Liquid fuel reforming using microwave plasma at atmospheric pressure

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Hydrogen meeting the requirements of being environment-friendly and renewable is one of the most promising alternative energy carriers. In contrast to conventional technologies of hydrogen production like water electrolysis or coal gasification, we propose a method based on the atmospheric pressure microwave plasma. In this paper we present results of the experimental investigations of the hydrogen production from liquid fuels using atmospheric pressure nozzleless waveguide-supplied metal-cylinder-based microwave plasma source (MPS).

1. Introduction

Decrease of natural reserves of fossil fuels as well as the greenhouse effect from CO_2 emissions exhorts searching of new energy sources meeting the requirements of being environment-friendly and renewable simultaneously. 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.

A variety of feedstock could be used for the production of hydrogen: fossil fuels [1], water [2], alcohols [3], biomass [4] or coal [5]. Hydrogen can be also produced from renewable sources: waste [6] or bio-ethanol [7], so it could be considered to be renewable fuel.

Hydrogen is produced by many methods [8]. The conventional technologies like coal gasification, hydrocarbon reforming and water electrolysis are well developed. The catalytic hydrogen production has been successfully operating in large scale industry for many decades. Nowadays it is the most developed and economical technique for hydrogen production. However, installations producing hydrogen for small scale applications requires also different features like: compactness, fast response and high durability for frequent startup-shutdown cycles [9]. 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.

The low pressure plasma could achieve high hydrocarbon conversion and good hydrogen selectivity but the low hydrogen production rate and extra energy requirement for vacuum device restrict its practical use. Various kind of atmospheric pressure plasmas were used experimentally in hydrogen production investigations: gliding arc plasma [10], dielectric barrier discharge [11], corona discharge [12], microwave plasma [13].

There are several hydrocarbon based methods of hydrogen production like: steam reforming, dry reforming, partial oxidation and thermal decomposition. All of these processes can be performed in plasma reactors [14].

In this paper we present results of the experimental investigations of the hydrogen production from liquid fuels (ethanol and isopropanol) using atmospheric pressure nozzleless metal-cylinder-based microwave plasma source (MPS). Our previous results showed that this type of MPS can be operated with addition of liquid vapours [15, 16] 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.

2. Experiment

Two microwave systems of 915 MHz and 2.45 GHz were used in this investigation. Both systems use the same frame setup and both were based on standard waveguides WR 975 and WR 430, respectively. The diagram of the experimental setup is shown in Fig. 1. It consisted of a magnetron generator, microwave power supplying and measuring system, microwave plasma source (MPS),

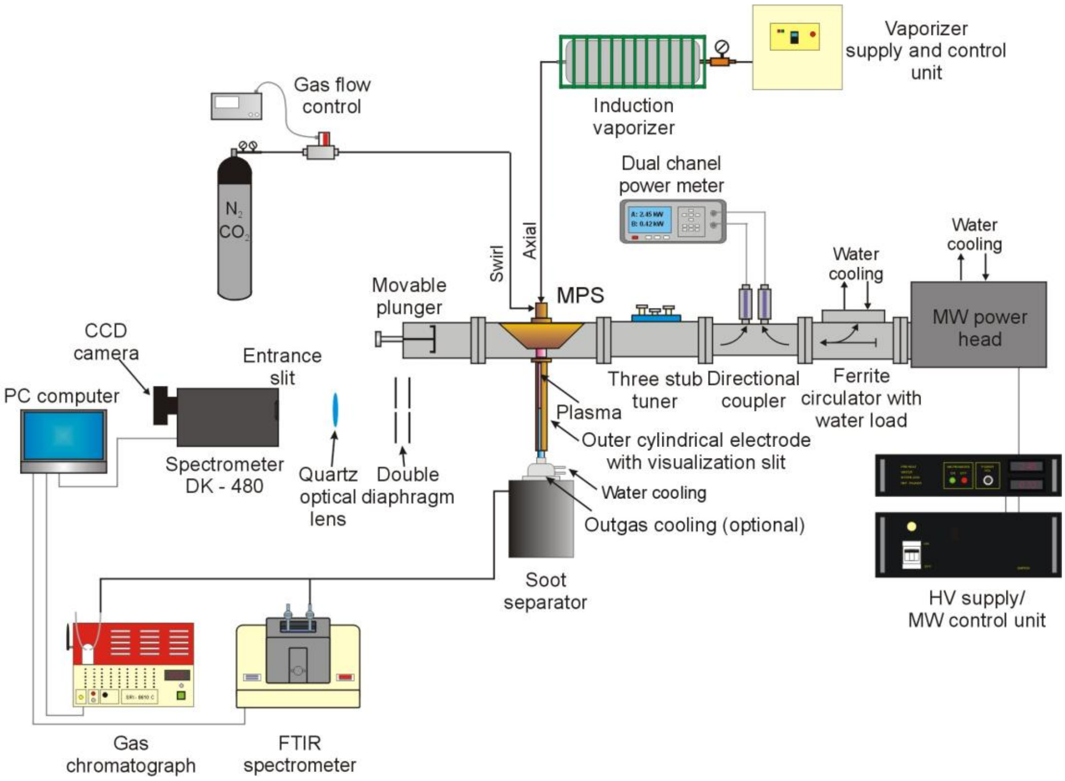

Fig. 1. Experimental setup

impedance matching elements, gas supplying and flow control system, gas analysis system and optical emission spectroscopy (OES) system.

The microwave generator was composed of a high voltage power supply, a control unit and a magnetron head. The magnetron head was equipped with a water cooled circulator which protects it against damages caused by the reflected microwave power. The microwave power measuring system includes a directional coupler, two power meter heads and a digital dual channel power meter. This system enabled direct measurements of an incident P_I and reflected P_R microwave powers. An absorbed power P_A was obtained from the subtraction of P_I - P_R.

The plasma was generated by waveguide-supplied nozzleless cylindrical type MPS based on a standard rectangular waveguide (WR 430 or WR 975) with a section of reduced-height, preceded and followed by tapered sections. 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 electrode with a slit for visualization. Working gas was introduced to the plasma by four gas ducts which formed a swirl flow inside the quartz tube. Liquid fuels were introduced into the plasma in form of vapours using an induction heating vaporizer. The vapours were introduced to the plasma axially. Optionally, at the outlet of the MPS the output gas was rapidly cooled. After cooling the gas was directed to a gas-soot separator.

The plasma generator was preceded by a three stub tuner and followed by a movable plunger. They play a role of impedance matching circuits between the plasma generator and the waveguide. Matching the impedance in the waveguide system improves efficiency of microwave power transfer from the microwave generator to the plasma generator.

For optical emission spectroscopy a spectrometer CVI DK-480 (1200 gr/mm and 3600 gr/mm grating) equipped with CCD (sensitivity calibrated) camera 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 in the range 300–600 nm were recorded. Gas temperature in plasma was estimated using Specair [17] and Lifbase [18] programs with relation to recorded spectra following a procedure described elsewhere [19**].**

Diagnostics 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 determined.

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.

All experimental tests were performed with the working gas flow rate Q ranged from 1200 to 3900 NL/h and absorbed microwave power P_A up to 5 kW. The working gases were nitrogen (N_2) and carbon dioxide (CO_2) . The amount of liquid vapours ranged from 0.4 to 2.4 kg/h.

3. Selected results

Two different plasma systems (915 MHz and 2.45 GHz) as well as various hydrocarbon production methods (thermal decomposition, steam reforming and dry reforming) and different liquid fuels (ethanol and isopropanol) were investigated in our studies. Best results were obtained for thermal decomposition of ethanol. They are presented below.

3.1. Spectroscopic results

In the 2.45 GHz system measured spectra of N_2 plasma without any addition of liquid fuels vapour contained bands of N_2+ first negative system ($B^2\Sigma \rightarrow X^2\Sigma$), N_2 first positive ($B^3\Pi \rightarrow A^3\Sigma$) and weak N_2 second positive system ($C^3\Pi \rightarrow B^3\Pi$). Intensity of the emitted N_2+ first negative system was dominant. Obtained rotational temperatures of N_2+ ranged from 4500 to 6000 K depending on the location in plasma and N_2 flow rate [19]. Similar temperatures were obtained for OH radicals (when a small amount of water vapour was added to the swirl gas flow in order to achieve detectable intensity of OH ($A^2\Sigma \rightarrow X^2\Pi$) spectra). In the case of the N_2 plasma with 0.8 kg of ethanol vapour the dominant spectrum was C_2 Swan system ($A^3\Pi \rightarrow X^3\Pi$). The spectrum contained also CN Violet system ($B^2\Sigma \rightarrow X^2\Sigma$) (see Fig. 2). Obtained rotational temperatures of CN ranged from 4000 to 6000 K. Lower rotational temperature was measured in the case of C_2 molecules (from 3500 to 4600 K). Similar results were obtained also in the 915 MHz plasma system [20].

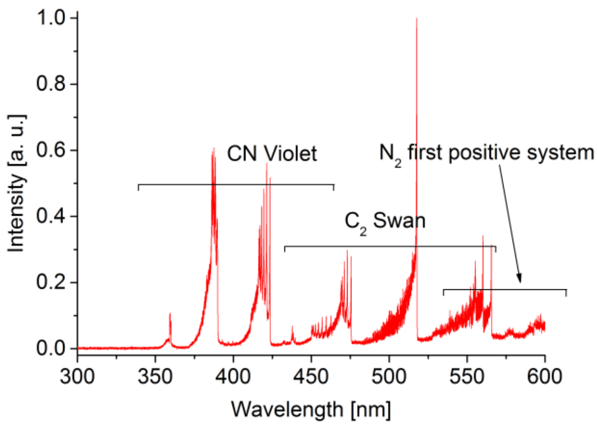

Fig. 2. Measured emission spectra of N_2 plasma with 0.8 kg/h of ethanol vapour addition. 2.45 GHz plasma system. Absorbed microwave power P_A - 4 kW. Working gas flow rate - 2700 NL/h.

3.2. Hydrogen production

Experiment showed that at comparable conditions the 915 MHz plasma system gives about 6 % better results than 2.45 GHz plasma system. It proved also that rapid cooling of the outgas improves results by about 17 %. Figure 3 presents results of thermal decomposition of ethanol in 915 MHz plasma system with rapidly cooled outgas. In this case the hydrogen production rate and energy yield of hydrogen production were 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], respectively. It should be noticed that under certain conditions, i.e.

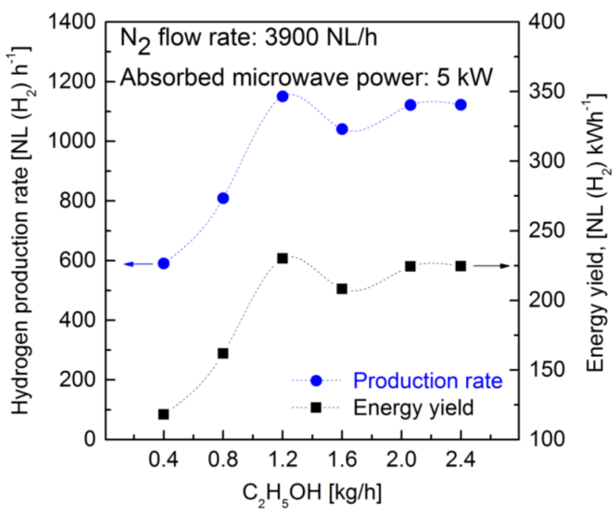

Fig. 3. Hydrogen production rate and energy yield for thermal decomposition of ethanol in N_2 plasma as a function of ethanol (C_2H_5OH) flow rate at N_2 flow rate 3900 NL/h.

when the absorbed microwave power, operating gas composition and flow rate the ethanol were properly set, the ethanol conversion degree could be almost 100%.

4. Summary

The production of hydrogen by conversion of liquid fuels using microwave plasma was studied experimentally. The waveguide-supplied nozzleless metal cylinder based MPS operated at atmospheric pressure was used.

The results showed that the investigated nozzleless waveguide-supplied cylindrical type MPSs for hydrogen production can be operated with a good power efficiency and stability. It can be operated in different gases like argon, nitrogen and carbon dioxide with microwave power of a few kW with gas flow rates of thousands NL/h [15, 16]. The temperature of heavy species (assumed to be close to gas temperature) was up to 6000 K (for N_2 plasma without ethanol) [19]. This encouraged us for performing tests of the hydrogen production via liquid hydrocarbons conversion. Addition of ethanol vapour into N_2 plasma caused the slight decrease of rotational temperatures of selected molecules. However these temperatures are still at the level of 4000 K.

The results of our investigations showed that hydrogen may be effectively produced by thermal decomposition of ethanol in a microwave nitrogen plasma. Our results are competitive compared to DBD discharge and also very competitive with other microwaves discharges [16, 21, 22]. It should be noticed that in contrast to arc plasmas which demonstrates higher hydrogen mass yield and higher energy yield the conversion rate in all microwave plasmas are almost 100% .

The presented MPS could work also with liquid fuels other than alcohols. Studies with kerosene are in the progress and results will be presented soon.

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