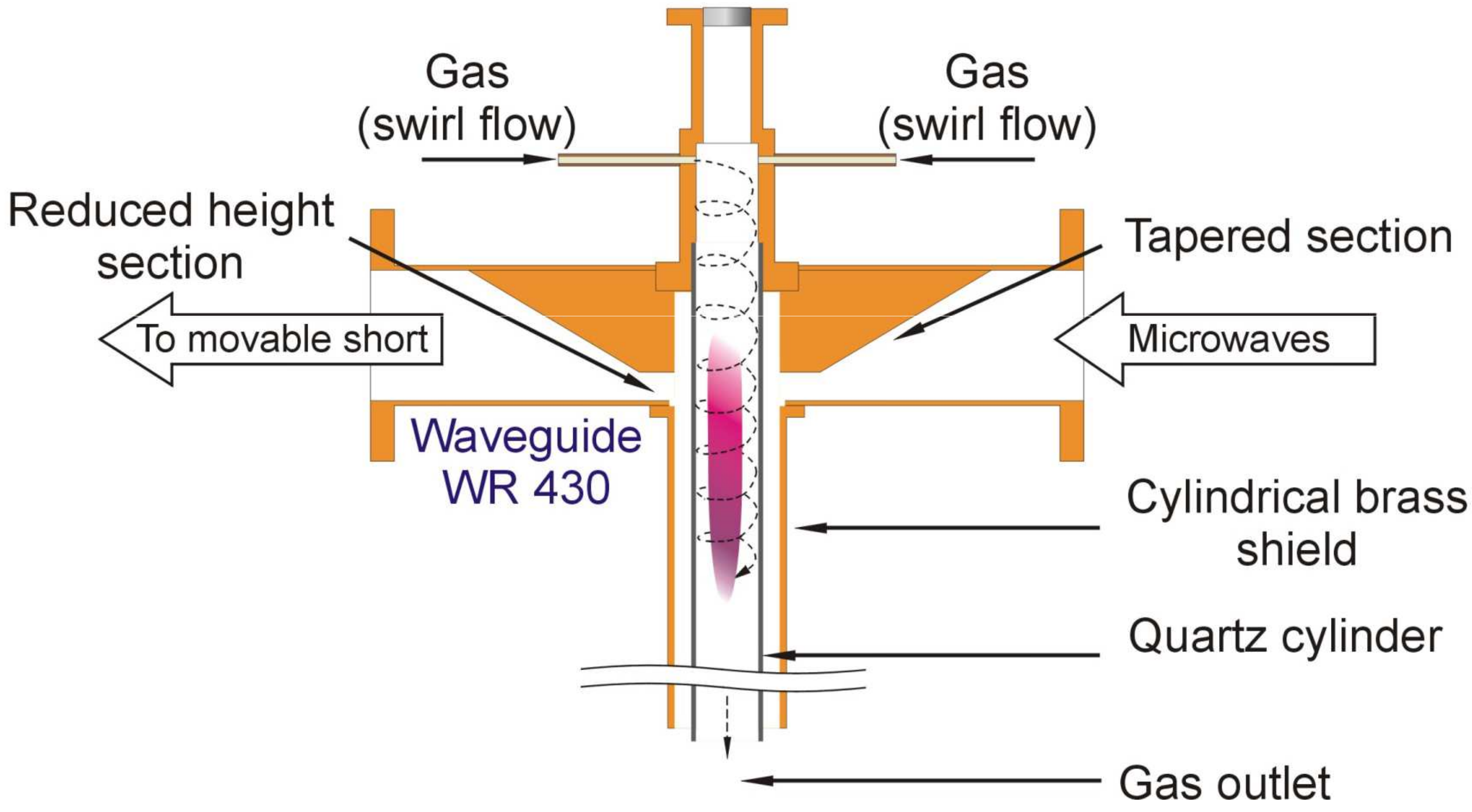
Selection of microwave plasma source

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

Waveguide-supplied metal-cylinder-based MPS

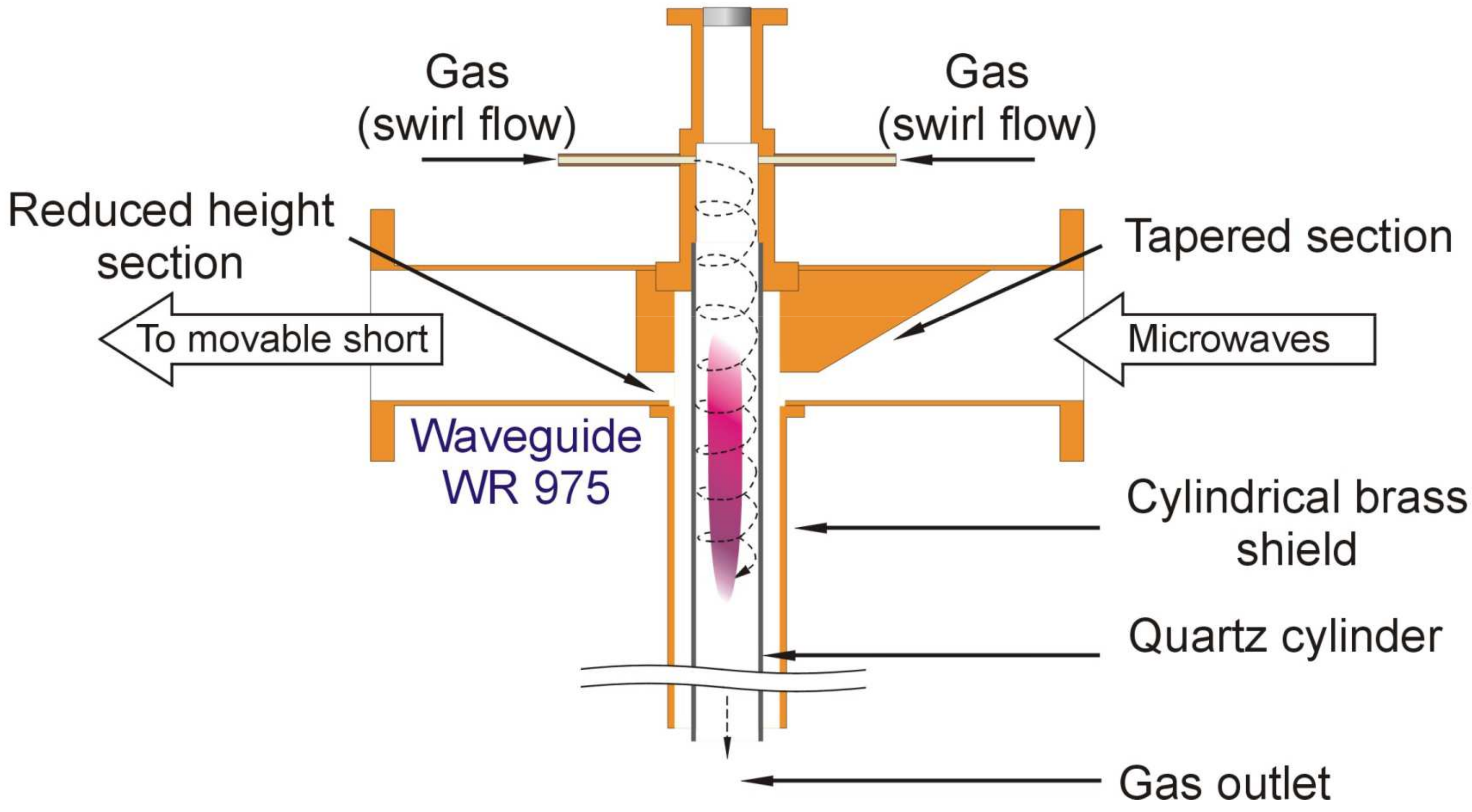
2.45 GHz system



Schematic view of the waveguide-supplied metal-cylinder-based MPS

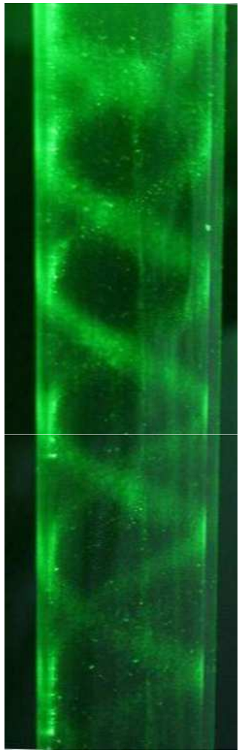
Waveguide-supplied metal-cylinder-based MPS

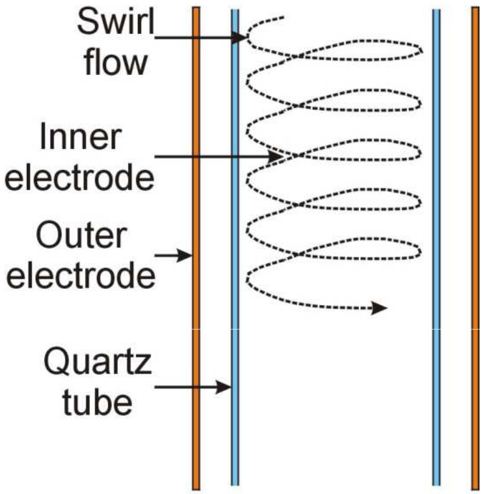
915 MHz system

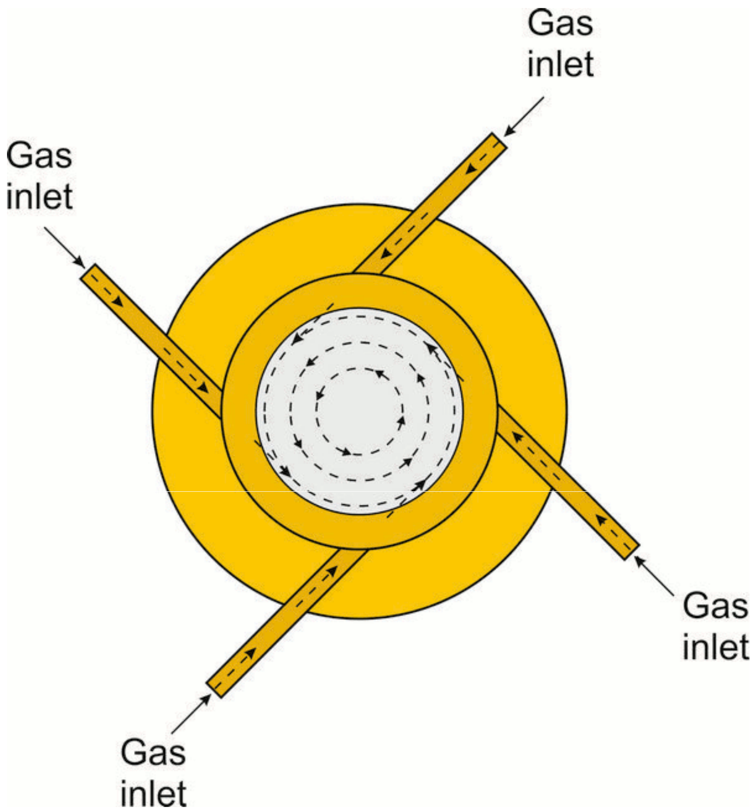


Schematic view of the waveguide-supplied metal-cylinder-based MPS

Waveguide-supplied metal-cylinder-based MPS





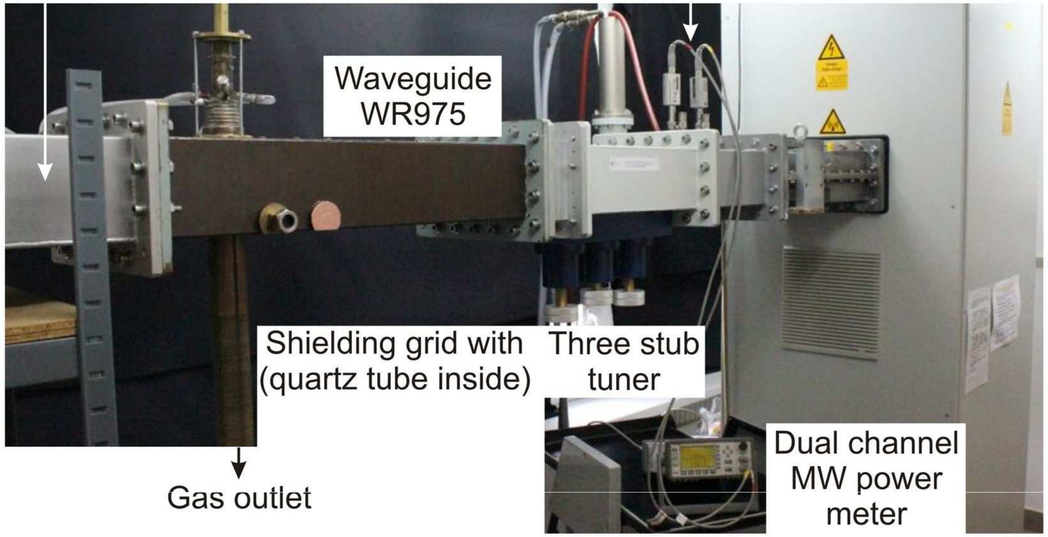


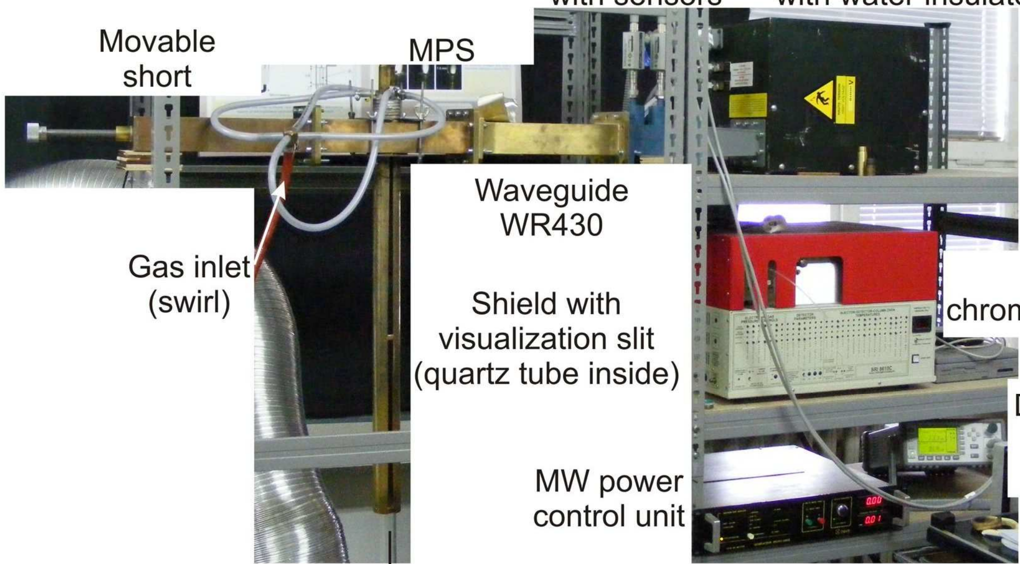
Laser visualization of the swirl flow without plasma

Illustrations of the gas swirl.
Inlet gas – mixed working gas with ethanol

Experimental setup

The 915 MHz system (up to 20 kW)





The 2.45 GHz system (up to 6 kW)

Experimental setup

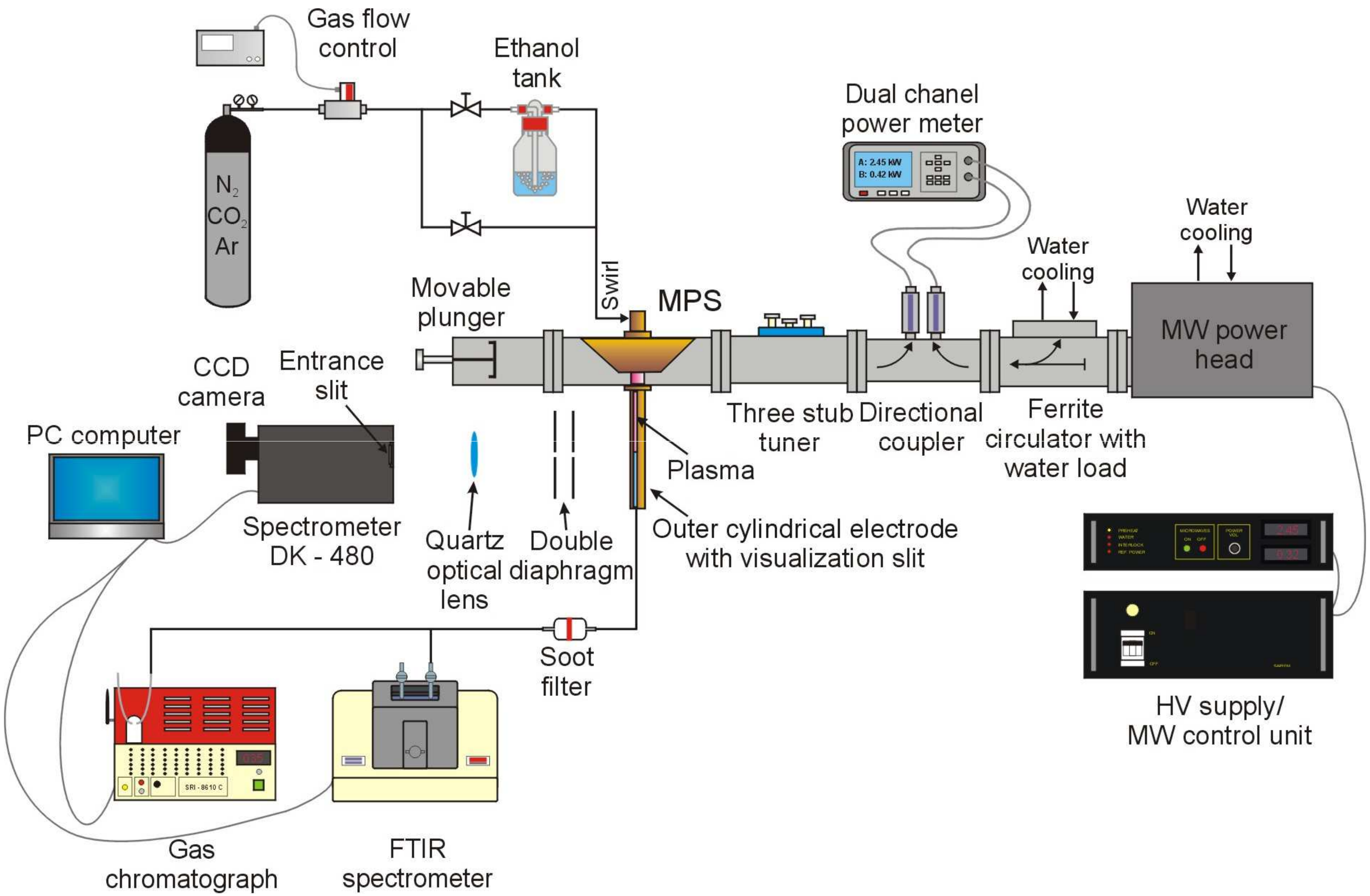


Diagram of the experimental setup for hydrogen production via ethanol conversion

Experiment parameters

Processes

- Thermal decomposition of etanol:

  $C_2H_5OH \rightarrow 3H_2 + CO + C$ (in N_2 and Ar plasma)

- Dry reforming of ethanol:

  $C_2H_5OH + CO_2 \rightarrow 3H_2 + 3CO$ (in CO_2 plasma)

Constant parameters

- Pressure: atmospheric
- C_2H_5OH addition: about 3 %

Variable parameters

- Microwave frequency: 915 MHz or 2.45 GHz
- Absorbed microwave power: 2 – 6 kW
- Working gas type: N_2, CO_2, Ar
- Working gas (N_2, CO_2, Ar) flow rate: 1500 – 3900 NL/min

Measured parameters

- 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 and C_2H_5OH
- Emission spectra of plasma in range of 300 – 600 nm

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

$$[(C_2H_5OH)_{converted} / (C_2H_5OH)_{initial} \times 100\%],$$

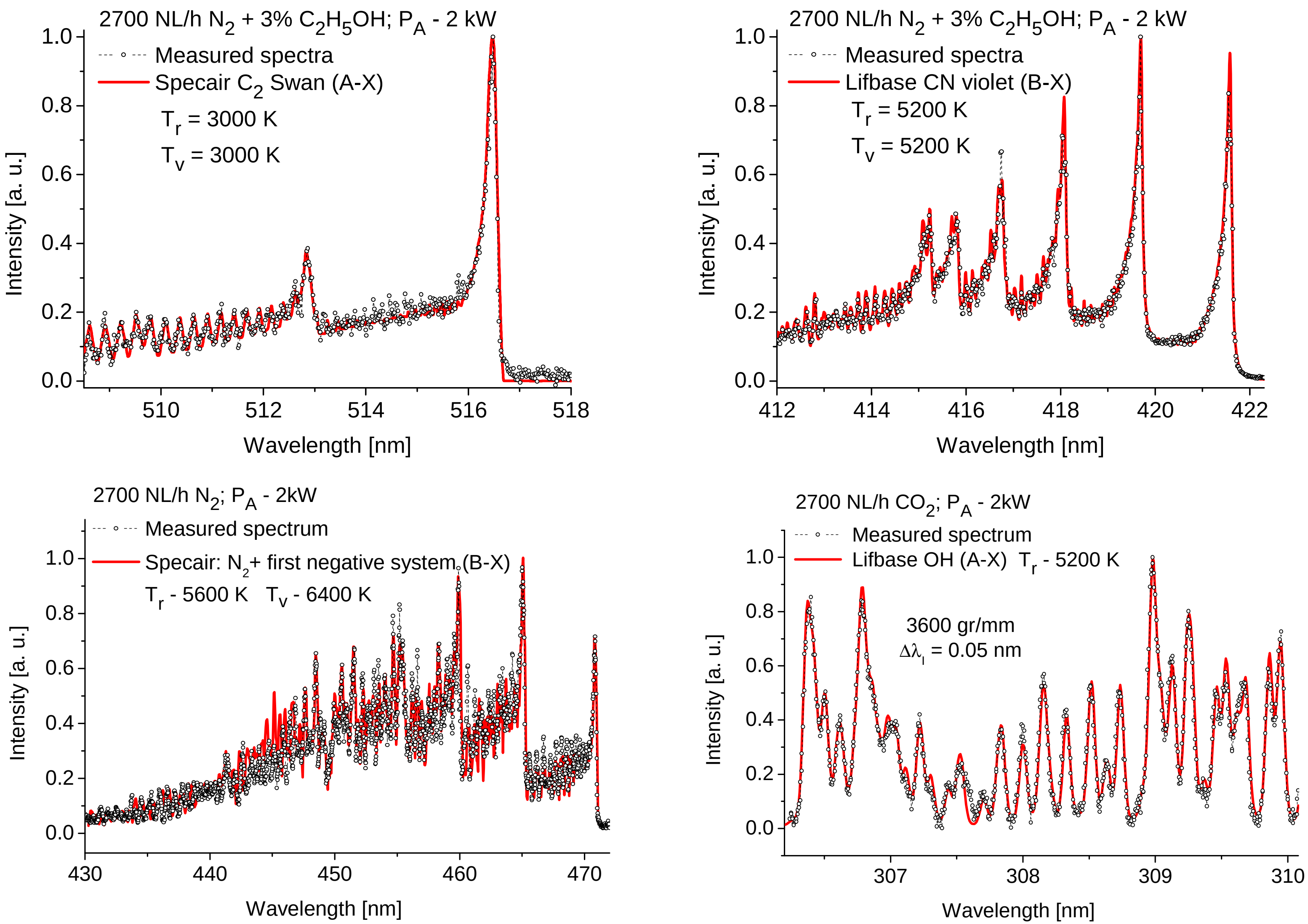
where $(C_2H_5OH)_{initial}$ is the total mass of ethanol and $(C_2H_5OH)_{converted}$ is the converted mass of etanol.

- Hydrogen concentration in the outgas is defined by relation

$$[Q(H_2)_{outgas} / Q(\text{working gas+ } H_2\text{+other products})_{outgas}] \times 100\%,$$

where $Q(H_2)_{outgas}$ is a hydrogen gas flow rate at the output of the MPS and Q(working gas+H_2+other products)$_{outgas}$ is the total gases flow rate at the output of the MPS.

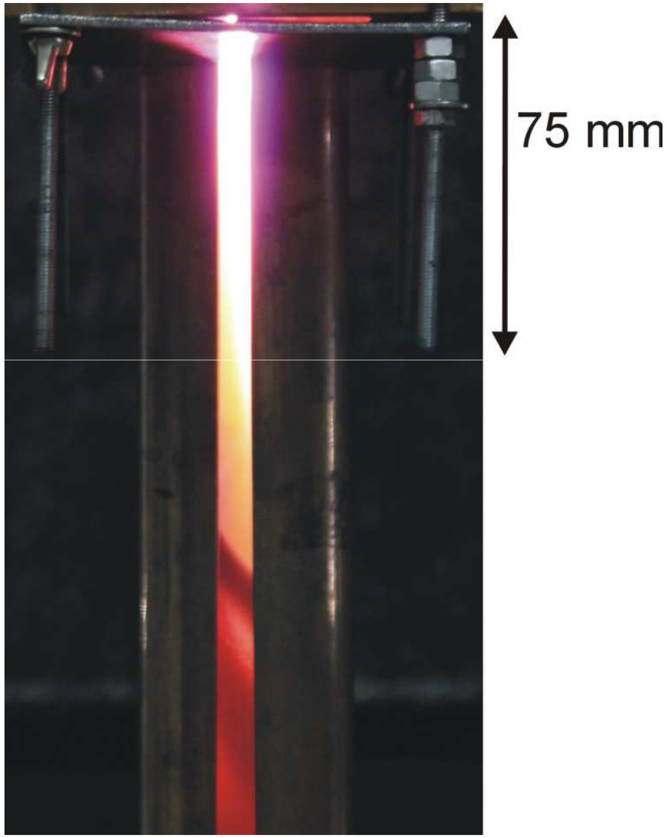
Spectroscopic diagnostics of plasma (rotational temperatures)



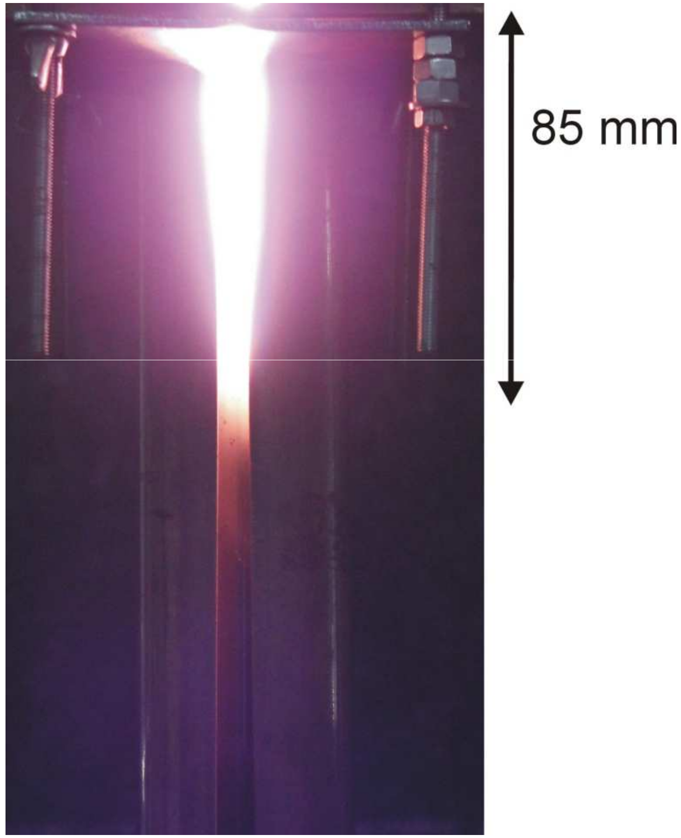
Comparison of the measured and simulated emission spectra of plasma. Absorbed microwave power P_A - 2 kW. 15 mm below the waveguide bottom.

N_2 and N_2/C_2H_5OH plasma

without C_2H_5OH



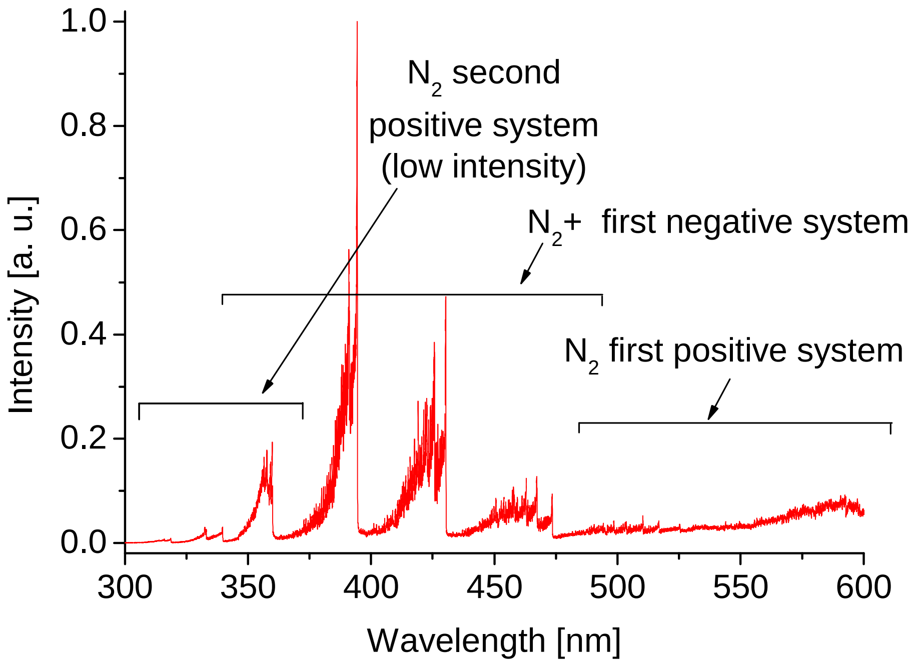
with C_2H_5OH



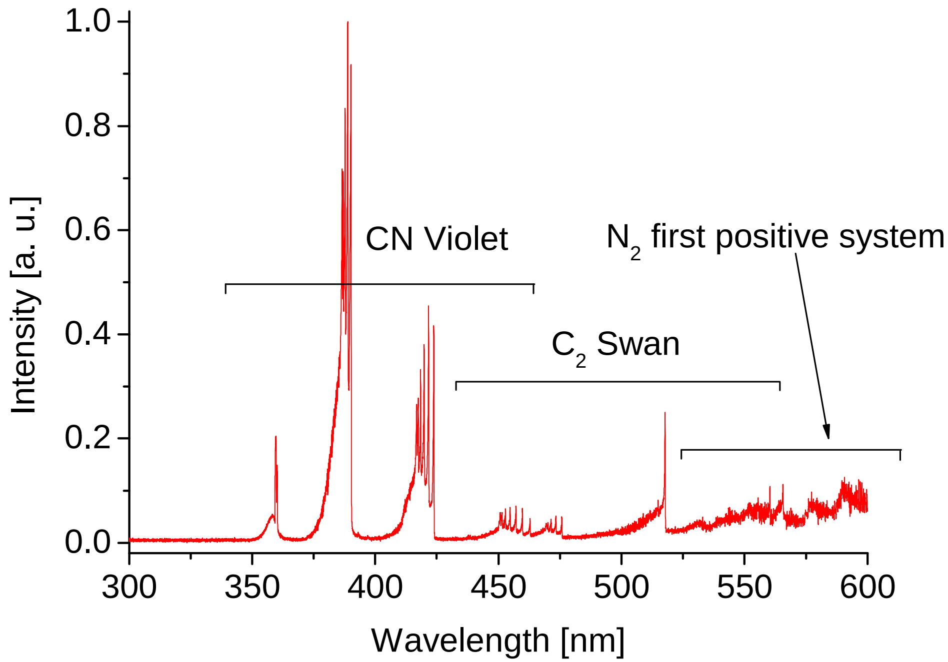
Photos of N_2 plasma with and without ethanol vapor addition (2.45 GHz plasma system, absorbed microwave power P_A - 2 kW, working gas flow rate - 2700 NL/h)

Spectroscopic diagnostics of N_2 and N_2/C_2H_5OH plasma

without C_2H_5OH



with C_2H_5OH



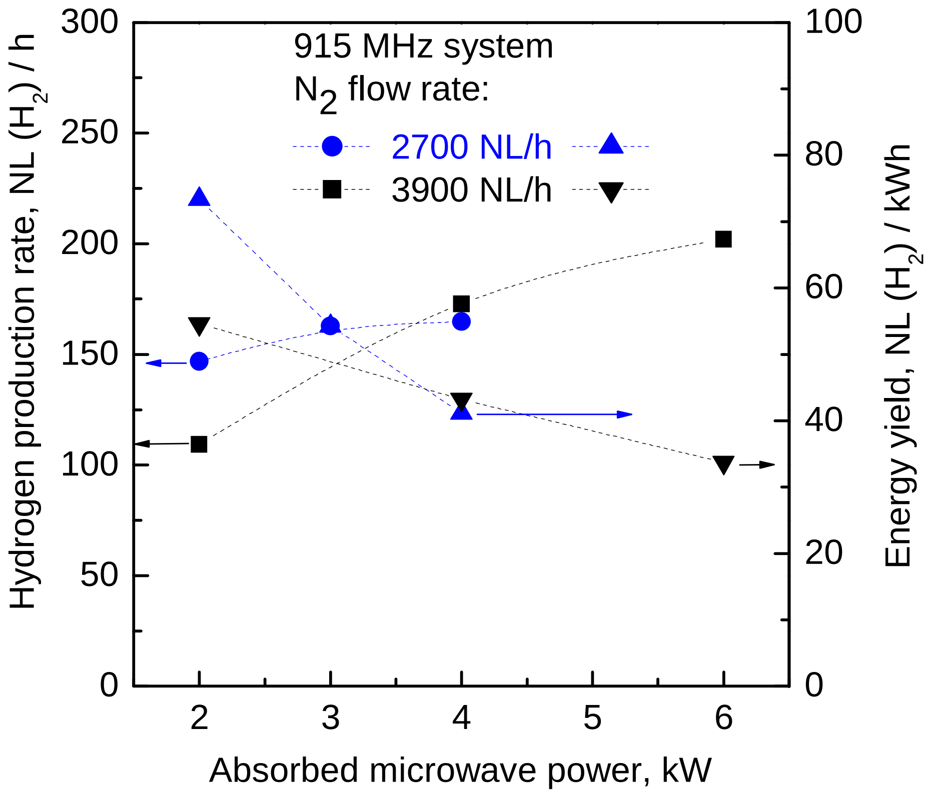
		at 15 mm and P_A – 2kW	ranged (dep. P_A & location)
T_r	N_2+	5000 K	4500 – 6000 K
	OH	4800 K	3300 - 5500 K

		at 15 mm and P_A – 2kW	ranged (dep. location)
T_r	CN	5400 K	4000 – 5400 K
	C_2	3500 K	3000 - 3500 K

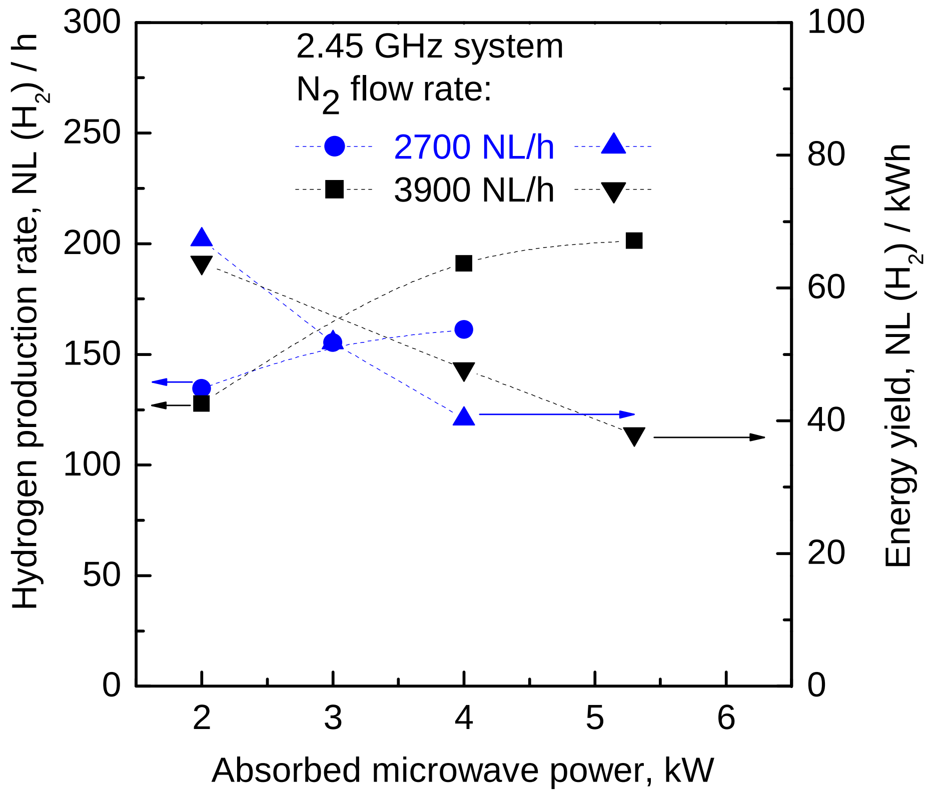
Measured emission spectra of N_2 plasma and rotational temperatures with and without ethanol vapor addition (2.45 GHz plasma system, absorbed microwave power P_A - 2 kW, working gas flow rate - 2700 NL/h, 15 mm below the waveguide bottom)

Ethanol conversion N_2/C_2H_5OH plasma

915 MHz system



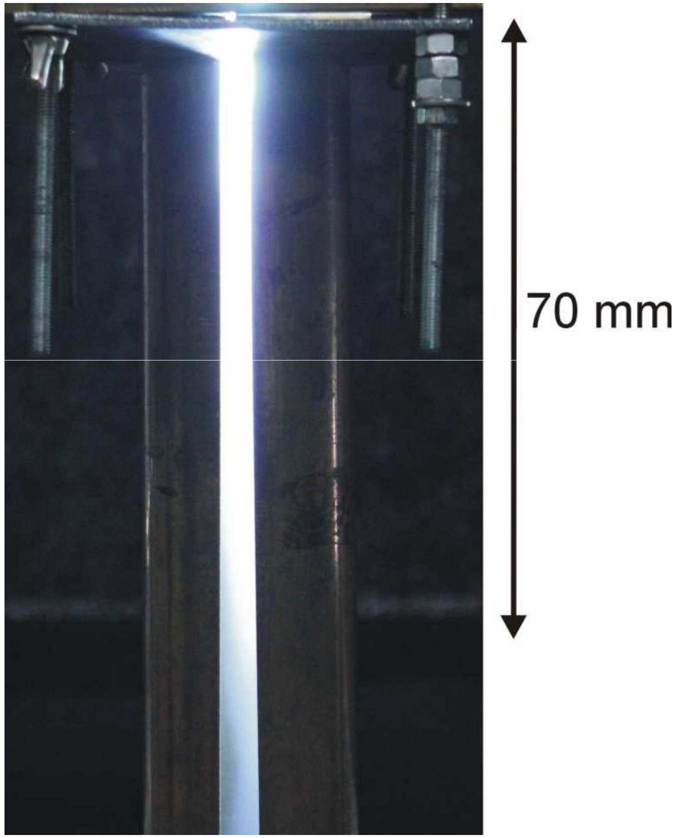
2.45 MHz system



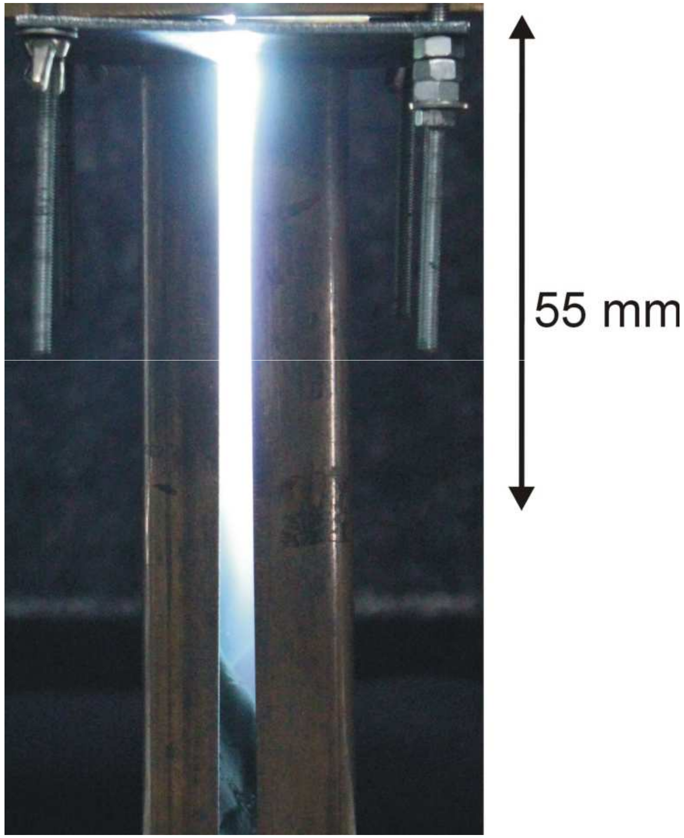
Hydrogen production rate and energy efficiency of hydrogen production as a function of absorbed microwave power for N_2 plasma in 915 MHz and 2.45 GHz systems.

CO_2 and CO_2/C_2H_5OH plasma

without C_2H_5OH



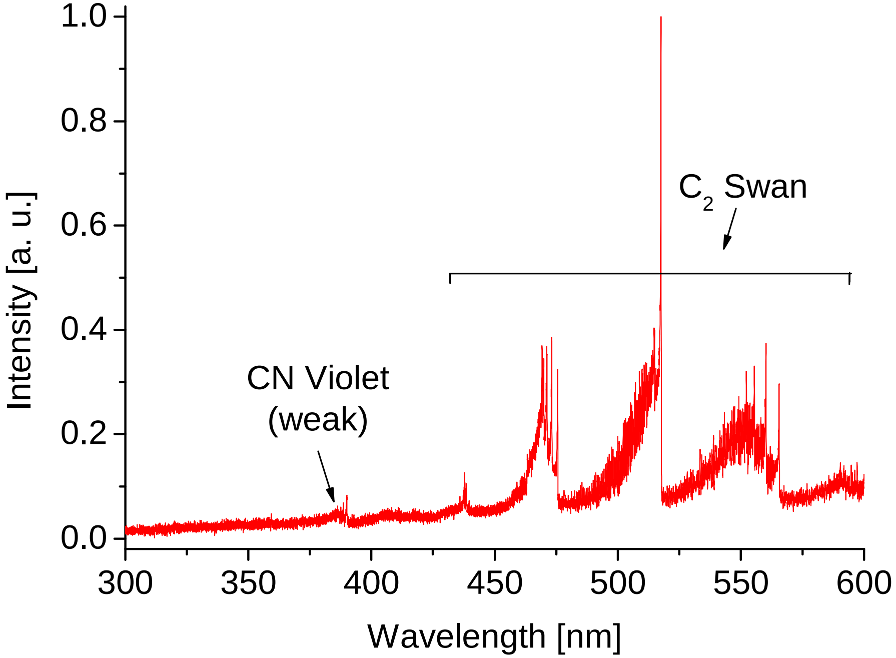
with C_2H_5OH



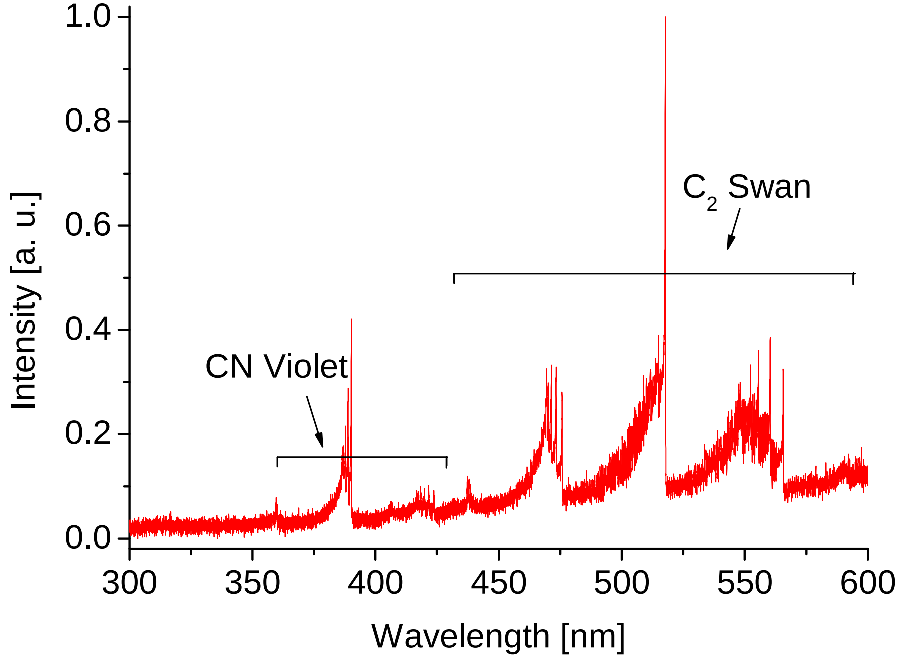
Photos of CO_2 plasma with and without ethanol vapor addition (2.45 GHz plasma system, absorbed microwave power P_A - 2 kW, working gas flow rate - 2700 NL/h)

Spectroscopic diagnostics of CO_2 and CO_2/C_2H_5OH plasma

without C_2H_5OH



with C_2H_5OH

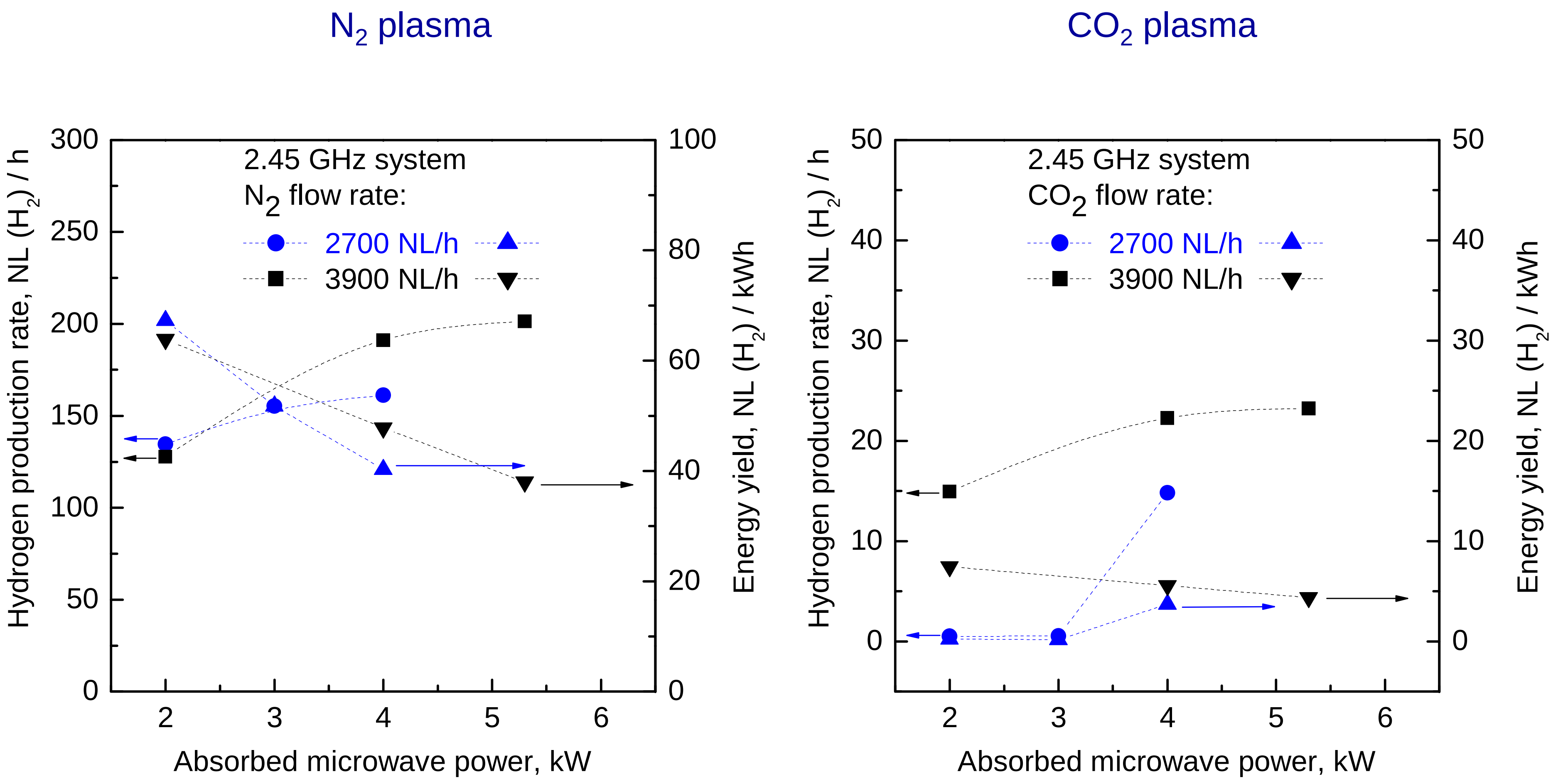


		at 15 mm and P_A – 2kW	ranged (dep. P_A & location)
T_r	C_2	5000 K	4500 – 6000 K
	OH	5000 K	3300 - 5500 K

		at 15 mm and P_A – 2kW	ranged (location)
T_r	C_2	5000 K	4500 – 5000 K

Measured emission spectra of CO_2 plasma and rotational temperatures 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, 15 mm below the waveguide bottom)

Ethanol conversion CO_2/C_2H_5OH plasma



Hydrogen production rate and energy efficiency of hydrogen production as a function of absorbed microwave power for N_2 and CO_2 plasma in 2.45 GHz system.

Ethanol conversion CO_2/C_2H_5OH plasma

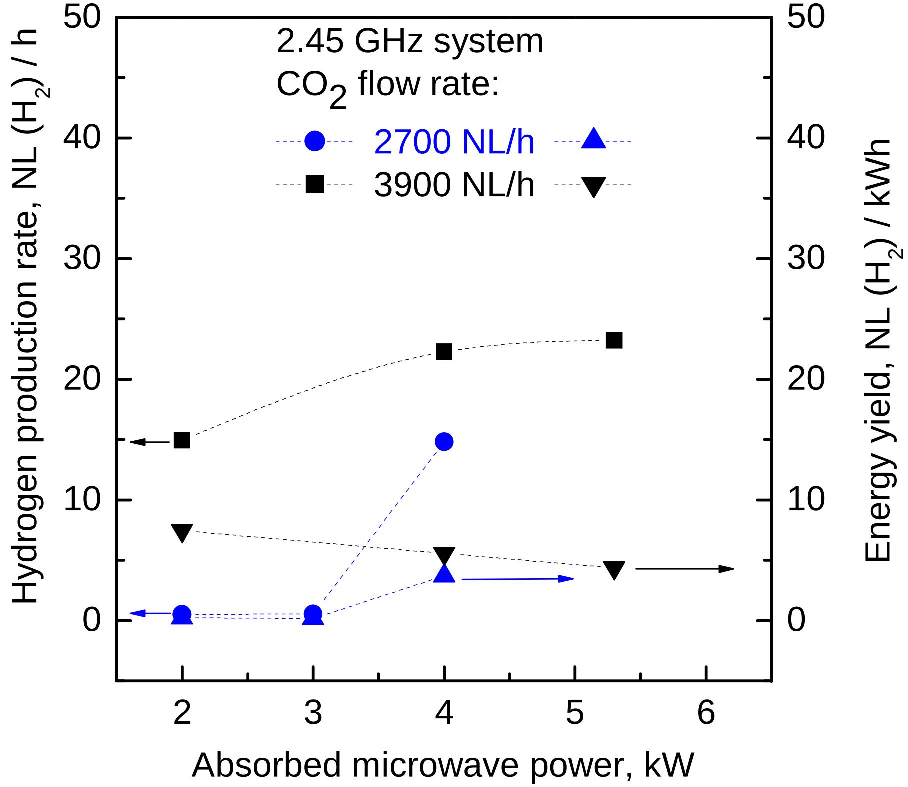
CO_2 plasma

CO_2 plasma without etanol (2700 NL/h of CO_2; P_A – 2kW):

2.35% of O_2 and 3% of CO at the output of the MPS ($CO_2 \rightarrow CO + {}^1/_2O_2$)

Instead of dry reforming, thermal decomposition or partial oxidation we achieved full oxidation:

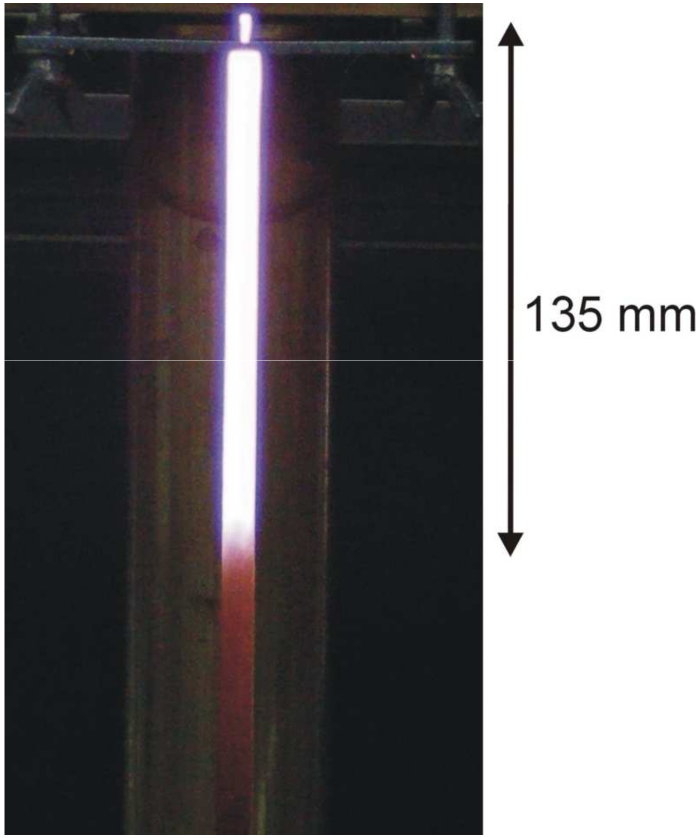
$C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2$



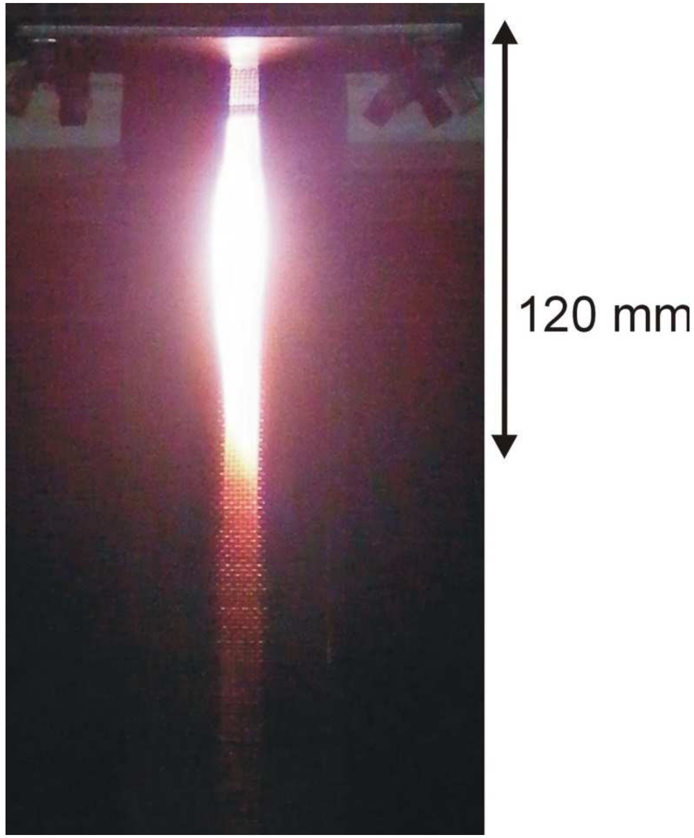
Hydrogen production rate and energy efficiency of hydrogen production as a function of absorbed microwave power for CO_2 plasma in 2.45 GHz system.

Ar and Ar/C_2H_5OH plasma

without C_2H_5OH



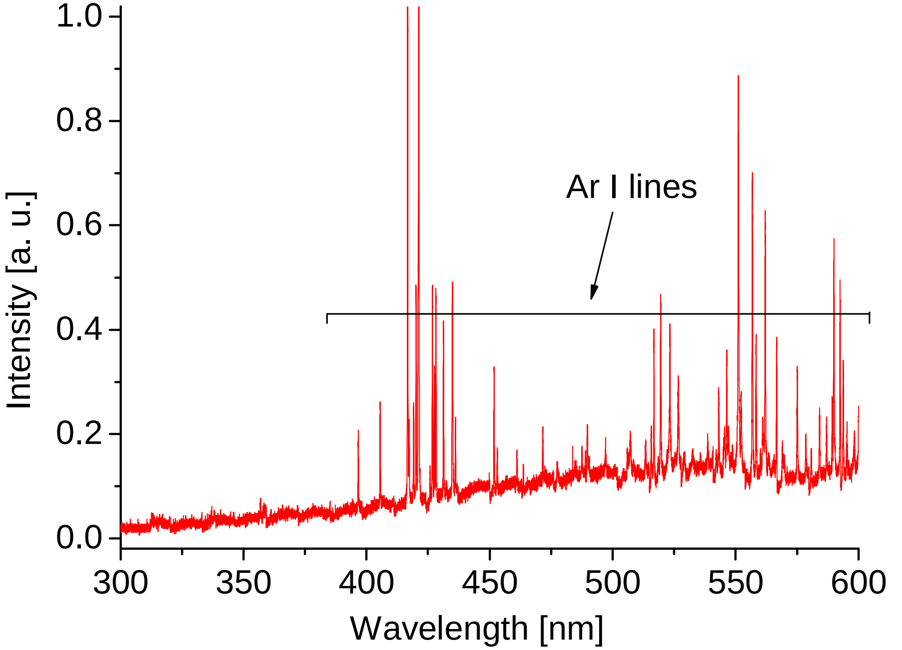
with C_2H_5OH



Photos of Ar 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)

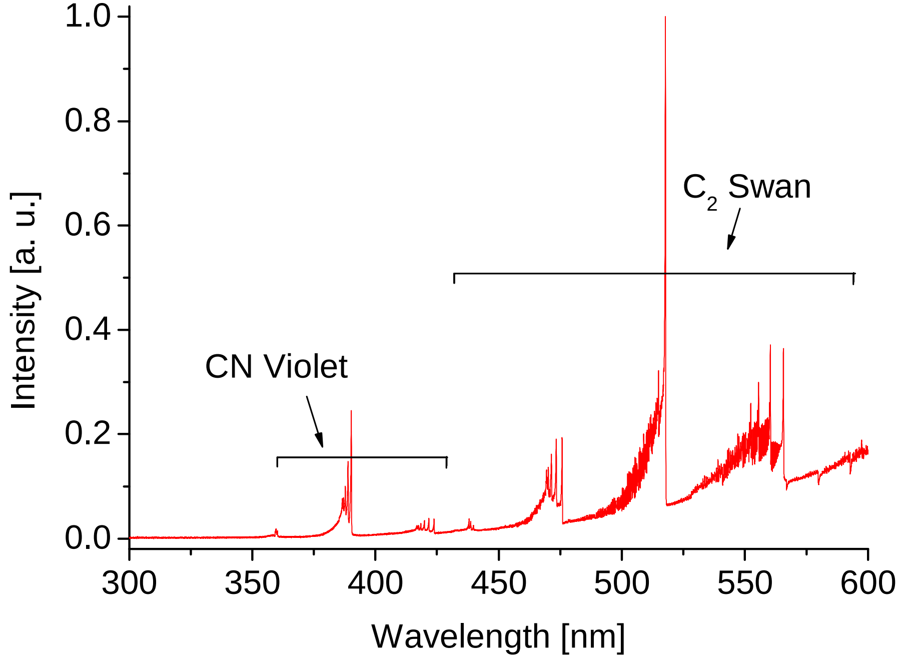
Spectroscopic diagnostics of Ar and Ar/C_2H_5OH plasma

without C_2H_5OH



T_r		at 15 mm and P_A – 2kW	ranged (dep. P_A & location)
	OH	2100 K	1900 - 4000 K

with C_2H_5OH

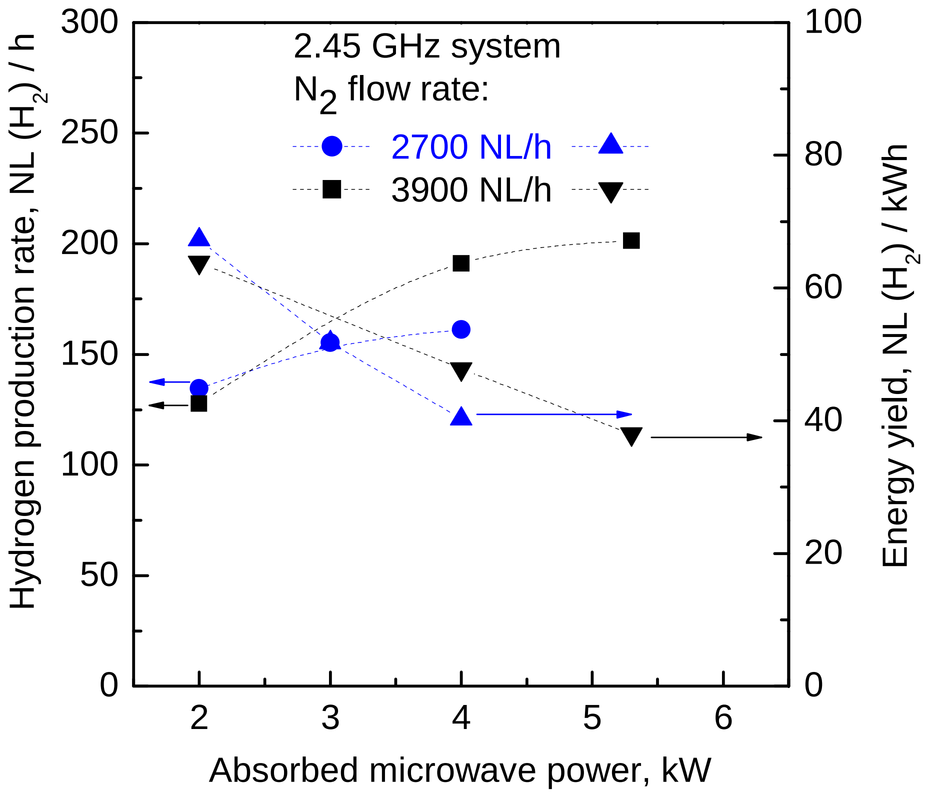


T_r		at 15 mm and P_A – 2kW
	CN	4500 K
	C_2	4500 K

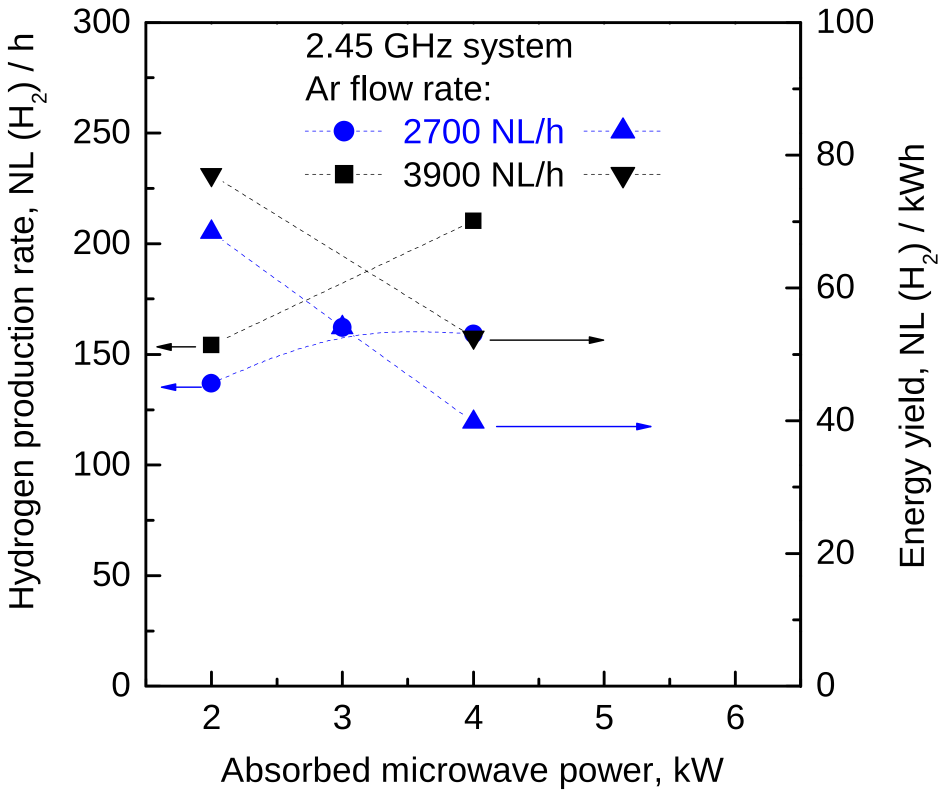
Measured emission spectra of Ar plasma and rotational temperatures with and without ethanol vapor addition (2.45 GHz plasma system, absorbed microwave power P_A - 2 kW, working gas flow rate - 2700 NL/h, 15 mm below the waveguide bottom)

Ethanol conversion Ar/C_2H_5OH plasma

N_2 plasma



Ar plasma

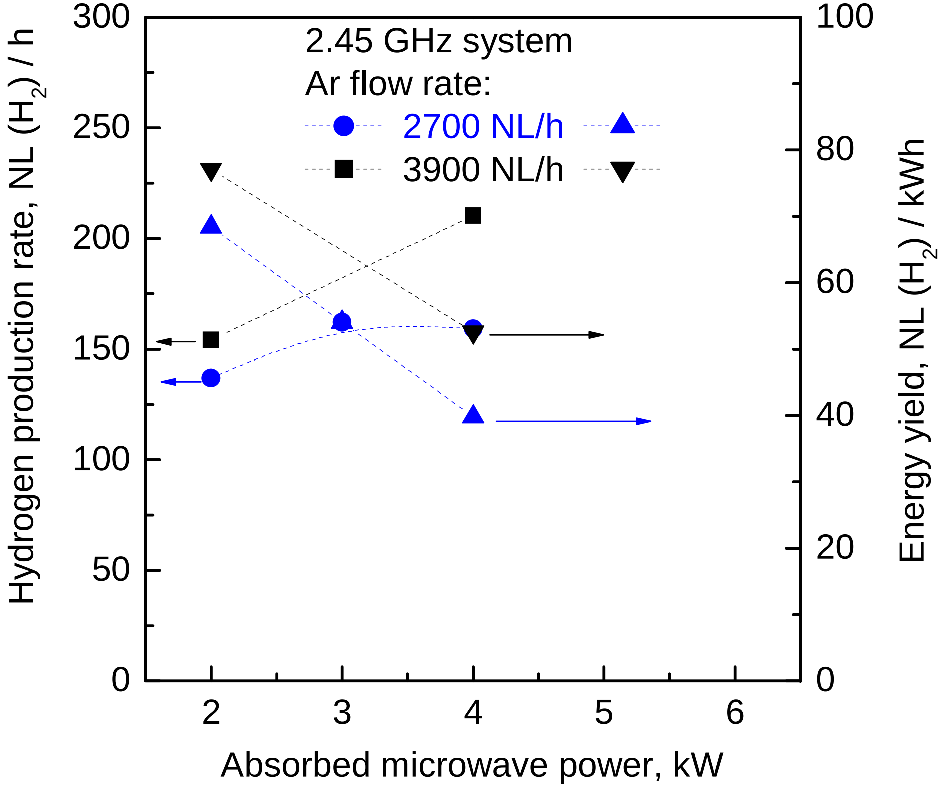


Hydrogen production rate and energy efficiency of hydrogen production as a function of absorbed microwave power for N_2 and Ar plasma in 2.45 GHz system.

Ethanol conversion Ar/C_2H_5OH plasma

Intensive soot production in plasma area

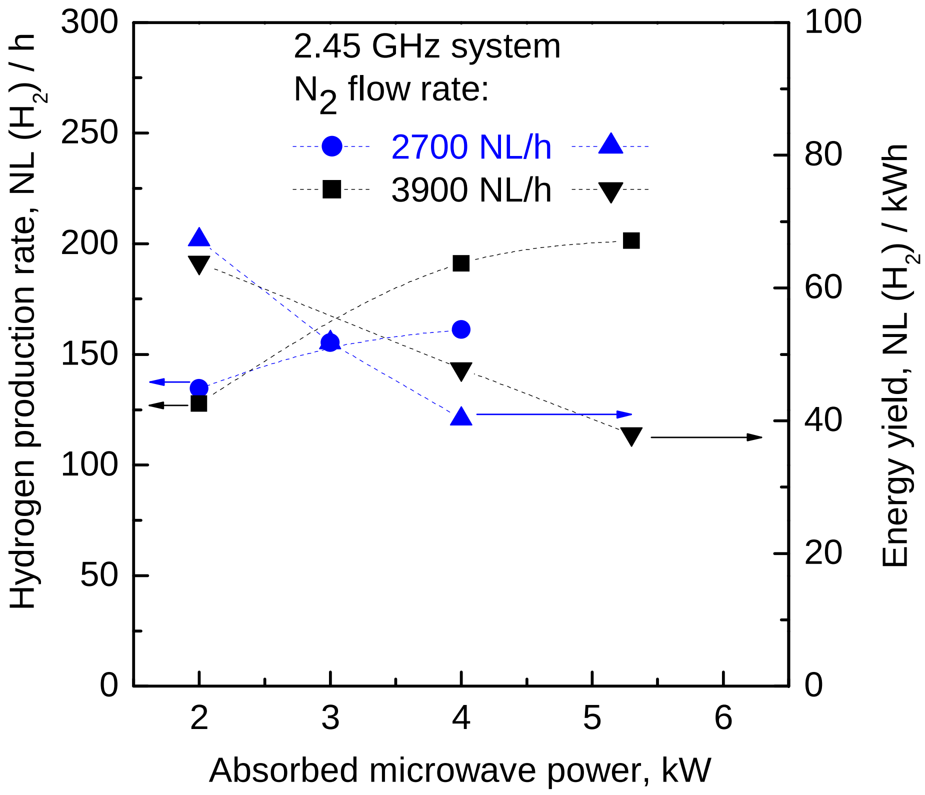
Ar plasma



Hydrogen production rate and energy efficiency of hydrogen production as a function of absorbed microwave power for Ar plasma in 2.45 GHz system.

Ethanol conversion Ar/C_2H_5OH plasma

N_2 plasma



Intensive CN molecules production

Hydrogen production rate and energy efficiency of hydrogen production as a function of absorbed microwave power for N_2 plasma in 2.45 GHz system.

Hydrogen production. The best results

Absorbed microwave power kW	Flow rate NL/h	Hydrogen production rate NL(H_2)/h [g(H_2)/h]	Energy yield NL(H_2)/kWh [g(H_2)/kWh]	Ethanol conversion degree %	Products in the outgas %
2	Ar - 3900	154 [12.8]	77 [6.3]	99.5	Ar - 93 H_2 - 3.78 CO_2 – 0.1 CO – 1.19 CH_4 – 0.28 C_2H_2 – 0.54 C_2H_4 – 0.26 C_2H_6 – 0.06
4	Ar - 3900	210 [17.5]	52.5 [4.4]	99.7	Ar - 91 H_2 - 5.08 CO_2 – 0.1 CO – 1.54 CH_4 – 0.25 C_2H_2 – 0.9 C_2H_4 – 0.105 C_2H_6 – 0.03

The best achieved results of hydrogen production via ethanol conversion using waveguide-supplied metal-cylinder-based MPS

Conventional and plasma methods of H_2 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
Cylindrical MPS	$Ar+C_2H_5OH$	6.4	present work

Summary and conclusions

- The etal-cylinder-based MPS can operate in different gases (nitrogen, carbon dioxide, argon) with high gas flow rates at atmospheric pressure and microwave power of a few kW
- The spectroscopic measurements showed the high gas temperature (1900-6000 K)
- The hydrogen production rate and energy yield were up to 210 NL(H_2)/h [180 g(H_2)/h] and 77 NL(H_2)/kWh [42.9 g(H_2)/kWh] in case of etanol thermal conversion using metal-cylinder-based MPS
- The ethanol conversion rate in all cases was greater than 99% (initial addition of ethanol have to be increased)
- The metal-cylinder-based MPS has a high potential for hydrogen production via liquid hydrocarbons (e.g. ethanol) conversion

Thank you for your attention!

Authors:


Bartosz Hrycak


Dariusz Czylkowski


Robert Miotk


Mirosław Dors


Mariusz Jasiński


Jerzy Mizeraczyk

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