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Conversion of Methane and Carbon Dioxide in a DBD Reactor: Influence of Oxygen

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Abstract A continuous plug flow reactor supported by a dielectric barrier discharge (DBD) is used to study the conversion of methane, carbon dioxide, and oxygen at different compositions. The three studied gases were diluted with helium to 3 % with an overall flow rate of 200 sccm. The 13.56 MHz plasma was ignited at atmospheric pressure. The product stream and the inlet flow were analyzed by a FTIR spectrometer equipped with a White-cell and by a quadrupole mass spectrometer. The DBD reactor generates hydrogen, carbon monoxide, ethane, ethene, acetylene, formaldehyde, and methanol. Additional oxygen in the feed has positive effects on the yield of methanol, formaldehyde and carbon monoxide and reduces the total consumed energy. The hydrogen yield reaches its maximum at medium amounts of oxygen in the inlet flow. The conversion of methane increases to a limiting value of about 35 %. Methane rich feeds increase the yield of hydrogen, ethane and methanol. On the other hand, additional oxygen has a negative influence on the produced amount of C2 hydrocarbons. The conversion of methane and carbon dioxide as well as the yield of synthesis gas components and C2 hydrocarbons increases by changing the plasma power to higher values.

Keywords Cold plasma · Dielectric barrier discharge · Methane · Oxygen · Online monitoring

Introduction

Fossil fuels like crude oil or natural gas will be exhausted in the near future. These substances are not only used as a power fuel or to generate heat or electricity, but also source for producing organic basic chemicals via thermal or fluid catalytic cracking [1].

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Our work deals with the development of a new technique to generate synthesis gas and basic organic chemicals like C2 hydrocarbons and oxygenated hydrocarbons i.e. methanol and formaldehyde from alternative sources.

The conversion of gas mixtures of the greenhouse gases carbon dioxide and methane is one solution for this problem. CO_2 is obtained by burning fossil fuels while methane is the main component of natural gas. A mixture of both gases is generated in biogas, landfill or sewage plants by anaerobic microbial mineralization of organic compounds. The regenerative starting material for this process is organic solids. The main products are methane (40–70 %) and carbon dioxide (30–50 %) with oxygen, hydrogen, nitrogen and hydrogen sulfide being generated in minor concentration [2, 3].

To effectively convert methane and carbon dioxide, their reactivity has to be increased. One way to achieve that is the use of a non thermal plasma like a dielectric barrier discharge (DBD), a gliding arc, a corona discharge or a microwave discharge. Here, the low temperature of the molecules and ions and the high energy of the free electrons (up to 10 eV) is an advantage [4]. In this work a DBD reactor powered by a RF generator was used to ignite the plasma. Advantages of this plasma source are the absence of sparks and arcs, the flexibility of the reactor geometry, and the scale up [5].

The conversion of methane and carbon dioxide in a DBD reactor has been studied in many research projects. Synthesis gas components [6–10] (hydrogen and carbon monoxide), hydrocarbons [11, 12] and oxygenates [13, 14] have been obtained as products. Some research groups [15–21] have already studied the influence of oxygen on the plasma assisted conversion of CH_4 and CO_2 mixtures in a DBD reactor in the low and high frequency (40–5,000 Hz) range. However, no investigations at radio frequencies have been performed up to date. Thus, our research concentrates on the hitherto unexplored radio frequency range at 13.56 MHz.

In our current research the effect of oxygen on the conversion of methane and carbon dioxide mixtures is analyzed. For this study the amounts of the three inlet gases and the plasma power have been altered. The primary aim of this work is to increase the conversion of the reactants and the yield of the products.

Experimental Setup

The experimental Setup has been described in detail in a previous paper [12]. A fourth mass flow controller (MFC) has been used in this research in comparison to the previous work. These four MFCs have been used to adjust the 200 sccm gas flow consisting of methane (1.25–2.5 %), carbon dioxide (0–1.25 %) and oxygen (0–1 %). The remaining volume is our carrier gas, helium. These gas mixtures have been converted in a cylindrical DBD reactor at atmospheric pressure. A RF-generator and a matching network have been used to ignite the 13.56 MHz plasma. An Octive VI probe has been used to measure the voltage, the current and the phase shift between them in order to calculate the total consumed energy (TCE). This device is located between the plasma generating unit and the reactor. The reactor has a capacity of 32 nF which has been determined via impedance spectroscopy.

The reactor temperature reaches about 100 °C at the highest plasma power (70 W). The details for this measurement are explained in an article representing previous work [6].

For the analysis of the inlet gas and the product stream of IR active species a FTIR spectrometer has been used at a resolution of 0.5 cm^{-1} and a pressure of 100 mbar equipped with a White-cell providing an optical path length of up to 6 m. All compounds

which do not show a characteristic IR peak or are IR inactive have been monitored by a quadrupole mass spectrometer at a pressure of 10^{-5} mbar.

Results and Discussion

We have analyzed the recorded IR spectra between 5,000 and 500 cm^{-1} and identified carbon monoxide, formaldehyde, methanol, ethene and acetylene [13]. Hydrogen, methane, ethane, oxygen and carbon dioxide have quantitatively been studied in the mass spectrometer. Methane and carbon dioxide have characteristic IR peaks, but they absorb too intensively and for methane the C–H stretch around 3,000 cm^{-1} is characteristic for all hydrocarbons.

Helium has been used for dilution and to facilitate the ignition of the plasma. It is important because it can transfer energy to other molecules such as methane or carbon dioxide in collisions. As it does not itself actively take part in the chemistry of the plasma process it is neglected in the following discussion of the chemical conversion process.

Two different kinds of measurements have been performed to study the influence of oxygen on the plasma assisted conversion of methane and carbon dioxide (see section "Influence of Oxygen on the Conversion of Methane and on the Product Distribution"). The concentration of oxygen has been altered between 0 and 29 % in the first set of measurements. In that case, the undiluted gas flow without oxygen has consisted of 100 % methane and the power has been fixed to 35 W.

At this plasma power the concentration of the oxygenated products reached the highest values (see section "Influence of Methane, Carbon dioxide, and Plasma Power on the Product Distribution"). In the second part of this work the power (0–70 W) and the composition of the inlet stream have been varied (see section "Influence of Methane, Carbon dioxide, and Plasma Power on the Product Distribution"). The concentration of methane has been altered between 41.5 and 83 % at a fixed amount of oxygen (17 %) and carbon dioxide has accordingly been added to reach 100 %.

All measurements were carried out three times in order to access reproducibility and experimental errors. The product yields, conversions of the starting material, selectivity's and the TCE were averaged, and the *error bars* represent the standard deviation of the three measurements.

The following formulas were used to calculate the conversion (C) of the starting material and the selectivity (S) of the particular products:

$$C_x = \frac{n_{x,conv.}}{n_{x,0}}, \text{ where x represents } CO_2,\ CH_4 \text{ or } O_2; \quad n_{x,conv} = n_{x,0} - n_{x,end} \tag{1}$$

$$S_{H_2} = \frac{n_{H_2}}{2 \cdot n_{CH_4,conv.}} \tag{2}$$

$$S_{CO} = \frac{n_{CO}}{n_{CH_4,conv.}} \tag{3}$$

$$S_{C_2H_b} = \frac{2 \times n_{C_2H_b}}{n_{CH_4,conv.}} \quad \text{with } b = 2, 4 \text{ or } 6 \tag{4}$$

$$S_{CH_3OH} = \frac{n_{CH_3OH}}{n_{CH_4,conv.}} \quad (5)$$

$$S_{CH_2O} = \frac{n_{CH_2O}}{n_{CH_4,conv.}} \quad (6)$$

The TCE is calculated by the following formula:

$$TCE = \frac{P}{\dot{n}_{CH_4,conv.} + \dot{n}_{CO_2,conv.} + \dot{n}_{O_2,conv.}} \quad (7)$$

with P = measured power (VI Probe) [W], $\dot{n}_{x,conv.}$ = molar flow rate of reactant X converted [mol/s].

Influence of Oxygen on the Conversion of Methane and on the Product Distribution

The conversion of methane and oxygen as a function of the added amount of oxygen is shown in Fig. 1. The conversion of oxygen reaches a maximum value of 79 % for measurements with at least 19 % oxygen in the inlet gas. Oxygen dissociates in the plasma zone via reaction (8) into two O radicals. For low O_2 concentrations the probability for a collision of an energy rich electron with an oxygen molecule is lower than for high concentrations, resulting in a smaller conversion for low amounts of oxygen. The conversion reaches a limiting value, because the mean free paths of the electrons are not sufficiently large to dissociate all oxygen molecules upon a collision. Molecular oxygen has a large electron affinity. Thus, this molecule easily captures electrons in the plasma region and reduces their number. In turn, the negatively charged ion (O_2^-) with a high reactivity is able to convert methane for example to carbon monoxide and hydrogen.

Additional O_2 increases the conversion of methane from 25 % (without O_2) to 35 % (17 % O_2). For higher oxygen concentrations the conversion also approaches a limiting value. These results are explainable by the following reactions occurring as a primary or a secondary reaction in the plasma region.

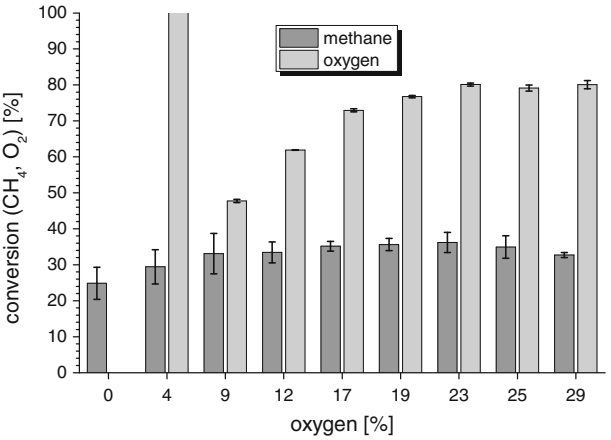

Fig. 1 Conversion of methane and oxygen as a function of the oxygen portion. The undiluted gas flow without oxygen consisted of 100 % methane. The power was adjusted to 35 W. The conversion of oxygen at 4 % oxygen is assumed to 100 %. The amount of oxygen is there out of the detection limit of the QMS. The *error bars* represent the standard deviation of the three measurements

$$O_2 \xrightarrow{e^-} O + O \tag{8}$$

$$CH_4 \xrightarrow{e^-} CH_3 + H \tag{9}$$

$$CH_4 + O \rightarrow CH_3 + OH \tag{10}$$

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{11}$$

Methane is dissociated through energy rich plasma electrons to a methyl and hydrogen radical [reaction (9)], regardless of the presence or absence of oxygen. In the presence of oxygen, the generated O radicals [reaction (8)] are very reactive and form an OH radical after a collision with methane [reaction (10)]. The OH radical can undergo another secondary reaction with methane to form water [reaction (11)]. Reactions (10) and (11) become more probable by increasing the concentration of oxygen, resulting in a higher conversion of methane.

Figures 2, 3, 4 illustrate the yields of the identified products as a function of the amount of oxygen in the inlet gas. The main products are hydrogen and carbon monoxide (Fig. 2), together known as synthesis gas. The generated amount of carbon monoxide grows from 1 to 18 % if the oxygen concentration in the inlet gas increases. The hydrogen yield (24 %) reaches a maximum at medium oxygen concentrations (17 %). These observations are explainable by the reactions (12–14) that lead to the formation of molecular hydrogen.

$$H + H + M \rightarrow H_2 + M \tag{12}$$

M represents another particle or the reactor wall.

$$H + CH_4 \rightarrow H_2 + CH_3 \tag{13}$$

$$CH_2 + O \rightarrow CO + H_2 \tag{14}$$

Molecular hydrogen can either be generated in a three body collision of two hydrogen radicals with another particle or the reactor wall [reaction (12)] or via reaction (13) following a collision of a hydrogen radical with a methane molecule. Reaction (14) comes into play for samples containing additional oxygen where CH_2 radicals are generated in a collision of the methyl radical with a plasma electron. This reaction requires an activation energy of 4.9 eV [22]. Since the free electrons of the plasma source have a temperature up to 10 eV [4] this is sufficient for an effective CH_2 generation. Reaction (14) becomes more relevant with increasing amount of oxygen in the feed resulting in an enhancement of the synthesis gas yield.

The hydrogen yield decreases again at even higher oxygen concentrations because oxygen is then able to react with methane to water [reactions (10) and (11)].

Another minor pathway is the formation of carbon dioxide following the collision of carbon monoxide with a hydroxyl radical forms carbon dioxide.

$$CO + OH \rightarrow CO_2 + H \tag{15}$$

The generated amount of carbon dioxide is small and therefore not illustrated in Fig. 2.

In addition to the yields of the synthesis gas components Fig. 2 also shows their ratio [n(H_2):n(CO)]. The H_2:CO ratio decreases with the addition of oxygen mainly because of the increase of the generated amount of carbon monoxide. Synthesis gas is needed in hydroformylations [23] of unsaturated alkenes or in Fischer–Tropsch reactions [24] to produce hydrocarbons. For these reactions particular ratios are required. A H_2:CO ratio of 1 is required for hydroformylation while a ratio of 2 is necessary to produce alkenes. Our

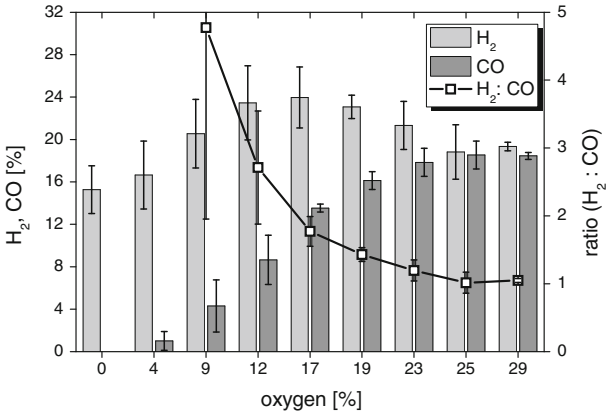

Fig. 2 Product distribution of the synthesis gas components (H_2 and CO), left scale, and their ratio (H_2:CO), right scale, for different amounts of oxygen in the inlet gas. The undiluted gas flow without oxygen consists of 100 % methane. The plasma power was fixed to 35 W at a total flow rate of 200 sccm. The *error bars* of the H_2 and the CO yield represent the standard deviation of the three measurements and *error bars* of the H_2:CO ratio are calculated by error propagation

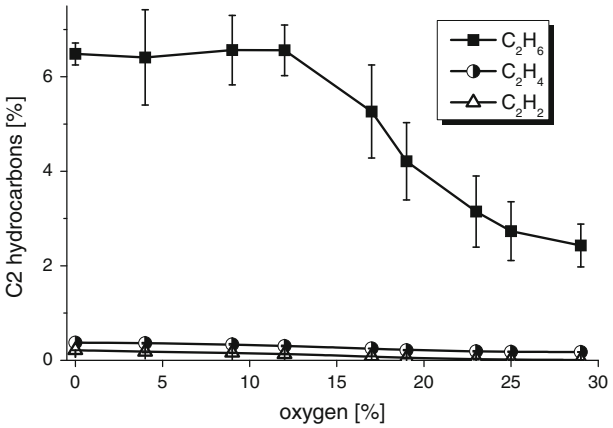

Fig. 3 Yield of C2 hydrocarbons as a function of the amount of oxygen. The undiluted gas flow without oxygen consists of 100 % methane. The plasma power was fixed at 35 W at a total flow rate of 200 sccm. The *error bars* represent the standard deviation of the three measurements

results provide the opportunity to adjust this ratio in a simple way by adding the required amount of oxygen.

The very large H_2:CO ratio at four percent oxygen content in the starting material is not displayed in Fig. 2 for clarity reason.

Ethane is the third important product in the conversion process beside the two synthesis gas components. Figure 3 shows the product distribution of the three C2 hydrocarbons (ethane, ethene, acetylene) for different amounts of oxygen.

A small amount of oxygen does not noticeably influence the product concentrations of these compounds as oxygen is not needed at all to generate these products. The starting point for this process is methane, dissociating via reaction (9) to CH_3. In order to form ethane, the methyl radical has then to collide with another methyl radical. For the generation of ethene and acetylene, additional steps are required in which CH_3 radicals have to collide one or several times with an energy rich electron to be dissociated to a CH_2 or CH

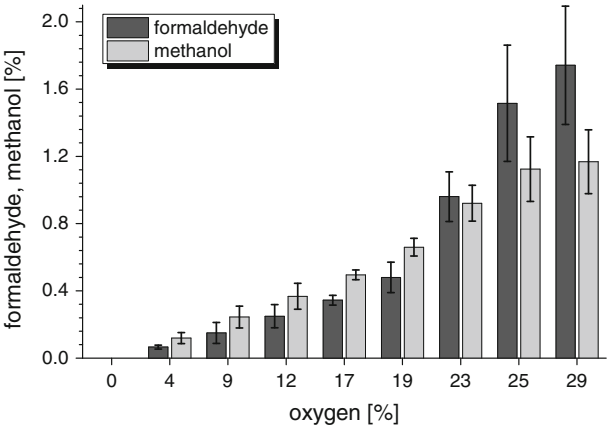

Fig. 4 Methanol and formaldehyde yields as a function of the amount of oxygen. The undiluted gas flow without oxygen consists of 100 % methane. The plasma power was fixed at 35 W at a total flow rate of 200 sccm. The *error bars* represent the standard deviation of the three measurements

radical. Those radicals will then undergo a reaction with a CH_2 or CH radical to form ethene or acetylene. Since multiple steps are required to generate the unsaturated hydrocarbons, this concentration is in our reactor generally low.

A higher percentage of oxygen has a negative effect on the production of ethane, ethene and acetylene. Two processes contribute to the inhibition of C2 hydrocarbons generated upon by adding oxygen. Firstly, the C2 hydrocarbons themselves can be destroyed in reactions with oxygen. Secondly, oxygen reduces the concentration of methane (water is formed) by reactions (10) and (11).

The striking contrast, oxygen has a large and positive effect on the produced amount of oxygenated hydrocarbons (methanol or formaldehyde). Our reactor generates maximally 3 % of these two products. Figure 4 illustrates the dependency of the methanol and formaldehyde yields on the concentration of oxygen in the inlet gas. The amounts of both oxygenated products rise to 1.2 % (MeOH) and 1.7 % (formaldehyde) by increasing the amount of oxygen to 29 %. The generation of these two products can be understood by the following reactions are [25, 26]:

$$CH_3 + O \rightarrow H_2CO + H \tag{16}$$

$$CH_3 + OH \rightarrow CH_3OH \tag{17}$$

Both reactions are the result of collisions of two radicals originating from methane and oxygen, respectively CH_3 radicals are generated via the primary reaction (9) or via the secondary reaction (10) which simultaneously generates the needed OH radical for reaction (17). O radicals are created via the primary reaction (8) by the action of plasma electrons. The concentration of each of the oxygenated products is <2 % because the radical concentration in weakly ionized plasmas is also low [5] and, therefore, the collision of two radicals is less likely. In addition, oxygenated products are easily destroyed because they are a highly reactive with radicals like OH, O, and H which are formed in large abundance in the DBD reactor during the plasma process.

Larger amounts of oxygen in the inlet gas lead to a higher conversion of the starting material in the DBD reactor; resulting in higher concentrations of the required radicals for

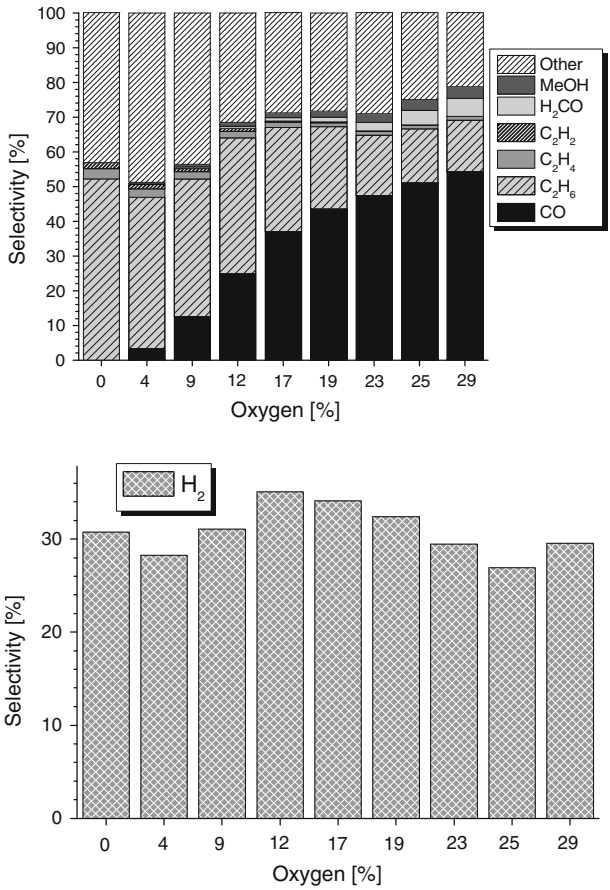

Fig. 5 *Above* selectivity calculated from C balance as a function of the added oxygen. *Below* selectivity of methane to hydrogen. The undiluted gas flow without oxygen consists of 100 % methane. The plasma power was fixed at 35 W at a total flow rate of 200 sccm

reactions (16) and (17). As a consequence an increase in the concentration of oxygenates is observed if the oxygen amount in the inlet gas is increased.

Another important aspect which is discussed in the following subsection is the selectivity of the relevant plasma processes. Figure 5 illustrates the dependence of the selectivity for methane conversion on the amount of oxygen in the inlet gas. The missing fraction to 100 % selectivity being calculated from C-balance is assumed to be due to the generation of higher hydrocarbons which cannot identified quantified with the used FTIR and mass spectrometer. All together, five selectivity effects are observed upon adding oxygen. Firstly, the selectivity for hydrogen formation remains constant with the experimental error since no additional reactions generating hydrogen occur after adding oxygen. Secondly, the selectivity for CO increases because of reaction (14). Thirdly, the selectivity to form ethane reaches a maximum at a low oxygen concentration. The reason is that starting radicals for the ethane generation are produced from reactions with O radicals with methane and that high concentrations of oxygen combust the methane, resulting in a decrease of the ethane selectivity. Fourthly, the selectivity of the unsaturated C2 hydrocarbons decreases after adding oxygen. Fifthly, the selectivity of the oxygenated hydrocarbons (methanol and formaldehyde) reaches a maximum at a high concentration of oxygen because O radicals are needed to form those products.

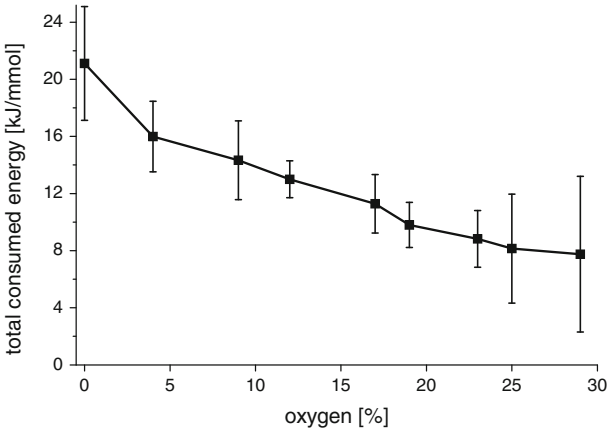

Fig. 6 Total consumed energy for different concentration of oxygen. The undiluted gas flow without oxygen consists of 100 % methane. The plasma power was fixed at 35 W at a total flow rate of 200 sccm. The *error bars* represent the standard deviation of the three measurements

The influence of oxygen in the inlet gas on the TCE is shown in Fig. 6. Additional oxygen decreases the consumed energy from 21 to 8 kJ/mmol. Even one oxygen molecule that is dissociated in the DBD reactor via reaction (8) into two O radicals will convert four methane molecules via reactions (10) and (11). Thus, the increase in the conversion efficiency goes along with a decrease of the TCE. Similar values of 5–10 kJ/mmol have been reported in the literature [4, 16] for a DBD reactor. However, the present work has not focused on minimizing the energy consumption, but instead to investigate and understand relative trends in product composition when oxygen is added.

Influence of Methane, Carbon Dioxide, and Plasma Power on the Product Distribution

In section "Influence of Oxygen on the Conversion of Methane and on the Product Distribution" we have analyzed the influence of different concentrations of oxygen on the conversion of methane and the product distribution in the DBD reactor at a fixed power (35 W). In this section we will discuss the influence of different concentrations of methane, carbon dioxide and the variation of the plasma power on the conversion process at a fixed amount of oxygen in the inlet gas (17 %).

Before discussing the product distribution the conversion of the starting materials will be analyzed. The conversion of methane and carbon dioxide as a function of the plasma power for different compositions of the inlet gas is shown in Figs. 7 and 8. As the number of micro filaments in the reactor rises by increasing the power in the plasma region, the conversion of both components also increases with increasing power.

Generally, the conversion of methane is always larger than the conversion of carbon dioxide. Methane is fragmented by plasma electrons via reaction (9), while carbon dioxide is converted by the following process:

$$CO_2 \xrightarrow{e^-} CO + O \tag{18}$$

For the electron assisted dissociation of CO_2 (5.52 eV [27]) more energy is required than for the fragmentation of CH_4 (4.45 eV [27]), reaction (9). Moreover, the additional oxygen from reaction (8) is another source to accomplish the conversion of methane via reaction (10) while there are no additional reactions of carbon dioxide with oxygen.

Negative conversions are observed for carbon dioxide at a power of 30 and 35 W, i.e. a production of CO_2 takes place. Carbon dioxide production occurs either via reaction (15)

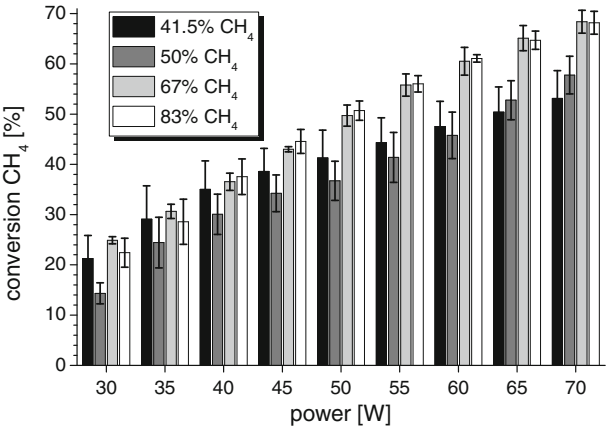

Fig. 7 Conversion of methane as a function of the concentration of the starting material (CH_4, CO_2 and O_2) and the plasma power. The amount of oxygen was fixed at 17 %. The *error bars* represent the standard deviation of the three measurements

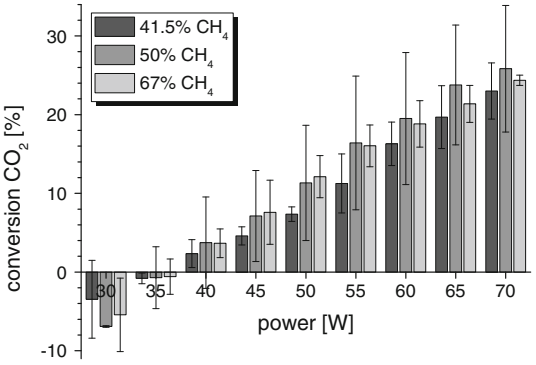

Fig. 8 Conversion of carbon dioxide as a function of the concentration of the starting material (CH_4, CO_2 and O_2) and the plasma power. The amount of oxygen was fixed at 17 %. The *error bars* represent the standard deviation of the three measurements

or via back reaction of reaction (18). For reaction (15) to occur, oxygen needs to form an OH radical first after a collision with methane [reaction (10)], which can then collide with CO to form carbon dioxide. The back reaction of reaction (18) becomes more likely because additional oxygen increases the concentration of O radicals significantly. At low plasma power, the energy of the plasma is not high enough to counter balance this CO_2 production by the conversion process.

For any fixed plasma power, the highest conversion of methane is reached at the highest concentration of methane and for low amounts of carbon dioxide. For this starting material composition, a collision of a methane molecule with a plasma electron, an O, or an OH radical is most probable.

The conversion of oxygen for different compositions of the inlet gas and the plasma power is listed in Table 1. The composition of the inlet gas does not significantly affect the conversion of oxygen because the amount of O_2 was fixed only for very large plasma powers a high methane concentration significantly increases the oxygen conversion. At low plasma power (30 W) little more than 50 % of O_2 is converted. An increase in the power above 30 W generally increases the conversion to a limiting value of around 75 % because the plasma electrons cannot dissociate all oxygen within the short residence time of only

Table 1 Conversion of oxygen as a function of the concentration of the starting material (CH_4, CO_2) and the plasma power

Power (W)	Conversion of oxygen (%)			
	41.5 % CH_4 41.5 % CO_2 17 % O_2	50 % CH_4 33 % CO_2 17 % O_2	67 % CH_4 16 % CO_2 17 % O_2	83 % CH_4 0 % CO_2 17 % O_2
30	64.3	54.8	58.2	65.1
35	64.4	70.9	65.4	72.0
40	74.7	74.3	70.0	74.1
45	76.2	74.7	71.5	74.3
50	76.5	74.7	72.1	75.1
55	76.6	74.7	72.0	75.2
60	77.0	75.3	72.5	75.6
65	77.3	75.5	73.9	100
70	77.6	77.8	100	100

The amount of oxygen was fixed at 17 %

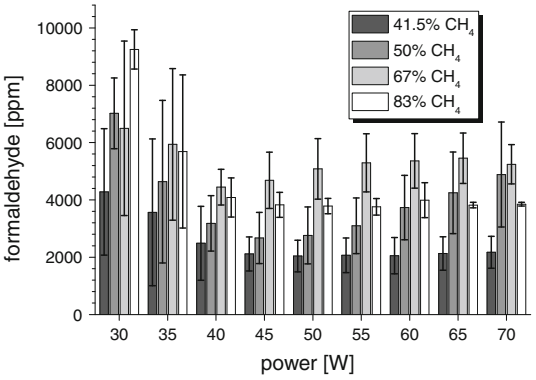

Fig. 9 Formaldehyde yield for different compositions of the inlet gas and plasma power. The amount of oxygen is fixed at 17 %. The *error bars* represent the standard deviation of the three measurements

320 ms of the starting material in the reactor. Only if the power was increased to 65 W with 83 % methane, and at 70 W for the measurement with 67 % methane all oxygen molecules could be converted. Under these conditions the concentration of hydrogen radicals in the reactor is very large which react with molecular oxygen to an oxygen radical and a hydroxyl radical.

The following part of this section addresses the product distribution. The components are discussed in the order of the influence of additional oxygen.

The influence of different compositions of the inlet gas and of the plasma power on the formaldehyde yield is shown in Fig. 9. The produced amount of formaldehyde reaches the highest values at the lowest power and decreases by increasing the power from 30 to 45 W. The mechanism for the formaldehyde generation has been discussed in section "Influence of Oxygen on the Conversion of Methane and on the Product Distribution". The collision of a methyl with an oxygen radical is the final reaction to form formaldehyde [reaction (16)] where carbon dioxide is another source for oxygen radicals.

Generally, radicals like OH, H, and O will destroy the formed formaldehyde. As the concentration of these radicals increases with the plasma power, the formaldehyde yield

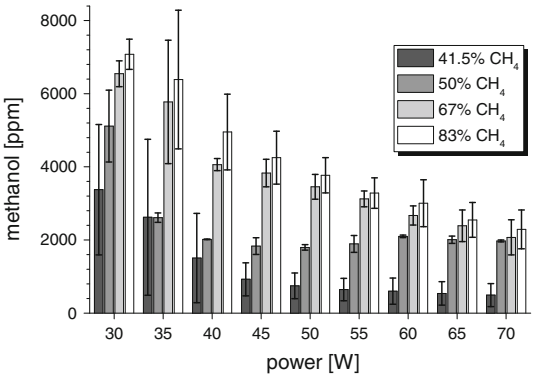

Fig. 10 Influence of the plasma power and the composition of the inlet gas on the concentration of methanol. The amount of oxygen is fixed at 17 %. The *error bars* represent the standard deviation of the three measurements

decreases. For plasma powers larger than 40 W and methane pure and rich inlet gas mixtures the H_2CO yield is independent of the plasma power. Here, the formaldehyde yield remains constant because the formation and decay reactions are in equilibrium: with increasing power more O radicals are available to produce CO, but at the same time the concentration of the destructive radicals increases in the same way. For the measurements with 50 or 67 % methane the concentration of formaldehyde slightly rises again after increasing the power to values beyond 45 W. Now, reaction (18) occurs with a higher probability because the electric field in the reactor rises with the plasma power. The result is a higher concentration of the O radicals which are required for reaction (16).

In general, the highest formaldehyde yield is found for measurements with 67 % methane, 16 % CO_2 and 17 % O_2 for any fixed plasma power. Only for the lowest power, a higher methane concentration leads to a higher formaldehyde concentration.

The concentration of the methanol product decreases with the power as shown in Fig. 10 for different compositions of the inlet stream. The formation process in this case is a collision of two radicals (CH_3 and OH) via reaction (17). The decrease of the methanol yield is explained by the formation of other reactive radicals in the DBD reactor. The details are discussed in the formaldehyde paragraph above.

In contrast to the case of formaldehyde the production of methanol increases with increasing concentration of methane in the inlet gas at any fixed plasma power. The concentration of CH_3 radicals in the DBD reactor is larger at a higher methane concentration. Thus, the collision of an OH radical with a CH_3 radical becomes more probable.

The highest concentration of methanol (7,100 ppm) is generated at a power of 30 W and for a carbon dioxide free inlet gas consisting of 83 % methane and 17 % oxygen only.

Figure 11 illustrates the dependency of the hydrogen and carbon monoxide yields on the composition of the inlet gas. For all inlet gas compositions, the yield of the synthesis gas components (hydrogen and carbon monoxide) increases when the plasma power rises from 30 to 70 W. The mechanism for the generation of these products is discussed in section "Influence of Oxygen on the Conversion of Methane and on the Product Distribution" for measurements without carbon dioxide. Carbon monoxide is generated via the primary plasma [reaction (18)], via reaction (14) reaction or by a collision of methanol or formaldehyde with an oxygen or hydroxyl radical. Reactions (19) and (20) illustrate the latter pathway for the example of the collision of formaldehyde with an O radical.

$$H_2CO + O \rightarrow CHO + OH \tag{19}$$

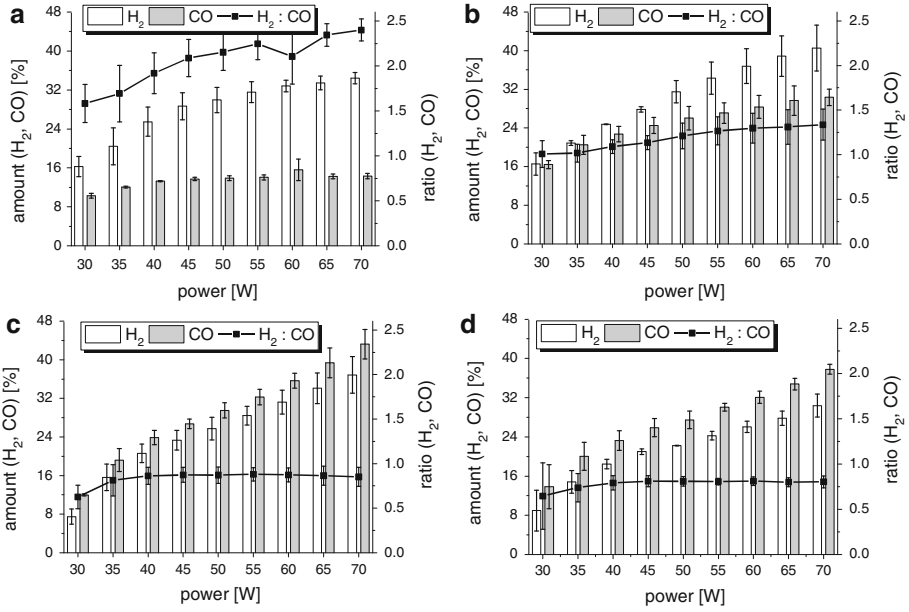

Fig. 11 Yield of the synthesis gas components as a function of the power and the composition of the inlet gas at a fixed amount of oxygen (17 %) (**a**) 83 % CH_4, 17 % O_2 (**b**) 67 % CH_4, 16 % CO_2, 17 % O_2 (**c**) 50 % CH_4, 33 % CO_2, 17 % O_2 (**d**) 41.5 % CH_4, 41.5 % CO_2, 17 % O_2. The *error bars* of the H_2 and the CO yield represent the standard deviation of the three measurements and *error bars* of the H_2:CO ratio are calculated by error propagation

$$CHO + O \rightarrow CO + OH \tag{20}$$

If the input energy is increased by increasing the power, the number of micro filaments is accordingly increasing resulting in a higher amount of radicals generated via reactions (8), (9) and (18). Some of the formed species are the starting point to form synthesis gas.

Figure 11a–d shows the synthesis gas formation for decreasing the concentration of methane in the inlet gas. The produced amount of hydrogen reaches a maximum for 67 % CH_4, 16 % CO_2, 17 % O_2 (see Fig. 11b). The formation of H_2 in the absence of carbon dioxide is discussed in section "Influence of Oxygen on the Conversion of Methane and on the Product Distribution" resulting from reaction (13) (collision of H with CH_4) and (14) ($CH_2 + O$). Additional CO_2 in the reaction mixture forms formaldehyde which is able to react with hydrogen radicals to form molecular hydrogen:

$$H_2CO + H \rightarrow HCO + H_2 \tag{21}$$

This reaction reaches the highest probability at low concentrations of carbon dioxide (Fig. 11b).

The concentration of product carbon monoxide does not reach its maximum for the highest concentration of reactant carbon dioxide. The CO product can be produced by one or more of the following mechanism:

1. Dissociating of CO_2 via plasma electrons [reaction (18)].
2. The reaction of a CH_2 radical with an O radical [reaction (14)].
3. The destruction reaction of formaldehyde and methanol via O or OH radicals [reactions (19) and (20)].

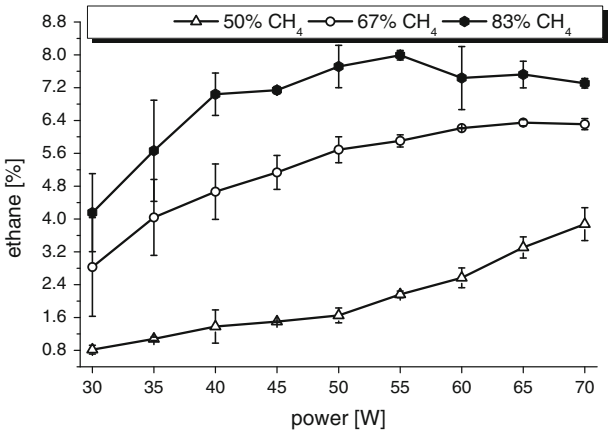

Fig. 12 Influence of the plasma power and the composition of the inlet gas on the ethane yield. The amount of oxygen is fixed at 17 %. The *error bars* represent the standard deviation of the three measurements

The optimum for the CO yield is achieved for a composition consisting of 50 % CH_4, 33 % CO_2, and 17 % O_2.

The ratio of the two synthesis gas components (H_2:CO) is an important factor for industrial application. This parameter decreases by increasing the amount of carbon dioxide in the inlet gas. In that case, the amount of hydrogen decreases, while the concentration of CO increases. The ratio is independent of the plasma power for measurements with a large carbon dioxide concentration in the inlet gas (Fig. 11c, d). A methane rich inlet stream generates a ratio of H_2:CO that increases by increasing the plasma power (Fig. 11a, b).

The highest yield of hydrogen (41 %) is generated in a mixture, consisting of 67 % CH_4, 16 % CO_2, and 17 % O_2 at a power of 70 W. 44 % is the highest produced amount of CO for the same power.

The amount of ethane rises with increasing the power from 30 to 70 W (Fig. 12). A higher plasma power represents a higher concentration of the required CH_3 radicals which are needed to form ethane:

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M \tag{22}$$

M represents another particle or the reactor wall.

A higher concentration of methane in the inlet gas increases the concentration of ethane at any fixed plasma power. Higher concentrations of the CH_3 radicals are generated in a reaction mixture consisting of mostly methane to undergo reaction (22). No ethane at all has been detected for measurements consisting of 41.5 % or less methane in the inlet gas. The unsaturated C2 hydrocarbons are not discussed in this section because their yield is smaller than 0.7 % and oxygen has only a minor effect on the distribution of these products.

Conclusion

Oxygen increases the yield of methanol by a factor of 10 and the yield of formaldehyde by a factor of 26 at a fixed plasma power of 35 W. The methane conversion rises from 25 % under oxygen free conditions to a limiting value of approximately 35 % with oxygen. The hydrogen yield reaches a maximum at 17 % of oxygen in the inlet gas. Additional O_2 is

able to combust methane to carbon monoxide, thus increasing the amount of CO. In contrast, the yield of C2 hydrocarbons drops by adding oxygen. While not in the focus of this work it is worth to note that the TCE is reduced by almost a factor of three by adding oxygen to the inlet gas flow.

The yield and the conversion of nearly all products are increased by changing the power to higher values. Only the concentrations of methanol and formaldehyde decrease under these conditions, with the latter approaching a lower limiting value. The concentrations of methanol, hydrogen and ethane rise with increasing concentrations of methane in the inlet gas, while carbon dioxide rich inlet gas increase the amount of produced CO.

It is possible to adjust the composition of the generated synthesis gas such that it can either be used for hydroformylation (H_2:CO = 1) or for Fischer–Tropsch synthesis of alkenes (H_2:CO = 2) by changing the amount of oxygen, methane and carbon dioxide in the inlet gas mixture and by controlling the plasma power.

The influence of water on the plasma assisted conversion of methane and carbon dioxide has been analyzed in a previous publication [27]. The H_2:CO ratio can be controlled by adding water to the inlet gas mixture. The ratio increases upon addition of water. The product gas composition in biogas conversion depends on the experimental conditions. Since the starting material for the conversion of CH_4 and CO originating from different regenerative sources (biogas, landfill, or sewage plants) has variable compositions, a required product ratio (H_2:CO) is adjustable by adding water or oxygen to mixtures of methane and carbon dioxide.

In addition, it is shown, that an oxygen free apparatus is not necessary for this DBD reactor, thus facilitating its use in every day applications.

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