

A combined study for turning CO₂ and H₂O into value-added products in a dielectric barrier discharge

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Abstract: A combination of experiments and extensive modelling, including a chemical kinetics analysis, was performed for a CO₂/H₂O plasma in a dielectric barrier discharge. This provides a better understanding of the mechanisms related to the reactivity of the plasma and of the conversions into value-added products, such as methanol.

Keywords: dielectric barrier discharge, CO₂/H₂O interaction, water vapour, syngas production, methanol

1. Introduction

It is becoming a central strategy in the chemical industry to increase the use of renewable energy as a replacement for fossil fuels, to become more resource and energy efficient. One of the key molecules considered to continue on this road is CO₂. The reactions which are of greatest interest are those leading to the production of short-chain olefins (ethylene, propylene) and the conversion of CO₂ to syngas, formic acid, methanol and dimethyl ether, hydrocarbons via Fischer-Tropsch Synthesis and methane [1].

At first sight, the reactions in which CO₂ is involved can be divided into two categories, chemicals and fuels. The latter is being considered as the most suited target for the conversion of large volumes of CO₂ since its market size is 12-14 times larger than the former. One of the most interesting compounds is methanol, which is positioned exactly in the middle, as it is at the same time a raw chemical and a fuel (in combustion engines and fuel cells) [2]. Moreover, it has been extensively discussed that methanol and dimethyl ether (DME) can play a pivotal role in the energy scenario under the “methanol economy” concept [1].

Methanol synthesis from syngas (CO and H₂) is a well-known commercial process, and can also be realized starting from CO₂ and H₂. The traditional approach consists of a two-catalyst system, such as Cu/oxides, to catalyse the reversed water gas shift reaction, followed by a CO reduction to methanol (a typical catalytic system is Cu/ZnO/Al₂O₃) [1]. This is however considered to be a 3-step renewable energy process, since first an energy vector, H₂, has to be produced from electricity, which is then consumed to produce the desired chemical (renewable energy → electricity → hydrogen → chemical/fuel).

The use of plasmas, on the other hand, could provide us with a more efficient 2-step renewable energy process (renewable energy → electricity → chemical/fuel) when starting from CO₂ and H₂O. Therefore, we carried out

experiments in a dielectric barrier discharge (DBD), as well as extensive modelling and a chemical kinetics analysis. This was achieved in order to obtain a better understanding of the mechanisms related to the reactivity of CO₂/H₂O plasmas and of their conversions into value added products.

2. Description of the Model

2.1. 0D Chemical Kinetics Model

The computational model used in this work to describe the plasma chemistry is a zero-dimensional (0D) kinetic model, called Global_kin, developed by Kushner and coworkers [3]. In this work the 0D plasma chemistry module and the Boltzmann equation module are used. The time-evolution of the species densities is calculated, based on production and loss processes, as defined by the chemical reactions. The rate coefficients of the heavy particle reactions depend on the gas temperature and are calculated by Arrhenius equations. The rate coefficients for the electron impact reactions are a function of the electron temperature, and are calculated in the Boltzmann equation module. Finally, the electron temperature is calculated with an energy balance equation.

2.2. Plasma Chemistry Included in the Model

The CO₂ chemistry used in this study is adopted from the work of Aerts *et al.* [4] and the hydrocarbon chemistry from the work of Snoeckx *et al.* [5], while the H₂O/O₂ chemistry was taken from the work of Van Gaens and Bogaerts [6] to take into account the corresponding reactions with CO₂. The total chemistry set considers 122 different species, which react with each other in 344 electron impact reactions, 930 ion reactions and 537 neutral reactions. Their corresponding rate coefficients and the references where these data were adopted from are listed in [4-6].

3. Experimental

The experiments are carried out in a coaxial DBD reactor (see Fig. 1). A stainless steel mesh (ground electrode) is wrapped over the outside of an alumina tube with an outer and inner diameter of 30 and 26 mm, respectively. A copper rod with a diameter of 22 mm is placed in the centre of the alumina tube and used as high voltage electrode. The length of the discharge region is 100 mm with a discharge gap of 2 mm, giving rise to a discharge volume of 15.1 cm³. The DBD is supplied with an AFS generator G10S-V for a maximum power of 1000 W, with peak-to-peak voltage of 5 kV and frequency of 28.06 kHz. The Q-U Lissajous method is used to calculate the discharge power. The energy input is defined as the SEI (specific energy input), which is equal to the ratio of the calculated plasma power to the gas flow rate.

CO₂ is used as feed gas with a flow rate of 250 and 500 mL_n min⁻¹ with a continuous flow of water vapour. This water vapour is generated in a controlled manner using a steam generator (CEM mixer Bronkhorst). Between 0 and 12 % of water vapour was added to the CO₂ plasma. Furthermore, the entire system is heated up to 50 °C to avoid condensation and to promote nebulization of the water through the discharge.

The CO₂ conversion is studied using mass spectrometry (Hiden Analytical QGA MS) and optical emission spectroscopy (Andor Shamrock 500i OES), while electrical characterisation is performed by means of an oscilloscope (Tektronix DPO 3032) to evaluate the properties of the discharge. A small amount of H₂ is always observed by mass spectrometry when the plasma contains H₂O.

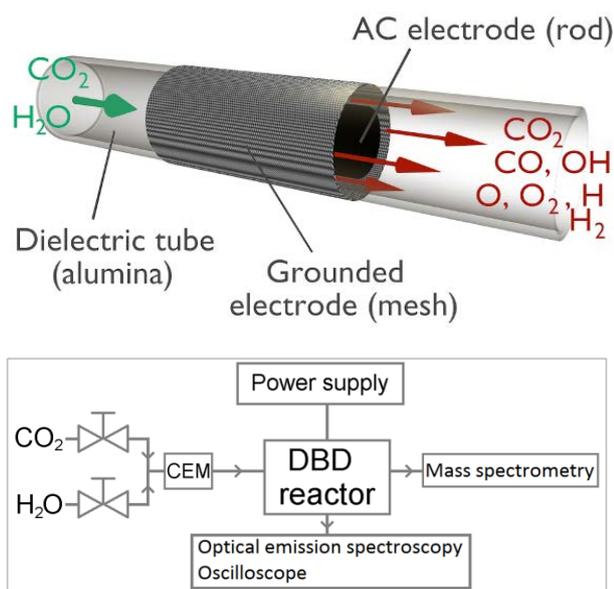


Fig. 1. Schematic of the experimental DBD reactor and the experimental setup.

4. Results

First, we will discuss the experimental results (section 4.1), explaining the effect of the water vapour and the residence time on the CO₂ and H₂O conversion. Subsequently we will compare these experiments with our modelling results, based on reactant conversion and product selectivity. This allows us to use the plasma chemistry in the model to describe and explain the observed trends (section 4.2).

4.1. Experimental Results

In Fig. 2 the experimental CO₂ and H₂O conversions are plotted as a function of water vapour percentage for a CO₂ flow rate of 250 mL_n/min. From these results it is clear that the CO₂ conversion is always the highest for pure CO₂, when no water vapour is added to the discharge. This behaviour may result from the destabilization of the discharge induced by the presence of water, since water has the tendency to trap free electrons. When going from 0 to 4 % water vapour the CO₂ conversion drops by a factor 2 for all SEI values investigated. When adding water vapour up to 12 % both the CO₂ and H₂O conversion continue to decrease slightly by 20-30 % and 10-20 %.

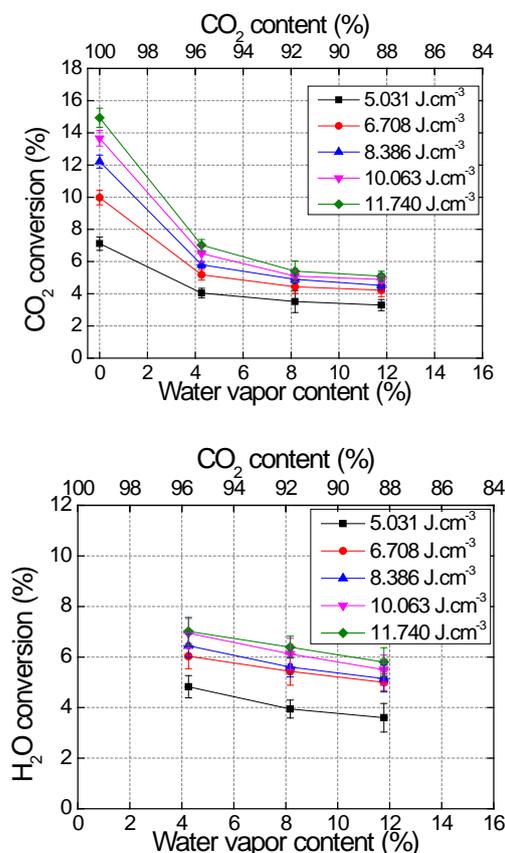


Fig. 2. CO₂ (top) and H₂O (bottom) conversion obtained by MS as a function of water vapour content for CO₂ flow rate = 250 mL_n.min⁻¹.

By increasing the flow rate from 250 mL_n/min to 500 mL_n/min, the residence time drops by a factor 2, thus the exposure time of the gas molecules to the discharge is shorter, and both the CO₂ and H₂O conversion decrease, as can be seen in Fig. 3. The presented results show that the CO₂ and H₂O conversion increase when the energy density, i.e. higher SEI, is applied for both CO₂ flow rates under study (see Figs. 2 and 3). For all investigated cases the main products formed are CO, H₂ and O₂.

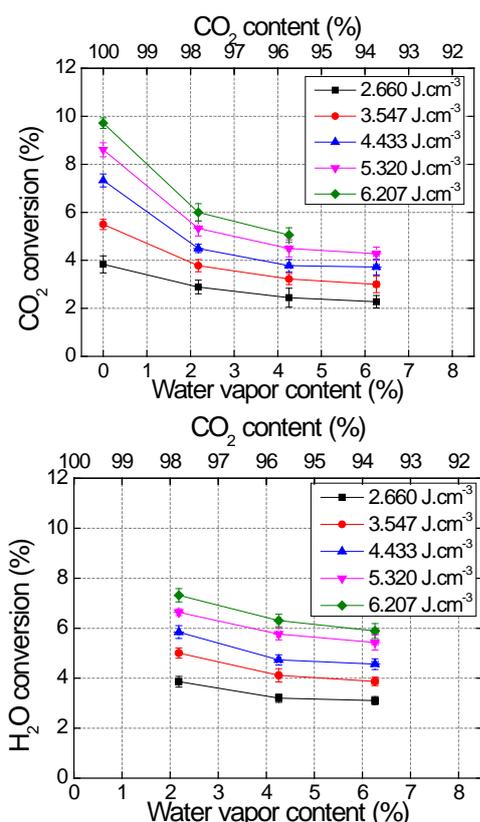


Fig. 3. CO₂ (top) and H₂O (bottom) conversion for obtained by MS as a function of water vapour content for CO₂ flow rate = 500 mL_n.min⁻¹.

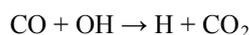
The increase in conversion with increasing SEI is however not strong enough to compensate for the higher energy use, resulting in a decrease of the energy efficiency. This effect is in line with other investigations, albeit for different gas mixtures [7-10]. In summary, the CO₂ and H₂O conversion show higher values at low concentrations of H₂O and high SEI, while the energy efficiency is higher at low SEI and low H₂O concentrations.

4.2. Analysis of the Plasma Chemistry

To obtain a one-to-one comparison between the experiments and our simulations, we performed simulations mimicking the exact experimental conditions.

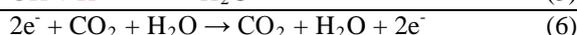
The same trends were observed as for the experiments with regard to the conversion of CO₂, H₂O and the selectivity towards CO, H₂ and O₂ (currently, the calculations are not all finished yet, but in the presentation, the calculation results will be compared in detail with the experimental data). This allows us to use the plasma chemistry in the model to describe and explain the observed trends.

The kinetic analysis reveals that the most important process is the reaction between CO and OH:



$$k = 5.4 \times 10^{-14} [\text{cm}^3/\text{molecule s}] (T/298 \text{ K})^{1.50} e^{250 [\text{K}]/T}$$

This reaction controls the ratio between the conversion of CO₂ and H₂O. To explain this in a very simple way, the following will be the main reaction path taking place:



Reactions (1) and (2) lead to the (electron impact) dissociation of CO₂ and H₂O, yielding the products OH and CO. However, due to the fast reaction rate constant of (3) these radicals will recombine to form again CO₂. Thus, two H atoms and one O atom are formed, and as explained before [10], these atoms recombine quickly to form OH and H₂O through reactions (4) and (5), respectively, which are both very fast reactions as well. In the end, this leaves us exactly where we started (6).

This is the reason why the conversion of CO₂ decreases when H₂O is added and especially why no production of methanol is observed. Indeed, all the hydrogen atoms that are needed to start forming CH and CHO fragments are being steered to OH and subsequently H₂O again.

5. Conclusions

We demonstrated that adding water to a CO₂ plasma in a DBD leads to a steep decrease in the CO₂ conversion, and when adding even more water both the CO₂ and H₂O conversion keeps decreasing slightly. As observed for other CO₂ mixtures, the conversion increases with increasing SEI, resulting from a decreasing residence time or increasing power. The energy efficiency shows the opposite trend and thus increases with decreasing SEI. The main products formed are CO, H₂ and O₂, and no methanol formation was observed experimentally. We were able to match the experimental results with our model calculations for an extensive chemistry set. The kinetic analysis of our model revealed why the CO₂

conversion decreases when adding water and especially why there was no methanol formation observed. In general, the main reactive species formed in the plasma are OH, CO, O and H. The problem is that the fastest reactions are the recombination reactions of OH and CO to CO₂ and H and the recombination reactions of O and H to OH and subsequently H₂O.

As we are able to correlate the lower CO₂ conversion with these reactions, this allows us to look for possible solutions. When combining the plasma with a catalyst, we should look towards a catalytic system, which is for example able to recombine the present H atoms to molecular hydrogen before it has the chance to recombine to OH and H₂O. Also a catalyst which is able to transform the CO together with H₂ to methanol before the CO recombines with OH to CO₂, would be interesting.

6. Acknowledgements

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