# Plasma technology for the electrification of chemical reactions

### **Annemie Bogaerts**

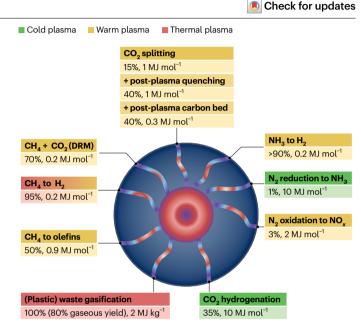
Plasma technology is gaining increasing interest in sustainable chemistry, by electrification of chemical reactions. This Comment discusses the potential and limitations of both cold and warm/thermal plasmas, challenges in plasma catalysis and reactor scale-up, and the status of start-up companies, and provides options for further performance improvement.

Plasma is a (partially) ionized gas, created by applying (electrical) energy to a gas. This causes gas breakdown into ions and electrons. The light electrons are accelerated by the electric field, and they 'activate' gas molecules, creating new ions, excited molecules and radicals. This reactive chemical cocktail makes plasma interesting for the conversion of stable molecules (such as  $CO_2$ ,  $N_2$  and  $CH_4$ ) into value-added compounds at atmospheric pressure. Furthermore, plasma can be quickly switched on and off, making it ideal for chemical conversions with (fluctuating) renewable electricity, hence 'power-to-X'.

The chemical industry is largely dominated by thermal catalysis, and large efforts are devoted to electrifying conventional chemical processes through electric heating (power-to-heat). While this is crucial and very valuable, one can also directly use electricity for the chemical reactions through generating electrons, as in electrocatalysis and electrochemistry and plasma technology ('electrification 2.0'). Thermal catalysis, and also electrocatalysis, find more widespread application in industry in contrast to plasma technology. However, the latter is gaining increasing interest, especially owing to its fast switch on/off capability, high reactivity and possibility to operate without catalysts. Its high reactivity makes it especially suitable for 'simple' reactions, breaking up molecules into a few smaller ones, rather than selectively producing more complex molecules, although the latter is possible in plasma-liquid systems. For the selective production of chemicals in gas-phase plasmas, a catalyst is needed, but, as described below, plasma catalysis is still at a low technology readiness level.

Plasma-based power-to-X finds application in  $CO_2$  splitting into CO and  $CO_2$ ,  $CH_4$  conversion into olefins,  $CO_2$  and valuable carbon (such as carbon black or carbon nanotubes), the combined  $CO_2$  and  $CO_2$  and  $CO_3$  hydrogenation, partial oxidation of  $CO_4$ ,  $CO_4$ ,  $CO_4$  hydrogenation, partial oxidation of  $CO_4$ ,  $CO_4$ ,

 $Various \ plasma\ reactor\ types\ have\ been\ developed\ for\ these\ applications,\ including\ dielectric\ barrier\ discharges\ (DBDs),\ microwave\ (MW),\ gliding\ arc\ (GA)\ and\ arc\ plasmas,\ nanosecond-pulsed\ discharges$ 



 $\label{eq:Fig.1} \begin{tabular}{l} \textbf{Fig. 1} & \textbf{Main applications of plasma-based power-to-X, with representative} \\ \textbf{performance metrics.} & \textbf{The color refers to the three main plasma types (see top),} \\ \textbf{and the performance metrics are conversion (in \%) and energy cost (EC, in MJ mol^-1).} \\ \textbf{The EC is with respect to conversion, and the conversion of DRM refers to total conversion.} & \textbf{The EC for waste gasification is given in MJ kg^{-1} processed waste.} \\ \textbf{The EC for N}_2 \ \text{reduction to NH}_3 \ \text{and CO}_2 \ \text{hydrogenation does not include the EC for H}_2 \ \text{production, but only for the plasma process, where H}_2 \ \text{is used as inlet gas.} \\ \textbf{Furthermore, the metrics for CO}_2 \ \text{hydrogenation correspond to CO formation.} \\ \textbf{Indeed, for some reactions (CO}_2 \ \text{splitting to CO, DRM to syngas, N}_2 \ \text{oxidation to NO}_x, \ N_2 \ \text{reduction to NH}_3, \ \text{and NH}_3 \ \text{cracking to H}_2), \ \text{the product selectivity is close to 100\%, and yield is equal to conversion.} \ \textbf{However, in the other reactions, several products can be formed.} \ \text{More information on the metrics stated in this figure, including the sources, and information on product selectivity and yield, can be found in Supplementary Information.} \\ \end{tabular}$ 

(NPDs), and atmospheric pressure glow discharges (APGDs). We can make a rough subdivision into cold (DBD), warm (MW, GA, NPD and APGD) and thermal (arc, MW) plasmas, although warm plasmas are also considered quasi-thermal (with temperatures ranging from about 3,000 K to above 6,000 K).

### Cold (DBD) plasmas, challenges in plasma catalysis

DBD plasmas are typically characterized by gas temperatures slightly above room temperature (about 400–500 K), although local temperatures might be higher than reported, owing to hotspots. Overall, DBDs are most useful for exothermic reactions, which benefit from low temperature, such as  $NH_3$  synthesis from  $N_2/H_2$  plasmas, and for the selective production of oxygenates by  $CO_2$  hydrogenation or DRM,

in combination with catalysts, in so-called in-plasma catalysis, where the reactive plasma species (radicals and excited molecules) can activate the catalyst. However, DBD plasmas exhibit low energy efficiency because the electron energy is typically too high for most efficient gas dissociation<sup>1</sup>.

While several papers report plasma–catalyst synergy<sup>6</sup>, that is, plasma catalysis yields higher performance than the sum of plasma and catalysis separately, or a high selectivity toward targeted compounds, such as methanol<sup>7</sup>, closer inspection indicates that synergy is not always reached, and the methanol (or other oxygenates) selectivity is largely overestimated when measured offline because this method does not properly account for mass balance. We therefore strongly advocate only reporting oxygenate selectivities from online measurements to allow fair comparison with thermal catalysis. A more detailed discussion on this can be found in ref. 8.

Overall, the underlying mechanisms of plasma catalysis are still far from understood $^\circ$ . First, there is limited insight into the optimal catalyst material tailored to the plasma environment. Many plasma catalysis studies are based on trial-and-error experiments, using insights from thermal catalysis, but the best thermal catalyst is not necessarily optimal in plasma catalysis. For instance, radicals are the main species in DBD, but microkinetic modeling suggests that metal catalysts may scavenge radicals, and thus rather act as 'anti-catalysts' in plasma catalysis $^\circ$ . Other materials are potentially more suitable, such as metal oxides, which may accommodate oxygen vacancies, and  ${\rm CO}_2$  could be activated by filling the oxygen vacancy, thus enhancing CO formation. However, the role of oxygen vacancies in plasma catalysis remains largely unexplored. Detailed insights needed to make progress in the field can be obtained from chemical kinetics modeling as well as in situ surface characterization.

Another way to enhance plasma-catalyst synergy would be tuning the plasma conditions to the catalyst needs, promoting (electronically and vibrationally) excited molecules. The latter can reduce the energy barrier for dissociative adsorption at the catalyst surface, enhancing the reaction rates compared with thermal catalysis. Promoting vibrational excitation could be realized by lowering the reduced electric field (that is, electric field divided by gas number density (E/N), expressed in Td). Typical E/N values in DBDs are above 100 Td, yielding electron impact dissociation, while vibrational excitation requires lower E/N(about 50 Td), like in warm plasmas. However, the latter exhibit higher gas temperatures (up to 6,000 K), far too high for direct catalyst implementation, and resulting in fast relaxation of the vibrational levels to the ground state. Hence, an intermediate plasma type would be needed, in between cold (DBD) and warm plasmas, with E/N around 50 Td, to promote vibrational excitation, but gas temperatures below 1,000 K, for vibrational-translational non-equilibrium, and to accommodate catalysts inside the plasma.

Finally, probably the most important is to improve plasma-catalyst contact. Indeed, even if we find the ideal catalyst tailored to the plasma environment, and the plasma conditions are optimally tuned to the catalyst needs, there is no guarantee of plasma-catalyst synergy because the plasma chemistry is often dominant over the catalytic chemistry. In addition, the catalyst also affects the discharge behavior (for example, change from filamentary to uniform plasma), which affects the plasma chemistry, potentially overshadowing possible chemical-catalytic effects<sup>8</sup>. The reason for the dominant plasma chemistry is the limited surface area available in plasma catalysis because plasma cannot penetrate catalyst pores below about 600 nm, and thus, reactive plasma species cannot be generated in such small pores.

Moreover, species diffusion from the plasma to within the pores is limited because of their short lifetimes. The void space between the catalytic packing should be below 100 µm so that reactive plasma species can reach the catalyst surface, and surface reactions are promoted above the plasma chemistry<sup>8</sup>. Hence, we should target improved reactor design, with smaller void space for better plasma-catalyst contact, for example, by using micrometer-sized catalyst/support beads (although care must be taken to avoid substantial pressure build-up due to a too dense packing) or by creating plasma inside micrometer-size 'structures' (for example, honeycomb and foams) coated with catalyst. More detailed discussion about these and other options to improve plasma-catalyst contact can be found elsewhere8. More insight is needed for developing improved reactors, for example, based on multi-scale plasma-catalysis models, that integrate plasma and surface chemical kinetics9, but also gas flow dynamics, plasma electrical behavior (streamer propagation) and species transport. Altogether, it is clear that plasma catalysis is very complex, and substantial progress will require multidisciplinary collaboration and merging of expertise, including plasma physics and chemistry, catalysis, and catalytic reactor engineering.

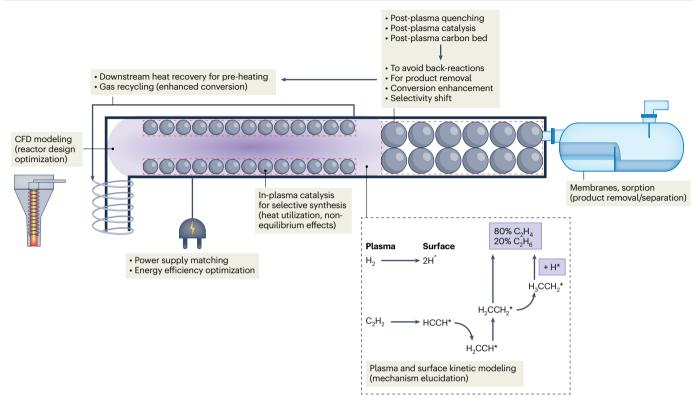
# Warm/thermal plasmas, a boost in research and start-up companies

There has been a clear increase in research efforts on warm plasmas for gas conversion, especially on MW, GA, NPD and APGD plasmas. As mentioned above, warm plasmas promote vibrational excitation, which is claimed to be the most energy-efficient dissociation process, by so-called vibrational ladder climbing¹. The best energy efficiency for  $CO_2$  splitting is reached in low-pressure MW plasmas, attributed to this mechanism. However, in practice, when operating at atmospheric pressure, the high gas temperature (3,000-6,000 K) causes vibrational–translational relaxation, and the chemistry of, for example,  $CO_2$  splitting, DRM,  $NO_x$  formation and  $NH_3$  cracking, proceeds mainly thermally  $^{5,10,11}$ . Nevertheless, it is quite efficient, as heating is induced directly in the gas by vibrational–translational relaxation and exothermic chemical reactions and not applied from an externally heated body (like resistive heating).

However, if the temperature is above the maximum needed for full conversion within the typical gas residence time, further heating does not speed up the reactions and is thus a waste of energy input. Likewise, heat can also be lost through the walls. Therefore, it is important to know the energy distribution, that is, how much energy is effectively consumed for chemical conversion, and present strategies to recover the excess heat as much as possible, for example, for gas preheating as discussed below.

Figure 1 shows the typical conversion and energy cost (EC) obtained for various applications, where endothermic reactions are most efficient in warm plasmas, while exothermic reactions are more suitable in cold (DBD) plasmas, and (plastic) waste gasification is carried out with thermal plasmas.

Because of the promising laboratory-scale results, more and more start-up companies are being established. In fact, plasma-based CH<sub>4</sub> conversion toward olefins has already been performed within the Huels process in Germany since 1938, using a thermal arc plasma at temperatures of 15,000–20,000 K for CH<sub>4</sub> conversion into C<sub>2</sub>H<sub>2</sub>, with single-pass-yields up to 40%. Plasma pyrolysis of CH<sub>4</sub> (natural gas) for the co-production of H<sub>2</sub> and carbon black was also performed already in the 1990s by Kvaerner using a thermal d.c. plasma torch<sup>3</sup>. In 1992, three MW plasma pilot installations were tested at ScanArc (Sweden).



**Fig. 2** | **Possible improvements in plasma and process design for gas conversion applications.** Computational fluid dynamics (CFD) modeling can help improve plasma reactor design (see text), while chemical kinetics modeling can reveal the underlying mechanisms and propose solutions to overcome limitations.

Catalyst implementation (in-plasma catalysis) can improve the selectivity toward value-added compounds. The other aspects focus on improving the overall

process: post-plasma quenching, catalysis or carbon beds, as well as membranes or sorption materials, can avoid back-reactions (that is, recombination of the products back into the reactants), and thus increase the conversion and product selectivity. Post-plasma quenching is ideally combined with heat recovery (for gas pre-heating). Gas recycling also improves the overall conversion, while the overall energy efficiency should be optimized by matching the power supply.

In 1997, Kvaerner built its first industrial unit (in Canada), producing 20,000 t of carbon black and 70 million  $\rm Nm^3$  of  $\rm H_2$  per year. However, they stopped activities in 2003. In 1997, Fulcheri and colleagues also started developing thermal plasma for the co-production of  $\rm H_2$  and carbon black in France. In 2012, the activities were continued at Monolith Materials with a pilot plant in California, and in 2016, Monolith developed its first commercial-scale facility in Nebraska (Olive-Creek I), which has been operational since 2020, providing a  $\rm H_2$  yield above 95%, a C yield above 90% and an EC of 25 kWh kg $^{-1}$   $\rm H_2$  (or about 0.2 MJ mol $^{-1}$  of  $\rm H_2$ ), which is only 42% of the EC by water electrolysis  $^3$ , and comparable to steam reforming of natural gas with CO $_2$  capture. In 2024, the Brightsite spin-off company Thoriant was established for plasma-based CH $_4$  conversion toward C $_2\rm H_2$  and  $\rm H_2$ .

There are also several start-up companies for plasma-based  $N_2$  fixation toward  $N_0$  for fertilizer production. In fact, one of the first industrial processes for fertilizer production was plasma based: the Birkland–Eyde process, using thermal air plasma. However, owing to the high EC and electricity price, compared with the cheap fossil fuel-based Haber–Bosch process, it was abandoned in 1920. Recently, however, several companies have entered the plasma-based  $N_2$ -fixation market because plasma allows full electrification of fertilizer production. N2 Applied (established in 2010) focuses on plasma-based  $N_2$  fixation to  $N_2$ , including enrichment of organic manure and synthesis of mineral fertilizers. VitalFluid (established in 2014) produces

plasma-activated water for food production, to reduce pathogenic activity and improve germination. Other, more recent, N<sub>2</sub>-fixation companies include NitroCapt (established in 2016), Nitricity (2018), PlasmaLeap (2019), Green Lightning, PlasNifix, Psymbios (all in 2021), NitroFix (2022) and DEBYE (2023).

Plasma-based CO<sub>2</sub> splitting is being pursued by our own spin-off company, D-CRBN (established in 2021). Their first pilot reactor had 7 GA plasma reactors in parallel, each powered by about 1 kW, but with a limited CO<sub>2</sub> processing capacity of 100 l min<sup>-1</sup> (that is, 100 t yr<sup>-1</sup>). The next-generation 'pilot XL' (with 18 plasma reactors in parallel) will be operational in 2025, and the aim is to reach 30 ktCO<sub>2</sub> yr<sup>-1</sup> by 2026, and 1 MtCO<sub>2</sub> yr<sup>-1</sup> by 2030. A recent techno-economic analysis for CO<sub>2</sub> conversion in GA plasma, for a pilot plant producing 100 tCO per day, reported an EC of 19.5 GJ tCO<sup>-1</sup> (or 0.55 MJ mol<sup>-1</sup>), which was estimated 43% lower than for electrolysis and conventional CO<sub>2</sub> conversion<sup>12</sup>. The CO production cost was about US\$670 tCO<sup>-1</sup> and is estimated to drop below US\$500 tCO<sup>-1</sup> in the future, based on affordable feedstocks and equipment.

Plasma reactors are typically made of cheap materials, and warm plasmas do not require catalysts, yielding relatively low capital expenditure (CAPEX), which is mainly determined by the power supply. The latter is still quite expensive today because it is still a 'niche product', and challenges exist, for example, in degradation, reproducibility, and tight control and energy efficiency for MW power supplies. Scale-up

also remains a challenge: current MW power supplies are limited to 150 kW per unit, although commercial set-ups exist up to 200 kW, but they comprise multiple MW power supplies chained together, which increases the CAPEX. However, we expect that the price of power supplies will drop upon further expansion of plasma technology in the above applications, yielding better economies of scale.

As mentioned above, plasma reactors can simply be scaled up by placing reactors in parallel, although this increases the CAPEX, and optimal communication between power supply and individual reactors is essential. An alternative way of upscaling is by increasing the reactor size, although care must be taken that the 'chemically active' plasma region for gas conversion also increases by applying higher power because otherwise the conversion is limited. This higher power will often make the plasma more thermal. It is noted that some industrial chemical processes (such as Haber–Bosch) are only cost- and energy-efficient at large scale, but this is accompanied by costly distribution, which contributes to the product price. In contrast, plasma technology allows decentralized production of value-added compounds from renewable electricity (for example, fertilizer production by local farmers, based on one wind turbine or a few solar panels), which minimizes the distribution costs.

# Opportunities for further improvement of plasma technology

Plasma-based electrification of chemical reactions is promising, as illustrated by the examples above. However, although many reactions are demonstrated as a proof of concept in laboratory plasmas (Fig. 1), they are not all promising enough to be further developed at a commercial scale. For example, DRM is not energy-efficient in DBD plasmas (Supplementary Information) and would only be commercially viable if high-value products, such as oxygenates, can be selectively produced in large amounts. In practice, however, syngas is the main product, due to the dominant plasma chemistry. Hence, dedicated catalysts must be developed, in combination with close plasma-catalyst contact, to promote selective catalyst surface reactions toward higher-value oxygenates, which should not be destroyed again in the plasma, for which clearly more research is needed (see above). In contrast, DRM in warm plasmas is much more energy-efficient (Supplementary Information), so this process is far more promising for upscaling. Although it also mainly produces syngas, this syngas can be combined with Fischer-Tropsch for the production of higher hydrocarbons or oxygenates. In summary, while several papers claim that plasma catalysis allows one-step selective production of oxygenates, this still remains to be demonstrated (see discussion above regarding offline measurements).

In parallel with industrial implementations, there are still several options to further improve the performance (Fig. 2). Improving plasma reactor design is needed to control chemical non-equilibrium and gas flow dynamics and its mixing with the chemically active plasma region for maximum conversion. This is not always the case<sup>11</sup>, and can explain the somewhat limited conversion in some applications (Fig. 1). Turbulence can help improve mixing, but it can also transport more heat from the hot central plasma filament outward, giving energy losses. Computational fluid dynamics modeling provides more insight into the complex interaction between plasma and gas flow dynamics, to optimize mixing and minimize energy losses, while chemical kinetics modeling can elucidate the chemical conversion pathways. Nevertheless, these models do not yet have predictive power due to the complex physics and chemistry and the intricate coupling between gas flow dynamics, heating, chemistry and plasma electrical behavior. In particular, chemical kinetics models are still subject to uncertainties, due to limited input data.

Besides optimizing plasma reactor design, research should also focus on what happens post-plasma, where product molecules often recombine back into the reactants. These back-reactions can be avoided by fast cooling (quenching) of the gas post-plasma, which has resulted in  $\mathrm{CO}_2$  conversion enhancements by sevenfold<sup>13</sup>. Ideally, the heat taken away by cooling should be recovered by preheating the inlet gas. Indeed, warm/thermal plasmas would benefit from gas preheating, so that less plasma power is needed to reach the same level of conversion, thus reducing the energy cost. However, this is only true in case of heat recovery, that is, combined with a heat exchanger, utilizing the excess heat that would otherwise be lost downstream from the hot plasma effluent. While heat integration is common in the chemical industry, it is still in its infancy in plasma technology.

Another way to avoid back-reactions is by removing one of the products, for example, by sorption materials or membranes. Specifically for CO<sub>2</sub> splitting, a post-plasma carbon bed is very powerful: the O/O<sub>2</sub> produced from plasma–CO<sub>2</sub> splitting reacts with the carbon bed, forming extra CO, and avoiding CO recombination with O/O<sub>2</sub> back into CO<sub>2</sub>, hence also improving the CO<sub>2</sub> conversion. Moreover, at temperatures above 1,000 K, the unconverted CO<sub>2</sub> also reacts with the C atoms through the reverse Boudouard reaction (CO<sub>2</sub>+C  $\rightarrow$  2CO), further improving the conversion and forming extra CO. Enhancements in CO<sub>2</sub> conversion and simultaneous reductions in EC by a factor of four to five have been reported, and all the O<sub>2</sub> can be removed from the outlet mix, thus reducing separation costs<sup>14</sup>.

In general, more research should be devoted to combining plasma with membranes or sorption materials, for post-plasma product separation. Indeed, the high plasma-chemical reactivity produces several different compounds simultaneously, for example, in CH<sub>4</sub> conversion (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, larger hydrocarbons and H<sub>2</sub>) or DRM (CO, H<sub>2</sub>, hydrocarbons and also oxygenates). Plasma catalysis can improve product selectivity, but still faces major challenges, as discussed above. Post-plasma catalysis, combined with warm plasmas (which are too hot for in-plasma catalysis), is promising, but still largely unexplored. Indeed, the hot gas leaving the plasma reactor can thermally activate catalysts, further enhancing the conversion, or changing product composition, as successfully demonstrated for the targeted production of C<sub>2</sub>H<sub>4</sub>, where CH<sub>4</sub> plasma mainly produces C<sub>2</sub>H<sub>2</sub>, but post-plasmacatalytic hydrogenation leads to C<sub>2</sub>H<sub>4</sub> (ref. 15). Overall, we believe there is a lot to gain from process integration, and, thus, the focus should be not only on plasma optimization but also on the entire process design.

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#### Competing interests

A.B. is co-founder and member of the board of directors (without remuneration) of D-CRBN (a spin-off company from her research group mentioned in this paper).

### Additional information

 $\textbf{Supplementary information} \ The online version contains supplementary material available at \ https://doi.org/10.1038/s44286-025-00229-3.$ 

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