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Conversion of biogas like mixtures to C2 hydrocarbon in a plug flow reactor supported by a DBD at atmospheric pressure

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A B S T R A C T

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.

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

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

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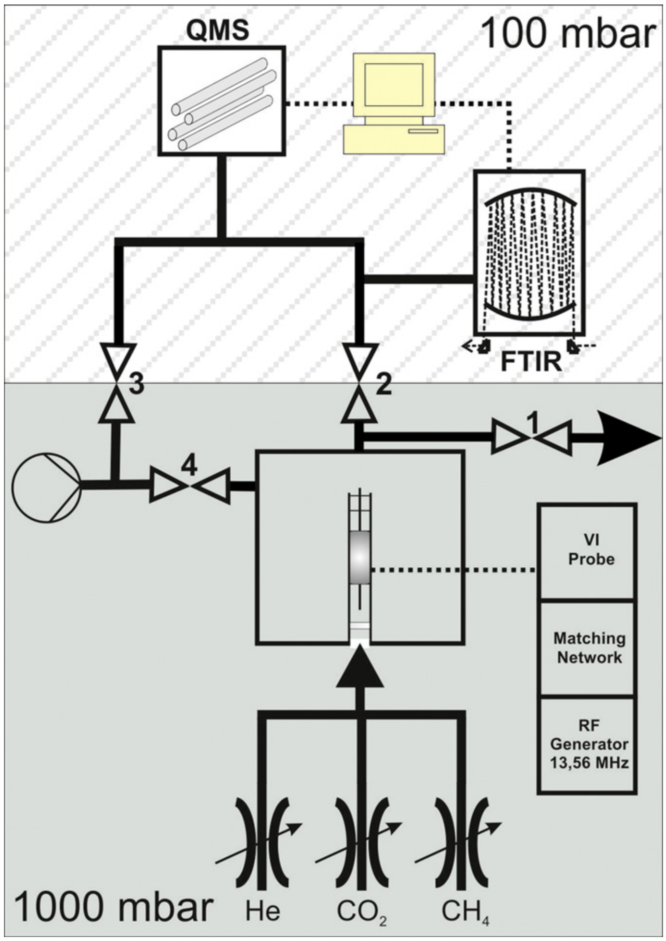

Fig. 1. Schematic setup; FTIR: fourier transform infrared spectrometer; QMS: quadrupole mass spectrometer; → gas flow system; dotted line: electrical interface.

fourier transform infrared spectrometer (FTIR) at a pressure of 100 mbar in the analysis domain and by a quadrupole mass spectrometer (QMS).

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 was 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 min 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 an 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 m. 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 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 s.

3. Results and discussion

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. The concentration ratio between ethane and ethen (and ethane and ethine) is approximately 13.

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:

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

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

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

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.

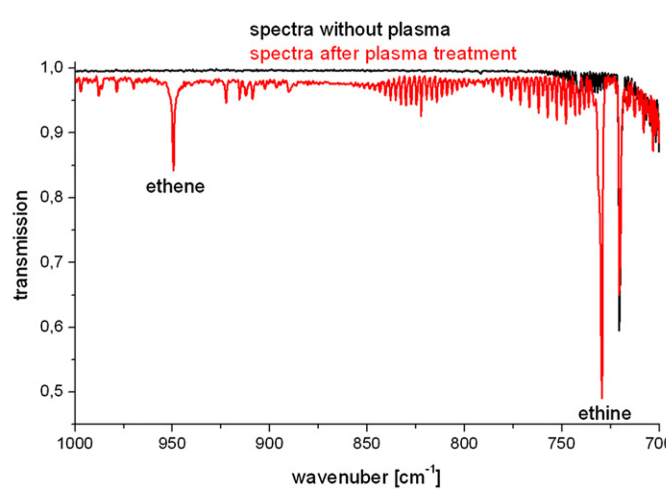

Fig. 2. Spectra of the inlet flow (7 sccm CH_4, 3 sccm CO_2, 390 sccm He) and the product stream (generator power: 65 W).