



THE INFLUENCE OF HYDROGEN SULPHIDE AND CONFIGURATION OF A DBD REACTOR POWERED WITH NANOSECOND HIGH VOLTAGE PULSES ON HYDROGEN PRODUCTION FROM BIOGAS

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Keywords: hydrogen; biomethane; dielectric barrier discharge; plasma; hydrogen sulphide.

The production of hydrogen from CH₄:CO₂:H₂S (70 % : 30 % : 1000 ppm) mixture, simulating dry biogas in a DBD reactor, supplied with nanosecond negative pulses, is presented. We have found that sulphur produced from H₂S during the process changes the electrical parameters of the reactor with a RVC electrode. As a result, the production of syngas and the selectivity of methane conversion into hydrogen, decreases. Due to changed electrical parameters of the reactors, radicals formed from methane recombine into C₂ and C₃ hydrocarbons more efficiently, resulting in lower production of hydrogen. Major by-product of the methane processing is propane, concentration of which is comparable to hydrogen.

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Introduction

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

Unfortunately, the plasma-catalytic systems are not useful when biogas containing sulphides (mainly H₂S) is going to be processed, due to the catalyst poisoning. There are several publications claiming to describe the production of hydrogen from the biogas, using plasma-catalyst systems.¹⁻⁴ However, the authors have used a mixture of methane and carbon dioxide simulating the biogas, without any additives which are present in the real biogas, such as water vapor, H₂S and NH₃. Such a simple simulation of the biogas is not adequate when the outlet gas is going to be used with fuel cells, which are very sensitive to H₂S traces. There are only 2 papers on using the real biogas and both of them were published by the same research group, in 2008 and 2010.⁵⁻⁶ Sekine et al studied the application of the pulsed corona discharge (PCD) reactor and the dielectric barrier discharge (DBD) reactor without any catalyst and they found, that the PCD could convert the biomethane into the syngas and H₂S into the solid sulphur simultaneously.⁵⁻⁶ This is due to the high electron energy of the PCD - the electron has enough energy to dissociate a C-C bond and a C-S bond. On the other hand, the DBD could convert H₂S into solid sulphur too, but methane and CO₂ in the biogas have not reacted at

the lower input power. In this work, we present the results of an experiment in which both the DBD and the pulsed power supply, are used. These results show the influence of the plasma reactor configuration, the catalyst typical for steam hydrocarbon reforming, and hydrogen sulphide polluting the biogas on the process of hydrogen production, methane conversion and its by-products formation.

Experimental set-up

In this paper the results obtained in three specific DBD reactors are presented. The schemes of the reactors are shown in Figs. 1-3. The reactor No. 1 represents basic construction which was used for the next two. 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 an aluminum foil, remaining a 4 mm wide slit along the reactor. The RVC electrode is formed as a tube of outer diameter 8 mm, inner diameter 3 mm and length of 150 mm. Through that RVC tube, a mixture of methane, carbon dioxide and hydrogen disulfide (70 %:30 %:1000 ppm, respectively), simulating a dry biogas, was introduced into the reactor. Due to the relatively low porosity of the RVC tube, which is 80 ppi (pores per inch), the gas flow was not disturbed and was kept at 200 cm³ min⁻¹ at the atmospheric pressure. An average residence time for the processed gas in the discharge space of the reactor No. 1 is about 5.7 s.

In the reactor No. 2, there is an additional dielectric barrier in the form of ceramic tube, covering tightly the RVC electrode (Fig. 2). Then, the gas gap in the reactor decreases from 3.5 mm to 2 mm, which results in the average residence time in the discharge space of about 1 s (at the flow rate of 200 cm³ min⁻¹). This additional barrier is also used as a support for Ni catalyst, incorporated into the ceramic via an impregnation method. The shorter residence time is compensated to some extent by more uniform and distributed non-thermal plasma generated by the DBD (Fig. 3).

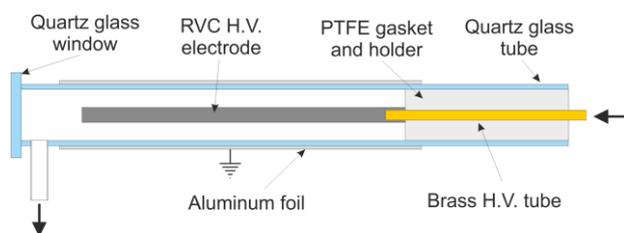


Figure 1. DBD reactor with RVC electrode (Reactor No. 1)

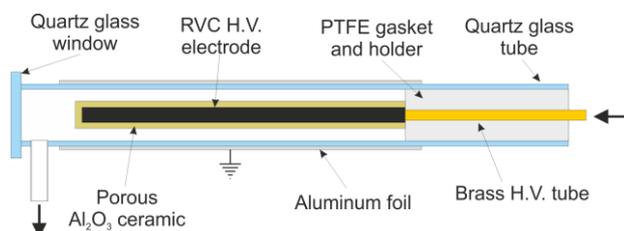


Figure 2. DBD reactor with RVC electrode and porous ceramic tube as the second dielectric barrier (Reactor No. 2)

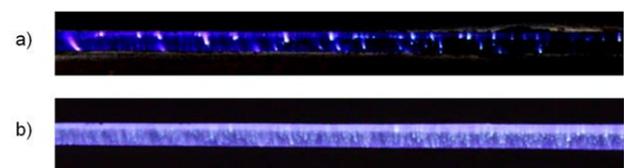


Figure 3. Images of DBD supplied by nanosecond pulses of 29 kV and 50 Hz in Reactor No.1 (a) and No.2 (b)

In the reactor No. 3 there is no additional dielectric barrier, but the gap between RVC electrode and the quartz glass tube is filled with glass beads (Fig. 4). This way, the DBD is transformed into the surface discharge developing on glass beads, instead of bridging the gas gap.

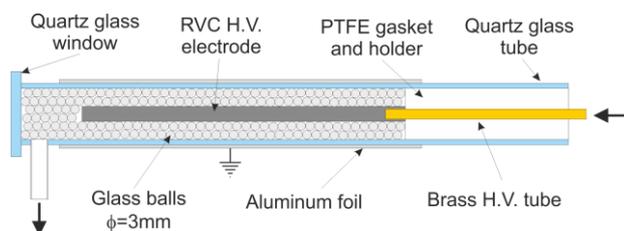


Figure 4. DBD reactor with RVC electrode and glass spheres

As a source of nanosecond pulses, we used the NPG-15/2000 pulse generator by Megaimpulse Ltd., producing negative voltage pulses of 29 kV with the repetition rate in the range of 50 Hz – 3.0 kHz. Typical voltage and current pulses are presented in Fig. 5. The voltage pulse is not influenced by the presence of H₂S in the gas, but the current pulse decreases significantly. Voltage pulses were measured using the Tektronix P6015A high voltage probe, whereas current pulses were measured using the Pearson 2877 coil. The discharge power was calculated by multiplying the repetition rate by a single discharge pulse energy (E_p), which was obtained after the experiment by the integration of the pulse voltage (U) times the current (I) over the pulse duration (t):

$$E_p = \int_{\text{pulse}} U(t)I(t)dt \quad (1)$$

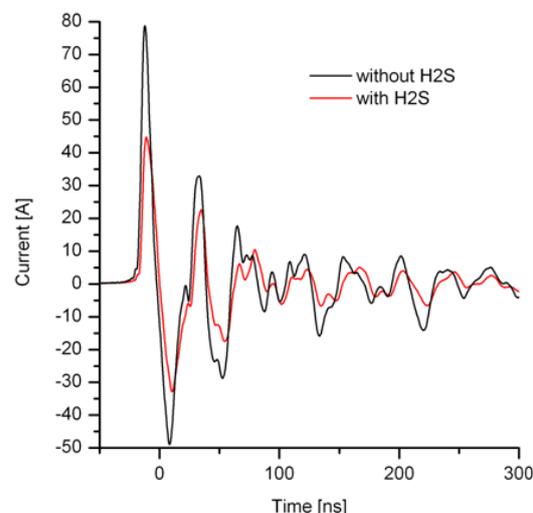
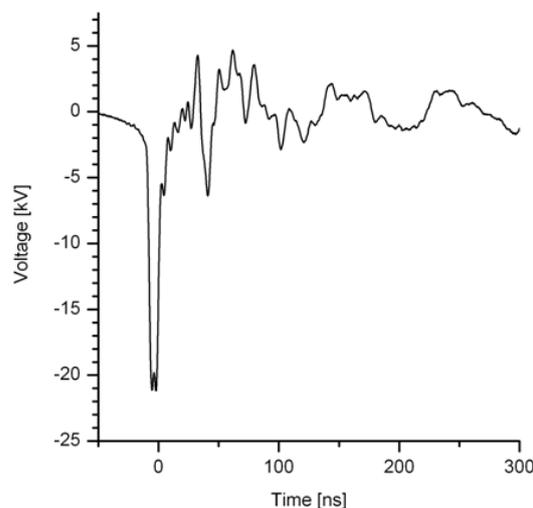


Figure 5. Typical voltage and current pulses in the Reactor No. 1 with and without H₂S in the processed gas

The gas composition before and after the processing in the DBD reactor was analyzed using FTIR spectrophotometer and gas chromatograph. For the measurements of CO₂, CO and CS₂, the FTIR Nicolet 380 spectrophotometer with gas cell of 10 cm optical path length and CaCl₂ windows was used. It was calibrated using certificated mixtures delivered by Linde Gaz Polska Ltd.: N₂:CO₂ (50 % : 50 %), N₂:CO (90 % : 10 %) and N₂:CS₂ (99 % : 1 %). Every single component was calibrated with a single mixture diluted in several proportions by nitrogen in a flowing regime, i.e. nitrogen stream was mixed with a stream of one compound and then introduced into the FTIR spectrophotometer. Mass flow controllers were used for accurate control of flow rates of each stream. The precision of the measurements of CO₂, CO and CS₂ was 90 ppm, 7 ppm, and 1.3 ppm, respectively.

The diagnostics of H₂ and CH₄ was carried out using the SRI 8610C gas chromatograph with the gas sampling valve, TCD, molecular sieve column and argon as a carrier gas. When the gas chromatograph was equipped with the FID and Hayesep Q column, then CH₄ and other hydrocarbons were detected. The gas chromatograph was calibrated towards H₂, CH₄, C₂H₂, C₂H₄, C₂H₆ and C₃H₈ with the same procedure as used for the FTIR spectrophotometer.

The calibration of hydrogen and methane was carried out with pure gases whereas C₂ and C₃ hydrocarbons were calibrated using certified mixtures composed of 5 % of each components and nitrogen. The precision of the measurements of H₂, C₂H₂, C₂H₄, C₂H₆ and C₃H₈ was 50 ppm, whereas for CH₄ it was only 450 ppm.

Unfortunately, hydrogen sulphide could not be measured neither with FTIR spectrophotometer (too low sensitivity when using 10 cm gas cell) nor GC (no detection available). For monitoring H₂S concentration we used colorimetric gas detection tubes by Dräger Safety AG, Germany.

Since the DBD formed in our reactor emits relatively strong light when applying high voltage, it was possible to apply optical emission spectroscopy. For that purpose, Mechelle 5000 spectrometer with ICCD i-Star camera by Andor Technology, equipped with UV transmitting optical fiber, was used.

The temperatures of the processed gas at the 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.

Results and discussion

A. Gas composition

The hydrogen production is exactly the same in the DBD reactor without and with the porous ceramic barrier when no catalyst and no H₂S is present (Fig. 6). It suggests the same mechanism of hydrogen formation from methane. In the presence of Ni, the highest H₂ concentration observed at the discharge power of 22 W, is also the same as in the other cases, but the shape of the curve describing the hydrogen production is different. After extrapolating all 4 curves obtained when using all of the reactors, and without H₂S, one can conclude that concentration of hydrogen is about to the highest value when no catalyst is used, i.e. the H₂ production is decreasing, whereas in the presence on Ni the production of hydrogen may still increase, with the potential of giving much more hydrogen. This leads to another conclusion, that the activity of Ni catalyst grows with the DBD power.

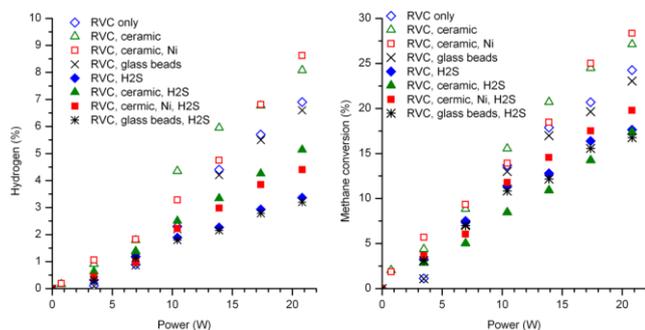


Figure 6. Concentrations of H₂ and methane conversion in the gas mixture processed by DBD with RVC electrode in Reactors No.1-3

Such a tendency is even better seen in the variations of the methane conversion degree (Fig. 6) and CO concentrations (Fig. 7). It is clear that at the highest discharge power of 22 W, in the experiment without the porous ceramic barrier, the CO concentration have reached the maximum, and with the ceramic free of the catalyst, it is close to a maximum, whereas in the presence of the catalyst in the porous ceramic the CO concentration still grows linearly. These differences in the shape of the curves may be explained by the different temperature of the gas in the plasma region. Simple modelling using a Thermodynamic Equilibrium Reactor (TER) shows a very similar tendencies at an assumption that the gas is heated up by the DBD to 300 K, 600 K and 800 K in the Reactor No. 2 with the catalyst, in the same reactor without the catalyst, and in the Reactor No. 1, respectively. This assumption is reasonable since, as seen in Fig. 3, the DBD in the reactor with the RVC electrode only forms a low number of filaments with plasma, which is more luminous and therefore hotter than uniform and less intensive plasma in the reactor with the additional ceramic barrier.

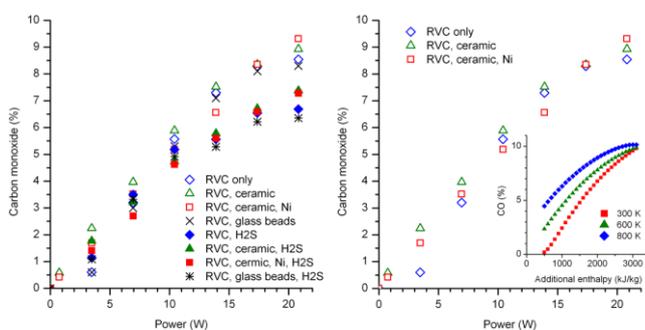
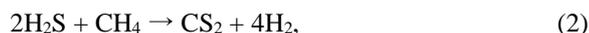


Figure 7. Concentrations of CO in the gas mixture processed by DBD with RVC electrode in Reactors No.1-3 and calculated using TER model.

It is clear from Figs. 6 and 7 that the addition of H₂S to the CH₄:CO₂ mixture inhibits the methane conversion and the production of hydrogen and CO in the DBD reactors. In the group of results obtained when H₂S was present in the gas mixture, the lowest production of hydrogen was observed in the reactor with RVC only (Reactor No. 1) and in the reactor packed with glass beads (Reactor No. 3), whereas the highest – in the reactor with ceramic tube but not saturated with Ni catalyst (Reactor No. 2). Hydrogen concentrations are 40-60 % lower comparing to the results for the mixture without H₂S. Such a high influence of H₂S on the hydrogen concentration cannot be explained by the gas phase reactions only, since the concentration of H₂S is almost 1000 times lower than methane. Hydrogen sulphide (Fig. 8) is decomposed in 90-96 % simply into hydrogen and solid sulphur. The contribution of H₂ from H₂S into the total balance of H₂ is small, i.e. below 1000 ppm, which and can be hardly distinguished. On the other hand, the formation of solid sulphur is clearly visible on the reactor wall (Fig. 9). The deposited sulphur forms a resistive layer which decreases the discharge current (Fig. 5). The only product of the H₂S reactions with CH₄, is CS₂ seen in the FTIR spectra (Fig. 10). Since CS₂ is well recognized in the spectra, it means that the reaction:



is the main one involving H₂S. This conclusion is supported by the results obtained experimentally and via modeling by Petherbridge et al.⁷ They proposed a scheme of subsequent reactions:



Carbon disulfide is an intermediate by-product. It is decomposed in reaction (3), causing a drop of CS₂ concentration when H₂S concentration is too low to support high CS₂ production. This process is well seen in Fig. 8, showing a peak in CS₂ concentration at the DBD power of 10 W. It is interesting that Sekine et al. have obtained exactly the same CS₂ profile, when increasing the DBD current.⁵ In their experiment, they were able to use much higher power and obtain the complete decomposition of carbon disulfide. They also found, that the final product of H₂S transformations is solid sulphur, depositing on the reactor wall.

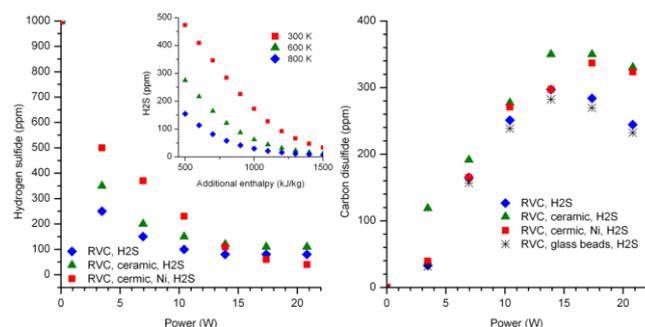


Figure 8. Concentrations of H₂S and CS₂ in the gas mixture processed by DBD with RVC electrode in Reactors No.1-3 and calculated using TER model (only H₂S)



Figure 9. Sulfur deposited on the reactor cylinder

It is interesting to note, that the decrease in H₂S concentration in all of the reactors (Fig. 8) is close to the results obtained from the TER model, similarly as in the case of CO. This may prove the conclusion on the different temperature of the gas in the plasma region in all studied reactors.

The concentrations of the hydrocarbon by-products detected in the gas mixture processed by the DBD in the different reactors are shown in Fig. 11. The formation of acetylene, as was observed in our previous experiments, is not related to the syngas production.⁸ The biogas processing in the DBD reactor with the RVC electrode only resulted in the small concentrations of acetylene, not exceeding 0.126 % at the maximum discharge power of 22 W.

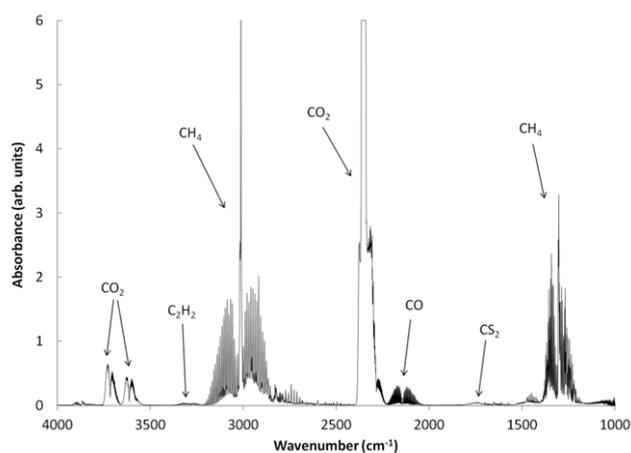


Figure 10. Typical FT-IR spectra of gas exiting DBD reactors with RVC electrode. Discharge power 22 W.

Adding the porous ceramic barrier caused the increased production of acetylene. Up to the level of 14 W of the discharge power, the concentrations of C₂H₂ are similar when the ceramic is free or impregnated with Ni. Further power increase reveals an activation of the Ni catalyst towards the decomposition of the acetylene, concentration of which drops dramatically down to 0.065 % at 22 W. In the presence of 1000 ppm H₂S in the processed gas, this drop is not observed. The most probable reason is poisoning of the Ni catalyst by sulphur, which suppresses the activation of the catalyst.

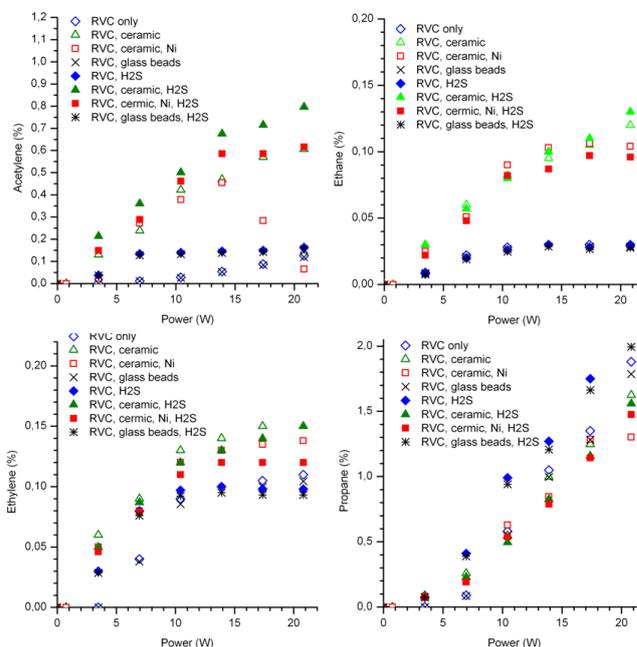


Figure 11. Concentrations of C₂H₂, C₂H₆, C₂H₄ and C₃H₈ in the gas mixture with H₂S processed by DBD with RVC electrode in Reactors No.1-3.

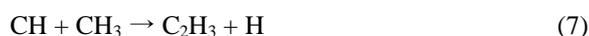
As seen from the linear growth of the ethane and ethylene concentrations, their production is constant up to 10 W of the DBD power. At the higher power levels the concentrations of those hydrocarbons reach plateau in the reactors with the RVC electrode only and in the reactor with the ceramic tube saturated with Ni catalyst.

In the reactor with the clean ceramic, the concentrations of C₂ hydrocarbons still grow. On the other hand, the production of propane is quite different. The concentration of C₃H₈ increases almost linearly till the last point of the DBD power.

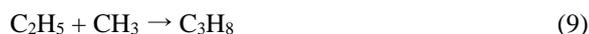
Generally, the lower concentrations of all detected hydrocarbons in the reactor with the RVC electrode only (Reactor No. 1) result from the lower methane conversion (Fig. 6), which also explains the differences in the results obtained using each of the reactors. According to the results of the modelling performed by De Bie et al., the increase in the methane conversion degree up to 20 % is accompanied with the increase in concentrations of acetylene, ethylene and ethane and decrease in propane concentration, exactly as we observed.⁹ Chemical reactions responsible for the production and the consumption of C₂H₂, C₂H₄, C₂H₆ and C₃H₈ are as follows. Acetylene and ethylene are produced mainly in one reaction:



where C₂H₃ radicals results from the recombination of CH and CH₃ radicals produced directly from CH₄ in the electronic reaction:



In reactions of recombination and hydrogenation of C₂H₅ radicals ethane and propane molecules are formed:



As predicted by the calculations of De Bie et al C₂H₅ is formed mainly by hydrogen attachment to C₂H₄:⁹



As can be seen in Fig. 11, hydrogen sulphide does not influence much higher hydrocarbons production, except acetylene. When comparing to the highly influenced methane conversion and hydrogen production, one can conclude that the formation of higher hydrocarbons is not controlled by the electronic reactions but by the gas temperature. Since in the experiment with H₂S we observed formation of the sulphur resistive layer causing the drop in the discharge current, it means that the rest of the power

delivered to the reactor dissipated as the heat. The increased gas temperature is enough to influence C₂ and C₃ hydrocarbons production, but not enough to play a role in CH₄ dehydrogenation. Therefore, still the key reaction in the methane conversion and hydrogen production is the dissociation of methane molecules by the energetic electrons.

The selectivity of the hydrogen production (Fig. 12) shows that only up to 21 % of hydrogen atoms from the methane molecule leaves the DBD reactors as H₂. The rest forms higher hydrocarbons and water vapour. The highest selectivity was recorded in the experiment with H₂S in the gas processed in the reactor with the ceramic tube not saturated with Ni catalyst at the DBD power of 11 W. At the higher DBD power, the selectivity in this reactor drops slightly, whereas in the other cases H₂ selectivity grows up to the highest values at 22 W. The influence of the DBD reactor configuration and the presence of H₂S on the hydrogen selectivity is not so well seen as in the case of concentrations of all the measured products.

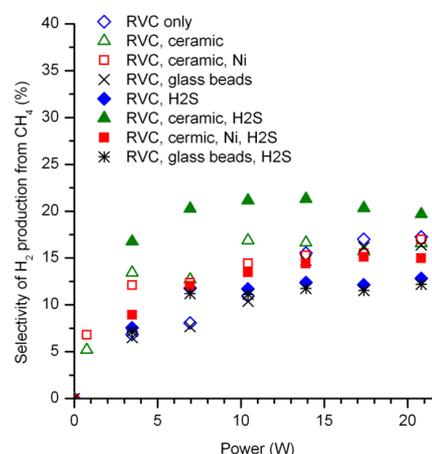


Figure 12. Selectivity of hydrogen production from methane in the gas mixture processed by DBD with RVC electrode in Reactors No.1-3.

B. Plasma diagnostics by OES

The typical spectra in the range of 250-450 nm recorded in this experiment are presented in Fig. 13. Increasing the DBD power results only in the increased intensity of each band. It means that more light from the increasing number of streamers generated during the discharge was emitted. At the same time the discharge energy transfer into the gas in the form of heat was very low. Temperature of the gas leaving the DBD reactors increased with the discharge power but only up to 38 °C (at 15 W delivered to the discharge).

In the recorded spectra most of the bands originated from N₂⁺ second positive system except those marked as CH bands and C triplet. The highest CH band is from CH (A-X) transition. What is important when analyzing an influence of the hydrogen sulphide presence on the DBD plasma is that the CH (A-X) band (as well as other bands marked in Fig. 13) is less intensive comparing to the experiment without H₂S (Fig. 14). The lower intensity of the bands can be caused either by the lower discharge current in the gas with H₂S or by the reaction (2), in which a portion of methane is consumed without the formation of CH radicals.

When comparing the spectra recorded in the experiments with 3 different reactor configurations, it is seen that in all cases plasma composition is similar (Fig. 15). There are no significant differences in those spectra except the CH (A-X) and CH (B-X) bands, which are higher in the reactor with the ceramic tube but without the Ni catalyst.

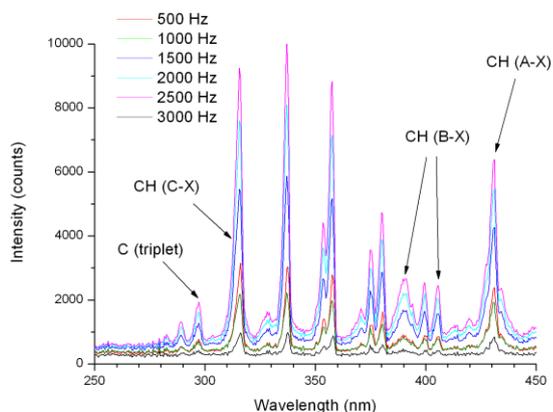


Figure 13. Optical emission spectra of the DBD in Reactor No. 1 for the repetition rate of nanosecond pulses 500-3000 Hz. Processed gas mixture CH₄:CO₂:H₂S

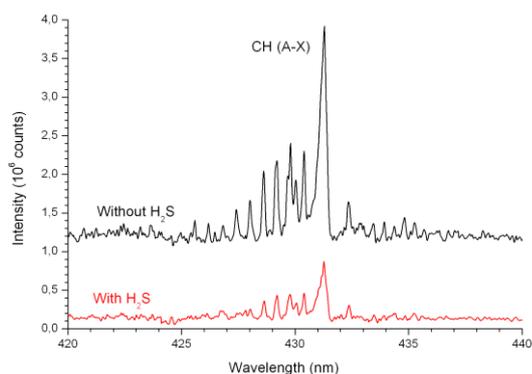


Figure 14. Comparison of optical emission spectra obtained in the DBD reactor No. 1 with and without H₂S in the CH₄:CO₂ mixture in the range of CH (A-X) band. Repetition rate of nanosecond pulses 1 MHz

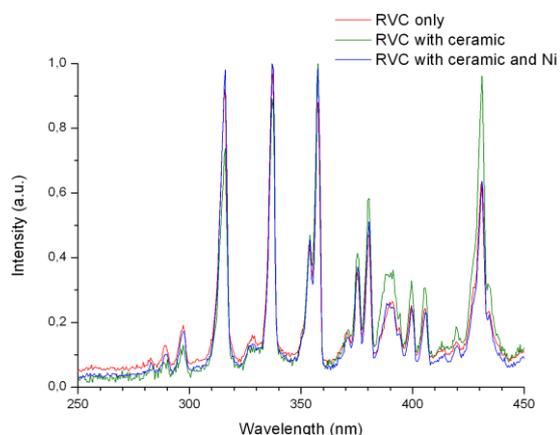


Figure 15. Optical emission spectra of DBD plasma generated in CH₄:CO₂:H₂S mixture processed in reactors No. 1-3. Repetition rate of nanosecond pulses 1 MHz.

Conclusions

Processing of the CH₄:CO₂: (70 % : 30 % : 1000 ppm) gas mixture simulating dry biogas, using different dielectric barrier discharge reactors with reticulated vitreous carbon high voltage electrode and nanosecond high voltage pulses showed, that:

- Presence of the additional ceramic barrier in the DBD reactor strongly influences plasma properties and consequently the production of syngas and higher hydrocarbons. The plasma is more uniform and colder, which results in different kinetics, comparing to the reactor without the additional barrier.
- Nickel catalyst incorporated in the additional ceramic barrier can be activated by the discharge at higher power. After being activated it supports acetylene decomposition.
- Sulphur produced from H₂S during the process changes the resistivity of the DBD reactor causing decrease in the discharge current. As a result, the production of syngas and methane conversion decreases.
- Electron impact dissociation of CH₄ resulting in the formation of CH₃ radical starts the conversion process. This radical initiates recombination reactions towards higher hydrocarbons such as C₂H₆ and C₃H₈. A further play of dissociation and recombination leads to the conversion towards C₂H₂ and C₂H₄. Finally, dissociation of CH₄ and the higher hydrocarbons also results in the formation of H₂. Production of CO is separated from the methane conversion.

This work was carried out using gas of room temperature and without water vapor normally present in the real biogas. Thus, in the real biogas we may expect much higher hydrogen production efficiency and methane conversion degree as observed by other researchers conducting the plasma assisted steam reforming of methane. Moreover, at such conditions the reactions involving hydrogen sulphide and its influence on by-products may be different than those described in this paper.

Acknowledgements

This work was supported by the National Science Centre under the project No. 2011/01/B/ST8/04131.

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Received:
Accepted:

10.07.2014.
25.07.2014.