Bartosz HRYCAK[1], Robert MIOTK[1], Dariusz CZYLKOWSKI[1], Mariusz JASINSKI[1], Jerzy MIZERACZYK[2], Mirosław DORS[1]

The Szewalski Institute of Fluid Flow Machinery Gdańsk, Centre for Plasma and Laser Engineering (1), Gdynia Maritime University, Faculty of Marine Electrical Engineering, Department of Marine Electronics (2)

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Hydrogen production by dry reforming of kerosene using microwave plasma

Abstract. *This paper presents results of study of dry reforming of kerosene using a microwave plasma. The plasma was generated in waveguide supplied metal-cylinder-based nozzleless microwave plasma source (MPS) operated at 915 MHz. The rotational temperature of heavy species (assumed to be close to gas temperature) was up to 5500 K (for plasma without kerosene). The hydrogen production rate was up to 470 NL[H_2]/h and the energy efficiency was 89.5 NL[H_2] per kWh of absorbed microwave.*

Streszczenie. *Artykuł przedstawia wyniki badań suchego reformingu nafty w plazmie mikrofalowej (915 MHz). Temperatura rotacyjna cząstek ciężkich (przyjmowana jako zbliżona do temperatury gazu) wynosiła do 5500 K (dla plazmy bez dodatku nafty). Uzyskana wydajność produkcji wodoru wynosiła do 470 NL [H_2]/h, natomiast efektywność energetyczna do 89,5 NL [H_2] na kWh zaabsorbowanej energii mikrofal. (**Produkcja wodoru na drodze suchego reformingu nafty w plazmie mikrofalowej**).*

Keywords: microwave plasma, hydrogen production, kerosene dry reforming.
Słowa kluczowe: plazma mikrofalowa, produkcja wodoru, suchy reforming nafty.

Introduction

The greenhouse effect from CO_2 emissions exhorts searching of new energy sources meeting the requirements of being environment-friendly. Hydrogen which has a high heating value per unit mass (120 kJ/g) and does not produce CO_2 in its combustion is a promising future energy carrier. Hydrogen is produced by many methods [1]. The conventional technologies of hydrogen production like coal gasification, hydrocarbon reforming and water electrolysis are well developed. Large scale catalytic hydrogen production has been successfully operating in industry for many decades. Currently it is the most developed and economical technique for hydrogen production. Alternative plasma technologies are very promising for hydrogen production using hydrocarbons conversions. Plasma ensures high chemical reactivity environment allowing to avoid expensive and impurity vulnerable catalysts. The high energy density of plasma results in the compactness of the plasma reformers. Further, the plasma system can be adapted for reforming various liquid hydrocarbons and their derivatives. With these advantages and low operational cost, when considering small scale distributed production systems, plasma technologies appear as an interesting alternative to the conventional methods.

Microwave sustained plasma has found practical applications in various fields. It could be used in sterilization [2] or technological processes like various materials surface treatment [3,4]. MPSs also found applications in the processing of various gases. Destruction of Freon HFC-134a [5] and production of hydrogen via methane conversion [6] in microwave atmospheric pressure plasmas were reported by us elsewhere.

A variety of feedstock could be used for the production of hydrogen: water [7], fossil fuels [8], biomass [9] or waste [10]. Methane [6] as well as ethanol [11, 12] can be a hydrogen source using microwave plasma processing. Kerosene also can be used for production of H_2 (also syngas: H_2 + CO). High temperature of microwave plasma in carbon dioxide [13] encouraged us for performing tests of the hydrogen production via conversion of heavier liquid hydrocarbons. This paper presents experimental results of study of dry reforming of kerosene using atmospheric pressure nozzleless waveguide-supplied metal-cylinder-based 915 MHz microwave plasma source (MPS). Our previous results showed that this type of MPS can be operated with addition of alcohol vapours [11, 12] and has potential for hydrogen production due to high heavy spices temperatures. Further, it can be operated with a good power efficiency and stability in different gases like argon, nitrogen and carbon dioxide using microwave power of a few kW with gas flow rates of thousands NL/h.

Experiment

The experimental setup (figure 1) consisted of a 915 MHz magnetron generator, microwave power supplying and measuring system, MPS, movable plunger and three stub tuner for impedance matching, gas supplying and flow control system, spectrometer for spectral emission measurements, and gas chromatograph. An absorbed power P_A was obtained from the P_I - P_R, where P_I and P_R are the incident and reflected microwave powers, respectively. The plasma was generated by waveguide-supplied nozzleless cylindrical type MPS based on a standard WR 975 rectangular waveguide with a section of reduced-height, preceded by tapered section. 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 shield with a slit for visualization.

The carbon dioxide (CO_2) was used as a plasma working gas. It was introduced to the plasma by four gas ducts which formed a swirl flow inside the quartz tube. The kerosene was introduced into the plasma axially in the form of vapour using an induction heating vaporizer. All experimental tests were performed with the working gas flow rate of 2700 NL/h and absorbed microwave power P_A from 4 up to 6 kW. The amount of kerosene vapour ranged from 0.2 to 1.2 kg/h and its temperature before injection into the microwave plasma was set at 720 K. The decomposition of kerosene was performed employing plasma dry reforming process.

For optical emission spectroscopy a spectrometer CVI DK-480 (1200 gr/mm grating) was used. In this experiment the light emitted by the plasma was focused with a quartz lens onto the entrance slit of the spectrometer. Double diaphragm of a 1 mm diameter was placed near the plasma. The diameter of the measured area was about 8 mm. The spectra at the range 300 – 600 nm were recorded and then corrected according to the wavelength sensitivity of CCD camera. The wavelength sensitivity of

CCD camera was determinated using a tungsten halogen calibration lamp. Using a Hg-Ne low-pressure calibration lamp we measured that the Gaussian instrumental line profile FWHM was about 0.12 nm. Gas temperature in plasma was estimated using Specair [14] program with relation to recorded spectra following a procedure described elsewhere [13]. In this experiment, for the temperatures determination we used the C_2 Swan system (A-X, 506 - 518 nm band).

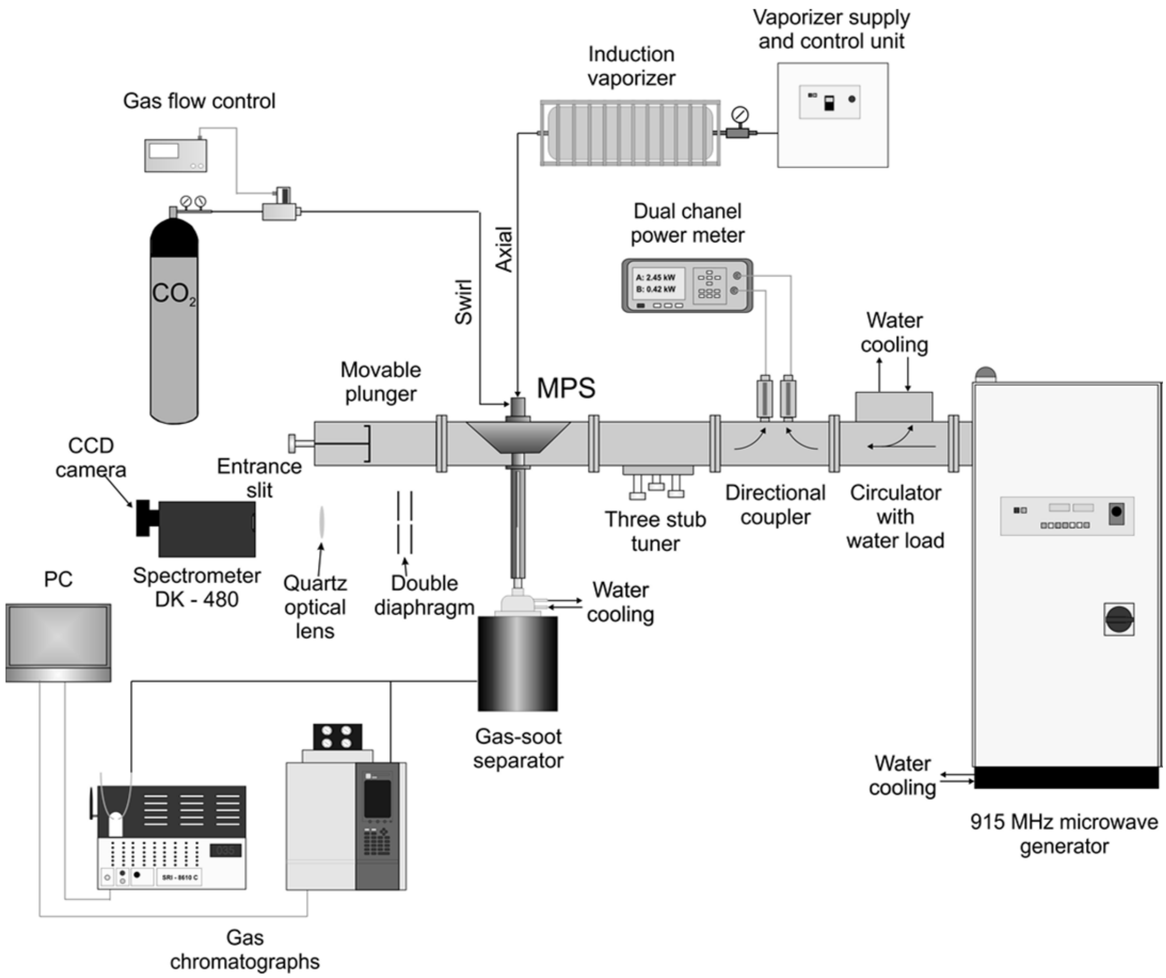

Fig.1. Experimental setup

Diagnostic of the working gas composition before and after the microwave plasma generator was carried out using gas chromatographs (Shimadzu GC-2014 and SRI 8610C). Concentrations of 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. Using the gas composition data hydrogen production rate and energy yield of hydrogen production were calculated. The hydrogen production rate (expressed in NL(H_2)/h or in g(H_2)/h) gives information about amount of hydrogen produced per unit of time. The energy yield (expressed in NL(H_2)/kWh or in g(H_2)/kWh) shows the volume or mass of hydrogen obtained from a unit of energy used for it. It have to be noticed that the energy used for calculation is the microwave energy.

Results

In measured spectra of CO_2 plasma without as well as with (see figure 2a) addition of kerosene vapour dominant spectrum was C_2 Swan system ($A^3\Pi \rightarrow X^3\Pi$). Using Specair [14] program determination of vibrational and rotational temperatures of the C_2 molecule were performed (figure 2b). The gas temperature can often be inferred from the rotational temperature of the heavy species of the gas [13, 15]. As seen in figure 3 rotational temperature of the C_2 molecule at 5 kW of absorbed microwave power measured 10 mm below waveguide without addition of kerosene vapour was 5500 K. It is higher of 500 K than with a kerosene vapour addition in comparable conditions. Addition of kerosene caused the slight decrease of the rotational temperature but the vibrational temperature increased up to 7500 K. Without kerosene both temperatures was in the equilibrium.

Figure 4a presents the hydrogen production rate and the energy efficiency of hydrogen production as a function of the absorbed microwave power. As it can be seen, for lower kerosene flow rate (0.4 kg/h) the hydrogen production rate do not vary significantly with the absorbed microwave power. Thus, the energy efficiency of hydrogen production decreased with the absorbed microwave power. In case of higher kerosene flow rate (0.8 kg/h) increase of the microwave absorbed power caused increase of the hydrogen production rate while the energy efficiency of hydrogen production was remaining at the same level.

As it could be observed in figure 4b increasing of kerosene vapour flow caused increase of hydrogen production parameters. However the increase is not linear. At higher kerosene flow rates saturation could be observed. The increase of kerosene vapour flow over 0.8 kg/h caused also problem with the intense soot production. The soot was forming on the quartz tube inner surface also in the plasma zone. This caused the problem with microwaves penetration and consequently damage the quartz tube. To avoid this problem the steam reforming or the combined steam [16] reforming should be tested in future.

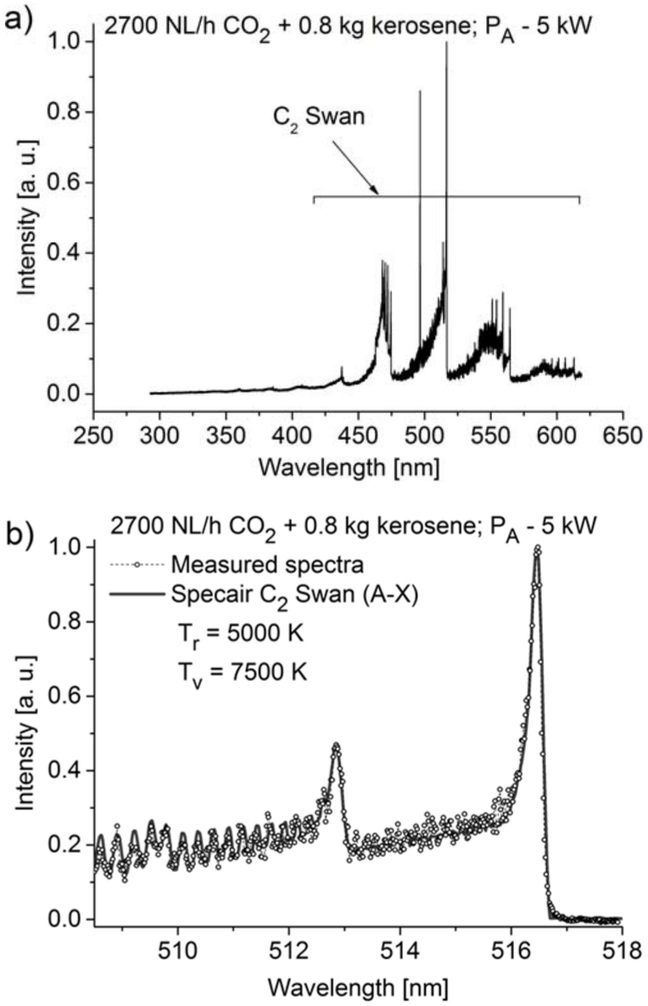

Fig.2. The measured emission spectrum of CO_2 plasma with kerosene vapour addition (a) and the comparison of the measured and simulated emission spectra of C_2 Swan system (b) at CO_2 flow rate - 2700 NL/h, kerosene vapour flow rate - 0.8 kg/h and absorbed microwave power P_A - 5kW, measured 15 mm below waveguide.

The soot production indicated that the kerosene reforming process in the microwave CO_2 plasma is more complex than dry reforming described with the reaction (1):

$$C_nH_m + nCO_2 \rightarrow 2nCO + \frac{m}{2}H_2 \quad (1)$$

The best achieved results of hydrogen production rate and energy efficiency of hydrogen production were 470 NL[H_2]/h and 89.5 NL[H_2] per kWh of microwave energy used, respectively.

As seen in figure 5 that from 1l of kerosene in proposed plasma method it is possible to obtain up to 470 NL[H_2].

It have to be noticed than increasing kerosene flow rate from 0.8 kg/h up to 1.2 kg/h caused the significant decrease of production of hydrogen from 1l of kerosene. This fact confirm the saturation effect mentioned before.

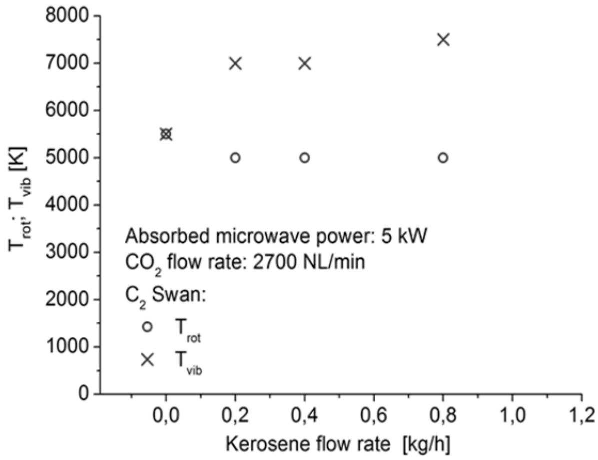

Fig.3. The rotational and vibrational temperatures of the C_2 molecule as a function of kerosene flow rate at CO_2 flow rate - 2700 NL/h and absorbed microwave power P_A - 5kW, measured 15 mm below waveguide.

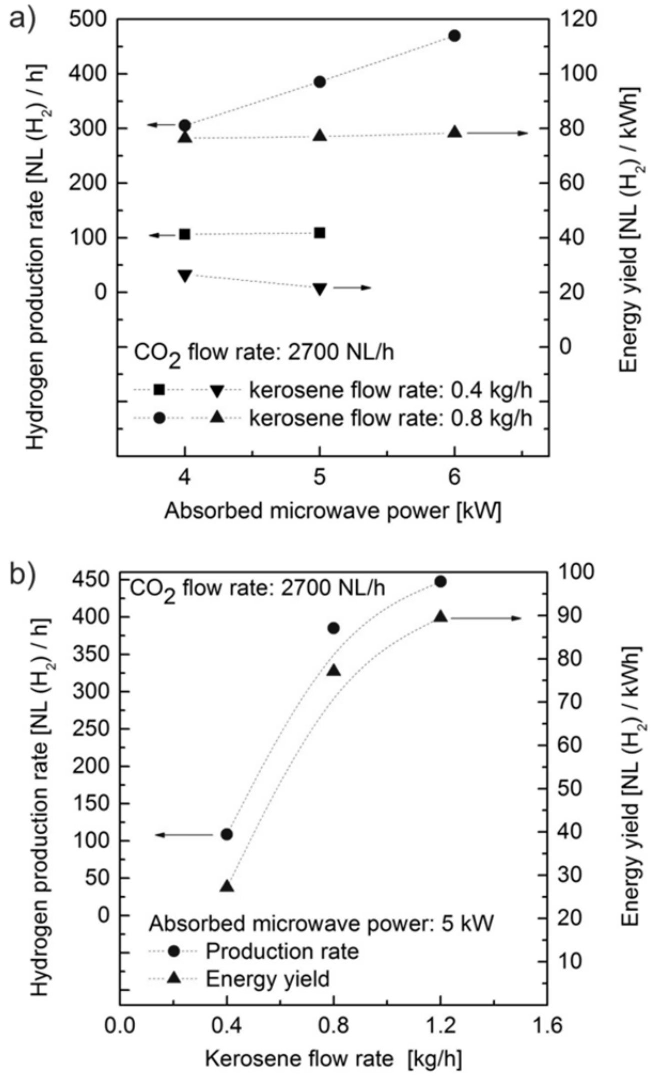

Fig.4. Hydrogen production rate and energy yield of hydrogen production as a function of absorbed microwave power at CO_2 flow rate – 2700 NL/h (a) and as a function of kerosene flow rate at CO_2 flow rate – 2700 NL/h and absorbed microwave power P_A – 5kW (b).

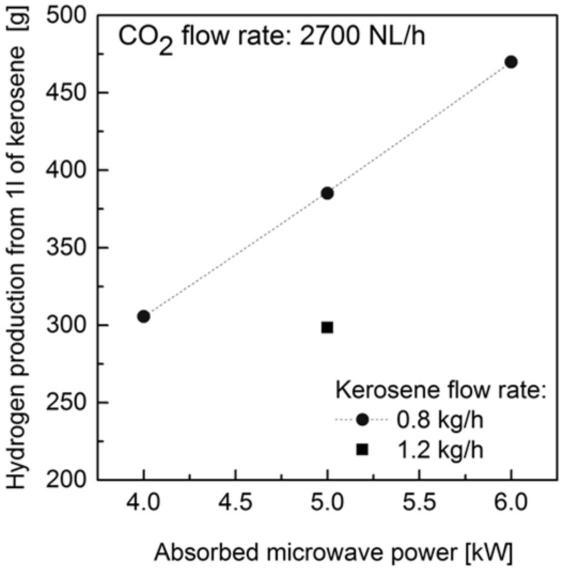

Fig. 5. Hydrogen production from 1 l of kerosene as a function of absorbed microwave power at CO_2 flow rate – 2700 NL/h obtained for two different kerosene flow rate.

Conclusion

Study of dry reforming of kerosene using a microwave plasma was presented in this work. The rotational temperature of heavy species (assumed to be close to gas temperature) was up to 5500 K (for plasma without kerosene). Addition of kerosene caused the slight decrease of the rotational temperature (about 500 K). The hydrogen production rate was up to 470 NL[H_2]/h (39.1 g[H_2]/h) and the energy efficiency was 89.5 NL[H_2] (7.44 g[H_2]) per kWh of absorbed microwave energy.

The investigated nozzleless, waveguide-supplied, cylindrical type MPS works very stable with various working gases. The high gas temperature makes it attractive tool for different gas processing at high flow rates [5, 6, 16]. The presented microwave plasma method can be also used for effective hydrogen production from methane [6, 16], alcohols [11, 12] and different other liquid fuels like gasoline, heavy oils and biofuels.

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***Authors:** mgr inż. Bartosz Hrycak, mgr. Robert Miotk, mgr inż. Dariusz Czylkowski, dr hab. inż. Mariusz Jasiński, dr hab. inż. Mirosław Dors, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, ul. Fiszera 14, 80-231 Gdańsk, E-mail: bartosz.hrycak@imp.gda.pl; rmiotk@imp.gda.pl; dczylkowski@imp.gda.pl; mj@imp.gda.pl; mdors@imp.gda.pl; prof. dr hab. inż. Jerzy Mizeraczyk, Gdynia Maritime University, Faculty of Marine Electrical Engineering, Morska 81-87, 81-225 Gdynia, E-mail: jmiz@imp.gda.pl*

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