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ABSTRACT

The conversion of biogas like mixtures of methane and carbon dioxide was studied in a plug flow reactor with a dielectric barrier discharge. A 13.56 MHz power supply generated the atmospheric plasma discharge. Studied concentration of methane ranged from 0 to 100%, with missing part filled up with carbon dioxide. This mixture was diluted with helium to 2.5% with small part of the product stream monitored online at a total pressure of 100 mbar by a Fourier transform infrared spectrometer supported by a White-cell and a quadrupole mass spectrometer. The reactor was driven at different flow rates. This DBD reactor produces all three hydrocarbons, with ethane being the major compound. The concentration of ethane increases when the power in the plasma region increases from 30 to 65 W. This product concentration also grows up, if the fraction of methane in the inlet flow is increased. The highest amount of ethane (5.4%) is produced, when the gas stream consist of 2.5% Methane and 97.5% helium at a flow rate of 200 sccm.

KEYWORDS: DBD, Biogas, Ethane, C2 Hydrocarbons, Atmospheric Pressure Discharge, Online Monitoring

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1. INTRODUCTION

C2 hydrocarbons (ethane, ethene and ethine) are important basic chemicals, especially the unsaturated one. Thermal cracking to ethene is an important range of application for ethane. This compound is also used as a fuel gas. Ethene is the starting material for industrial manufacturing of Ethanol or for the production of plastics like polyethylene [1]. Organic syntheses are the main application area of ethine. This compound is often used to prepare base material for most plastics.

The starting point for industrial manufacturing of ethane, ethene and ethine is natural gas or crude oil. New technologies are needed to prepare C2 hydrocarbon. One way is to convert a mixture of Methane and Carbon dioxide in a dielectric barrier discharge (DBD). The advantage for such type of plasma is the potential to activate thermodynamically unfavorable reactions through energy rich plasma electrons. In a DBD is the entire electrode area effectively used for generating the discharge. [2]

Intense research with DBDs have been done in the last years to convert methane and carbon dioxide to other useful chemicals like synthesis gas [3], [4], hydrocarbons [5], [6] or oxygenated hydrocarbons [7], [8]. Different techniques have been used. T. Kroker et al. [9] analyzed the produced amount of formaldehyde in a DBD reactor at a 100 mbar. The highest quantity of this product (1.25%) has been observed at low investigated plasma power (ca. 25 W). A Palladium catalyst increases the yield of formaldehyde at higher plasma power from 0.9% (without a catalyst) to 1.05%.

There are many sources for the starting material which is used in this process. Mixtures of methane and carbon dioxide are for example known as biogas or landfill gas. Biogas is independent from natural gas, because animal and vegetable materials are used for this process, i.e. corn, sugar beets, grain or slaughterhouse waste. These materials are manly transformed in an anaerobe microbial mineralization to methane and carbon dioxide. The biogas composition can be actuated by using different starting materials or varying the process conduct.

This work focuses on the conversion of methane and carbon dioxide to C2 hydrocarbons in a 13.56 MHz DBD reactor. The plasma power, flow rate and the mixture of the inlet flow have been varied. Additionally the influence of high frequencies to generate the plasma has been studied.

2. EXPERIMENTAL PROCEDURE

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The schematic setup of the current experiment is shown in **Fig.1**. This setup can be divided into two parts. The first part is the area of operation which works at ambient pressure. The reaction chamber with the DBD reactor is there located. The gas stream is analyzed by fourier transform infrared spectrometer (FTIR) at a pressure of 100 mbar in the analysis domain and by a quadrupole mass spectrometer (QMS).

Fig.1 Schematic setup; FTIR: fourier transform infrared spectrometer; QMS: quadrupole mass spectrometer; → gas flow system; dotted line: electrical interface.

The gas flow for this experiment consists of methane and carbon dioxide. Helium was used as a carrier gas to dilute the gas mixture to 2.5%. These three components were adjusted by three mass flow controllers. The influence of different compositions of the gas mixture (0 - 2.5% methane and 0 - 2.5% carbon dioxide) and flow rates (200 – 800 sccm) on the product distribution were analyzed. The cylindrical Duran glass DBD reactor is located in a cubic reaction chamber. The reactor has a length of 150 mm, an external diameter of 8 mm and an internal diameter of 5.8 mm.

A 140 mm long welding rod with a diameter of 3 mm forms the inner electrode for igniting the plasma. This electrode is fixed on the top with two glass frits and on the bottom with glass wool. The reactor is covered over the length of 50 mm with a conductive silver varnish to create the outer electrode. A RF-generator (ENI ACG-6B) and a matching network (ENI MW-10D) come in operation to generate 13.56 MHz plasma at atmospheric pressure. The input power has been adjusted in 5 W steps between 30 and 65 W. The reactor is driven for 15 minutes until the power is increased by 5 W.

Most of the gas flow leaves the reaction chamber through valve 1. A small stream is sidelined by the needle valve 2 to analyze the starting material and the product distribution. This occurs online at 100 mbar in the analysis domain. The pressure is realized with a XDS 10 dry scroll pump (Edwards) and valve 3. All IR active species have been researched in the FTIR spectrometer (Equinox 55, Bruker) in a White Cell with a path length of 6 meters. The resolution of this application is 0.5 cm^{-1}. All spectra consist of 16 scans (double sided, forward-backward). IR inactive or substances which have no characteristic IR

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peak were studied in the QMS (Balzer, QMS 200 Prisma). The measuring range is between m/z = 0 (mass per charge) to m/z = 90. All m/z would be measured for 2 seconds.

3. RESULTS AND DISCUSSION

Fig.2 Spectra of the inlet flow (7 sccm CH_4, 3 sccm CO_2, 390 sccm He) and the product stream (generator power: 65 W).

In a previous work [9] we analyzed the recorded IR spectra between 500 and 5000 cm^{-1}. The present paper focuses on C2 hydrocarbons. Ethene (949.5 cm^{-1}) and ethine (729,4 cm^{-1}) have isolated IR peaks. They are shown in **Fig.2.** It is not possible to analyze ethane via IR spectroscopy, because this compound has a characteristic peak around 3000 cm^{-1}. All hydrocarbons have their CH-valance vibration in this region. Therefore, ethane and the conversion of methane are quantitatively analyzed by mass spectroscopy. For the representation of the produced amount of the C2 hydrocarbon the buffer gas helium is ignored.

The produced amounts of the three C2 hydrocarbons as a function of the power which is adjusted on the RF generator are illustrated in **Fig.3**. The inlet flow for this measurement consists of 1.75% methane, 0.75% carbon dioxide and 97.5% helium. Ethane is the main and ethene the lowest C2 product. Between the produced amount of ethane and ethene and accordingly ethane and ethine is approximately a factor of 13.

Fig.3 Produced amount of C2 hydrocarbons as a function of the adjusted generator power. The 400 sccm inlet gas stream consists of 1.75% methane, 0.75% carbon dioxide and 97.5% helium. The produced amount of ethane is illustrated on the left axis (solid points) and the right axis shows the produced amount of ethene and ethine (open points).

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These results can be explained by the mechanism [5] for this reaction. The bond between hydrogen and carbon in a methane molecule are broken during the plasma treatment. The following reactions continue during this process:

$CH_4 + e^- \rightarrow CH_3 + H + e^-$ (1)

$CH_3 + e^- \rightarrow CH_2 + H + e^-$ (2)

$CH_2 + e^- \rightarrow CH + H + e^-$ (3)

The required energy to start these reactions is moderately, 4.37 – 4.90 eV [10]. The CH radical of reaction (3) can dissociate to form carbon black. However, no carbon black has been observed for this kind of measurements.

The produced radicals (CH_3, CH_2, CH) have to undergo a non elastic collision with the most abundant methane molecule to form ethane, ethene or ethine.

$CH_4 + CH_3 \rightarrow C_2H_6 + H$ (4)

$CH_4 + CH_2 \rightarrow C_2H_4 + 2H/H_2$ (5)

$CH_4 + CH \rightarrow C_2H_2 + H + H_2$ (6)

There are two reasons why ethane is the major C2 product. First only two steps (Reaction 1 and 4) are required to get this product. At least three collisions are necessary to form ethene (reaction 1, 2 and 5). The formation of ethine requires at least four reactions (reaction 1, 2, 3 and 6). The generated methyl radical (reaction 1) has to collide one or rather two times with energy rich electrons to form the starting material for reaction (5) and (6). The dwell time of the compounds in the DBD reactor is approximately 0.3 s and, thus, the probability of the collision of electrons with methane is rather low.

The second reason is that the average energy of one electron is between 0 and 10 eV for our plasma reactor. More energy is required (15.06 eV or rather 19.87 eV [11]) to create CH_2 or CH in one step from methane.

The reaction of two similar radicals for example two CH_3 radicals to ethane is thinkable but plasma in a DBD reactor has a small degree of ionization. The probability of a collision of two radicals is smaller than the collision of a radical and a molecule like in reaction 4 to 6.

There are not only reactions which generates C2 hydrocarbons. It is also possible to destroy these compounds in the plasma region (reaction 7 to 9).

$C_2H_6 + e^- \rightarrow 2\ CH_3 + e^-$ (7)

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$C_2H_4 + e^- \rightarrow C_2H_3 + H + e^-$ (8)

$C_2H_2 + e^- \rightarrow C_2H + H + e^-$ (9)

To dissociate ethine via reaction 9 more energy is needed (5.72 eV [12]) as for reaction 8 (4.60 eV [12]) to destroy ethene. Thus ethine is in the plasma region more stable than ethene. The amount of acetylene is for this reason higher than the amount of ethene for power above 45 W.

Fig.4 Conversion of methane as a function of the adjusted generator power.

The produced amount of the three C2 hydrocarbons increases with the adjusted generator power as shown in Fig 3. The ethane amount rises from 2.25% to 4.64%. There is an elevation of the ethene amount from 0.22% to 0.36% and 0.19% to 0.42% for ethine. These results can be explained by the conversion of methane. **Fig.4** illustrates the conversion of methane as a function of the adjusted generator power. The conversion of methane increases with the input power. The methane conversion has a value of 11.8% at a plasma generator power of 30 W and rise to 36.5% at the highest power. The number of electron increases with the power, which means a greater number of micro filaments. A larger number of micro filaments imply also a larger volume in which the starting material has been converted. A higher conversion of the starting material stands for more reactive species like CH_3, CH_2 or CH. These radicals collide with other methane molecules to form C2 hydrocarbons. The fraction of these products rises, if the concentration of the radical increases.

Fig.5 Influence of the flow velocity on the ethane yield. The gas stream consists of 1.75% Methane and 0.75% carbon dioxide.

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The first paragraphs of this section have shown the produced amount of C2-hydrocarbons at a flow rate of 400 sccm. **Fig.5** illustrates the dependency of the ethane yield on the velocity of the gas stream. The starting streams for these experiments consist of 1.75% methane and 0.75% carbon dioxide and the gas flow was variegated between 200 and 800 sccm. If the flow is decreased, the amount of ethane increases from 3.0% (800 sccm) to 5.4% (200 sccm) at a power of 60 W. This result can be explained by the dwell time of the compounds in the plasma region. A shorter flow implies a longer time to convert methane by energy rich plasma electrons in the reactor. The concentration of the required CH_3 radicals increases in this case and reaction (4) becomes more likely.

The dwell time of the particles in the 1.06 cm^3 plasma volume has been variegated between 80 ms (800 sccm) and 320 ms (200 sccm). If the power of the plasma generator reaches 65 W and the gas flow has a value of 200 sccm, an arc is and, thus, no ethane is shown in **Fig. 5**. No measurements are done at these parameters to protect the reactor.

The following results have been originated at a flow rate of 200 sccm. The dependence of the produced amount of ethane from the composition of the inlet flow is shown in **Fig.6**. The concentration of methane was changed from 1.25% to 2.5%. The highest concentration (5.7%) of ethane is produced, if the flow of the starting material consists of 5 sccm methane and 195 sccm of the buffered gas helium and the power of the plasma has a value of 60 W. In this situation is the concentration of the needed methyl radicals (reaction 6) higher than for inlet flows which have beside methane a small amount of carbon dioxide. The probability of a collision of one methyl radical with a methane molecule increases, if the concentration of methane in the starting flow increases. This figure shows an increasing of the ethane concentration with increasing power of the plasma generator to higher values.

Fig.6 Produced amount of ethane as a function of the ceased generator power for different inlet mixtures at a flow rate of 200 sccm.

Ethene and ethine show similar results, if the flow rate and the composition of the starting material have been varieed.

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The results for the selectivity of this reactor to the three C2 hydrocarbons (**Fig.7**) are shown for a starting stream which consists of 5 sccm methane and 195 sccm helium.

Selectivity of a reaction is another important factor to characterise the DBD reactor. For the C2 hydrocarbons it is calculated by the following formula:

$$S_{H_2} = \frac{2 \cdot n_{C_2H_X}(\text{produced})}{n_{CH_4}(\text{converted})} \qquad (7)$$

An increase of the inlet power leads to a decrease of the ethane selectivity from 50.9% at 30 W to 24.5% at 65 W. Similar results have been observed for ethene and ethine. The reaction selectivity for these two products is lower than for ethane; the values range between 2.5% and 4.5%. Two effects explain the decline of the selectivity: 1) Higher hydrocarbons are created at a higher power and 2) it is easier to create hydrogen at a higher input power. The selectivity of ethene is lower than the selectivity of ethane by about a factor of ten. The reason is the number of reactions to get the compounds. Ethane needs at least two and the other two products need three or rather four different reactions.

Fig. 7 Selectivity of this reactor for the three C2 hydrocarbons as a function of the inlet power. The left graph shows the selectivity for this reaction to ethane and the right the selectivity of ethene and ethine.

4. CONCLUSION

1) This DBD reactor generates the three C2 hydrocarbons. The main component of these three compounds is ethane. The relative amount of ethene and ethine isless than 1%.

2) The produced amount of three hydrocarbons is dependent of the adjusted generator power. There is an increase of the concentration, if the power rises.

3) A lower flow stream leads to a higher generated amount of the C2 hydrocarbons.

4) An increase of the amount of methane in the starting stream results in an increase of the produced amount of ethane, ethene and ethine.

5) The highest amount of ethane (5.4%) has been generated, if the inlet flow consists of 5 sccm methane and 195 sccm helium.

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4) The selectivity of the three interesting products reaches a high value at a low plasma power in the DBD reactor. The selectivity for the plasma assisted reaction of methane to ethane reaches a value of 51% at 30 W, if the stream consists of 2.5% methane and 97.5% helium at a flow rate of 200 sccm.

5) A higher input plasma power raises the conversion of methane.

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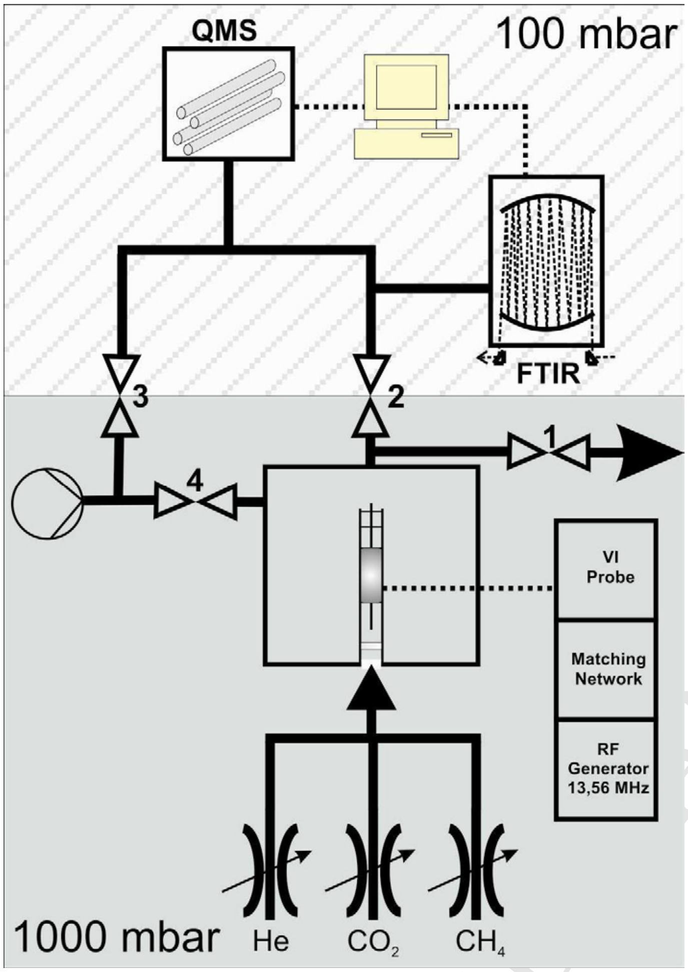

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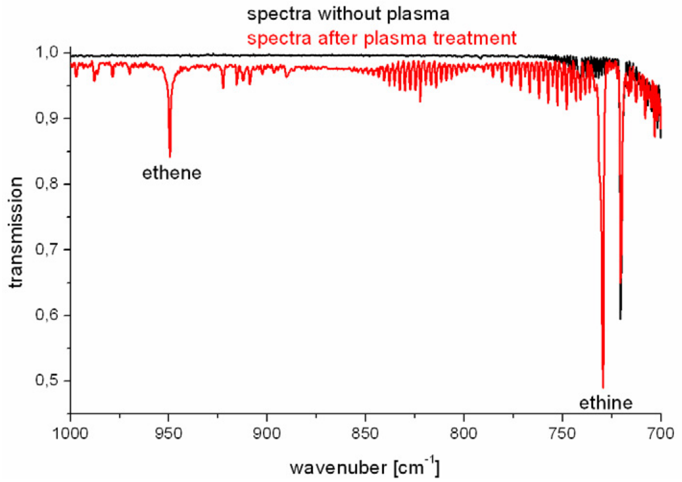

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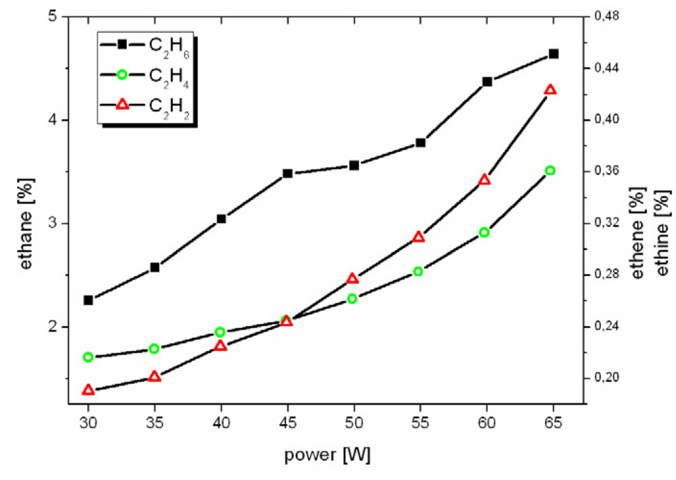

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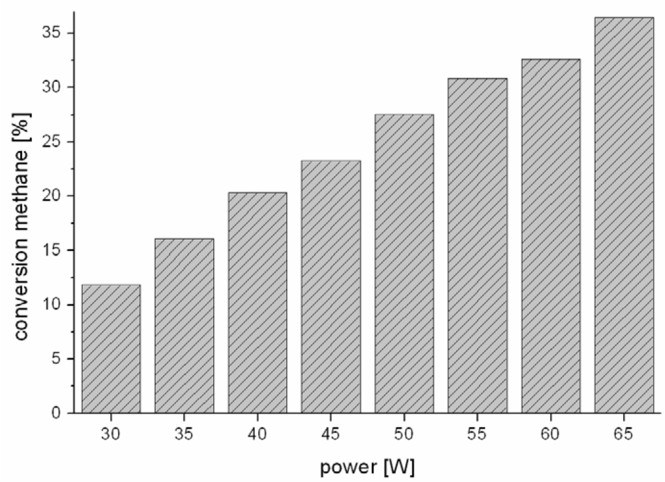

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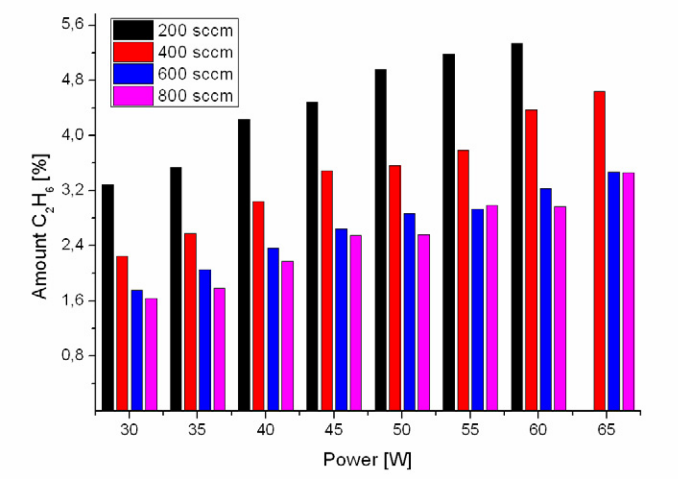

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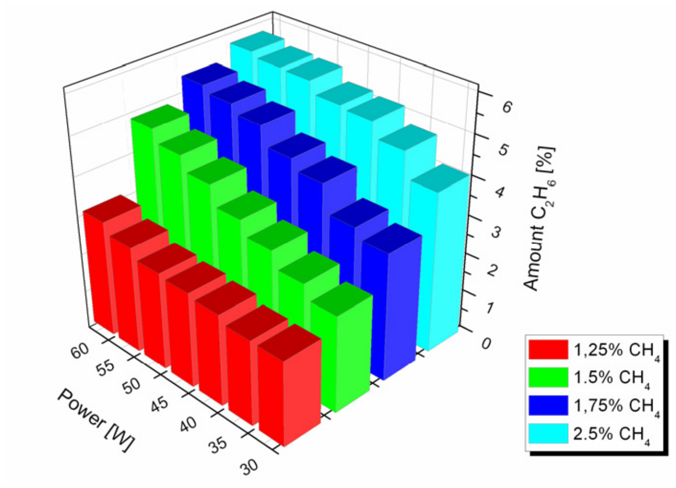

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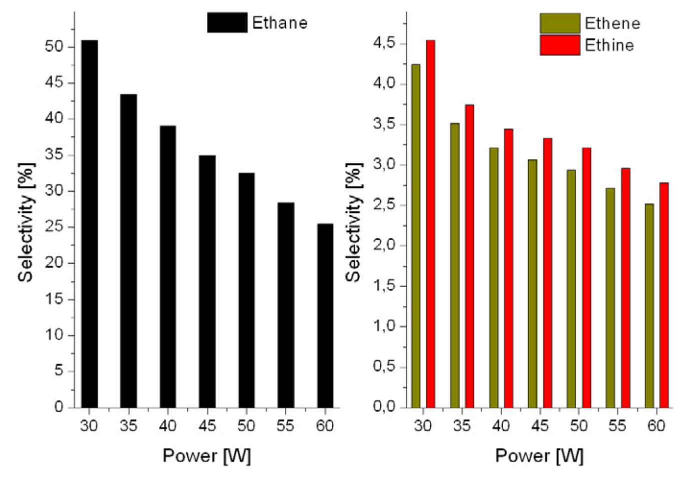

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