Hydrogen production via methane conversion in an atmospheric pressure microwave (2.45 GHz) plasma

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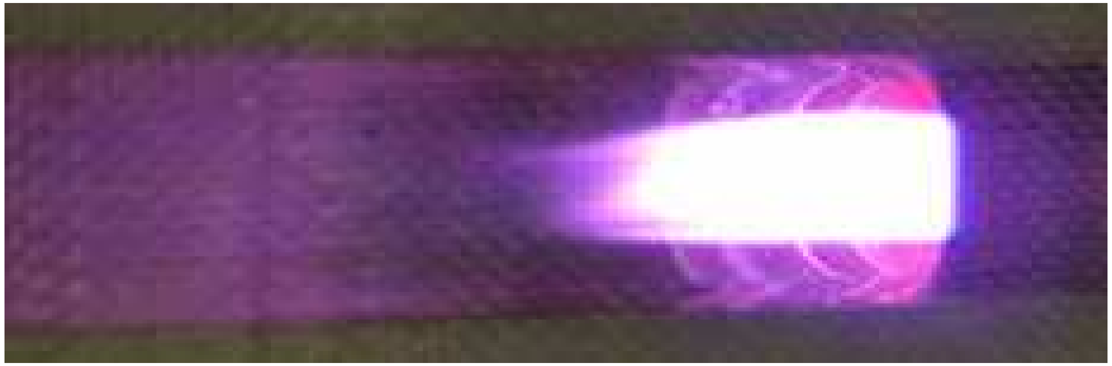

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Contents

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

- European roadmap for hydrogen and fuel cells published by European Commission in "Hydrogen Energy and Fuel Cells: A vision of our future" (EUR 20719, EN 2003)
    - from fossil fuel-based economy to hydrogen oriented economy
    - developing and implementing systems for hydrogen production from renewable electricity and biomass
    - research and development of other carbon-free hydrogen sources, such as solar thermal and advanced nuclear should be continued

- United States Department of Energy „Toward a more secure and cleaner energy future for America. National hydrogen energy roadmap" (2002)
    - lower the hydrogen production cost and to improve efficiency
    - improving existing commercial processes (e.g. steam methane reformation) and development new advanced production techniques (e.g. biological methods, nuclear and solar-powered)
    - cost of 1 kWh electric energy in the USA in April 2012 – $0.12
      $2/kg(H2) → kg(H2)/$2 → **60 g(H_2)/kWh** – Target of US DoE by 2020

Introduction

- Our motivation arises from the growing interest in the hydrogen production technologies
- 96% of hydrogen is produced from fossil fuels
- Industrial primary hydrogen sources
    - 48 % from natural gas
    - 30 % from oil
    - 18 % from coal
    - 4 % from water electrolysis
- Methane is a main constituent of natural gas
- Hydrogen production reactions from methane:
    - $CH_4 \rightarrow C+2H_2$ (pyrolysis)
    - **$CH_4+CO_2 \rightarrow CO+2H_2$ (dry reforming)**
    - **$CH_4+H_2O \rightarrow CO+3H_2$ (steam reforming)**
    - $CH_4+0.5O_2 \rightarrow CO+2H_2$ (partial oxidation)
    - $2CH_4+O_2+CO_2 \rightarrow 3CO+3H_2+H_2O$ (auto-thermal reforming)
    - $4CH_4+O_2+2H_2O \rightarrow 4CO+10H_2$ (auto-thermal reforming)

Conventional and plasma methods of H_2 production

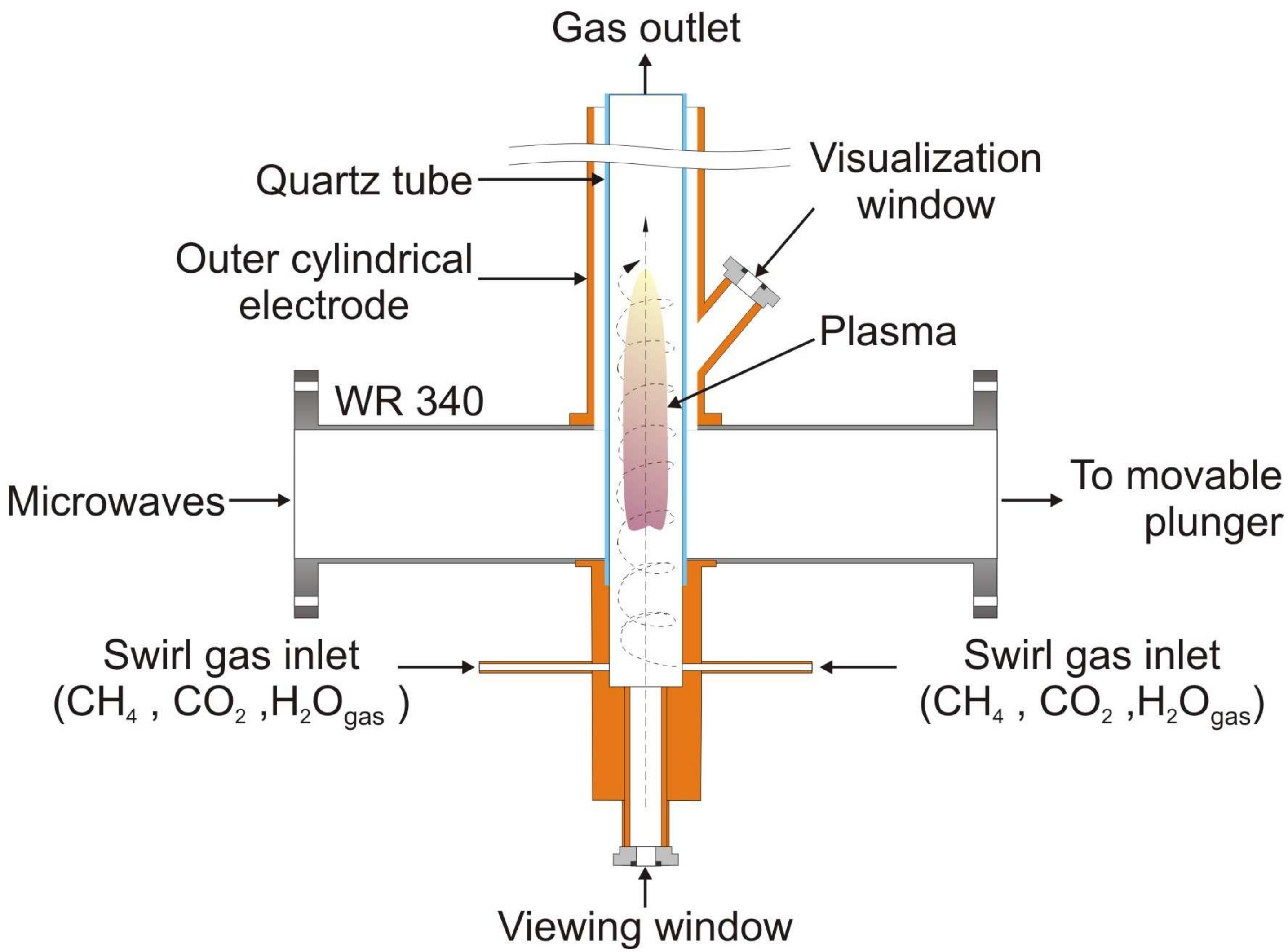
Production method	Initial composition	Energy yield $g(H_2)/kWh$	Reference
Conventional steam reforming of methane (catalyst)	CH_4 +H_2O+ air	60 Established Industrial Process	Katie Randolph, U.S. DOE, Hydrogen Production, 2013 Annual Merit Review and Peer Evaluation Meeting, May 16, 2013
Water electrolysis	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
Metal-cylinder-based MPS	CH_4 +CO_2+H_2O	42.9	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

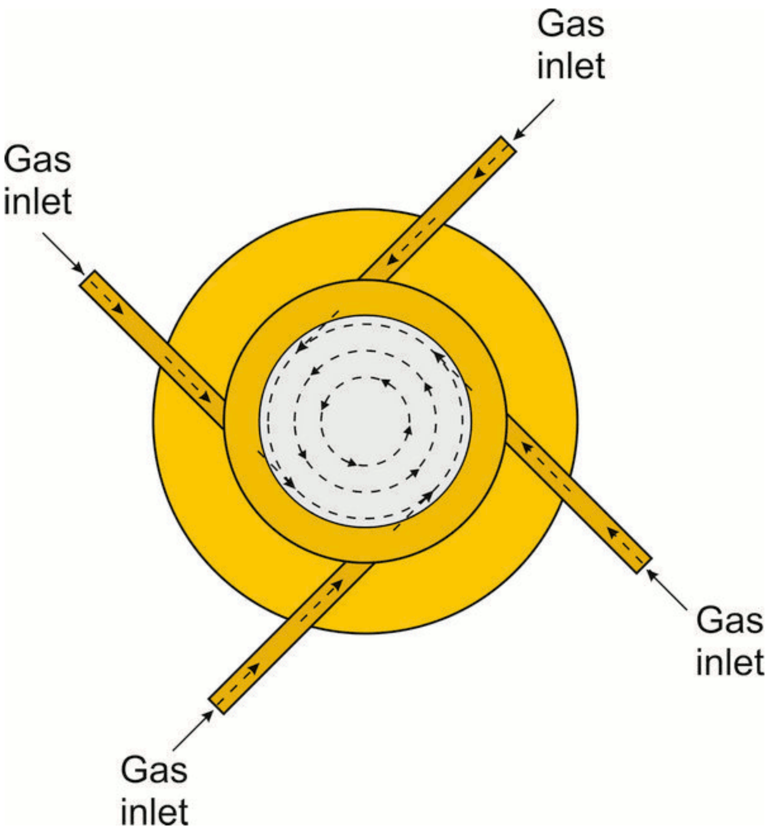
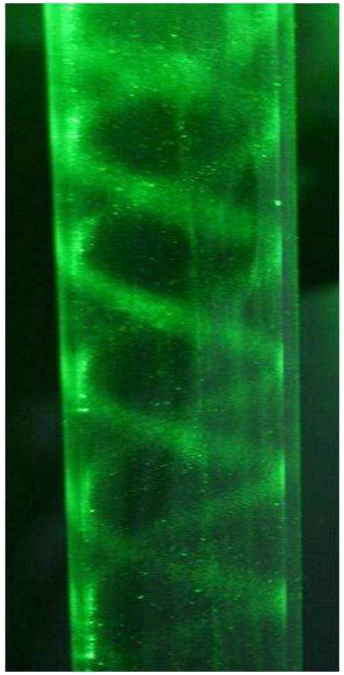


Illustration of the gas swirl.
Inlet gas – mixed (CH_4 , CO_2 , H_2O)



Laser visualization of the swirl flow without plasma

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

Waveguide-supplied metal-cylinder-based MPS

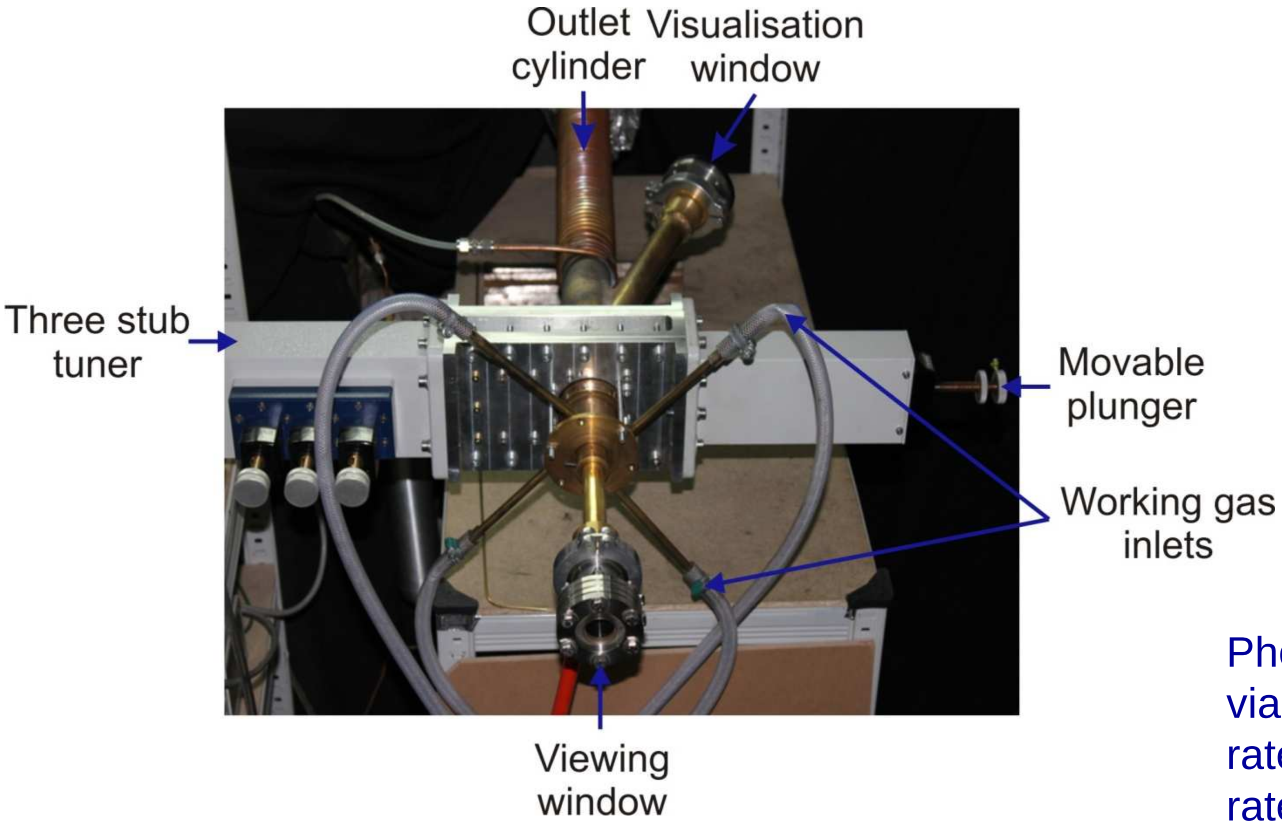


Photo of the waveguide-supplied metal-cylinder-based MPS

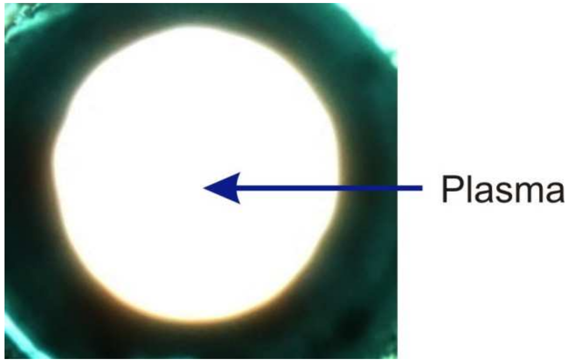


Photo of the plasma flame taken via viewing window. CH_4 swirl flow rate of 3000 NL/h. CO_2 swirl flow rate of 3000 NL/h. The absorbed microwave power 2800 W

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

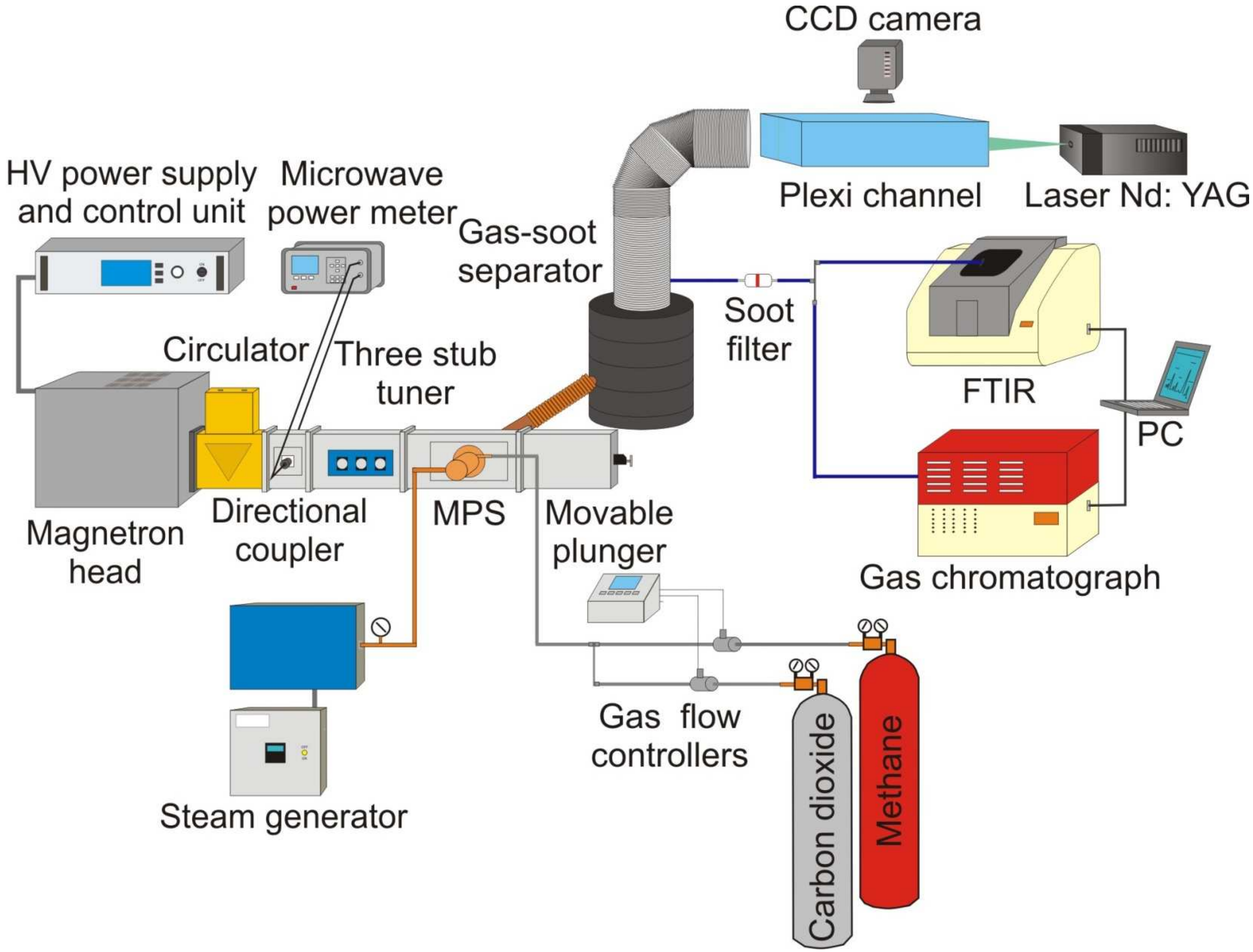


Diagram of the experimental setup for hydrogen production via methane conversion

Experimental setup

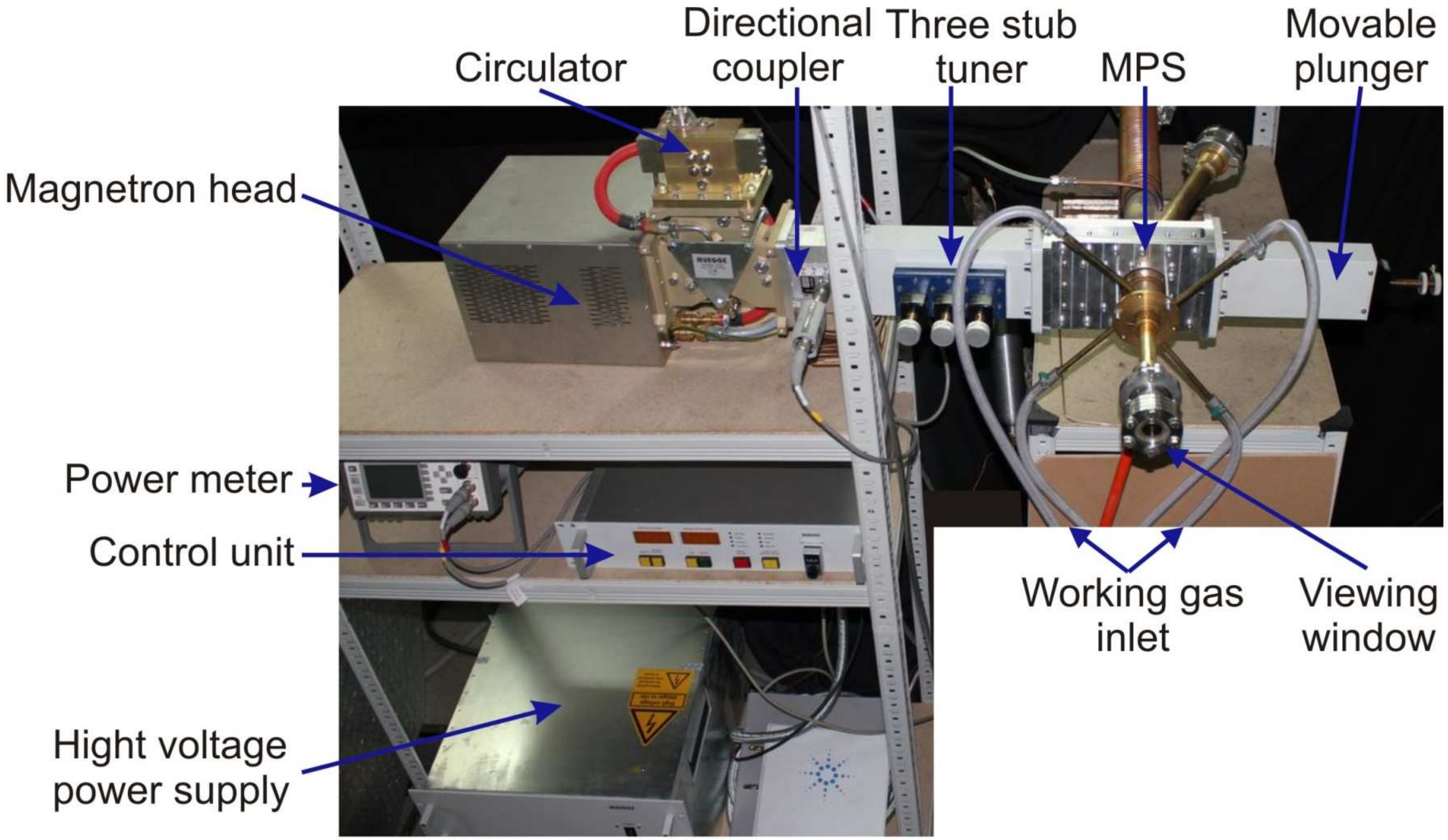
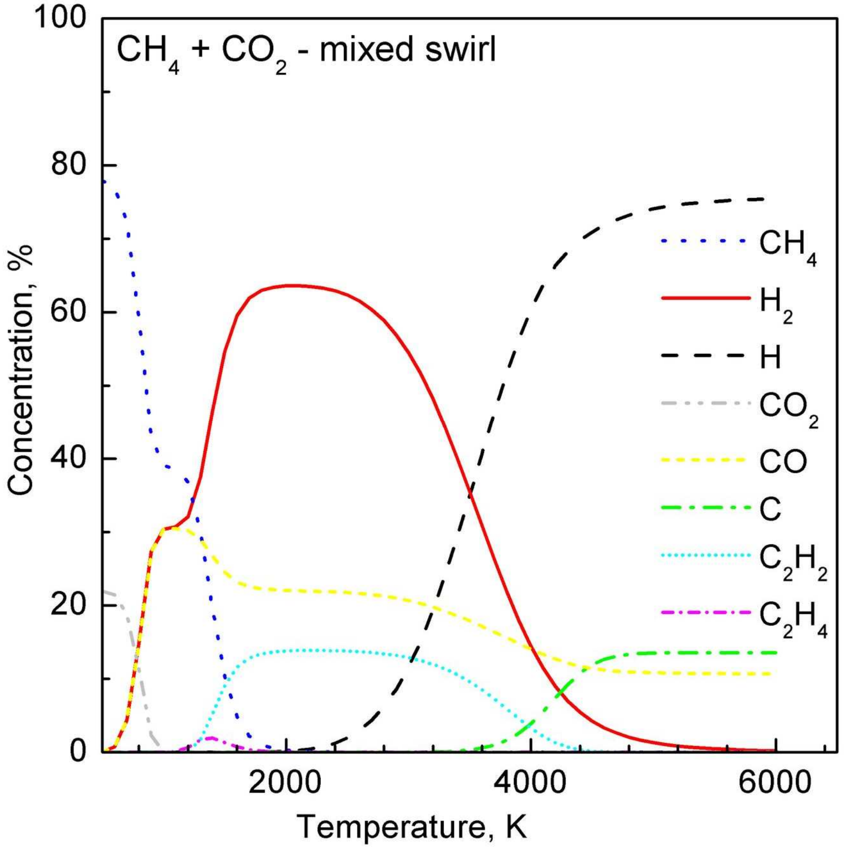
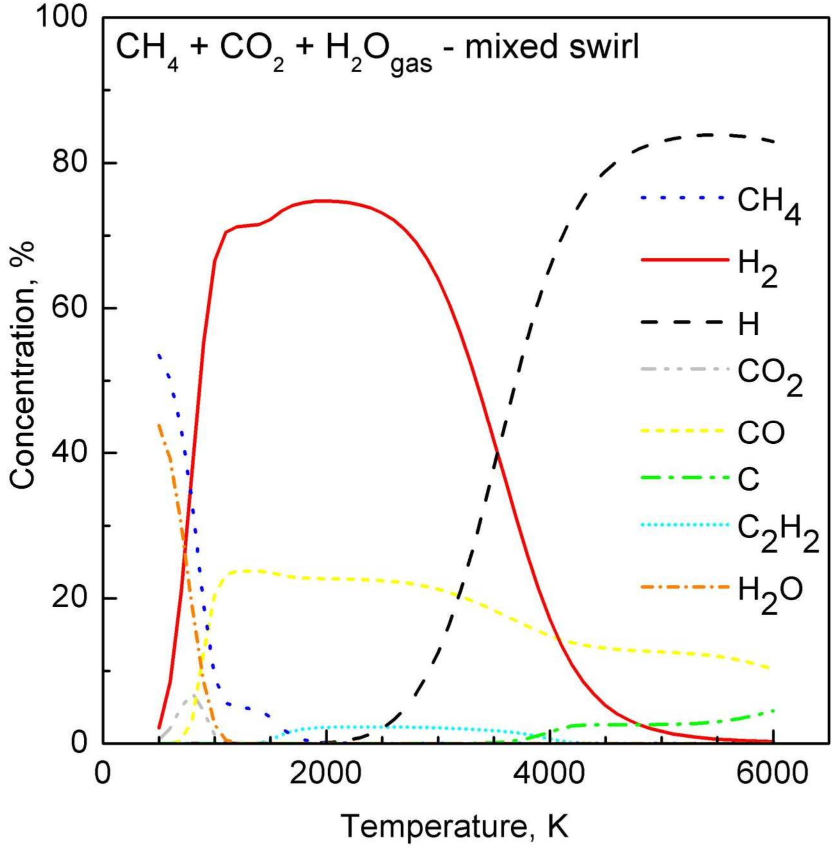


Photo of the experimental setup with the waveguide-supplied metal-cylinder-based MPS

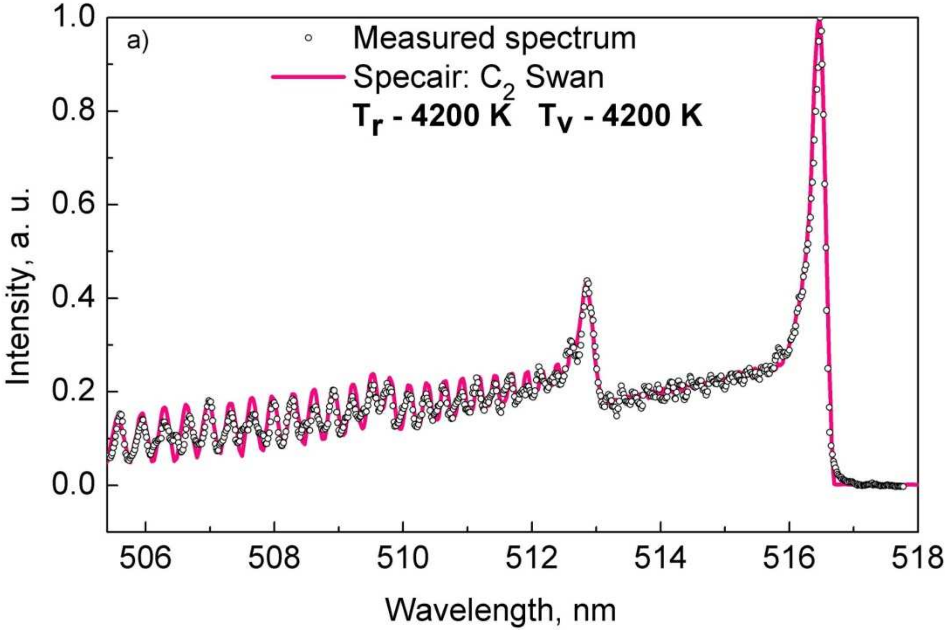
Methane reforming products. Thermodynamic modelling



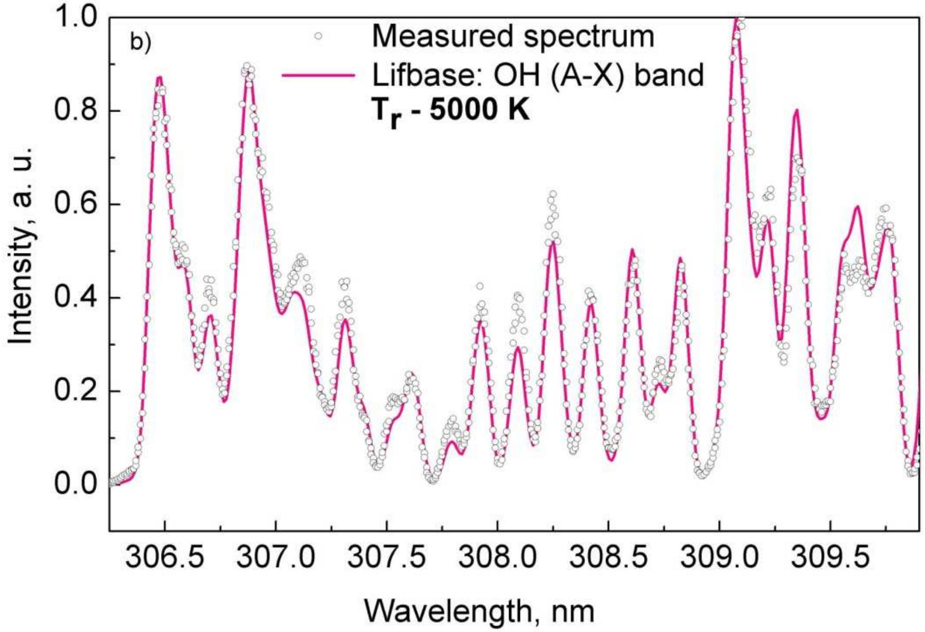


Results of the thermodynamic modelling of the methane dry and steam reforming products concentration (volume % in the outgas).Thermodynamic Equilibrium Reactor model (TER) by Kintech Ltd., Chemical Workbench 4.0, Moscow, Russia

Spectroscopic diagnostics of methane plasma



Comparison of the measured and simulated emission spectra of C_2 Swan band in CH_4/CO_2 plasma. Absorbed microwave power P_A=4.5 kW. Methane swirl flow rate - 50 NL/min. Carbon dioxide swirl flow rate - 50 NL/min. 15 mm below the waveguide bottom wall.



Comparison of the measured and simulated emission spectra of OH (A-X) band in CH_4/CO_2 plasma. Absorbed microwave power P_A=4.5 kW. Methane swirl flow rate - 50 NL/min. Carbon dioxide swirl flow rate - 50 NL/min. 15 mm below the waveguide bottom wall.

Hydrogen production. Experiment parameters

MPS type

- Waveguide-supplied metal-cylinder-based MPS

Processes

- Dry reforming of methane

  $CH_4 + CO_2 \rightarrow 2CO + 2H_2$, ($CH_4 + CO_2$) - mixed swirl flow

  Thermodynamic limit - 58 g(H_2)/kWh

- Steam reforming of methane

  $CH_4 + H_2O \rightarrow CO + 3H_2$, $CH_4 + CO_2 \rightarrow 2CO + 2H_2$, ($CH_4 + H_2O + CO_2$) - mixed swirl flow

  Thermodynamic limit - 105 g(H_2)/kWh

Constant parameters

- Microwave frequency: 2.45 GHz
- Pressure: atmospheric
- Catalyst: no catalyst

Variable parameters

- Absorbed microwave power (1 – 5 kW)
- CH_4 swirl flow rate (1500 – 9000 NL/min)
- CO_2 swirl flow rate (1200 – 9000 NL/min)
- H_2O_{aq} flow rate (0.5 – 3 L/h) [H_2O_{gas} flow rate (740 – 3700 NL/h)]

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 methane conversion degree is given by

$$[(CH_4)_{converted} / (CH_4)_{initial} \times 100\%],$$

where $(CH_4)_{initial}$ is the total mass of CH_4 and $(CH_4)_{converted}$ is the converted mass of CH_4.

- Hydrogen concentration in the outgas is defined by relation

$$[Q(H_2)_{outgas}) / Q(CH_4+H_2+C_2H_2+\text{other products})_{outgas}] \times 100\%,$$

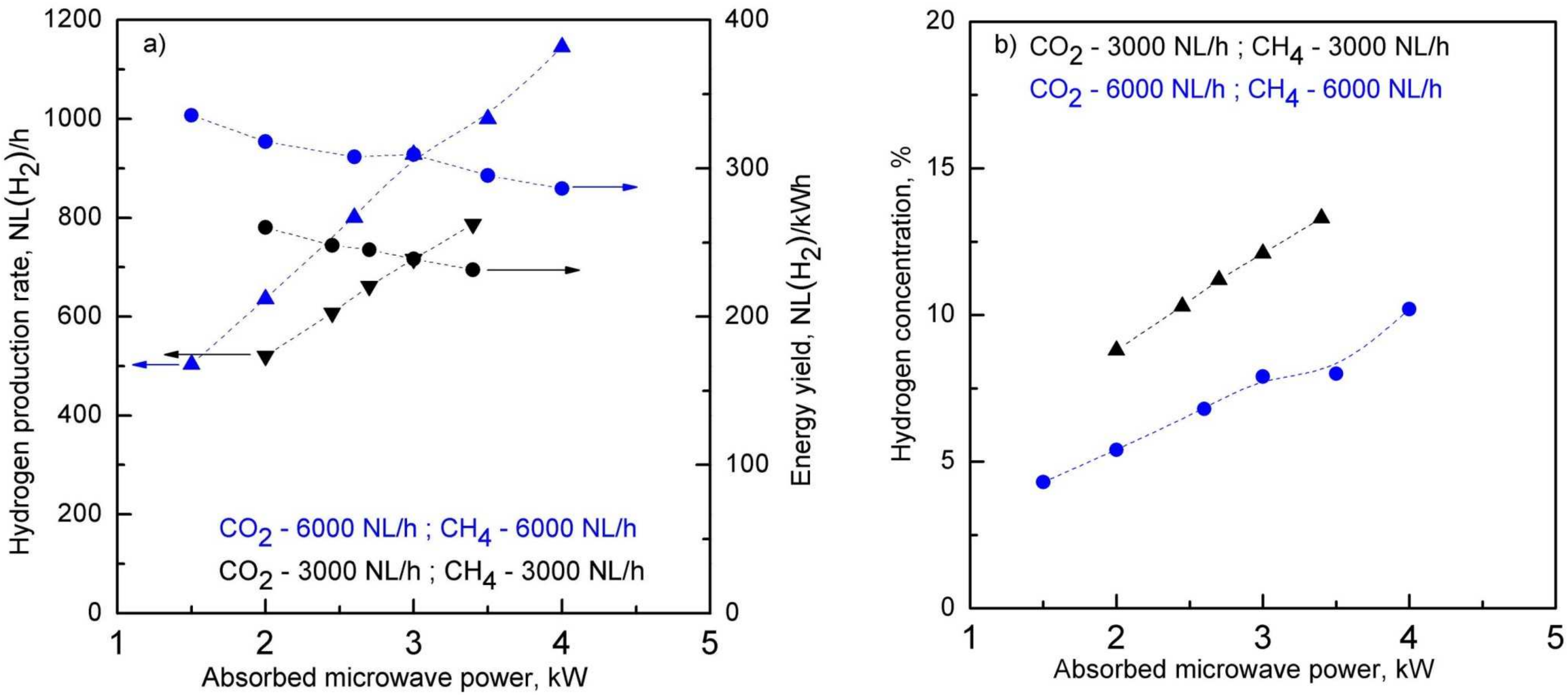
where $Q(H_2)_{outgas}$ is a hydrogen gas flow rate at the gases output of the MPS and $Q(CH_4+H_2+C_2H_2+\text{other products})_{outgas}$ is the total gases flow rate at the output of the MPS.

- The above listed parameters were calculated from methane mass balance of its conversion products.

Hydrogen production. Processing performance

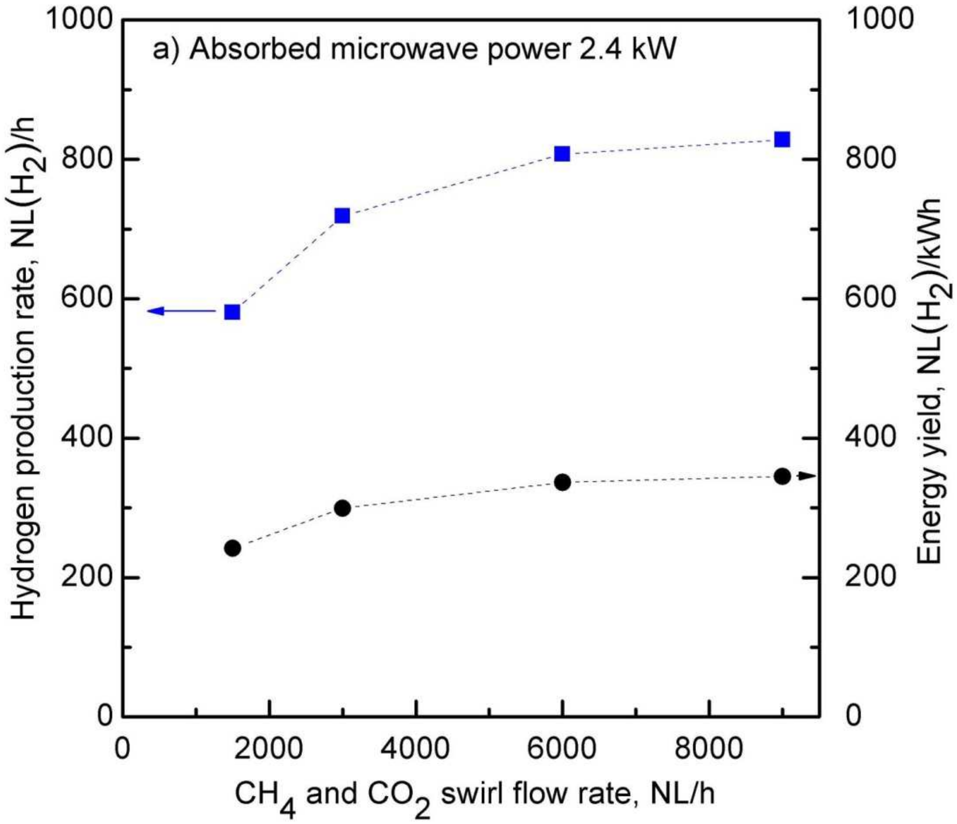
Process	Variable parameter	Hydrogen production rate	Energy yield	Methane conversion degree	Hydrogen concentration	Remarks
Dry reforming	Increasing absorbed microwave power	Increases almost linearly	Decreases slightly	Increases almost linearly	Increases slightly, almost linearly	Carbon powder (graphite) production
	Increasing CH_4 and CO_2 swirl flow rate	Increases slightly	Increases slightly	Decreases	Decreases	H_2 concentration decreases almost linearly
Steam reforming	Increasing absorbed microwave power	Increases slightly	Almost constant	Increases	Slightly increases	Water vapour condensation
	Increasing CO_2 swirl flow rate	Decreases slightly	Decreases slightly	Decreases	Decreases	
	Increasing H_2O_{gas} swirl flow rate	Almost constant	Almost constant	Almost constant	Almost constant	

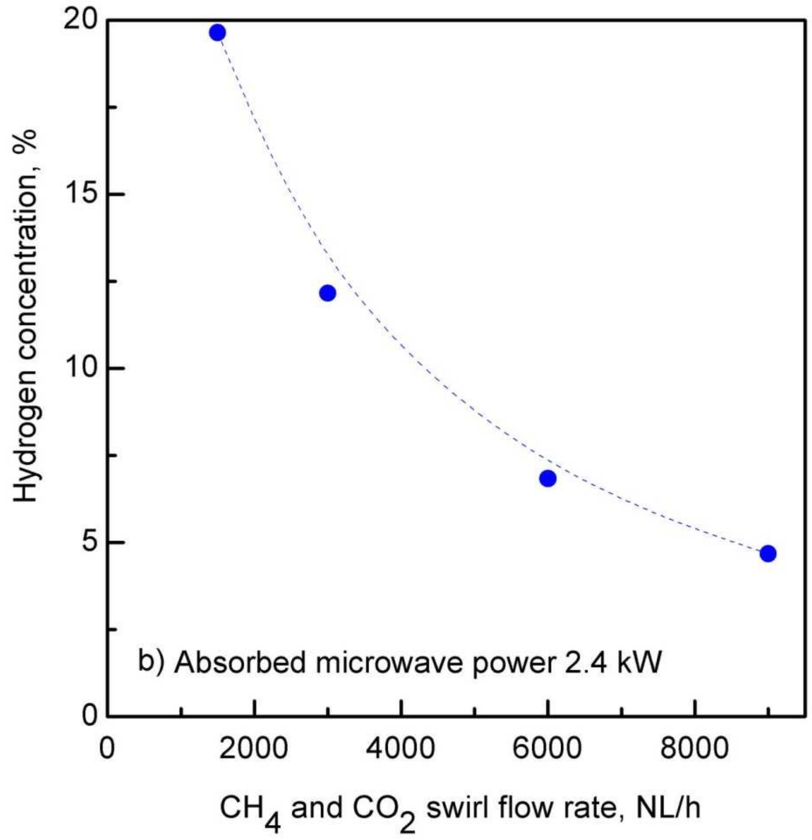
Methane dry reforming



Comparison of the hydrogen production rate, energy yield and hydrogen concentration as a function of absorbed microwave power for different CH_4 and CO_2 flow rates

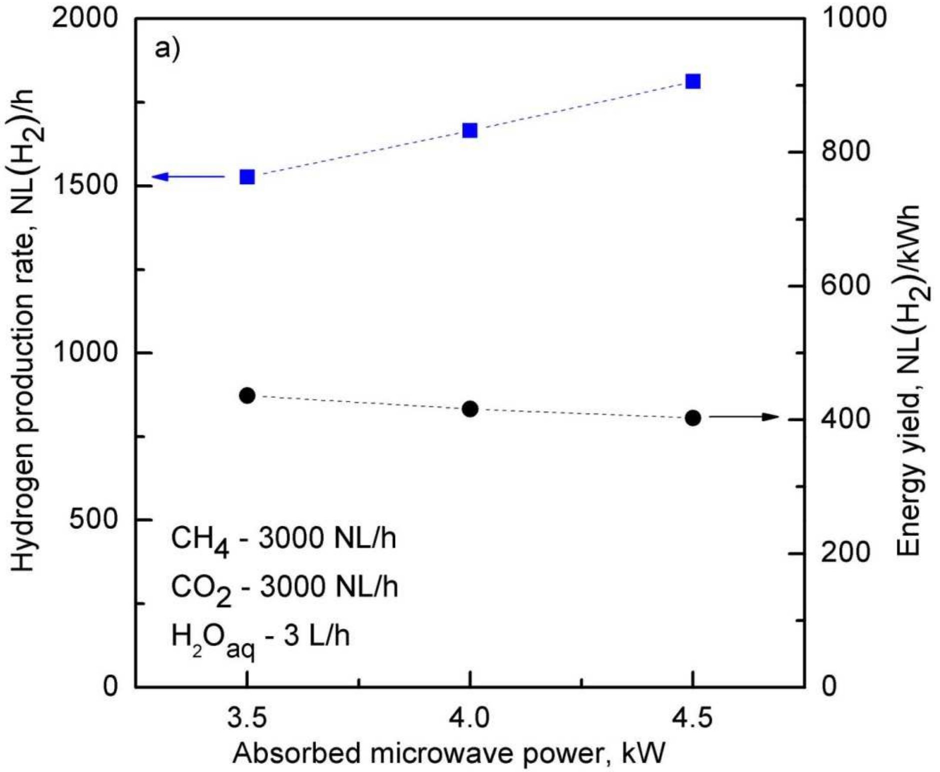
Methane dry reforming

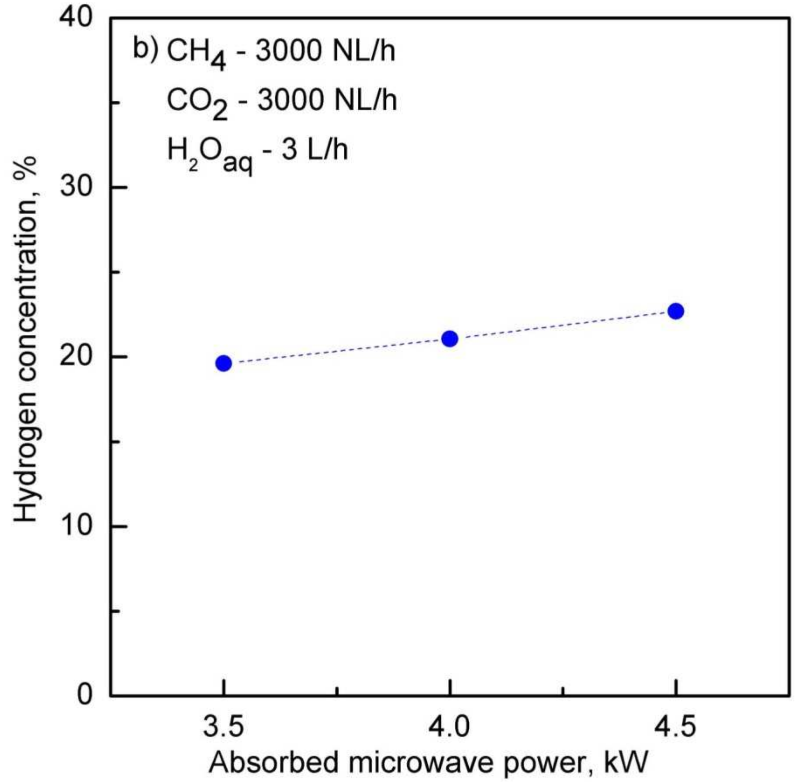




Hydrogen production rate, energy yield and hydrogen concentration as a function of CH_4 and CO_2 flow rates. Absorbed microwave power of 2.4 kW.

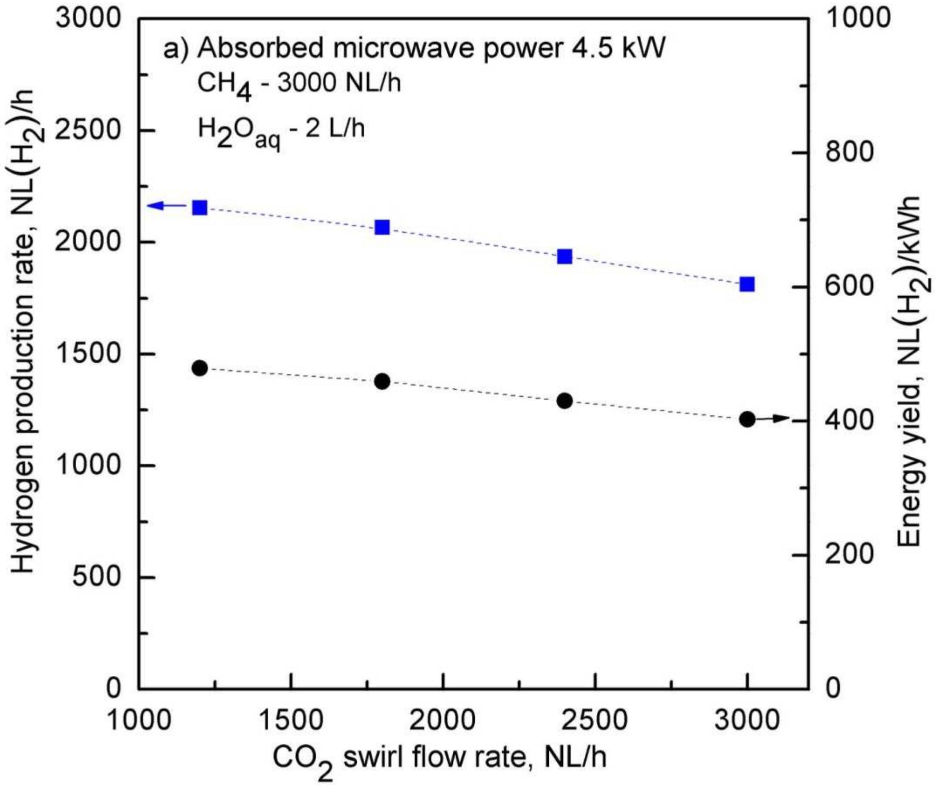
Methane steam reforming

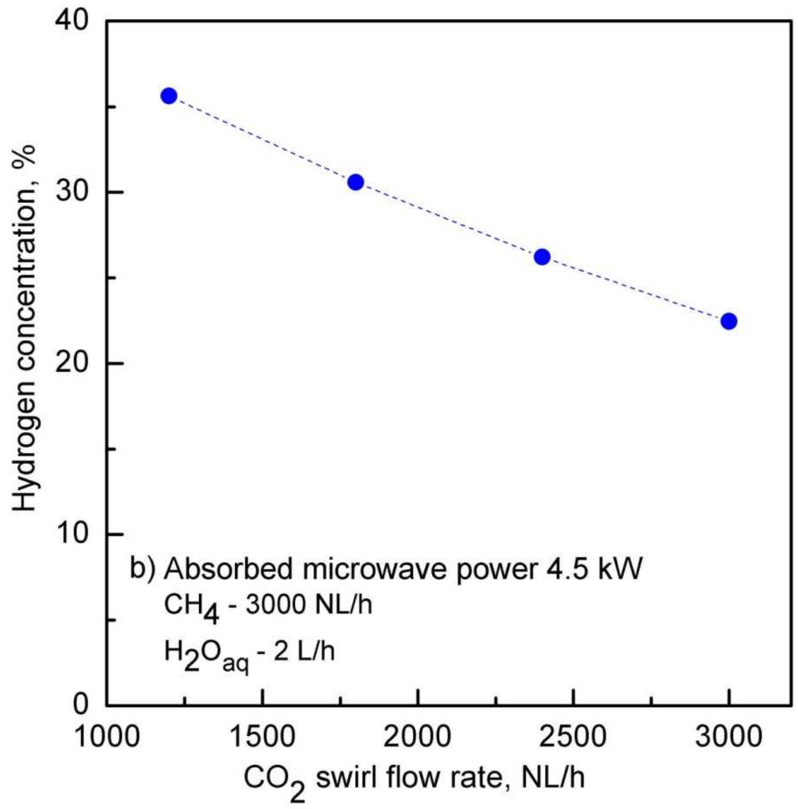




Hydrogen production rate, energy yield and hydrogen concentration as a function of absorbed microwave power. CH_4 swirl flow rate - 3000 NL/h. CO_2 swirl flow rate 3000 NL/h. H_2O_{aq} swirl flow rate – 3 L/h.

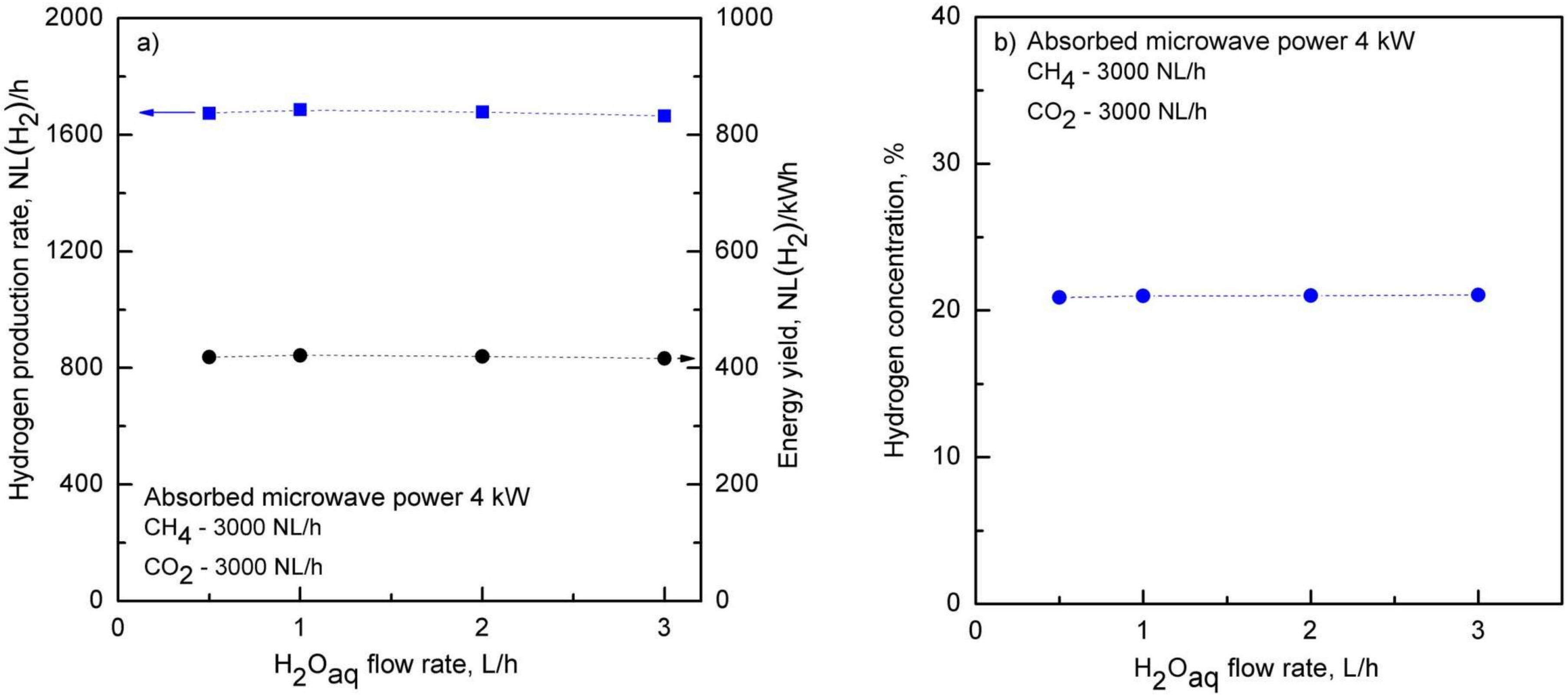
Methane steam reforming





Hydrogen production rate, energy yield and hydrogen concentration as a function of CO_2 flow rate. CH_4 swirl flow rate - 3000 NL/h. H_2O_{aq} swirl flow rate – 2 L/h. Absorbed microwave power of 4.5 kW.

Methane steam reforming



Hydrogen production rate, energy yield and hydrogen concentration as a function of H_2O_{aq} flow rate. CH_4 swirl flow rate - 3000 NL/h. CO_2 swirl flow rate - 3000 NL/h. Absorbed microwave power of 4 kW.

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]	Methane conversion degree %	Products in the outgas %
4.5	CH_4 - 3000 CO_2 - 1200 H_2O_{aq} - 2 L/h	2150 [180]	480 [42.9]	22	H_2 - 35.62 CH_4 – 38.23 CO_2 – 18.6 CO – 2.32 C_2H_2 – 0.84 C – 258 g/h

The best achieved results of hydrogen production via methane 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, air, carbon dioxide, methane) with high gas flow rates at atmospheric pressure and microwave power of a few kW
- The spectroscopic measurements showed the high gas temperature (4000-6000 K) which makes the MPS an attractive tool for hydrogen production via gaseous and liquid hydrocarbon conversion
- The hydrogen production rate and energy yield were up to 2150 NL(H_2)/h [180 g(H_2)/h] and 480 NL(H_2)/kWh [42.9 g(H_2)/kWh] in case of methane steam reforming using the metal-cylinder-based MPS
- The achieved energy yield of hydrogen production is close to DOE target 672 NL(H_2)/kWh [60g(H_2)/kWh] for 2020
- The metal-cylinder-based MPS has a high potential for hydrogen production via gaseous (and liquid) hydrocarbons conversion but adding catalysts also may improve its performance

Thank you for your attention





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Acknowledgment

This research was supported by The National Center for Research and Development under the program NR14-0091-10 /2010 and The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences under the program IMP PAN O3Z1T1

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