Combining CO₂ conversion and N₂ fixation in a gliding arc plasmatron

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A B S T R A C T

Industry needs a flexible and efficient technology to convert CO₂ into useful products, which fits in the Carbon Capture and Utilization (CCU) philosophy. Plasma technology is intensively being investigated for this purpose. A promising candidate is the gliding arc plasmatron (GAP). Waste streams of CO₂ are often not pure and contain N₂ as important impurity. Therefore, in this paper we provide a detailed experimental and computational study of the combined CO₂ and N₂ conversion in a GAP. Is it possible to take advantage of the presence of N₂ in the mixture and to combine CO₂ conversion with N₂ fixation? Our experiments and simulations reveal that N₂ actively contributes to the process of CO₂ conversion, through its vibrational levels. In addition, NO and NO₂ are formed, with concentrations around 7000 ppm, which is slightly too low for valorization, but by improving the reactor design it must be possible to further increase their concentrations. Other NO-based molecules, in particular the strong greenhouse gas N₂O, are not formed in the GAP, which is an important result. We also compare our results with those obtained in other plasma reactors to clarify the differences in underlying plasma processes, and to demonstrate the superiority of the GAP.

1. Introduction

“A penny saved is a penny earned” is one important saying in industry. It is in this view that industry is looking for an easy and energy-efficient method to convert CO₂ from their waste streams. A technology intensively investigated for this purpose is based on plasma [1,2]. Plasma is created by applying electric power to a gas, causing breakdown of the gas into ions and electrons. It is thus a (partially) ionized gas, consisting of molecules, but also a large number of other species, such as various radicals, ions, excited species, and electrons. This makes plasma a highly reactive cocktail, useful for many applications [1,3]. The major advantage of plasma is that mainly the electrons are heated by the applied power, because of their small mass, and the energetic electrons can activate the gas by electron impact excitation, ionization, and dissociation, creating reactive species that can easily form new molecules. In this way, the gas as a whole does not have to be heated. Furthermore, owing to the fact that plasma can be switched on and off very easily, this technique also has great potential to store intermittent renewable energy, like solar and wind [2].

A very promising candidate for plasma-based CO₂ conversion is the gliding arc plasmatron (GAP). This is a three-dimensional gliding arc reactor [4,5]. A gliding arc (GA) plasma is created by applying a potential difference between two electrodes (cathode and anode), and typically moves (or glides) along these electrodes as a result of a gas flow. The GAP is a non-thermal plasma with different electron, and likely different vibrational, rotational and translational temperatures [6–8]. In the GAP under study here, the cathode forms the reactor body, while the reactor outlet is at anode potential. The gas enters through 6 tangential inlets so that a vortex flow is obtained. This stabilizes the arc plasma in the center of the reactor and part of the gas flow is actually forced to go through the plasma, while only limited heat loss occurs to the reactor walls. Note that the plasma column is actually not just one reference, but moves slower than the gas flow surrounding the plasma column [9,10]. The splitting of pure CO₂ and the dry reforming of methane (DRM) have already been investigated in this GAP [4,5,11], as well as in similar designs [12–20], and showed very promising results in terms of energy efficiency (i.e. up to 46% for pure CO₂ splitting and up to 67% for DRM). However, most industrial gas flows contain impurities, or even large gas admixtures, and it is often economically not feasible to separate them from the gas stream [21].

Aiming for the industrial implementation of this technology, it is crucial to study the effect of these impurities on the CO₂ conversion and on the formation of byproducts.

Most often, N₂ is the main compound in gas effluents [22]. Therefore, we study in this paper the effect of N₂ on the plasma chemistry of CO₂ conversion. We have performed experiments in a broad range of N₂...
concentration to find out how it affects the CO₂ conversion, as well as the energy cost and energy efficiency. Furthermore, we analyzed which useful or harmful byproducts are formed. This is specifically interesting to find out whether purification is needed and whether pre- or post-purification steps would economically be most viable. Besides that, we also evaluate for the first time whether a mixture of CO₂ and N₂ could be a starting point for combined CO₂ conversion and N₂ fixation, i.e., the conversion of N₂ molecules into simple nitrogen compounds, that form the building blocks for life on Earth [23,24]. If sustainable electricity can be utilized for the plasma generation and further conversion of NOx into NH₃ can be realized, this can offer opportunities as a green alternative for the Haber-Bosch process [24,25] and more in general for the arc discharge (indicated in purple) in the center of the reactor and forces the latter clearly affects the plasma chemistry, and thus the CO₂ conversion and byproduct formation. This will also be illustrated in this paper.

To our knowledge, such a comprehensive experimental and computational study for the addition of N₂ to CO₂ in a GAP has never been performed. In addition, only a few papers have reported on the effect of N₂ on CO₂ conversion in other types of plasmas [16,26–28]. However, in the paper by Snoeckx et al. [28], a detailed analysis of the byproduct formation in this mixture was never performed, which is of course crucial for practical applications. Furthermore, Snoeckx et al. [28] carried out this analysis for a dielectric barrier discharge (DBD), which has completely different plasma properties than a GAP [2].

The latter clearly affects the plasma chemistry, and thus the CO₂ conversion and byproduct formation. This will also be illustrated in this paper.

2. Description of the experiments

2.1. Gliding arc setup

The experiments were performed with a gliding arc plasmatron (GAP), which was developed at Drexel University by Nunnally et al. [4] and was previously described in detail [5]. A schematic picture of the GAP is shown in Fig. 1. The cathode (reactor body) has a length of 10.20 mm and a diameter of 17.50 mm, while the anode has a length of 16.30 mm and a diameter of 17.50 mm, respectively. These dimensions give rise to a GAP that was developed at Drexel University by Nunnally et al. [4].

A schematic picture of the gliding arc plasmatron in reverse vortex flow configuration. Both the forward and reverse vortex flows are indicated (with full and dashed spirals, respectively). This vortex flow configuration stabilizes the arc discharge (indicated in purple) in the center of the reactor and forces the reverse gas flow to go through the plasma.

Mass Flow Controllers (Bronkhorst) were used to insert CO₂ and N₂ into the GAP. The total flow rate was kept constant at 10 L/min. The N₂ concentration was varied between 5 and 95%. The reactor was powered by a DC current source type power supply. The plasma voltage and current were measured by a high-voltage probe (Tektronix P6015A) and a current sense resistor of 6 Ω, respectively. The electrical signals were sampled by a two-channel digital storage oscilloscope (Tektronix TDS2012C). The current was set at 0.23 A. The plasma power was calculated as the product of the plasma voltage and current over a certain time. All the experiments were performed three times. Subsequently, a propagation of uncertainty was applied to the results, to calculate the error bars.

2.2. Product analysis

The output gas composition is analyzed with three different gas analysis techniques: gas chromatography (GC) [5], Fourier Transform Infrared spectroscopy (FTIR) [28] and Quantum Cascade Laser (QCL) technology. The feed and main product gases (CO₂, N₂, CO, O₂) were analyzed by a three-channel compact gas chromatograph (CGC) from Interscience. Besides CO and O₂, some other products, like O₃ and NOx compounds (i.e., NO, NO₂, N₂O, N₂O₃ and N₂O₅) can be formed. We used a Nicolet 380 Fourier-Transform Infrared (FTIR) spectrometer (Thermo Fischer Scientific, Waltham, MA) and a CTS800 Analyzer (Emerson, Stirling, UK) based on Quantum Cascade Laser (QCL) technology to qualitatively and quantitatively analyze these products, respectively. These techniques, as well as the associated formulas to calculate the conversion, energy cost and energy efficiency, are described in detail in the Supplementary Information (Suppl. Info.).

3. Description of the model

The model used to simulate the chemical reactions in the GAP, is a 0D chemical kinetics model. It solves a set of conservation equations (Eq. 1) for all individual species included in the model:

\[
\frac{dn_i}{dt} = \sum_j \left( (a_{ij}^+ - a_{ij}^-)k_j \prod_{k} n_k \right)
\]

where \(n_i\) is the density of species \(i\), \(a_{ij}^+\) and \(a_{ij}^-\) are the stoichiometric coefficients of the species \(i\) on the right and left hand side of the reaction \(j\), respectively, \(n_k\) is the density of the species \(k\) on the neutral side of reaction \(j\), and \(k_j\) is the reaction rate coefficient of reaction \(j\). For example, for the 0th reaction \(A + B \rightarrow C + D\), the conservation equation for the density of species \(B\) is:

\[
\frac{dn_B}{dt} = (0 - 1)k_A n_A n_B.
\]

An extensive chemistry set, containing 18180 reactions and 134 species, is included in the model. The species interact with each other through electron impact reactions, electron-ion recombination, ion-ion, ion-neutral and neutral-neutral reactions, as well as vibration-translation (VT) and vibration-vibration (VV) relaxation. More information on these reactions and the list of species, as well as more details on the model, can be found in the Suppl. Info., including the GAP geometry as treated in the 0D model (Figure S1).

4. Results and discussion

4.1. CO₂ conversion, energy cost and energy efficiency

Fig. 3(a) shows that the absolute CO₂ conversion rises from 5 to 18% with increasing fraction of N₂ in the mixture. Hence, N₂ helps to convert CO₂ by the transfer of vibrational energy, as explained in section ‘Simulation results’ below. Indeed, CO₂ conversion in a GAP is most effective through the vibrational levels [5,29], and the N₂ vibrational levels help to populate these CO₂ vibrational levels. The same mechanism was also found for a microwave (MW) plasma [26], while in a DBD plasma, another mechanism is more prominent, i.e., energy transfer from the electronically excited N₂ molecules [28].

The effective CO₂ conversion is obtained by accounting for the initial fraction of CO₂ in the mixture (see Eq. (2) in the Suppl. Info.). Until
a N₂ fraction of 50%, the effective conversion only slightly decreases, while above 50%, the effective conversion drops quite fast from 5 to 1% (see Fig. 3(b)). Thus, at N₂ fractions below 50%, the increase in absolute CO₂ conversion can more or less compensate for the lower CO₂ concentration in the mixture, but at higher N₂ fractions, this is not true anymore. Indeed, not all the energy of the vibrationally excited N₂ is transferred into CO₂ dissociation, and part of it also remains stored in the N₂ vibrational levels or gets lost by collisions with ground state molecules (so-called VT relaxation). Thus, at higher N₂ fractions in the mixture, a larger portion of the applied power is used to activate the N₂ molecules, without converting all this energy into CO₂ dissociation.

The energy cost of CO₂ conversion is calculated with equation (4) in the Suppl. Info., and is shown in Fig. 3(c). Until a N₂ fraction of 70%, the energy cost is about 40 kJ/L (or 10 eV/molec). At higher N₂ fractions, it rises dramatically to 210 kJ/L (or 52.5 eV/molec). The energy efficiency of CO₂ conversion (see Fig. 3(d)) more or less follows the trend of the effective CO₂ conversion, since it is approximately proportional to it. The fact that it does not exhibit exactly the same trend is due to a small drop in specific energy input (SEI) upon N₂ addition (see Figure S3 in the Suppl. Info.), as the energy efficiency is inversely proportional to the SEI (see equation (5) in the Suppl. Info.). The energy efficiency remains more or less constant around 28% until 50% N₂, after which it decreases rapidly to a value of 5%. Thus, upon increasing N₂ fraction, more energy is consumed by the N₂ molecules, which cannot be used anymore for CO₂ conversion. We can thus conclude that up to 50%, N₂ has little effect on the effective (i.e., overall) CO₂
conversion, its energy cost and energy efficiency. In this respect, there is no need to separate N₂ from CO₂ in waste streams containing at maximum 50% N₂.

The energy cost and energy efficiency reached in our GAP are very good compared to other plasma reactors, i.e., DBD and MW plasma [26,28]. This is clearly demonstrated from Figure S4 in the Suppl. Info., where the energy efficiency is plotted against CO₂ conversion in GAP, DBD and MW plasma. The best energy efficiency is reached in our GAP, but for the CO₂ conversion, there is still room for improvement, and the MW plasma reaches higher conversion. Nevertheless, the experiments with MW plasma were performed at reduced pressure (2660 Pa), while the GAP and DBD both operate at atmospheric pressure. If the pressure in the MW plasma would be increased, the conversion and energy efficiency would drop [2,30,31], and in addition the plasma would become less stable [2,31]. When operating at reduced pressure, the energy cost of pumping should also be accounted for, and this would lower the overall energy efficiency (not yet included in Figure S4). For industrial application of this technology, it would be beneficial to work at atmospheric pressure or higher.

4.2. Analysis of the byproducts - NOx concentrations

Not only conversion and energy efficiency are important for evaluation of this technology, but also the formation of byproducts. We used FTIR as qualitative analysis method for the byproducts, i.e., O₃ and NOx compounds (NO, NO₂, N₂O, NO₃, N₂O₃ and N₂O₅). Note that in terms of N₂ fixation, the NOx compounds are products rather than byproducts. However, as the main goal of the research was CO₂ conversion (in the presence of N₂ from a waste stream), the NOx compounds can be considered as byproducts, which can be of added value as well, if produced in sufficient amounts. The components that could be clearly distinguished from the FTIR-spectrum are CO, NO, and NOx. There were no signals visible for other components, like O₃, NO₂, NO₃, N₂O₃, N₂O₄ and N₂O₅. The influence of N₂ fraction on the NO and NOx concentration in arbitrary units is plotted in Figure S5 of the Suppl. Info. To quantitatively analyze the NOx compounds, we used a CT5800 Analyzer based on Quantum Cascade Laser (QCL) technology. The QCL could not detect any N₂O, in agreement with the FTIR analysis, indicating that the concentration of N₂O was never higher than 1 ppm. The concentrations of NO and NO₂ as well as the sum of both, are plotted in Fig. 4 as a function of N₂ fraction. The error bars are too small to be visible, as they were typically below 1% of the actual concentrations. These may be attributed to the error in the absolute concentration, as the NOx signals were below the detectability limit of the detector.

For a DBD reactor with [32,42] and without catalyst [28], the NOx yield reported in literature ranges from 0.06 – 1638 MJ/mol NOx. Thus, the GAP seems to perform at the lower limit for the NOX yield, but it performs quite well in terms of energy consumption, with a moderate value around 7 MJ/mol NOX. To make a fair comparison, however, we have to take into account that our starting mixture is CO₂/N₂. Therefore, the NOX yield is limited by the CO₂ conversion, which supplies the oxygen for NOX formation. In addition, this also affects the energy consumption, since part of the energy input is also used for CO₂ conversion and not only for NOX production. The real energy consumption for NOX formation in the GAP will thus be lower than 7 MJ/mol NOX.

For a DBD reactor with [32,42] and without catalyst [28], the NOX yield is lower with considerably higher energy consumption than for microwave (MW) and gliding arc (GA) discharges (although the energy consumption of 442 MJ/mol NOx from ref [28] is again obtained for a
Calculations we know that the fraction of gas passing through the arc is CO2/N2 instead of N2/O2, and part of the energy is consumed by CO2, as energy consumption is quite similar. However, we produce NOx from the need of a good vortex of 10 L/min is necessary for obtaining a stable plasma, because of the pattern was presented in the SI (Fig. 6) of reference [5]. From previous vide more energy-e...tronically excited species are involved in NOx production, which is thus higher reduced electric...explained above. We can conclude that NOx production from a CO2/N2 mixture, explaining the higher value). The reason is that MW and GA plasmas are characterized by a reduced electric field (i.e., ratio of electric field over gas number density) between 5 and 100 Td, where the dominant electron-induced process is vibrational excitation of N2, [24] similar as for CO2 [2]. Thus, in GA and MW discharges large amounts of vibrationally excited N2 molecules are present, which provide more energy-efficient N2 dissociation. DBDs are characterized by higher reduced electric fields, above 100–200 Td, where mostly electronically excited species are involved in NOx production, which is thus limited by the higher energy cost for the formation of these species (see more details below).

Comparing our results with those of the milliscale GA from Patil et al. [32,33], their NOx yield is more than twice as high, while the energy consumption is quite similar. However, we produce NOx from CO2/N2 instead of N2/O2, and part of the energy is consumed by CO2, as explained above. We can conclude that NOx production from a CO2/N2 mixture in a GAP is worth investigating further, since it has similar energy consumption than starting from an N2/O2 mixture and it can solve two problems at the same time. Some ways to increase the NOx yield in our GAP are suggested below.

The best results up to now were obtained in MW plasmas [43–45] but only at reduced pressure, which requires pumping, making it less attractive for industrial implementation, and it should be accounted for in the calculation of the energy consumption, which was not the case for the values in Table 1. Unfortunately, the cost for pumping was not mentioned in these references, so we cannot make a fair comparison between these and our data, which were obtained at atmospheric pressure.

To make the process effective for N2 fixation, the NOx concentration should increase to about 1% [23,50]. Indeed, such low concentrations can already provide high concentrations of HNO3 [50]. The CO2 conversion in our GAP is limited to 8–18%, due to the limited amount of gas passing through the actual arc plasma [5,11,51]. If this fraction can be enhanced by optimizing the reactor design or the gas inlet system, it would yield higher CO2 conversions, and thus the NOx concentration could also rise further. Previously we found that lowering the flow rate also increases the CO2 conversion [5]. However, a minimum flow rate of 101 L/min is necessary for obtaining a stable plasma, because of the need of a good vortex flow pattern. Such a calculated vortex flow pattern was presented in the SI (Fig. 6) of reference [5]. From previous calculations we know that the fraction of gas passing through the arc is 15% [11], meaning that the conversion inside the arc is about 71%. Hence, we have to increase the fraction of gas passing through the arc to up to minimum 22%, which results in a CO2 conversion of 16%, if we want to reach a NOx concentration above 1% (see more details in the Suppl. Info.). A way to increase this fraction is by decreasing the radius of one or more tangential inlets in order to create a higher flow velocity so that more gas is forced into the central vortex. Besides this approach, we also want to change the cathode design to increase the electric field, which also increases the plasma production and arc stability. Dedicated fluid dynamics simulations are needed to evaluate these approaches, which is the subject of our future work.

The selectivity towards NO and NO2 (see Eqs. (2) and (3)) are plotted as a function of N2 fraction in Fig. 5.

\[
\text{NO selectivity} = \frac{\text{NO concentration}}{\text{concentration of (NO + NO2)}} \times 100\% \tag{2}
\]

\[
\text{NO2 selectivity} = \frac{\text{NO2 concentration}}{\text{concentration of (NO + NO2)}} \times 100\% \tag{3}
\]

The NO selectivity rises from 93 to 99% with increasing N2 fraction, while the NO2 selectivity decreases from 7 to 1%. These trends are similar as in Wang et al. [24] for NOx formation from a N2/O2 mixture in a milli-scale classical (planar) GA, but the absolute values are clearly

Table 1
Overview of measured values for NOx yield and energy consumption for various plasma types.

<table>
<thead>
<tr>
<th>Plasma type</th>
<th>NOx concentration</th>
<th>Energy consumption</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gliding arc plasmatron (GAP)</td>
<td>0.7 % NOx</td>
<td>7.02 MJ/mol NOx</td>
<td>this work</td>
</tr>
<tr>
<td>DBD (*)</td>
<td>0.06 % NOx</td>
<td>442 MJ/mol NOx</td>
<td>28</td>
</tr>
<tr>
<td>DBD with MoO3 catalyst</td>
<td>0.5 % NOx</td>
<td>18 MJ/mol NOx</td>
<td>32,42</td>
</tr>
<tr>
<td>Milliscale GA with pulsed power</td>
<td>2 % NOx</td>
<td>7.2 MJ/mol NOx</td>
<td>32,33</td>
</tr>
<tr>
<td>Milliscale GA with pulsed power</td>
<td>0.8 % NOx</td>
<td>2.8 MJ/mol NOx</td>
<td>32,33</td>
</tr>
<tr>
<td>Pulsed arc discharge</td>
<td></td>
<td>10.6 MJ/mol NOx</td>
<td>36</td>
</tr>
<tr>
<td>Plasma arc jet</td>
<td>6.5 % NO</td>
<td>4.0 MJ/mol NO</td>
<td>37</td>
</tr>
<tr>
<td>Laser-produced plasma</td>
<td></td>
<td>8.96 MJ/mol NO</td>
<td>38</td>
</tr>
<tr>
<td>Exploding water jet discharge</td>
<td>1 % NOx</td>
<td>47.2 MJ/mol NOx</td>
<td>39</td>
</tr>
<tr>
<td>Negative pulsed corona discharge</td>
<td></td>
<td>1638 MJ/mol NOx</td>
<td>40</td>
</tr>
<tr>
<td>Positive pulsed corona discharge</td>
<td></td>
<td>1060 MJ/mol NOx</td>
<td>40</td>
</tr>
<tr>
<td>Spark discharge</td>
<td></td>
<td>20.2 MJ/mol NOx</td>
<td>40</td>
</tr>
<tr>
<td>Spark discharge</td>
<td>1 % NOx</td>
<td>2.41 MJ/mol NOx</td>
<td>41</td>
</tr>
<tr>
<td>MW discharge with MoO3 catalyst</td>
<td>6 % NO</td>
<td>0.84 MJ/mol NO</td>
<td>43</td>
</tr>
<tr>
<td>MW discharge</td>
<td>6 % NO</td>
<td>0.60 MJ/mol NO</td>
<td>44</td>
</tr>
<tr>
<td>MW discharge with N2</td>
<td>14 % NO</td>
<td>0.30 MJ/mol NO</td>
<td>45</td>
</tr>
<tr>
<td>MW discharge</td>
<td>0.6 % NOx</td>
<td>4.05 MJ/mol NOx</td>
<td>46</td>
</tr>
<tr>
<td>Shielded sliding discharge</td>
<td>0.1 % NO</td>
<td>15.4 MJ/mol NO</td>
<td>47</td>
</tr>
<tr>
<td>Electric arc (original Birkeland-Eyde process)</td>
<td>1 – 2 % NO</td>
<td>2.41 MJ/mol NO</td>
<td>48</td>
</tr>
<tr>
<td>Electric arc with water injection</td>
<td>4.7 % NO</td>
<td>3.50 MJ/mol NO</td>
<td>49</td>
</tr>
</tbody>
</table>

*(1) CO2/N2 as starting mixture.

*(2) N2/O2 as starting mixture.
different. Indeed, Wang et al. [24] obtained more or less equal selectivities of 50% for NO and NO2, except at very high or low N2 concentrations, while in our GAP the selectivity towards NO is much higher than towards NO2. This is attributed to the much higher temperature in our GAP (i.e., nearly 3000 K [51], vs. 1000–1500 K in the classical GA [24]), favoring NO above NO2, as well as the different starting mixture, and hence different reaction mechanisms for the formation of NO and NO2, as explained in the ‘Simulation results’ section.

In fact, the separate NO and NO2 concentrations are not so important, as NO can easily be oxidized into NO2 after plasma, so it is the total NOx concentration that counts. When the NOx concentrations will still be a bit higher and thus effective for N2 fixation, the NO/NO2 mixture can be separated from the unconverted fraction by taking part in the Ostwald process, thereby producing nitric acid [50]. This can be used as precursor for the synthesis of more complex molecules, such as mineral fertilizers. In the industrial Ostwald process, NH3 is first oxidized to NOx and then absorbed by H2O to form HNO3. The typical yield from NH3 to NOx is about 98%. In our case, HNO3 would also be made from NOx absorption by H2O, but the yield from N2 to NOx is considerably lower than in the industrial Ostwald process, so our process is by far not yet competitive with the Haber process, without producing NH3 as an intermediate step. Hence, we believe our plasma process is a unique concept.

4.3. Underlying mechanisms as revealed by numerical simulations

We developed a chemical kinetics model to investigate the mechanisms of the combined CO2 and N2 conversion in our GAP (see brief explanation above and more details in the Suppl. Info.). The model has been validated against the experimental data for conversion, energy efficiency and NOx concentrations. In all cases, the trends and absolute values predicted by the model were in reasonable agreement with the experimental results, as illustrated in Figures S6 and S7 in the Suppl. Info. Indeed, on average the relative difference between calculated and experimental data was 5% for the CO2 conversion, 27% for the N2 conversion, 5% for the energy efficiency, 34% for the NO concentration, and 72% for the NO2 concentration. The largest deviation was found for NO2 concentration, but keeping in mind the complexity of the underlying chemistry, this is still reasonable. Therefore, we can use the model to predict the underlying mechanisms. In Figures S8, S10 and S12 in the Suppl. Info., we present the net time-integrated rates of the most important reactions for the loss and formation of CO2, NO and NO2, respectively. For additional insight, we also plotted the net contributions of these reactions in Figures S9, S11 and S13 in the Suppl. Info.
For pure CO₂ the most important loss mechanism is the reaction of vibrationally excited CO₂ with O atoms, see Figure S8(a). This agrees well with earlier model predictions [5]. However, as soon as N₂ is added, the reaction of vibrationally excited CO₂ with NO becomes dominant, with an overall contribution of 50–60 % (Figure S9). Other reactions, such as the collision of vibrationally excited CO₂ with CN or any molecule M in the plasma, and electron impact dissociation of both CO₂ ground state and vibrationally excited levels, also play a role, with contributions of 5–60 %, depending on the N₂ fraction (Figure S9). CO₂ formation is mainly caused by recombination of CO and O₂ (Figure S8(b)), with contributions up to 80% (Figure S9). To prevent this recombination and thus enhance the CO₂ dissociation, we could separate O₂ from the mixture, e.g., by membrane technology or oxygen scavengers.

NO is initially formed upon reaction of vibrationally excited N₂ with O atoms, i.e., the so-called Zeldovich mechanism, in agreement with the dominant formation mechanisms in a milli-scale classical GA [24]. Subsequently, NO reacts with vibrationally excited CO₂, forming CO and NO₂ (Figure S10). In return, the reaction of NO₂ with O atoms will further produce NO.

We summarize the most important reaction pathways in Fig. 6. Reactants are indicated in color according to the time-integrated rate of their reaction (red \( \geq 10^{17} \text{ cm}^{-3} \); green \( \geq 10^{16} \text{ cm}^{-3} \); blue \( \geq 10^{15} \text{ cm}^{-3} \)), while the thickness of the arrow lines corresponds to the overall importance of the reaction. The most important reactions, ranked by importance based on the average time-integrated rates, are listed in Table S5 in the Suppl. Info.

Both CO₂ and N₂ are easily excited from ground state to vibrational levels, and vice versa, upon electron impact (de)excitation, vibration-vibration (VV) and vibration-translation (VT) relaxation. The vibrational distribution functions (VDFs) of both CO₂ and N₂ are plotted in Figure S14. Overall, the VDF of both molecules is thermal, with a vibrational temperature of 3174 K and 3333 K for CO₂ and N₂, respectively (Figure S15), which is more or less equal to the gas temperature (3140 K). We should be able to increase the energy efficiency of CO₂ conversion and N₂ fixation if the VDFs of both CO₂ and N₂ would be more non-thermal, with higher populations of the higher vibrational level [5,29]. To realize this, the temperature in the arc should be reduced, so that VT relaxation, which depopulates the vibrational levels, can be reduced. On the other hand, the vibrational levels in our GAP are clearly more populated than in other types of plasmas, such as a DBD, where the VDF dramatically drops for the higher vibrational levels [58–60]. This explains why the CO₂ conversion and N₂ fixation are high rate in the DBD flow rate of 10 L/min, while the thickness of the arrow lines corresponds to the overall importance of the reaction. The most important reactions, ranked by importance based on the average time-integrated rates, are listed in Table S5 in the Suppl. Info.

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4.4. Comparison of GAP with DBD

As mentioned in the Introduction, Snoeckx et al. [28] have also analyzed the byproducts formed in a CO₂/N₂ mixture, but for a DBD plasma, which has completely different plasma properties than a GAP, [2] hence affecting the plasma chemistry. Therefore, we compare here both plasma reactors in terms of conversion efficiency and byproduct formation, at typical GAP and DBD conditions, i.e., a specific energy input (SEI) of around 2 kJ/L and 12 kJ/L, respectively. These values originate from a plasma power of 350 W and a total flow rate of 10 L/min for the GAP, while the plasma power and total flow rate in the DBD reactor are around 120 W and 611 mL/min, respectively. Note that we cannot compare the results in the GAP and DBD at the same SEI,
because the flow rate in the GAP is much higher, which is necessary to obtain a good vortex flow pattern, while such a high flow rate would result in very small residence times, and thus virtually no conversion, in a DBD. However, this difference in flow rate (and power) must be accounted for when we compare the results in the GAP and DBD.

4.4.1. CO₂ conversion, energy cost and energy efficiency

In Fig. 8(a), the absolute CO₂ conversion is plotted for both plasma reactors as a function of N₂ fraction. The GAP shows a slightly more than linear trend with increasing N₂ fraction, while the trend of the DBD is more exponential. The absolute values in the GAP are somewhat higher than in the DBD, even at much lower SEI (cf. above). Thus, in general the CO₂ conversion is higher in the GAP, but the addition of large amounts of N₂ in a DBD enhances the CO₂ conversion more compared to in a GAP. To explain this, we should compare the main dissociation mechanisms of CO₂ in DBD and GAP. In a DBD the main dissociation mechanism is electron impact dissociation of ground state CO₂, but with increasing N₂ fraction, the reaction of CO₂ with metastable N₂ molecules becomes more important, and is the most important dissociation mechanism above 70% N₂ addition. [28] In our GAP, the reaction of vibrationally excited CO₂ with dissociated N₂ products, i.e., mainly NO but also CN (Figure S8(a)), is the most important CO₂ dissociation process. The reaction with NO is dominant up to 80% N₂, while above 80%, the reaction with CN becomes most important, but its absolute rate is quite low (Figure S8(a)), because CN also needs C to be formed, which is low at low CO₂ fractions. Thus, at high N₂ fractions, the contribution of N₂ is more important in a DBD than in a GAP, explaining why the GAP and DBD curves intersect at ca. 80% N₂. As is clear from Fig. 8(b), the effective CO₂ conversion is higher in the GAP than in the DBD, except again at N₂ fractions above 80%, where the values are comparable. The energy cost in the DBD is on average 6 times higher than in the GAP; see Fig. 8(c). Indeed, the effective conversion is slightly lower, but the SEI in the plasma is much higher (12 kJ/L vs 2 kJ/L). Thus, our GAP is much more promising than a DBD for plasma-based CO₂ conversion [2]. The energy efficiency in both plasma reactors decreases with increasing N₂ fraction (see Fig. 8(d)). In addition, the energy efficiency is 7 times higher in the GAP than in the DBD, for N₂ fractions up to 50%, i.e., around 27–31 % for the GAP vs. 4% for the DBD. At N₂ fractions above 50%, the difference becomes smaller, as the values drop to 5.9% for the GAP and 1.3% for the DBD, at 95% N₂. Indeed, in the DBD, the main mechanism of CO₂ dissociation is electron impact dissociation from ground state CO₂ molecules [28], which requires much more energy than the vibrational pathway in the GAP, this explains the better energy efficiency in the GAP than in the DBD.

4.4.2. Byproduct formation

We can conclude from above that the GAP is definitely superior for CO₂ conversion in the presence of N₂, in terms of conversion efficiency. However, for industrial application, also the formation of byproducts is important. The concentrations of NO and NO₂ obtained in the GAP and DBD are compared in Fig. 9, as a function of N₂ fraction in the mixture. Both the NO and NO₂ concentrations follow the same trend as a function of N₂ fraction in the GAP and DBD, with a maximum around 50–60% N₂. This is striking, as the formation mechanisms in both plasma types are quite different (see ref. [28]). However, the reason is that in both mechanisms important in GAP and DBD, both N₂ and CO₂ first have to be split into reactive species needed for NO formation, and this condition is fulfilled most when both N₂ and CO₂ are present in somewhat equal amounts. Indeed, in both GAP and DBD, when there is mainly N₂ in the mixture, CO₂ will be the limiting reactant for NO formation, while in case of mainly CO₂ in the mixture, N₂ will be the limiting reactant.

However, the NO and NO₂ concentrations are more than 10 times and about 6 times higher in the GAP than in the DBD. This can only partly be explained by the higher effective CO₂ conversion (Fig. 8(b)). Indeed, the N₂ dissociation – also needed for NOx formation – is a factor 4 higher in the GAP than in the DBD (i.e., 4% vs. 1%). In addition, the selectivity towards NO and NO₂ is significantly higher in the GAP than...
in the DBD, where also other NOx compounds were formed [28].

It is indeed remarkable that in our GAP no N2O, N2O3 and N2O5 could be detected, while they were clearly detected in the DBD, with the same measuring equipment (FTIR) [28]. Our simulation results also indicate NO and NO2 as the major byproducts of CO2 and N2 conversion in the GAP, in agreement with our experiments, while N2O (0.1–3 ppm), N2O3 (10^{-8} – 10^{-7} ppm), N2O4 (10^{-11} – 10^{-9} ppm) and N2O5 (10^{-12} – 10^{-10} ppm) have much lower concentrations (Figure S16 (a)). In comparison, in a DBD, next to NO and NO2 also N2O and N2O5 are formed in relatively high concentrations, i.e., calculated up to 115 ppm for NO, 34 ppm for NO2, 55 ppm for N2O, and even up to 1000 ppm for N2O5; see Figure S16(b) and also ref. [28]. The N2O3 and N2O4 concentrations are calculated to be much lower.

The reason we only detected NO and NO2 in our experiments, while in the DBD also N2O, N2O3 and N2O5 were detected, is attributed to the different plasma temperature. It is predicted to be around 3000 K inside the arc [51] in our GAP (for pure CO2), which is too high to form N2O, N2O3, and N2O5. Indeed, at higher temperatures the formation rates of these species increase but the loss rates are even higher (Figure S17), which results in lower net concentrations (Figure S16). On the other hand, a DBD operates around room temperature, yielding higher formation than loss rates (Figure S17), resulting in higher net concentrations (Figure S16). Furthermore, DBD plasmas are characterized by streamers, with short lifetime (order of 30 ns [61]), in which mainly electron impact reactions occur, but in between these streamers, NO2 can interact with NO or NO3 to form N2O and N2O5, respectively [28]. This is not the case in a GAP, because the arc is continuously stabilized in the center, explaining why only NO and NO2 are detected in our experiments.

Taking into account that N2O is a very potent greenhouse gas, with a global warming potential (GWP) of 298 CO2 equivalents, it is highly beneficial that its concentration in the GAP does not exceed the detection limit of 1 ppm. After all, the production of N2O would void the greenhouse gas mitigation potential of plasma technology if no denox purification step would be added.

Overall we can conclude that the GAP is far superior for CO2 conversion in the presence of N2 than the DBD, due to the higher conversion, but especially the absence of N2O, N2O3, N2O5 formation, and the significantly higher energy efficiency.

5. Conclusions

We have investigated the effect of N2 on CO2 conversion in a GAP, by combining experiments and simulations. The addition of N2 has a positive effect on the absolute CO2 conversion up to 50%, while at higher N2 fractions, the effective CO2 conversion and energy efficiency drop. Our simulations reveal that the CO2 conversion mainly proceeds through the vibrational levels, which are populated through collision with the N2 vibrational levels. In addition, NO and NO2 are formed in the CO2/N2 mixture, initiated by the reaction between N2 vibrational levels and O atoms (so-called Zeldovich mechanism [24]).

Combining CO2 and N2 in a GAP thus can lead to combined CO2 conversion and N2 fixation. The highest amount of NOx obtained is 6761 ppm, which is still below the minimum threshold of 1% to make it effective for N2 fixation. By improving our reactor and gas inlet design, we should be able to enhance the gas fraction that passes through the arc, and thus the CO2 conversion and NOx production. This optimization will need dedicated fluid dynamics simulations, which are planned in our future work.

We compared the performance of our GAP with other plasma types. The best energy efficiency for CO2 conversion is reached in our GAP, but the conversion itself needs further improvement. In terms of NOx production, the NOx yield is still quite low (attributed to the limited CO2 conversion), but the energy consumption is reasonable compared to other plasma types, certainly if we take into account that our energy consumption also includes the cost for CO2 conversion.

Finally, we made a more detailed comparison with a DBD, which is the only other work in literature where NOx production was also studied from a CO2/N2 mixture. The energy efficiency was 7 times higher in our GAP than in the DBD, next to a somewhat higher CO2 conversion. Indeed, CO2 dissociation in the GAP proceeds through vibrationally excited states, while in a DBD it occurs mainly by electronic excitation, which is less efficient [2]. Furthermore, our GAP only produces NO and NO2, while N2O, N2O3, and N2O5 are also formed in a DBD. Keeping in mind that N2O is a very potent greenhouse gas, it is highly beneficial that its concentration in the GAP does not exceed the detection limit of 1 ppm. Overall, the GAP is superior for CO2 conversion in the presence of N2 compared to a DBD, due to its higher conversion, but especially the absence of N2O, N2O3, N2O5 formation and the much higher energy efficiency.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jcou.2019.05.015.