Hydrogen Production via Biomethane Reforming in DBD Reactor

M. Dors[1], T. Izdebski[1], A. Berendt[1], and J. Mizeraczyk[1, 2]
[1]Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid Flow Machinery, Poland
[2]Department of Marine Electronics, Gdynia Maritime University, Poland

Abstract—Production of hydrogen from CH_4:CO_2 (70%:30%) mixture simulating dry biogas in a DBD reactor supplied with AC of 1.0-2.0 kHz or nanosecond negative pulses is presented. We have found that hydrogen production and methane conversion degree increase linearly with discharge power in the range of up to 50 W. Nanosecond voltage pulses are much more efficient in hydrogen production than sine AC voltage.

Keywords—Hydrogen, biomethane, dielectric barrier discharge, plasma

I. Introduction

So far most plasma methods of hydrogen production use such substrates as natural gas, gasoline, heavy oils, and kerosene. Many of them uses combination of plasma with catalysts either as single-stage or two-stage system. The single-stage type is constructed by packing catalyst pellets within the plasma zone or coating catalyst on the surface of electrode(s). As for the two-stage type, the plasma zone is located either upstream or downstream the catalyst bed, which is termed as plasma preprocessing and plasma postprocessing, respectively.

Unfortunately, plasma-catalytic systems are not useful when biogas containing sulfides (mainly H_2S) are going to be processed due to catalyst poisoning. There are several publications claiming to describe production of hydrogen from biogas using plasma-catalyst systems [1-4]. However, the authors have used a mixture of methane with carbon dioxide simulating a biogas but without any additives which are present in real biogas such as water vapor, H_2S and NH_3. Such a simple simulation of biogas is not appropriate when the outlet gas is going to be used with fuel cells, which are very sensitive to H_2S traces. There are only 2 papers on using real biogas and they were published by one research group in 2008 and 2010. Sekine *et al*. [5, 6] studied application of pulsed corona discharge (PCD) reactor and dielectric barrier discharge (DBD) reactor without any catalyst and they found that PCD could convert biomethane into syngas and H_2S into solid sulfur simultaneously. This is due to the high electron energy of PCD and the electron has enough energy to dissociate C-C bond and C–S bond. On the other hand, DBD could convert H_2S into solid sulfur too, but methane and CO_2 in the biogas were not reacted at lower input power. The investigation by Sekine *et al*. showed that proper choice of electrical discharge can brings effective reaction for dry reforming of biomethane and desulfurization, and this is due to the correlation between the bond dissociation energy of each molecule and electron energy level of each discharge. Our proposal is to verify this conclusion by parametrical studies of biomethane reforming using DBD and real biogas or a mixture simulating biogas with its trace components (influence of voltage pulses shape, duration and frequency, influence of reactor geometry).

In this work a first stage of our studies concerning hydrogen production from simple biogas-like mixture of methane and carbon dioxide is presented.

Corresponding author: Miroslaw Dors
e-mail address: mdors@imp.gda.pl

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II. Experimental set-up

A. DBD Reactor

In this paper results obtained in one specific DBD reactor are presented. The scheme of the reactor is shown in Fig. 1. It is made of a quartz glass tube of inner diameter 15 mm in which a high voltage RVC (Reticulated Vitreous Carbon) electrode is placed. The glass tube is covered with aluminum foil remaining a 4 mm wide slit along the reactor. RVC electrode is formed in a tube of outer diameter 8 mm, inner diameter 3 mm and length 150 mm. Through that RVC tube a mixture of methane and carbon dioxide (70%:30%, respectively) simulating dry biogas was introduced into the reactor. Due to relatively low porosity of the RVC tube, which is 80 ppi (pores per inch), it does not obstruct the gas flow which was kept at 200 cm^3/min at atmospheric pressure.

B. High Voltage Power Supply

Two different type of supply for DBD reactor have been used. The first one is composed of function generator Tektronix AFG3101 and amplifier TREK

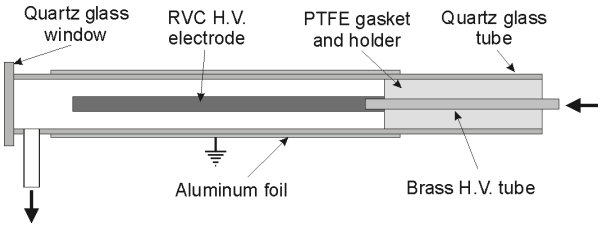

Fig. 1. DBD reactor with RVC electrode.

40/15. It allows to modify voltage pulses shape and frequency up to 2 kHz. In this work results for AC sine voltage of up to 35 kV_{p-p} and repetition rate of 1 kHz, 1.5 kHz and 2 kHz are presented. Discharge power was determined from Lissajous curves (Fig. 2).

The second power supply for DBD reactor was a nanosecond pulse generator NPG-15/2000 by Megaimpulse Ltd. Typical negative voltage pulse shape obtained from that power supply is shown in Fig. 3a. In this work we used voltage pulses of 29 kV and repetition rate in the range 50 Hz-2.5 kHz. Voltage pulses were measured using high voltage probe Tektronix P6015A whereas current pulses (Fig. 3b) were measured using Pearson 2878 coil. Discharge power was calculated by multiplying repetition rate by single discharge pulse energy (E_p), which was obtained after experiment by integration of the pulse voltage (U) times the current (I) over the pulse duration (t):

$$E_p = \int_{pulse} U(t)I(t)\mathrm{d}(t) \quad (1)$$

C. Diagnostics

Gas composition before and after the processing in the DBD reactor was analyzed using FTIR spectrophotometer and gas chromatograph. For measurements of CO as well as for detection of other heterogenic molecules the FTIR Nicolet 380 spectrophotometer with gas cell of 10 cm optical path length and $CaCl_2$ windows was used. Diagnostics of H_2 and CH_4 was carried out using SRI 8610C gas chromatograph with TCD and molecular sieve column and argon as a carrier gas.

Since the DBD formed in our reactor when applying sine high voltage emits relatively strong light, as shown in Fig. 4, it was possible to apply optical emission spectroscopy. For that purpose a spectrometer Maya 2000Pro by Ocean Optics equipped with UV transmitting optical fiber was used.

Temperature of the processed gas at inlet and outlet of the DBD reactor was measured with thermocouples. Initial gas temperature was kept at 19°C all the time during the experiment.

III. Results

A. AC Sine Supply

Processing the mixture simulating dry biogas in the DBD reactor with RVC high voltage electrode results in formation of hydrogen, carbon monoxide and acetylene as the only gaseous products. Production of hydrogen in the DBD reactor supplied with sine high voltage shows typical dependence on discharge power and frequency. As it is seen in Fig. 5, hydrogen concentration in the outlet gas grows linearly when increasing discharge power. The highest concentration of hydrogen of 4.4% was recorded at 1.5 kHz sine voltage of 30 kV_{p-p} which corresponds to discharge power of 46.5 W which is the

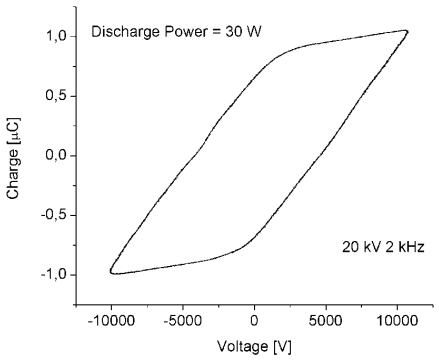

Fig. 2. Typical Lissajous curve obtained during DBD. Presented curve concerns sine voltage of 20 kV and 2 kHz. Determined discharge power was 30 W.

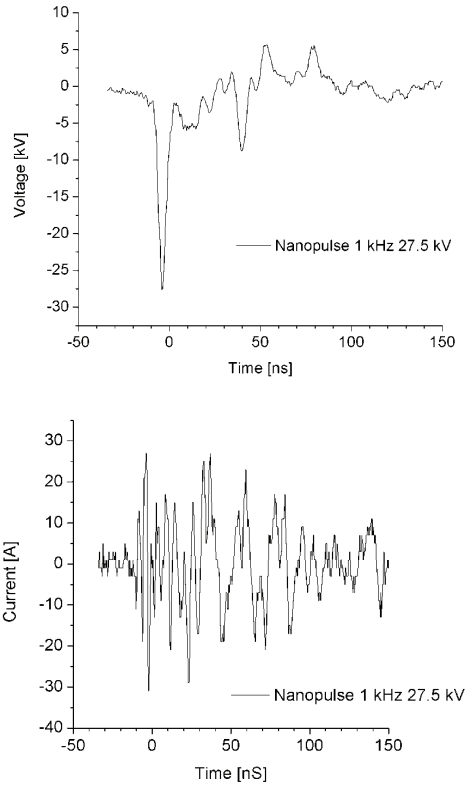

Fig. 3. Typical voltage and current pulses generated by nanosecond pulse generator NPG-15/2000 in our DBD reactor. Pulse energy $E_p = 5$ mJ.

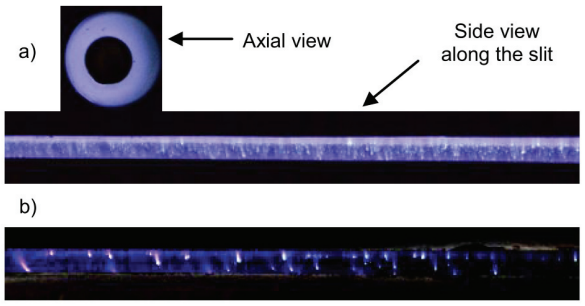

Fig. 4. Images of DBD in the reactor with RVC high voltage electrode supplied by a) sine AC voltage of 35 kV_{p-p} and 2 kHz, b) nanosecond pulses of -29 kV and 50 Hz. Images from DBD generated with nanosecond pulses at higher repetition rates were not recorded due to strong interference generated by HV power supply.

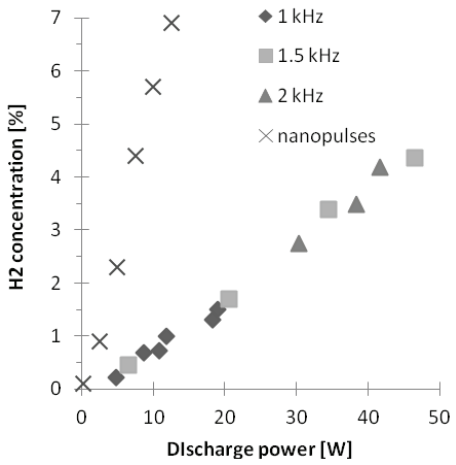

Fig. 5. Hydrogen concentration produced in CH_4:CO_2 (70%:30%) gas mixture as a function of discharge power for different discharge frequency. Sine AC voltage.

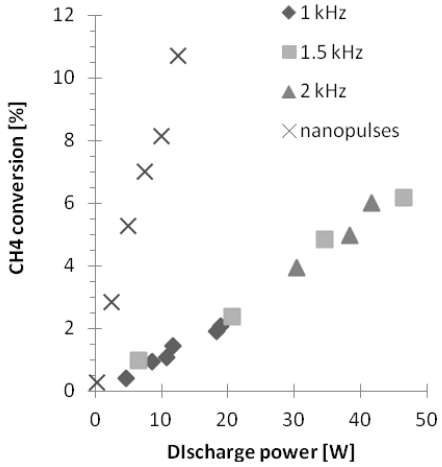

Fig. 6. Methane conversion degree in CH_4:CO_2 (70%:30%) gas mixture for different discharge power and frequency. Sine AC voltage.

maximum discharge power used in the experiment. Resulted efficiency of hydrogen production is 0.94 g/kWh.

As methane is the only source of hydrogen, the production of hydrogen corresponds to consumption of methane. Relation of methane conversion degree on the discharge power and frequency is shown in Fig. 6. The conversion degree is low but it must be noted that the experiment was conducted using gas of room temperature and without water vapor normally present in the real biogas. Similar methane conversion degree was observed in CH_4:CO_2 mixture processed in DBD reactor by Sekine *et al*. [6].

When methane conversion proceeds in the thermodynamic equilibrium then concentrations of products are governed by the summary reaction:

$$CH_4 + CO_2 = 2\ CO + 2\ H_2, \qquad (2)$$

and can be calculated for a wide range of temperature (Fig. 7). It is clear that ratio CO:H_2 should be as 1:1. In

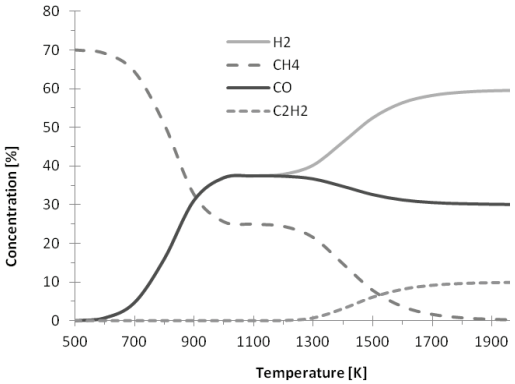

Fig. 7. Concentrations of CH_4 and its conversion products calculated for thermodynamic equilibrium.

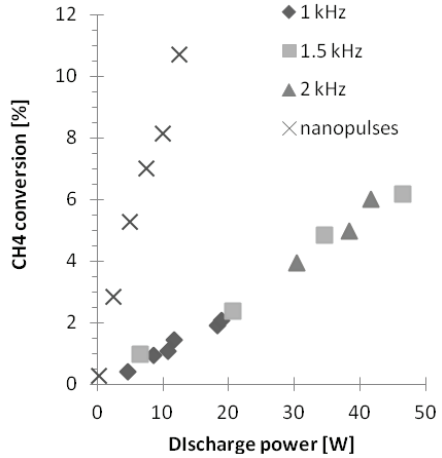

Fig. 8. Carbon monoxide concentration produced in CH_4:CO_2 (70%:30%) gas mixture for different discharge power and frequency. Sine AC voltage.

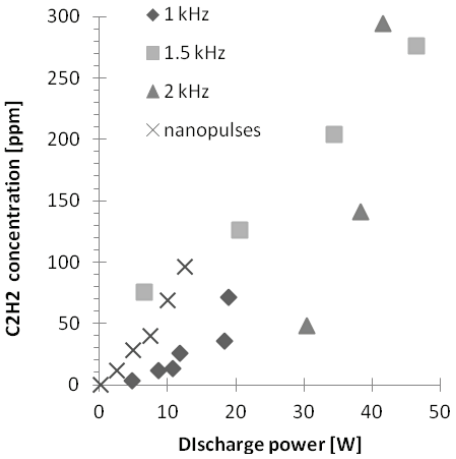

Fig. 9. Acetylene concentration produced in CH_4:CO_2 (70%:30%) gas mixture for different discharge power and frequency. Sine AC voltage.

such a case, basing on experimentally obtained concentration of H_2, one can conclude that temperature of gas in the DBD plasma, i.e. in filaments, is close to 700K.

However, experimentally measured concentration of CO is much lower than hydrogen concentration. Concentration of carbon monoxide formed from CO_2 in

the DBD is shown in Fig. 8. From non-linear increase of CO concentration as well as from the ration of CO:H_2, which is much higher than 1:1, it is seen that CO is not produced in a dry reforming reaction (1) but in a dissociation reaction typical for non-thermal plasma. The same ratio CO:H_2 was observed by Nagazoe *et al*. [7] in their experiment with CH_4:CO_2 processed by microwave plasma.

Concentrations of acetylene produced from methane in the DBD reactor with RVC high voltage electrode do not exceed 300 ppm (Fig. 9) and again increase linearly with discharge power.

B. Supply by Nanosecond High Voltage Pulses

When the DBD is generated using nanosecond high voltage pulses production of hydrogen and corresponding methane conversion increases linearly with pulse repetition rate (Figs. 5 and 6). Obtained concentration of H_2 and conversion of CH_4 are slightly higher comparing to those for the DBD generated by sine AC voltage. Maximum hydrogen concentration is 6.9% at 2.5 kHz repetition rate. However, resulted efficiency of hydrogen production is 5.47 g/kWh which is 5.8 times higher than that obtained when applying sine AC voltage.

Concentration of CO formed from CO_2 in the DBD supplied with nanosecond pulses is shown in Fig. 8. Both non-linear CO concentration increase and ratio CO:H_2 is similar to that observed when applying AC voltage.

Concentrations of acetylene do not exceed 100 ppm (Fig. 9) and again increase linearly with discharge power. In contrast to AC voltage supplied DBD nanosecond pulses results in 3 times lower acetylene concentration.

C. Optical Emission Spectroscopy

Typical emission spectrum recorded during CH_4:CO_2 processing in the DBD reactor with RVC high voltage electrode is shown in Fig. 10. Dominant light originates from N_2 second positive system. Similar spectrum of DBD in biogas was recorded by Sekine *et al*. [6].

However, it is also seen that continuous spectrum and other bands overlaps the N_2 band. It is well seen when comparing a spectral region 250-450 nm of measured spectrum with calculated one (Fig. 11). Bands that particularly do not fit N_2 second positive system are: 390 nm and 430 nm.

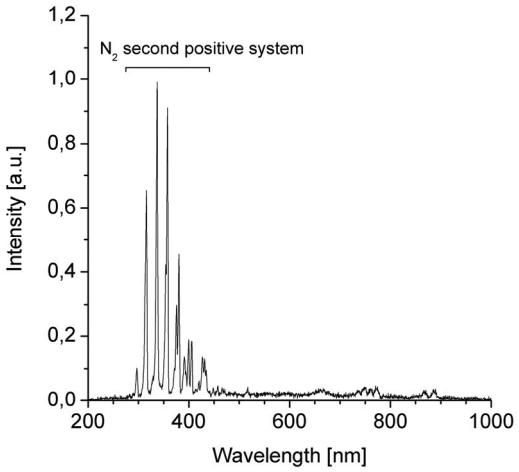

Fig. 10. Hydrogen concentration produced in CH_4:CO_2 (70%:30%) gas mixture as a function of pulse repetition rate. Nanosecond voltage pulses.

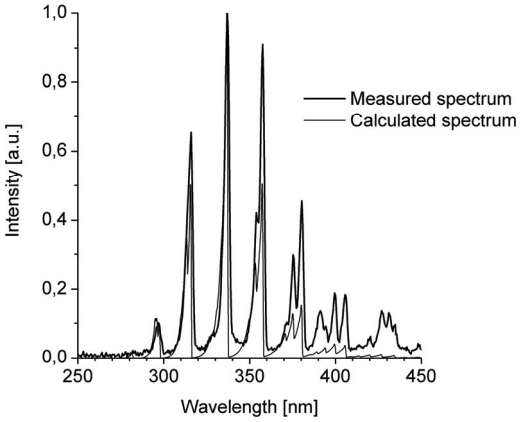

Fig. 11. Methane conversion degree in CH_4:CO_2 (70%:30%) gas mixture as a function of pulse repetition rate. Nanosecond voltage pulses.

IV. CONCLUSION

Processing of CH_4:CO_2 (70%:30%) gas mixture simulating dry biogas using dielectric barrier discharge reactor with reticulated vitreous carbon high voltage electrode showed that:

- Hydrogen production and methane conversion degree increase linearly with discharge power in the range of up to 50 W. Thus, the discharge power controlled by the pulse repetition rate is the most important parameter influencing the hydrogen production;
- Nanosecond voltage pulses are much more efficient in hydrogen production than sine AC voltage;
- DBD supplied with nanosecond voltage pulses produces much lower acetylene than in the case of sine AC voltage supply;
- Conversion of methane in DBD exhibits different chemistry than that typical for thermodynamic equilibrium.

This work was carried out using gas of room temperature and without water vapor normally present in the real biogas. Thus, in real biogas we may expect much higher hydrogen production efficiency and methane conversion degree as observed by other researchers conducting plasma assisted steam reforming of methane.

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REFERENCES

[1] T. Nozaki, H. Tsukijihara, W. Fukui, and K. Okazaki, "Kinetic analysis of the catalyst and nonthermal plasma hybrid reaction for methane steam reforming," *Energy & Fuels*, vol. 21, pp. 2525-2530, 2007.

[2] V. Goujard, J. M. Tatibouet, and C. Batiot-Dupeyrat, "Use of a non-thermal plasma for the production of synthesis gas from biogas," *Applied Catalysis A: General*, vol. 353, pp. 228–235, 2009.

[3] Y. C. Yang, B. J. Lee, and Y. N. Chun, "Characteristics of methane reforming using gliding arc reactor," *Energy*, vol. 34, pp. 172–177, 2009.

[4] Y. N. Chun, Y. C. Yang, and K. Yoshikawa, "Hydrogen generation from biogas reforming using a gliding arc plasma-catalyst reformer," *Catalysis Today*, vol. 148, pp. 283–289, 2009.

[5] Y. Sekine, J. Yamadera, M. Matsukata, and E. Kikuchi, "High-efficiency dry reforming of biomethane directly using pulsed electric discharge at ambient condition," *Energy & Fuels*, vol. 22, pp. 693–694, 2008.

[6] Y. Sekine, J. Yamadera, M. Matsukata, and E. Kikuchi, "Simultaneous dry reforming and desulfurization of biomethane with non-equilibrium electric discharge at ambient temperature," *Chemical Engineering Science*, vol. 65, pp. 487-491, 2010.

[7] H. Nagazoe, H. Naito, M. Kobayashi, T. Yamaguchi, H. Kimuro, and K. Onoe, "CH_4 reforming with CO_2 using microwave plasma technique," in *Proc. of 16th International Symposium on Plasma Chemistr*y, 2003, Taormina, Italy, pp. 321-326.