Catalytic Conversion of Biogas in a Fluidized Bed Reactor Supported by a DBD

[1]Thorsten Kroker, [1]Torsten Kolb, [2]Krzysztof Krawczyk, [2]Michal Młotek [1]Andreas Schenk, [1]Karl Heinz Gericke

[1]Institute of Physical and Theoretical Chemistry, Braunschweig, 38106, Germany

[2]Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskieo 3, 00-664 Warszawa

Abstract

The catalytic conversion of biogas (60% CH_4 + 40% CO_2) and other mixtures of methane and carbon dioxide was studied in a fluidized bed reactor supported by a RF driven dielectric barrier discharge. The discharge was realized in a coaxial DBD-reactor, driven by a 13.56 MHz power supply unit. A powder of 3% palladium carried by Al_2O_3 was used as catalyst with a grain size between 0.16 and 0.32 mm. The investigated gas mixtures consisted of 5% of different combinations of CH_4/CO_2 in helium. The influence of temperature, dwell time and power on the product yield were studied. The reaction was monitored online by quadrupole mass spectroscopy and infrared spectroscopy supported by a White-cell. The aim is to create optimal reactor conditions and catalysts for producing special products. Formaldehyde was produced in this way, with a yield up to 1.2% and selectivities of more than 12%. Additionally the formaldehyde yield, was investigated by using a Pd/Al_2O_3 catalyst and the influence of the temperature of the catalyst was studied.

Keywords: Biogas recycling, DBD, catalyst, fluidized bed reactor, online analysis, greenhouse gas.

1. Introduction

Biogas is a renewable resource consisting mainly of methane (average concentration 60%) and carbon dioxide (average concentration 35%). Using biogas as an energy source or for producing synthesis gas is a very active research field. The Fischer-Tropsch synthesis is a well known method for the production of hydro carbons and alcohols [1]. It seems to be a good idea to use biogas for producing the synthesis gases for Fischer-Tropsch by plasma treatment [2,3,4], but this two step process requires a significant amount of energy to build the CO/H_2 mixture and form the products.

The direct conversion of biogas into other useful chemicals like methanol and formaldehyde [5,6,7] seems to be more promising. For industrial applications a continuous method, like the plug-flow-reactor, is useful. To use Biogas for the production of useful chemicals combines two major advantages: Biogas is a very cheap starting material and is available in huge amounts. A very interesting source of Biogas is landfill, because in most cases the disposal gas would be wasted in the atmosphere. This way the concentration of greenhouse gases is increased. From this follows the second advantage: to catch and refine the biogas reduces the amount of the greenhouse gases that were wasted into the atmosphere.

In addition, online monitoring allows to change the reactor conditions whenever it is necessary. This online monitoring is helpful because the composition of Biogas is not constant. Therefore it is beneficial when this disadvantage can be countered by changing the reactor conditions to obtain the best possible product yield and selectivity. Furthermore, catalysts allow to optimize product distribution and to adjust the biogas compositions. In order to save energy a catalyst heater was added to the reactor to selectively heat the catalyst. The main aim of the project is to characterise all products qualitatively and quantitatively and to search for conditions to optimize the selectivity and the product yield. As a side effect, we created an online monitoring system in order to study the whole process. This work investigates the yield of formaldehyde under different conditions.

2. Experimental Procedure

The experiment was performed in a fluidized bed reactor supported by a dielectric barrier discharge. The DBD reactor (**Fig.1**) was a Duran glass-tube with 8 mm external diameter and 5 mm inner diameter. The whole reactor is 150 mm long. The top of the reactor was extended with a Duran glass-ball with 20 mm diameter. The catalyst was laid on the bottom atop a piece of glass wool. The catalyst was a powder of 3% palladium carried by Al_2O_3 with grain size between 0.16 and 0.32 mm [8]. The catalyst can be heated up to 250°C.
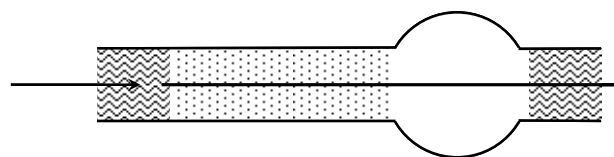

Fig.1 Schematic picture of the reactor. Dotted area = Plasma/catalyst area, shaded area = glass wool, dashed line = iron conductor.

The plasma was ignited over an area of 10-50 mm and was realized by silver paint and an iron conductor with a length of 100 mm and a diameter of 2 mm.

This leads to average dwell times of 10 to 50 ms (10 ms per cm). The iron conductor was fixed by glass wool. The plasma was driven by a RF-generator (ENI ACG-6B) and an impedance controller (ENI MW-10D) at a frequency of 13.56 MHz. The pressure in the reactor chamber was 100 mbar and was realized with a XDS dry pump (Edwards).

A needle valve controls the gas flow and the pressure in the reaction chamber. The gases were adjusted by three mass flow controllers (MFC), at a total flow rate of 100 sccm per minute. The content of CH_4 and CO_2 was 5% in Helium as carrier gas. The products were analyzed online by FTIR-spectroscopy (Equinox 55, Bruker) in a White-cell with a path length up to 8 meters and a QMS (Balzer, QMS 200 Prisma). A thermo couple was used for analyze temperature measurements. **Figure 2** shows the schematic setup.
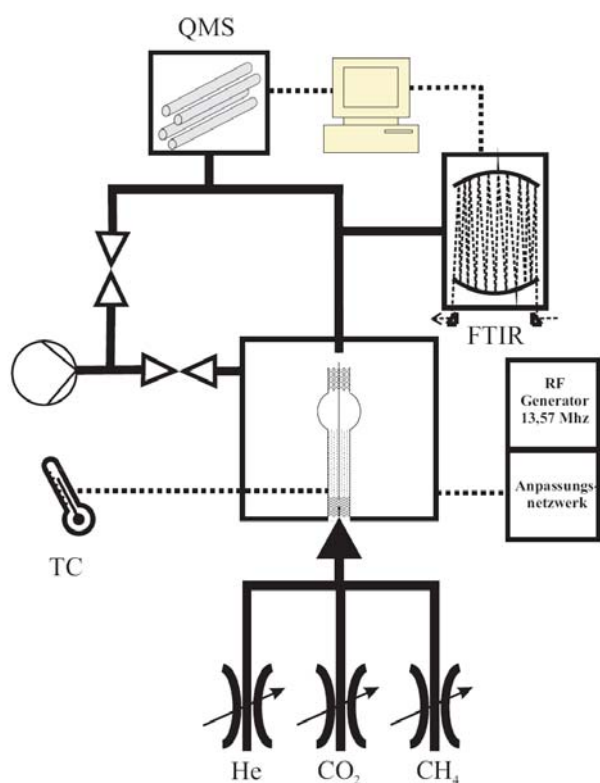

Fig.2 Schematic setup of the gas flow system (solid lines) and electronical interfaces (dashed lines). The three MFC's (He, CO_2, CH_4) feed the experiment with the gases. MS = mass spectrometer, IR = FT-infrared spectrometer, PC = personal computer, TC = thermo couple, IM = impedance controller, RF = RF-Generator, FR = Fluidized Bed reactor.
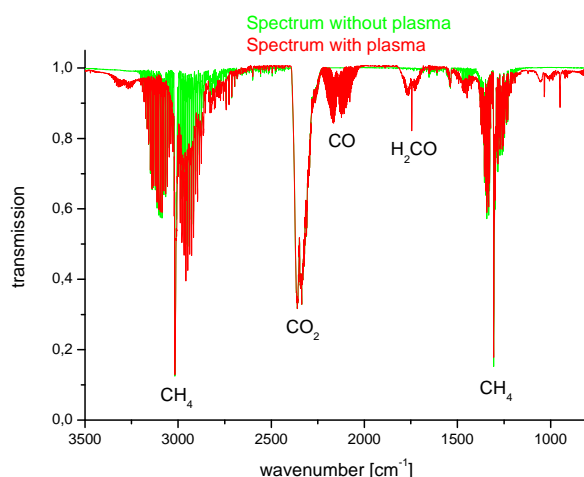

Fig.3 Spectrum of starting material (green, 3% CH_4 and 2% CO_2 in Helium) overlap with the product stream spectrum (red).

3. Results and Discussion

Spectra were recorded in the range from 600 to 5000 cm^{-1}, with a resolution of 1 cm^{-1}. **Figure 3** shows an FTIR spectrum of a mixture of 3% methane and 2% carbon dioxide in helium with and without plasma. After switching on the plasma many new peaks can be found. **Fig.4** shows the most interesting range of the spectrum. It shows a peak at 1745 cm^{-1} which was identified as the sym. C-O stretch vibration of formaldehyde. This peak was used for monitoring formaldehyde quantitatively. The detected concentration of CH_2O is shown in **Figs.5, 6, 12** and **13**.

Figure 5 shows the detected amount of formaldehyde after plasma treatment for several gas mixtures as function of the plasma power. The results indicate that the highest formaldehyde production rate
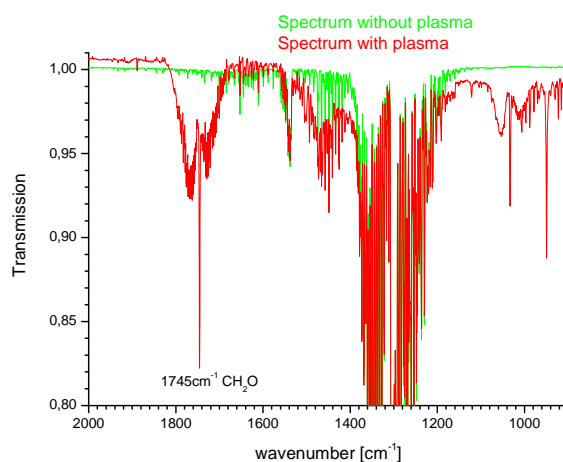

Fig.4 Detail spectrum of the most interesting region (green = starting material, red = product stream).
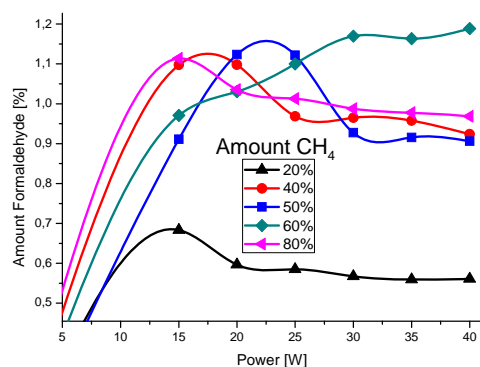
Fig.5 Formaldehyde yield at several gas mixtures.

is achieved at a gas concentration of 2.5-3% Methane and 2-2.5% CO_2 and at plasma power between 20 and 30 W. The amount of formaldehyde is decreased significantly at higher plasma power treatment. These results can be explained by the increasing amount of electrons and radicals, when the plasma area is extended. The results show that the methane/carbon dioxide ratio is essential for the produced amount of formaldehyde. A nearly optimum CH_2O yield is realized for a gas ratio similar to the biogas composition (see blow). **Figure.6** compares the product yield of formaldehyde by using the fluidized Pd-catalyst with the product yield at catalyst free conditions.

The investigated gas mixture was 3% methane and 2% carbon dioxide, which is the extrapolated mean biogas composition (60% methane and 40% carbon dioxide). **Figure 6** shows an example of reproducibility. Two series of measurement are pictured.

The highest product yield was be found at medium power rates without the palladium catalyst. Interestingly the catalyst affects the product yield negatively at smaller power, but it increases the formaldehyde yield at higher plasma power. Additionally, the amount of formaldehyde is more or less constant above 30 Watt threshold.
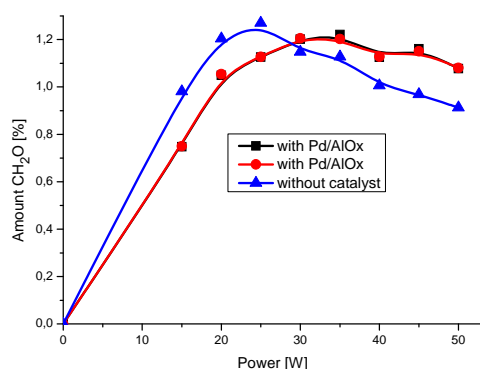

Fig.6 Formaldehyde yield with and without Pd-catalyst.
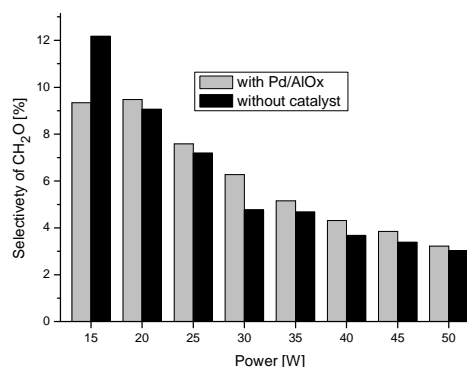

Fig.7 Selectivity of formaldehyde for the series of measurements.

A big advantage in using the palladium catalyst is that the product yield is less dependent of power. In this way a constant product yield can be assured easily. The CH_2O molecule is involved in more than 40 building and depletion reactions [9]. Therefore an exact declaration is questionable. It is well-known that palladium can absorb huge amounts of hydrogen, thus the Pd/Al_2O_3 could affected the reaction mechanism significantly. The Palladium catalyst could be involved directly, as a hydrogen radical source, or indirectly in the reaction mechanism. **Fig.7** compares the selectivity of the data former shown. The selectivities are related to the conversion rates of methane and carbon dioxide (see **Fig.8** and **9**).

The highest selectivity could be found at very low plasma power without a palladium catalyst. At the same time the lowest conversion rates of methane and carbon dioxide were observed. The selectivity of formaldehyde was 12.2% at 15 Watt during the conversion rate of methane was 8.3%, while the conversion rate of carbon dioxide was 7.1%. The selectivity of formaldehyde decreases with the plasma power. It should be mentioned that preliminary results indicate an increase of other products like synthesis gas and C2 Hydrocarbons, with increasing power (see later works). Therefore, a feedback reactor is promising.

The conversion rates of methane by using the fluidized Pd/Al_2O_3 are smaller than those without catalyst. However, the conversion rate of carbon dioxide becomes higher above 40 Watt threshold by using the Pd-catalyst. The selectivity of formaldehyde decrease with increasing power. At 20 Watt the selectivity of formaldehyde by using the Pd/Al_2O_3 catalyst is 9.5% in contrast to 9.1% without the catalyst.

There is a linear correlation between the conversion rates of methane and carbon dioxide (**Fig. 8 and 9**) with the catalyst. Without a catalyst the conversion rates converge to a maximum.
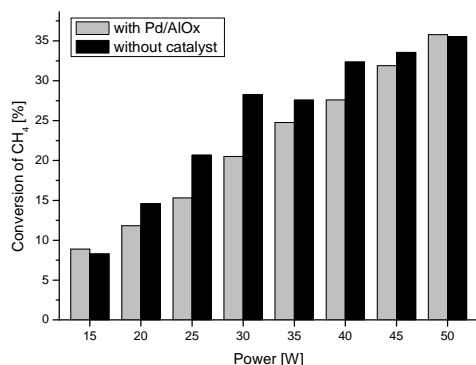
Fig.8 Conversion rates of methane after plasma treatment at different power.

At the highest power rates synthesis gas (H_2/CO) will be generated with very high product yields and selectivities. Therefore, the application of the palladium catalyst is very promising.

An interesting feature from an environmental point of view is to reduce the carbon dioxide concentration of the biogas mixture, since CO_2 and CH_4 belong to the greenhouse gases. **Figure 9** shows the conversion rates of carbon dioxide after several plasma treatments. Unfortunately the Pd/Al_2O_3 catalyst decreases the conversion rate of CO_2 like CH_4. At low plasma power the conversion rate of carbon dioxide decreases from 7.1% without a catalyst to 5.1% by using the fluidized Pd-catalyst.

The temperature is an important factor, because it affects the absorption and desorbtion rates of the intermediates. For characterizing the effect of the temperature a catalyst heater was used (see blow). **Fig. 10** shows temperature of the reactor wall as a function power. To analyze the effect of the catalyst temperature a special catalyst heating system was built. **Fig. 11** shows the temperature as a function of power of electrical the heating system. In this way the catalyst can be heated up to 250°C.
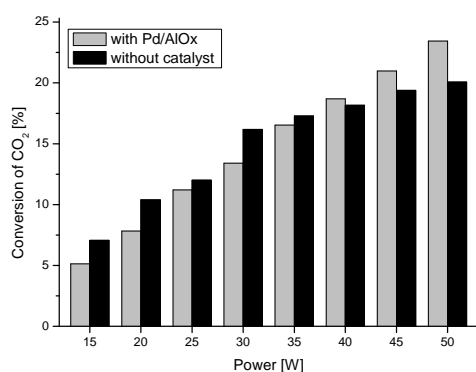

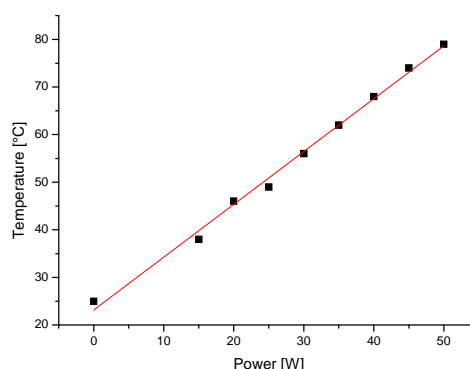**Fig.9** Conversion rates of carbon dioxide after plasma treatment at different power.

Fig.10 Temperature of the reactor wall as function of power of the plasma generator.

Fig.12 shows the conversion rate of carbon dioxide and the amount of formaldehyde as a function of the temperature of the catalyst. The power of plasma was 25 Watt. While the temperature is increased the conversion rates of carbon dioxide decrease significantly. The amount of formaldehyde decreases in the same way. High catalyst temperatures affect the formaldehyde production negatively. In later works the effect of the temperature on other catalysts will be investigated.

Another essential area is the duration of the plasma treatment and the concentration of radicals per volume. The plasma area of the reactor was reduced leading to dwell times of $10 - 50$ ms. The former results were realized with dwell times of 50 ms. The reduction of the area of plasma leads to an increase of micro discharges per area at the same power. The amount of radicals per volume is increased and therefore their concentration. The reaction kinetic depends strongly of the concentration of the radicals. Therefore, the concentration of several intermediates is changed, resulting in other product yields. **Fig. 13** shows the amount of formaldehyde as a function of plasma power for several dwell times.
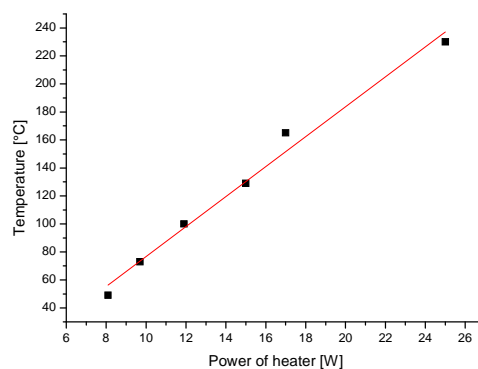

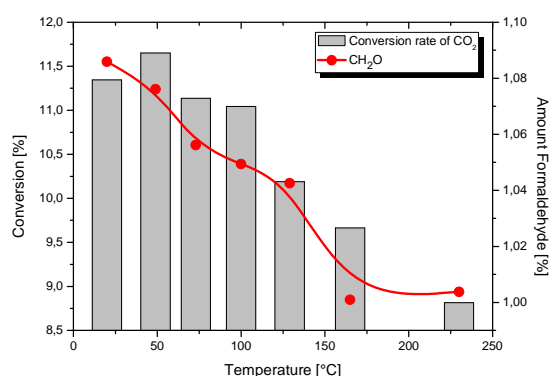**Fig. 11** Temperature of the Pd/Al_2O_3 catalyst using the heating system.

Fig.12 Conversion rate of carbon dioxide and the yield of formaldehyde as function of the temperature of the catalyst at 25 Watt plasma power.

The results predict a maximum yield of formaldehyde of above 40ms dwell time. The product concentration does not decrease linearly, therefore one can suppose that a part of the formaldehyde is built in the afterglow of the plasma.

4. Conclusions

1. The gas ratios are essential for the produced amount of formaldehyde. A nearly optimum product rate of CH_2O can be achieved for a methane/carbon dioxide mixture similar to the biogas composition.
2. The highest product rates of CH_2O can be observed at medium powers of the investigated plasma power. The highest selectivity is found at small plasma power.
3. The used Pd/Al_2O_3 affects the conversion rates of methane and carbon dioxide and increases the amount of formaldehyde at medium power and increases the selectivity in this yield of plasma power.
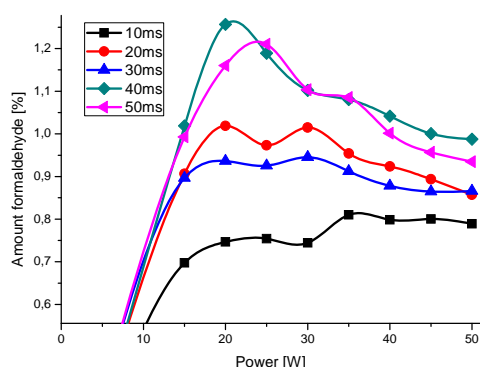4. The results point to a connection between the temperature of the catalyst and the product yield.

Fig.13 Yield of formaldehyde as a function of plasma for different times of plasma treatment.

5. It was demonstrate that the product yield depends strongly on the dwell time. The highest amount of formaldehyde was be found at 40 ms.

The next step is to use the QMS data for H_2 in order to obtain the synthesis gas concentration. Furthermore, other possible products such as higher hydrocarbons or acids are identified and monitored. After that other catalyst will be check for their activity and their effect on the selectivities and the product yield.

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