Hydrogen production by conversion of ethanol using atmospheric pressure microwave plasmas

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Introduction

- Hydrogen is more and more attractive as an efficient and environmental friendly source of energy. It 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
- Our motivation arises from the growing interest in the hydrogen production technologies
- Plasma technologies on hydrocarbon reforming to generate hydrogen has been gradually attracting attention (no expensive and impurity vulnerable catalysts)
- Investigation concerns microwave (915 MHz, 2.45 GHz) atmospheric pressure plasma source (MPS) for hydrogen production via ethanol conversion
- Hydrogen production reactions from ethanol:

$C_2H_5OH \rightarrow 3H_2 + CO + C$ (thermal decomposition)
$C_2H_5OH + CO_2 \rightarrow 3H_2 + 3CO$ (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)
$C_2H_5OH + {}^1/_2O_2 \rightarrow 3H_2 + 2CO$ (partial oxydation)

- 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

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	$N_2+C_2H_5OH+H_2O$	21.4	present work

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

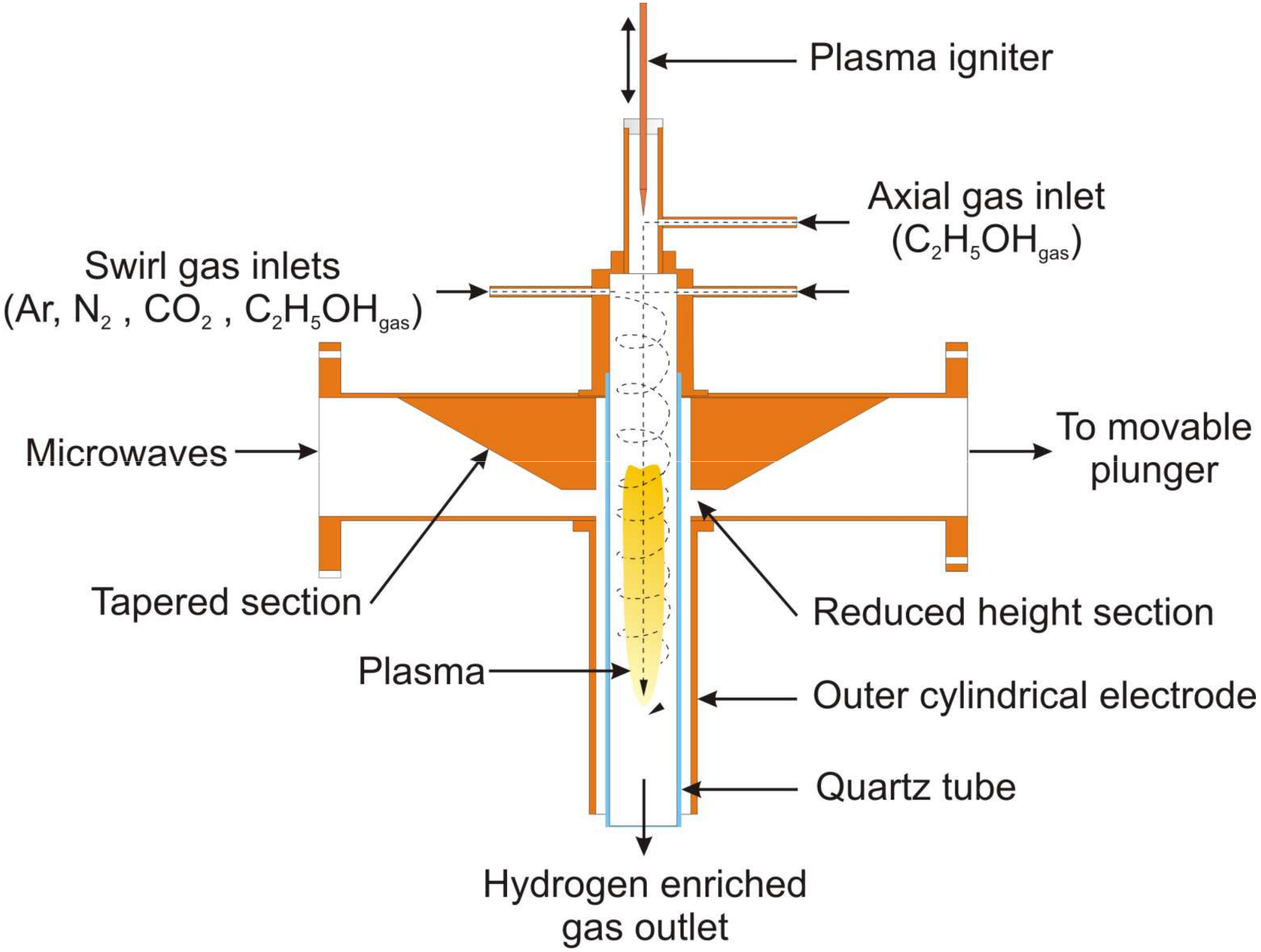
- nozzle-type MPSs:
  - coaxial-line-supplied coaxial-line-based (low gas flow rate)
  - waveguide-supplied coaxial-line-based (low and high gas flow rate)

- nozzleless MPSs:
  - waveguide-supplied coaxial-line-based (with or without an inner dielectric tube)
  - waveguide-supplied metal-cylinder-based (with or without an inner dielectric tube)
  - 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



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

Waveguide-supplied metal-cylinder-based MPS

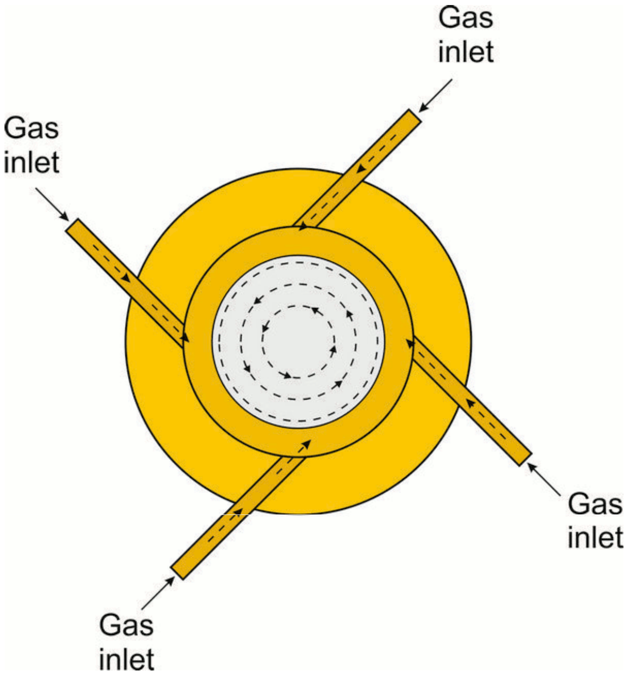
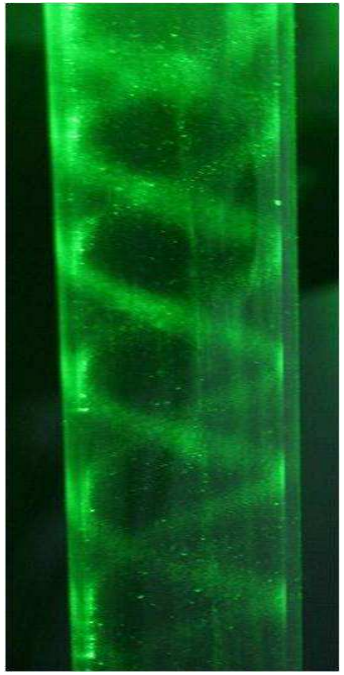


Illustration of the gas swirl.
Inlet gas – mixed
(C_2H_5OH , N_2, CO_2 , H_2O)



Laser visualization of the swirl flow without plasma

Visualization of the swirl: the discharge quartz tube covered with the soot after plasma processing of ethanol

Features of the MPS:

- waveguide-based structure allowing to operate with microwaves of power of the order of a few kW
- nozzleless eliminating the nozzle erosion due to high temperature and thus prevent plasma contamination
- possibility of processing large volume of gases (several thousands NL/h)

Experimental setup

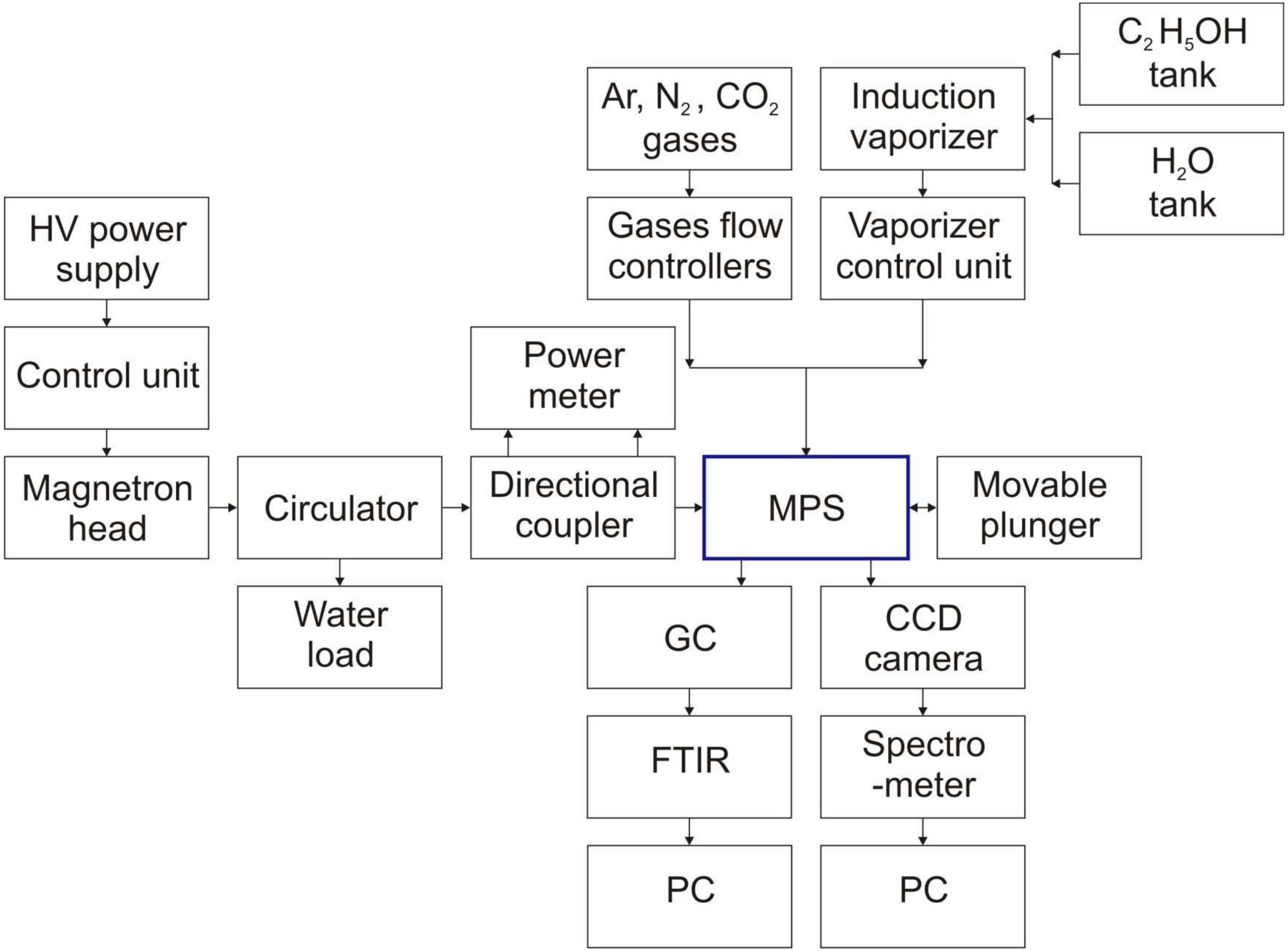
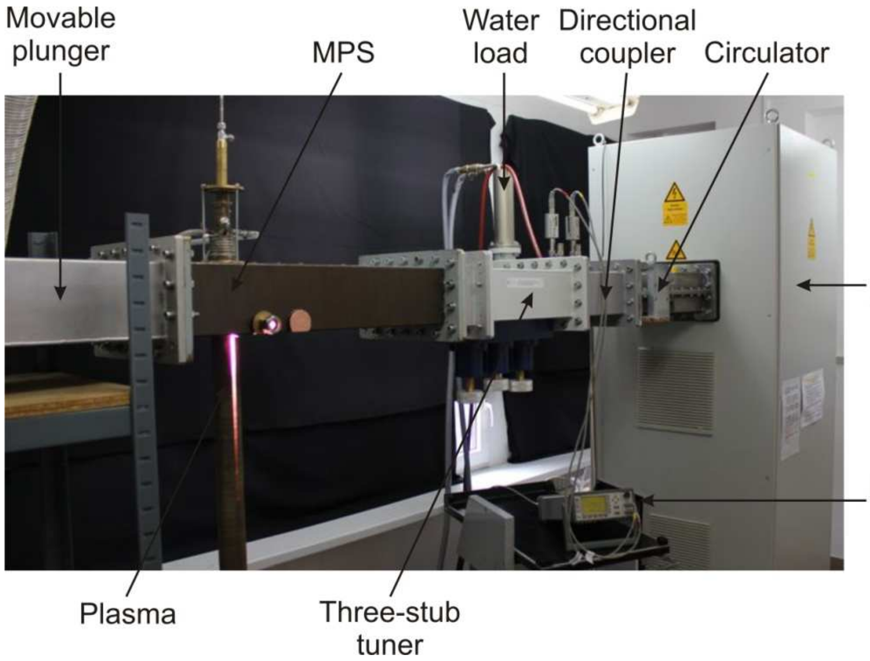


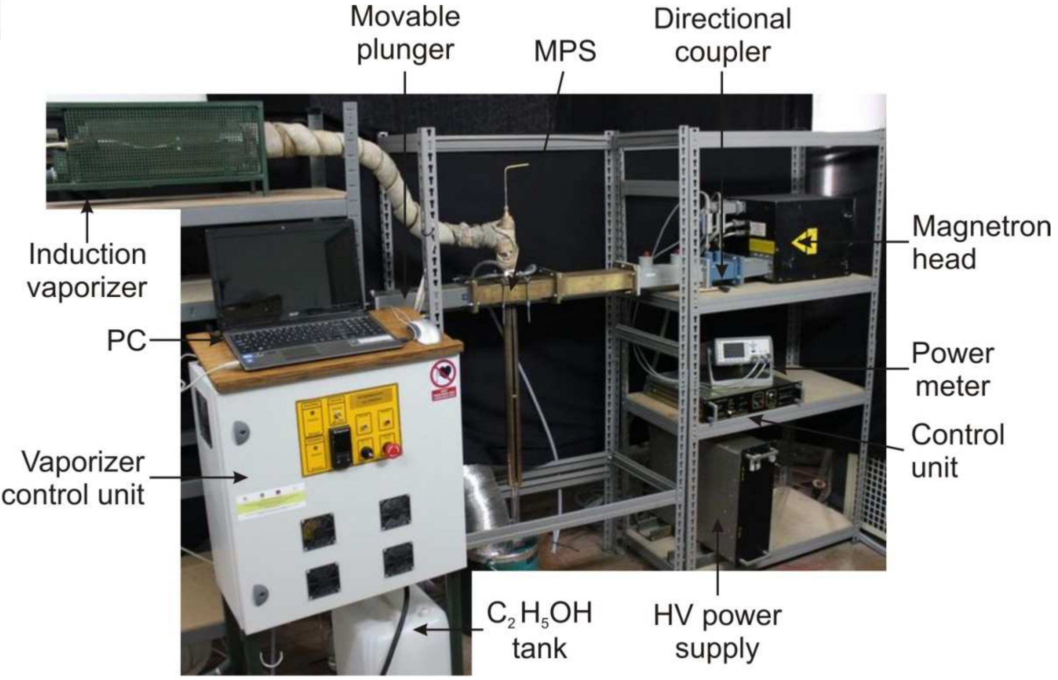
Diagram of the experimental setup for hydrogen production via ethanol conversion

Experimental setup



915 MHz microwave system

2.45 GHz microwave system



Photos of the 915 MHz and 2.45 GHz experimental setup for hydrogen production by conversion of ethanol using atmospheric pressure plasma

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 – 6 kW)
- Working gas type: Ar, N_2, CO_2
- 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

Parameters tested

- Hydrogen production rate in NL(H_2)/h
- Energy yield of hydrogen production in NL(H_2)/kWh
- Ethanol conversion degree in %
- Volume concentration of hydrogen in the outlet gas in %

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.

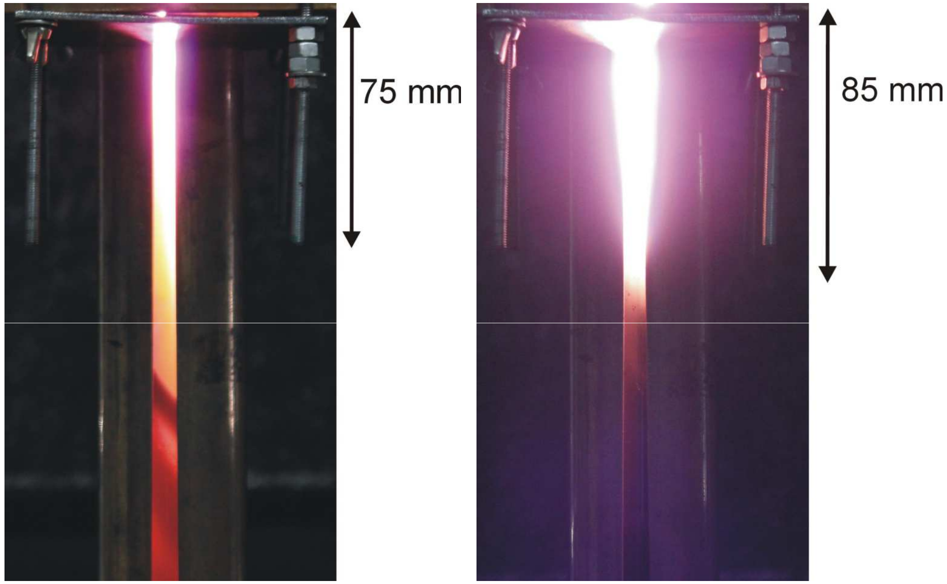
- Hydrogen concentration in the outgas is defined by relation

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

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.

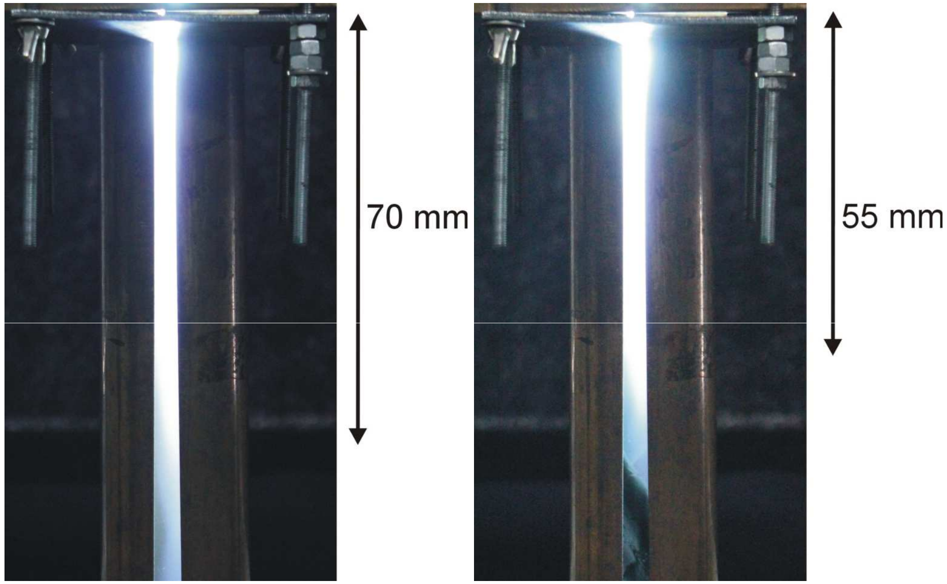
Visualization of the plasma flame

without C_2H_5OH with C_2H_5OH



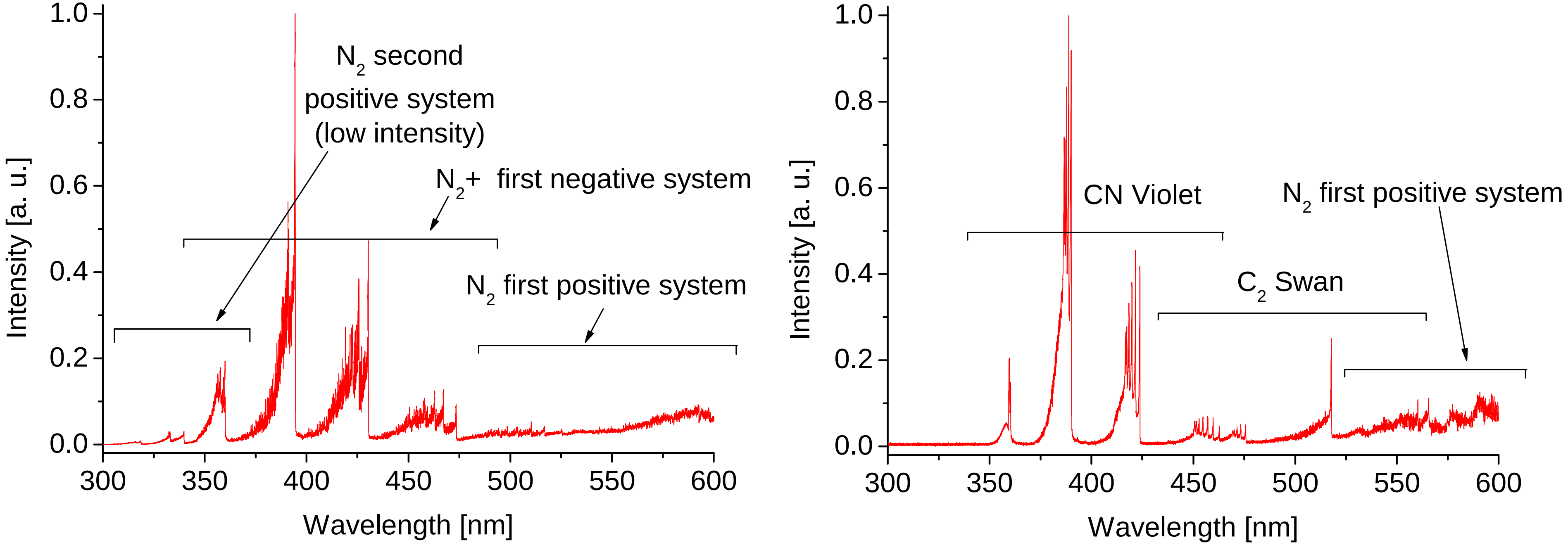
Front view of the of N_2 plasma with and without ethanol vapor addition. 2.45 GHz plasma system, absorbed microwave power P_A - 2 kW, working gas flow rate - 2700 NL/h.

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.

Plasma spectroscopic diagnostics



without C_2H_5OH

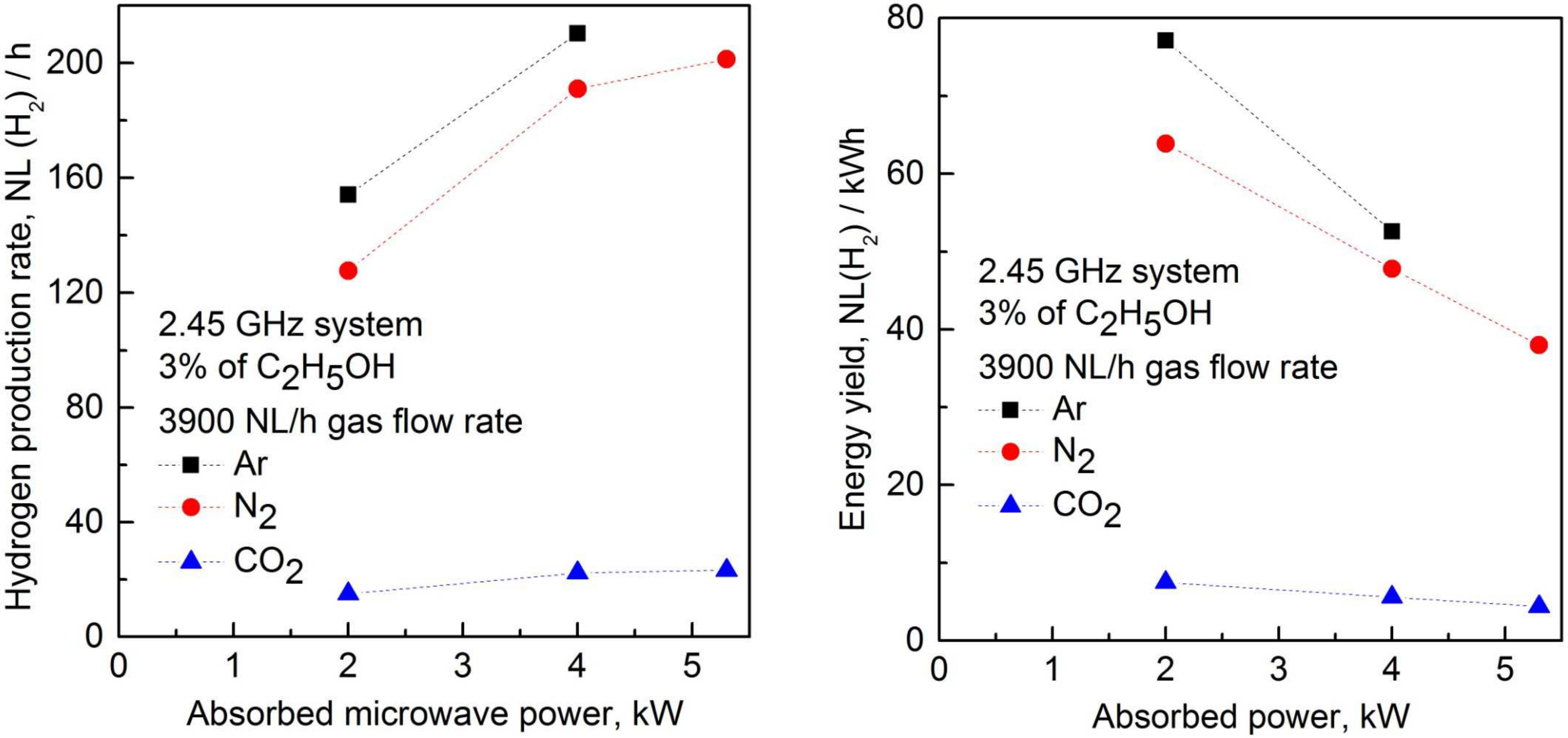
with C_2H_5OH

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

T_r		at 15 mm and P_A – 2kW	ranged (dep. location)
	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.

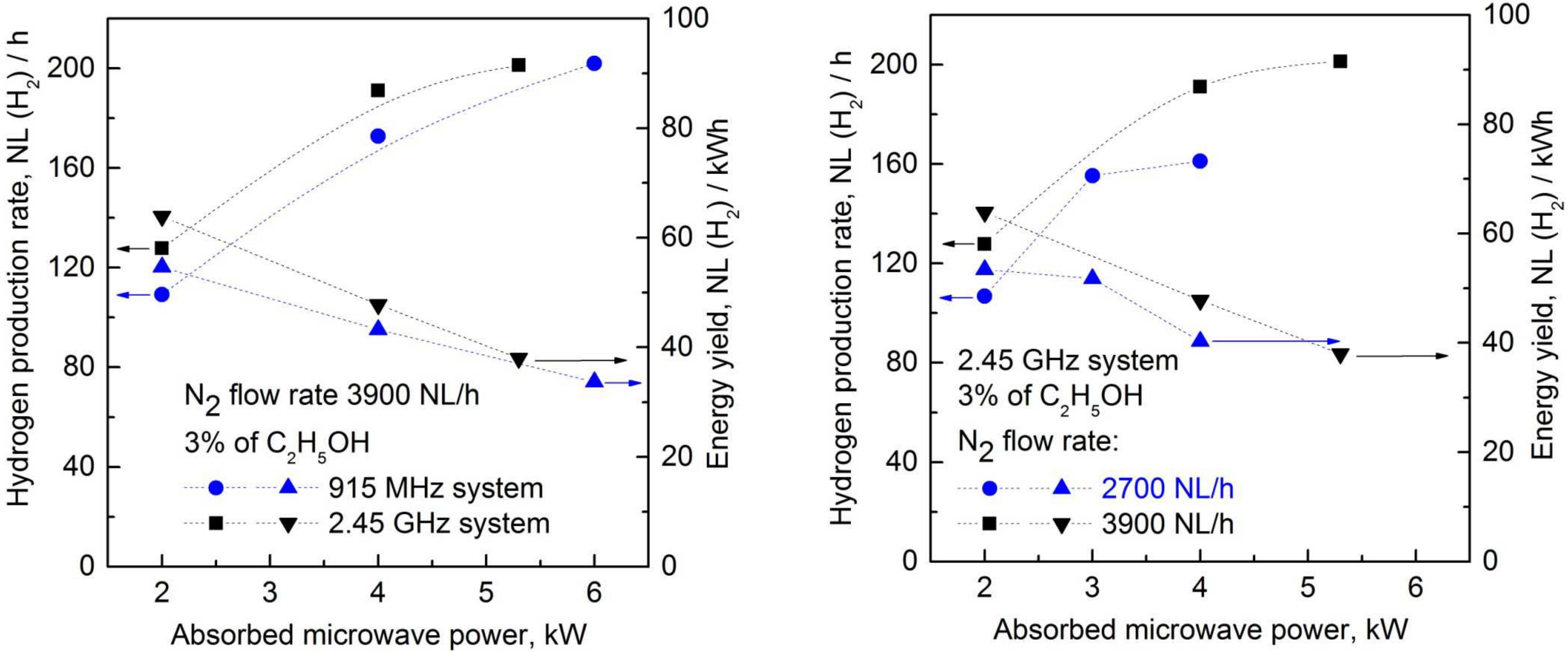
Thermal decomposition of ethanol



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. C_2H_5OH swirl flow.

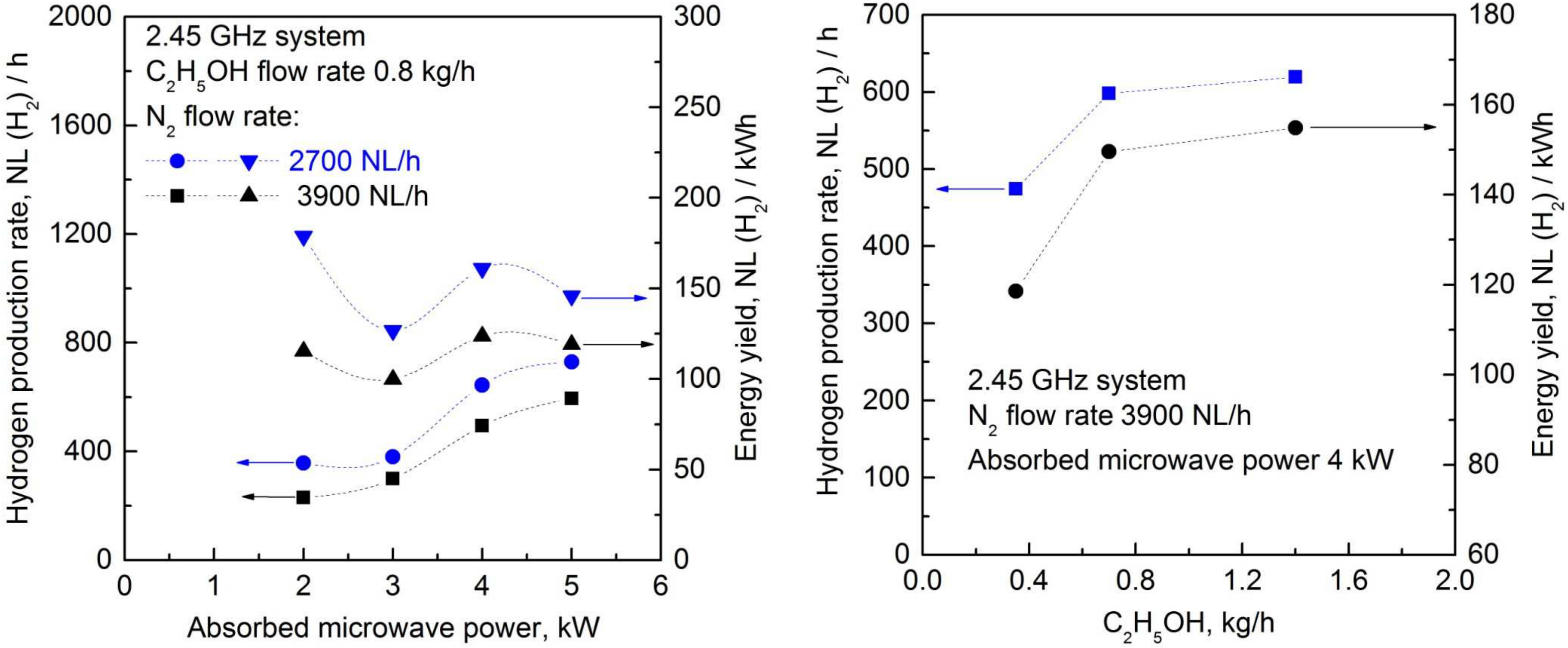
Comment: In the case of CO_2 plasma 2.35% of O_2 and 3% of CO at the output of the MPS was observed ($CO_2 \rightarrow CO + {}^1/_2O_2$). Instead of dry reforming, thermal decomposition or partial oxidation we achieved full oxidation: $C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2$

Thermal decomposition of ethanol



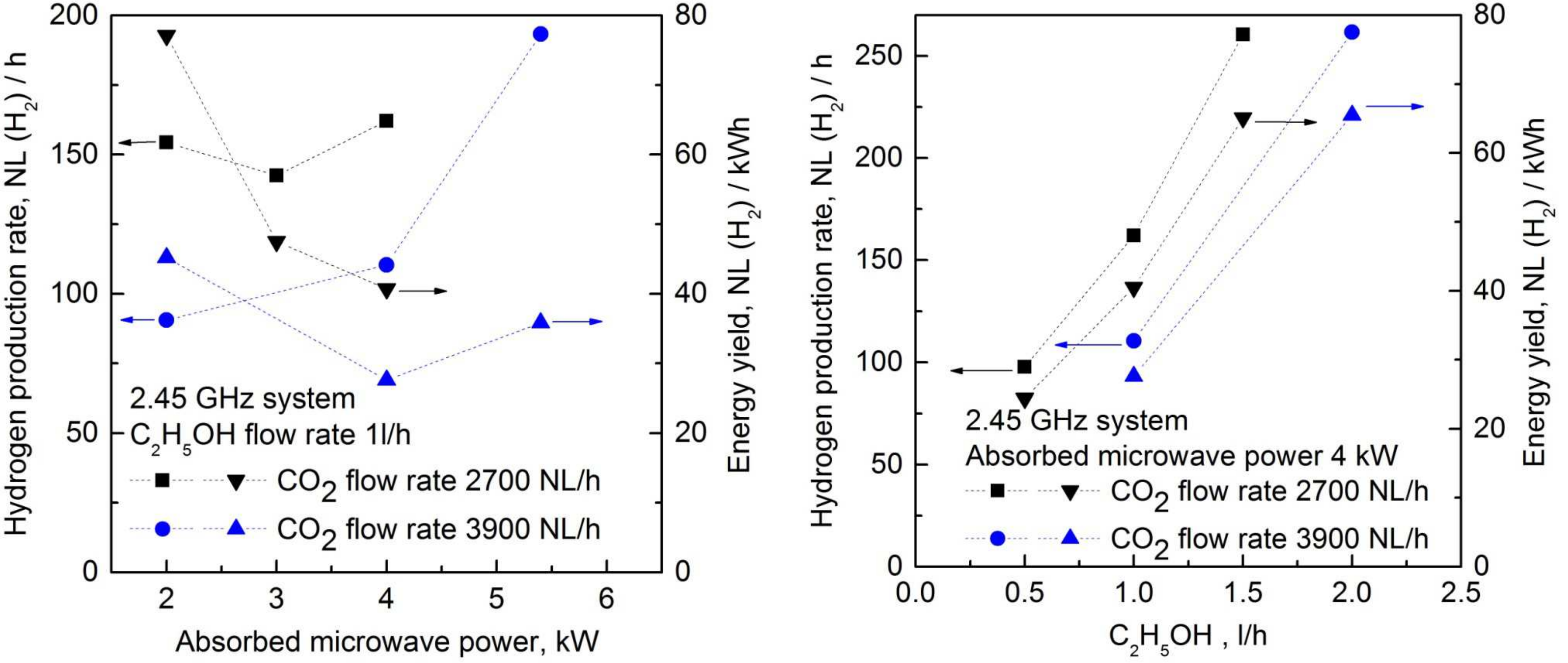
Comparison of the hydrogen production rate and energy yield as a function of absorbed microwave power for N_2 plasma. Different microwave systems (915 MHz, 2.45 GHz) – on the left and different N_2 flow rate (2700, 3900 NL/h) – on the right. C_2H_5OH swirl flow.

Thermal decomposition of ethanol



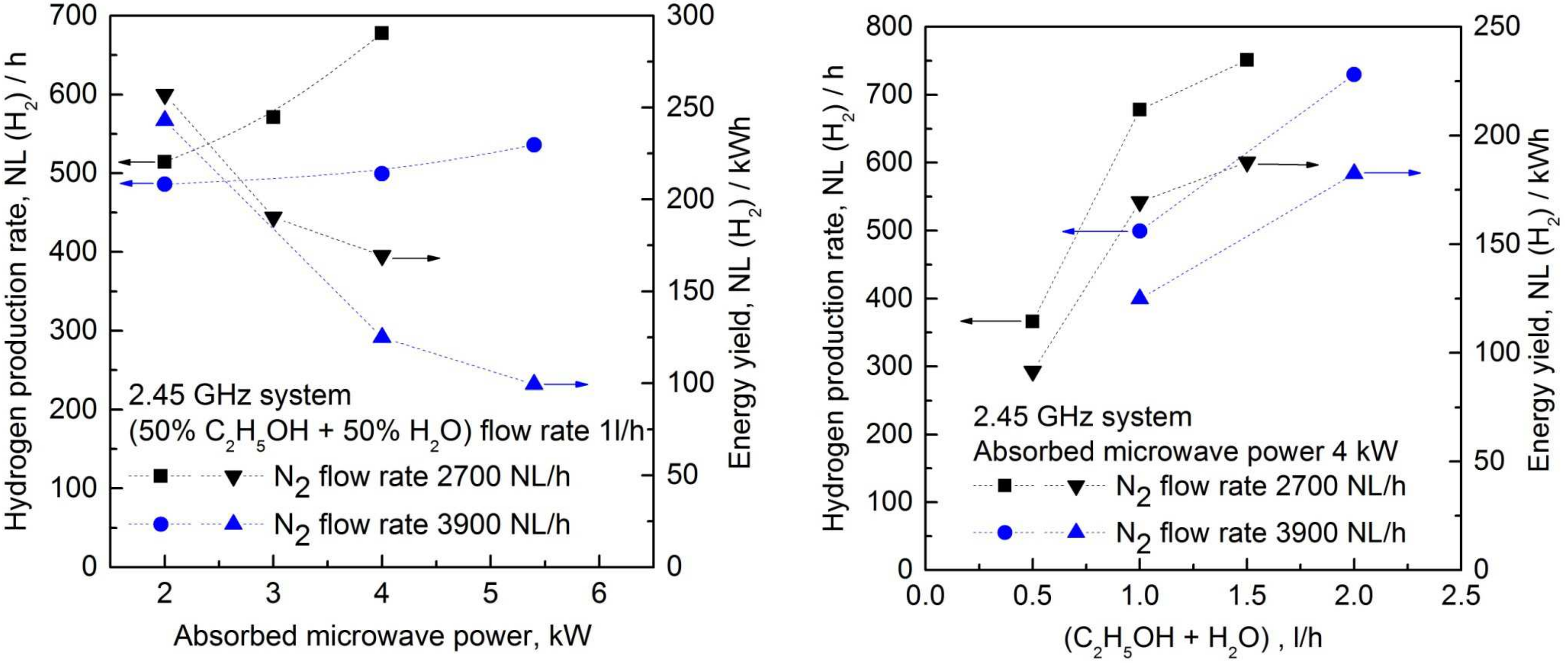
Hydrogen production rate and energy yield for N_2 plasma as a function of absorbed microwave power (on the left) and as a function of C_2H_5OH flow rate (on the right). C_2H_5OH swirl flow.

Ethanol dry reforming



Comparison of the hydrogen production rate and energy yield as a function of absorbed microwave power (on the left) and as C_2H_5OH flow rate (on the right). Different CO_2 flow rate (2700, 3900 NL/h). C_2H_5OH axial flow.

Ethanol steam reforming



Comparison of the hydrogen production rate and energy yield as a function of absorbed microwave power (on the left) and as C_2H_5OH flow rate (on the right). Different N_2 flow rate (2700, 3900 NL/h). C_2H_5OH axial flow.

Processing performance

Variable parameter	**Hydrogen production rate**	**Energy yield**
Increasing absorbed microwave power	Increases	Decreases
Increasing working gas swirl flow rate	Generally decreases	Generally decreases
Increasing C_2H_5OH axial flow rate	Increases	Increases

Dependence of the hydrogen production rate and energy yield on variable parameters

Hydrogen production. The best results

MPS type	Hydrogen production method	Flow rate	Hydrogen production rate NL(H_2)/h	Energy yield		Remarks
				NL(H_2)/kWh	g(H_2)/kWh	
Waveguide-supplied metal-cylinder-based MPS	Thermal decomposition	N_2 - 2700 NL/h C_2H_5OH - 1 l/h	728	145	12.1	C_2H_5OH swirl flow
	Dry reforming	CO_2 – 3900 NL/h C_2H_5OH - 2 l/h	262	65	5.4	C_2H_5OH axial flow
	Steam reforming	N_2 – 2700 NL/h (C_2H_5OH + H_2O) - 1 l/h	751	257	21.4	C_2H_5OH axial flow

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

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 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 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 best achieved results of hydrogen production rate and energy yield were 751 NL(H_2)/h and 257 NL(H_2)/kWh, respectively (ethanol steam reforming)
- The metal-cylinder-based MPS has a high potential for hydrogen production via other liquid hydrocarbons conversion

Thank you for your attention

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