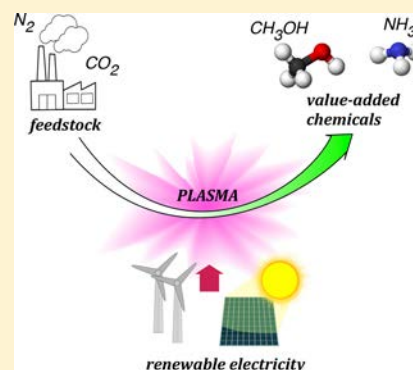


Plasma Technology: An Emerging Technology for Energy Storage

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ABSTRACT: Plasma technology is gaining increasing interest for gas conversion applications, such as CO₂ conversion into value-added chemicals or renewable fuels, and N₂ fixation from the air, to be used for the production of small building blocks for, e.g., mineral fertilizers. Plasma is generated by electric power and can easily be switched on/off, making it, in principle, suitable for using intermittent renewable electricity. In this Perspective article, we explain why plasma might be promising for this application. We briefly present the most common types of plasma reactors with their characteristic features, illustrating why some plasma types exhibit better energy efficiency than others. We also highlight current research in the fields of CO₂ conversion (including the combined conversion of CO₂ with CH₄, H₂O, or H₂) as well as N₂ fixation (for NH₃ or NO_x synthesis). Finally, we discuss the major limitations and steps to be taken for further improvement.



Recently, the production of renewable electricity is rapidly growing. This wide-scale adoption and especially the intermittent character of solar and wind energy, however, pose challenges for the efficient storage and transport of this electricity. There is a need for peak shaving, as well as for grid stabilization. This requires technologies that can follow in a flexible manner the irregular and sometimes intermittent supply of renewable electricity. Such technologies must easily be switched on/off to follow the supply. A so-called “turnkey” process that might be able to use this renewable electricity in a flexible way and convert it into fuels or chemicals is provided by plasma technology.

Plasma, also called the “fourth state of matter”, is an ionized gas. There exist different types of plasmas. In fact, more than 99% of the visible universe is in the plasma state, with the most well-known example being our Sun. Closer to Earth, natural plasma manifests itself in the form of lightning, the Auroras, or Saint-Elmo’s fire. In addition, plasma can also artificially be created by supplying energy to a gas. A distinction can be made between fusion plasmas and gas discharge plasmas. Fusion plasmas operate at millions of degrees to mimic the conditions of the Sun in order to realize nuclear fusion as a future energy source. Gas discharge plasmas, on the other hand, operate at much lower temperature, even close to room temperature, and are created by applying electrical energy to a gas. This explains why they are potentially interesting for use as renewable electricity.

In recent years, there is growing interest in the use of plasma for gas conversion applications.^{1,2} Two major application fields, which will be covered in this Perspective article, are (i) CO₂ conversion into value-added chemicals or renewable fuels and (ii) N₂ fixation from the air, to be used for the production of small

Plasma, i.e., ionized gas, has great potential for gas conversion applications because the energetic electrons can activate inert molecules, like CO₂ and N₂, enabling thermodynamically difficult reactions to occur at ambient conditions of temperature and pressure.

building blocks for, e.g., mineral fertilizers. Plasma allows the activation of these stable molecules in an energy-efficient way. Indeed, the gas does not have to be heated as a whole. The applied electrical energy will selectively heat the electrons due to their small mass. Subsequently, these energetic electrons will collide with the gas molecules (e.g., CO₂ or N₂), causing excitation, ionization, and dissociation. The excited species, ions, and/or radicals will quickly react further, creating new molecules. Thus, there is thermal nonequilibrium between the highly energetic electrons on the one hand (typically with energy of a few eV, i.e., several 10 000 K) and the gas molecules on the other hand (virtually at room temperature up to a maximum of a few 1000 K). This allows thermodynamically unfavorable or energy-intensive chemical reactions, such as N₂ or CO₂ splitting, or dry reforming of methane (DRM; i.e., the combined conversion of CO₂ and CH₄), to proceed in an energy-efficient way by making

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use of (renewable) electricity. It should be noted that there exist also thermal plasmas, where all species (electrons, gas molecules, excited species, ions, ...) have the same temperature, but they are typically less energy-efficient for gas conversion applications.¹

In the remainder of this Perspective, we will present the state-of-the-art of plasma technology for this emerging application. We will present the plasma types most often used for gas conversion applications, with their characteristic features. This is necessary to explain later why some plasma types exhibit better energy efficiency than others. We will provide a brief state-of-the-art and highlight some characteristic examples of both CO₂ conversion and N₂ fixation, based on which we provide a critical analysis of this emerging technology. Finally, we will discuss what is needed to bring this technology closer to industrial application.

Different Plasma Types Used for Gas Conversion Applications. In its simplest form, a gas discharge plasma is created by applying an electric potential difference between two electrodes, positioned in a gas. The gas pressure can range from a few Torr up to (above) 1 atm. The potential difference can be direct current (DC), alternating current (AC), ranging from 50 Hz over kHz to MHz (radio frequency, RF), or pulsed. In addition, the electrical energy can also be supplied in other ways, e.g., by a coil (inductively coupled plasma, ICP) or as microwaves (MWs). We briefly present here the three types of plasmas most often studied for gas conversion applications, i.e., dielectric barrier discharges (DBDs), MW plasmas, and gliding arc (GA) discharges. It is worth mentioning, however, that also other plasma types are explored for these applications, such as nanosecond (ns) pulsed discharges, spark discharges, corona discharges, and atmospheric pressure glow discharges. More information about these plasma types can be found in the recent review paper of Snoeckx and Bogaerts.²

Dielectric Barrier Discharges (DBDs). A DBD operates at atmospheric pressure and is created by applying an AC potential difference between two electrodes, of which at least one is covered by a dielectric barrier. The latter limits the amount of charge transported between both electrodes, and thus the electric current, preventing the discharge from undergoing a transition into a thermal regime (cf. above). The electrodes can be two parallel plates, but for gas conversion applications, two concentric cylindrical electrodes are most often used (cf. Figure 1a). Typically, such a reactor consists of an inner electrode

surrounded by a dielectric tube, yielding a gap of a few millimeter, and the outer electrode is typically a mesh or foil that is wrapped around the dielectric tube. One of the electrodes is connected to a power supply, while the other electrode is grounded. The gas flows in from one side and is gradually converted along its way through the gap between the inner electrode and dielectric tube, like in a plug flow reactor, and flows out from the other side.

A DBD has a very simple design, making it suitable for upscaling and thus industrial implementation, as has been demonstrated already for ozone synthesis.³ The upscaling is realized by placing a large number of DBD reactors in parallel. Furthermore, a DBD operates at atmospheric pressure, which is also beneficial for industrial applications.

On the other hand, the energy efficiency for gas conversion (e.g., CO₂ splitting or DRM or N₂ fixation) is quite low, as will be demonstrated and explained in the “Highlights of Ongoing Research” below. The energy efficiency can sometimes be enhanced by introducing packing of dielectric material in the gap between the electrodes, creating a so-called packed-bed DBD reactor. The reason for the improved energy efficiency is the polarization of the dielectric packing beads as a result of the applied potential difference, enhancing the electric field near the contact points of the packing beads, and thus the electron energy.⁴ Hence, for the same applied power, a higher electron energy can be obtained, giving rise to more electron impact excitation, ionization, and dissociation and thus activation of the gas molecules, explaining the better energy efficiency.

Furthermore, the packing beads can have catalytic properties or be covered by a catalytic material to enable the selective production of targeted compounds by so-called plasma catalysis.^{5,6} Indeed, a plasma on its own is very reactive due to the cocktail of chemical species (electrons, various types of molecules, atoms, radicals, ions, and excited species), but for the same reason, it is not selective in the production of targeted compounds. Plasma catalysis combines the high reactivity of a plasma with the selectivity of a catalyst, so that targeted compounds can be formed with high product yield and selectivity. However, more research is needed to effectively design catalysts tailored for the plasma environment (as discussed in the “Highlights of Ongoing Research”).

Microwave (MW) Plasmas. A MW plasma is created by applying MWs, i.e., electromagnetic radiation with frequency between 300 MHz and 10 GHz, to a gas, without using electrodes. There are different types of MW plasmas, such as cavity-induced plasmas, free expanding atmospheric plasma torches, electron cyclotron resonance plasmas, and surface wave discharges. The latter type are most frequently used for gas conversion applications. The gas flows through a quartz tube, which is transparent to MW radiation, intersecting with a rectangular waveguide, to initiate the discharge (see Figure 1b). The MWs propagate along the interface between the quartz tube and the plasma column, and the wave energy is absorbed by the plasma.

MW plasmas can operate from reduced pressure (e.g., 10 mTorr) up to atmospheric pressure. When operating at low pressure, they exhibit very good energy efficiency (as will be demonstrated and explained in the “Highlights of Ongoing Research”), but when operating above 0.1 atm, they approach thermal equilibrium, with gas temperatures of a few 1000 K, greatly reducing their energy efficiency (see below).

Gliding Arc (GA) Discharges. A GA discharge is a transient type of arc discharge. A classical GA discharge is formed between two flat diverging electrodes (see Figure 1c). The arc is initiated at the

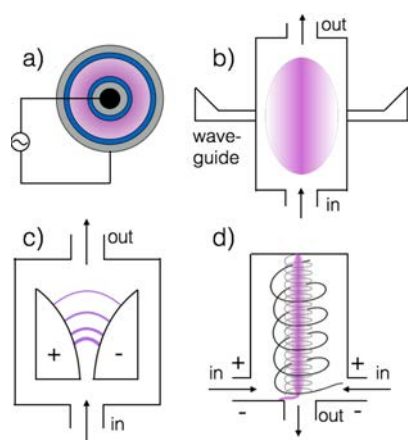


Figure 1. Schematic illustration of the three plasma reactors most often used for gas conversion applications, i.e., DBD (a), MW plasma (b), and GA discharge, in classical configuration (c) and cylindrical geometry, called GAP (d).

shortest interelectrode distance, and under the influence of the gas blast, which flows along the electrodes, the arc “glides” toward a larger interelectrode distance until it extinguishes and a new arc is created at the shortest interelectrode distance.

This type of (two-dimensional) GA discharge yields only limited gas conversion because a large fraction of the gas does not pass through the arc discharge. Therefore, other types of (three-dimensional) GA discharges have been designed, such as a gliding arc plasmatron (GAP) and a rotating GA, operating between cylindrical electrodes. The GAP is schematically illustrated in Figure 1d. The cylindrical reactor body operates as a cathode (powered electrode), while the reactor outlet acts as an anode and is grounded. The gas enters tangentially between the two cylindrical electrodes. When the outlet diameter is (significantly) smaller than the diameter of the reactor body, the gas flows in an outer vortex toward the upper part of the reactor body, and subsequently, it will flow back in a reverse inner vortex with smaller diameter because it has lost some speed, and thus, it can leave the reactor through the outlet. The arc is again initiated at the shortest interelectrode distance and expands until the upper part of the reactor, rotating around the axis of the reactor until it (more or less) stabilizes in the center after about 1 ms. In the ideal scenario, the inner gas vortex passes through this stabilized arc, allowing a larger fraction of the gas to be converted than in a classical two-dimensional GA discharge. Nevertheless, the fraction of gas passing through the active arc is still somewhat limited, as will be demonstrated in the “Highlights of Ongoing Research”.

The GA discharge operates at atmospheric pressure, making it also suitable for industrial implementation. Furthermore, it exhibits a rather high energy efficiency for gas conversion applications, as demonstrated and explained in the “Highlights of Ongoing Research”. However, the gas temperature is also fairly high (typically a few 1000 K), limiting the energy efficiency, like in a MW plasma, because the plasma approaches thermal equilibrium (see below).

Highlights of Ongoing Research. *CO₂ Splitting into CO and O₂.* CO₂ conversion into value-added chemicals and fuels is considered one of the great challenges of the 21st century. Due to limitations of the traditional thermal approaches, several novel technologies are being developed, such as electrochemical, solar thermochemical, photochemical, and biochemical pathways, either with or without catalysts, and all of their possible combinations. Plasma chemical conversion can be seen as an additional novel technology, but it has received less attention up to now than the other upcoming technologies.

Research on plasma-based CO₂ splitting into CO and O₂ started already in the 1980s, when a lot of experiments were performed in the former Soviet Union, in various types of plasma reactors.¹ Extremely high energy efficiencies were reported at that time, i.e., up to 90% for MW plasmas operating at very specific conditions, i.e., supersonic gas flow and reduced pressure (~100–200 Torr), but increasing the pressure to 1 atm significantly reduced the energy efficiency. In the past decade, there has been renewed interest in plasma-based CO₂ conversion, with various groups around the world actively searching for optimized conditions in various types of plasma reactors and trying to understand the underlying mechanisms. Up not now, however, the high energy efficiencies obtained in the 1980s have not yet been reproduced, and the highest values reported more recently are around 50–60%. All results obtained up to now in the literature are summarized in Figure 2, in terms of energy efficiency vs CO₂ conversion, indicated per plasma type.

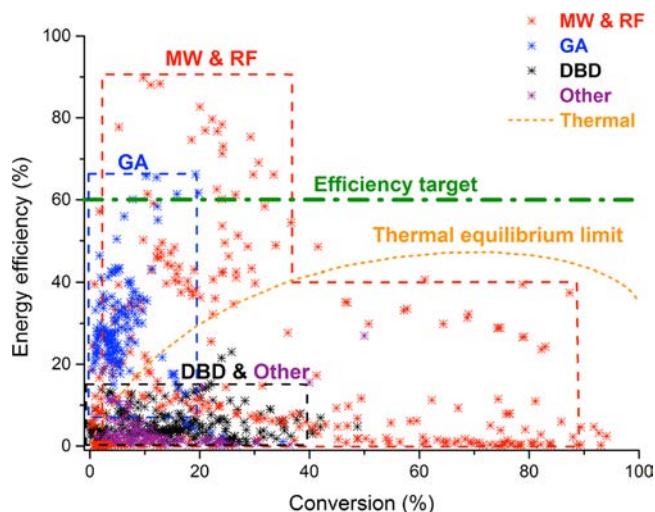


Figure 2. Comparison of all data collected from the literature for CO₂ splitting in the different plasma types, showing the energy efficiency as a function of conversion. The thermal equilibrium limit and the 60% efficiency target are also indicated. Adopted from ref 2 with kind permission; published by The Royal Society of Chemistry.

This figure is adopted from the recent review paper on CO₂ conversion by plasma technology, published by Snoeckx and Bogaerts.² The latter paper critically evaluated the capabilities of all types of plasma reactors for CO₂ splitting, as well as the combined conversion of CO₂ with CH₄, H₂, or H₂O acting as the H-source for the production of syngas (CO/H₂) or even the direct production of oxygenates or higher hydrocarbons. Therefore, we refer to ref 2 for a complete overview of the state-of-the-art.

Figure 2 also indicates the thermal equilibrium limit, as calculated in ref 2, as well as an energy efficiency target, defined to be at least 60%.² The latter is determined based on two criteria. The first one is the comparison with the main competitor of plasma technology for renewable energy storage, being electrochemical water splitting, which reaches commercial energy efficiencies of 65–75%. The second criterion is based on comparison with other novel technologies, as mentioned above, which make use of direct solar energy, such as solar thermochemical conversion, for which a solar-to-fuel conversion efficiency of 20% is considered industrially competitive.² Thus, taking a solar panel efficiency of 25%, an energy efficiency of 60–80% for plasma-based CO₂ conversion would yield a competitive solar-to-fuel efficiency of 15–20%.

Here, we present some characteristic examples for the three different plasma types discussed previously to illustrate their capabilities and limitations.

As is clear from Figure 2, a DBD typically yields CO₂ conversions up to 30%, with energy efficiencies up to 5–10%,^{2,7} although the energy efficiency can be enhanced up to 20% (record values) by applying the power in a so-called burst mode.⁸ However, a high conversion is typically accompanied by a low energy efficiency, and vice versa.^{2,7} As mentioned previously, the performance can also be improved in a packed-bed DBD. Van Laer et al.⁹ and Mei et al.¹⁰ reported a simultaneous increase in both conversion and energy efficiency by a factor 2 for ZrO₂ and for TiO₂ and BaTiO₃ packing, respectively, attributed to the enhanced electric field due to polarization of the packing beads. Moreover, for TiO₂ and BaTiO₃ packing, this was also attributed to a (photo)catalytic effect, i.e., the formation of electron–hole

pairs due to the plasma electrons, causing oxygen vacancies, which are active sites for adsorption and activation of the reactants.¹⁰

However, it should be stressed that a packed-bed DBD does not always yield better performance.^{2,9–12} Figure 3 illustrates a

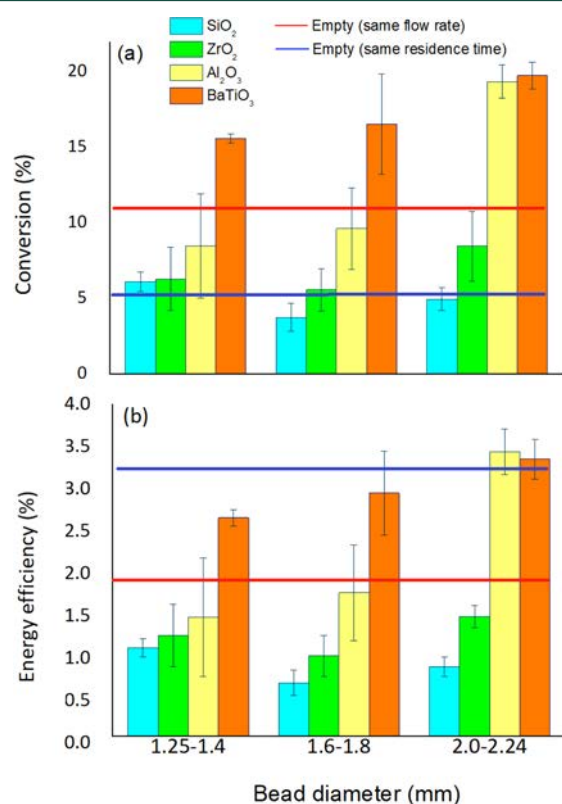


Figure 3. CO₂ conversion (a) and energy efficiency (b) in a DBD, with and without dielectric packing, for four different packing materials (legend) and three different bead sizes (*x*-axis), in the case of a DBD reactor with an Al₂O₃ dielectric barrier, 4.5 mm gap, stainless steel outer electrode, applied frequency of 23.5 kHz, 10 W input power, and 50 mL/min gas flow rate.¹² The error bars are defined based on 12 gas chromatography measurements. Comparison is also made with the results of an unpacked reactor, at the same flow rate (red line) and the same residence time (but much higher flow rate of 192 mL/min; blue line).

typical CO₂ conversion and the corresponding energy efficiency for a DBD reactor, with and without dielectric packing.¹² Both the conversion and energy efficiency are quite limited, i.e., around 5–20 and 1–3%, respectively. They are somewhat better in a packed-bed DBD due to the electric field enhancement, as explained in “Different Plasma Types Used for Gas Conversion Applications”, but not for all conditions. Indeed, introducing the packing reduces the residence time at constant flow rate due to a reduced plasma volume, and this will negatively affect the conversion. Thus, depending on the conditions (i.e., applied power and flow rate, discharge gap, packing material, and bead size), either the electric field enhancement or the effect of reduced plasma volume might be dominant, resulting in higher or lower CO₂ conversion and energy efficiency. Indeed, when compared at the same flow rate (cf. red horizontal line in Figure 3), some packing materials (e.g., Al₂O₃ and BaTiO₃) and bead sizes (typically larger beads) yield higher conversion and energy efficiency than in the unpacked reactor, while others yield lower results, as is clear from Figure 3. When compared with the

unpacked reactor at the same residence time (and thus much higher flow rate, cf. blue horizontal line in Figure 3), the conversion is nearly always higher as a result of the enhanced electric field, but the energy efficiency is lower because it is defined by the conversion and the specific energy input (SEI), which is determined by the flow rate

$$\eta (\%) = \frac{\Delta H_R (\text{kJ/mol}) \times X_{\text{CO}_2} (\%)}{\text{SEI (kJ/L)} \times 22.4 (\text{L/mol})}$$

where η stands for the energy efficiency, ΔH_R is the reaction enthalpy of the reaction under study (i.e., 279.8 kJ/mol for CO₂ splitting at room temperature, i.e., temperature of the input and output gas), X_{CO_2} is the CO₂ conversion, and SEI is the specific energy input

$$\text{SEI (kJ/L)} = \frac{\text{Plasma power (kW)}}{\text{Flow rate (L/min)}} \times 60 (\text{s/min})$$

Note that the results of Figure 3 do not represent the best performance found in the literature for (packed-bed) DBD reactors, but they illustrate that inserting a packing does not always lead to better performance and that the results greatly depend on the packing material and geometry, as well as the reactor geometry.¹²

In a MW plasma, a much higher conversion and/or energy efficiency can be reached, but only when operated at reduced pressure.^{13–17} The best results presented in the literature are summarized in Figure 4. As mentioned, in the 1980s, Rusanov

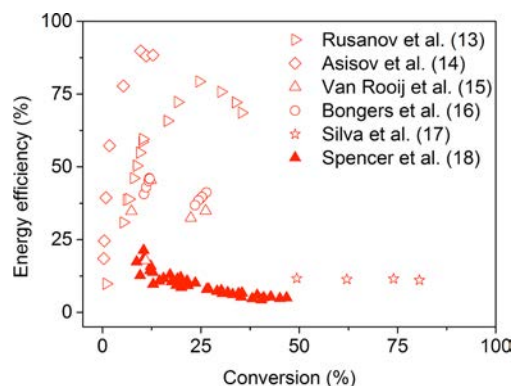


Figure 4. Summary of the best results published in the literature for energy efficiency vs CO₂ conversion in a MW plasma, at both reduced pressure (open symbols) and atmospheric pressure (full symbols).

and colleagues reported energy efficiencies up to 80% with conversions around 20% in a MW plasma at reduced pressure and subsonic flow,¹³ while Asisov and colleagues reported values of energy efficiency and conversion of 90% and 10% for reduced pressure and supersonic flow.¹⁴ These results have not yet been reproduced since then, as mentioned above, but more recently, van Rooij, Bongers, and colleagues reached energy efficiencies around 40–50%, with conversions around 10–20%,^{15,16} while Silva et al. reported conversions of 50–80% but at corresponding energy efficiencies of 10%.¹⁷ All of these results were obtained at reduced pressure (typically up to a few 100 mbar). At atmospheric pressure, Spencer et al. reported much lower values, i.e., energy efficiencies up to 20% for conversions of 10% or conversions up to 50% for energy efficiencies of 5%.¹⁸

A GA plasma operates at atmospheric pressure and provides good energy efficiencies around 30–40%, with some exceptions up to 60%, but the conversion is typically limited to a maximum of 10% (see Figure 2).^{19–24} Figure 5 illustrates the energy

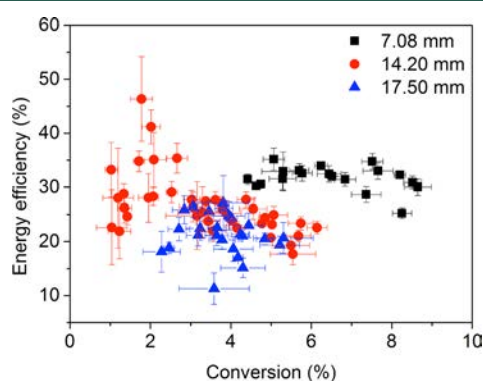


Figure 5. Energy efficiency vs CO₂ conversion in a GAP for three different configurations with different anode diameters (cf. legend) and different combinations of power and gas flow rate.²²

efficiency as a function of CO₂ conversion for a GAP for different anode (i.e., gas outlet) diameters. As explained previously, in a GAP, the gas enters tangentially, and when the anode (outlet) diameter is smaller than the cathode (reactor) diameter, it flows in an outer vortex toward the upper end of the reactor, followed by a reverse vortex with smaller diameter toward the outlet (see Figure 1d). This reverse vortex gas flow passes through the active arc in the middle of the reactor, yielding better conversion and energy efficiency than in the case of an anode (outlet) with larger diameter, comparable to the reactor diameter. This is indeed obvious from Figure 5. Nevertheless, the fraction of gas passing through the arc is still quite limited, like in a classical GA (as explained in “Different Plasma Types Used for Gas Conversion Applications”), and this limits the CO₂ conversion in both a classical GA and GAP. We believe that this gas fraction could be enhanced by smart design of the GAP reactor or the gas inlet. Likewise, in a classical GA, this gas fraction might be enhanced by modifying the reactor setup and hence the gas flow configuration to realize a higher relative velocity between the arc and gas flow, as demonstrated by model calculations.^{23,24}

In general, it is clear that a MW (when operating at reduced pressure) and a GA provide much better energy efficiency than a DBD, and this is attributed to the role of vibrational kinetics.^{1,2,25,26} Indeed, MW and GA plasmas are characterized by reduced electric fields (= ratio of the electric field over gas density) below 100 Td (1 Td = 10⁻²¹ V m²). This yields electron energies around 1 eV, which are most beneficial for vibrational excitation of CO₂.^{1,2,26} On the other hand, the reduced electric field in a DBD reactor is typically above 100–200 Td, creating electrons with higher energy, which mainly give rise to electronic excitation, ionization, and dissociation.

Hence, in a MW and GA plasma, the electrons populate the lower vibrational levels of CO₂. Subsequently, these levels collide with each other in so-called vibrational–vibrational (VV) relaxation, gradually populating the higher levels.^{2,26} This so-called ladder climbing requires 5.5 eV for CO₂ dissociation, which is exactly the C=O bond dissociation energy. On the other hand, electronic excitation to a dissociative level, which is the main process in a DBD reactor, would require 7–10 eV. This is much more than the C=O bond dissociation energy, and this extra energy is just a waste of energy, thus explaining why the

energy efficiency in a DBD is much more limited than that in a MW and GA plasma.

It should be mentioned, however, that the vibrational levels can also get lost by vibrational–translational (VT) relaxation. This becomes especially important at high gas temperature, as revealed by computer simulations,²⁷ where it results in a vibrational distribution function (VDF) that is (nearly) in thermal equilibrium with the gas temperature. Unfortunately, a GA and MW plasma operating at atmospheric pressure exhibit a quite high gas temperature on the order of several 1000 K, resulting in a VDF that is indeed close to thermal.^{24,27} Increasing the power density and reducing the pressure and the gas temperature can make the VDF deviate more from a thermal distribution.²⁷ This explains why a MW plasma performs much better at reduced pressure, as discussed above (cf. Figure 4). At atmospheric pressure, realizing a lower gas temperature is not so straightforward. One option is to use a supersonic gas flow, as demonstrated by Asisov et al.,¹⁴ so that the gas does not have enough time to be heated. A possible alternative could be to apply a pulsed power, so that the gas can cool down in between the applied pulses. A higher power density can be obtained by reducing the dimensions, i.e., applying the same power over a smaller plasma volume, but this will negatively affect the gas throughput, unless several reactors could be placed in parallel.

An alternative to improve the conversion and energy efficiency, as revealed by model predictions,^{23,24} is to remove O₂ from the gas mixture to avoid the back-reaction, i.e., the recombination with CO into CO₂. To remove O₂ from the gas mixture, scavenging materials or chemicals²⁸ or membranes could be applied, as demonstrated by Mori et al. for a hybrid reactor of a DBD with solid oxide electrolyzer cell (SOEC),²⁹ but more research is needed to fully explore all of the possibilities.

CO₂ Conversion in Combination with a H-Source. Contrary to pure CO₂ splitting, the combined conversion of CO₂ with CH₄, H₂, or H₂O, acting as a H-source, can yield a wide variety of products. Typically, the main product is syngas (CO/H₂), but the direct production of oxygenates or higher hydrocarbons is also possible. Most research in the literature has been performed up to now with CH₄ as the H-source, i.e., DRM. Figure 6 presents an overview of all results obtained up to now in the literature for DRM, plotting the energy cost vs total conversion.² The reason why the energy cost is plotted here, instead of the energy efficiency, is because the true energy efficiency can only be determined if all formed products—both gaseous and liquids—are taken into account in the theoretical reaction enthalpy (see the formula above) or, alternatively, if the higher (or lower) heating values of all products are accounted for, but in the literature, typically only the selectivity (or yield) toward CO and H₂ and light hydrocarbons is mentioned, making it impossible to deduce the true energy efficiency.

Figure 6 also indicates the thermal equilibrium limit, as well as the efficiency target. Keeping in mind that syngas is the main product in DRM, the same 60% efficiency target is considered here (see arguments in the beginning of “CO₂ Splitting into CO and O₂”), which equals an energy cost of 4.27 eV/molecule for general stoichiometric DRM.² However, it should be realized that this efficiency target only applies to syngas production. When directly forming liquids (such as methanol), the energy efficiency requirements would be drastically reduced because the energy-intensive step of further processing syngas into the desired liquid products can be circumvented. For instance, a solar-to-methanol conversion efficiency of 7.1% is stated to be already economically feasible. Hence, a plasma-based conversion

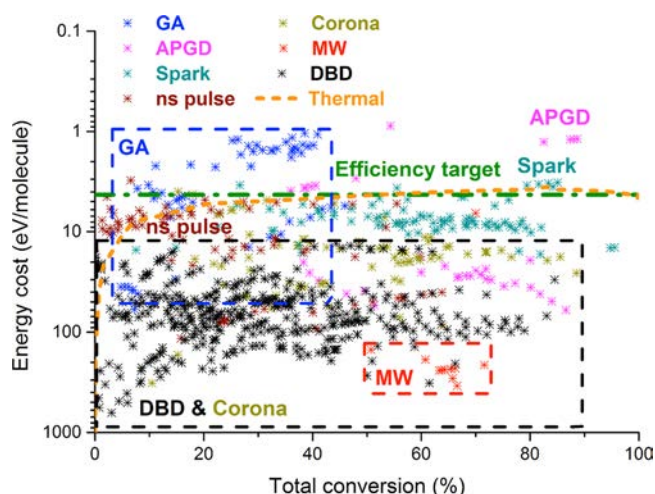


Figure 6. Comparison of all data collected from the literature for DRM in the different plasma types, showing the energy cost as a function of the conversion. The thermal equilibrium limit and an target energy cost of 4.27 eV/molecule for the production of syngas (corresponding to 60% efficiency target) are also indicated. The y-axis is reversed to allow comparison with Figure 2. Adopted from ref 2 with kind permission; published by The Royal Society of Chemistry.

energy efficiency of 30% (instead of the above 60%) would already be sufficient in that case.²

Although DRM indeed mainly yields syngas, when combined with a suitable catalyst, it is also possible to selectively produce oxygenates. Scapinello et al.³⁰ reported enhanced selectivity toward the formation of carboxylic acids in a DBD used for DRM when using copper or nickel electrodes instead of stainless steel. The selectivity for formic acid was found to be four and three times higher with nickel and copper, respectively, than that with stainless steel. This was attributed to a chemical catalytic effect of the metals, more specifically, hydrogenation of chemisorbed CO_2 , which has a rather high barrier in the gas phase, and seems to play a key role in the synthesis of these carboxylic acids.³⁰

Figure 7 illustrates the conversion of CO_2 and CH_4 (top), as well as the selectivity of gaseous products (middle) and liquid products (bottom), for the catalyst alone, plasma alone, and plasma + catalyst using different catalyst materials, keeping the experimental conditions constant (30 °C and atmospheric pressure), again in a DBD reactor, obtained by Wang et al.³¹ The results with catalyst alone were obtained with a $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst and show no conversion at this low temperature. Plasma catalysis yields a slightly lower conversion of CO_2 and CH_4 than plasma alone, which might be attributed to the change in discharge behavior due to the full packing of the catalysts in the plasma reactor. Consequently, also the total energy efficiency for conversion slightly drops, from 12.4% (plasma alone) to 8.7, 11.7, and 11.1% for Cu, Au, and Pt catalyst, respectively.³¹

The results of plasma alone and plasma catalysis were found to be similar in terms of selectivity of the gaseous products, with H_2 , CO , and C_2H_6 being the major ones. The main liquid compounds are acetic acid, methanol, and ethanol and some fractions of acetone, with a total selectivity of 59% in the plasma-only case. The combination of plasma with catalyst yields the same products but with some potential to tune the distribution of the different liquid products due to the presence of both gas-phase reactions and plasma-assisted surface reactions. For example, compared to plasma-only, the $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst

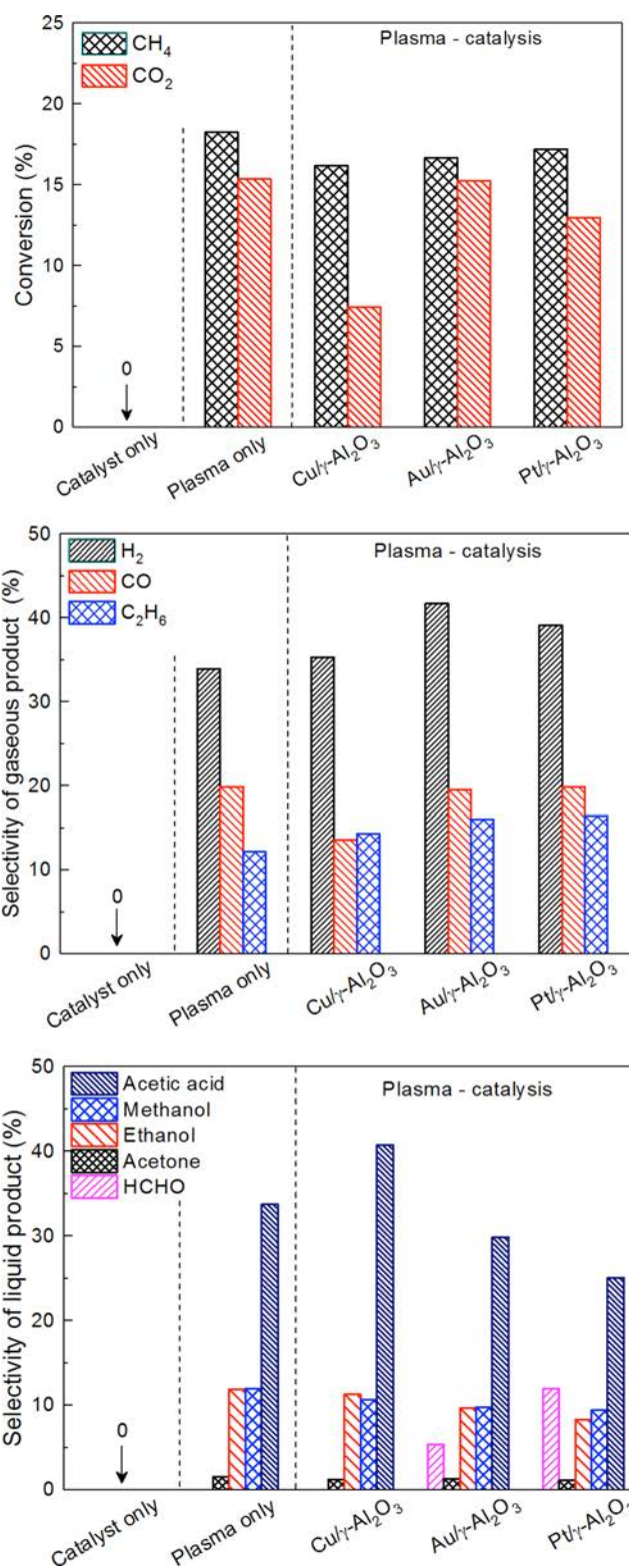


Figure 7. Conversion of CO_2 and CH_4 (top) and selectivity of gaseous products (middle) and liquid products (bottom) for catalyst only, plasma only, and plasma catalysis for three different catalyst materials in a DBD at 30 °C and atmospheric pressure.³¹

increases the selectivity of acetic acid to 40%. In addition, HCHO was not detected in the case of plasma alone but was only formed when using the supported noble catalysts ($\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Au}/\text{Al}_2\text{O}_3$). Nevertheless, the total fraction of liquids was only

around 1%.³¹ It must be stressed that our knowledge of selecting appropriate catalysts for directly converting CO₂ and CH₄ into value-added oxygenates using plasma catalysis is still very limited. It will be crucial to specifically and rationally design catalysts tailored for the plasma environment with high selectivity toward desired liquid chemicals.

Most results for DRM have been obtained with a DBD, with or without (catalyst) a packed bed. Just like for pure CO₂ splitting (cf. “CO₂ Splitting into CO and O₂”), the energy efficiency for this conversion is quite limited (typically up to 10%), as is clear from Figure 6. Furthermore, as indicated in Figure 6, only a few experiments have been reported for DRM with a MW plasma, which is a bit surprising in view of the good results obtained for pure CO₂ splitting (cf. previous section). On the other hand, Figure 6 illustrates quite promising results for GA plasma reactors.

Plasma can easily be switched on/off; therefore, it will be very suitable to combine with renewable electricity for the production of renewable fuels or value-added chemicals.

As an example, Figure 8a presents the effective CO₂ and CH₄ conversion in a GAP as a function of the CH₄ fraction in the mixture for a total gas flow rate of 10 L/min and a plasma power of 500 W, yielding a SEI of 3 kJ/L or 0.75 eV/molecule.³² Both the effective CO₂ and CH₄ conversion and thus also the total conversion rise upon increasing CH₄ fraction. Note that the absolute conversions (i.e., with respect to the amount of gas entering the reactor) are higher than the effective conversions, i.e., up to 60% for CH₄,³² because the effective conversions account for the gas fraction in the mixture. The energy efficiency increases as well (see Figure 8b) and reaches values up to above 60%. The corresponding energy cost is then ca. 10 kJ/L or 2.6 eV/molecule.³² Also in other GA plasmas, maximum conversions in the range of 30–50% have been reported, with energy costs as low as 1–2 eV/molecule.^{33–35} The best reported result was obtained for a rotating GA reactor, yielding a total conversion of 39% with an energy cost of 1 eV/molecule.³³ Finally, the combination of a GA plasma with Ni-based catalysts in a heat-insulated reactor operating in a CO₂/CH₄/O₂ (2/3/1.8) mixture yielded a dramatic rise in energy efficiency (up to 86%), with absolute CH₄ conversion of 92% and absolute CO₂ conversion of 23%.³⁴ Thus, it is clear that the GA easily reaches the energy efficiency target of 60% for syngas production by DRM, or a corresponding energy cost of 4.27 eV/molecule, defined by Snoeckx and Bogaerts,² as a criterion to be competitive with other technologies (see the beginning of this discussion).

Figure 8c also depicts the product selectivity, obtained without catalyst. The C-based selectivity for CO is around 100%. The fact that it appears slightly above 100% at low CH₄ fraction is due to uncertainties associated with the measurements. The CO selectivity slightly drops upon higher CH₄ fraction due to the formation of some C₂ hydrocarbons (mainly C₂H₂, as also revealed from plasma chemistry modeling³²) and probably higher hydrocarbons or other carbon-based products not detected by the gas chromatograph. The O-based selectivity of O₂ is about 60% in pure CO₂ and strongly drops upon addition of (5%) CH₄, indicating that the O atoms formed from CO₂

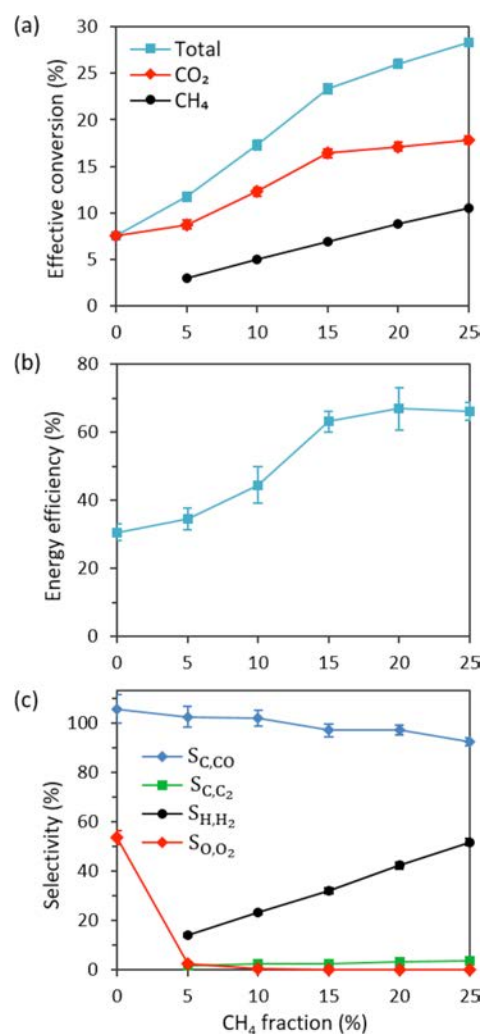


Figure 8. Conversion of CO₂ and CH₄ and total conversion (a), energy efficiency (b), and product selectivity (c) as a function of the CH₄ fraction in the mixture for a GAP at a total gas flow rate of 10 L/min and plasma power of 500 W, yielding a SEI of 3 kJ/L or 0.75 eV/molecule (kept constant for all CH₄ fractions).³²

splitting mainly yield O₂ and CO in pure CO₂ but are converted into other compounds (e.g., oxygenates but also H₂O) upon addition of a H-source. The H-based selectivity of H₂ increases with increasing CH₄ fraction; the remaining H atoms give rise to higher hydrocarbons and H₂O. In general, CO and H₂ (or syngas) are the major compounds formed in the absence of a catalyst.²

Finally, also other plasma reactors have been investigated for DRM, and especially ns-pulsed discharges, spark discharges, and atmospheric pressure glow discharges (APGDs) showed quite promising results (see Figure 6).² Ns-pulsed discharges yield total conversions in the 40–60% range, with energy costs around 3–10 eV/molecules.³⁶ The most abundant hydrocarbon formed is C₂H₂, like in a GA reactor (see above) but different from a DBD where mainly C₂H₆ is formed (cf. Figure 7, middle panel). Spark discharges and APGDs yielded conversions up to 80–90%, with minimum energy costs around 3 eV/molecules (for spark discharges³⁷) and 1.2 eV/molecules (for APGDs³⁸). However, only limited results have been reported in the literature for this type of discharge, and more research is needed to better understand their underlying mechanisms and to further exploit their possibilities.

Besides CH_4 , also H_2O and H_2 can be used as the H-source for the conversion of CO_2 into value-added compounds. The conversions reported in CO_2 hydrogenation and the corresponding energy efficiency are, however, a factor of 2–3 lower (and thus the energy cost is the same factor higher) than those for DRM and pure CO_2 splitting.² The same applies to a mixture of CO_2 and H_2O . This mixture could in principle be very interesting as H_2O is the cheapest H-source available, and this process could mimic the natural photosynthesis process. However, it appears that H_2O addition leads to a severe drop in the CO_2 conversion because the OH radicals formed from H_2O splitting react with CO molecules, forming again CO_2 and H atoms.³⁹ Moreover, only a limited amount of oxygenated hydrocarbons is formed in the absence of a catalyst.² This can be explained by chemical reaction pathway analysis, carried out for a DBD plasma reactor.³⁹ Indeed, the H atoms react with O to form OH and subsequently H_2O , instead of forming CH and CHO fragments, which are essential to create, e.g., methanol and other oxygenated hydrocarbons. Therefore, plasma chemistry modeling reveals that H_2O might not be a suitable H-source for the direct formation of oxygenated hydrocarbons from CO_2 because of the abundance of O atoms, O_2 molecules, and OH radicals in the plasma, trapping the H atoms. We believe that a catalyst or scavenging material will be needed in order to produce significant amounts of oxygenated hydrocarbons in a $\text{CO}_2/\text{H}_2\text{O}$ plasma and, more specifically, a material that is able to (i) scavenge the O atoms, so that the H atoms can recombine into H_2 before they react with O atoms to form OH and H_2O , and (ii) transform the H_2 together with CO into methanol before CO recombines with OH into CO_2 .

Finally, H_2O is also stated to quench the CO_2 vibrational levels,¹ thus reducing the most energy-efficient CO_2 dissociation process in a MW and GA plasma reactor (cf. “ CO_2 Splitting into CO and O_2 ”). This was indeed confirmed in a GA discharge at atmospheric pressure.^{40,41} On the other hand, in a MW plasma at reduced pressure (30–60 Torr), the addition of H_2O yielded better CO_2 conversion,⁴² which can be explained by a cooling effect upon introducing H_2O , reducing the loss of the CO_2 vibrational levels by VT relaxation (cf. “ CO_2 Splitting into CO and O_2 ”) and by the fact that the quenching process of the CO_2 vibrational levels by H_2O molecules might be less effective at this reduced pressure.

N_2 Fixation. Besides CO_2 conversion, plasma also has great potential for N_2 fixation.^{43–45} N_2 is the main constituent of the Earth’s atmosphere and is a crucial element in the growth of plants and living organisms (e.g., for fertilizers). It forms an essential part of amino acids and nucleotides, which lead to the formation of proteins, DNA, and RNA, the building blocks of all life on Earth. Unfortunately, N_2 has a very strong triple $\text{N}\equiv\text{N}$ bond, which requires very high activation energies to break. Therefore, atmospheric N_2 is hardly accessible to most living beings. The process to convert N_2 into small molecules (like NH_3 or NO_x) that can be more easily used as building blocks for life on Earth is called N_2 fixation.

N_2 fixation by chemical processes started in the beginning of the 20th century. In 1903, Birkeland and Eyde successfully developed thermal arc furnaces to convert air into nitrogen oxides.^{46,47} This process was based on a thermal plasma and was used in industry until 1940, but only at small scale. It suffered from a low NO_x yield and a low energy efficiency due to the high temperature. In 1908, the Haber–Bosch (H–B) process was successfully developed as an alternative N_2 fixation technique.⁴⁸ In this process, NH_3 is synthesized from N_2 and H_2 using iron as a

catalyst, at relatively high temperature (400–500 °C) and high pressure (~30 MPa). The H–B process was commercialized in 1913 and gradually took over the Birkeland–Eyde process because of its lower energy consumption and high NH_3 production. It has been extensively used over the last century, and about 135×10^{12} g of N_2 per year is currently fixed by the H–B process.⁴⁹ It sustains over 40% of the global population by producing >130 million tons of NH_3 per year. This process has been significantly optimized over the last century to reduce its environmental footprint and increase its energy efficiency, and currently, it almost reaches its theoretical limits. However, this process still consumes almost 2% of the world’s total energy production; it emits 300 million metric tons of CO_2 and utilizes 3–5% of the total natural gas output.^{50,51} The high energy consumption is due to the large swings in pressure and temperature.⁵² The commercial H–B process is mostly operated for mass production of about 2000 tons NH_3 /day, and the efficiency of this process is known to decrease upon decreasing plant size. The changing social and environmental conditions worldwide create significant challenges for more environmentally friendly NH_3 synthesis based, e.g., on renewable energy-based H_2 production. If NH_3 production would be matched to such a renewable energy-based H_2 production, the typical process size would be <10 tons NH_3 /day, thus affecting its efficiency.⁵² Therefore, further improvements in the environmental impact of N_2 fixation can only be reached by searching for alternative approaches.

Plasma-based N_2 fixation is a very promising alternative because of its thermal nonequilibrium between the light electrons and the gas molecules, as explained in the introduction, which allows one to perform N_2 fixation at lower temperature and relatively low energy consumption. Indeed, the theoretical limit of the energy consumption of plasma-based N_2 fixation is more than 2.5 times lower than the energy consumption of the H–B process.⁴⁸ Furthermore, the process can be conducted at ambient temperature and atmospheric pressure, in contrast to the high pressure and temperature of the H–B process, which could lead to improved process safety, combined with lower operational costs. Two processes are mainly investigated in plasma-based N_2 fixation, i.e., (i) NH_3 synthesis from N_2 and H_2 and (ii) NO_x formation from air. A detailed overview of plasma-based N_2 fixation can be found in the very interesting review papers by Hessel and co-workers.^{43–45}

NH_3 synthesis from N_2 and H_2 is an exothermic reaction and therefore favored at low temperature, making nonthermal plasma very attractive. However, the dissociation of N_2 is a strongly endothermic reaction, which requires high energy input. To our knowledge, no plasma-based NH_3 synthesis process has been developed and implemented on the industrial or pilot scale, but numerous efforts have been reported on the lab scale.^{52–63}

As an example, Figure 9 shows the results of NH_3 synthesis in a single-stage plasma catalysis reactor packed with Ru–Mg/ γ - Al_2O_3 pellets at different temperatures from experiments of Kim et al.³² While the stoichiometry of the H–B process is a $\text{H}_2:\text{N}_2$ ratio of 3:1, the optimum ratio in plasma catalysis appears to be 1:4, hence N_2 -rich conditions. For temperatures below 150 °C, where thermal catalysis does not occur, the NH_3 yield is low (ca. 1.1–1.3 g of NH_3 /kWh). The effect of the plasma only becomes prominent when the catalyst reaches the so-called light-off temperature (200 °C). Only 10 ppm of NH_3 is formed without plasma, compared to 810 ppm with plasma (at an SEI of 220 J/L); see Figure 9. Similar trends can be observed at higher temperatures. The energy yield obtained in these experiments

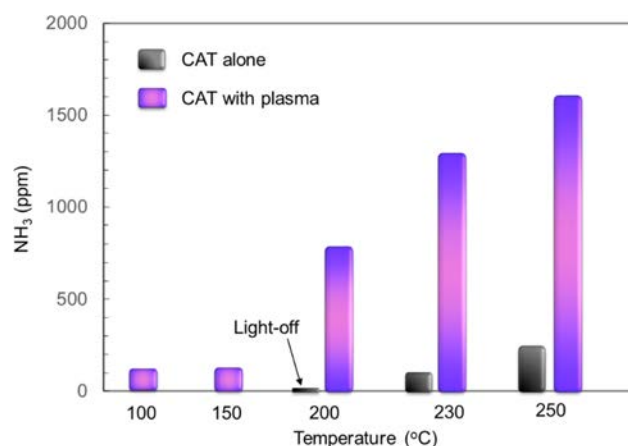


Figure 9. NH₃ concentration obtained in a packed-bed DBD plasma reactor with Ru–Mg/γ-Al₂O₃ packing at a gas flow rate of 2 L/min and a H₂:N₂ ratio of 1:4, compared with and without plasma at different temperatures.⁵²

was 25–30 g of NH₃/kWh.⁵² This corresponds to an energy consumption of about 2 MJ/mol (cf. Table 1). The net energy yield of the H–B process is estimated to be about 500 g of NH₃/kWh, but considering the low adaptivity of the H–B process for downsizing, the benchmark energy yield for 10 ton of NH₃/day (cf. above) is in the range of 150–200 g of NH₃/kWh.⁵² This

Table 1. Overview of Measured Values for NH₃ Yield and Energy Consumption for Various Plasma Types^a

plasma type	NH ₃ yield	energy consumption (MJ/mol)	ref
catalytic DBD with MgO + glass pellets	max NH ₃ conc: 0.57%	576	53
	max H ₂ conversion: 4.2%		
catalytic DBD with carbon coatings on α-Al ₂ O ₃	max NH ₃ conc: 1.2%	–	54
ferroelectric packed DBD	max N ₂ conversion: 7%	408	55
	max N ₂ conversion: 2.7%	136	56
membrane-like Al ₂ O ₃ DBD	max N ₂ conversion: 4%	192	57
catalytic DBD with 2%Rh/γ-Al ₂ O ₃	max NH ₃ conc: 1.4%	32	58
	max H ₂ conversion: 6.5%		
microgap DBD	max NH ₃ conc: 1.25%	34	59
DBD with MCM-41 as catalyst (10 wt % Ru/MgO with Cs promoter)	NH ₃ yield: 3.75%	27	60
catalytic DBD with Ru–Mg/γ-Al ₂ O ₃ and AC or pulsed source	–	5.32 (AC)	61
	–	1.71 (pulsed)	61
	max NH ₃ conc: 0.16%	2.04	52
catalytic DBD with wool-like metal electrodes	NH ₃ yield: 3.5%	93	62
packed DBD with glass or BaTiO ₃ beads or porous Ni-based catalyst	NH ₃ yield: 9.0%	81	63

^aIn some references, only the NH₃ yield (or maximum NH₃ concentration or N₂ or H₂ conversion) or energy consumption was mentioned.

means that the yield of plasma-based NH₃ synthesis is still a factor 6–7 too low to be competitive with the H–B process. It must be mentioned, however, that the value reported by Kim et al.⁵² was obtained at a single-pass under atmospheric pressure and can probably be further increased upon rising pressure and when recirculating the process gas.

Table 1 illustrates the measured values for NH₃ yield and energy consumption for various plasma types. This is not a complete overview of all literature results because the latter is not in the spirit of this Perspective article; it only gives an indication of typical values obtained by different groups. Note that the energy consumption values reported are only for the reactors and not for the overall process. The maximum H₂ or N₂ conversions are mentioned per pass; therefore, they can be further improved in a recirculating reactor.

The maximum N₂ or H₂ conversions and maximum NH₃ concentrations obtained are typically in the % range. The energy consumption, however, seems to vary in a wider range, with values reported of several 100 MJ/mol, down to the order of 1 MJ/mol, as obtained by Kim et al.⁶¹ As mentioned above, these values are still not competitive with the highly optimized H–B process, which has an energy consumption of 0.48 MJ/mol,⁴⁸ but it is worth stressing that the results of Table 1 are typically obtained under ambient conditions of pressure and temperature. Furthermore, we believe that plasma-based NH₃ synthesis still has room for improvement as this application is recently gaining significant interest for sustainable energy storage and several research groups are starting activities in this field. Especially plasma catalysis seems to be promising in this respect, as is clear from Table 1. Finally, we should perhaps not use the H–B process as a benchmark as plasma-based N₂ fixation has potential for distributed production plants, as discussed below.

For plasma-based NO_x formation, a larger number of different plasma types have been investigated, including various thermal and nonthermal discharges.^{64–79} Table 2 gives a nonexhaustive overview of some characteristic results. Again, the energy consumption values reported are only for the reactors and not for the overall process, except for the Birkeland–Eyde process (first row in the table). Quite some work was performed several decades ago (cf. Table 2), but only very recently has research on the topic been picked up again, in the framework of a large EU project called “Microwave, Acoustic and Plasma Syntheses” (MAPSYN).^{43–45,58,77–80}

Again, the results reported in the literature vary a lot among different plasma types (see Table 2). The NO yields are typically in the % range, with energy consumption values varying from 0.3 up to 1600 MJ/mol. Thermal plasmas, such as arc discharges as also used in the Birkeland–Eyde process but also laser-produced plasmas, RF discharges, and arc jets, provide reasonable NO_x yields but typically at fairly high energy costs because the energy in a thermal system is distributed over all degrees of freedom, including those not effective for the NO_x synthesis (see below).

The best results are obtained in MW plasmas operating at reduced pressure. Pulsed MW plasmas yield a low energy cost of 0.6 MJ/mol, corresponding to an energy efficiency of 16%, for an NO yield of 6%.⁷³ The same NO yield was obtained in a MW plasma with a catalyst at an energy cost of 0.84 MJ/mol.⁷² The highest NO yield of 14% and lowest energy cost of 0.3 MJ/mol, were reported for a low-pressure MW plasma with a magnetic field (so-called electron cyclotron resonance),⁷⁴ but this value for the energy cost only accounts for the plasma power and not for the energy-intensive process of generating liquid nitrogen for

Table 2. Overview of Measured Values for NO_x Yield and Energy Consumption for Various Plasma Types^a

plasma type	NO _x yield	energy consumption	ref
electric arc (original Birkeland–Eyde process)	1–2% NO	2.41 MJ/mol NO	46
electric arc with water injection	4.7% NO	3.50 MJ/mol NO	64
pulsed arc discharge	–	10.6 MJ/mol NO _x	65
plasma arc jet	6.5% NO	4.0 MJ/mol NO	66
radio-frequency discharge	–	11.6 MJ/mol HNO ₃	67
laser-produced plasma	–	8.96 MJ/mol NO	68
exploding water jet discharge	1% NO _x	47.2 MJ/mol NO _x	69
pulsed corona discharge	–	180 MJ/mol HNO ₃	69
negative pulsed corona discharge	–	1638 MJ/mol NO _x	70
positive pulsed corona discharge	–	1060 MJ/mol NO _x	–
spark discharge	–	20.2 MJ/mol NO _x	70
spark discharge	1% NO _x	2.41 MJ/mol NO _x	71
MW discharge with MoO ₃ catalyst	6% NO	0.84 MJ/mol NO	72
Pulsed MW discharge	6% NO	0.60 MJ/mol NO	73
MW discharge with magnetic field	14% NO	0.30 MJ/mol NO	74
MW discharge	0.6% NO _x	4.05 MJ/mol NO _x	75
shielded sliding discharge	0.1% NO _x	15.4 MJ/mol NO _x	76
DBD with γ -Al ₂ O ₃ catalyst	0.5% NO _x	18 MJ/mol NO _x	77
milliscale GA with pulsed power	2% NO _x	2.8 MJ/mol NO _x	78, 79

^aIn some references, only the energy consumption was mentioned, and not the NO_x yield.

reactor cooling, which also needs to be included for a fair comparison. Furthermore, the low-pressure operation of these MW plasmas requires vacuum equipment, which makes it more difficult to be applied in industrial-scale processes, and the energy requirements of this vacuum equipment should in fact also be included when calculating the energy consumption.

GA discharges and DBDs have been applied by the Hessel group in the MAPSYN project,^{77–79} with very promising results for GA discharges, i.e., up to 2% NO_x yield and 2.8 MJ/mol energy consumption, certainly keeping in mind that these results were obtained at atmospheric pressure. DBDs have not been investigated so often as for NH₃ synthesis (see Table 1), and the yields reported are relatively low, with higher energy costs than for MW and GA discharges, even when combined with catalysts.

The reason why GA plasmas and MW discharges yield better results than for DBDs is the same as that for CO₂ conversion (see “CO₂ Splitting into CO and O₂”). Indeed, these plasma types are characterized by reduced electric field (E/n) values between 5 and 100 Td, where vibrational excitation of N₂, just like for CO₂, is the dominant electron-induced process. This is illustrated in Figure 10 (region between the dashed lines). This means that GA and MW discharges contain large amounts of vibrationally excited N₂ molecules, which provide the most energy-efficient N₂ dissociation pathway, just like for CO₂. Indeed, vibrational excitation of N₂ can help to overcome the reaction energy barrier of the nonthermal Zeldovich mechanism ($O + N_2(v) \rightarrow NO + N$) and can thus significantly enhance the NO synthesis, as revealed by recent computer modeling.⁸¹ Further NO₂

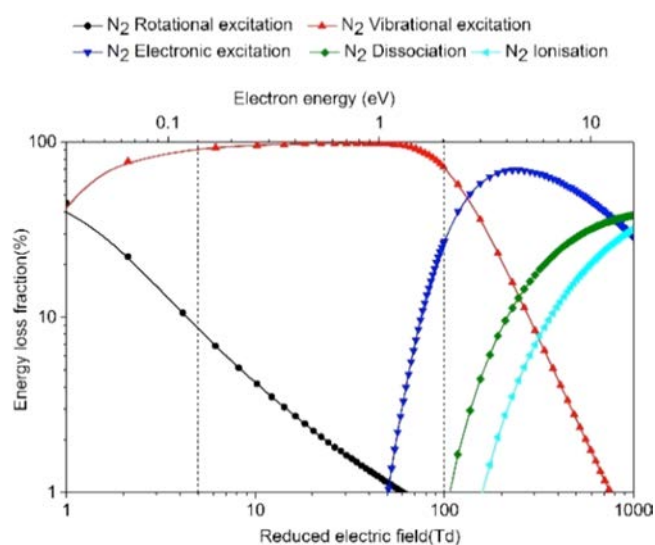


Figure 10. Fraction of electron energy transferred to different channels of excitation, as well as ionization and dissociation of N₂, as a function of the reduced electric field (bottom x -axis) and electron energy (top x -axis). The region between the two vertical dashed lines, i.e., between 5 and 100 Td, corresponds to GA and MW plasmas, while the region above 100 Td corresponds to a DBD.

production then occurs by oxidation of NO. DBDs are characterized by reduced electric fields above 100–200 Td and are expected to be less efficient in N₂ vibrational excitation, as can be seen in Figure 10. Indeed, the mechanism of NO_x synthesis in a DBD involves charged and electronically excited species, and thus, it is limited by the high energy cost for the formation of these species, just like for CO₂ conversion (cf. “CO₂ Splitting into CO and O₂”). Nevertheless, DBDs are interesting to further exploit because they can easily be combined with catalysts, operate at atmospheric pressure, and are easy to scale up.

As mentioned above, the H–B process for NH₃ synthesis still has a lower energy consumption, i.e., 0.48 MJ/mol; therefore, major efforts should be taken for nonequilibrium plasma-based N₂ fixation to further increase the yield and decrease the energy consumption if we want to become competitive with the industrial-scale H–B process. Computer simulations⁸¹ can help to improve the process as they elucidate the limiting factors for energy-efficient NO_x synthesis, and thus, they can help to provide solutions to overcome these limitations.

On the other hand, it might be difficult to compete with the H–B process, which has been well established for so many years and benefits from its large scale. However, we believe that plasma-based N₂ fixation has great potential for modular, small-scale reactors, e.g., for localized production of fertilizers from air, using renewable electricity. This could, for instance, be of great interest for local farmers in regions where a wealth of under-used wind and solar resources exists. In general, we believe that plasma technology opens new windows of opportunities for small-scale NH₃ and NO_x production (cf. also initiatives of N₂ Applied in Norway for a small-scale Birkeland–Eyde process and Siemens for small-scale NH₃ production technology).

Critical Analysis of the Performance of Plasma Technology. It is clear from “Highlights of Ongoing Research” that a DBD plasma provides too low energy efficiency for industrial implementation, certainly for pure CO₂ splitting (“CO₂ Splitting into CO and O₂”). Indeed, to compete with classical as well as other emerging technologies, Snoeckx and Bogaerts stated that

an energy efficiency of 60% would be required (see also Figure 2).² Thus, a DBD, with typical energy efficiencies of 5–10%, is far below this target. GA and MW plasmas, on the other hand, provide energy efficiencies for CO₂ splitting above the thermal equilibrium conversion for CO₂ and close to the defined target of 60%, showing their great potential for this application. This is attributed to the important role of vibrational excitation for energy-efficient dissociation of CO₂ in this type of plasmas.

For DRM, the performance of a DBD plasma is again far below the defined efficiency target of 60% (or above the target energy cost of 4.27 eV/molecule) to be competitive with existing technologies (see Figure 6). For MW plasmas, very limited results have been reported in the literature, but GA discharges, as well as ns-pulsed discharges, spark discharges, and APGDs, show very promising results, close to or above the efficiency target, as discussed in “CO₂ Conversion in Combination with a H-Source” and shown in Figure 6.

However, we want to stress again that this efficiency target of 60% for DRM was defined for the production of syngas, which is indeed the major product in plasma-based DRM. On the other hand, in combination with suitable catalysts, plasma also allows the direct production of higher-value compounds, such as higher hydrocarbons or oxygenates. This is a clear advantage, and it would significantly reduce the energy efficiency target to be competitive with other technologies if the latter would need a two-step process for this purpose. In this sense, even DBD plasmas could become suitable, especially because they have a simple design, allowing easy upscaling and straightforward implementation of catalysts. However, more research is needed to search for the precise mechanisms at play (which may differ from the thermal mechanisms⁸²) and, based on this knowledge, to specifically and rationally design catalysts to be implemented in plasma reactors. The latter is the case not only for DRM but certainly also for CO₂ hydrogenation (CO₂/H₂) and artificial photosynthesis (CO₂/H₂O mixtures), where the reported data indicate obvious limitations for high conversion, but we believe that catalysts tailored for the plasma environment could help solve these limitations.

For N₂ fixation, the same types of plasmas appear to be most promising as those for CO₂ conversion, i.e., MW and GA discharges, because they again allow vibrational excitation of N₂, providing the most energy-efficient pathway for N₂ dissociation. This is most apparent for NO_x synthesis, while for NH₃ synthesis nearly all results obtained in the literature are for DBD plasmas, mostly in combination with catalysts. However, there are indications that the higher gas temperatures in MW and GA reactors might be advantageous for NH₃ production, based on the kinetic modeling of Hong et al. including surface reactions⁸³ and the experimental results of Kim et al.⁵² Indeed, Hong et al. noted the importance of H₂ dissociation on catalytic surfaces at low surface temperatures because the dissociative adsorption of H₂ has a much higher reaction probability than dissociative adsorption of N₂.^{83,84} Hence, this hinders the dissociative adsorption of N₂, which is critical for NH₃ production. In order to provide available active surface sites for N₂ and other NH_x intermediate species, the authors suggested increasing the surface temperature, which will accelerate the recombination of surface-adsorbed H(s). Because the surface temperature equilibrates with the plasma gas (or heavy species) temperature, this can be achieved by increasing the gas temperature of the plasma, as is the case for MW and GA plasmas.

On the other hand, although MW and GA plasmas yield higher N₂ vibrational populations, it was recently demonstrated that

even in DBD plasmas N₂ dissociation at catalyst surfaces is enhanced by the N₂ vibrational levels, which enables one to overcome typical classical NH₃ synthesis scaling relations.⁸⁵ Indeed, the usual constraints for catalysts to simultaneously have a low activation energy for N₂ dissociation and a weak interaction with surface intermediates can be circumvented by the DBD plasma, thus showing the great potential of DBD-based plasma catalysis for NH₃ synthesis.⁸³ Therefore, as MW and GA discharges exhibit more pronounced vibrational excitation, it would be interesting to explore their performance for NH₃ synthesis as well, although their combination with catalysts is less straightforward than those for DBD plasmas.

In general, an industrial process for plasma-based NO_x synthesis might be more successful in the end than for plasma-based NH₃ synthesis as it can utilize air as feed gas, while NH₃ synthesis requires H₂ as co-feed, and the cost for H₂ production is still quite high. In this respect, it would be interesting to perhaps use CH₄ or H₂O as the H-source, just like for CO₂ conversion, and maybe this would give rise to other value-added chemicals, such as amines. Clearly more research is needed to exploit these possibilities.

When comparing the energy efficiencies (or energy costs) reported in the literature for both NH₃ and NO_x synthesis with those for the H–B process, it is clear that plasma-based N₂ fixation is not yet competitive. However, we should probably not compare with the H–B process as one cannot fight against the economy of scale at thermodynamic equilibrium. However, as the world is changing and creates new economies, we should follow new business models, and we believe that, in this respect, plasma-based N₂ fixation, in contrast to the H–B process, has great potential for distributed production plants based on renewable energy sources, including fertilizer production in underdeveloped countries.

Snoeckx and Bogaerts² recently made a detailed comparison with other (emerging) technologies, such as electrochemical, solar thermochemical, photochemical, biochemical, and catalytic conversion, for the application of CO₂ conversion, but similar arguments apply to N₂ fixation as well. It was concluded that plasma technology is quite promising, for the following reasons:

- (1) **Process versatility**, allowing different types of reactions to be carried out. For CO₂ conversion, this includes pure CO₂ splitting, as well as CO₂ conversion in the presence of a H-source, such as CH₄, H₂, or H₂O, although the latter two seem only viable if suitable catalysts can be found. In contrast, most other emerging technologies have only been investigated up to now for CO₂/H₂O or pure CO₂ splitting.² Moreover, when combined with a suitable catalyst, plasma allows the direct production of oxygenates in a one-step process, circumventing the need for additional Fischer–Tropsch or methanol synthesis and subsequent methanol/ethanol-to-olefins synthesis. However, clearly more research is needed to specifically and rationally design catalysts tailored for the plasma environment. The same applies to N₂ fixation, where research is performed for both NH₃ and NO_x synthesis. Moreover, if the appropriate catalysts can be designed, other N-containing compounds could be targeted as well (e.g., amines). This process versatility allows plasma technology to be used at a wide variety of locations, independent of the available feed gas composition and even adjustable to a variable-feed gas composition. Indeed, for instance, in the case of CO₂ conversion, large amounts of N₂, as present in

- CO₂ effluent gases, can even be beneficial to enhance the CO₂ conversion.⁸⁶
- (2) **No use of rare earth metals**, which is currently a limiting factor (and thus the subject of many investigations) for various other technologies.
 - (3) **Turnkey process**: plasma can be turned on and off very quickly as it requires no preheating or long stabilization times and no cool-down times. In fact, the gas conversion starts immediately after plasma ignition, i.e., from the first second. This makes plasma technology very suitable for converting intermittent renewable energy into fuels or chemical building blocks. Furthermore, there is no risk of damaging the plasma reactors with repeated on/off cycles.
 - (4) **Low investment and operating costs**. Furthermore, plasma technology can be applied in a very modular setting as there is almost no economy of scale. Indeed, plasma tubes scale up linearly with the plant output. Thus, plasma technology allows for local on-demand production schemes. This can be of special interest for fertilizer production from air (N₂ fixation) and renewable energy, even by local farmers, e.g., in underdeveloped countries.
 - (5) Finally, plasma allows the use of **various types of renewable energy** and is thus not limited only to solar energy, like other emerging technologies (solar thermochemical, photochemical and biochemical). The advantage of the latter technologies is that they directly use renewable energy (solar radiation), thus skipping an energy conversion step, which always leads to energy losses. In contrast, plasma technology only employs indirect renewable electricity, but this allows use also of other renewable energy sources, such as wind, hydro, wave, and tidal power. This increases its application versatility as it can be installed and operated independent of the availability of solar radiation (although it needs to be noted that photochemical and biochemical technologies may also rely on indirect renewable energy when used in combination with artificial lighting).

Van Rooij et al. recently evaluated the potential of a particular plasma process for CO₂ splitting into CO to help integrating renewable energy in the chemical industry, and they estimated the manufacturing cost price of CO at 1.2 kUS\$/ton CO.⁸⁷ Note that all assumptions made in this estimation were chosen conservatively, and a more progressive process and commercial parameters would reduce the estimated cost. Still, it is obvious that this particular plasma process of CO₂ splitting into CO is not yet competitive with the bulk CO price, which was estimated around 228 US\$/ton.⁸⁷ Product separation turns out to be the dominant cost factor, concluding that improving the conversion is currently more effective to lower the price rather than improving the energy efficiency of the plasma process. It should be realized, however, that in the case of direct production of liquid fuels or higher-value chemicals, for which the reference price is much higher, the business case would be much more optimistic, also because product separation would be easier. This again stresses the need for rational design of catalysts tailored for the plasma environment to selectively produce these target compounds.

Conclusions and Future Directions. In this Perspective article, we discussed the possibilities of plasma technology for storage of renewable electricity, showing two examples, i.e., CO₂ conversion (either pure CO₂ splitting or in combination with a H-source) and N₂ fixation.

For further improvement, more research efforts are needed, especially to design catalysts tailored to the plasma environment.

Strictly speaking, the term “storage” typically refers to a temporary holding spot, and upon retrieval, the original item is in its same state. When applying this to storage of renewable electricity, it should still be electricity when it is retrieved. This definition does not apply to all of the examples given in this article. It may be possible with CO₂ conversion into fuel, which is subsequently burned for electricity, but in the case of producing value-added chemicals and fertilizers from CO₂ or N₂, the term “use” of renewable electricity might be more appropriate than “storage”. On the other hand, while we refer in this article to fertilizer production from N₂, it should be realized that NH₃ (produced from N₂ fixation) clearly has more potential than only for fertilizer purposes. Indeed, it is also widely viewed as an energy storage and transportation medium, where it is transformed back into H₂ for fuel cell vehicles or alternatively utilized directly in solid oxide fuel cells in an internal combustion engine or a gas turbine.⁸⁸

The general advantage of plasma technology for renewable electricity storage or use is its overall flexibility. This includes flexibility in terms of feed gas (i.e., for CO₂ conversion, both pure CO₂ splitting and mixtures with any H-source are possible; likewise, for N₂ fixation, mixtures with O₂ and H₂ are mainly explored, but CH₄ or H₂O should also be possible), flexibility in terms of energy source (solar, wind, hydro, wave, and tidal power, as well as nuclear power), and flexibility in terms of operation (fast on/off switching and modular upscaling capabilities).

However, further research is needed to improve the capabilities of this application. Major efforts should go to improving the energy efficiency. The latter largely depends on the type of plasma reactor and operating conditions. In summary, what is needed for energy-efficient CO₂ conversion or N₂ fixation is (i) a reduced electric field of 5–100 Td but still high enough plasma power, yielding sufficient vibrational excitation of the gas molecules, as this provides the most energy-efficient dissociation pathway, (ii) in combination with a low gas temperature to minimize vibrational losses upon collision with other gas molecules (so-called VT relaxation) or, in other words, a strong thermal nonequilibrium.

Besides further improving the energy efficiency, research should also focus on enhancing the conversion (e.g., by increasing the fraction of gas treated by the plasma, which is a limitation, for instance, in GA plasmas; cf. “CO₂ Splitting into CO and O₂”) as well as the product yield/selectivity. Indeed, perhaps the major disadvantage of plasma technology for gas conversion purposes is the need for a postreaction separation step as the gas conversion is typically (far) below 100%, and in addition, a plethora of reaction products can be formed due to the nonselective character of the plasma chemical reactions.

In the case of N₂ fixation, mainly NH₃ or NO/NO₂ is formed, and not so many byproducts, but the conversions are typically low due to the strong N≡N bond that needs to be broken. Operating at conditions that promote the vibrational kinetics (cf. above) will improve not only the energy efficiency but also the conversion. It should be stressed, however, that the H–B process for NH₃ production also requires such a separation step because the single-pass conversion is only 15–20%.

In the case of CO₂ splitting, the separation of CO and O₂ is rather energy-intensive and provides the largest energy cost, as demonstrated by van Rooij et al.⁸⁷ In the case of DRM (or CO₂/H₂ or CO₂/H₂O), mainly syngas is formed, but some minor side-products are observed as well, like hydrocarbons and oxygenates. The syngas mixture does not really pose a problem when it is subsequently used for Fischer–Tropsch or methanol synthesis. Moreover, plasma technology is able to deliver a wide variety of syngas ratios, depending on the initial feed gas mixing ratio. Furthermore, when the plasma conversion would enable direct production of liquid compounds (e.g., oxygenates), the post-reaction separation step would not be so critical as these liquid compounds are easier to separate. However, as discussed above, clearly more research is needed toward specific and rational design of catalysts tailored for the plasma environment.

To conclude, we can identify three specific areas where advances are needed for further improvement, i.e., (i) in plasma operation design to tailor the reduced electric field, plasma power, and gas temperature, (ii) in reactor design to tailor the gas flow and conversion, and (iii) in catalyst design to tailor the chemistry.

We want to stress that when plasma converts CO₂ into renewable fuels, the CO₂ will later be emitted again. Hence, the whole process can at most be carbon-neutral, which is certainly better than using fossil fuels, but it does not realize negative CO₂ emissions, which is crucially needed to stop global warming.⁸⁹ The latter could, however, be realized when plasma is combined with CO₂ capture technology, and the CO₂ is converted into value-added chemicals that can be kept away from the carbon-cycle for a very long time (up to centuries), like construction materials, monomers for plastics to be used in housing, etc. However, as mentioned above, much more research will be needed for this to design the right catalysts, yielding the selective production of such value-added chemicals.

In general, we believe that plasma technology can play an important role in the future energy infrastructure as it has great potential in combination with renewable energies for storage or use of peak energies and stabilization of the energy grid, and in this way, it contributes indirectly to CO₂ emission reductions. Finally, this is of interest not only for the production of renewable fuels (so-called solar fuels) but also for the production of chemicals. Indeed, we hope that the concepts of modular plants and decentralized chemical production facilities will soon gain acceptance in the chemical industry.

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