

Plasma technology for the electrification of chemical reactions

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This supporting information document provides more information on the performance metrics data summarized in Figure 1 of the main paper, for the various reactions, i.e., how we obtained this data based on literature. Figure 1 presents the conversion and energy cost (EC) of the conversion. In many of the reactions, there is only one (main) product, with selectivity (close to) 100%, so that the product yield is equal to the conversion. However, in some reactions, more products can be formed. For those reactions, we also discuss the typical product distribution in this document. We took the data from literature, but always checked whether the correct formulas are used to calculate these performance metrics (e.g., accounting for gas expansion/contraction in the reaction, and whether the products are correctly detected, not by offline measurement), and if needed, we recalculated them based on the raw data. We refer to [1] for using the correct formulas.

1. Plasma-based CO₂ splitting

1.1. Plasma-only process

CO₂ splitting is one of the most studied reactions in plasma technology, by various types of plasma reactors, ranging from cold plasmas (mainly dielectric barrier discharges; DBDs) to warm plasmas, including microwave (MW), gliding arc (GA), low-current arc, spark, atmospheric pressure glow discharge (APGD) and nanosecond pulsed plasmas, and a few papers also report on the use of thermal plasmas. A very complete overview of the state-of-the-art, based on all data published up to 2017 for all types of plasmas, was provided in our Chemical Society Reviews paper [2], and it was updated more recently in 2023 [3].

In general, MW plasmas at reduced pressure exhibit the highest EC, i.e., up to 80%, and even up to 90% when using supersonic expansion. However, this data was obtained in the 1980s in the former USSR, and have not been reproduced since then. Moreover, the EC did not include the cost of the vacuum system. Therefore, we do not report this data here, also because we prefer to focus on atmospheric pressure plasmas, which have more potential for commercial exploitation.

At atmospheric pressure, the very best values reported for conversion are about 20%, at an EC of ~ 0.4-0.5 MJ/mol [3]. Note, in the overview figures of [2,3], the EC was not plotted, but the energy efficiency (EE). The best EE values are somewhat above 60%, which (for CO₂ splitting) corresponds to an EC around (below) 4.9 eV/molecule or 0.49 MJ/mol [2]. However, we decided to not report the very best performance metrics in Figure 1, but more representative values that have been reported by several groups in various plasma types. Indeed, as can be seen in the overview figures of [2,3], the conversion and EC (or EE) can vary in a wide range. Thus, we wrote in Figure 1: **conversion = 15% and EC = 1 MJ/mol**, based on an extensive study, evaluating various different warm plasmas, including various GA plasmas, but also APGD and MW plasmas [3].

Note that the performance metrics written in Figure 1 indeed apply to warm plasmas, while in cold (DBD) plasmas, the EE is typically four times lower (up to 15%), and hence the EC four times higher (thus around 4 MJ/mol), although the conversion can range up to 50% [2,3].

1.2. Post-plasma quenching

Post-plasma quenching can greatly improve the conversion, by avoiding the back-reactions, i.e., recombination of CO with O/O₂ into CO₂, as explained in the main paper. The best results, i.e., **conversion ~40%, at an EC of ~1 MJ/mol**, were reported by Hecimovic et al. for (near) atmospheric pressure MW plasmas [4], but they are representative for the numbers presented by other authors as well, in other warm plasmas at similar SEI values.

1.3. Post-plasma carbon bed

Placing a carbon bed post-plasma also significantly improves the performance, by removing the formed O/O₂, and thus again avoiding the back-reactions to CO₂. In addition, at temperatures above 1000 K (which is feasible for the hot effluent gas after warm plasmas) the unconverted CO₂ can react with the C atoms from the carbon bed via the reverse Boudouard reaction ($\text{CO}_2 + \text{C} \rightarrow 2 \text{CO}$), further enhancing the conversion. Importantly, not only the conversion, but also the EC, greatly improves upon combination with post-plasma carbon bed. Note that EE is less straightforward to be defined in this case, because one needs to know the exact contributions of the CO₂ conversion inside the plasma and the reverse Boudouard reaction, as explained in [5]. The best results were recently obtained by O'Modhrain et al. [5] (conversion ~41%, EC ~0.41 MJ/mol) and by Biondo et al. [6] (conversion >40%, EC ~0.28 MJ/mol), hence we took as best (but representative) values: **conversion = 40%, EC = 0.3 MJ/mol**; see Figure 1.

As CO₂ splitting typically only produces CO and ½ O₂, with negligible solid carbon formation (at most conditions investigated) or other products, the CO selectivity is typically 100%, and the CO yield is equal to the CO₂ conversion.

2. Plasma-based CH₄ and CO₂ conversion: Dry reforming of methane (DRM)

The combined CO₂ and CH₄ conversion (DRM) typically yields higher conversion and lower EC than pure CO₂ splitting, because of the easier conversion of CH₄. The conversion defined here refers to the total conversion, or weighted average of CH₄ and CO₂ conversion. We also made a very complete overview of the state-of-the-art for DRM, based on all data published up to 2017 for all types of plasmas, as reported in our Chemical Society Reviews paper [2], and updated in 2022 [7]. As can be seen in the overview figures of [2,7], the conversion and EC again vary in a wide range, but we consider a **total conversion of 70%, at an EC of 0.2 MJ/mol** (or 2 eV/molecule) as representative values (although not the best ever reported, but representative for several types of warm plasmas, such as GA, MW, APGD, spark and nanosecond pulsed plasmas. The conversion in cold (DBD) plasmas is similar, but the EC is at least five times higher, with more representative values being 50 times higher, in the order of 10 MJ/mol [7].

Typically, CO and H₂ (or syngas) are the main products, with selectivities reaching up to 100%, although DRM is prone to solid carbon formation, especially at CH₄ fractions of 50% and higher (which typically makes the plasma unstable), and also higher hydrocarbons (typically C₂H₂ in warm plasmas, and C₂H₆ in DBD) are also detected in smaller amounts. Oxygenates can also be formed in principle, but when correctly measured (i.e., with online gas chromatography), their yields are typically negligible, although these products have been reported in DBD plasmas (with and without catalysts), but typically by offline measurements, which largely overestimates their selectivities. Nevertheless, as different products can be formed, it is not straightforward to define the EE, because one needs to account for the reaction enthalpy of all possible reactions occurring, or the lower heating value of all possible products (depending on the formula used for

calculating EE, see [1] for details). Hence, we recommend using EC instead of EE as more accurate performance metric.

3. Plasma-based CH₄ conversion to H₂

Plasma-based CH₄ conversion to H₂ reaches the best results in thermal plasmas, where conversions above 95% are typically achieved under optimal conditions, as demonstrated by Fulcheri et al. for thermal plasma-based CH₄ pyrolysis [8]. The lowest reported EC for H₂ is reported by Monolith Materials through their thermal plasma CH₄ pyrolysis process, reaching ~ 0.2 MJ/mol H₂. Hence, we put in Figure 1: **conversion of 95%, at an EC of 0.2 MJ/mol H₂**. Monolith's commercial-scale facility (Olive Creek I, operational since 2020) achieves CH₄ conversions above 99%, producing H₂ and solid carbon as the primary products, with negligible formation of other hydrocarbons or CO₂ emissions. The quality of the produced solid carbon can vary significantly, from amorphous carbon black suitable for industrial applications, to higher-value structured carbons such as graphite or graphene. In this case, the solid product depends on the specific plasma operating conditions and reactor design.

4. Plasma-based CH₄ conversion to olefins

For plasma-based CH₄ conversion to olefins, the conversion is typically lower, often ranging from around 10% to over 70%, depending strongly on the plasma type and operating conditions [9]. The reason it is lower than for CH₄ conversion into H₂ is attributed to the fact that the latter typically operates at higher power, in thermal plasmas.

The product distribution is broad, encompassing not only the most valuable product, C₂H₄, but also significant amounts of C₂H₂, C₂H₆, C₃ and even C₄ hydrocarbons. C₂H₄ is thermodynamically challenging to synthesize selectively from CH₄ coupling due to its intermediate position in the reaction pathways. The product selectivity is highly dependent on the plasma source employed: warm plasmas (e.g., pulsed, GA and MW plasmas) typically favor unsaturated hydrocarbons like C₂H₂, while non-thermal plasmas (e.g., DBD) tend to yield more saturated and longer-chain hydrocarbons. Recent state-of-the-art studies exemplifying these trends include the catalyst-free hybrid plasma system by Delikonstantis et al., achieving an EC of approximately 1.64 MJ/mol C₂H₄ at around 25% yield per pass [10], while the plasma-catalytic approach of Cameli et al. reported an EC of approximately 0.87 MJ/mol C₂H₄ [11]. While these values are towards C₂H₄, the authors reported the same EC towards C₂H₂, which is by far the main plasma product, but it is quite selectively hydrogenated into C₂H₄ post-plasma, using the hot plasma effluent to thermally activate the catalyst (so at no extra EC). For that reason, we write in Figure 1: “CH₄ to olefins”, with performance metrics of: **conversion of ~50%, at an EC of 0.9 MJ/mol**.

5. Plasma-based (plastic) waste gasification

Waste gasification by plasma is carried out with a much larger variety of plasma systems (both warm and thermal), and feedstock (municipal solid waste, sewage sludge, sorted or unsorted plastic waste) than other processes described herein. Specifically, the commonly used plasma types are DC and AC arc torches, and MW plasmas, although the differences in specific configuration result in a large variety of setups used. The plasma power also differs within a few orders of magnitude, from 1 to 120 kW. Likewise, the plasma feed gases (used both as plasma-sustaining and gasifying agent) can also vary from inert gases (Ar, N₂) to CO₂, steam (H₂O), or their combination [12, 13]. Plasma gasification with air/O₂ (i.e., effectively plasma incineration) has

also been studied [14]. Such a wide span of conditions gives rise to very different process metrics and syngas yields. A typical EC cost reported is **2 MJ/kg processed waste**, which reflects the difference between the energy input and the (potentially usable) energy recovered as syngas [12-14].

The gasification extent (i.e., gaseous yield in Figure 1 of the main paper) depends on the type of waste, and ranges from 50 to 99% [15], with the remains being ash or inert slag. We chose **80% as the average gaseous yield**: it is closer to the higher values, which is more representative of more recent studies and plastic waste (which, obviously, results in higher gasification ratio due to its chemical composition).

The syngas composition is also a function of the plasma gas (gasifying agent). Steam-containing plasmas usually yield syngas with higher H₂:CO ratio (up to 2:1 H₂:CO) [12,15], whereas CO₂ plasmas may result in H₂ relative concentration of merely 10 vol%. In general, the output stream is comprised of up to 95% syngas, the other constituents being usually H₂O, CO₂, CH₄, and unsaturated C2-C3 hydrocarbons, but this again depends on the conditions used (plasma type, temperature, gasifying agent, etc.) [15].

6. Plasma-based CO₂ hydrogenation

Plasma-based CO₂ hydrogenation is mainly carried out in DBD plasmas (typically with catalysts) and involves three different reactions, i.e.,

(i) the reverse water-gas shift (RWGS) reaction:



(ii) the methanation reaction (or Sabatier process):



(iii) methanol formation:



Thermodynamics equilibrium considerations reveal that low temperatures (< 900 K) mainly yield CH₄, while CO is the major product at high temperature (> 900 K). The direct production of CH₃OH from CO₂ hydrogenation would however be desirable, because it is a valuable fuel and chemical intermediate. Nevertheless, at room temperature and ambient pressure, the equilibrium gas phase CH₃OH yield from CO₂/H₂ is near 0 %. Therefore, in thermal catalysis, CH₃OH production from CO₂ (or syngas: CO/H₂) operates at higher pressure, being favorable due to the reaction stoichiometry. However, thermodynamically, the process would benefit from lower temperature due to the exothermicity (-50 kJ/mol). This is however kinetically unfavorable, because of the high dissociation barrier of CO₂ that must be overcome. A compromise is made in thermal catalysis by operating at ~200 °C and 50 bar.

Plasma catalysis offers a unique way to enable kinetically limited processes, while maintaining thermodynamically favorable temperatures. Therefore, plasma-catalytic CO₂ hydrogenation into CH₃OH has attracted interest by several authors [16-30], but most of them reached very low CH₃OH yield. In recent years, some authors reported very high selectivities towards CH₃OH or other oxygenates, namely around 50% [19-25], but they were measured offline, which artificially overestimates the values to a large extent. In practice, when measured correctly (online), the

CH₃OH selectivities are still quite low, and more research is needed to find the best catalysts tailored to the plasma environment, for the selective production of such oxygenates. Therefore, in practice, the RWGS and methanation reactions are dominant, with the former being the most important (especially at higher temperatures).

For instance, Eliasson et al. [16] reported CO and H₂O as major products in plasma-alone, while CH₄ and CH₃OH were only detected with a selectivity of 3-4 % and 0.4-0.5 %, respectively. Adding a CuO/ZnO/Al₂O₃ catalyst resulted in a 10 times and 10-20 times higher CH₃OH yield and selectivity, respectively, but the maximum CH₃OH yield was still limited to ~1 %. Zeng and Tu [17] reported a CO₂ conversion of 7.5 % without catalyst, with the main products being CO and CH₄ at 46 % and 8 % selectivity, respectively. Adding a Cu/ γ -Al₂O₃, Mn/ γ -Al₂O₃ or Cu-Mn/ γ -Al₂O₃ catalyst improved the CO₂ conversion to 8-10 % and the CO selectivity and yield to 76-80 % and 6.4-7.9 %, respectively, but no CH₃OH was detected. Parastaev et al., [18] used a Cu/CeZrO₄ catalyst, and reported that the hydrogenation is mostly selective towards CO and CH₄, while CH₃OH formation was not monitored. Wang et al. [19], on the other hand, reported a high CH₃OH yield and selectivity, up to 11% and 54%, respectively. These record values were achieved in a DBD plasma reactor with water-cooled electrode and packed with a Cu/ γ -Al₂O₃ catalyst. The water-cooled electrode was claimed to control the temperature in the plasma, favouring the formation of CH₃OH (at low temperature), but the exact mechanisms are not yet understood. Moreover, the CH₃OH selectivity was measured offline, and therefore largely overestimated, like in other papers using the same principle (e.g., [20-25]). Recently, there is growing awareness that liquid oxygenates must be measured online to be correct, so the above selectivities of 50% must be reconsidered. Overall, most studies still report either CO or CH₄ to be the dominant products (e.g., [26-30]), with CO being predominant, especially at somewhat higher temperatures (400-800 K).

The numbers of conversion and EC written in Table 1 are based on work by Sun et al. [29,30], reporting an energy yield of ~ 0.1 mmol/kJ, which corresponds to an **EC = 10 MJ/mol, at a conversion ~ 35%**. CO was the dominant product formed, with selectivities above 90%. Note that this EC does not include the EC for H₂ production, but only for the plasma process itself, where H₂ is used as inlet gas.

7. Plasma-based N₂ oxidation to NO_x

Plasma-based N₂ oxidation to NO_x has been studied in a wide range of plasma reactors, including DBD and various warm/thermal plasmas. In fact, NO_x production by plasma is not new. A century ago already, the Birkeland-Eyde (BE) process was developed, using thermal plasma [31]. It was one of the first industrial N₂ fixation methods, but never played a big role, due to the lower EC of the Haber-Bosch process for fertilizer production. However, recently, plasma-based NO_x formation has gained renewed interest, due to reduced EC and the emergence of renewable electricity, making plasma technology more viable (as also illustrated by the many startup companies on plasma-based NO_x production that have been launched in recent years, as mentioned in the main paper), and many different plasma types are being explored [32,33].

A comprehensive overview of the state-of-the-art of the performance metrics reported in literature up to 2021 in all types of plasma reactors, was provided in [32]. Since then, however, significant improvements have been reported, which are briefly mentioned here, to motivate the numbers put in Figure 1.

Warm, or (quasi-)thermal plasmas are clearly the most promising. In a rotating gliding arc (RGA), NO_x yields up to 5.5 % were reported, at an EC of 2.4 MJ/mol [34]. These results were further improved, reaching NO_x yields of 5.9 %, at an EC of 2.1 MJ/mol [35], by placing a so-called “effusion nozzle” at the end of the RGA reactor, which was claimed to act as heat sink, causing fast quenching of the gas after reaction, thereby preventing the decomposition of the produced NO_x back into N_2 and O_2 . Furthermore, operating the RGA at elevated pressure (up to 4 bar) yielded maximum NO_x yields of around 5 % and lowest EC of 1.8 MJ/mol (in oxygen-enriched air) [36]. Furthermore, MW plasmas also yield fairly high NO_x yields of 3.8% at a low EC of 2 MJ/mol [37], while an even lower EC of 1.6 MJ/mol, at a NO_x yield of 1.5%, was reported for ns-pulsed plasma [38]. Note that the lowest EC reported to-date is 0.45 MJ/mol, obtained in a pulsed spark plasma jet [39]. However, this was accompanied by a very low NO_x yield (< 0.1%), and with low potential for scalability. For the latter reasons, it is not considered in the numbers put in Figure 1.

Note that NO and NO_2 (collectively called NO_x) are virtually the only products detected upon N_2 oxidation in (warm) plasmas, with typically NO being dominant, although elevated pressure produces almost exclusively NO_2 (highly interesting for fertilizer applications) [36]. Based on the above numbers, and considering that the NO_x yield is twice the N_2 conversion, we define a **N_2 conversion of 3%, at an EC of 2 MJ/mol** as representative values for N_2 oxidation into NO_x in Figure 1.

8. Plasma-based N_2 reduction to NH_3

In contrast to plasma-based N_2 oxidation to NO_x , plasma-based N_2 reduction to NH_3 is mostly performed in DBD plasmas (with catalysts). Indeed, this is an exothermic reaction, which benefits from the low temperature of DBD plasmas. A comprehensive overview of the state-of-the-art, based on all papers published till 2020, was provided in [40]. Since then, the performance metrics have not been spectacularly improved. More recent works provided an updated EC overview, as summarized in several reviews [41-44]. In plasma-catalytic NH_3 synthesis in a DBD reactor from N_2 and H_2 , the values of N_2 conversion and EC range from <0.1% to 12%, and from ca. 2 to 450 MJ/mol, respectively [41-44]. There is also often an empirical counter-correlation between EC and production rate: a lower EC corresponds to an extremely low production rate, and vice versa: reasonable production rates (e.g. in the order 100-1000 mg/h) are usually accompanied by a higher EC [45]. Instead of focusing on the production rate, we here present the two metrics most often addressed in plasma-based N_2 fixation with H_2 : EC and N_2 conversion. Our values in Figure 1, i.e., a **N_2 conversion of 1%, at an EC of 10 MJ/mol**, are based on the values collated in the aforementioned reviews. We note that this is not an exact value corresponding to a specific report; rather, it is an average value for the lower end of EC (see above) and typical conversion of 1 %. Note that NH_3 is the sole product of N_2 reduction with H_2 , so the NH_3 selectivity is virtually 100%. Furthermore, just like for CO_2 hydrogenation, the EC does not include the EC for H_2 production, but only for the plasma process, where H_2 is used as inlet gas.

9. Plasma-based NH_3 cracking to H_2

Plasma-based NH_3 cracking is gaining increasing interest in recent years. Early experiments with thermal radio frequency plasma [46] showed high EC and limited practical use, because NH_3 was diluted in Ar/H_2 . More recently, various plasma types are being investigated for NH_3 cracking, but

most research has been performed with DBD plasmas, often combined with catalysts (e.g., [47-50]). While they can reach NH_3 conversion up to 100% (at least when combined with catalysts, otherwise not above 20%), their EC is excessively high, typically in the order of 2-10 MJ/mol (and even more) without catalysts, and 0.3-1 MJ/mol with catalysts.

Warm plasmas are not so often used for NH_3 cracking up to now, although they exhibit much better performance, with EC down to 0.2 MJ/mol, albeit at relative low conversion (around 20%) [51,52]. We recently compared four different warm plasmas (two different GA plasmas, an APGD and a pin-to-pin low-current arc plasma) in a wide range of conditions, and we also benchmarked our results with the existing literature [53]. We obtained a quite low EC around 0.2 MJ/mol, for an NH_3 conversion up to 50%. The conversion obtained was limited by the power supply, and based on our measurements, we expect it to further increase upon higher power, for the same EC. Recently, we performed experiments in a MW plasma where we could apply higher power, indeed reaching conversion close to 100%, at an EC down to ca. 0.2 MJ/mol. Hence, we inserted the following data in Figure 1: **conversion > 90%, EC = 0.2 MJ/mol**, demonstrating the best (but representative) performance in warm plasmas. Again, H_2 (and N_2) are the only products formed.

10. References

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