This paper brings the comparison of performances of CO₂ conversion by plasma and plasma-assisted catalysis based on the data collected from literature in this field, organised in an open access online database. This tool is open to all users to carry out their own analyses, but also to contributors who wish to add their data to the database in order to improve the relevance of the comparisons made, and ultimately to improve the efficiency of CO₂ conversion by plasma-catalysis. The creation of this database and database user interface is motivated by the fact that plasma-catalysis is a fast-growing field for all CO₂ conversion processes, be it methanation, dry reforming of methane, methanolisation, or others. As a result of this rapid increase, there is a need for a set of standard procedures to rigorously compare performances of different systems. However, this is currently not possible because the fundamental mechanisms of plasma-catalysis are still too poorly understood to define these standard procedures. Fortunately however, the accumulated data within the CO₂ plasma-catalysis community has become large enough to warrant so-called “big data” studies more familiar in the fields of medicine and the social sciences. To enable comparisons between multiple data sets and make future research more effective, this work proposes the first database on CO₂ conversion performances by plasma-catalysis open to the whole community. This database has been initiated in the framework of a H2020 European project and is called the “PIONEER Database”. The database gathers a large amount of CO₂ conversion performance data such as conversion rate, energy efficiency, and selectivity for numerous plasma sources coupled with or without a catalyst. Each data set is associated with metadata describing the gas mixture, the plasma source, the nature of the catalyst, and the form of coupling with the plasma. Beyond the database itself, a data extraction tool with the open access performance data of plasma-catalysis reactors with the open access PIONEER database.
1. Introduction

Although the first article mentioning the association of a non-thermal plasma source with catalysts dates back to 1921 [1], studies on this subject have increased dramatically since the 1990s, see for instance [2–21] and references therein. An overview of the growth of the number of plasma-catalysis publications per year obtained from different popular search engines is shown in Fig. 1. The plasma-catalysis coupling can be used either to decontaminate a gas (indoor air treatment, NOx destruction, etc.) or to realise the synthesis of a molecule (NH3 synthesis, CO2 conversion into CO, hydrocarbons and alcohols, etc.). In the particular case of CO2 conversion, a plasma-catalyst coupling can increase the yield of different molecules (e.g. methane, methanol, ethanol, and other hydrocarbons) compared to plasma-only conversion depending on the gas mixture and the catalysts used. All these processes, whether methanation, dry reforming, or others, are also studied in thermal catalysis. However, the reaction pathways and the performances obtained are fundamentally different in plasma-catalysis. In thermal catalysis, the reactant molecules in their ground state adsorb on the catalyst, then react only on the surface, and finally desorb, possibly after several steps. In plasma-catalysis, excited species and radicals are created in the gas phase by the plasma, which can then reach the catalyst surface and alter the kinetics, promoting different reaction pathways compared to thermal catalysis. In addition, the interaction between the plasma and the catalyst may open up new reaction pathways, which are not available in thermal catalysis. For example, the strong electric fields induced by the plasma can affect the adsorption energies and the mobilities on the catalyst surface [23]. Alongside this, the presence of charged species and high-energy photons results in reactions that are occasionally compared to photo-catalysis or electro-catalysis [24]. However, as will be explained later, the reaction pathways within plasma-catalysis cannot be simply categorised as either thermal-catalytic, electro-catalytic, or photo-catalytic. Instead, the unique combination of reaction pathways within plasma-catalysis may constitute a new form of non-equilibrium catalysis worthy of a separate category of its own.

The fast-increasing number of plasma-catalysis publications, as shown in Fig. 1, puts pressure on the development of tools for benchmarking and performance comparison. However, plasma-catalysis is still lacking in standardised tools and benchmarks to allow relevant performance comparison for different catalytic materials. Appropriate examples may be model reactors, systematic characterisation methods, or fully-characterised reference materials, openly available to the community as being done for conventional catalysis [25]. The complexity of plasma-catalysis is such that systematic procedures are yet to be established. To do
so, two approaches, complementary to each other, have to be developed in parallel.

1. in situ and time-resolved measurements in combination with modelling to get a deeper, fundamental understanding of plasma-catalyst interactions.
2. developing meta-analysis tools and approaches to capture key parameters for performance improvement from existing conversion studies, even if the experiments were not conducted under standardised conditions.

The first approach generally imposes the use of specific reactor geometries that are dedicated to the study of a particular phenomenon and are thus not focusing on high CO2 conversion. On the contrary, reactors designed for high conversion performance have more complex geometries and are typically not well-suited for advanced in situ diagnostics, making comparisons between different reactors more challenging. To compensate for this and make the second approach listed above more effective, a detailed description of the experimental conditions must be provided to ease the comparison. Thus, this work proposes a meta-analysis tool, suitable for CO2 plasma-catalysis, with the aim of facilitating the identification of key parameters and trends for performance improvement. The proposed tool is an open access database collecting all the relevant performance data from the literature. The database is the result of a joint effort between 13 PhD students (first authors of this work), part of the European PIONEER project [26], and is therefore called the PIONEER database (abbreviated as CO2-PDB from now on). In addition, an online user interface, allowing the extraction, filtering and plotting of the data from the database has been developed and is accessible via http://db.co2pioneer.eu (and aliases http://pdb.co2pioneer.eu or http://database.co2pioneer.eu or http://pioneer.database.co2pioneer.eu). More details, e.g., practical information to get started, using and referencing the CO2-PDB, can be found in the online documentation: https://docs.co2pioneer.eu. The CO2-PDB is exclusively limited to plasma-(catalysis) CO2 conversion results. This is motivated by the specificity of plasma-catalysis for CO2 conversion, as will be discussed in Section 2. CO2 capture and storage technologies can also sometimes rely on the use of catalysts (or adsorbents), which are sometimes even produced using plasma processes [27], but these technologies, although certainly useful in the context of reducing CO2 emissions, are not included in the database proposed here. The positioning compared to other existing databases, the graphical interface and the type of data set to be provided to the CO2-PDB are described in Section 3. One of the ambitions of this work is to propose a minimal set of parameters that should be reported in any work dedicated to plasma-catalysis coupling for CO2 conversion. This minimal set of parameters must include enough information/parameters to characterise the experiments and enable a comparison with other experimental works. This set can be divided into four main subsets, namely, (i) the plasma source, (ii) the catalytic material, (iii) the type of coupling configuration, and (iv) the gas mixture. The selection criteria of these subsets and the parameters therein included will be explained in Section 3.2, together with general information about the data set already included in the CO2-PDB at the time of publication. The main features of the CO2-PDB and the graphical interface developed to extract data will be presented in Section 3.3. The explanation of how to use the basic and more advanced features of the CO2-PDB will be explained in Sections 3.3.1 and 3.3.2, respectively. Section 4 provides first examples of data extraction from the CO2-PDB. A comparison with figures from previously published review papers in the field of plasma-catalysis is first shown in Section 4.1. Section 4.2 explains in a broad manner the use of the CO2-PDB web interface. The caveats and disclaimers are explained in details in Section 4.3. To illustrate the possibilities offered by the numerous input parameters of the database, Sections 4.4 and 4.5 highlight the role of the support vs. the role of the active phase for CO2 conversion performances and also the behaviour of C2H4 molecules in various plasma-catalytic reactor configurations. The graphs that will be discussed in these data extraction examples are obtained from the data set already included in the CO2-PDB at the time of submission of this paper. It is important to reiterate that this data set is intended to be developed by contributions from the whole community. The trends observed will therefore need to be confirmed against a larger and perhaps better defined data set when future publications in the field provide more complete information on the experimental conditions and characterisation of the materials used. Currently many publications suffer from a lack of characterisation of either the plasma source or the catalytic material used. This is an important obstacle to more detailed comparisons of the results obtained in different research groups. Section 5 will therefore propose some ways to enrich future work with minimal parameter sets (which can be included in the CO2-PDB) that seem important to gain more understanding from cross comparison of results of different works.

2. Specificity of plasma-catalysis for CO2 recycling

2.1. Plasma sources used for CO2 conversion

As stated in the introduction, the practical applications of plasma-catalysis are predominantly gas decontamination and molecular synthesis. Despite their different end goals, these applications frequently share a common aspect, which is the use of a dielectric barrier discharge (DBD) as the plasma source and, more specifically, a “packed bed DBD” in coaxial geometry. The extensive use of packed bed DBDs is because they are easy to implement, relatively cheap, and provide simple catalyst coupling. However, in the context of CO2 conversion, DBDs often have the drawback of being unable to exploit the more efficient vibrationally excited dissociation. This is due to the high electric field induced by the
plasma filament favouring direct electron-impact dissociation over vibrational excitation [28]. As a result, other plasma sources have been studied with or without catalyst coupling. They can be discharges often used at atmospheric pressure such as gliding arc (GDA), or nanosecond repetitive pulsed (NRP) plasma, but discharges such as microwave (MW), radio frequency (RF), or glow discharge (Glow) can operate at reduced and atmospheric pressure. These plasma sources generate conditions different from DBDs in terms of electric field, charge density, vibrational excitation, gas temperature, radical densities, etc. For example, the high gas temperature involved in GDA and MW plasma sources means that direct coupling with catalysts is not feasible. However, it is possible to place a catalyst downstream of the plasma where the gas temperature is low enough to not cause any degradation. It should be noted however that if the catalyst is positioned too far from the plasma, only molecules stable in their fundamental state will be likely to reach the surface of the catalyst and the surface reactivity which can then be obtained will not be different from what can be observed in conventional catalysis with the same molecules. Nevertheless, the benefits of adding a catalyst often outweigh the difficulty of coupling it with the plasma, and as such, increasing amounts of research are being conducted on plasma-catalysis reactors rather than pure plasma reactors. Using low (or reduced) pressure is often disregarded in conventional catalysis because catalytic phenomena, typically described by Langmuir-Hinshelwood equations, are less efficient as a result of the lowering of adsorbed species concentration. However in plasma-catalysis, this effect could be compensated in some cases for instance because of a stronger vibrational excitation at reduced pressure enhancing the efficiency of surface reaction.

The diversity of the considered plasma sources raises questions on the relevance of the operating parameters that can be compared between them, for instance, power, flow rate, pressure, etc. As such, we have included Section 3.2 dedicated to the types of parameters included in the database so that sensible comparisons can be made between the different plasma sources. In all cases though, the reactivity of these plasma sources combines the effects of charged species, excited electronic and vibrational states, strong electric fields, and often strong spatio-temporal gradients, resulting in chemical reactivity fundamentally different from that obtained in thermal catalysis.

To be able to compare different plasma sources ideally, it would be necessary to know the energy distribution function of the electrons, or at least the electric field and the electron density. It would also be necessary to characterise the spatial inhomogeneity of the energy deposited. However, these quantities are in general difficult to determine, especially when the plasma is in direct contact with a catalyst. Alternatively, more macroscopic parameters such as power or specific energy input (SEI) and gas temperature should at least be known so that one can study the conversion performances collected in the database.

2.2. Catalytic materials in contact with a plasma

A catalyst is a substance that increases the rate of a chemical reaction without modifying the overall standard Gibbs energy change in the reaction. The structure of a catalyst often consists of a support with a large specific surface area to improve exchanges with the gas phase, and an active phase dispersed on its surface. Additionally, there may be a promoter to improve the performance of the active phase. Despite containing typically three components, each of them has many parameters that can influence the efficiency of the resulting catalytic material for a given reaction. For example, there is the adsorption capacity of the material towards the reactants, the accessibility of the surface to the reactants by diffusion, or the potential poisoning of the surface during the reaction.

In thermal catalysis, good practices to ensure relevant comparison of performances between catalysts require that the measured quantities are really “intrinsic” rates and selectivities [25]. This necessitates the use of “ideal” reactors, such as a “plug flow”, “batch”, or “continuously stirred tank” reactor. These “ideal” reactors also need the determination of well-defined parameters such as turnover frequency, site-normalised catalytic reaction rates, turnover numbers, or site-normalised catalytic productivities. Limitations of mass and heat transfer within the catalyst bed must also be ensured to not affect the conversion or the selectivity results.

All these thermal catalysis “good practices” impose constraints on the reactor geometries and the type of catalytic bed that can be used to determine fundamental parameters. Predominantly though, these “ideal” catalyst bed configurations are not suitable for plasma-catalysis. As plasma cannot develop on lengths smaller than the Debye length, which is in general larger than a few microns, reactors are therefore constrained by this length scale. Therefore the important parameter in thermal-catalysis of macro, meso-, micro-, or nanoporosity (all defined at nanometric scales) is not the only surface parameter to be considered in plasma-catalysis. Specifically, the length of the pores is just as important as their diameter, as the length will determine which species reach the active sites present on the catalyst. This is a situation typical to plasma-catalysis, where the lifetime of the plasma species results in different processes. Thus, one can have a situation rather different from thermal catalysis, where the modification of the porosity at the nanometric scale can greatly improve the efficiency of a catalyst but could be irrelevant for certain cases in plasma-catalysis. Nevertheless, macroscopic structure at the scale of a few hundred microns or even millimeters can affect the way that the plasma develops along the catalyst surface, and consequently improve the access of short-lived species to the catalytic surface.

Furthermore, the very definition of certain parameters considered as intrinsic properties of a given catalytic material in thermal catalysis must be reconsidered when this material is under direct exposure to a plasma. Specifically, this is the case for the density of “active sites”. The nature and number of which can be modified according to the properties of the plasma used, and therefore can no longer be treated as a characteristic property of a given material. Even an a priori chemically inert surface like SiO2 can gain new adsorption sites under plasma exposure. As an example, oxygen atoms chemisorbed on a SiO2 surface exposed to a glow discharge can then convert NO to NO2 [29]. The number and nature of the active sites present on a given material can thus depend on the properties of the plasma to which it is exposed, and a material usually considered as a simple support can act as a catalyst with reactive species created in the plasma.

Even a notion like the yield, Y, can be misleading within plasma-catalysis. Y is defined as the mole fraction of initial limiting reactant that is transformed into a given product. In plasma-catalysis however, the limiting reactant of a reaction happening on the catalyst surface is not necessarily one of the gases introduced into the reactor, it can also be a product of a reaction occurring in the plasma which is not necessarily known.

The complexity of the mutual interaction mechanisms between a plasma source and a catalyst was recently described in a review article [10]. This work makes it clear that to enable data comparison from different plasma-catalysis works, it is essential to consider other parameters than those used in thermal catalysis. If the pre-existing tools in thermal catalysis are insufficient to derive information from plasma-catalysis measurements, the question arises whether techniques used for other non-conventional heterogeneous catalysis processes, such as electro-catalysis and photo-catalysis, could be suitable for plasma-catalysis instead.
2.3. Differences and similarities between plasma-catalysis and electro- or photo-catalysis

Despite being a unique technique, plasma-catalysis shows similarities with other types of catalysis. For example, photo-catalysis relies on the transfer of charges caused by the absorption of photons of suitable energy by a catalyst, creating electron-hole pairs. The catalyst can then participate in the reactions of interest by transferring these charges to reagents and/or intermediates. The obvious similarity with plasma-catalysis is that plasma emits light and such light could, at least theoretically, induce photocatalytic processes as previously reported [32]. However, this potential application requires further study, since it is generally accepted that the photon flux in plasma-catalysis reactors is too low to significantly activate photo-catalysts as seen in previous reports [33,34].

Nevertheless, this does not necessarily mean that there are no other intersections between the two types of catalysis. For instance, it was proposed that electron impact on the catalyst may induce electron-hole pairs as well, particularly in the case of DBD plasmas where the electron energy is similar to photon energies used in photo-catalytic processes (around 3 eV to 4 eV) [35]. Furthermore, it has been shown in some cases that plasma can create oxygen vacancies in the catalysts and electrons can be trapped in those vacancies, which in turn would favour photo-catalytic processes. In that sense, plasma- and photo-catalysis are not only similar, but can potentially exhibit synergy [36].

In the same way as in photo-catalysis, electron transfer is at the core of electro-catalysis, and potentially plays a role in plasma-catalysis. For example, it is possible that the electrons deposited by the plasma on a catalyst surface can result in charge being transferred to molecules such as CO₂. Indeed, it has been observed that this effect substantially impacts the ability of the material to perform reduction reactions [37] and it can be assumed to work in a similar way as in electro-catalysis. Nevertheless, it is worth highlighting that both photo-catalytic and electro-catalytic reduction of CO₂ are performed more frequently in aqueous media, being water (or aqueous species) oxidised either by the holes generated in the photo-catalysts or at the anode in the electro-catalysis. However, so far few studies reported on the plasma reduction of CO₂ in aqueous media, owing to the fact that H₂O-derived species in plasma, especially reactive oxygen species, are usually taken as detrimental. This happens because there is still no established strategy to properly separate them from the products and they tend to hinder the production of larger molecules [38]. Comparatively, in photo-catalysis this separation is usually performed by strategies like heterojunctions that can effectively separate holes from electrons, while, in electro-catalysis, this is done by separating the anode and cathode within the electrochemical cell.

Additionally, a drawback of reducing CO₂ in aqueous media is the low solubility of CO₂ in water [39], limiting the efficiency. From an operational point of view, plasma-catalysis and electro-catalysis can be switched on and off much more quickly than thermal catalysis. As such, both represent an opportunity to use intermittent electricity from renewable sources, creating an energy buffer that stabilises the electricity grid by peak shaving.

Unlike the other methods, photo-catalysis enables the direct use of solar irradiation for CO₂ conversion, reducing the amount of steps involved in energy conversion. That being said, it is not necessary to limit a chemical process to one type of catalysis. For instance, some catalysts may be suitable for both photo-catalysis and plasma-catalysis, which could allow for hybrid reactors that perform photo-catalysis in the day and plasma-catalysis at night. In this regard, oxides or a mixture of oxides are commonly used as photo-catalysts; provided their bandgap is suitable for absorbing light at the appropriate wavelengths [40]. However, as mentioned before, electron-hole separation is one of the crucial points of development for photo-catalysis. A common strategy to tackle this problem includes the addition of a conductive material (e.g. metallic nanoparticles) on the surface of the metal oxides to “drain” the generated electrons, creating the so-called Schottky junction [41]. In that sense, the resulting material can be a metal oxide acting as a catalyst for photo-catalysis and as a “support” for plasma-catalysis, and a metal working as an electron drainer in photo-catalysis and as an active phase in plasma.

Therefore, all three techniques can be complementary and useful under different conditions, but in no way they are interchangeable. The relevant parameters to analyse the performances of electro- and photo-catalysis may sometimes overlap with the ones for plasma-catalysis (electrical current, photon flux, etc.), but plasma-catalysis remains a separate field, characterised by the high reactivity of the gas phase to which the catalyst is being exposed. In plasma-catalysis, the flux of species to the catalyst surface is a complex mixture of excited states and radicals, whereas, in the other forms of catalysis, the flux of species reaching the surface is composed of stable molecules in their ground states. As a result, the tools developed for analysing performances and comparing results in thermal, electro- and photo-catalysis cannot be easily used on a plasma-catalytic system. From the great uniqueness and complexity of plasma-catalysis processes for CO₂ conversion comes the motivation to develop the CO2-PDB, which is presented in this publication.

3. The PIONEER database: positioning, graphical interface and type of data set

3.1. Motivation for the creation of the CO2-PDB and positioning

The usefulness of creating a database dedicated to plasma-catalysis for CO₂ conversion arises from two main points. Firstly, the complexity of plasma-catalyst interactions discussed in previous sections necessitates large amounts of data in order to identify trends which indicate fundamental mechanisms. Secondly, the number of works in the field is becoming large and, without comparison tools, potentially useful information can be missed. Therefore, the CO2-PDB is a first attempt to fulfill these two objectives by filling a gap with respect to existing tools in other scientific communities.

The performance data on plasma-catalysis experiments gathered in the CO2-PDB represent a valuable contribution to the research field as no comparable database exists. Even in conventional catalysis, we are unaware of a global performance database for given catalysts. The list of catalysis databases available online includes: the Open Materials Database [42], the Materials Project [43], AFLLOW [44], the Open Quantum Materials Database [45], Aida [46], the Catalysis-Hub [47], the Open Crystallography Database [48], NoMaD CoE [49], and the Computational Materials Repository [50]. They come with high-quality interfaces, Python modules for data handling and access, and extensive data compared to the CO2-PDB. Nevertheless, these databases focus on data derived from computational methods (e.g. density functional theory) with the goal of discovering new materials, particularly catalysts. Comparatively, the CO2-PDB focuses on experimental performance data from plasma-(catalytic) CO₂ conversion.

On the plasma side, databases are even more scarce. A popular example is the LXCat database for electron and ion scattering cross sections and swarm parameters [51], which provides valuable input for plasma kinetic simulations. The extension to plasma-catalysis is however not straightforward. In this regard, it is worth mentioning the Korean data center for plasma properties that provides data for the plasma-wall interaction, and other aspects [52].
Likewise the LXCat database, this database is meant to serve as input for modelling, and no performance data is included. Therefore, the CO2-PDB bridges the gap between large-scale/big-data studies and well-controlled, ideal, comparable, small-scale studies. In fact, all the catalysis databases presented above follow the “big-data” approach and usually come with some machine learning utility [42–44, 47, 49, 50]. However, when it comes to plasma-catalysis performance, machine learning approaches become much more delicate. This is because results obtained by so-called machine learning techniques will never be valid if the data sets used are not complete, balanced, and well-distributed. In order to build such a data-set, a better definition of the parameters controlling the performance in plasma-catalysis is required. For example, there is significant progress in using machine learning for materials discovery in the fields of adsorbents [53], superionic conductors [54], electro- and photocatalysis [55], perovskite materials [56], etc. However, in these cases, the performance parameters or the expected properties are much better understood. Also, given the broad characteristic of plasma experiments in CO2 conversion, using different gas compositions, catalytic materials, reactor designs, and plasma sources, the spatial coverage of possible target variables is also very broad, which machine learning models usually have trouble dealing with. For example, a catalyst can perform well for the dry reforming of methane in a microwave plasma. Still, its performance may be completely different in a DBD, which has a lower working temperature, or for another reaction, such as CO2 hydrogenation. In its current form, it is quite challenging to compartmentalise the available data to have its coverage referring to similar cases while still maintaining a training data-set that is large enough to drive materials design or discovery. While the comparability between different experiments and reactors is currently limited, small-scale studies isolate certain fundamental parameters, enabling a comparison with other small-scale studies, but are intrinsically limited in parameter space. The CO2-PDB therefore connects disparate experimental studies in literature, and thus creates an environment for more systematic studies on the most promising directions. Over time, the practices used to study plasma catalysis will become more comparable because the database will make it easier for everyone to be aware of the critical parameters needed to cross-check data from one system to another. New contributions from the entire community will improve the quality and completeness of the data sets in the database. Ultimately, this will make it possible to identify the physico-chemical properties that are really beneficial to plasma-catalyst coupling, in order to define new materials, probably quite different from the catalysts usually used in thermal catalysis, that are really capable of improving the performance of the plasma itself as well as taking advantage of the short-lived species generated by the plasma.

3.2. Scope of the database

The research fields of plasma and catalysis feature an enormous versatility of characterisation that only expands when the two merge. Thus, any attempt to cover everything in one plasma-catalysis database is unlikely to succeed. For that reason, we...
prioritise comparability and importance of included data over quantity, leading to a manageable set of data for each measurement series. An in-depth discussion of included data is given in the Supplementary Material while this section gives a brief overview and focuses on some selected metrics. Table 1 gives an overview of the amount and diversity of the data included in the CO2-PDB at the time of submission of this manuscript. In short, the CO2-PDB reports on so-called “process parameters”, i.e. x-values in Table 2, against so-called “performance parameters”, i.e. y-values in Table 3, which are backed up by metadata to facilitate the interpretation and comparison of trends. Note that all data sets in the CO2-PDB report on plasma experiments on CO2 conversion, of which 2012 are plasma-catalytic experiments. No data of conventional thermal catalysis is included. Insights obtained in this section are used in Section 5 to give some best practice advice.

The data collected in the CO2-PDB must have been previously published in a peer-reviewed journal in English. As such, the validity of the measurements is ensured by the classical peer reviewing process and is in no way the responsibility of the CO2-PDB authors. Beyond the simple identification of the article in which the data were published, the CO2-PDB metadata allows the characterisation of the gas mixture studied, the plasma source, the nature of the catalyst, and the way in which the catalyst is coupled to the plasma. Each data set (i.e. set of (x,y) pairs that comprise a measurement, line, or equivalent) in the CO2-PDB is associated to all these parameters when the information is available in the published article.

The fraction of data sets in the CO2-PDB providing certain information focusing on the plasma in Fig. 2(a) and on the catalyst in Fig. 2(b). Hence, each bar in the chart corresponds to one column in the database. For Fig. 2(a), all data sets in the CO2-PDB are considered as all studies include a plasma (i.e. 3041 data sets at the date of submission of this paper, see Table 1), while Fig. 2(b) includes only plasma-catalytic studies (i.e. 2012 data sets). All data are considered important such that the closer a bar is to 100%, the better. Note that only a selection of all data columns in the CO2-PDB is shown, namely, those data columns that are crucial to each and every data set. For instance, power always has to be deposited to ignite the plasma. Conversely, MW discharges do not rely on an applied voltage, which is not included in Fig. 2.

From the comparison of Fig. 2 (a and b), it becomes apparent that in the general perspective of the database, the plasma is more exhaustively characterised than the catalyst. In fact, the average fraction of provided data for plasma is 89%, while it is only 45% for the catalyst. A possible rationale is that the field of plasma-catalysis is still relatively young, needs significant interdisciplinary efforts, and is still being led mostly by the plasma community, which has less experience in catalyst characterisation. Therefore, the characterisations provided for the catalysts are still not in the standard of other more established fields of catalysis. From Fig. 2 (a), it can be seen that parameters that are best documented mainly concern what is put into a reactor and in what quantity, for example, gas composition, and flow rate. Conversely, the physical properties of the plasma studied are limited except for power.

### Table 3
Overview of performance parameters in the database, i.e. the y-axis values, discussed in more detail in the Supplementary Material.

<table>
<thead>
<tr>
<th>Performance parameter</th>
<th>Unit</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>%</td>
<td>CO2, CH4</td>
</tr>
<tr>
<td>Selectivity</td>
<td>%</td>
<td>CO, H2, CH4, CH2OH, CH3COOH, C2H2, C2H4, C2H6, C3H6, C3H8, C4H10, C2H5OH</td>
</tr>
<tr>
<td>Yield</td>
<td>%</td>
<td>CO, H2, CH4, CH2OH, CH3COOH, C2H2, C2H4, C2H6, C3H6, C3H8, C4H10, C2H5OH</td>
</tr>
<tr>
<td>Carbon balance</td>
<td>%</td>
<td>CO2, CH4</td>
</tr>
<tr>
<td>Energy efficiency</td>
<td>molecule J⁻¹</td>
<td>CO2, CH4</td>
</tr>
<tr>
<td>Energy efficiency ratio</td>
<td>%</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 2. The fraction of data sets that provide information about individual plasma parameters with respect to the total number of sets in the CO2-PDB in (a). The fraction of data sets that provide information on catalyst parameters with respect to the total number of data sets including a catalyst in (b).
and SEI. Parameters such as electron densities, electric fields, or vibrational temperatures would provide great value, but unfortunately these parameters are unknown in the vast majority of cases and therefore are not included as CO2-PDB metadata for the moment. However, as previously mentioned, plasma-catalysis is an interdisciplinary field, and drawing reliable conclusions requires a complete and comprehensive characterisation of both the plasma and the catalyst. Unfortunately, many crucial parameters are underreported. For example, only 65% of papers report the gas temperature $T_g$ in the plasma despite its importance for assessing residence time, non-equilibrium characteristics [57], and the role of thermal versus plasma-catalysis [2]. Even when a temperature value is given, the various methods used to measure this temperature can lead to inconsistencies when comparing studies, see also the discussion of Fig. 15 in Section 5.1.

It is interesting to note that the SEI, calculated as the ratio of power over flow rate, is one of the most popular process parameters, i.e. the most frequent $x$-coordinate, as it allows for maximum comparability across different plasma sources. However, the total fraction of data sets reporting the SEI is only around 90%, which is probably because studies on fundamental mechanisms tend not to document the SEI, whereas those on process optimisation do. For the sake of comparability, we recommend always reporting it.

In panel Fig. 2(b), we see that the catalyst composition and its proportions are usually reported. However, information on the remaining fields is scarce and the bulk density of the catalyst material is almost never reported. To a lesser extent the data scarcity also concerns the size and surface area of the particles, which are crucial parameters in all fields of catalysis but were reported in less than half of the papers. More generally, the macroscopic characteristics of the catalyst bed (dimensions greater than typically a hundred microns) are not sufficiently described despite their impact on plasma initiation.

It is worth emphasising that following the definition used here, the catalyst data do not include any process parameters. Process parameters are regarded as the “control knobs” of the experiment that are tuned to optimise the performance. There is no doubt that advanced catalyst design is a key element in the further development of plasma-catalytic CO2 conversion. However, the design of the catalyst and reactor occurs before CO2 processing, while the plasma process parameters can be adjusted in real time. Nonetheless, no data is lost. Literature data reporting performance parameters against catalyst properties are rearranged: the catalyst properties end up in the catalyst metadata and a new ($x,y$) pair is created, with $x$ preferably being the SEI, see also the Supplementary Material.

The database also foresees developments in the separation of the plasma reaction products. Few publications have dealt with separation of products, specifically oxygen atoms as they can participate in the back reaction to CO2 [58,59]. At the time of publication, it is hard to estimate which possible input data would be interesting for the database. So far, separation type and position are the only parameters included but this can change and extend according to future developments. More is discussed in the Supplementary Material.

To summarise, the CO2-PDB comprises data extracted from a large and wide-ranging collection of peer-reviewed publications arranged into an easy-to-use format (Table 1). However, we have not included all possible items from the reported data. Instead, we only included data that we deemed important and comparable. This means that vital parameters that only appear in a small number of studies will not be included. Therefore, the data selected for the CO2-PDB are proposed as a minimum parameter set for comparing CO2 plasma-catalysis performance results. We chose a minimum collection so that the CO2-PDB can evolve over time with the addition of new parameters proposed by the plasma-catalysis community.

3.3. The PIONEER database web interface

The PIONEER database contains a wealth of useful data on plasma and plasma-catalytic CO2 conversion. To make the information within the database accessible and provide a platform for the
community to compare results, an online front-end point providing access to the database can be found at https://db.co2pioneer.eu. This tool provides functionalities for visualising data from the database, as well as selecting, filtering, and exporting data and/or graphs from the database. It is also possible to overlay user data on top of the main visualisation. In the following subsections a brief overview of the interface and some of its features are highlighted. These sections also serve as a primer for basic operation of the database, which are complemented by the Supplementary Material and the online documentation. The ambition is to continue adding new data to this online platform and contributions of (newly) published scientific results are strongly encouraged. The only conditions for proposing new data to be included in the CO2-PDB are that the results have first been published in a peer-reviewed journal, and that the authors provide (i) the metadata in the template provided here, and (ii) the corresponding data sets as two-columns (x, y) ASCII files formatted as described in detail in the online documentation. The CO2-PDB app (shown in Fig. 3) provides two main modes of interacting with the database. The first is the main visualisation section, which allows users to explore performance (Table 3) versus process parameters (Table 2) for plasma-catalytic conversion. The second is the advanced database inspection interface, which provides features for more advanced data interaction, such as selection, inspection, and export. However, we have developed the main visualisation section so that there are sufficient features to effectively analyse the data in a visual manner both within the app and offline via a vector quality export of the graphs in *.svg format.

Nevertheless, if more granular control, or an export of the underlying data is desired, the advanced inspection interface can be used. These two modes of interacting with the database are discussed in more detail below, with further information also provided via the online documentation.

### 3.3.1. The main interface for graphing performance versus process data

The main user interface consists of two regions: A central viewport with widgets for filtering the database and an $Y$ vs. $X$ graph of the selected data, and a sidebar containing controls for the plot appearance and normalisation applied to the selected data, see Fig. 3.

<table>
<thead>
<tr>
<th>Panel</th>
<th>Filter criterion</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>Source type</td>
<td>Relevant diagnostic used to determine power</td>
</tr>
<tr>
<td></td>
<td>Plasma main diagnostic</td>
<td>Relevant diagnostic used to determine plasma or gas temperature</td>
</tr>
<tr>
<td></td>
<td>Plasma power diagnostic</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plasma/gas temperature diagnostic</td>
<td></td>
</tr>
<tr>
<td>Catalysts</td>
<td>Catalyst used</td>
<td>True/False</td>
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<tr>
<td></td>
<td>Coupling</td>
<td></td>
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<tr>
<td></td>
<td>Catalyst support material class</td>
<td>Filtering on classes like Perovskites</td>
</tr>
<tr>
<td></td>
<td>Catalyst active phase</td>
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<td></td>
<td>Catalyst support</td>
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<td>Catalyst promoter</td>
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<tr>
<td></td>
<td>Catalyst active phase search by element</td>
<td>Allow filtering materials based on custom string</td>
</tr>
<tr>
<td></td>
<td>Catalyst support search by element</td>
<td>Allow filtering materials based on custom string</td>
</tr>
<tr>
<td>Catalyst properties</td>
<td>Surface area ($m^2g^{-1}$)</td>
<td>Numeric setting of upper/lower threshold (based on secondary widget)</td>
</tr>
<tr>
<td></td>
<td>Permittivity</td>
<td>Numeric setting of upper/lower threshold (based on secondary widget)</td>
</tr>
<tr>
<td></td>
<td>Gas species</td>
<td>Select which elements to in/exclude, if ‘None’ is chosen, does not filter</td>
</tr>
<tr>
<td></td>
<td>Gas combinatoric operator</td>
<td>Controls how to filter the selected gas species</td>
</tr>
<tr>
<td></td>
<td>Gas pressure (mbar)</td>
<td>Numeric slider to control the pressure range</td>
</tr>
<tr>
<td></td>
<td>Gas flow (sccm)</td>
<td>Upper (if negative) or lower (if positive) bound for flow rate</td>
</tr>
<tr>
<td>Misc.</td>
<td>Author</td>
<td>Last name of the listed first author of a publication</td>
</tr>
<tr>
<td></td>
<td>Goal</td>
<td>The outcome of the process under investigation, e.g., CO₂ splitting, methanation, etc.</td>
</tr>
<tr>
<td></td>
<td>Separation type</td>
<td>Method of output product separation such as a carbon bed or membrane</td>
</tr>
<tr>
<td></td>
<td>Separation position</td>
<td>The position where the separation is applied</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
<td>Whether some form of calculation has been applied to the data</td>
</tr>
</tbody>
</table>

The main viewport The “Main UI” tab in the main viewport constitutes what will be called the main interface, which consists of three parts. The top row consists of a set of widgets that allow the desired parameters of the $Y$ vs. $X$ graph to be selected, which are tabulated in Tables 2 and 3 respectively. It also includes indicators for the number of data points, data sets and papers that are either shown or contained in the database. Since the core feature of the tool is to create $Y$ vs. $X$ plots, these widgets are always shown in the main user interface.

The second part provides more granular filtering options. These options are located in several “contextual” tabs and contain filter widgets related to the same context, for instance, plasma metadata. An overview of how these filters are structured can be found in Table 4. Most of these filters are inclusive categorial filters, i.e., they serve to restrict the data in the graph to a particular subset or category. Data exclusion is performed by clicking on a label in the graph, which will toggle the visibility of the corresponding data. The exception to this are filters for the gas composition, gas flow, pressure, catalyst specific surface and relative permittivity, and catalyst active phase or support containing element, which behave differently, see Table 4. Whenever a filter widget is set to NA (Shorthand for Not Applicable), no filtering will occur on that particular category. Note that this is distinct from the “None” option, which can be the absence of a property, for instance, the absence of an active phase. Finally, the third part contains the graph element that displays the data that have been selected by the various filtering widgets.

The visibility of individual or groups of lines in the plot can be controlled by clicking on the corresponding legend entry, as stated. A toolbar to the right of the figure provides access to various tools related to the plot and its underlying data, for instance, data inspection, zooming and panning. Although *.png images can be exported from here as well, their use is discouraged in favour of annotated *.svg exports (see below). Further control over the graph and displayed data can be exercised via the assorted widgets in the sidebar, which are discussed next.

The sidebar menu The collapsible sidebar contains buttons for opening the documentation, updating the loaded database model, plotting the data, and exporting the current plot view in vector format, or a BibTeX of included references in the plot. This vector export is the intended way of exporting graphs, since it contains...
important metadata and minimal annotation on applied normalisation, which is crucial for comparison. Alongside these buttons, there are two tabs for further control over the plot and data. The “Plot setup” tab contains the widgets that control the appearance of the database plot. Using these widgets, it is possible to control the scale of the axes, the colour map of the plot and toggling automatic redrawing of the plot after each filter change. Special attention should be given to the “Group data by” widget, which allows the selection of one or more categorical columns by which the data are grouped and colour mapped in the plot. By allowing the user to custom create custom groupings, insights into how certain groups and categories of experiments compare against each other can be made, see Fig. 4(a) as an example.

The “Normalisation” tab provides control over several different normalisation functions that can be applied to either the X or Y axis of the graph. Further input to some normalisation functions is controlled by the “Normalise species” and “Normalise aggregate func.” widgets, which respectively control the species to normalise (e.g., normalising for CO2 or H2O partial pressure) and how to aggregate array-like metadata where applicable (e.g., taking the minimum, maximum or mean of the temperature if a range is defined). The same aggregation will be applied to all numeric columns that are needed for a calculation. The effect of applying a normalisation to the data can be seen in Fig. 4(b), which shows the same filters and grouping as Fig. 4(a), but now with the data normalised for the CO2 fraction in the initial gas mixture. In Section 4.2, a discussion of the benefits of this normalisation is presented.

It is important to note that normalisations only return data for which the necessary metadata used in calculation is present. In other instances, NaN values are returned. Consequently, applying a normalisation can result in a decrease in the amount of data shown.

Fig. 4. Comparison of example graphs as they can be directly exported from the CO2-PDB app graphical user interface (left as-is, save for moving the legend) showcasing the CO2 conversion (in %) versus the SEI (in J L-1) with data grouped by the “main goal” and use of catalyst (either “True” or “False”). Both figures in principle show the same data, but in (b) the SEI has been normalised by dividing by the CO2 fraction in the gas flow.

3.3.3. A note on calculations, assumptions and features

It is important to note that the database is not just a catalogue of data, but also a tool that allows quick comparisons of (normalised) data. However, there are some core assumptions and approximations that are made to compare as much data as possible across a wide range of conditions.

For example, SEI is seen as a macroscopic process parameter that inputs power into a given amount of flow rate regardless of the plasma conditions. Within the database, SEI values directly extracted from publications appear alongside values calculated from reported powers and flow rates, and are labelled accordingly. Contrary to the direct calculation of SEI, the adjustment with respect to standard conditions is barely mentioned in the publications used to build the database. Therefore, we can only assume that temperature and pressure inside the plasma or reactor are not considered when SEI or energy efficiencies are calculated in standard conditions. It is crucial to know how much time a molecule spends under plasma conditions. Similarly for the energy efficiency calculations, the correction of the SEI used here had to be applied to the data, but in (b) the SEI has been normalised by dividing by the CO2 fraction in the gas flow.
The normalisation feature allows for easy calculation and comparison of data sets within the same interface. Several functions are available with the corresponding equations described in more detail in the Supplementary Material. In particular, we would like to highlight the application of “abundance”. This term attempts to give an approximate amount or abundance of molecules without knowing the real density of molecules. In the case that real density is needed however, then functions using “partial density” should be used. Again, \( \phi \) is assumed to not be corrected to standard conditions, as in many publications this is not indicated. Therefore, for the functions with \( \phi_{\text{std}} \), the data is normalised by flow at standard conditions. A deeper discussion about standard conditions is given in Section 5.

On the other hand, some parameters are given on a range instead of a defined value such as in temperature and flow rate. For these cases, a mean value is used for subsequent calculations, although in the normalisation feature in the interface, such ranges can be considered for plotting as max, min, and mean values. For more details of the equations followed, the Supplementary Material should be consulted.

### 4. First examples of data extraction

This section shows some examples of meta-analysis that can be done with the CO2-PDB and the developed App, demonstrating the potential of the tool. However, this is just a sample of the different process- and performance parameters, and grouping options available. For example, Section 4.1 compares graphs produced from the CO2-PDB with previous review papers on CO2 conversion [60, 61]. Such a comparison serves as benchmark of the CO2-PDB. Nevertheless, the comparison is limited to the parameters CO2 conversion, energy efficiency and SEI, since no other combinations of performance and process parameters have been thus far compared in any review paper to our knowledge. Section 4.2 demonstrates how quickly insights can be obtained from the data by simply using the basic features of the CO2-PDB App’s main interface (see Section 3.3.1). Despite the versatility of the CO2-PDB, some precautions, discussed in Section 4.3, need to be taken. Furthermore, Section 4.4 illustrates the benefit of using some representation techniques, popular in statistics, to analyse large data sets and elucidate any synergistic effect of plasma-catalysis. Finally, Section 4.5 provides an example of new analysis that can be performed with the CO2-PDB. Particularly, the focus is on the production of hydrocarbons CxHy, in plasma-based dry reforming of methane, taken as illustration of a topic that is growing in interest.

In the coming sections, there are plots using data contained in the database. In some special instances, these plots are the direct exports of the database app for demonstrative purpose, which is noted explicitly in their caption.

#### 4.1. Comparison with graphs from previous review papers

The plasma-catalysis community has already understood the importance of collecting a vast array of experimental results on plasma-based CO2 conversion, and this is evidenced by the number of review articles available in the literature. In this section, the extraction of CO2-PDB data is compared with the collected data from two review papers [60, 61], with the aim of.

![Fig. 5. CO2 conversion (top) and energy efficiency of CO2 conversion (bottom) as a function of SEI, either in eV/molecule −1 in (a) reproduced from Snoeckx and Bogaerts [60] or in J L−1 in (b) for data extracted from the CO2-PDB [36, 38, 62–89]. In both panels, only data for DBD discharges for CO2 splitting are shown. Open symbols and crosses correspond to packed bed DBD results in Fig. 5(a) and (b), respectively. The pressure range in Fig. 5(b) goes from 300 mbar to 2500 mbar, with only 12 out of 1210 data points not at atmospheric pressure.](image-url)
1. Assessing the reliability of the data already available in the CO2-PDB at the date of publication of this paper.

2. Checking the progress that has been made in the field since the publication of previous review papers.

In fact, one of the missions of the CO2-PDB is to become the reference point for the CO2 plasma-catalysis community, aiming at becoming the largest and most up-to-date database available.

One of the review articles often used as a reference to illustrate the differences in conversion performance between different plasma sources is Snoeckx and Bogaerts [60]. Fig. 5 shows the CO2 conversion and the corresponding energy efficiency (both in %) for DBD reactors, with a distinction made between plasma-only (or empty) reactors and those with a catalyst-coupling (or packed bed). Fig. 5(a) is reproduced from Snoeckx and Bogaerts [60] with full markers corresponding to plasma-only experiments while empty marker show packed bed (PB) experiments. In comparison, Fig. 5(b) displays data extracted from the CO2-PDB with circles corresponding to plasma-only experiments while plasma-catalytic studies are shown as crosses. Note that Fig. 5(b) is not directly obtained from the CO2-PDB App, but shows extracted data from the CO2-PDB that has been plotted to resemble Fig. 5(a).

Fig. 5 displays the same overall trends, with CO2 conversion increasing and energy efficiency decreasing with SEI. The SEI is the most commonly used parameter to compare the performance of one reactor to another. Note that Snoeckx and Bogaerts [60] in Fig. 5(a) give the SEI in eVmolecule⁻¹ while Fig. 5(b) uses J L⁻¹. The latter is the default in the CO2-PDB as the majority of included papers report the SEI in that unit. In fact, there are almost six times as many data sets in the CO2-PDB, directly extracted from literature without any processing, providing the SEI in J L⁻¹ than in eVmolecule⁻¹. It is worth emphasising that the SEI in J L⁻¹ can always be calculated from the power divided by the total gas flow at the inlet. This maximises the amount of data for comparison. The interpretation of this SEI is potentially ambiguous though, since the temperature and pressure conditions must be defined as well as the reactant concentration to accurately describe the amount of reactant treated. It is, then, an entirely external process parameter which does not reflect the specificity of the plasma properties in the reaction zone (gas temperature, time- and space-inhomogeneity, etc.).

To motivate the SEI in eVmolecule⁻¹ instead, we have to remember that a mass flow controller (MFC), often displays a volumetric flow rate at conditions specified by the manufacturer (“normal” or “standard” flow) which actually correspond to a mass/molar flow rate, i.e. a number of particles per time that is independent of temperature and pressure. Thus, the SEI in energy (eV or J) per number of particles as presented in Fig. 5(a) reduces the ambiguity regarding the absolute amount of reactants really being processed. In principle, the same argument of computability given for J L⁻¹ holds for eVmolecule⁻¹. However, the calculation needs to take into account the correct conditions to translate the MFC reading to molar flow by means of the molar volume Vmol. Even for what is commonly referred to as standard conditions there is some ambiguity depending on the regulatory body which is usually not clearly stated. The most frequent choices are a pressure of pstd = 1013.25 mbar and a temperature of Tstd = 273.15 K or Tstd = 293.15 K. Note that the use of the wrong temperature already leads to a 7% deviation. Using the former definition of standard conditions, the SEI axis in Fig. 5 spans from 2.5 × 10⁻⁴ eVmolecule⁻¹ (for 10 J L⁻¹) to 75 eVmolecule⁻¹ (for 3 × 10⁵ J L⁻¹), which is similar to the plot from Snoeckx and Bogaerts [60].

However, for an accurate unit conversion, more detailed information about pressure/temperature as well as “standard” or “normal” conditions used (e.g., temperature at 273.15 K or 293.15 K) would need to be known for all articles. Nonetheless, J L⁻¹ is used as a unit throughout this paper and in the interface to simplify data comparisons across publications. Finally, another relevant parameter for cross-comparison of the data is the dilution factor of CO2 in the initial feed mixture. The SEI refers to the energy spent on the whole input gas flow, independent on the species. Thus, a reaction with a feed mixture of 10% CO2—in a noble gas buffer for instance—would better be compared as a function of the energy cost (i.e. the energy spent per CO2 molecule converted). The data displayed in graphs from Snoeckx and Bogaerts [60] correspond to the absolute conversion and not the effective conversion, which accounts for the dilution of CO2 in the gas mixture. For the energy efficiency, however, the dilution is taken into account. Therefore, for the sake of comparison, the same criterion has been applied to Fig. 5(b).

Despite the similar trends displayed in Fig. 5, the data sets considered in Snoeckx and Bogaerts [60] and in the CO2-PDB are different, with the latter including also data from recent publications, from 2017 on. Fig. 6 shows the number of publications in Fig. 6(a) and the corresponding number of data sets in Fig. 6(b), included in the CO2-PDB (up to March 2023), for a function of the year of publication. Interestingly, almost half of the data included in the CO2-PDB is more recent than the review paper from Snoeckx and Bogaerts [60] (green), demonstrating the usefulness of an online database that is constantly updated.

In 2021, Chen et al. [61] published another review article on plasma-based CO2 conversion. The performance results collected by the authors, namely the CO2 conversion as a function of the energy efficiency, are compared with the data extracted from the CO2-PDB in Fig. 7. The comparison immediately reveals that the CO2-PDB, shown in Fig. 7(b), contains a larger number of data sets, and covers a wider range of plasma sources and reactions. For example, spark and NRP discharges are not included by Chen et al. [61]. Moreover, it is worth noticing that subgroups of data, e.g. “MW (1983)” in Fig. 7(a), can also be recovered from the CO2-PDB metadata. It is also worth noticing that the calculated efficiencies shown in our figure are plotted for every type of
reaction (CO₂ splitting, methanation, dry reforming, etc.) using the CO₂ splitting enthalpy, while in [61] there are only papers dealing with the CO₂ splitting reaction. The direct implication is that our plot aims to be more referential than an exact measure of the energy efficiency of the system. This was done to further demonstrate how powerful the tool can be and the fundamental differences between the two plots (for example the outliers with high conversion and efficiency) are taken into account and will be discussed further.

First, a closer comparison shows that the energy efficiency extracted from the CO₂-PDB is about one order of magnitude lower than the energy efficiency reported by Chen et al. [61], especially for MW plasmas, coloured in green in Fig. 7. However, it must be pointed out that the subset of publications directly reporting the energy efficiency is less diverse and covers only MW discharges, NRP discharge and DBDs [90–92, 88, 93]. Such discrepancy may arise from the back-end energy calculations carried out by the CO₂-PDB (which are explained in Section 4.3 and in the Supplementary Material) and the added papers coming from these calculated data. In effect, the plot gathers a total of 1431 data points, of which only 53 were directly included from the reference papers, while the rest is calculated by the CO₂-PDB (see the discussion in Section 4.3). Furthermore, while Chen et al. [61] also include calculated data, further comparison cannot be made because the authors do not report whether any normalisation was applied to account for CO₂ admixing with other gases in the calculation of conversion and energy efficiency.

Fig. 7 shows that the most common plasma source coupled with a catalyst is the DBD, although some studies on GDA and corona discharges coupled with catalysis have also been reported. In general, the addition of a catalyst enhances both conversion and efficiency for all plasma types, although the clearest activity enhancement is achieved by DBDs packed with catalysts. Indeed, according to the results gathered in the PBD, plasma-catalysis with DBDs can yield conversion above 50%, with the energy efficiency ranging from 10% to 90%.

Nevertheless, high conversion and energy efficiency displayed by DBDs are exclusively obtained for CO₂ methanation, with the addition of catalysts. A possible explanation is that this reaction is exothermic and suitable catalysts can harvest the released heat to perform thermal catalysis. Furthermore, methanation is both thermodynamically favoured compared to pure CO₂ splitting. In addition, while DBD plasmas usually have less heating effect, good-performing catalysts based on Ru and Ceria can have the onset of this reaction as low as 443 K [94], thus being perfectly achievable in DBD reactors. Indeed, all three DBDs with excellent performance used thermally active catalysts for methanation, namely Ru/MgAl layered double hydroxide (CO₂/H₂/Ar = 1.428/42.86/42.86) [95], doped Ni/CeZrO₂ (CO₂/H₂ = 20/80) [96], and Ni or Ni-Ce supported on zeolites (CO₂/H₂ = 20/80) [97]. Although the number of reports is limited, this trend can indicate a comprehensive pathway towards improved performance in CO₂ methanation by plasma-catalysis. This is because there is a significant number of sophisticated catalysts designed for thermal methanation that can also be tested in plasma-catalysis. On the other hand, the coupling of GDA with a catalyst (magenta in Fig. 7) seems to improve only the conversion maintaining the same efficiency range. However, the number of data sets, in general, is low for GDAs, so any conclusion on GDA applications to plasma-catalysis should be tentative. Other high-performance cases include spark for dry reforming of biogas (CO₂/CH₄ = 40/60) [98], DBD with catalyst bed (not packed) for pure CO₂ splitting [36], (un)catalysed power-modulated MW for CO₂ splitting (CO₂/N₂ = 95/5) [90], dry reforming of methane using a corona discharge coupled with Ni/Al₂O₃ and HZSM-5 zeolite (CO₂/CH₄ = 66.7/33.3) [99], and dry reforming of methane using NRP (CO₂/CH₄ = 50/50) [100]. Such a variety of results in the best-performing region (10% to 100% energy efficiency and CO₂ conversion) shows that there is still plenty of room for development not only in catalyst innovation but also in reactor design and plasma sources.

4.2. Simple tricks with the CO₂-PDB web interface

An important feature of the CO₂-PDB App is the possibility to quickly visualise how new data compares to the literature. Fig. 8 illustrates the possibilities of the overlay feature of the CO₂-PDB web interface. Fig. 8(a) shows the overlay of experimental data (labelled “Garcia Soto2022a” in the legend) with literature data, shown here for the CO₂ conversion against the initial fraction of CO₂ in the gas mixture in CH₄-containing DBDs. As stated in previous sections, only peer-reviewed data is accepted in the CO₂-PDB. However, with the overlay feature, users still have the option to put their results into context. Data can be provided as multiple files to the appropriate widget in the “Custom overlay” tab, using comma separated values without any header (i.e. the CO₂-PDB data format). Thus, the overlay can then serve as a sanity check before submitting data to be included in the CO₂-PDB, which can be done using the procedure described at https://docs.co2pioneer.eu/contribute.
With the same feature, the CO2-PDB App can be used to verify the validity of the data, as showcased in Fig. 8(b) which demonstrates how insights can be obtained from a comparison with functional relations with the example of the CO yield against the CO2 conversion. The CO yield is equal to the conversion of CO2 times the CO selectivity [101]. When all CO2 is converted to CO, i.e. 100% selectivity, the CO yield as a function of the CO2 conversion would be a line through the origin with slope 1 as shown in the overlay. Interestingly, there are also points above this line which should not be possible.

Another useful feature of the CO2-PDB App is the normalisation of data as discussed already in previous sections. Fig. 4(a) has already shown the CO2 conversion against the SEI with the data grouped according to the declared goal of the study and whether a catalyst is used (True) or not (False). Generally, the expected increase in conversion with SEI is observed. However, some lines seem to decrease with increasing SEI which is counter intuitive. In Fig. 4(b), the SEI has been normalised to the initial fraction of CO2 in the gas mixture. This operation clearly filters out some data sets with peculiar shapes by moving them to high SEI of $10^6$ JL/C0 to $10^8$ JL/C0. Closer inspection shows that these points belong to [67] that report gas mixtures of only 0.03% CO2 diluted in Ar. This highlights the fact that the database and visualisation tool proposed here (the CO2-PDB and the CO2-PDB App) is not a substitute for keeping a critical eye on the graphs generated as output. Indeed, when data seems to be out of line with the general trends, it is essential to always try to understand which parameter could be responsible for this difference. In the example of Fig. 4(b), the extreme dilution of CO2 in argon explains the difference observed for the data from [67]. Beyond the choices made by the CO2-PDB App user, one should also not forget the problems inherent to the lack of data standardisation in the plasma-catalysis community which are discussed below.

4.3. Caveats and disclaimers

Despite our best efforts to create a harmonised data set across a large selection of parameters, there are caveats and problematic data in the CO2-PDB. These issues are reported in literature and how they are entered into the CO2-PDB. The clear outline of the undertaken steps allows any user of the database to retrieve data and perform their own calculations. For illustration, an article by Martini et al. [102], containing a comprehensive clarification of parameters used and assumptions made, is discussed here. In their work, they establish the conversion in the effluent by gas chromatography, even accounting for the change in molecule number density as a consequence of the conversion by using N2 as an internal standard, whilst also performing in situ time-resolved measurements by laser spectroscopy. However, the large spatiotemporal gradients in the used NRP discharge make this work one of the most extreme discharges included in the CO2-PDB. An appropriate treatment of [102] assures an even better treatment of most other included publications.

To begin with, the gas temperature $T_g$ is a prominent input that is rarely given, see also the discussion in Sections 3.2 and 5.1. When given, a value of $T_g$ measured in situ is considered more valuable for the purpose of the CO2-PDB, in order to identify working conditions for maximum performance and highlight the real benefit of plasma-catalysis compared to thermal-catalysis. However, herein lies a subtle conflict with the common practice of measuring conversion downstream of the discharge. To understand this, first the change of volumetric flow when passing through

Fig. 8. Showcase of the overlay feature of the CO2-PDB App. (a) Exemplifies the overlay of experimental data while (b) illustrates a cross check against a simple functional relation. Graphs obtained with the CO2-PDB App graphical user interface in May 2023.

Fig. 9. Discrepancy between originally reported (green) and calculated (cyan) energy efficiency of CO2 conversion as a function of SEI for Martini et al. [102], as a consequence of assuming 300 K for the effluent conditions in the CO2-PDB calculation. The dotted magenta line showcases the consequence of relying on the in situ $T_g$ of the NRP discharge when using the stable conversion as measured by gas chromatography in the effluent for the efficiency calculation.
the plasma needs to be considered. In fact, the real volumetric flow rate \( \Phi_{\text{vol}} \) is

\[
\Phi_{\text{vol}} \text{[m}^3\text{ s}^{-1}] = \Phi_{\text{vol}} \text{[sccm]} \frac{p_{\text{std}}}{T_{\text{plas}}} \frac{T_{\text{plas}}}{T_{\text{std}}}/(60 \text{ s min}^{-1} \cdot 1 \times 10^6 \text{ cm}^3 \text{ m}^{-3}),(1)
\]

where \( p' \) and \( T' \) are the pressure and temperature in the plasma \((i = \text{plas})\) or at standard conditions \((i = \text{std})\), see the discussion in Section 4.1, and \( \Phi_{\text{vol}} \) is the volumetric flow rate at standard conditions. This change in volumetric flow rate depending on the conditions is essential for instance in the calculation of the residence time in the plasma region. However the gas composition is most of the time measured downstream the reactor. The fraction of the gas corresponding to a given molecule is then determined at room temperature in a gas which can have more (or less) molecules and atoms than the inlet gas mixture, due to the conversion of initial reactants. Several pitfalls can then arise when calculating for instance the energy efficiency of CO\(_2\) conversion. In the example of [102] the authors clearly state that 273 K has been used in the calculation of the energy efficiency but this is not always clearly specified in publications. The energy efficiency calculation performed in the back-end with the CO2-PDB tool must then be based on an assumption about the temperature. We argue that ambient conditions are a realistic assumption for the downstream effluent measurements and 300 K is taken into account by default in all back-end calculation of energy efficiencies. Fig. 9 illustrates the consequences of this procedure. Here, the green line corresponds to the data directly extracted from [102] with the temperature taken at 273 K, and the cyan line shows the calculation assuming 300 K performed by default with the CO2-PDB tool. The CO2-PDB also allows users to extract data and perform any post-processing they wish. It is important to be aware that the "temperature" column of the CO2-PDB corresponds to the temperature in situ when it is available. So if the user tries to recalculate the Martini energy efficiency from the dissociation rate column and the mean temperature measured in situ at 1400 to 2500 K, this time the dotted magenta line is obtained in Fig. 9. Due to the higher temperature in the discharge compared to the exhaust, the calculated efficiency seems now considerably lower which is due to the inconsistency of the data used for this particular calculation. It is impossible to anticipate all the uses that can be made by users of the data extracted from the CO2-PDB but it is essential to always refer to the real meaning of each parameter (see in particular the Supplementary Material) before exploiting them.

In conclusion, the discrepancy in reported and calculated values is highlighted to further address the implications that metadata in the database can have, and how it should be carefully considered alongside the data itself. There are competing interests between a more complete, faithful description of the actual conditions of a measurement, whilst also associating—and preserving for inspection—crucial information on the in-plasma conditions. The CO2-PDB focuses on trends in measurements and ensures wide comparability between different studies.

Another point arises from calculating the energy efficiency of CO\(_2\) conversion, which compares the SEI spent to achieve an amount of conversion of CO\(_2\), to the standard reaction enthalpy of \( \Delta H_{\text{CO2}} \). In the strictest sense, this calculation only makes sense in an experimental context that solely aims for CO\(_2\) splitting; for the overall energy efficiency of methanation, or dry reforming of methane for instance, the total reactant conversion needs to be taken into account.

When dealing with reactions other than CO\(_2\) dissociation such as methanation or dry reforming of methane, using reaction enthalpies is not straightforward because the total reactant conversion needs to be taken into account and it is generally impossible to write a correct stochiometric equation. To define the process efficiency, various definition can then be used depending on the effect the authors aim at emphasising. For instance, the energy conversion efficiency defined as the ratio between the energy contained in the products and the sum of the energy of the converted reactants with the energy injected in the plasma is used for dry reforming of methane in [100]. Since these definitions of "efficiency" are not unique from one author to another and the number of articles using a given definition is still too limited, this type of parameter based on energy content of product is not included in the CO2-PDB for the moment. However, since the definition based on the standard reaction enthalpy valid for the pure CO\(_2\) case can...
still be retrieved from the CO2-PDB data by way of filtering the database on only CO2 splitting experiments, the other experimental goals are not excluded from the CO2-PDB, see Fig. 10(a). As such, by using the energy efficiency of CO2 conversion, at least some comparison can be made between different experimental goals, but due care is again warranted before drawing conclusions.

As shown in Fig. 10(a), there is some clustering of data by their goal, with mainly methanation experiments showcasing strong outliers that showcase high conversion and efficiency. However, this may be partially due to the exothermic nature of the methanation process, further enhanced by (thermal) catalytic reactions. Another observation can be made based on the applied methodologies and/or region for establishing the plasma or gas temperature, as is illustrated in Fig. 10(b). There is merit to the argument that the accuracy of the reported temperature plays a key role when underestimating (or not accounting for a rise in) the temperature for the process in the reactor, which is used in calculating the efficiency. Conversely, the opposite holds for experiments reporting in situ temperatures and effluent conversions which will result in an underestimated efficiency, for reasons discussed above. As a final remark, it should also be pointed out that the graphs in Fig. 10 show the CO2 conversion and do not normalise for the amount of CO2 put into the system. For experiments dealing with gas mixtures or dilution, such as methanation, this changes the situation considerably, making the outliers more in line with the rest of the data.

4.4. Influence of support and active phase shown through statistical data

The advanced data extraction functionalities presented in Section 3.3.2 enable easy cross-comparisons with all database input parameters. In this section, examples of extraction graphs and their corresponding analyses are given. However, it is essential to keep in mind that all the insights available from a database rely on the quantity and value range of the data with respect to the parameters considered. The conclusions that can be drawn from a data extraction must therefore always be considered with a critical eye on the amount of data available for a specific combination of input parameters. It is obvious that the more data the database will contain thanks to the contribution of the whole community, the more trustworthy the conclusions that can be drawn from it will become. To date, the data sets are sometimes still too limited to allow certain analyses, as will be illustrated in the following.

Fig. 11(b) shows the CO2 conversion and energy efficiency for different types of discharges, distinguishing between results obtained with plasma alone and those obtained with a catalytic material.

The width of the distributions at a given conversion rate (or energy efficiency) and for a given plasma source depends on the amount of data available at that value. However for sake of visibility, the relative areas between the different distributions are not related between each other. Experiments containing catalysts (Fig. 11a, in magenta) are clearly shifted towards higher conversion rates compared to those without catalyst (in cyan) in the case of Spark, Glow, GDA and MW plasma, which are all plasma sources that tend to heat the gas at atmospheric pressure. The observed conversion gain could therefore be partially due to the thermal activation of the catalyst in these plasmas. The conversion energy efficiency (Fig. 11b) also shows a benefit from the presence of catalyst in MW and GDA but these data are unfortunately not currently available in the CO2-PDB for the Spark and Glow discharges. This absence of data is due to the lack of information concerning the power dissipation available in some plasma configurations. Other factors include the uncertainty of the real temperature in the system, alongside the inherent difficulties of inhomogeneous energy deposition between plasma sources (see Sections 3.2 and 5). The class of NRP plasmas is generally investi-
The input parameters of the database allow one to push the analysis further, in particular thanks to the parameters describing the properties of the catalyst. At the time of writing there is still a paucity of data on the support shape, pore volume, or specific surface which precludes any trustworthy conclusions. These parameters are intentionally tracked to improve the capabilities of the database in future work. Currently, the available data allow users to discriminate the effect of the supports from the effect of the active phase added to supports.

To that end, Fig. 13 shows again the CO2 conversion rates and energy efficiency like Fig. 11, but this time restricted to solely DBDs, whilst comparing the performances obtained in plasma either with the support alone (cyan), or with an active phase on the same support (green). The range of conversion rates in Fig. 13(a) is correlated to the support used. In the case of alumina for example, the conversion does not vary significantly with the addition of an active phase, reaching a maximum of 40% conversion. Zeolites exhibit a larger range of conversion rates with a second peak above 50% once the material with the active phase is considered. The same is also true for the SiO2 class of supports. Ceria-based supports alone do not aid CO2 conversion reactions (conversion restricted below 20%), and in the presence of an active phase these catalysts seem to be the most efficient among those reported in Fig. 13(b). BaTiO3, which is a material characterised by large dielectric permittivity, has been used so far in literature without an active phase, yielding low conversion and efficiency. However, it should be noted that the number of publications used to build Fig. 13 is not sufficient to reach general conclusions. The discussion presented here is therefore at this stage too premature and aims only at illustrating the usefulness of the CO2-PDB. The real physico-chemical trends on conversion performance will naturally become increasingly valid and relevant as the community adds data.

4.5. General behaviour of C\textsubscript{2}H\textsubscript{4} molecules

The performance data in the CO2-PDB is not limited to pure CO2 conversion. Beyond the conversion rates of the main reactants (CO2 and CH\textsubscript{4}), the CO2-PDB also includes data on the selectivity or production rate of other products that are increasingly claimed to be of interest in the recent literature. For instance, CO\textsubscript{2} is often investigated as a softer oxidant than O2 for light alkane partial oxidation reactions [104,105]. Its use as an oxygen source for light alkane activation is attractive due to the high content of CO\textsubscript{2} in biogas [106] and due to the rise of vast new shale gas resources [107]. The conversion of CH\textsubscript{4} to C\textsubscript{2} hydrocarbons is a side reaction of dry reforming of methane, in which C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{4} can be produced according to Eqs. (2) and (3).

\begin{equation}
2 \text{CH}_4(g) + \text{CO}_2 \rightarrow \text{C}_2\text{H}_6(g) + \text{H}_2\text{O}(g) + \text{CO}(g) \quad \text{with} \quad \Delta H_r^\circ = 111.9 \text{ kJ mol}^{-1}
\end{equation}

\begin{equation}
2 \text{CH}_4(g) + 2 \text{CO}_2 \rightarrow 2 \text{C}_2\text{H}_4(g) + 2 \text{H}_2\text{O}(g) + 2 \text{CO}(g) \quad \text{with} \quad \Delta H_r^\circ = 287 \text{ kJ mol}^{-1}
\end{equation}

The endothermic nature of these reactions implies that the use of CO\textsubscript{2} as an oxidant requires more energy than the reaction driven by O\textsubscript{2} [105]. To increase conversion and decrease reaction temperature, plasma technology has been proposed for CO\textsubscript{2}/CH\textsubscript{4} activation. However, the main product of CO\textsubscript{2}/CH\textsubscript{4} discharges is typically syngas (H\textsubscript{2} + CO), as in Eq. (4).

\begin{equation}
\text{CH}_4(g) + \text{CO}_2(g) \rightarrow 2 \text{H}_2(g) + 2 \text{CO}(g) \quad \text{with} \quad \Delta H_r^\circ = 247.3 \text{ kJ mol}^{-1}
\end{equation}
Fig. 14 shows the selectivity towards the main C2 hydrocarbons as a function of the SEI, for different types of plasma sources extracted from the CO2-PDB. Fig. 14 shows that for all C2 hydrocarbons the maximum selectivity is reached at low SEI values and, beyond that, the selectivity tends to 0% as can be expected since C\textsubscript{x}H\textsubscript{y} molecules get decomposed by the plasma if the energy density is too high. Snoeckx and Bogaerts\cite{60} reviewed the literature available up to 2017 and found that the selectivity to C2 hydrocarbons tends to increase with the feed flow rate, and thus with decreasing SEI, in line with Fig. 14. Moreover, maximum selectivities to C2H\textsubscript{2} and C2H\textsubscript{4} are typically achieved by thermal discharges (i.e. GDA and spark discharges in Fig. 14a and b), whereas C2H\textsubscript{6} is significantly produced only by non-thermal discharges (i.e. DBD and corona discharge in Fig. 14c). The SEI is generally much larger in DBD than in thermal plasmas; therefore, the inclination of the former towards higher C2H\textsubscript{6} selectivity seems counter-intuitive. In thermal plasmas, higher SEI means higher residence time in the plasma and higher gas temperature \cite{109,110}, promoting the pyrolysis of hydrocarbons to solid carbon and H\textsubscript{2}. We must point out that this is not always the case, as higher power density (e.g. upon discharge contraction with increasing pressure \cite{111}) can also cause an increase in gas temperature. However, DBDs typically feature a filamentary behaviour, meaning that the actual gas residence time in the microdischarges is much lower than the overall gas residence time in the DBD reactor, and resulting only a fraction of the gas flow comes into contact with the discharge. Hence, the filamentary regime enables both low gas temperature and high SEI, resulting in more electron impact dissociation and three-body recombination processes, thus driving the selectivity towards C2H\textsubscript{6} and higher hydrocarbons \cite{112}. However, C2H\textsubscript{6} is more valuable than C2H\textsubscript{4} for the chemical industry, and Fig. 14 shows that thermal plasmas may provide good selectivity at low SEI (and thus low energy cost), although little research has been carried out so far.
5. Suggestions of good practices

The choice of metadata currently included in the CO2-PDB is an image of what is most commonly reported in the plasma-catalysis literature. As such, the CO2-PDB gives not only a comprehensive overview of the state of the art but also serves as template of what data should be provided to facilitate the comparison between studies.

A critical assessment of this template might lead to the conclusion that there is the plasma characterisation on the one hand and the catalyst characterisation on the other. Within that narrative, Fig. 2 seems to show in general a more complete description of the plasma-related parameters than the catalyst-related ones. In reality, neither the plasma source nor the catalyst are easily characterised because of the presence of each other. Indeed, the great specificity of plasma-catalysis, as described in Section 2, is that the chemical reactivity takes place as much in the plasma phase as on the catalyst surface. For instance, any comparison of efficiency between two catalysts, even when used in the same plasma reactor, therefore raises the question of whether the observed effect is really due to the surface reactivity of the catalyst, or whether the used materials have modified the plasma reactivity. At the same time, reactor configurations aiming at optimising conversion performances are rarely compatible with advanced in situ diagnostics allowing for a thorough characterisation of key parameters. The relevance of any cross-comparison is thus limited by the knowledge of these key parameters.

In the following, two aspects are addressed for better comparability. For one thing, lessons learned from the status quo of the CO2-PDB are recapitulated. In brief, we argue that if future studies would adhere to the template of metadata established by the CO2-PDB, a significant amount of comparability would be obtained. For another thing, with relatively simple methods elaborated on in the following, even more essential information could be exploited in a more systematic way. Note that these methods occasionally go into the details and beyond what is currently included in the database. The CO2-PDB is meant to evolve and grow though, allowing it to become a guideline for future research rather than a mere image of it.

5.1. Parameters to characterise the plasma phase

Ideally, to properly describe the properties of a plasma source, one would need to know for example the electron density or the electric field. Even if new techniques now allow to determine the electric field in filamentary plasmas at atmospheric pressure, both in the plasma (E-FISH technique [113,114]) and in dielectric surfaces exposed to these plasmas (Mueller polarimetry [115]), these techniques do not yet allow to assess the electric field inside a plasma-catalysis reactor designed for achieving good conversion performances. The plasma behaviour in plasma-catalysis reactors must therefore mostly be deduced from electrical diagnostics and sometimes from emission spectroscopy. As it can be seen in Fig. 2, the parameters most often reported to describe the plasma source used are above all: the frequency, the power (and the SEI which are linked), then the volume and the temperature; the other parameters describing rather the gas mixture.

**Volume**

The volume is an important notion when the chemical reactivity is controlled by short-lived species. When the volume is given, it is often the geometrical volume of the plasma reactor between the electrodes which is the easiest to determine, see Fig. 15(c). Two other volumes would nevertheless be important to know: (i) the real volume of the plasma when it is ignited (which does not always correspond to the volume delimited by the electrodes), (ii) the volume of the “voids”, i.e. the geometrical volume of the reactor minus that of the catalyst particles. The effective volume of the plasma can vary according to the experimental conditions used. In a microwave plasma for example, the plasma volume can expand with the injected power, but a constriction of the plasma can also appear when the pressure increases [116]. In a DBD, the volume over which the streamers manage to ignite also depends on the injected power (see comments on the Lissajous figures below), and on the configuration of the catalytic bed [117]. This effective plasma volume affects the residence time of the gas in the plasma zone which is decisive for the conversion efficiency if the short-lived species generated by the plasma are involved. For the same reason, the volume of voids in the zone where the plasma is initiated should be known as well. More pre-
cise information on the geometric volume of the reactor, the effective plasma volume, and the interstitial volume between the catalyst particles would be important to describe for any plasma-catalysis study.

**Temperature**

A re-occurring theme throughout this work is the importance of temperature. In Section 3.2, we have seen that the temperature is the most sparsely reported plasma parameter despite its importance for the reaction kinetics [118]. In Fig. 9, it was furthermore demonstrated that it also plays a crucial, not entirely unambiguous, role in evaluating process output. The scope of the issue is further illustrated in Fig. 15(a), which shows the fraction of each temperature determination method with respect to the total amount of data sets reporting the temperature. A more in-depth elaboration on each method is given in the Supplementary Material, but two aspects are worth mentioning here. Firstly, moving in Fig. 15(a) from the optical emission spectroscopy (OES) bar to the right, the methods become more ex situ and/or invasive. In other words, the determined temperature is less representative of the environment where the conversion takes place or the measurement method even perturbs the environment. Secondly, for most cases the temperature is in fact measured/imposed ex situ or even of unknown origin \((T_0)\). We argue that the ex situ case has only limited added value compared to no temperature information at all when it comes to tuning the conditions for optimal conversion.

When a temperature value is given, it is important to be precise in specifying which temperature it is (external surface temperature, catalyst bed surface temperature, reactor exit gas temperature, plasma gas temperature etc.). Recent work with materials having a thermo-sensitive spectral response has shown that the surface temperature of the catalyst is not even necessarily thermalised with the plasma temperature [119,120]. Any available information on one of these temperatures is always important to know, but it is essential to be specific about its meaning. In particular, when the conversion performance is compared with and without plasma for different temperatures imposed with an external furnace, it is essential to take into account this comparison the heating of the catalyst bed induced by the plasma itself.

However, an accurate in situ temperature measurement is often impeded by the reactor geometry with a diagnostic-optimised design usually coming at the expense of conversion performance. In addition, the gas temperature is typically not constant in the reactor but there is a temperature profile. A potential compromise is a more thorough thermal characterisation of the reactor itself. The thermal properties of the catalyst are important as they govern the thermal energy transport in the reactor. Particularly, knowledge of the thermal conductivity of the catalyst (and gas) allows for the determination of the temperature change in the discharge gap due to plasma depending on the power. In turn, this helps assessing whether a catalyst performance increase in the presence of a plasma originates in a gas temperature increase, or actual synergy [121,122]. Despite this potential, none of the publications in the CO2-PDB report the thermal conductivity of the used catalyst. As such, this parameter is not included in the database yet.

In conclusion, we recommend a thorough thermal characterisation of the plasma-catalytic system, preferably involving the two following types of measurements. Firstly, the measurement of the gas temperature \(T_g\), preferably non-invasively in situ at the location of conversion under as many experimental conditions as possible, and secondly the determination of the thermal conductivity of the catalyst in order to estimate the temperature in the bed from the power dissipated and the outer surface temperature. Likewise for effluent measurements, the conditions of the effluent need to be considered and specified. This also includes taking into account an increase in the number of molecules due to conversion [123].

**Power**

A similar argumentation holds for the way the power is measured. In Fig. 2, it is shown that about 90% of data sets report the deposited power but Fig. 15(b) shows that for 18% of those cases, it is not clear how the power is determined \((T_{in})\). Therefore, the first recommendation is to always report the power determination method. The best way to determine the power strongly depends on the system in use, and on the purpose of the value being given.

Before going into detail of different power determination methods, it is worth mentioning here that applied voltage is sometimes reported instead of power (or SEI). The voltage is a fairly easily accessible process parameter which makes it a popular \(x\)-value in experimental studies. We argue though that it is of little help for comparison between different plasma sources. When, for whatever reason, determined to report a performance parameter against voltage, our advice is to always also present a corresponding graph of power vs. voltage. Preferably, results should be presented against power directly or even better against the SEI.

If the objective is to prove the energy efficiency of a CO2 conversion process for an industrial application context, then the power consumed “at plug”, i.e. including the energy efficiency of the voltage generator should be given. However, so far only one publication in the CO2-PDB reports the power at plug [124]. This is because the generators used for the studies aiming to understand the plasma-catalysis coupling are not optimised for a specific reactor configuration, and it is therefore more relevant to compare plasma-catalyst performance depending on the power really transferred to the gas, where power losses in the electrical circuit between the generator and the plasma reactor should always be made explicit.

For example, in the case of an RF reactor, the reflected power must be explicitly subtracted from the power supplied by the generator to be able to compare the plasma performance with only the power injected to the gas. In the case of NRP discharges, powered by voltage pulses whose rise time is faster than the characteristic development time of a streamer, thus less than a few nanoseconds, the accuracy of the measurement of the time shift between the applied voltage signal and the discharge current signal should always be mentioned (as well as bandwidth and sampling rate of the electrical measurement equipment) because of its influence on the product of voltage and current signals on these time scales. The use of the product \(U \cdot I\) seems justified in the case of NRP discharges without dielectric barrier for which the current that is measured is directly the discharge current.

In the case of DBDs which in general generates multiples randomly distributed current spikes during each half period of the power supply, the use of \(U \cdot I\) is at best very challenging as explained in details in [125,126]. Indeed the duration of each current spike is within 1–10 ns while typical period of power supply is 10–100 ms. The bandwidth and rise times of current probes are limited, and so is the maximum sampling rate of commonly available oscilloscopes. Furthermore, the position of the current probe in the circuit can affect the influence of parasitic inductances and capacitances that induce peak current oscillations which do not correspond to the real discharge current, and which can overlap with other current peaks when the number of streamer per half period is too high. Finally, since DBDs are essentially capacitive dividers, it is also important to ensure that the displacement current is correctly subtracted to successfully extract the discharge current. All these difficulties make in general the \(U \cdot I\)-method more inaccurate in DBD reactors aiming for CO2 conversion performances. Despite these limitations, no less than 17% of the data dealing with DBDs currently included in the CO2-PDB rely on the
product of voltage and current, while only 66% of DBD data sets give a power using the Lissajous figure method [127]. Since DBDs make up the majority of plasma sources in the CO2-PDB, it is worth elaborating further on the Lissajous figure which is one the main source of information about the plasma in packed bed DBD.

The Lissajous cycle area is always a good estimate of the energy dissipated during a period of the high voltage supply, and multiplying it by the generator frequency gives the power. It is intrinsically a method integrating the current signal which therefore allow for the use of lower bandwidth electrical measurement systems than the \( U-I \)-method. On the other hand, if instead of integrating the cycle area, the power is calculated with the classical formula given by Manley [127], under certain conditions the power obtained may be wrong. First, if the voltage is too low, the plasma will not cover the entire surface of the dielectric and in this case it is necessary to take into account the proportion of the surface on which the streamer is really ignited. Secondly, the addition of a catalytic material in the inter-electrode space can affect both the effective area on which the plasma can ignite, and also add parasitic capacitances as explained in details in [128,129]. Two simple methods grant further insight into the influence of the catalyst. Firstly, from the shape of Lissajous figures the effective capacity of the system, and the minimum ignition voltage can be obtained [129]. Secondly, the statistical behaviour of the current peaks over a large number of periods can give information on the influence of the catalyst on the streamer distribution in the reactor provided that the comparisons from one condition to another are made with always the same temporal resolution on the electrical measurements (the bandwidth and the sampling rate of the measurement system must be related to the measurements made) [130]. It is therefore recommended that the integration of the Lissajous cycle is always preferred to determine the power, and if possible, to work with a sufficient voltage to ensure that the plasma initiates over the entire surface of the dielectric barrier.

The homogeneity—or lack thereof—of the energy deposition over the whole volume of the plasma reactor at a given power is not a problem limited to the case of DBDs. For example, the shape of the electrodes used in a GDA configuration will influence the number of plasma filaments experienced by the gas even at constant power. The homogeneity of energy deposition in a MW reactor also depends on the experimental conditions and the reactor geometry [116]. It is therefore difficult to propose at this stage general rules to better characterise the way energy is transferred to the gas but more detailed information in this direction would be valuable. In particular, an estimate of the proportion of gas that passes through the reactor without being in direct contact with the plasma is important.

### 5.2. Parameters to characterise the catalytic bed

Beyond the information on the composition of the catalyst, which is obviously essential, Fig. 2 shows that relatively few works characterise in a complete way the catalysts used. When characterisation is done, it is mainly parameters relevant to thermal catalysis that are reported (porosity, pore volume, nanoparticle size, and specific surface area). These parameters remain important in plasma-catalysis but they are not the only ones, as the catalyst could constrain the ability to ignite the plasma and modify the way it propagates.

To properly compare the performance of different catalysts, it would be necessary to be able to determine the intrinsic properties of these catalysts when they are exposed to plasma. In order to obtain these intrinsic kinetic properties, any mass transfer limitation should be avoided. It would also be necessary to well control the concentrations and the temperature at the “active sites”, and the results from one catalyst to another should be compared while remaining at conversion rate low enough to avoid significant contribution of back reactions. Some of the “good practices” are still applicable even in plasma-catalysis. For instance, comparing selectivity at equal conversion rates, remaining at low conversion rates to compare the benefit on conversion from one material to another, or comparing results only if the carbon balance measured is better than 95% complete are recommended practices in both conventional and plasma-catalysis. Unfortunately, other conditions taken from good practices in thermal-catalysis, are incompatible with direct plasma exposure. Indeed, first of all the concentration of the reactants and the temperature at the surface of the catalyst is very difficult to know and control accurately in a plasma-catalytic reactor. Moreover, the very notion of “active site” must be reconsidered under plasma exposure because the plasma can modify the surface and the number or nature of active sites. In turn, this leads to reconsider also the notion of “support” and “active phase”. In addition, the ideal conditions to study the intrinsic properties of a catalyst require the use of small particles (a few nanometers or tens of nanometers) to limit mass transfer limitations, but this leads to problem of the plasma ignition in the core of the catalytic bed. It is therefore not possible to conclude that the surface reactivity of one catalyst is better than another if the macroscopic shape of one and the other generates different properties of the plasma in contact with them. For this reason, the influence of the macroscopic shape of the catalyst (or its support) on the plasma development should be systematically studied. This includes in particular a careful study of the relative permittivity (or dielectric constant) of the material used.

It is thus difficult to really trace the intrinsic properties of the catalysts in plasma-catalysis. Nevertheless, for each of the difficulties just mentioned, some suggestions are made below to better highlight the real benefit of plasma-catalysis compared to thermal catalysis, and to better control the influence of the catalyst on the generated plasma. The ideas mentioned below only concern feasible practices with complex reactors designed to test conversion performances. It is clear that fundamental studies dedicated to the in situ study of certain mechanisms of interaction between the plasma and the catalyst are also essential for this research to develop, but it is not the object of the remarks made here.

**Role of support**

Support materials make up the largest proportion of the catalyst composition and they could have a chemical, physical and/or catalytic activity on their own when exposed to a plasma. Sometimes this activity is overlooked and not studied in detailed, as the field of plasma-catalysis often relies on paradigms of other types of catalysis, where such supports often act more as substrates for the active phase than as an active player in the reaction. For instance, the basicity of this support material is rarely reported while it can be of significant importance for CO2 plasma conversion. Therefore, we recommend that these materials should be systematically tested alone in the plasma configuration under study. Indeed, the support itself can already (i) have surface reactivity in particular with short lived species produced by the plasma, and (ii) modify the plasma properties. This last point is related, in particular, to the macroscopic shape and to the physical properties such as the permittivity of the support.

**Size and shape**

As discussed already, in thermal catalysis the use of small particles (a few nanometers or tens of nanometers) is recommended to cope with mass transfer issues in the bulk of the catalytic material. For plasma-catalysis, using small particles would also be beneficial to ensure that short-lived species generated by the plasma can reach the active sites of the catalyst particles. Unfortunately, while surface reactivity would definitely improve when compared to larger particles, the plasma needs voids between the particles larger than the Debye length to ignite, typically corresponding to
spaces of several 100 nm at least [131]. The use of larger particles is then necessary to promote a well distributed plasma in the catalyst bed. However, since plasma does not form in smaller pores and interstices, in turn the short-lived species can not diffuse to the interior of large particle. As a consequence, a large proportion of catalytic material does not make use of short lived “plasma species” but can only react with stable molecules, as it would happen in conventional thermal catalysis. In order to really exhibit the specificity of plasma-catalysis, the ideal size and shape for a system of support/active phase will always be the one that can maximise the surface area and the number of active sites that can be effectively reached by plasma generated species. Therefore, contrary to the best practices in thermal-catalysis, larger catalyst particles (typically several hundred microns) should be used for plasma-catalysis. It is therefore advisable to keep the same macroscopic shape (same support for example) to compare the efficiency of different catalysts in the plasma.

The use of large particles creates mass transport problems for two main reasons: (i) the diffusion limitations in the particle bulk, and (ii) the gas flow distribution in the catalytic bed.

If these relatively large particles are completely porous, then concentration gradients will appear in their bulk depending on the characteristic diffusion length of the different species, in particular for short lived species created in the plasma. One possibility to infer the relative contribution of long or short lived species reactivity would be to have a reference material consisting of particles with the same macroscopic shape and composition as the catalyst under study but without internal porosity. Ideally, to better comprehend the role of particle size and porosity it would be useful to have several comparisons: varying porosity but keeping particle size constant and the other way around, while analysing thoroughly the electrical data to analyse the resulting plasma behaviour (as described in Section 5.1).

The good distribution of the gas flow in the catalytic bed is also important. To ensure this in the case of a catalytic bed with relatively large particles, a rough order of magnitude is to ensure that the diameter of the reactor is at least ten times the diameters of catalyst particles. Depending on the size of the particles and the type of plasma source used this is not always possible due to the electric fields needed to ignite the plasma, but it is a parameter that should also be considered.

In any case, any plasma-catalyst coupling study should give precise and detailed information on the macroscopic characteristics of the catalytic bed. Due to the lack of information available in most of the papers, the only parameter related to this “macroscopic shape” in the CO2-PDB is currently the “shape” parameter which roughly differentiates the type of support (aerogels, beads, powder, monoliths etc.), without giving more information about the characteristic dimensions. We argue that such information would be important to mention systematically in addition to the microscopic characterisations of the catalyst. All these considerations on the shape and the size of the particles of the catalytic bed are obviously important for the “packed bed DBD” which is the most studied configuration, but all these remarks remain valid whatever the type of plasma associated with the catalytic bed.

Relative permittivity (or dielectric constant)

The relative permittivity is often mentioned in plasma-catalysis papers because of the electric field re-enforcement induced at the surface of high permittivity material. If the reinforcement of the field at the surface of a high permittivity material can indeed allow the initiation of a plasma at lower applied voltage, one should not forget that the permittivity also plays on the capacity of the material, and thus on the quantity of charge that the plasma must deposit on the surface which is not always an advantage for the development of the plasma on a large volume. In any case, many of the typical supports used in heterogeneous catalysis for CO2 conversion deal with metal oxides or mixtures of metal oxides, as CeO2 or Al2O3. These materials usually have a high relative permittivity (or dielectric constant). However, the permittivity not only depends on the composition but also on the size, shape, temperature, frequency, etc. In the particular case of DBDs that are essentially a capacitive configuration, the presence of high permittivity material will affect the capacitance of the reactor. Such effect can be observed easily on the slope of the plasma OFF phase in the Lissajous figure which corresponds to the capacitance of a DBD reactor including the dielectric barriers, gas and catalyst. However, few publications measure this constant for the materials prepared for plasma-catalytic reactions. Following the procedure given in [129] for instance, the change in reactor capacitance depending on the reactor configuration should be reported. Furthermore, it should be further considered that the addition of a metallic material (often the active phase) over the metal oxide will modify the relative permittivity of the overall catalyst. Therefore, when possible it is encouraged to measure both the dielectric constant of the support alone and the whole catalyst tested.

Catalyst modifications induced by the plasma

Finally, the plasma is very likely to modify the nature of the catalyst due to local heating, surface reactions, sputtering, etc., either reversibly or irreversibly. Such modifications can be chemical, morphological, topographical, micro-structural, etc. However, it is often difficult to characterise the surface state of the catalyst in situ. By default, it is still important to carry out all the usual methods of surface characterisation before and after exposure to the plasma, and to specify in the publications the method used to transfer the samples from the plasma reactors to the analysis tools. This would at least allow for the assessment of irreversible modifications which does not necessarily correspond to the surface state existing under direct exposure to plasma, but it remains a source of information relatively easy to obtain which should be more systematically reported. While this can be a way to rapidly improve our knowledge about the effects of plasma on catalytic materials, future developments on the application of diverse spectroscopic techniques will dictate what could be implemented in the case of material characterisation under plasma conditions.

The notion of “blank” measurement

The recommendations discussed above lead to question the notion of “blank” for performance comparisons. Obviously, comparing the situation of plasma alone or in the presence of a catalyst does not directly highlight a certain chemical reactivity of the catalyst surface, because the plasma will be very different due to the presence of the catalyst. To gain insight into the real benefits of combining a plasma with a catalyst, it is probably necessary to compare several types of “blank” aimed at addressing different contributions of this combination. It can be a support with the same macroscopic shape but not the same permittivity just to check the impact on the plasma development, or the same material with the same particle size but with or without internal porosity to look at the influence of the species diffusion in the core of the material, to list some examples. In any case, particular attention should be paid to the type of materials that are used as “reference” in the comparisons aiming to highlight a better conversion efficiency in the presence of a catalyst in the plasma.

6. Conclusions

There are a lot of nuances involved with any critical appraisal of plasma-catalytic CO2 experiments. Comparing experiments conducted across a large range of conditions and configurations is already a non-trivial task, which is further complicated by the manner in how—and also which—parameters are reported in literature. A concerted effort has been made to compile the experimen-
tal outcomes of a large body of literature in the field, along with descriptive metadata. This effort has been crystallised in the form of the CO2 PIONEER Database (CO2-PDB), containing data from almost 200 publications spanning roughly two decades at the date of submission of this paper. The information contained within the CO2-PDB reproduces previously observed trends from review papers, which can be trivially replicated using the dedicated web application (https://db.co2pioneer.eu). It furthermore facilitates a more statistical assessment of the literature, allowing tentative trends to be already observed. With further contributions of the community, the descriptive power will only grow. Submission of new data to grow the CO2-PDB is widely encouraged for the benefit of the entire community by following the submission requirements described at https://docs.co2pioneer.eu/contribute.

However, care must be taken to critically assess the data that is extracted from the CO2-PDB. First of all, it is inherently limited by the details that are reported in literature. The data currently available in the community are still disparate, and whatever trends appear in a CO2-PDB data extraction, it is important to keep a critical eye on the possibly incomplete or even missing information that would explain the observed trend. Moreover choices had to be made for the CO2-PDB, and some limitations stem from a compromise between accurate descriptions of measurement conditions, whilst also maintaining descriptive metadata of the experiments that were conducted.

These metadata are for the moment limited on the one hand by what is reported so far in the articles (it would not make sense to include in the CO2-PDB a parameter that is so far only mentioned by a few articles), and on the other hand by the lack of fundamental understanding of the plasma-catalysis interaction (e.g. the notion of “active site” in the case of plasma-catalysis is still vague). The CO2-PDB must therefore be an evolving tool to adapt to what research results the community will identify as new key parameters, allowing better comparison of data. Conversely, the CO2-PDB can highlight the need for more rigorous practices on already well identified parameters. For instance, parameters as critical to plasma-catalyst coupling as gas temperature or power dissipation should always require a critical analysis of the method used to obtain them, coupled with a discussion of their accuracy or homogeneity across the reactor, for example.

A final important point to keep in mind is the biases related to the amount of data available for a given type of configuration/material compared to others. With the data currently available in the CO2-PDB, there is, for example, an overrepresentation of DBD data with catalysts having a Nickel active phase. The fact that more studies have focused on this configuration should not lead to exclude a priori the possible interest of other configurations and other metallic active phases. This is in fact one of the basic ideas of any statistical study, which is to try to have data sets as complete, balanced and well distributed as possible. The data currently available in plasma-catalysis do not yet allow this in a satisfactory way. This is why, whereas the use of machine learning algorithms is so widespread nowadays, it does not seem relevant for the moment to implement such tools on the currently available data sets for plasma catalysis. If the limitations previously mentioned must be kept in mind, the CO2-PDB nevertheless offers for the first time the possibility to cross-reference the state-of-the-art results on CO2 conversion by plasma-catalysis with all the filters offered by the included metadata. This tool is bound to develop over time and should allow everyone to put their own results in the current context of the discipline, but also to the community to improve the understanding of this complex phenomenon that is the plasma-catalyst interaction. The CO2-PDB represents a comprehensive overview of the literature on plasma-catalytic conversion of CO2, based on which some recommendations are made to progress the field.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jechem.2023.07.022.

References
