Plasma-based dry reforming of methane:
What role does N_2 play in a dielectric barrier discharge?

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Abstract: Plasma technology is considered to have great potential as a gas conversion and reforming technique. A lot of studies have already been performed on dry reforming of methane. However, a key aspect—that can have major consequences—hasn't been properly addressed yet; the fact that lab-scale studies generally use pure gases. Therefore, a combined computational and experimental study is presented to investigate the effects of N_2 on the plasma-based dry reforming of methane process using a dielectric barrier discharge.

Keywords: CH_4, CO_2, N_2, DBD, dry reforming, plasma modelling.

1. Introduction

The conversion of greenhouse gases (mainly CO_2 and CH_4) into value-added chemicals and fuels is one of the main challenges of the 21st century.[1-2] An efficient process capable of converting both gases can be considered to fit into the visionary "cradle-to-cradle" concept, converting waste (greenhouse gases) into a new feedstock (esp. fuels and raw materials).[3]

As a result, the combined reforming of both CH_4 and CO_2, dry reforming of methane (DRM), has gained significant interest over the years. Its main advantages over other reforming processes are the use of CO_2 as both a carbon source and oxidizing agent and the production of syngas (H_2/CO) in a ratio which is easily controllable. The main disadvantage for implementing catalytic DRM on an industrial scale is its inherent carbon deposition, which leads to catalyst poisoning. Nevertheless the formation of syngas by dry reforming of methane could provide a substantial use for CO_2 from industrial and natural sources.[4]

This led to a booming interest in alternative reforming technologies; based on biochemical, solar thermochemical, photochemical, electrochemical and last but not least plasmachemical conversion processes. As a matter of fact non-thermal plasma technology is among the most promising technologies.[5]

Numerous analyses and comparisons between these different technologies have been made in the literature; however, they all overlook a key aspect that has major consequences, i.e. the fact that lab-scale studies generally use pure gases (99.999 % purity), whereas industrial gases (with some exceptions) usually contain N_2. In our previous work we have already shown that the presence of N_2 can significantly influence the plasma physics and chemistry. In the case of CH_4/N_2 mixtures we found that the presence of N_2 enhances soot formation.[6] While in the case of CO_2/N_2 mixtures the presence of N_2 leads to the formation of harmful NO_x compounds.[7] Here we investigate the next logical step, the effect of N_2 on the plasma-based dry reforming of methane process.

2. Description of the model
2.1. 0D Chemical Kinetics Model

The model used in this work is a zero-dimensional (0D) plasma chemical kinetics model, called ZDPlaskin.[8] In this model, the time-evolution of the species densities is calculated by balance equations, taking into account the various production and loss terms by chemical reactions. Transport processes are not considered; hence, the species densities are assumed to be constant in the entire simulation volume. Although this means that the plasma is treated as a "batch reactor", we can convert this to represent a "plug-flow reactor", which is indeed close to the real situation, by translating the temporal behavior into a spatial behavior, as described below. The rate coefficients of the heavy particle reactions (i.e., atoms, molecules, radicals, ions, excited species) are assumed to be constant and adopted from the literature (see below), whereas the rate coefficients for the electron impact reactions are calculated with a Boltzmann solver, BOLSIG+,[9] which is integrated into ZDPlaskin. For a more detailed description of the model, we refer to the work of Panchesniy et al.[8]

The plasma chemistry used in this model was developed previously.[10]

2.2. Application of the 0D model to a DBD reactor

0D models can only calculate the species densities as a function of time, and thus they neglect spatial variations. Nevertheless, by using the gas flow rate, the time evolution can be translated into a spatial evolution (i.e. as a function of position in the DBD reactor). This spatial evolution is necessary to mimic the typical filamentary behavior found in DBDs used for CO_2 conversion. On their way throughout the reactor the gas molecules will pass through several micro-discharge filaments. This is mimicked in the model by applying a large number of consecutive triangular micro-discharge pulses, in the same way as described in our previous work.[11] This approach has already proven to be applicable for a variety of conditions, gas mixtures and different 0D simulation codes.

3. Description of the experiments

The experimental apparatus consisted of a dielectric barrier discharge (DBD) reactor, a power supply system, a reactant supply system, and measurement system. The DBD reactor was composed of a coaxial DBD with a quartz tube with an inner diameter of 44 mm. A stainless-steel rod with a diameter of 38 mm, was used as high voltage electrode, resulting in a 3 mm discharge gap. A 50 mm wide stainless-steel mesh was wrapped around the outside of the quartz tube to serve as a ground electrode. CH_4, CO_2 and N_2 are used as feed gases with a constant total flow rate of 200 sccm. The reactor is supplied by an adjustable high voltage AC power supply (Trek), which could supply voltage and current up to 20 kV. The discharge power was set to be 20–24 W, providing a specific energy input for all investigated cases of 6-7 J/cm³.

4. Results

Effluent gas flows from industrial and Carbon Capture Sequestration/Utilization/Recycling (CCS/U/R) often contain impurities, of which in most cases N_2 is the main component. Furthermore, in some cases research on plasma-based DRM is being performed in diluted N_2 streams, without accounting for its effects on the presented results. Therefore, it is of great importance to study the effect of N_2 on the plasma based conversion. The following specific questions need to be answered: how does N_2 affect the conversion (and thus energy efficiency), and which (by)products (e.g., useful products or harmful compounds) are formed. In our previous work we already investigated the effect of N_2 for both pure CH_4 reforming,[6] and pure CO_2 splitting.[7] In both cases the presence of N_2 led to unwanted effects, i.e., soot deposition and NO_x production, respectively. In theory, from a chemical kinetics point of view, this can be explained by the absence of an oxidant and the absence of a hydrogen source, respectively. As such, we hypothesize that both unwanted effects should not present themselves for the DRM process and the presence of N_2 might have no significant effect.

First we will show which effect varying the N_2 content in the mixture has on the conversions (section 4.1), then we will discuss the effects it has on the by-product formation (Section 4.2), and finally we will discuss our progress on modelling these results (Section 4.3).

4.1. Effect on the conversion

Interestingly, upon adding 25 % N_2 the absolute conversions of CH_4 and CO_2, decrease significantly by a factor 3 approximately. Upon adding 50 and 75 % N_2 they start increasing again, as shown in Figure 1(a). The effective conversion (which is the absolute conversion multiplied with the gas fraction) of CH_4 and CO_2 shows a similar 3–4 fold decrease upon adding 25 % N_2 to the mixture. The conversions slightly increase upon adding 50 % N_2 and decrease again upon adding 75 % N_2.

This behavior is rather unexpected. From our previous work on CH_4/N_2 and CO_2/N_2 such strong drop in the conversions when adding N_2 was not observed. The increase in absolute conversions—and steady behavior of the effective conversions—upon adding more N_2, on the other hand, are in line with the observations for CH_4/N_2 and CO_2/N_2.
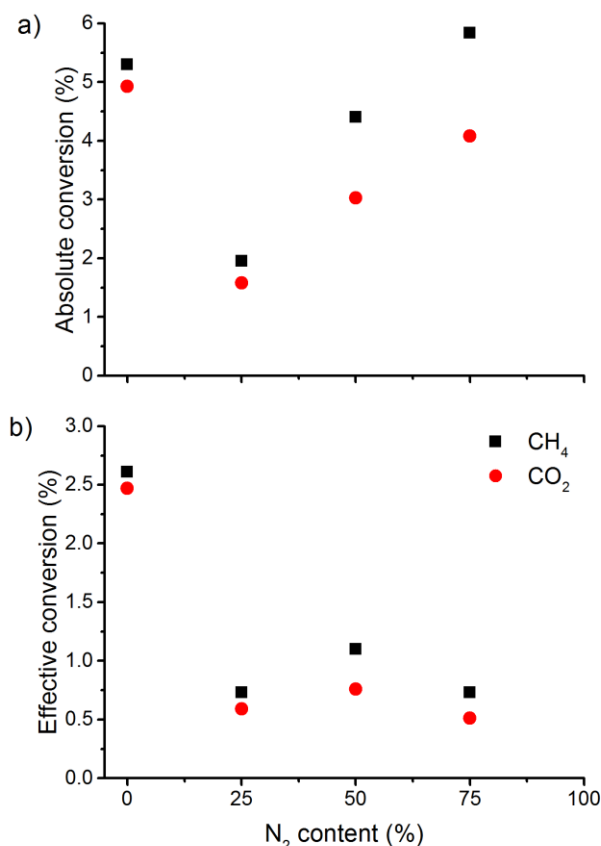

Fig. 1. Experimental absolute (a) and effective (b) conversion of CH_4 and CO_2 as a function of the N_2 content, for a 1:1 CH_4/CO_2 ratio, a fixed total flow rate of 200 sccm and a corresponding SEI of 6–7 J/cm³.

4.2. Effect on by-product formation

An overview of the different FTIR spectra for the experimental results is given in Figure 2. From these spectra it becomes clear that we do not form NO_x, since no peaks for NO (1875 cm^{-1}) and NO_2 (1599 cm^{-1}) emerge upon adding N_2 to the mixture. This is as expected due to the presence of CH_4 which can inhibit the formation of NO_x. This inhibition can be explained by the chemical pathways constructed based on the previous chemical kinetics modelling results. Indeed, whereas in a CO_2/N_2 mixture the O/O_2 species react with N/N_2 to form NO_x, in the presence of a hydrogen source they form H_2O due to the faster reaction rates of the reactions involved in the latter process. Additionally, any formed NO_x will also be reduced by the hydrogen containing species.[12]

The unwanted effect for CH_4/N_2 mixtures was the high soot formation. In the present study, as expected, this soot production does not present itself. However, we do clearly observe the deposition of a coating sticking on the reactor walls (Figure 3) for all the experiments with N_2.
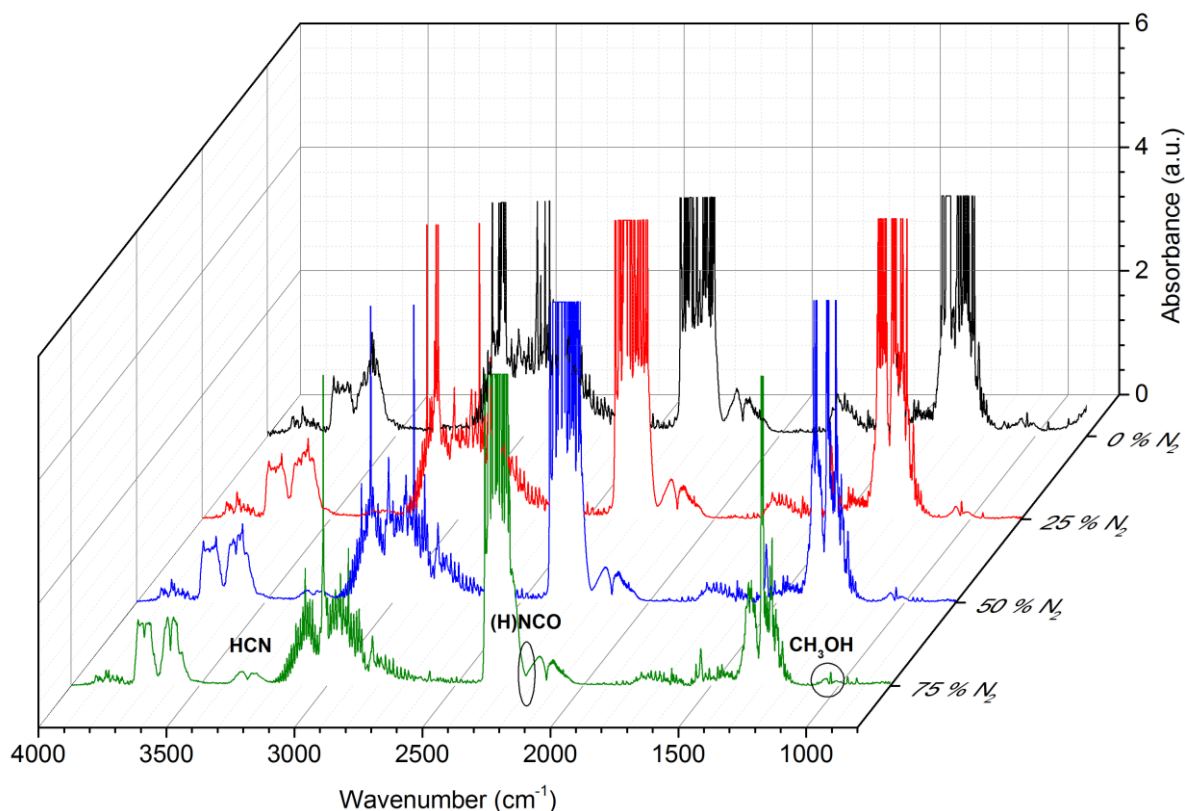
Fig. 2. FTIR spectra of a 1:1 mixture of $CH_4:CO_2$ with 0, 25, 50 and 50 vol% N_2 added. The peaks corresponding to HCN, (H)NCO and CH_3OH peaks are indicated.

An additional by-product created when adding N_2 is HCN, as can be identified from the FTIR spectra in Figure 2 and as also confirmed using GCMS analysis. The concentration of HCN increases with increasing N_2 addition. Another possible by-product that can be identified based on the FTIR spectra and the analysis in our previous work[12] is (H)NCO.
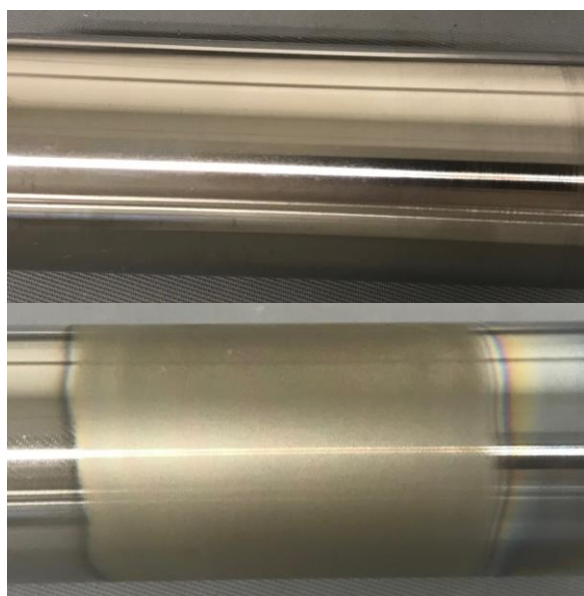

Fig. 3. Image of the inner electrode before (upper) and after (lower) plasma operation of a $CH_4/CO_2/N_2$ mixtures.

4.3. Modelling results

Regarding the CH_4 and CO_2 conversions, the preliminary modelling results show the same trends as found experimentally. The modelling results indicate that the severe drop in CH_4 and CO_2 conversion upon adding N_2 is partially the result of a decrease in the electron density by more than a factor 2.

When it comes to the by-product formation the model needs to be further optimized and validated, but at the moment it is able to predict the trends of the HCN formation.

Additional experiments for a lower and higher N_2 content are being performed, as well as a further optimization of the chemistry set used in the model. This will allow us to clearly show the pathways behind this severe decrease in conversions and the pathways towards these by-products.

5. Conclusions

We have shown that the presence of N_2 strongly influences the plasma chemistry of the plasma-based dry reforming of methane process and have taken the first steps in identifying the underlying reasons.

As expected, the addition of N_2 to a 1:1 mixture of $CH_4:CO_2$ does not lead to the formation of NO_x or soot deposition. We did, however, identify HCN (and possibly (H)NCO) as a by-product. Although, HCN is a very poisonous compound, it might not pose as big a problem as NO_x, since it could be easily separated through

condensation. Nevertheless, the presence of N_2 severely diminishes the conversion of both CO_2 and CH_4. The effective conversion and hence the energy efficiency are a factor 3–4 lower than for the mixture without N_2. Hence, it is highly probable that the plasma-based dry reforming process will only be viable if the feed gases do not contain N_2.

Future work will focus on further optimizing the chemical kinetics model to further evaluate the effect of other impurities on a wide range of plasma-based reforming processes.

6. Acknowledgements

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