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Plasma-based CO₂ conversion: How to correctly analyze the performance?

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Abstract

Plasma-based CO₂ conversion is promising for carbon capture and utilization. However, inconsistent reporting of the performance metrics makes it difficult to compare plasma processes systematically, complicates elucidating the underlying mechanisms and compromises further development of this technology. Therefore, this critical review summarizes the correct definitions for gas conversion in plasma reactors and highlights common errors and inconsistencies observed throughout literature. This is done for pure CO₂ splitting, dry reforming of methane and CO₂ hydrogenation. We demonstrate that the change in volumetric flow rate is a critical aspect, inherent to these reactions, that is often not correctly taken into account. For dry reforming of methane and CO₂ hydrogenation, we also demonstrate inconsistent reporting of energy efficiency, and through numerical examples, we show the significance of these deviations. Furthermore, we discuss how to measure changes in volumetric flow rate, supported by data from two experimental examples, showing that the sensitivity inherent to a standard component and a flow meter is essential to consider when deriving the performance metrics. Finally, some general recommendations and good practices are provided. This paper aims to be a comprehensive guideline for authors, to encourage more consistent calculations and stimulate the further development of this technology.

Keywords

Plasma; CO₂; Dry reforming of methane; CO₂ hydrogenation; Conversion; Performance

List of symbols

Symbols (incl. sub- and superscripts)	Description
*	Incorrect expression
<i>A</i>	Atom
abs	Absolute
app	Applied
α	Flux ratio
<i>b</i>	Balance
β	Dilution ratio
chem	Chemical
conv	Converted
corr	Corrected
des	Desired
DF	Dissociation fraction
ΔH°	Standard reaction enthalpy (kJ mol ⁻¹)
<i>E</i>	Energy (kJ ⁻¹ , eV)
EC	Energy cost (kJ mol ⁻¹ , kJ L ⁻¹ , eV molecule ⁻¹)
eff	Effective
EY	Energy yield (mol kJ ⁻¹ , L kJ ⁻¹ , molecule eV ⁻¹)
fin	Final
H_f	Formation enthalpy (kJ mol ⁻¹)
<i>i</i>	Reactant
in	At reactor inlet/before reactor
init	Initial
<i>j</i>	(Gaseous) product
<i>k</i>	Condensed/deposited product
LHV	Lower heating value (kJ mol ⁻¹)
meas	Measured
μ	Stoichiometric coefficient
\dot{n}	Molar flow (mol min ⁻¹)
N_A	Avogadro's constant (molecule mol ⁻¹)
η	Energy efficiency
out	At reactor outlet/after reactor
<i>p</i>	Pressure (bar, atm)
<i>P</i>	Power (kW)
RE	Relative error
reac	Reaction
rep	Reported
<i>s</i>	Diluting agent/standard component
<i>S</i>	Selectivity
SEI	Specific energy input (kJ mol ⁻¹ , kJ L ⁻¹ , eV molecule ⁻¹)
<i>T</i>	Temperature (K, °C)
tot	Total

\dot{V}	Volume flow (L min ⁻¹)
V_m	Molar volume (L mol ⁻¹)
χ	Conversion
y	Molar/volume fraction
Y	Product yield

1. Introduction

The transition to a more sustainable society requires innovative management of CO₂ to minimize environmental risks [1]. Carbon capture and utilization (CCU) aims to both capture CO₂ from emission sources, as well as use it as a feedstock for cleaner processes [2]. Various CCU pathways are under development, and a wide variety of methods for chemical CO₂ conversion into, e.g., liquid fuels have been extensively investigated, including thermal, electrochemical or photochemical conversion pathways [3–8].

A CO₂ conversion technology that has gained increasing interest over the past decades is plasma technology [9]. Plasma is an ionized gas that is able to convert stable molecules into value-added chemicals at ambient conditions, e.g., carbon dioxide (CO₂ conversion) [9,10], but also molecular nitrogen (N₂ fixation, for fertilizer production) [11–14]. This technology is very flexible in terms of input gases and instant control over the process, which makes it suitable for electrified production in combination with the fluctuating renewable electricity supply [9]. Furthermore, it does not require using scarce materials [9] and has already been demonstrated in various industrial applications, such as ozone production and arc plasma furnaces for steelmaking [15].

The performance of plasma technology, also with respect to other CCU technologies, has been extensively reported in the review paper by Snoeckx and Bogaerts [9]. As is clear from their work, there is a variety of plasma reactors used for gas conversion, differing in terms of design, applicable currents, voltages, pressures, flow rates, etc. In their paper (as well as in more recent literature, e.g., Refs. [16–19]), a comparison of these reactors in terms of their performance towards CO₂ conversion is presented, which is extremely important for developing this technology. To make this comparison, it is imperative to have an objective, consistent and correct methodology for determining the performance metrics.

Ideally, a plasma reactor can be considered as a plug flow reactor, i.e., a tubular reactor where the composition of the gas is uniform in the radial direction, but changes as a function of the axial position. This also means that the total number of molecules, the concentrations and the total volumetric flow rate change along the reactor. Indeed, a change in volumetric flow rate is inherent to any reaction where the total number of molecules changes and should be considered when determining the performance metrics. For example, in the case of CO₂ splitting, the overall reaction proceeds as follows:



One molecule of reactant splits into 1.5 molecules of product. In other words, upon conversion of CO₂ there will be an increase in the volumetric flow rate. Hence, the performance metrics (such as conversion, product yield and selectivity, but also energy efficiency and cost) cannot be based solely on the number density without considering the change in volumetric flow rate, but should be based on the number of species entering/exiting the reactor per unit of time. These flow rates are well-defined at the inlet of a reactor with mass flow controllers. At the exit of a reactor, however, this is not straightforward to measure. Indeed, common analytical tools (e.g., Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC) and mass spectrometry (MS)) sample the gas flow and measure the concentration of species, but not the volumetric flow rates. To calculate the performance metrics, one should carefully consider whether the flow rate or the concentration is needed.

However, Pinhão et al. [20] found that so-called “gas expansion” (i.e., an increase in the volumetric flow rate) is often neglected when analyzing the performance of plasma reactors. They found errors

up to 20% on the performance metrics for CO₂/CH₄/He mixtures. Therefore, they introduced a new technique to determine the gas expansion ratio, defined as the flux ratio α , alongside a set of formulas to correctly define the performance metrics.

Despite this fundamentally important work, several researchers in the field still neglect gas expansion or provide no information on how it has been taken into account, as will be demonstrated in this paper (see examples and references in Sections 3 and 5). Even when it is accounted for, a wide variety of formulas and interpretations are reported, also within our own group. Furthermore, inconsistent formulas are found in literature for all performance metrics, not only for the conversion, but also for the energy efficiency and energy cost. This complicates the comparison of the results of different works in literature, and hence, further development of this technology.

In this critical review, we aim to clarify the correct definitions for performance metrics in plasma-based gas conversion. In Section 2, we derive the stoichiometric equations for pure CO₂ conversion, and we provide the correct definitions for the energy-related performance metrics. In Section 3, we discuss our equations in relation to other terminology in literature and demonstrate how some other formulas used in literature provide incorrect values, by means of a numerical example. In addition, we illustrate these inconsistencies with a literature review. Section 4 presents the equations for other CO₂ reforming processes, such as dry reforming of methane (DRM) and CO₂ hydrogenation. They typically require more elaborate calculations, since various products can be formed, and simple stoichiometry is typically not sufficient, and thus, the concept of flux ratio should be used. In Section 5, we discuss our equations again in relation to other terminology that exists in literature for various CO₂ reforming processes (with a co-reactant), and show the large inconsistency towards how energy efficiency is defined through a numerical example, as well as through a review of some of the available recent literature. Section 6 presents different analytical methods to obtain the flux ratio, supported by two experimental examples, both for pure CO₂ conversion and with co-reactants, to evaluate their accuracy and choose the best method. Finally, in Section 7, we provide some research recommendations and good practices for plasma-based CO₂ conversion, followed by the overall conclusion in Section 8. It is worth stressing that the presented definitions here are valid for any type of gas conversion in a plug flow reactor and not limited to plasma processes; however, a detailed analysis of the equations used in other gas conversion fields is beyond the scope of this paper.

2. CO₂ conversion: definitions and terminology

Pure CO₂ splitting is the first reaction that we will discuss as a baseline for different reactant mixtures later in Section 4. Thanks to the simple stoichiometry, we can derive all performance metrics directly from the measured output fractions. Besides the theoretical derivation in this section, we will also test these formulas in an experimental example in Section 6.2.

2.1 Conversion

The conversion χ can be deduced from the stoichiometry of the reaction for pure CO₂ splitting, as indicated in Table 1.

Table 1. Reaction equation for pure CO₂ conversion, expressed in flow rates relative to the total inlet flow rate.

Reaction	CO ₂	CO	O ₂
in	1	0	0
out	$1 - \chi$	χ	$\chi/2$

After the reaction, we can express the measured concentration of CO₂ as the CO₂ output fraction $y_{\text{CO}_2}^{\text{out}}$:

$$y_{\text{CO}_2}^{\text{out}} = \frac{\dot{n}_{\text{CO}_2}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{out}}} = \frac{\dot{n}_{\text{CO}_2}^{\text{out}}/\dot{n}_{\text{tot}}^{\text{in}}}{\dot{n}_{\text{tot}}^{\text{out}}/\dot{n}_{\text{tot}}^{\text{in}}} = \frac{1 - \chi}{(1 - \chi) + \chi + \frac{\chi}{2}} = \frac{1 - \chi}{1 + \frac{\chi}{2}} \quad (1)$$

with $\dot{n}_{\text{CO}_2}^{\text{out}}$ and $\dot{n}_{\text{tot}}^{\text{out}}$ the CO₂ and total molar flow rate at the reactor outlet, respectively, and $\dot{n}_{\text{tot}}^{\text{in}}$ the total molar flow rate at the reactor inlet (which in the case of pure CO₂ splitting is equal to the CO₂ molar flow rate at the reactor inlet $\dot{n}_{\text{CO}_2}^{\text{in}}$). For the other components, we obtain

$$y_{\text{CO}}^{\text{out}} = \frac{\chi}{1 + \frac{\chi}{2}} \quad (2)$$

$$y_{\text{O}_2}^{\text{out}} = \frac{\frac{\chi}{2}}{1 + \frac{\chi}{2}} \quad (3)$$

The conversion is calculated from any of these measured fractions by simply rearranging the equations (see Supporting Information (SI), Section S1). When the output fraction of CO₂ is measured, we calculate the conversion as follows:

$$\chi = \frac{1 - y_{\text{CO}_2}^{\text{out}}}{y_{\text{CO}_2}^{\text{out}} + \frac{1}{2}} \quad (4)$$

This formula inherently accounts for gas expansion and can be calculated similarly from the other measured output fractions, as presented in the SI (Section S1). In the rest of the paper, we name the equations of this section “stoichiometric equations”, since they were derived from the stoichiometric reaction.

2.2 Flux ratio

Often, the conversion is presented in terms of the fraction at the inlet (i.e., measured as a “blank” at the outlet when the plasma is OFF) and outlet of the plasma (i.e., measured when the plasma is ON):

$$\chi = \frac{y_{\text{CO}_2}^{\text{in}} - \alpha \cdot y_{\text{CO}_2}^{\text{out}}}{y_{\text{CO}_2}^{\text{in}}} \quad (5)$$

Here, $y_{\text{CO}_2}^{\text{in}}$ is the input fraction of CO₂ (which is 1 for pure CO₂) and the factor α is the so-called “flux ratio” introduced by Pinhão et al. [20]. In the case of pure CO₂ splitting, this is also called the “gas expansion factor”, and it represents how much the total molar flow rate $\dot{n}_{\text{tot}}^{\text{out}}$ has increased due to the reaction (i.e., $\dot{n}_{\text{tot}}^{\text{out}} > \dot{n}_{\text{tot}}^{\text{in}}$). If the ideal gas law is considered valid, then at the same pressure and temperature, this is equal to the ratio of the total volumetric flow rate at the outlet $\dot{V}_{\text{tot}}^{\text{out}}$ relative to the inlet $\dot{V}_{\text{tot}}^{\text{in}}$:

$$\alpha = \frac{\dot{n}_{\text{tot}}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{in}}} = \frac{\dot{V}_{\text{tot}}^{\text{out}}}{\dot{V}_{\text{tot}}^{\text{in}}} \quad (6)$$

Note that it is a general assumption in this work to consider the ideal gas law as valid, as well as that the values for the volumetric flow rates are always obtained at the same temperature and pressure.

For pure CO₂ conversion (with $\dot{n}_{\text{tot}}^{\text{in}} = \dot{n}_{\text{CO}_2}^{\text{in}}$), we can couple this back to the stoichiometric equations (Table 1):

$$\alpha = \frac{\dot{n}_{\text{tot}}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{in}}} = \frac{\dot{n}_{\text{CO}_2}^{\text{out}} + \dot{n}_{\text{CO}}^{\text{out}} + \dot{n}_{\text{O}_2}^{\text{out}}}{\dot{n}_{\text{CO}_2}^{\text{in}}} = \frac{(1 - \chi) + \chi + \chi/2}{1} = 1 + \frac{\chi}{2} \quad (7)$$

This result fits the intuitive understanding of gas expansion. Every CO molecule replaces exactly one CO₂ molecule after the reaction, but in addition, half of an O₂ molecule is formed as well. In other words, it is equal to the initial volume of CO₂ (=1) plus half of the converted CO₂ (to account for the “extra” ½ O₂ molecule). If we fill the result of Eq. (7) back into Eq. (5):

$$\chi = \frac{y_{\text{CO}_2}^{\text{in}} - \left(1 + \frac{\chi}{2}\right) \cdot y_{\text{CO}_2}^{\text{out}}}{y_{\text{CO}_2}^{\text{in}}} \quad (8)$$

$$\chi = \frac{1 - \left(1 + \frac{\chi}{2}\right) \cdot y_{\text{CO}_2}^{\text{out}}}{1} \quad (9)$$

and rearrange to extract the conversion, we obtain the same result as Eq. (4). It is clear that all these Eqs. (1)–(9) are related to one another. Moreover, only one of the parameters must be known to calculate the others if we assume a perfect reaction like pure CO₂ splitting. The relation between all the different parameters is summarized in the SI (Section S1). This approach is similar for all reactions that have no side reactions or no significant amount of by-products, such as NH₃ synthesis from N₂ and H₂ or the formation of H₂O from H₂ and O₂.

2.3 Diluted CO₂

In some cases, a dilution gas, such as argon or helium, is added to the feed gas to improve plasma stability and performance. However, this dilution factor is not always considered when comparing the performance, and thus, the real gas conversion might be overestimated.

To take this dilution of CO₂ into account, we introduce the “dilution ratio” β , expressed as

$$\beta = \frac{\dot{n}_s}{\dot{n}_{\text{CO}_2}^{\text{in}}} = \frac{\dot{V}_s}{\dot{V}_{\text{CO}_2}^{\text{in}}} \quad (10)$$

With \dot{n}_s and \dot{V}_s the molar and volumetric flow rate, respectively, of the diluting agent (the subscript s refers to “standard component”, for which the same derivation of the conversion applies as for the diluting agent, as we will explain in more detail in Section 6.1.3). With this dilution ratio, one can again derive the conversion from any of the measured output fractions, including the fraction of the diluting agent y_s . This is also presented in the SI (Section S2). When the output fraction of CO₂ is measured, we calculate the conversion as follows:

$$\chi^{\text{abs}} = \frac{1 - (1 + \beta) \cdot y_{\text{CO}_2}^{\text{out}}}{1 + \frac{y_{\text{CO}_2}^{\text{out}}}{2}} \quad (11)$$

The derivation of this equation can also be found in the SI (Section S2). We define this parameter as the absolute conversion, which only considers the conversion of a single reactant of interest. When considering the whole input mixture, we define the effective conversion χ^{eff} :

$$\chi^{\text{eff}} = \chi^{\text{abs}} \cdot y_{\text{CO}_2}^{\text{in}} \quad (12)$$

Where the absolute conversion χ^{abs} is multiplied by the fraction of CO₂ at the inlet $y_{\text{CO}_2}^{\text{in}}$. This definition of the conversion is important for the comparison of different reactant mixtures. It can help in understanding how the conversion of one specific reactant is affected by dilution in different gases. Moreover, the effective conversion is the correct input for calculating the energy cost and energy efficiency, while the absolute conversion would give too optimistic results (underestimated energy cost and overestimated energy efficiency). Indeed, the energy is applied to the full gas mixture, not only to CO₂. We discuss these definitions of interest next.

2.4 Energy cost, energy yield and energy efficiency

The two most important experimental input parameters in any plasma-based gas conversion process are the plasma power and the input flow rate. The plasma power is determined according to the specific plasma type. For example, in a dielectric barrier discharge (DBD) reactor, the area of the Lissajous figures is calculated [21]. In contrast, in a gliding arc reactor, the time-averaged product of voltage and current is taken [22], and in a radiofrequency (RF) or microwave (MW) reactor, the difference between forward and reflected power determines the plasma power [23]. The input flow rate is determined with mass flow controllers (MFCs). It is crucial to pay special attention to the manufacturer and calibration of the MFCs, since the definitions of “standard” and “normal” liter per minute can differ depending on the region or institute; for instance, American standard liters per minute is the same as European normal liters per minute [24–27]. These differences can have a significant effect, as demonstrated with the molar volume in Table 2 when assuming the ideal gas law.

Table 2. Various definitions for standard and normal conditions and the corresponding values for the molar volume V_m . The EPA is the Environmental Protection Agency of the USA. The IUPAC definitions for standard temperature and pressure (STP) and standard ambient temperature and pressure (SATP) are also given.

Definition	T (K)	T (°C)	p (atm)	p (bar)	V_m (L mol ⁻¹)
normal EU = standard USA	273	0	1	1.01325	22.41
standard EU = normal USA	293	20	1	1.01325	24.06
EPA	298	25	1	1.01325	24.47
STP IUPAC	273	0	0.987	1	22.71
SATP IUPAC	298	25	0.987	1	24.79

These two input parameters are combined into the specific energy input SEI . The specific energy input is the dominant determining factor for the conversion and energy efficiency in a plasma process and is defined as the ratio of plasma-deposited power P to the inlet gas flow rate. SEI can be expressed in different units, depending on the units of the power and the inlet gas flow rate, as shown through Eq. (13) in kJ mol^{-1} , (14) in kJ L^{-1} and (15) in eV molecule^{-1} :

$$SEI (\text{kJ mol}^{-1}) = \frac{P (\text{kW})}{\dot{n}_{\text{tot}}^{\text{in}} (\text{mol min}^{-1})} \cdot 60 (\text{s min}^{-1}) \quad (13)$$

$$SEI (\text{kJ L}^{-1}) = \frac{P (\text{kW})}{\dot{V}_{\text{tot}}^{\text{in}} (\text{L min}^{-1})} \cdot 60 (\text{s min}^{-1}) = \frac{SEI (\text{kJ mol}^{-1})}{V_m (\text{L mol}^{-1})} \quad (14)$$

$$SEI (\text{eV molecule}^{-1}) = \frac{SEI (\text{kJ mol}^{-1}) \cdot 6.24 \cdot 10^{21} (\text{eV kJ}^{-1})}{N_A (\text{molecule mol}^{-1})} \quad (15)$$

Where V_m is the molar volume of an ideal gas, calculated at the same conditions as the measurement of the flow rate (see Table 2), and N_A is Avogadro's constant (i.e., $6.02214076 \times 10^{23} \text{ mol}^{-1}$). For clarity, in the following definitions throughout this paper, we assume the specific energy input to be defined in kJ mol^{-1} , as in Eq. (13), but of course the units are readily interchangeable.

Based on the specific energy input, we calculate the energy cost EC as the amount of energy that is consumed by the process:

$$EC (\text{kJ mol}_{\text{conv}}^{-1}) = \frac{SEI (\text{kJ mol}^{-1})}{\chi^{\text{eff}}} \quad (16)$$

As written above, note that the energy cost can also be expressed in kJ L^{-1} and eV molecule^{-1} , depending on the unit of the specific energy input. An alternative is to express the inverse of the energy cost, i.e., the energy yield EY :

$$EY (\text{mol}_{\text{conv}} \text{kJ}^{-1}) = \frac{1}{EC (\text{kJ mol}_{\text{conv}}^{-1})} \quad (17)$$

The energy efficiency η is the third main property that describes the effectiveness of the applied energy during the process, next to energy cost and energy yield. It is a measure of how efficiently the process performs compared to the standard reaction enthalpy ($+283 \text{ kJ mol}^{-1}$ for pure CO_2 splitting):

$$\eta = \frac{\chi^{\text{eff}} \cdot \Delta H^\circ (\text{kJ mol}^{-1})}{SEI (\text{kJ mol}^{-1})} \quad (18)$$

3. Confusing terminology and errors in literature for pure CO₂ splitting

In the previous section, we gave an overview of the correct definitions and calculations for determining CO₂ conversion, and the corresponding energy cost and energy efficiency, in a plasma reactor. In this section, we discuss some common definitions used in literature for gas conversion and the errors that they introduce in the reported values (Section 3.1). As an illustration, we present a numerical example and demonstrate the difference between the formulas in Section 3.2. Finally, in Section 3.3, we give an overview of the literature, and we refer to numerous papers that report a wide variety of both correct and incorrect results. Note that in Section 3.1, we only discuss the formulas, while in Section 3.3, we refer to the corresponding papers that use these formulas, for a critical literature analysis.

3.1 Alternative and/or incorrect definitions

3.1.1 Most common definition

First, we discuss the most common definition of conversion in plasma literature, expressed as follows:

$$\chi = \frac{\dot{n}_{\text{CO}_2}^{\text{conv}}}{\dot{n}_{\text{CO}_2}^{\text{in}}} = \frac{\dot{n}_{\text{CO}_2}^{\text{in}} - \dot{n}_{\text{CO}_2}^{\text{out}}}{\dot{n}_{\text{CO}_2}^{\text{in}}} \quad (19)$$

This formula is correct, but the problem is that analytical equipment typically measures concentrations and not molar or volumetric flow rates. As mentioned in Section 0, the latter is easily defined at the inlet, but it is not straightforward to obtain them at the outlet. Often, the following equation is applied instead, using the measured fractions:

$$\chi^* = \frac{y_{\text{CO}_2}^{\text{in}} - y_{\text{CO}_2}^{\text{out}}}{y_{\text{CO}_2}^{\text{in}}} \quad (20)$$

Although Eq. (19) is correct, it is not correct to simply replace the CO₂ flow rates with the CO₂ fractions, as in Eq. (20), and we indicate the incorrect conversion with an asterisk χ^* . This fallacy can be explained as follows. When we rewrite the concentrations again in terms of molar flow rates, we get an equation that is only valid if $\dot{n}_{\text{tot}}^{\text{in}}$ and $\dot{n}_{\text{tot}}^{\text{out}}$ are equal:

$$\chi^* = \frac{\frac{\dot{n}_{\text{CO}_2}^{\text{in}}}{\dot{n}_{\text{tot}}^{\text{in}}} - \frac{\dot{n}_{\text{CO}_2}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{out}}}}{\frac{\dot{n}_{\text{CO}_2}^{\text{in}}}{\dot{n}_{\text{tot}}^{\text{in}}}} \quad (21)$$

In the CO₂ splitting reaction, however, the molar flow rates at in- and outlet are not equal, as discussed in Section 0. The total number of moles per unit of time $\dot{n}_{\text{tot}}^{\text{out}}$ increases with a factor between 1 and 1.5, depending on the amount of CO₂ that is converted. As a result, $\dot{n}_{\text{tot}}^{\text{in}}$ and $\dot{n}_{\text{tot}}^{\text{out}}$ are not equal and thus, Eqs. (20) and (21) are false. The problem lies in using the relative values of concentration. Indeed, for every CO₂ molecule that reacts away, it creates an additional dilution of the remaining CO₂ molecules. The correct definition follows from introducing a new factor in Eq. (21) as follows:

$$\chi = \frac{\frac{\dot{n}_{\text{CO}_2}^{\text{in}}}{\dot{n}_{\text{tot}}^{\text{in}}} - \left(\frac{\dot{n}_{\text{tot}}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{in}}}\right) \frac{\dot{n}_{\text{CO}_2}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{out}}}}{\frac{\dot{n}_{\text{CO}_2}^{\text{in}}}{\dot{n}_{\text{tot}}^{\text{in}}}} = \frac{y_{\text{CO}_2}^{\text{in}} - \alpha \cdot y_{\text{CO}_2}^{\text{out}}}{y_{\text{CO}_2}^{\text{in}}} \quad (22)$$

where α is the flux ratio, exactly as described in Section 2.2; in other words, Eq. (22) is the same as Eq. (5). If this factor is neglected by simply applying equation (20), the conversion is overestimated, as we will show with a numerical example in Section 3.2.

3.1.2 Measured conversion

A second common definition in literature describes a “corrected” conversion χ^{corr} . The overestimation of equation (20) is thereby often attributed to the sampling procedure of analytical equipment. However, gas expansion is inherent to chemical reactions, as shown by the stoichiometric formulas in Section 2.1. More specifically, Eq. (20) was defined as the “measured” conversion χ^{meas} that must be recalculated to the corrected conversion. For example, the following equation is common:

$$\chi^{\text{meas}} = \frac{y_{\text{CO}_2}^{\text{in}} - y_{\text{CO}_2}^{\text{out}}}{y_{\text{CO}_2}^{\text{in}}} = 1 - \left(\frac{1 - \chi^{\text{corr}}}{1 + \frac{\chi^{\text{corr}}}{2}} \right) \quad (23)$$

and can be rearranged to obtain the corrected CO₂ conversion:

$$\chi^{\text{corr}} = \frac{2 \cdot \chi^{\text{meas}}}{3 - \chi^{\text{meas}}} \quad (24)$$

It is important to note that the resulting value is correct, but the explanation is somewhat ambiguous and might be confusing. This is especially true because of the term measured conversion, while we demonstrated in Section 2 that simple stoichiometric formulas suffice to calculate the conversion.

Taking a closer look at Eq. (23), we want to make it clear that this is not a conversion, just like Eq. (20) is not a conversion. Instead, what is calculated is the product fraction:

$$\frac{y_{\text{CO}_2}^{\text{in}} - y_{\text{CO}_2}^{\text{out}}}{y_{\text{CO}_2}^{\text{in}}} = \frac{1 - y_{\text{CO}_2}^{\text{out}}}{1} = \sum_j y_j^{\text{out}} \quad (25)$$

With j representing any product, in this case CO and O₂. Note that Eq. (25) is only valid in case of pure CO₂ because $y_{\text{CO}_2}^{\text{in}}$ has to be equal to 1. The value of $y_{\text{CO}_2}^{\text{out}}$ can be derived from the stoichiometry as in Eq. (1):

$$\sum_j y_j^{\text{out}} = 1 - \frac{1 - \chi}{1 + \frac{\chi}{2}} \quad (26)$$

Rearranging this equation to extract the conversion χ :

$$\chi = \frac{2 \cdot \sum_j y_j^{\text{out}}}{3 - \sum_j y_j^{\text{out}}} \quad (27)$$

gives the same result as Eq. (24). To verify our new definition, i.e., Eq. (4), we can check that the product fraction, according to the definitions in Section 2, is as follows:

$$\sum_j y_j^{\text{out}} = y_{\text{CO}}^{\text{out}} + y_{\text{O}_2}^{\text{out}} \quad (28)$$

Inserting Eqs. (2) and (3) in Eq. (28) gives:

$$\sum_j y_j^{\text{out}} = \frac{\chi}{1 + \frac{\chi}{2}} + \frac{\frac{\chi}{2}}{1 + \frac{\chi}{2}} = \frac{\frac{3 \cdot \chi}{2}}{1 + \frac{\chi}{2}} = \frac{3 \cdot \chi}{2 + \chi} \quad (29)$$

After rearranging this equation to extract the conversion, this gives the same expression as equation (27).

3.1.3 Dissociation fraction

The third definition that is commonly applied in literature to express conversion is the dissociation fraction χ_{DF} , as follows:

$$\chi_{\text{DF}} = \frac{y_{\text{CO}}^{\text{out}}}{y_{\text{CO}_2}^{\text{out}} + y_{\text{CO}}^{\text{out}}} \quad (30)$$

When these values are replaced by the stoichiometry from Eqs. (1) and (2), this gives

$$\chi_{\text{DF}} = \frac{\frac{\chi}{1 + \chi/2}}{\frac{1 - \chi}{1 + \chi/2} + \frac{\chi}{1 + \chi/2}} \quad (31)$$

The equation can be rearranged as follows:

$$\chi_{\text{DF}} = \frac{\chi}{1 - \chi + \chi} = \chi \quad (32)$$

This proves that the dissociation fraction is an alternative to calculate the conversion in pure CO₂. Of course, this requires an accurate determination of both CO and CO₂ in the analytical equipment, as opposed to the simpler definition of Eq. (4) where only the output CO₂ fraction is needed.

However, a misleading variation of the dissociation fraction is sometimes applied, which we label with an asterisk in the following equations to highlight the difference. The equation goes as follows:

$$\chi_{\text{DF}}^* = \frac{y_{\text{CO}}^{\text{out}}}{y_{\text{CO}_2}^{\text{in}}} \quad (33)$$

However, if the stoichiometric principles are applied, this gives

$$\chi_{\text{DF}}^* = \frac{\frac{\chi}{1 + \chi/2}}{1} = \frac{\chi}{1 + \chi/2} = y_{\text{CO}}^{\text{out}} \quad (34)$$

This is not equal to the conversion; instead, this dissociation fraction expresses the output fraction of CO (Eq. (2)). After rearranging equation (34), the conversion becomes

$$\chi = \frac{\chi_{\text{DF}}^*}{1 - \frac{\chi_{\text{DF}}^*}{2}} = \frac{y_{\text{CO}}^{\text{out}}}{1 - \frac{y_{\text{CO}}^{\text{out}}}{2}} \quad (35)$$

Hence, as we will show in the next section, authors who apply this formula underestimate their real conversion.

An important observation is that the error made in Eq. (33) is a result of neglecting the change in volumetric flow rate. Indeed, one can derive the following expression from Eq. (19) and Table 1:

$$\chi = \frac{\dot{n}_{\text{CO}_2}^{\text{conv}}}{\dot{n}_{\text{CO}_2}^{\text{in}}} = \frac{\dot{n}_{\text{CO}}^{\text{out}}}{\dot{n}_{\text{CO}_2}^{\text{in}}} = \frac{\dot{n}_{\text{tot}}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{in}}} \cdot \frac{\dot{n}_{\text{CO}}^{\text{out}}}{\dot{n}_{\text{CO}_2}^{\text{in}}} = \alpha \cdot y_{\text{CO}}^{\text{out}} \quad (36)$$

This shows that Eq. (33) can only be correct when the flux ratio is 1, which is inherently never the case for CO₂ splitting. Essentially, this is the exact same fundamental error that is made as with Eq. (20), indicating that the aspect of determining the flow rates of the output gases (through the fractions of the output gases and the flux ratio) is still poorly understood by some authors, despite being so important.

3.2 Numerical example

As an illustration, we present a numerical example to compare our correct (stoichiometric) formula from Section 2 (Eq. (4)) with the alternative formulas from Section 3.1, and demonstrate which formulas give the same or different results as our stoichiometric calculation. We consider CO₂ conversions in a wide range from 10% to 90%. From this range, we calculate the conversion according to the various definitions and present these in Table 3. We also plot the reported conversions as a function of the real conversion in Fig. 1, where it is clear that the stoichiometric conversion from Eq. (4) forms a perfectly straight line, as it is the correct method for calculating the conversion. This is also true for Eqs. (27) and (30), as explained in Section 3.1. However, Eqs. (20) and (33) deviate. The dashed lines indicate the relative error of these other definitions, as denoted by the y-axis on the right. Indeed, Eq. (20) overestimates the conversion, while Eq. (33) underestimates it. Note that the relative error on the conversion RE_χ , similar to the work of Pinhão et al. [20], is calculated as follows:

$$RE_\chi = \frac{\chi^{\text{rep}} - \chi}{\chi} \times 100 \text{ (\%)} \quad (37)$$

Where χ^{rep} is the reported conversion and χ is the real conversion. If the reported conversion overestimates the real conversion, the relative error is positive; on the contrary, if it is an underestimation, the relative error is negative. It is clear from Fig. 1 that the relative errors of Eq. (20) are larger for smaller conversions, i.e., a relative error of 40% is obtained for a conversion of 10%. In Eq. (33), the relative error is the largest (most negative) at higher conversions, i.e., a relative error of -25% is reached for a conversion of 70%. Furthermore, these errors propagate to other performance metrics, such as the energy efficiency and energy cost.

This example demonstrates the importance of using the correct formulas for consistency when comparing the performance of plasma-based CO₂ conversion in different types of plasma reactors, and more in general, for moving this technology forward.

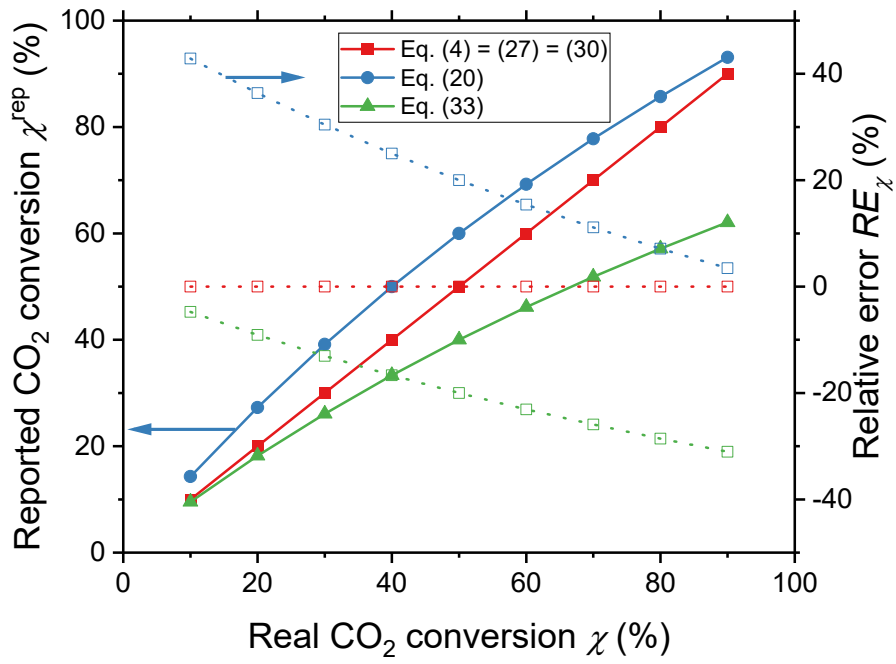


Fig. 1. Numerical example of the reported conversion calculated according to the different equations (see legend; full lines, left axis) and the relative error (dotted lines, right axis). Since the correct formulas report the real CO₂ conversion, their relative error is equal to zero. Eq. (20) yields a positive error, while Eq. (33) gives a negative relative error.

Table 3. Numerical example of the conversion as calculated by the different equations. The first row gives the reference to the equation number in the paper, while the second row gives the symbols and formulas. The comparison to the real conversion is indicated as overestimated (+), equal (=) or underestimated (-) values. For clarity, all values are given in %.

Real CO ₂ conversion	Measured fractions				Stoichiometric conversion (4)		(20)		(27)		(30)		(33)	
	$y_{CO_2}^{in}$	$y_{CO_2}^{out}$	y_{CO}^{out}	$y_{O_2}^{out}$	$\frac{1 - y_{CO_2}^{out}}{1 + \frac{y_{CO_2}^{out}}{2}}$		$\frac{y_{CO_2}^{in} - y_{CO_2}^{out}}{y_{CO_2}^{in}}$		$\frac{2 \cdot \sum_j y_j^{out}}{3 - \sum_j y_j^{out}}$		$\frac{y_{CO}^{out}}{y_{CO_2}^{out} + y_{CO}^{out}}$		$\frac{y_{CO}^{out}}{y_{CO_2}^{in}}$	
10.0	100	85.7	9.5	4.8	10.0	=	14.3	+	10.0	=	10.0	=	9.5	-
20.0	100	72.7	18.2	9.1	20.0	=	27.3	+	20.0	=	20.0	=	18.2	-
30.0	100	60.9	26.1	13.0	30.0	=	39.1	+	30.0	=	30.0	=	26.1	-
40.0	100	50.0	33.3	16.7	40.0	=	50.0	+	40.0	=	40.0	=	33.3	-
50.0	100	40.0	40.0	20.0	50.0	=	60.0	+	50.0	=	50.0	=	40.0	-
60.0	100	30.8	46.2	23.1	60.0	=	69.2	+	60.0	=	60.0	=	46.2	-
70.0	100	22.2	51.9	26.9	70.0	=	77.8	+	70.0	=	70.0	=	51.6	-
80.0	100	14.3	57.1	28.6	80.0	=	85.7	+	80.0	=	80.0	=	57.1	-
90.0	100	6.9	62.1	31.0	90.0	=	93.1	+	90.0	=	90.0	=	62.1	-

3.3 Critical evaluation of literature reports

While the example in Section 3.2 highlights the importance of applying the correct formulas, we illustrate the lack of uniformity in this section with some examples from literature.

Luckily, many recent studies on plasma-based CO₂ conversion do report the correct values for conversion and energy efficiency, although the simple stoichiometric derivation (Eq. (4)) is rarely applied (e.g., in Refs. [28,29]). Many authors, including from our own group, e.g., Refs. [22, 30-35], apply the confusing terminology of “measured” conversion and then “corrected” this conversion in the next step (i.e., Eq. (27) of Section 3.1). In the present work, we demonstrated in Eqs. (25)–(29) that it is not a “measured” conversion, but the product fraction $\sum_j y_j^{\text{out}}$ that can be used to calculate the real CO₂ conversion χ . Although the definitions are confusing, the reported values remain correct.

Another common definition is the dissociation fraction (as in Eq. (30)), which is indeed equivalent to the conversion, see Refs. [36–38]. Various other derivations for the CO₂ conversion can be found in literature (e.g., Refs. [39–46]). Despite these inconsistent explanations, the formulas can be validated when applying the simple stoichiometric principles from Section 2.1. Hence, the reported values are correct, but for transparency and consistency reasons, we strongly recommend using the simple stoichiometric Eq. (4), or one of the other stoichiometrically derived expressions (SI; Section S1) in future work.

Unfortunately, some papers in the field report overestimated values for the CO₂ conversion when they apply the incorrect equation (20) (e.g., Refs. [47–50]). As demonstrated in Section 3.1, these studies report the product fraction, which is not equal to the conversion (Eq. (27)). Some other sources underestimate their CO₂ conversion when they apply an alternative form of the dissociation fraction (Eq. (33)) (e.g., Refs. [51,52]). In addition, some authors claimed that the GC sampling method was responsible for the deviation in the “measured” conversion. This incorrect explanation in previous work from our group [30] has led to misunderstandings in later work. In one example, also from our group [47], it is even mistakenly declared that gas expansion does not play a role in their analytical method, even though it is inherent to the reaction and independent of the setup. Another observation is that, very often, the correct formula is given (based on molar flow rates), but the reported diagnostics, such as GC, are not able to measure the molar flow rates directly, and no details are given on how these values were obtained (e.g., Refs. [53–59]).

Several authors derive the flux ratio through a flow meter [60–64] or a standard component (either as part of the feed gas or introduced in the exhaust gas stream) [65–69], and do not use a stoichiometrically derived expression, but, e.g., Eq. (5) or (19). Some authors also use a combination of both a stoichiometrically derived expression and a flow meter, to validate their approach [42,70]. These methods will be discussed and compared with each other in more detail in Section 6.

Finally, accounting for the dilutions is important. Many studies (e.g., Refs. [61, 71-74]) report the absolute conversion, and it has been demonstrated that, e.g., the absolute CO₂ conversion increases in the presence of argon [75]. While this is not an error, we do advise to report the effective conversion as well, as this value takes into account the dilution of CO₂ and hence, is the value that should be compared with other reactors.

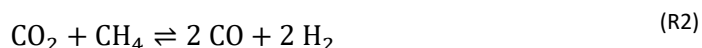
This section has clearly demonstrated how the correct formulas are essential to analyze the performance of different plasma reactors. Although inconsistent formulas are not always a problem when authors are transparent in their data and calculations, and do not always change the conclusions significantly, they become problematic when authors compare their results to other experiments, as we demonstrated with significant deviations in a numerical example. Therefore, we hope that this

paper can elucidate the correct formulas for CO₂ conversion and help authors to report more consistent, correct values for the performance of plasma reactors.

4. CO₂ conversion with a co-reactant: definitions and terminology

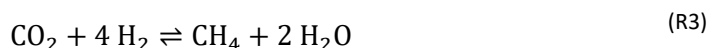
In the previous section, we described the conversion of pure CO₂, but many recent studies add a co-reactant to the feed to facilitate the conversion. Indeed, the reaction enthalpy of pure CO₂ splitting ($\Delta H^\circ=+283 \text{ kJ mol}^{-1}$) is higher than the enthalpy of DRM ($\Delta H^\circ=+247 \text{ kJ mol}^{-1}$), for example. Moreover, the addition of co-reactants allows for direct targeting of valuable reaction products like syngas or oxygenates, decreasing the number of subsequent processing steps like the Fischer-Tropsch synthesis, and therefore lowering the target for the energy efficiency [9].

The presence of the co-reactant does not change the definition of α as written in Eq. (6), but it will certainly affect its value. For example, the DRM reaction is usually expressed with reaction (R2):



As can be seen, the gas flow will expand upon increasing conversion, with a theoretical maximum flux ratio of 2, i.e., higher than the maximum value of 1.5 in the case of pure CO₂ splitting.

Another example is plasma-based CO₂ hydrogenation. The most common reactions are the CO₂ methanation reaction (R3) and the reverse water gas shift (RWGS) reaction (R4):



In this case, the total volumetric flow rate will not increase but decrease, or at least remain the same. Hence, the value for the flux ratio will be lower than or equal to 1.

The change in volumetric flow rate is important for these reaction mixtures, since the gas can contract or expand even more than for pure CO₂. As already pointed out by Pinhão et al. [20] for CO₂/CH₄/He mixtures, neglecting the effect of gas expansion or contraction can cause significant errors. As indicated in their paper, several authors reported incorrect values, and some authors still do not report all performance metrics correctly, as illustrated in Section 5.3.

In the following section, we summarize how to derive these performance metrics, specifically for the most studied reactions in plasma, i.e., DRM and CO₂ hydrogenation. Nevertheless, almost all formulas are generally applicable. The chemistry inside the plasma might be complex, but the formulas to calculate the overall performance metrics, such as conversion, product selectivity and yield, are valid for all reactions between two or more gases in a plug flow reactor (as described in Section 0).

It should be noted that in some cases, a reactant that is not in the gas phase is used, which also affects the experimental methods. An example is the reverse-Boudouard reaction, which describes the conversion of CO₂ together with solid carbon, and we present the correct formulas for this case in the SI (see Section S3). Again, the latter formulas generally apply for every reaction between one or more gases and a solid component in a plug flow reactor.

4.1 Change in total gas flow rate

Although Eq. (6) for the flux ratio remains valid, deriving a specific formula for mixtures of CO₂ with a co-reactant is more complex than for pure CO₂ splitting (R1). Some critical considerations influence the value of the flux ratio. Firstly, reactions (R2), (R3) and (R4) only represent the ideal reaction, but many researchers report several by-products, depending on the exact plasma conditions.

Moreover, the stoichiometric derivation of the flux ratio α is not always possible, but only in some specific cases (e.g., Section 6.3). This is due to liquid or solid products formed during the reaction. Water, methanol, etc. could condense at the reactor walls or gas lines, and sometimes a cold trap deliberately initiates the condensation of liquids. In addition, carbon deposition is typical in CO₂/CH₄ plasmas with a high CH₄ content. For both liquid and solid products, it is often impossible to trace back their original fraction in the gas stream, since they accumulate over time. Even when they remain in the gas phase, components like water are usually difficult to quantify with common analytics like GC. Because of these effects, deriving a clear stoichiometric relationship can be challenging, and in many cases impossible. This is in contrast to pure CO₂ splitting, where it is clear from Section 2 that stoichiometric equations can always be derived.

Therefore, other methods are applied to determine the flux ratio, such as using a volumetric flow meter, or introducing a standard component in the outlet gas stream. These experimental methods will be discussed in more detail in Section 6.1. To first give a more streamlined overview of the correct formulas, we will treat the flux ratio as a known parameter in the following sections.

4.2 Conversion

In both DRM and CO₂ hydrogenation, an additional reactant next to CO₂ is present, so Eq. (5) changes to the more general equation form Eq. (11). Depending on the reaction, the reactant i can be CO₂, CH₄ (in case of DRM), or H₂ (in case of CO₂ hydrogenation). The effective conversion as defined in Eq. (12) remains the same. Additionally, the total conversion χ^{tot} is introduced as the sum of all the effective conversions:

$$\chi^{\text{tot}} = \sum_i \chi_i^{\text{eff}} \quad (38)$$

The advantage of Eq. (38) is that the overall conversion of the entire gas mixture can be quantified and compared. Note that in Section 2.3, the effective and total conversion is the same, since the dilution is a consequence of an inert gas component that is (virtually) not converted, as opposed to these reaction mixtures where multiple components are converted.

4.3 Energy cost, energy yield and energy efficiency

The definitions from Section 2.4 for the specific energy input, energy cost and energy yield remain valid. The only difference here in terms of energy cost and energy yield is that the total conversion should be used, because it represents the overall conversion of the gas mixture:

$$EC \text{ (kJ mol}_{\text{conv}}^{-1}) = \frac{1}{EY \text{ (mol}_{\text{conv}} \text{ kJ}^{-1})} = \frac{SEI \text{ (kJ mol}^{-1})}{\chi^{\text{tot}}} \quad (39)$$

The correct formula to calculate the energy efficiency is a bit more complicated. In theory, Eq. (18) can be used again, with the corresponding reaction enthalpy for DRM or CO₂ hydrogenation. However, as we will discuss in detail in Section 5, this equation is not always ideal to use for DRM and CO₂ hydrogenation. Hence, an alternative definition is introduced, expressing the energy efficiency η (also sometimes called the “energy conversion efficiency”) as the fraction of the total energy that goes to the formation and breaking of chemical bonds. In other words, it is the fraction of energy that effectively carries out the reaction and is not lost (e.g., as heat). In general, this is written as

$$\eta = \frac{\sum_j E_j^{\text{chem}}}{E^{\text{app}} + \sum_i E_i^{\text{chem}}} \quad (40)$$

Here, E^{app} is equal to the applied energy to the system, which can be determined through the measured applied power. $\sum_i E_i^{\text{chem}}$ and $\sum_j E_j^{\text{chem}}$ are the chemical energy, intrinsically present in the reactants i and the products j , respectively. However, while a reaction enthalpy can be measured, e.g., with a calorimeter, the energy intrinsically present in the reactants and products cannot. To solve this issue, another definition represents the chemical energy of products and reactants by a lower heating value LHV , which is a measure for the energy that is released upon full oxidation of the specified species. This is the so-called “fuel energy efficiency”:

$$\eta = \frac{\alpha \cdot \sum_j (y_j^{\text{out}} \cdot LHV_j (\text{kJ mol}^{-1}))}{SEI (\text{kJ mol}^{-1}) + \sum_i (y_i^{\text{in}} \cdot LHV_i (\text{kJ mol}^{-1}))} \quad (41)$$

with LHV_i and LHV_j the lower heating value of reactant i and product j , respectively. As mentioned, this value represents the reaction enthalpy for the conversion of i or j upon reacting with O_2 to their most thermodynamically stable products [20,76]. In this case, these products are CO_2 and/or H_2O , which by definition have a lower heating value equal to 0 kJ mol^{-1} , together with O_2 . Note that Eq. (41) still resembles the general form of Eq. (40), with the specific energy input representing the applied energy and the lower heating values the chemical energies, all in units of kJ mol^{-1} . The fact that the reaction enthalpy upon full oxidation is used for all reactants and products, makes this a valid method to express the chemical energy present in both reactants and products and, consequently, the energy efficiency of the reaction. Finally, note that lower heating values describe the reaction enthalpy with the produced H_2O considered to remain in the gas phase. When considering H_2O in the liquid phase, and thus taking into account the additional energy released upon condensation, higher heating values for the different components are used instead.

When all products are included (condensed and deposited products as well), Eq. (42) should be used

$$\eta = \frac{\alpha^{\text{fin}} \cdot \sum_j (y_j^{\text{out}} \cdot LHV_j (\text{kJ mol}^{-1})) + \alpha^{\text{init}} \cdot \sum_k (y_k^{\text{out}} \cdot LHV_k (\text{kJ mol}^{-1}))}{SEI (\text{kJ mol}^{-1}) + \sum_i (y_i^{\text{in}} \cdot LHV_i (\text{kJ mol}^{-1}))} \quad (42)$$

Where the condensed and deposited products are indicated by the subscript k . Note that we now have two flux ratios. When we have condensation or deposition of products from the gas stream, the total number of molecules in the gas flow will decrease. This means a decrease of the final gas flow rate from $\dot{V}_{\text{tot}}^{\text{out,init}}$ to $\dot{V}_{\text{tot}}^{\text{out,fin}}$, and thus, following Eq. (6), a decrease in flux ratio from α^{init} to α^{fin} . The relationship between α^{init} (with all products still in the gas phase) and α^{fin} (after condensation and/or deposition of certain products) is given by Eq. (43)

$$\alpha^{\text{init}} = \frac{\alpha^{\text{fin}}}{(1 - \sum_k y_k^{\text{out}})} \quad (43)$$

When the only product that is significantly lost is H_2O ($LHV_{\text{H}_2\text{O}} = 0 \text{ kJ mol}^{-1}$), it does not require quantification in order to solve Eq. (42). However, if other components such as methanol, ethanol etc. are a significant part of the condensed fraction, they need to be quantified. Specifically, the fraction of these components while they were still in the gas stream needs to be traced back, which is practically impossible. However, alternative equations are available in literature where this is not strictly needed, which we will discuss in more detail in Section 5.1.

4.4 Product selectivity and yield

Aside from conversion, product yield and selectivity are two other critical performance metrics. As discussed before, the conversion states how much of a reactant has reacted away. Product selectivity expresses how much of one specific product is formed, relative to all other products. The product yield is the combination of conversion and product selectivity, and shows how much a particular product is formed, relative to the theoretical maximum amount that could have been formed. When there are no significant side reactions, as in pure CO₂ splitting, expressing a selectivity or yield is not necessary. For (R1), all CO₂ is converted into CO and O₂ (with negligible amounts of other products, such as O₃), and thus, there is a fixed selectivity towards CO and O₂. The yield of CO or O₂ is not fixed, but it gives no extra information compared to the conversion.

On the other hand, by-products can be formed in case of DRM and CO₂ hydrogenation. Therefore, it is more interesting to report values that express the degree to which a desired product is produced, and even necessary when comparing conditions in one setup or comparing setups with each other. The atom-based (*A*-based, in this case either the carbon-, hydrogen- or oxygen-based) selectivity for product *j* is defined as

$$S_j^A = \frac{\mu_j^A \cdot \alpha \cdot y_j^{\text{out}}}{\sum_i (\mu_i^A \cdot (y_i^{\text{in}} - \alpha \cdot y_i^{\text{out}}))} \quad (44)$$

With μ_i^A and μ_j^A the stoichiometric coefficients (i.e., the number of atoms *A* per reactant *i* and product *j*, respectively). The sum of the selectivities for the same base-atoms should be 100% when all products are considered, because it represents the distribution of the atoms among the products that are formed.

The atom-based yield of product *j* is defined as

$$Y_j^A = \frac{\mu_j^A \cdot \alpha \cdot y_j^{\text{out}}}{\sum_i (\mu_i^A \cdot y_i^{\text{in}})} \quad (45)$$

In this case, the sum of the yields for the same base-atom should be equal to the conversion of the reactants containing the same base-atom, when all products are considered. Indeed, product yield expresses the actual amount of a product relative to the theoretical maximum amount that can be formed of that same product. Mathematically, it can be considered as the product of conversion and selectivity for the same base-atom:

$$Y_j^A = S_j^A \cdot \chi_i^A = \frac{\mu_j^A \cdot \alpha \cdot y_j^{\text{out}}}{\sum_i (\mu_i^A \cdot (y_i^{\text{in}} - \alpha \cdot y_i^{\text{out}}))} \cdot \frac{\sum_i (\mu_i^A \cdot (y_i^{\text{in}} - \alpha \cdot y_i^{\text{out}}))}{\sum_i (\mu_i^A \cdot y_i^{\text{in}})} \quad (46)$$

When there are condensed products, selectivity and yield can be expressed in the same way, but then a distinction between the initial and final flux ratio must be made, just as was the case for Eq. (42). However, when the lost products cannot be quantified (or even qualitatively detected), the selectivities and yields towards all the other products only require knowledge of the final flux ratio (which can be experimentally measured) and they can therefore still be obtained.

5. Confusing terminology and errors in literature for CO₂ conversion with a co-reactant

In the previous section, we presented the correct definitions and calculations for determining the performance metrics in plasma-based CO₂ conversion with a co-reactant. In this section, we discuss some alternative and some incorrect definitions reported in literature for energy cost, energy efficiency and product yield (Section 5.1). As an illustration, we present a numerical example in Section 5.2 and demonstrate the difficult interpretation and comparison of the reported values. Finally, in Section 5.3, we provide a critical overview of some of the available literature.

5.1 Alternative and/or incorrect definitions

5.1.1 Energy cost

The energy cost in DRM is sometimes defined as a “syngas energy cost”:

$$EC_{\text{syngas}}(\text{kJ mol}^{-1}) = \frac{SEI(\text{kJ mol}^{-1})}{\alpha \cdot (y_{\text{CO}}^{\text{out}} + y_{\text{H}_2}^{\text{out}})} \quad (47)$$

This value should be interpreted as the amount of energy needed to form a certain amount of syngas. Note that this definition, where the amount of the desired product is used as reference, is quite common for other reactions too, like NH₃ or NO_x formation [23, 77, 78], and is also interesting to report from an economic perspective. However, it is important to notice that Eq. (47) will never give the same result as Eq. (39), even for “ideal” DRM as described by reaction (R2), due to the increase in flow rate:

$$EC_{\text{syngas}}(\text{kJ mol}^{-1}) = \frac{SEI(\text{kJ mol}^{-1})}{\alpha \cdot (y_{\text{CO}}^{\text{out}} + y_{\text{H}_2}^{\text{out}})} = \frac{SEI(\text{kJ mol}^{-1})}{2 \cdot \chi^{\text{tot}}} = \frac{EC(\text{kJ mol}^{-1})}{2} \quad (48)$$

with Eq. (48) only valid for ideal DRM, where only syngas is formed and the syngas flow rate equals the total inlet flow rate multiplied with a factor ($2 \cdot \chi^{\text{tot}}$).

5.1.2 Energy efficiency

In many cases (see references in Section 5.3), an adapted version of Eq. (41) expresses the energy efficiency. The first variant is Eq. (49):

$$\eta = \frac{\alpha \cdot \sum_j (y_j^{\text{out}} \cdot LHV_j(\text{kJ mol}^{-1}))}{SEI(\text{kJ mol}^{-1}) + \sum_i ((y_i^{\text{in}} - \alpha \cdot y_i^{\text{out}}) \cdot LHV_i(\text{kJ mol}^{-1}))} \quad (49)$$

The amount of converted reactants is now written in the denominator, instead of the initial fraction. This does not fully correspond with the general definition (see Eq. (40)). Instead, Eq. (49) defines the fraction of the “transformed” energy that carries out the reaction, while the remaining fraction of “transformed” energy is equal to the energy lost as heat. In other words, this equation gives a (theoretical) value of 1 when the reaction proceeds without heat losses, independent of how much reactant is converted.

A second (and third) variant is when only the desired products (represented by subscript j , des) are considered (i.e., syngas for DRM, CH₄ or CO for CO₂ hydrogenation), similar to the syngas energy cost in Section 5.1.1. This can be expressed both relative to the total energy at the inlet (as in Eq. (41)) as well as the “transformed” energy (as in Eq. (49)). Both variants are defined through Eqs. (50) and (51), respectively:

$$\eta = \frac{\alpha \cdot \sum_{j,\text{des}} \left(y_{j,\text{des}}^{\text{out}} \cdot LHV_{j,\text{des}} (\text{kJ mol}^{-1}) \right)}{SEI (\text{kJ mol}^{-1}) + \sum_i \left(y_i^{\text{in}} \cdot LHV_i (\text{kJ mol}^{-1}) \right)} \quad (50)$$

$$\eta = \frac{\alpha \cdot \sum_{j,\text{des}} \left(y_{j,\text{des}}^{\text{out}} \cdot LHV_{j,\text{des}} (\text{kJ mol}^{-1}) \right)}{SEI (\text{kJ mol}^{-1}) + \sum_i \left((y_i^{\text{in}} - \alpha \cdot y_i^{\text{out}}) \cdot LHV_i (\text{kJ mol}^{-1}) \right)} \quad (51)$$

Note that Eqs. (50) and (51) consider the chemical energy attributed to the by-products also as a form of “lost” energy. This offers the advantage that, when not all by-products can be quantified, these equations can still be solved.

Indeed, Eqs. (41), (49), (50) and (51) are all correct, but should be interpreted differently nonetheless. Simply stated, an energy efficiency of 1 (or 100%) would mean for:

- Eq. (49) : a reaction that proceeds without heat losses
- Eq. (41) : a reaction that proceeds without heat losses and 100% conversion
- Eq. (51) : a reaction that proceeds without heat losses and 100% product selectivity towards the desired products
- Eq. (50) : a reaction that proceeds without heat losses and 100% product yield of the desired products

Another alternative definition for the energy efficiency is based on the standard formation enthalpies, also sometimes called the “chemical energy efficiency”, for each component:

$$\eta = \frac{\alpha \cdot \sum_j \left(y_j^{\text{out}} \cdot H_{f,j} (\text{kJ mol}^{-1}) \right) - \sum_i \left(\chi_i^{\text{eff}} \cdot H_{f,i} (\text{kJ mol}^{-1}) \right)}{SEI (\text{kJ mol}^{-1})} \quad (52)$$

$H_{f,i}$ and $H_{f,j}$ are the standard formation enthalpies of the various reactants i and products j , expressed in kJ mol^{-1} . In fact, Eq. (52) does not correspond to the general definition presented through Eq. (40). Rather, Eq. (52) compares the energy difference corresponding to the reaction, relative to the applied energy:

$$\eta = \frac{\Delta E^{\text{reac}}}{E^{\text{app}}} \quad (53)$$

Note that Eq. (18) also corresponds to this general equation. For an endothermic reaction, this ratio is a correct representation of the energy efficiency (i.e., 0 when no reaction is proceeding, and 1 when all applied energy is absorbed and used to carry out the reaction). However, as is clear from comparing Eq. (40) with Eq. (53), the chemical energy efficiency does not represent a “fraction” of the total energy that carries out the reaction. Additionally, the chemical energy efficiency on the one hand (Eq. (52)) and the fuel energy efficiency on the other hand (Eqs. (41), (49), (50) and (51)) describe the “chemical energy” differently. In fact, for an exothermic reaction (such as reactions (R3) and (R4) when considering H_2O in its liquid state) the chemical energy efficiency will become negative, even when a relatively good conversion and energy cost is obtained. This makes the results from Eq. (52) sometimes difficult to interpret without any additional information on other performance metrics.

In Eq. (52), the reaction enthalpy ΔH° is constructed from the individual formation enthalpies, following Hess’s law. However, a consequence of using a reaction enthalpy is that one has to include all products and reactants to determine it correctly, including all the liquid products that are present

in non-negligible amounts. This makes the chemical energy efficiency not always applicable, in contrast to (some of) the fuel energy efficiency equations. In addition, often a single reaction enthalpy is taken from literature and used, similar to Eq. (18), instead of deriving it through the formation enthalpies. For example, for DRM often the reaction enthalpy of 247.3 kJ mol⁻¹ is used. However, this value is only correct for 1 mole CO₂ reacting with 1 mole CH₄, forming only syngas, as shown in reaction (R2). Any deviation from this will alter the value for the reaction enthalpy. Hence, this approach is incorrect in all cases, except one theoretically ideal situation.

Finally, note that for pure CO₂ splitting, all equations will lead to the same value (given by Eq. (18)):

$$\eta = \frac{\alpha \cdot (y_{\text{CO}}^{\text{out}} \cdot LHV_{\text{CO}}(\text{kJ mol}^{-1}) + y_{\text{O}_2}^{\text{out}} \cdot LHV_{\text{O}_2}(\text{kJ mol}^{-1}))}{SEI(\text{kJ mol}^{-1}) + y_{\text{CO}_2}^{\text{in}} \cdot LHV_{\text{CO}_2}(\text{kJ mol}^{-1})} \quad (54)$$

$$= \frac{\chi_{\text{CO}_2}^{\text{eff}} \cdot 283 \text{ kJ mol}^{-1}}{SEI(\text{kJ mol}^{-1})}$$

$$\eta = \frac{\alpha \cdot (y_{\text{CO}}^{\text{out}} \cdot LHV_{\text{CO}}(\text{kJ mol}^{-1}) + y_{\text{O}_2}^{\text{out}} \cdot LHV_{\text{O}_2}(\text{kJ mol}^{-1}))}{SEI(\text{kJ mol}^{-1}) + (y_{\text{CO}_2}^{\text{in}} - \alpha \cdot y_{\text{CO}_2}^{\text{out}}) \cdot LHV_{\text{CO}_2}(\text{kJ mol}^{-1})} \quad (55)$$

$$= \frac{\chi_{\text{CO}_2}^{\text{eff}} \cdot 283 \text{ kJ mol}^{-1}}{SEI(\text{kJ mol}^{-1})}$$

$$\eta = \frac{\alpha \cdot y_{\text{CO}}^{\text{out}} \cdot H_{\text{f,CO}}(\text{kJ mol}^{-1}) + \alpha \cdot y_{\text{O}_2}^{\text{out}} \cdot H_{\text{f,O}_2}(\text{kJ mol}^{-1}) - \chi_{\text{CO}_2}^{\text{eff}} \cdot H_{\text{f,CO}_2}(\text{kJ mol}^{-1})}{SEI(\text{kJ mol}^{-1})} \quad (56)$$

$$= \frac{\chi_{\text{CO}_2}^{\text{eff}} \cdot 283 \text{ kJ mol}^{-1}}{SEI(\text{kJ mol}^{-1})}$$

Hence, the correct determination of the energy efficiency depends mostly on the correct determination of the effective CO₂ conversion, which we described in detail in Sections 2.3 and 2.4.

5.1.3 Product yield

For product yield there is also an alternative, but incorrect definition:

$$Y_j^{A*} = \sum_i (\mu_i^A \cdot \chi_i^{\text{eff}}) \cdot \frac{1}{\mu_j^A} \cdot S_j^A \quad (57)$$

This equation uses the product of conversion and selectivity to calculate the yield, as was described in Section 4.4. However, when implementing Eqs. (12) and (44) in Eq. (57), we get

$$Y_j^{A*} = \alpha \cdot y_j^{\text{out}} = \frac{\dot{n}_{\text{tot}}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{in}}} \cdot \frac{\dot{n}_j^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{out}}} = \frac{\dot{n}_j^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{in}}} \quad (58)$$

This is not in line with the general definition of yield, which considers the theoretical maximum amount of product j that could have been formed (Eq. (45)). Yield depends on the amount of atoms A both per molecule of product j and per molecule of reactant i , while Eq. (58) is independent of this, and therefore incorrect (e.g., for DRM, $\dot{n}_{\text{tot}}^{\text{in}}$ is not by definition equal to the theoretical maximum amount that can be formed of H₂, as CO₂ will not contribute to its formation).

5.2 Numerical example

As discussed in Section 5.1, the determination of energy efficiency in literature is ambiguous. Different definitions can be theoretically correct, but result in very different values nonetheless. In this section, we present a numerical example to illustrate the variety in results. Specifically, we consider a DRM experiment, based on previous research from our group [79], but the values are generally valid for any warm plasma (e.g., gliding arc, microwave, etc.); see Table 4. We calculate the energy efficiency according to the various definitions, as presented in Fig. 2. An additional example for CO₂ hydrogenation, with values typical for a cold plasma, is presented in the SI, along with more details regarding the calculations for both examples (see SI, Section S4).

Table 4. Numerical example for DRM in a warm plasma with a specific energy input of 240.6 kJ mol⁻¹; flow rates of gases at the inlet, and unreacted gases and products at the outlet.

Flow rate (mL min ⁻¹)	CO ₂	CH ₄	H ₂	CO	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	H ₂ O	Total
In	650	350	0	0	0	0	0	0	1000
Out	300	90	375	575	15	2	0.4	125	1482

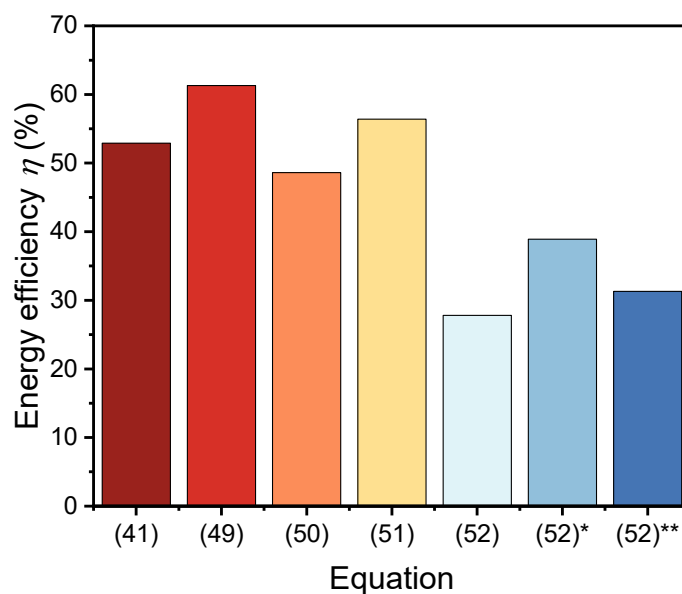


Fig. 2. Numerical example of the energy efficiency calculated according to the various definitions for DRM. Eq. (52)* represents the chemical energy efficiency without taking all products into account, Eq. (52)** represents the chemical energy efficiency when the reaction enthalpy corresponding to the “ideal” stoichiometry is used (described by reaction (R2) for DRM).

As can be seen, the results vary significantly depending on the applied definition, for both the DRM example (Fig. 2) and the CO₂ hydrogenation example (see SI, Section S4). Note again that all fuel energy efficiency formulas (Eqs. (41), (49), (50) and (51)) are correct, if interpreted correctly. Indeed, referring back to Section 5.1.2, some definitions depend on e.g., the conversion, while some do not. As a result, the definition yielding the highest value is Eq. (49), which expresses the fraction of energy that is not lost as heat, and the definition giving the lowest value is Eq. (50), which expresses the fraction of energy that is not lost as heat, unconverted reactants and by-products.

A large drop in energy efficiency is observed when comparing the fuel energy efficiencies to the chemical energy efficiency presented through Eq. (52). This is because Eq. (52) applies to a different general formula (Eq. (53)), where the endo- or exothermicity of the reaction determines the energy

efficiency. For example, for the same specific energy input, the energy efficiency drops significantly when the selectivity towards very stable products (e.g., H₂O during DRM) increases, as it lowers the endothermicity of the reaction. Therefore, it is no surprise that there is such a large difference when not all products are considered when deriving the reaction enthalpy (Eq. (52)* in Fig. 2), which is overestimated with 11.1% (equal to a relative deviation of 39.9%). Taking the reaction enthalpy for the “ideal” stoichiometry for DRM (Eq. (52)** in Fig. 2) described by reaction (R2), leads to an overestimated value of 3.5% (equal to a relative deviation of 12.6%). Finally, in the case of CO₂ hydrogenation, the same general trends are observed, with the chemical energy efficiency even reaching a negative value. More details on this can be found in the SI, Section S4.

From this numerical example, it is clear that a one-on-one comparison of reported energy efficiencies becomes challenging. Authors should always check the applied definitions and, if necessary, recalculate the values from other studies to allow for a fair comparison.

5.3 Critical evaluation of literature reports

In contrast to pure CO₂ splitting (Section 3.3), there is not much recent literature for plasma-based DRM and CO₂ hydrogenation where the effect of gas expansion or contraction is completely ignored and where the conversion is determined incorrectly. Hence, the paper of Pinhão et al. [20] had a good impact. Even though some authors explain the necessity of the flux ratio in their calculations incorrectly, also within our own group, they still do apply it in the correct way (e.g., Ref. [80]). Three different methods are described in literature to determine the flux ratio, i.e., using a standard component (e.g., Refs. [80–90]), a flow meter (e.g., Refs. [91–96]) and a stoichiometrically derived expression (e.g., Ref. [97]). We compare these three methods in detail in Section 6. Some authors define their formulas correctly (based on molar flow rates and not on fractions), but provide no details on the method used to determine the flux ratio (e.g., Refs. [98–104]), so we can only assume that they used one of these methods correctly. When the flux ratio is measured, the performance metrics, as described in Section 4, can be calculated. However, the example in Section 5.2 demonstrates that it can be difficult to interpret the results of various definitions. Therefore, we illustrate the lack of uniformity in this section with some examples from literature.

First is the energy cost, for which most definitions align with our general equation in Eq. (39). Sometimes it is defined relative to a product of interest, such as the syngas energy cost of Eq. (47) in Refs. [85, 88, 105], which is a valuable alternative. The same is true for the energy yield (e.g., a “methanol energy yield” is defined in Ref. [96]).

Second, as discussed in Sections 5.1.2 and 5.2, there is not one correct definition of energy efficiency, but a wide variety of them. For instance, Eq. (41) is used in Ref. [20], Eq. (49) in Ref. [82], Eq. (50) in Ref. [101], Eq. (51) in Refs. [84, 87, 89, 93, 97, 103] and Eq. (52) in Ref. [20]. However, there are some cases where an incorrect form of Eq. (52) is used. In Ref. [80], not all products are considered. While these authors motivate using their equation, i.e., excluding the hydrocarbons due to their negligible effect, they have a significant fraction of H₂O, which they exclude as well. However, it heavily alters the result, as shown in Section 5.2. In Refs. [86,102], multiple “ideal” reaction enthalpies are used. As explained in Sections 5.1.2 and 5.2, this is very often an incorrect expression. Indeed, in Ref. [86], other products are formed that are not described by the reaction equations corresponding to the used enthalpies. In Ref. [102], it seems that the by-products are not present in significant amounts, and then (and only then!) one can assume the ideal stoichiometry for the two main reactions to be valid. Nevertheless, the energy efficiency in this specific case is overestimated, since the reaction enthalpy is not describing the amount of energy per mole reactant. Rather, it describes the energy per 2 mole reactant, as it is 0.427 eV that is consumed when 1 mole CO₂ reacts with 1 mole H₂ towards CO and

H₂O. When dividing by the energy cost in eV per 1 mole reactant converted, they do not refer to the same amounts of moles, and the resulting energy efficiency value should be divided by 2 to correct for this error.

Importantly, some authors express an energy efficiency in units of mmol kJ⁻¹ (e.g., [86,91,93,95,98,99,101,103,104]). However, as mentioned in Sections 2.4 and 4.3, this should be called energy yield (see Eq. (17)). Alternatively, the energy yield can also be defined in units of g(H₂) kW h⁻¹, as in Ref. [92].

Notably, to compare energy efficiencies for DRM or CO₂ hydrogenation, one needs to carefully check whether the same formulas are used. Otherwise, the energy efficiency should be re-calculated with available raw data. In Refs. [56,93,101], the authors report a comparison of energy efficiencies from literature, but the values from literature are not the same as those reported, so we conclude the authors indeed re-calculated these values themselves, using the same formulas as used for their own energy efficiency. However, in Ref. [18], the authors refer, e.g., to values from Ref. [80], where different formulas were applied, hence this comparison is incorrect. Nevertheless, the impact on their conclusions remains limited because they also compared energy costs, which were calculated through the same formula. Due to the lack of a uniform definition for energy efficiency, we generally recommend comparing energy costs instead of energy efficiencies, as was also recommended in Ref. [9].

Third, the product selectivity and yield are reported more consistently in the field, with some exceptions, e.g., an incorrect definition of yield is used in Ref. [82] as explained in Eq. (58) (see Section 5.1). However, overall, literature reviews typically do not compare the yield in plasma reactors, but the conversion (e.g., Refs. [9,79]). Yet, plasma-based CO₂ conversion with a co-reactant is complex, and many products can be formed. It is therefore interesting to compare the yield of the desired product as well. Indeed, for the same energy cost, a high conversion is only meaningful when it is combined with a high selectivity toward the desired product. We will discuss this performance metric in more detail in our recommendations in Section 7.

We can conclude that although the effect of gas expansion and contraction is widely acknowledged in literature for plasma-based CO₂ conversion with a co-reactant, it remains challenging to interpret the variety of definitions, specifically for energy cost and energy efficiency. Again, transparency in data and calculations is key to facilitate an accurate comparison of literature reports, and we hope that this paper can provide insights to report more consistent and correct values for plasma technology.

6. Analysis of the available methods for determining the flux ratio

In the previous sections, we described the formulas for determining the different performance metrics for pure CO₂ conversion, DRM and CO₂ hydrogenation. The flux ratio is a fundamental part of these calculations. In addition, the stoichiometric equations, as presented in Section 2.1 for pure CO₂ splitting, are typically not applicable for more complex reactions, when by-products can be formed that cannot all be easily quantified or even detected. In that case, knowledge of the flux ratio is essential.

In Section 6.1, we describe the three main experimental methods to determine the flux ratio: (i) the stoichiometric relationships (when they are possible, i.e., as extension of Section 2.1), the use of (ii) a flow meter and of (iii) a standard component. All other performance metrics can be determined when the flux ratio is known, as described in Section 4. In literature, several researchers report one of these methods, as described in Section 5.3. However, to our knowledge, a detailed comparison between the different methods and specifically, the sensitivity of the performance metrics to these measurements, has not been reported. We will proceed with such a comparison in Section 6.2, supported by an experimental example for CO₂ splitting in a DBD reactor, and in Section 6.3, again supported by an experimental example for the conversion of CO₂-CH₄-O₂ mixtures, in an atmospheric pressure glow discharge (APGD) reactor.

6.1 Description of the methods

6.1.1 Stoichiometric relationships

In Section 2.1, we discussed the stoichiometric relationships between the fractions of CO₂, CO and O₂ and the conversion for pure CO₂ splitting. Measuring only one of the fractions (y_{CO_2} , y_{CO} or y_{O_2}), or otherwise the flux ratio (α) (cf. Section 2.2), is sufficient to derive the conversion and each of the remaining parameters, as shown in the SI (Section S1). The advantage of this method is that the experimental setup can be simple. In theory, e.g., one accurate O₂-sensor is sufficient to determine all other parameters, but ideally, more than one parameter should be measured to validate the method. When the measurement is done accurately, the performance metrics derived from each measured parameter should all be the same (within the experimental error margin). To measure y_{CO_2} , y_{CO} and y_{O_2} , there are a number of techniques available. Dedicated sensors for each of these three components are widely available, and GC or FTIR spectrometers can be used to measure multiple components simultaneously.

Similar analytics are also applicable for DRM or CO₂ hydrogenation. However, with these reactions, stoichiometric relationships can only be derived if one is able to solve one of the three atom balance equations towards the flux ratio. The general formula for the atom balance b_A (where A can be C, H or O) is written as:

$$b_A = \frac{\alpha^{\text{fin}} \cdot (\sum_i (\mu_i^A \cdot y_i^{\text{out}}) + \sum_j (\mu_j^A \cdot y_j^{\text{out}})) + \alpha^{\text{init}} \cdot \sum_i (\mu_i^A \cdot y_i^{\text{out}})}{\sum_i (\mu_i^A \cdot y_i^{\text{in}})} \quad (59)$$

By definition, the atom balance should always be 1. In other words, solving Eq. (59) towards α^{fin} (and hence: using this method) is only possible if all reactants and products containing atom A , at inlet and outlet, are identified and their fraction quantified. Such an example will be discussed in more detail in Section 6.3.

6.1.2 Flow meter

A more direct measurement of the flux ratio can be done by means of a flow meter. The simplest example is a bubble flow meter, where the movement of a soap bubble across a certain distance is timed to derive the flow rate. By measuring this value before and during plasma reaction, at the same temperature and pressure, α is obtained through Eq. (6) in Section 2.2. In fact, any device that can directly or indirectly provide an accurate volumetric flow rate is suitable for this method.

6.1.3 Standard component

An indirect measurement of the flow rate can be performed by adding a standard component to the outlet stream of the reactor, as introduced by Pinhão et al. [20]. This standard component can be any gas (e.g., Ar, N₂) that does not react in the outflow. While the volumetric flow rate of the standard component does not change, its fraction will, but only due to the change in total flow rate. Please note that it is important for this method to introduce the standard component in the effluent gas and not in the feed gas. The addition of any gas to the inlet of the reactor will interfere with the plasma properties and influence the effective and total conversion, as well as the energy cost, energy yield and energy efficiency.

For pure CO₂ splitting, the same formulas for diluted CO₂ of Section 2.3 are valid to derive the conversion from the product fractions. Calculating the flux ratio, however, will not be the same when the standard is added to the outlet stream instead of as part of the feed gas. This is explained in more detail in the SI (Section S5.1).

The situation becomes more complex for reactions such as DRM or CO₂ hydrogenation, since the total gas flow rate and the fractions of the components change consecutively due to gas expansion, removal of liquid products and the addition of a standard, before finally reaching the analytical equipment. The simplest way to define the flux ratio is as the ratio of the measured fractions of the standard y_s^{in} and y_s^{out} :

$$\alpha_s^{\text{meas}} = \frac{y_s^{\text{in}}}{y_s^{\text{out}}} \quad (60)$$

Eq. (60) can then be used together with the measured input and output fractions to calculate all performance metrics presented in Section 4. However, there are multiple ways to express the flux ratio and the fractions that will lead to a correct determination of conversion, energy cost etc. For example, one can choose to work with the fractions in the gas stream before the standard is added, together with the flux ratio at that stage. Or, as explained in Section 4.3, one might need to derive the “initial” flux ratio (before condensation occurs). How this should be done is presented in detail in the SI (Section S5.2).

6.2 Example of pure CO₂ splitting in DBD plasma

We performed two separate series of experiments (one with a standard, one with a flow meter) with pure CO₂ flowing in a DBD plasma reactor. Experimental details can be found in the SI (Section S6). The performance metrics are calculated according to the formulas described in Section 2, and in the SI (Sections S1, S2 and S5.1).

The absolute CO₂ conversion and flux ratio in the first series of experiments are presented in Fig. 3(a), comparing the stoichiometrically derived values (based on the fraction of CO₂, CO and O₂) with the values obtained using the standard component (N₂). The same parameters from the second series of experiments are presented in Fig. 3(b), comparing the stoichiometrically derived values with the values derived from the flow meter. To avoid confusion, we emphasize that the stoichiometric values (and

their error margins) in Fig. 3(a and b) are obtained through two separate series of experiments and are therefore not completely equal. The numerical data and results for all remaining performance metrics are given in the SI (Section S6).

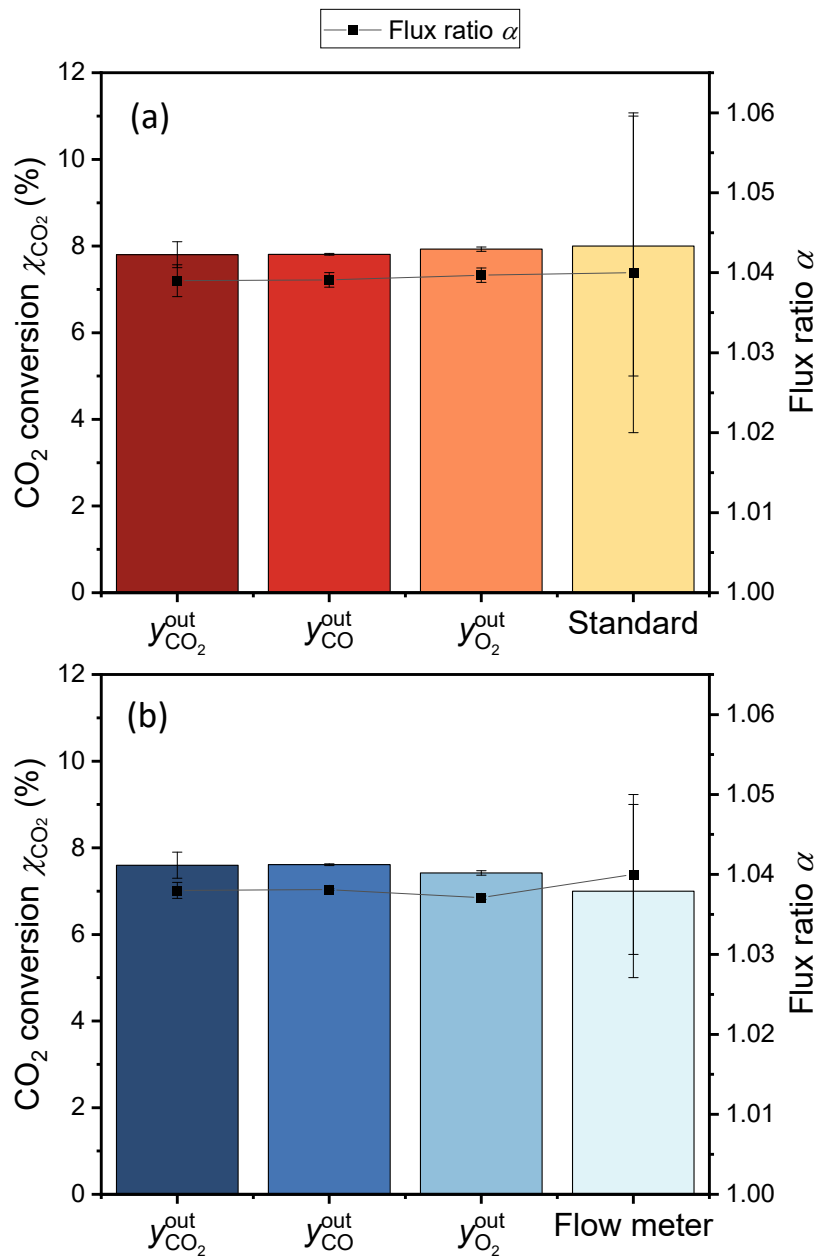


Fig. 3. CO₂ conversion (left axis) and flux ratio (right axis) for pure CO₂ splitting in a DBD reactor. The results are determined by means of the stoichiometric formulas (based on the CO₂, CO and O₂ fractions, first three bars), and the standard component (a) and bubble flow meter (b) (last bar in both cases). Error bars are added but some might be too small to be visible.

From both figures, it is clear that the CO₂-, CO- and O₂-based conversion and flux ratio are always very close to one another, almost always within each other's error margin. Hence, this data indicates that the stoichiometric relationships are suitable to derive the conversion with high accuracy. Notably, the results based on the N₂ standard and the flow meter are not very accurate, given that the error bar is significantly larger for these values. To explain this observation, we provide the relative errors on the fractions used to derive the conversion and flux ratio, as well as the relative error on the conversion

and flux ratio itself, in Table 5. The relative error is calculated similarly as was done in Eq. (37) in Section 3.2 for the conversion, now with the experimental absolute error used in the numerator.

Table 5. Relative errors on the output fractions, flux ratio and conversions, for both the experiments performed with the standard added and the flow meter used. Note that the relative error on β , used in the experiments with the standard, is 0.5%.

	CO₂	CO	O₂	Standard
y^{out}	0.4%	0.3%	0.6%	1%
α	0.2%	0.09%	0.09%	2%
χ	4%	0.3%	0.6%	38%
	CO₂	CO	O₂	Flow meter
y^{out}	0.4%	0.3%	0.6%	–
α	0.1%	0.01%	0.02%	1%
χ	4%	0.3%	0.7%	29%

It is important to note that the relative error on the fractions, used to calculate the conversions and flux ratio, are all very comparable. After propagation of this error to the flux ratio, the majority of the errors decrease and all remain acceptable, with a maximum relative error of 2% on the flux ratio obtained through the fraction of the standard. However, when propagating these errors to the conversion, we see that the relative errors all increase significantly. The errors based on the measured fractions remain acceptable, but the ones based on the flow measurement propagate to a relative error of 38% and 29% with the standard and the flow meter, respectively. This proves that any small error on the flow rate and consequently flux ratio, will propagate to a much more significant error on the conversion, independent of the technique used and the reproducibility of the experiment. Hence, the conversions based on the measured CO₂, CO and O₂ fractions are in this case much more reliable.

Therefore, we conclude that using a standard component or a flow meter leads to more errors due to the sensitivity inherent to these methods. Instead, accurate diagnostics such as a GC should be used to determine all product fractions when possible, so that the more reliable stoichiometric values can be applied. They are easier to validate and obviously require less effort from the operator.

6.3 Example of DRM in the presence of O₂ in APGD plasma

We again performed two separate series of experiments (one with a standard, one with a flow meter) similar to the experiments in the DBD reactor. Here, we use a mixture of CO₂, CH₄ and O₂ (so-called oxidative CO₂ reforming of methane (OCRM)) in an APGD plasma reactor. Experimental details can be found in the SI (Section S7).

As explained in Section 6.1.1, to derive a stoichiometric relationship for DRM, one of the three atom balances needs to be solved to derive the final flux ratio. In this example, the APGD plasma is a so-called warm plasma, and under these conditions, by far the dominant product is syngas. High-value liquid products such as methanol can also be formed, but their fraction is often negligible. We used a cold trap between the reactor and the GC in these experiments, and the liquid fraction was analyzed after each experiment. Since the liquid consisted mainly of H₂O, with a fraction of 99.95%, the fraction of other components was negligible. In addition, a small amount of solid carbon was deposited in the experiments, specifically at the electrodes. However, this was less than a few milligrams, accumulated over time, so we conclude that its concentration is also negligible in the entire exhaust gas flow. Finally, all peaks on the chromatograms obtained with the GC were identified and quantified. This resulted in H₂O being the only significant product of which the fraction could not be measured. Hence, all C-based

products could be identified, and therefore, the carbon balance equation (i.e., Eq. (52) of Section 6.1.1) can be re-arranged (considering that $b_c = 1$), to result in Eq. (61):

$$\alpha^{\text{fin}} = \frac{\sum_i (\mu_i^{\text{C}} \cdot y_i^{\text{in}})}{\sum_i (\mu_i^{\text{C}} \cdot y_i^{\text{out}}) + \sum_j (\mu_j^{\text{C}} \cdot y_j^{\text{out}})} \quad (61)$$

The formulas described in Section 4 were used to calculate the performance metrics. When the standard was added, the flux ratio as described in Section 6.1.3 was used, but also the other flux ratios were calculated, as described in the SI (Section S5.2).

The total conversion (i.e., the sum of the effective CO₂, CH₄ and O₂ conversions) and final flux ratio obtained with the first series of experiments are presented in Fig. 4(a), comparing the stoichiometrically derived values with the values derived by the standard component. The same parameters obtained with the second series of experiments are presented in Fig. 4(b), comparing the stoichiometrically derived values with the values obtained by the flow meter. To avoid confusion, we emphasize again that the stoichiometric values (and their error margins) in Fig. 4(a and b) are obtained through two separate series of experiments and are therefore not completely equal. The numerical data and results for all remaining performance metrics are given in the SI (Section S7).

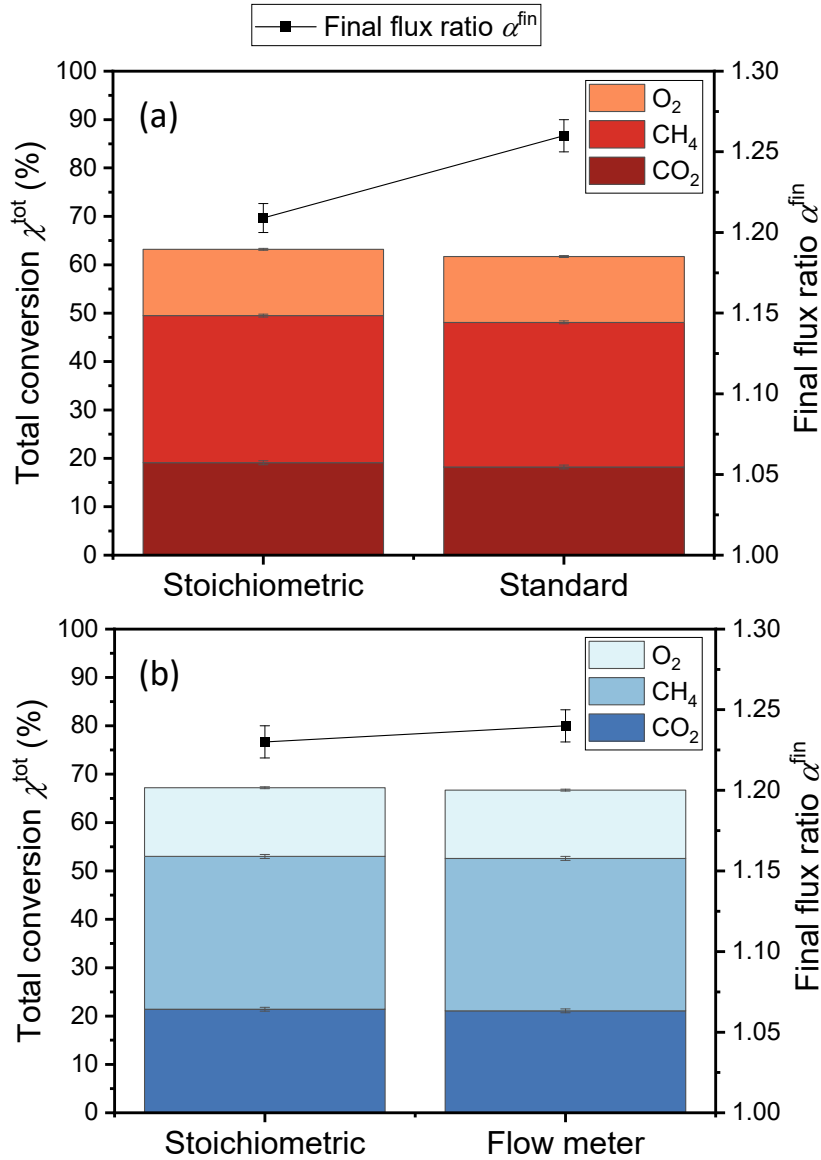


Fig. 4. Total conversion and the effective CO₂, CH₄ and O₂ conversions (left axis), and flux ratio (right axis) with OCRM in an APGD reactor. The results are determined by means of the stoichiometric formulas (based on the assumption of a perfect C-balance) (left bar), and the standard component (a) and bubble flow meter (b) (right bar in both cases).

Both the effective and total conversions obtained with the standard component and bubble flow meter are in good agreement with the values obtained by the stoichiometric formula. Indeed, the agreement, also in terms of error margins, is better than in Section 6.2, because in contrast to CO₂ splitting, the conversion here is much higher (i.e., 60%–70% total conversion). As a consequence, for the same absolute difference on the conversion, the relative difference becomes almost ten times smaller.

The difference between the flux ratios for the second series of experiments is negligible (0.01 ± 0.01), but for the first series of experiments, obtained with the standard component, the difference is a bit larger (i.e., 0.05 ± 0.01 , or a relative difference of around 4%–5%). For the values derived through the standard, it is also observed that the sum of all C-based selectivities is equal to $107 \pm 2\%$, and the sum of the C-based yields is higher than the C-based conversion. This is impossible because it implies a violation of the law of mass conservation. To explain this issue, we show the atom balances from the first series of experiments in Fig. 5(a), comparing the stoichiometrically derived values with the values obtained by using the standard component. The same is done for the values of the second series of

experiments in Fig. 5(b), comparing the stoichiometrically derived values with the values derived by the flow meter.

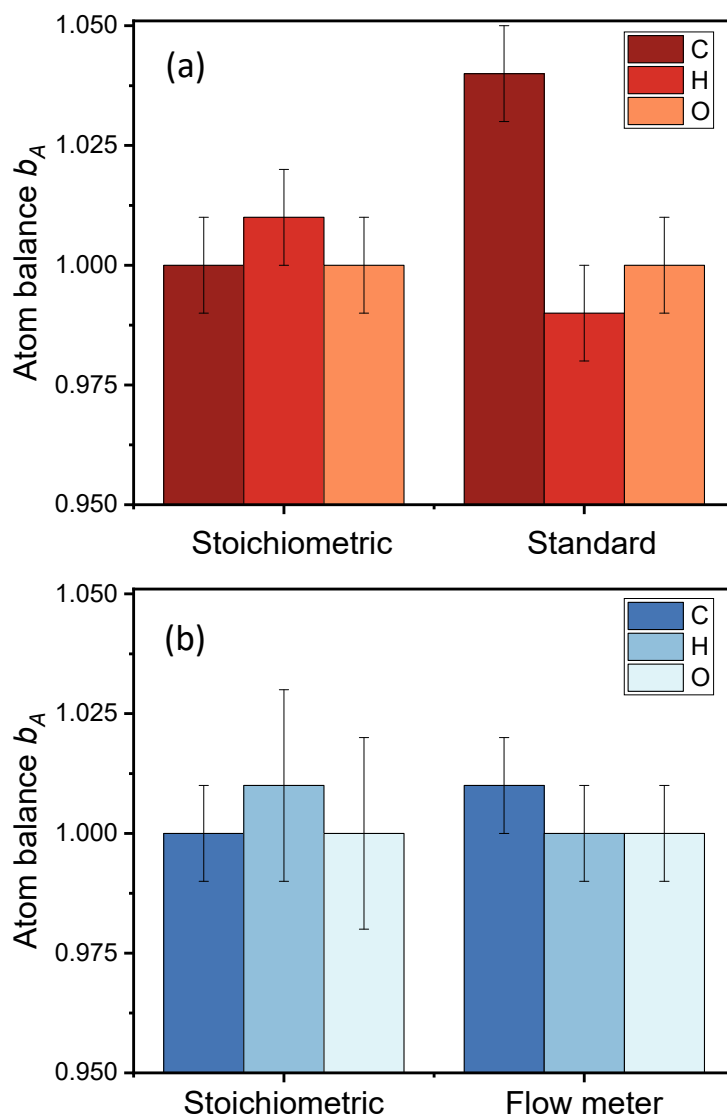


Fig. 5. Atom balance for C, H and O with OCRM in an APGD reactor. The results are determined by means of the stoichiometric formulas (based on assuming a perfect C-balance) (left bar), and the standard component (a) and bubble flow meter (b) (right bar in both cases).

Fig. 5 illustrates that all atom balances are close to 1 for the stoichiometric method (within their error margin). However, the C-balance obtained with the standard component, as shown in Fig. 5(a), clearly exceeds the theoretical maximum value of 1 (i.e., 1.04 ± 0.01). Since the fractions and the calibration of the different components are all the same, this deviation can only originate from an incorrect measurement of the flux ratio. While the effect on the conversion was nearly negligible (see Fig. 4a), the error of the flow measurements is now more apparent when looking at (the sum of) the product selectivities and the atom balances. Hence, results that would otherwise be inexplicable (like a violation of the law of mass conservation) can be traced back to a small error on the measurement of the flux ratio.

Based on these observations, we can again conclude that the stoichiometrically derived values seem to be the most reliable, similar to Section 6.2. Nevertheless, we want to stress again that it is often not

possible to apply the stoichiometric formulas for DRM (and similar reactions, like OCRM), because the composition of the liquid and solid fraction has to be known, and their original fraction in the gas mixture needs to be estimated at least.

Next, the bubble flow meter turned out to be more reliable in our experiments than the use of the standard component, although it is also less convenient to use. Not only does it require careful control of temperature and pressure, but it also requires manual action, prone to human error and limited to a certain maximum flow rate. An accurate digital flow meter is a better alternative, since it usually corrects for temperature and pressure effects, and yields a continuous reading of the flow rate. However, in our experience, a flow meter that provides the total volumetric flow without prior knowledge on the gas composition (as is the case at the reactor outlet) and that can be used for almost any gas mixture, is not easy to find. Moreover, it is not as affordable as the other methods described in this section.

The use of a standard component is more simple, because it can be analyzed together with the other components, can be very cheap and is easily introduced. However, it performs clearly the worst in this example. There are several plausible reasons: a small error on the MFC regulating the flow rate of the standard could already cause a small deviation on its measured fraction and the flux ratio, and propagate to a significant error on certain performance metrics such as the product selectivity. Another possibility is that the mixing of the standard with the rest of the gas mixture is not sufficient. We observed different results when introducing the standard at different positions (i.e., very close to the reactor outlet compared to more downstream), which could indicate a mixing issue. Finally, the way it is described by Pinhão et al. [20], there is no need to calibrate the analytics for the standard component itself. While this is true when the response of the analytic device on the standard component is a linear trend as function of its fraction, with the intercept at the y-axis equal to zero, we believe it is better to calibrate for this standard component as well. Not all analytics have a perfect linear response, and assuming so could have a significant impact on the flux ratio and the performance metrics.

Altogether, we advise checking the available methods for each new set of experiments. A comparison as in this section is relatively easy, and in our opinion, it is the best way to validate the chosen experimental method.

7. Recommendations and good practices

When reporting the performance of plasma-based CO₂ conversion, there are some important good practices to keep in mind. We recommend the excellent topical review by Alves et al. [106] on best practices in the field of low-temperature plasmas. Discussing challenges ranging from plasma diagnostics to computer models, the authors also address the importance of validation and reporting. Overall, they lay a clear foundation on how to improve communication, reproducibility and transparency within the field. In the following discussion, we present our own recommendations more specifically for measuring and reporting the performance for plasma-based CO₂ conversion, for pure CO₂ but also with co-reactant, such as in DRM and CO₂ hydrogenation.

In first instance, all details on the experimental setup should be provided. For the power, it is important to note the difference between (i) the plasma power, which is the true power dissipated in the plasma, (ii) the applied power, which is the power delivered by the PSU, and (iii) the plug power, which is the overall power consumed by the PSU during plasma operation. The applied power is equal to the plasma power plus the power related to the losses in the electronic circuit, while the plug power also accounts for the efficiency of the PSU itself. The relation between the plug power and the plasma power is given by the so-called plug-to-plasma power efficiency. Typically, the measured plasma power is used for calculating the energy efficiency and energy cost, as it reflects the efficiency of the plasma process itself. However, in an industrial context, the plug-to-plasma power efficiency should be accounted for, and thus, the applied power should be used to calculate the overall energy efficiency and energy cost [107]. In addition, the reported power should also include the duty cycle when a pulsed power is applied [108]. Special care should be taken to describe the electrical components (i.e., voltage probe, current sensor, ...) and calculations that were used to obtain the plasma power.

Moreover, when measuring the outlet gas composition in a wide range of conditions, all analytical equipment should be carefully calibrated, starting with the MFCs, because small deviations can lead to large errors for determining the flux ratio. Regular calibrations are needed according to the manufacturer's recommendations, but at least before every new set of experiments.

Furthermore, the sampling position in the setup should be specified, especially for warm plasmas. Most experiments measure the outlet gas downstream from the reactor, where possible recombination reactions (e.g., CO+O₂ reacting back into CO₂) have reached equilibrium with the forward (splitting) reactions, and the gas composition has reached a steady state. The conversions downstream are thus typically lower than compared to sampling right after the plasma reactor and one should pay special attention that the sampling position is the same when comparing different experiments. In general, all details of the experiment should be described for transparency and repeatability. Although this may seem evident, not all authors in the field provide the proper descriptions.

When all the experimental details are specified, presenting the data in a clear and transparent way is equally important. For each presented data point, all experimental conditions should be specified: the flow rates of both the input gases and dilution agents, as well as the power, and the fractions of the output gases, together with the flux ratio, to derive the flow rates of the output gases. Ideally, the raw data should be open access to allow other researchers to reanalyze the data at a later stage and to comply with the FAIR principles [109]. How to present data with statistical relevance and other detailed recommendations for plasma research in general, can be found in the review by Alves et al. [106].

Last but not least, when all experimental details are provided, the correct formulas should be used for the calculation of the performance (i.e., conversion, yields, selectivity, energy cost and energy

efficiency), and they should be clearly reported. When doing a comparison of different setups, we recommend to pay special attention to the product yield and the energy cost or yield. The product yield of the desired products is a very informative parameter, because it is the product of both conversion and selectivity. Secondly, energy cost or yield should be compared, rather than energy efficiency, due to the lack of a uniform definition for the latter.

We hope that this section, together with the correct formulas presented in previous sections, can provide a guideline for more consistent calculations, and can stimulate a correct comparison of different plasma reactors and conditions described in literature.

8. Conclusions

Over the past decades, plasma technology has gained increasing interest as possible CCU technology. However, the formulas used in literature to calculate the performance metrics are often inconsistent, and sometimes even incorrect, leading to serious deviations from the real performance. This makes it challenging to compare the performance of plasma processes between different experiments (e.g., different conditions and plasma reactors) from different research groups, and hinders the development of this technology on both a fundamental and more applied level. In this critical review, we summarized the correct formulas for the performance metrics and highlighted common inconsistencies and errors, alongside general points of attention and recommendations.

We presented stoichiometrically derived expressions to simply and correctly calculate the conversion for pure CO₂ splitting, which are rarely used in literature so far, alongside with the correct definitions for energy cost, energy yield and energy efficiency. Furthermore, we showed that incorrect definitions for conversion are common in literature, due to neglecting the change in volumetric flow rate, confirming earlier findings [20]. This leads to relative errors on the conversion as high as 40%, which we demonstrated with a numerical example.

Next, we summarized the correct definitions for the performance metrics of CO₂ conversion with a co-reactant, specifically for the dry reforming of methane and CO₂ hydrogenation. We showed that a wide variety of definitions exists for energy cost and especially energy efficiency. As a consequence, a direct comparison of energy efficiencies obtained with different reactors is complicated, which we demonstrated through a numerical example. Therefore, when comparing different studies for CO₂ mixtures, we recommend comparing energy cost or energy yield rather than energy efficiency, due to the inconsistent definitions for the latter, as was also recommended in Ref. [9]. Apart from the energy cost, the product yield is the second most informative performance metric in case of CO₂ conversion with a co-reactant, and more suitable than the conversion for a comparison between processes, because it also includes the selectivity to the desired products.

For CO₂ mixtures with a co-reactant, taking into account the flux ratio is crucial. It should be determined by means of a direct measurement (e.g., flow meter) or an indirect measurement (e.g., adding a standard component in the outlet stream of the reactor), and in some cases it can be derived stoichiometrically. We presented a detailed comparison of these methods, supported by two experimental examples, and investigated the experimental error on the conversion and the flux ratio. We found that for the same error, the uncertainty on the performance metrics can propagate to a much larger extent when using one method compared to another, and it is an important aspect that needs to be considered prior to any series of experiments. Therefore, we advise to always do such a simple comparison, as was also performed by Refs. [42,70].

Finally, we provided some general recommendations. Specifically, we advise to always report essential parameters, such as the plug-to-plasma power efficiency, all experimental input conditions, the flux ratio, the fractions of the output gases and the formulas used to calculate all performance metrics.

We can conclude that besides the clear importance of reporting all experimental details and applied formulas, more consistent formulas are essential to correctly analyze the performance in the field of plasma-based CO₂ conversion. We hope that this paper can provide a guideline for authors and facilitate objective and correct comparisons of different reactors, to stimulate further development of plasma technology and contribute to a more sustainable future.

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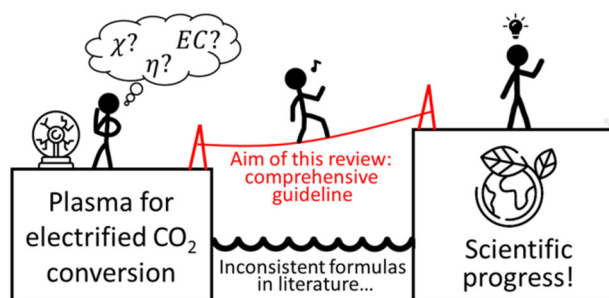
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Graphic abstract

This review aims to provide a comprehensive guideline for authors to encourage more consistent calculations in plasma-based CO₂ conversion and stimulate the further development of this technology.



Supporting information: Plasma-based CO₂ conversion: How to correctly analyze the performance?

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S1. Formulas for pure CO₂ conversion: Relationships between conversion, CO₂/CO/O₂ fractions and flux ratio

The equations in Sections 2.1 and 2.2 in the main paper give the basic outline of the conversion calculation based on the fractions of CO₂, CO and O₂ (Section 2.1) as well as the relationship with the flux ratio (Section 2.2). Depending on which information is available in the experiment, the other values can be deduced, as summarized in Table S.1. For example, when we measure the CO₂ output fraction $y_{\text{CO}_2}^{\text{out}}$, we can obtain the conversion, by rearranging Eq. (1) in the main paper to Eq. (4) as follows:

$$y_{\text{CO}_2}^{\text{out}} = \frac{1 - \chi}{1 + \frac{\chi}{2}}$$

$$y_{\text{CO}_2}^{\text{out}} \cdot \left(1 + \frac{\chi}{2}\right) = 1 - \chi$$

$$y_{\text{CO}_2}^{\text{out}} + \frac{y_{\text{CO}_2}^{\text{out}} \cdot \chi}{2} = 1 - \chi$$

$$\chi + \frac{y_{\text{CO}_2}^{\text{out}} \cdot \chi}{2} = 1 - y_{\text{CO}_2}^{\text{out}}$$

$$\chi \cdot \left(1 + \frac{y_{\text{CO}_2}^{\text{out}}}{2}\right) = 1 - y_{\text{CO}_2}^{\text{out}}$$

$$\chi = \frac{1 - y_{\text{CO}_2}^{\text{out}}}{1 + \frac{y_{\text{CO}_2}^{\text{out}}}{2}}$$

Table S.1. Overview of formulas for pure CO₂ conversion: How to obtain the conversion, flux ratio, or output fraction of CO₂, CO or O₂, when one of the other values is known.

Known → Unknown ↓	χ	α	$y_{\text{CO}_2}^{\text{out}}$	$y_{\text{CO}}^{\text{out}}$	$y_{\text{O}_2}^{\text{out}}$
$\chi =$	χ	$2 \cdot \alpha - 2$	$\frac{1 - y_{\text{CO}_2}^{\text{out}}}{1 + \frac{y_{\text{CO}_2}^{\text{out}}}{2}}$	$\frac{y_{\text{CO}}^{\text{out}}}{1 - \frac{y_{\text{CO}}^{\text{out}}}{2}}$	$\frac{2 \cdot y_{\text{O}_2}^{\text{out}}}{1 - y_{\text{O}_2}^{\text{out}}}$
$\alpha =$	$1 + \frac{\chi}{2}$	α	$\frac{3}{2 + y_{\text{CO}_2}^{\text{out}}}$	$\frac{2}{2 - y_{\text{CO}}^{\text{out}}}$	$\frac{1}{1 - y_{\text{O}_2}^{\text{out}}}$
$y_{\text{CO}_2}^{\text{out}} =$	$\frac{1 - \chi}{1 + \frac{\chi}{2}}$	$\frac{3 - 2 \cdot \alpha}{\alpha}$	$y_{\text{CO}_2}^{\text{out}}$	$\frac{(y_{\text{CO}}^{\text{out}} - 2) \cdot (3 \cdot y_{\text{CO}}^{\text{out}} - 2)}{4 - 2 \cdot y_{\text{CO}}^{\text{out}}}$	$1 - 3 \cdot y_{\text{O}_2}^{\text{out}}$
$y_{\text{CO}}^{\text{out}} =$	$\frac{\chi}{1 + \frac{\chi}{2}}$	$\frac{2 \cdot \alpha - 2}{\alpha}$	$\frac{-(y_{\text{CO}_2}^{\text{out}} + 2) \cdot (y_{\text{CO}_2}^{\text{out}} - 1)}{3 + \frac{3 \cdot y_{\text{CO}_2}^{\text{out}}}{2}}$	$y_{\text{CO}}^{\text{out}}$	$2 \cdot y_{\text{O}_2}^{\text{out}}$
$y_{\text{O}_2}^{\text{out}} =$	$\frac{\frac{\chi}{2}}{1 + \frac{\chi}{2}}$	$\frac{\alpha - 1}{\alpha}$	$\frac{1 - y_{\text{CO}_2}^{\text{out}}}{3}$	$\frac{y_{\text{CO}}^{\text{out}}}{2}$	$y_{\text{O}_2}^{\text{out}}$

S2. Formulas for CO₂ conversion with a diluting agent

When adding a diluting agent to the feed gas, the dilution effect needs to be taken into account when calculating the performance metrics. When applying the same approach as described in Section 2.1 in the main paper, we obtain Table S.2. Note that these values are the flow rates of each species relative to the input CO₂ flow rate.

Table S.2. Reaction equation for pure CO₂ conversion, expressed in flow rates relative to the CO₂ flow rate at the reactor inlet, in the presence of a diluting agent.

Reaction	CO ₂ →	CO	O ₂	Diluting agent
in	1	0	0	β
out	1 - χ	χ	χ/2	β

When expressing the fraction of CO₂ at the outlet, we obtain the following expression:

$$y_{\text{CO}_2}^{\text{out}} = \frac{\dot{n}_{\text{CO}_2}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{out}}} = \frac{\dot{n}_{\text{CO}_2}^{\text{out}}/\dot{n}_{\text{CO}_2}^{\text{in}}}{\dot{n}_{\text{tot}}^{\text{out}}/\dot{n}_{\text{CO}_2}^{\text{in}}} = \frac{1 - \chi}{(1 - \chi) + \chi + \frac{\chi}{2} + \beta} = \frac{1 - \chi}{1 + \frac{\chi}{2} + \beta} \quad (\text{S.1})$$

Rearranging this equation to express conversion as function of the CO₂ output fraction is done as follows:

$$y_{\text{CO}_2}^{\text{out}} = \frac{1 - \chi}{1 + \frac{\chi}{2} + \beta}$$

$$y_{\text{CO}_2}^{\text{out}} \cdot \left(1 + \frac{\chi}{2} + \beta\right) = 1 - \chi$$

$$y_{\text{CO}_2}^{\text{out}} + \frac{y_{\text{CO}_2}^{\text{out}}}{2} \cdot \chi + y_{\text{CO}_2}^{\text{out}} \cdot \beta = 1 - \chi$$

$$\chi + \frac{y_{\text{CO}_2}^{\text{out}}}{2} \cdot \chi = 1 - y_{\text{CO}_2}^{\text{out}} - y_{\text{CO}_2}^{\text{out}} \cdot \beta$$

$$\left(1 + \frac{y_{\text{CO}_2}^{\text{out}}}{2}\right) \cdot \chi = 1 - (1 + \beta) \cdot y_{\text{CO}_2}^{\text{out}}$$

$$\chi = \frac{1 - (1 + \beta) \cdot y_{\text{CO}_2}^{\text{out}}}{1 + \frac{y_{\text{CO}_2}^{\text{out}}}{2}}$$

This is the same equation as presented by Eq. (11) in the main paper. The relationships between the conversion, the flux ratio and the CO₂, CO and O₂ fraction, as well as the fraction of the diluting agent, are presented in Table S.3.

Table S.3. Overview of formulas for pure CO₂ conversion in the presence of a diluting agent, and how to obtain the conversion, flux ratio, or output fraction of CO₂, CO, O₂ or the diluting agent, when one of the other values is known. Note that β is the dilution ratio, as defined by Eq. (10) in the main paper.

Known → Unknown ↓	χ	α	$y_{\text{CO}_2}^{\text{out}}$	$y_{\text{CO}}^{\text{out}}$	$y_{\text{O}_2}^{\text{out}}$	y_s^{out}
$\chi =$	χ	$(2 \cdot \alpha - 2) \cdot (1 + \beta)$	$\frac{1 - (1 + \beta) \cdot y_{\text{CO}_2}^{\text{out}}}{1 + \frac{y_{\text{CO}_2}^{\text{out}}}{2}}$	$\frac{(1 + \beta) \cdot y_{\text{CO}}^{\text{out}}}{1 - \frac{y_{\text{CO}}^{\text{out}}}{2}}$	$\frac{2 \cdot (1 + \beta) \cdot y_{\text{O}_2}^{\text{out}}}{1 - y_{\text{O}_2}^{\text{out}}}$	$\frac{2 \cdot \beta - 2 \cdot (1 + \beta) \cdot y_s^{\text{out}}}{y_s^{\text{out}}}$
$\alpha =$	$\frac{1 + \frac{\chi}{2} + \beta}{1 + \beta}$	α	$1 + \frac{1 - (1 + \beta) \cdot y_{\text{CO}_2}^{\text{out}}}{2 \cdot (1 + \beta) \cdot \left(1 + \frac{y_{\text{CO}_2}^{\text{out}}}{2}\right)}$	$\frac{2}{2 - y_{\text{CO}}^{\text{out}}}$	$\frac{1}{1 - y_{\text{O}_2}^{\text{out}}}$	$\frac{\beta}{(1 + \beta) \cdot y_s^{\text{out}}}$
$y_{\text{CO}_2}^{\text{out}} =$	$\frac{1 - \chi}{1 + \frac{\chi}{2} + \beta}$	$\frac{1 - (1 + \beta) \cdot (2 \cdot \alpha - 2)}{\alpha \cdot (1 + \beta)}$	$y_{\text{CO}_2}^{\text{out}}$	$\frac{2 - (3 + 2 \cdot \beta) \cdot y_{\text{CO}}^{\text{out}}}{2 \cdot (1 + \beta)}$	$\frac{1 - (3 + 2 \cdot \beta) \cdot y_{\text{O}_2}^{\text{out}}}{1 + \beta}$	$\frac{(1 + 2 \cdot (1 + \beta)) \cdot y_s^{\text{out}} - 2 \cdot \beta}{\beta}$
$y_{\text{CO}}^{\text{out}} =$	$\frac{\chi}{1 + \frac{\chi}{2} + \beta}$	$\frac{2 \cdot \alpha - 2}{\alpha}$	$\frac{-(y_{\text{CO}_2}^{\text{out}} + 2) \cdot (\beta \cdot y_{\text{CO}_2}^{\text{out}} + y_{\text{CO}_2}^{\text{out}} - 1)}{\left(\frac{3}{2} + \beta\right) \cdot y_{\text{CO}_2}^{\text{out}} + 3 + 2 \cdot \beta}$	$y_{\text{CO}}^{\text{out}}$	$2 \cdot y_{\text{O}_2}^{\text{out}}$	$\frac{2 \cdot \beta - 2 \cdot (1 + \beta) \cdot y_s^{\text{out}}}{\beta}$
$y_{\text{O}_2}^{\text{out}} =$	$\frac{\frac{\chi}{2}}{1 + \frac{\chi}{2} + \beta}$	$\frac{\alpha - 1}{\alpha}$	$\frac{-(y_{\text{CO}_2}^{\text{out}} + 2) \cdot (\beta \cdot y_{\text{CO}_2}^{\text{out}} + y_{\text{CO}_2}^{\text{out}} - 1)}{(3 + 2 \cdot \beta) \cdot y_{\text{CO}_2}^{\text{out}} + 6 + 4 \cdot \beta}$	$\frac{y_{\text{CO}}^{\text{out}}}{2}$	$y_{\text{O}_2}^{\text{out}}$	$\frac{\beta - (1 + \beta) \cdot y_s^{\text{out}}}{\beta}$
$y_s^{\text{out}} =$	$\frac{\beta}{1 + \frac{\chi}{2} + \beta}$	$\frac{\beta}{(1 + \beta) \cdot \alpha}$	$\frac{\beta \cdot (2 + y_{\text{CO}_2}^{\text{out}})}{1 + 2 \cdot (1 + \beta)}$	$\frac{\beta \cdot (2 - y_{\text{CO}}^{\text{out}})}{2 \cdot (1 + \beta)}$	$\frac{\beta \cdot (1 - y_{\text{O}_2}^{\text{out}})}{1 + \beta}$	y_s^{out}

S3. Formulas for the reverse Boudouard reaction

The reverse Boudouard reaction (RBR) is defined as follows:



For this reaction, the standard reaction enthalpy ΔH° is equal to +172 kJ mol⁻¹, which is already 111 kJ mol⁻¹ lower compared to pure CO₂ splitting. For more general information on the plasma-based RBR, we refer to the available literature (e.g., Refs. [1-4]).

The volumetric gas flow rate again increases and needs to be taken into account. However, with respect to using the correct formulas, the main difference with CO₂ splitting is that the reactants are not all in gas phase. Furthermore, because the carbon material is usually in a fixed bed positioned after the plasma, there is no fraction of carbon at the inlet and $y_{\text{C}_{(\text{s})}}^{\text{in}}$ is zero.

Another difference is that O₂ will still be present in low amounts as by-product, originating from pure CO₂ splitting. Hence, there is some deviation from the “ideal” RBR reaction (R.S1). This means that the conversion cannot be determined solely based on the output CO₂ fraction $y_{\text{CO}_2}^{\text{out}}$, as was the case for pure CO₂ splitting. In case of the RBR, the fractions of all gaseous components need to be determined. Afterwards, the flux ratio can be derived through the O-balance equation, as all species containing O-atoms are quantified:

$$\alpha = \frac{2 \cdot y_{\text{CO}_2}^{\text{in}}}{2 \cdot y_{\text{CO}_2}^{\text{out}} + y_{\text{CO}}^{\text{out}} + 2 \cdot y_{\text{O}_2}^{\text{out}}} \quad (\text{S.2})$$

With $y_{\text{CO}_2}^{\text{in}}$ equal to 1 if no other gas is present at the inlet. Hence, the absolute CO₂ conversion, O-based selectivities and yields can already be determined in the same way as described in Sections 4.2 and 4.4 of the main paper.

To derive the consumption rate of solid carbon, we write down the carbon balance equation as:

$$\frac{\alpha \cdot (y_{\text{CO}_2}^{\text{out}} + y_{\text{CO}}^{\text{out}})}{y_{\text{CO}_2}^{\text{in}} + \frac{\dot{n}_{\text{C}_{(\text{s})}}}{\dot{n}_{\text{CO}_2}^{\text{in}}}} = 1 \quad (\text{S.3})$$

With $\dot{n}_{\text{C}_{(\text{s})}}$ equal to the consumption or loss rate of solid carbon from the fixed bed, expressed through Eq. (S.4):

$$\dot{n}_{\text{C}_{(\text{s})}} = \dot{n}_{\text{CO}_2}^{\text{in}} \cdot (\alpha \cdot (y_{\text{CO}_2}^{\text{out}} + y_{\text{CO}}^{\text{out}}) - y_{\text{CO}_2}^{\text{in}}) \quad (\text{S.4})$$

The advantage of this expression is that one can follow in real-time how much carbon is consumed and from which point the bed starts to get saturated. Weighing of the carbon material before and after reaction can still serve as validation.

The “fraction” of solid carbon consumed $y_{\text{C}_{(\text{s})}}^{\text{in}}$ is then expressed as:

$$y_{\text{C}_{(\text{s})}}^{\text{in}} = \frac{\dot{n}_{\text{C}_{(\text{s})}}}{\dot{n}_{\text{C}_{(\text{s})}} + \dot{n}_{\text{CO}_2}^{\text{in}}} \quad (\text{S.5})$$

Hence, the total conversion is defined through Eq. (S.6):

$$\chi^{\text{tot}} = y_{\text{C(s)}}^{\text{in}} + \frac{\dot{n}_{\text{CO}_2}^{\text{in}}}{\dot{n}_{\text{C(s)}} + \dot{n}_{\text{CO}_2}^{\text{in}}} \cdot \chi_{\text{CO}_2}^{\text{abs}} \quad (\text{S.6})$$

The definitions for energy cost and energy efficiency remain the same as described in Section 4.3 of the main paper.

S4. Additional details for the comparison of energy efficiency with different equations, for DRM and CO₂ hydrogenation

The numerical example in Section 5.2 of the main paper describes the different energy efficiency equations applied to a dataset for DRM in a typical warm plasma, based on earlier experiments from our group [5]. An additional numerical example for a theoretical CO₂ hydrogenation dataset in a typical cold plasma (e.g., dielectric barrier discharge) is presented below.

Table S.4. Numerical example for CO₂ hydrogenation in a typical cold plasma with a SEI = 240.6 kJ mol⁻¹: flow rates of gases at the inlet, and unreacted gases and products at the outlet.

Flow rate (mL min ⁻¹)	CO ₂	H ₂	CH ₄	CO	H ₂ O	Total
in	15	25	0	0	0	40
out	13	21.5	0.5	1.5	2.5	39

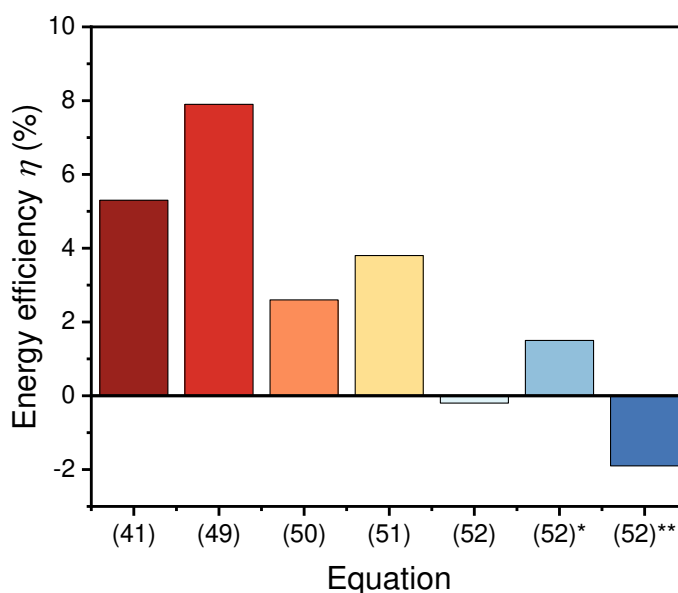


Fig. S.1. Numerical example of the energy efficiency calculated according to the various definitions for CO₂ hydrogenation. The different equation numbers refer to the equations presented in the main paper. Eq. (52)* represents the chemical energy efficiency without taking all products into account, Eq. (52)** represents the chemical energy efficiency when the reaction enthalpy corresponding to the “ideal” stoichiometry is used (described by reaction (R3) for CO₂ methanation in the main paper).

The same conclusions from the main paper remain valid for this example. In fact, due to the overall lower energy efficiency, the relative differences between the formulas are even more striking. Also note that the chemical energy efficiency (Eq. (52)) is slightly negative in this case, confirming even more that this definition is not so convenient compared to the fuel energy efficiency equations (Eqs. (41), (49), (50) and (51)).

The energy efficiency values from Fig. 2 in the main paper and Fig. S.1 are listed in Table S.5. The lower heating values, formation enthalpies and reaction enthalpies used for the calculation of the energy efficiency values are listed in Table S.6.

Table S.5. Energy efficiency values, obtained through the various equations presented in the main paper, for both the DRM (see Fig. 2 from the main paper) and CO₂ hydrogenation (Fig. S.1) numerical example.

Energy efficiency η (%)	DRM (Fig. 2 main paper)	CO ₂ hydrogenation (Fig. S.1)
Eq. (41)	52.9	5.3
Eq. (49)	61.3	7.9
Eq. (50)	48.6	2.6
Eq. (51)	56.4	3.8
Eq. (52)	27.8	-0.2
Eq. (52)*	38.9	1.5
Eq. (52)**	31.3	-1.9

Table S.6. Overview of lower heating values [6], as well as the formation enthalpies & reaction enthalpies [7], used in the energy efficiency calculations.

	CO ₂	0
	CH ₄	802
	CO	283
	H ₂	242
Lower heating values (kJ/mol)	C ₂ H ₂	1255
	C ₂ H ₄	1324
	C ₂ H ₆	1428
	H ₂ O	0
	CO ₂	-393.5
	CH ₄	-74.8
	CO	-110.5
	H ₂	0
Formation enthalpies (kJ/mol)	C ₂ H ₂	226.7
	C ₂ H ₄	52.4
	C ₂ H ₆	-83.8
	H ₂ O	-241.8
Reaction enthalpy for "ideal" stoichiometry (kJ/mol)	DRM	247.3
	CO ₂ methanation	-164.9

S5. Derivation of flux ratio in the presence of a standard

S5.1. CO₂ splitting

When the standard component is present as part of the feed gas, the same equations can be used as the ones presented in Table S.3 in section S2. However, when the standard is added in the exhaust stream, the flux ratio at the end, α_s , is given by:

$$\alpha_s = \frac{\dot{n}_{\text{tot}}^{\text{out}} + \dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}}} = \frac{\alpha + \beta}{1} = 1 + \frac{\chi}{2} + \beta \quad (\text{S.7})$$

Note that this is different from the equation in Table S.3, expressing the flux ratio as a function of conversion, due to the standard component not being present in the feed gas. As a result, all expressions for the flux ratio as a function of the conversion or one of the fractions, and vice versa, change compared to the ones presented in Table S.3. The equations to derive the flux ratio from each of the fractions are:

$$\alpha_s = 1 + \beta + \frac{1 - (1 + \beta) * y_{\text{CO}_2}^{\text{out}}}{2 + y_{\text{CO}_2}^{\text{out}}} \quad (\text{S.8})$$

$$\alpha_s = (1 + \beta) * \left(1 + \frac{y_{\text{CO}}^{\text{out}}}{2 - y_{\text{CO}}^{\text{out}}} \right) \quad (\text{S.9})$$

$$\alpha_s = (1 + \beta) * \left(1 + \frac{y_{\text{O}_2}^{\text{out}}}{1 - y_{\text{O}_2}^{\text{out}}} \right) \quad (\text{S.10})$$

$$\alpha_s = \frac{\beta}{y_s^{\text{out}}} \quad (\text{S.11})$$

Note that the equations in Table S.3 to derive the conversion from one of the measured fractions and vice versa do not change, as they are independent from the position where the standard is added. Also, it should be kept in mind that the flux ratio before the standard component is added is still defined as $1 + \frac{\chi}{2}$. The relationship between the flux ratio before (α) and after (α_s) addition of the standard can be derived from Eq. (S.7):

$$\alpha_s - \beta = 1 + \frac{\chi}{2} = \alpha \quad (\text{S.12})$$

S5.2. DRM & CO₂ hydrogenation

Fig. S.2 shows the different stages in the gas pathway for DRM or CO₂ hydrogenation with a cold trap and GC (or any other device for gas analysis):

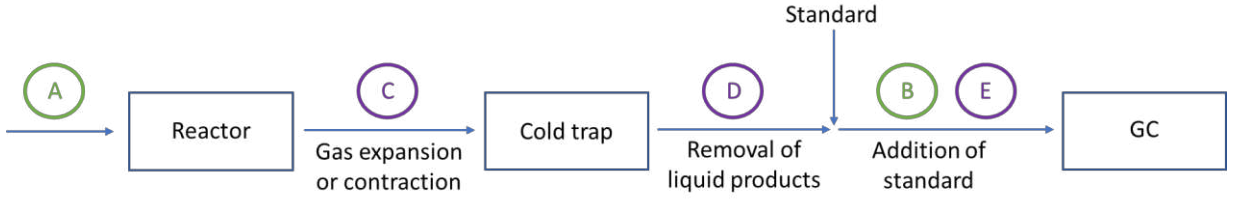


Fig. S.2. Gas pathway for a DRM/CO₂ hydrogenation experiment with cold trap and GC. The green A and B represent the initial stages (i.e. during a blank measurement, when the plasma is off) of the gas mixture, before and after dilution of the feed gas by the standard, respectively. The purple C, D and E represent the stages of the gas mixture when the plasma is on: gas expansion or contraction due to the reaction stoichiometry (C), gas contraction through removal of liquid products (D) and again dilution of the gas stream by adding the standard (E).

During the different stages of the gas pathway, the total molar and volumetric flow rate changes several times, and along with the total flow rate also the fractions of the gaseous components. When expressing a flux ratio and a fraction of a certain component, it is important to use the corresponding values, that refer to the same situations. For example, when expressing the flux ratio between situation B (flow in) and E (flow out), both the measured input and output fractions can be used directly, and the flux ratio is equal to the ratio of the obtained fractions of the standard, during the blank and plasma measurement:

$$\alpha_s^{\text{meas}} = \frac{y_s^{\text{in}}}{y_s^{\text{out}}} \quad (\text{S.13})$$

When expressing the flux ratio between situation A (flow in) and E (flow out), the measured output fractions can still be used directly, but the measured input factors not, since they do not represent the situation at the reactor inlet where no standard is present. To account for this, the factor $(1 + \beta)$ is multiplied with the measured input fractions, as well as the flux ratio:

$$y_i^{\text{in}} = y_i^{\text{in,meas}} \cdot (1 + \beta) \quad (\text{S.14})$$

$$\alpha_s^{\text{fin}} = \alpha_s^{\text{meas}} \cdot (1 + \beta) \quad (\text{S.15})$$

With β still representing the dilution ratio, generally defined as:

$$\beta = \frac{\dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}}} \quad (\text{S.16})$$

With \dot{n}_s the molar flow rate of the standard s and $\dot{n}_{\text{tot}}^{\text{in}}$ the total molar flow rate at the reactor inlet. Indeed, expressing Eq. (S.15) in terms of molar flow rates becomes:

$$\alpha_s^{\text{fin}} = \frac{\dot{n}_{\text{tot}}^{\text{out}} + \dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}} + \dot{n}_s} \cdot \left(1 + \frac{\dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}}} \right) \quad (\text{S.17})$$

With $\dot{n}_{\text{tot}}^{\text{out}}$ the total molar flow rate before addition of the standard, but after removal of liquid components (stage D in Fig. S.2). After rearrangement this results in:

$$\alpha_s^{\text{fin}} = \frac{\dot{n}_{\text{tot}}^{\text{out}} + \dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}}} \quad (\text{S.18})$$

This proves that Eq. (S.15) represents the ratio of the flow rate in stage E relative to the flow rate in stage A. A similar derivation can be performed for Eq. (S.14) expressing the input fractions.

Note that in the main paper, we defined an “initial” flux ratio (after reaction, but before condensation/deposition of certain products) and a “final” flux ratio (after condensation/deposition of certain products) in the main paper. In this context, this corresponds with the flux ratio between stage A and C, and between A and D, respectively. The relationship between the two was given by Eq. (43) in the main paper:

$$\alpha^{\text{init}} = \frac{\alpha^{\text{fin}}}{(1 - \sum_k y_k^{\text{out}})} \quad (\text{S.19})$$

In order to determine the initial flux ratio, the relationship between the flux ratio after condensation, but before the standard is added (α^{fin}) and the flux ratio after the standard is added (α_s^{fin}) has to be derived.

Consider again Eq. (S.17). When we divide every value by the total molar flow rate at the reactor inlet, we obtain:

$$\alpha_s^{\text{fin}} = \frac{\frac{\dot{n}_{\text{tot}}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{in}}} + \frac{\dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}}} + \frac{\dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}}} \cdot \left(\frac{\dot{n}_{\text{tot}}^{\text{out}}}{\dot{n}_{\text{tot}}^{\text{in}}} + \frac{\dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}}} \right)}{\frac{\dot{n}_{\text{tot}}^{\text{in}}}{\dot{n}_{\text{tot}}^{\text{in}}} + \frac{\dot{n}_s}{\dot{n}_{\text{tot}}^{\text{in}}}} \quad (\text{S.20})$$

We can rewrite this as:

$$\alpha_s^{\text{fin}} = \frac{\alpha^{\text{fin}} + \beta + \beta \cdot (\alpha^{\text{fin}} + \beta)}{1 + \beta} \quad (\text{S.21})$$

Note that the ratio of the total outflow over the total inflow is indeed equal to α^{fin} . This results in:

$$\alpha_s^{\text{fin}} = \alpha^{\text{fin}} + \beta \quad (\text{S.22})$$

All expressions for the flux ratios and fractions are summarized in Table S.7. Note that a single row gives a flux ratio and an in- and output fraction that needs to be used together, when calculating each performance metric. In other words, when one uses for example the measured in- and output fractions to calculate the absolute conversion, the corresponding flux ratio (Eq. (S.13)) should be used. The only exception is the calculation of the effective conversion, where always the fraction at the reactor inlet (Eq. (S.14), corresponding to stage A in Fig. S.2) has to be used, even when the measured fractions and flux ratio are used to calculate the absolute conversion:

$$\chi_i^{\text{eff}} = y_i^{\text{in,meas}} \cdot (1 + \beta) \cdot \chi_i^{\text{abs}} = y_i^{\text{in,meas}} \cdot (1 + \beta) \cdot \frac{y_i^{\text{in,meas}} - \alpha_s^{\text{meas}} \cdot y_i^{\text{out,meas}}}{y_i^{\text{in,meas}}} \quad (\text{S.23})$$

Using only the diluted fraction of the reactants $y_i^{\text{in,meas}}$ without the factor $(1 + \beta)$ will lead to an underestimation of the effective conversion, and hence also an underestimation of the total conversion, an overestimated energy cost, etc.

Table S.7. Expressions for flux ratio, input fraction and output fraction at each stage of the gas pathway for DRM/CO₂ hydrogenation. The parameters on the same row should be used together to calculate the performance metrics.

Stages	Flux ratio	Input fraction $y_i^{\text{in}} =$	Output fraction $y_{i/j}^{\text{out}} =$
In: B Out: E	$\alpha_s^{\text{meas}} = \frac{y_s^{\text{in}}}{y_s^{\text{out}}}$	$y_i^{\text{in,meas}}$	$y_{i/j}^{\text{out,meas}}$
In: A Out: E	$\alpha_s^{\text{fin}} = \alpha_s^{\text{meas}} \cdot (1 + \beta)$	$y_i^{\text{in,meas}} \cdot (1 + \beta)$	$y_{i/j}^{\text{out,meas}}$
In: A Out: D	$\alpha^{\text{fin}} = \alpha_s^{\text{fin}} - \beta$	$y_i^{\text{in,meas}} \cdot (1 + \beta)$	$y_{i/j}^{\text{out,meas}} \cdot \left(1 + \frac{\beta}{\alpha^{\text{fin}}}\right)$
In: A Out: C	$\alpha^{\text{init}} = \frac{\alpha^{\text{fin}}}{1 - \sum_k y_k^{\text{out}}}$	$y_i^{\text{in,meas}} \cdot (1 + \beta)$	$y_{i/j}^{\text{out,meas}} \cdot \left(1 + \frac{\beta}{\alpha^{\text{fin}}}\right) \cdot \left(1 - \sum_k y_k^{\text{out}}\right)$

S6. Experimental details for pure CO₂ splitting in DBD plasma

Two separate series of experiments were performed (one with a standard component, one with a flow meter) with CO₂ (Air Liquide, purity 99.999 %) flowing in a DBD plasma reactor with an input flow rate of 100 mL_s min⁻¹. When using a standard, an input flow rate of 20 mL_s min⁻¹ N₂ was used. An Agilent 990 Micro GC was calibrated for CO₂, CO, O₂ and N₂ to analyze the fractions in the output gas mixture. The flow rate was regulated by Bronkhorst mass flow controllers, which were calibrated manually with a Sensidyne Gilibrator-3 calibrator, before the GC calibration and experiments.

For each experimental run, three samples of the input gas mixture were injected on the GC, with 5 minutes between each sample. At least eleven samples were taken of the output gas mixture, of which at least seven after reaching a steady-state. From the latter, the average of the obtained peak areas was used for further calculations. When the bubble flow meter was used, two flow rate measurements were performed for each GC sample taken. After performing these experimental runs in triplicate, the weighted averages of the performance metrics were taken. For the errors on each individual measurement, we consider both the errors on the GC calibration factors, and the standard deviation on the obtained peak areas. The plasma power was monitored and confirmed to remain constant (approximately 60 W) during the different experiments.

The output fractions of CO₂, CO, O₂ and the standard (if present), as well as the dilution factor β (obtained through the MFC calibration), the measured plasma power and specific energy input (SEI) are presented in Table S.8. Each value is a weighted average of three separate experiments. The weighted averages of the flux ratio('s) and performance metrics, calculated through the different methods, are presented in Table S.9 for the experiments with the standard, and in Table S.10 for the experiments with the flow meter.

Table S.8. Weighted averages of all measured values and the SEI (kJ/mol), for both the experiments with the standard and the flow meter.

	Standard	Flow meter
$y_{\text{CO}_2}^{\text{out}}(\%)$	73.8 ± 0.3	88.9 ± 0.4
$y_{\text{CO}}^{\text{out}}(\%)$	6.25 ± 0.02	7.34 ± 0.02
$y_{\text{O}_2}^{\text{out}}(\%)$	3.17 ± 0.02	3.58 ± 0.02
$y_s^{\text{out}}(\%)$	16.8 ± 0.2	/
β	0.211 ± 0.001	/
P (W)	59.8 ± 0.1	59.93 ± 0.06
SEI (kJ/mol)	832 ± 2	808 ± 7

Table S.9. Weighted averages of the conversion, flux ratio's, energy cost, energy yield and energy efficiency, calculated from each output fraction (incl. the standard) for the experiments performed with a standard component added.

Known → Unknown ↓	$y_{\text{CO}_2}^{\text{out}}$	$y_{\text{CO}}^{\text{out}}$	$y_{\text{O}_2}^{\text{out}}$	y_s^{out}
$\chi(\%) =$	7.8 ± 0.3	7.81 ± 0.02	7.93 ± 0.05	8 ± 3
$\alpha_s =$	1.250 ± 0.002	1.2496 ± 0.0006	1.2502 ± 0.0007	1.25 ± 0.02
$\alpha =$	1.039 ± 0.002	1.0391 ± 0.0009	1.0397 ± 0.0009	1.04 ± 0.02
$EC(\text{kJ/mol}) =$	$(10.6 \pm 0.4) \cdot 10^3$	$(10.65 \pm 0.04) \cdot 10^3$	$(10.49 \pm 0.07) \cdot 10^3$	$(10 \pm 4) \cdot 10^3$
$EY(\text{mol/kJ}) =$	$(9.4 \pm 0.4) \cdot 10^{-5}$	$(9.39 \pm 0.03) \cdot 10^{-5}$	$(9.53 \pm 0.07) \cdot 10^{-5}$	$(10 \pm 4) \cdot 10^{-5}$
$\eta(\%) =$	2.7 ± 0.1	2.66 ± 0.01	2.70 ± 0.02	3 ± 1

Table S.10. Weighted averages of the conversion, flux ratio, energy cost, energy yield and energy efficiency, calculated from each measured output fraction and the measured flux ratio for the experiments performed with a flow meter.

Known → Unknown ↓	$y_{\text{CO}_2}^{\text{out}}$	$y_{\text{CO}}^{\text{out}}$	$y_{\text{O}_2}^{\text{out}}$	α
$\chi(\%) =$	7.6 ± 0.3	7.61 ± 0.02	7.42 ± 0.05	7 ± 2
$\alpha =$	1.038 ± 0.001	1.0381 ± 0.0001	1.0371 ± 0.0002	1.04 ± 0.01
$EC(\text{kJ/mol}) =$	$(10.6 \pm 0.4) \cdot 10^3$	$(10.62 \pm 0.09) \cdot 10^3$	$(10.9 \pm 0.1) \cdot 10^3$	$(11 \pm 4) \cdot 10^3$
$EY(\text{mol/kJ}) =$	$(9.5 \pm 0.3) \cdot 10^{-5}$	$(9.42 \pm 0.08) \cdot 10^{-5}$	$(9.2 \pm 0.1) \cdot 10^{-5}$	$(9 \pm 3) \cdot 10^{-5}$
$\eta(\%) =$	2.68 ± 0.09	2.67 ± 0.02	2.60 ± 0.03	2.5 ± 0.8

S7. Experimental details for DRM in the presence of O₂, in APGD plasma

For this second example, we look at CO₂ conversion in the presence of CH₄ and O₂, specifically in a 42.5/42.5/15 CO₂/CH₄/O₂ ratio. This reaction is also called oxidative CO₂ reforming of methane (OCRM). Again, two separate series of experiments were performed (one with a standard, one with a flow meter). The gases were again provided by gas bottles from Air Liquide (purity 99.999 %), and were sent to an APGD plasma reactor through Bronkhorst MFCs, which were calibrated manually with the bubble flow meter. An Agilent 990 Micro GC was calibrated for CO₂, CH₄, CO, H₂, C₂H₂, C₂H₄, C₂H₆, O₂ and N₂ to analyze the fractions in the output gas mixture. A sample of the input gas mixture was sent three times onto the GC, with 5 minutes between each sample. The same procedure was done for the output gas mixture, after the plasma reached a steady-state. The average of the obtained peak areas was used for further calculations. Each experimental run was repeated three times, and the weighted average of the performance metrics was taken. For the errors on each individual measurement, we consider both the errors on the GC calibration factors, and the standard deviation on the obtained peak areas.

The total reactant input flow rate with the standard method was 1 L_nmin⁻¹, and the standard was again N₂, with a flow rate of 100 mL_n min⁻¹ added to the effluent gas mixture between the cold trap and the GC sample point. For the experiments that were performed with the bubble flow meter, the flow rate was changed to 1 L_smin⁻¹. The plasma power was monitored through the readings on a DC Technix power supply, and confirmed to remain constant (91-94 W) during the different experiments.

The different fractions for each component (incl. the standard, if present), as well as the dilution ratio β (obtained through the MFC calibration), the measured plasma power and specific energy input (SEI) are presented in Table S.11 for both the experiments with the standard (left) and the flow meter (right). Each value is a weighted average of three separate experiments. The weighted averages of the flux ratios, atom balances and performance metrics, calculated through the different methods, are presented in Table S.12 for both the experiments with the standard (left) and the flow meter (right).

Table S.11. Weighted averages of all measured values and the SEI (kJ/mol), for both the experiments with the standard and the flow meter.

	Standard	Flow meter
$y_{\text{CO}_2}^{\text{in}}(\%)$	38.4 ± 0.2	43.0 ± 0.2
$y_{\text{CH}_4}^{\text{in}}(\%)$	38.3 ± 0.1	42.2 ± 0.2
$y_{\text{O}_2}^{\text{in}}(\%)$	14.41 ± 0.03	16.05 ± 0.03
$y_s^{\text{in}}(\%)$	9.37 ± 0.02	/
$y_{\text{CO}_2}^{\text{out}}(\%)$	17.7 ± 0.2	17.5 ± 0.2

$y_{\text{CH}_4}^{\text{out}} (\%)$	8.9 ± 0.2	8.7 ± 0.3
$y_{\text{O}_2}^{\text{out}} (\%)$	1.6 ± 0.1	1.5 ± 0.1
$y_{\text{CO}}^{\text{out}} (\%)$	34.3 ± 0.3	40.0 ± 0.3
$y_{\text{H}_2}^{\text{out}} (\%)$	28.5 ± 0.2	31.5 ± 0.3
$y_{\text{C}_2\text{H}_2}^{\text{out}} (\%)$	1.31 ± 0.02	1.41 ± 0.03
$y_{\text{C}_2\text{H}_4}^{\text{out}} (\%)$	0.376 ± 0.008	0.389 ± 0.007
$y_{\text{C}_2\text{H}_6}^{\text{out}} (\%)$	0.0929 ± 0.0006	0.0800 ± 0.0006
$y_s^{\text{out}} (\%)$	7.57 ± 0.07	/
β	0.0977 ± 0.0004	/
P (W)	91.3 ± 0.9	94 ± 1
SEI (kJ/mol)	117 ± 1	127 ± 2

Table S.12. Weighted averages of all calculated values based on the different methods, for both the experiments with the standard and the flow meter.

	Stoichiometric	Standard	Stoichiometric	Flow meter
α_s^{meas}	1.102 ± 0.008	1.24 ± 0.01	/	/
α_s^{fin}	1.307 ± 0.009	1.36 ± 0.01	/	/
α^{fin}	1.209 ± 0.009	1.26 ± 0.01	1.23 ± 0.01	1.24 ± 0.01
α^{init}	1.42 ± 0.01	1.43 ± 0.02	1.45 ± 0.01	1.45 ± 0.02

$\chi_{\text{CO}_2}^{\text{abs}}(\%)$	45.2 ± 0.8	43.1 ± 0.8	49.9 ± 0.8	49.0 ± 0.9
$\chi_{\text{CH}_4}^{\text{abs}}(\%)$	72.3 ± 0.6	71.3 ± 0.6	74.9 ± 0.8	74.6 ± 0.9
$\chi_{\text{O}_2}^{\text{abs}}(\%)$	87 ± 1	86 ± 1	88.3 ± 0.9	88.1 ± 0.9
$\chi_{\text{CO}_2}^{\text{eff}}(\%)$	19.1 ± 0.4	18.2 ± 0.4	21.4 ± 0.4	21.1 ± 0.4
$\chi_{\text{CH}_4}^{\text{eff}}(\%)$	30.4 ± 0.3	29.9 ± 0.3	31.6 ± 0.4	31.5 ± 0.4
$\chi_{\text{O}_2}^{\text{eff}}(\%)$	13.7 ± 0.2	13.6 ± 0.2	14.2 ± 0.2	14.1 ± 0.2
$\chi^{\text{tot}}(\%)$	63.1 ± 0.5	61.7 ± 0.5	67.4 ± 0.6	66.9 ± 0.6
$S_{\text{CO}}^{\text{C}}(\%)$	91 ± 2	97 ± 2	92 ± 2	93 ± 2
$S_{\text{C}_2\text{H}_2}^{\text{C}}(\%)$	6.9 ± 0.2	7.4 ± 0.2	6.4 ± 0.2	6.6 ± 0.2
$S_{\text{C}_2\text{H}_4}^{\text{C}}(\%)$	1.99 ± 0.05	2.12 ± 0.06	1.82 ± 0.05	1.86 ± 0.06
$S_{\text{C}_2\text{H}_6}^{\text{C}}(\%)$	0.491 ± 0.009	0.52 ± 0.01	0.365 ± 0.007	0.38 ± 0.01
$S_{\text{H}_2}^{\text{H}}(\%)$	61 ± 1	65 ± 1	61 ± 1	62 ± 1
$S_{\text{C}_2\text{H}_2}^{\text{H}}(\%)$	2.82 ± 0.06	2.97 ± 0.06	2.70 ± 0.07	2.75 ± 0.07
$S_{\text{C}_2\text{H}_4}^{\text{H}}(\%)$	1.63 ± 0.04	1.71 ± 0.04	1.51 ± 0.04	1.54 ± 0.04
$S_{\text{C}_2\text{H}_6}^{\text{H}}(\%)$	0.600 ± 0.009	0.63 ± 0.01	0.459 ± 0.009	0.47 ± 0.01
$S_{\text{H}_2\text{O}}^{\text{H}}(\%)$	34.3 ± 0.05	28.7 ± 0.5	35 ± 2	33.4 ± 0.7

$S_{CO}^0(\%)$	68 ± 1	73 ± 1	68 ± 1	70 ± 1
$S_{H_2O}^0(\%)$	31.7 ± 0.4	26.9 ± 0.4	32 ± 2	30.1 ± 0.6
$Y_{CO}^C(\%)$	53.1 ± 0.6	55.0 ± 0.7	57.4 ± 0.7	57.9 ± 0.9
$Y_{C_2H_2}^C(\%)$	4.05 ± 0.07	4.21 ± 0.07	4.03 ± 0.09	4.1 ± 0.1
$Y_{C_2H_4}^C(\%)$	1.17 ± 0.03	1.21 ± 0.03	1.12 ± 0.02	1.13 ± 0.03
$Y_{C_2H_6}^C(\%)$	0.288 ± 0.003	0.299 ± 0.004	0.231 ± 0.003	0.235 ± 0.004
$Y_{H_2}^H(\%)$	44.3 ± 0.5	45.9 ± 0.5	45.9 ± 0.6	46.5 ± 0.7
$Y_{C_2H_2}^H(\%)$	2.03 ± 0.04	2.11 ± 0.04	2.03 ± 0.05	2.06 ± 0.05
$Y_{C_2H_4}^H(\%)$	1.17 ± 0.03	1.21 ± 0.03	1.13 ± 0.02	1.14 ± 0.03
$Y_{C_2H_6}^H(\%)$	0.433 ± 0.005	0.449 ± 0.005	0.350 ± 0.005	0.356 ± 0.006
$Y_{H_2O}^H(\%)$	24.7 ± 0.3	20.0 ± 0.3	27 ± 2	25.1 ± 0.5
$Y_{CO}^O(\%)$	38.6 ± 0.5	40.0 ± 0.5	41.4 ± 0.5	41.8 ± 0.6
$Y_{H_2O}^O(\%)$	17.9 ± 0.2	14.5 ± 0.2	19 ± 1	17.9 ± 0.3
b_C	1.00 ± 0.01	1.04 ± 0.01	1.00 ± 0.01	1.01 ± 0.01
b_H	1.01 ± 0.01	0.99 ± 0.01	1.01 ± 0.02	1.00 ± 0.01
b_O	1.00 ± 0.01	1.00 ± 0.01	1.00 ± 0.02	1.00 ± 0.01

<i>EC</i> (kJ/mol)	179 ± 3	183 ± 3	186 ± 3	188 ± 3
<i>EY</i> (mol/kJ)	(5.60 ± 0.08)·10 ⁻³	(5.47 ± 0.08)·10 ⁻³	(5.37 ± 0.09)·10 ⁻³	(5.33 ± 0.09)·10 ⁻³
η (%) (Eq. (41))	54.8 ± 0.6	56.7 ± 0.6	56.2 ± 0.6	56.9 ± 0.8
η (%) (Eq. (49))	69.4 ± 0.9	73 ± 1	68 ± 1	70 ± 1
η (%) (Eq. (50))	48.2 ± 0.5	49.9 ± 0.5	50.0 ± 0.6	50.6 ± 0.7
η (%) (Eq. (51))	61.0 ± 0.8	63.9 ± 0.9	60.7 ± 0.9	62 ± 1
η (%) (Eq. (52))	2 ± 1	5 ± 1	3 ± 3	3 ± 2

S8. References

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List of symbols

Symbols (incl. sub- and superscripts)	Description
*	Incorrect expression
<i>A</i>	Atom
abs	Absolute
app	Applied
α	Flux ratio
<i>b</i>	Balance
β	Dilution ratio
chem	Chemical
conv	Converted
corr	Corrected
des	Desired
DF	Dissociation fraction
ΔH°	Standard reaction enthalpy (kJ mol ⁻¹)
<i>E</i>	Energy (kJ ⁻¹ , eV)
EC	Energy cost (kJ mol ⁻¹ , kJ L ⁻¹ , eV molecule ⁻¹)
eff	Effective
EY	Energy yield (mol kJ ⁻¹ , L kJ ⁻¹ , molecule eV ⁻¹)
fin	Final
H_f	Formation enthalpy (kJ mol ⁻¹)
<i>i</i>	Reactant
in	At reactor inlet/before reactor
init	Initial
<i>j</i>	(Gaseous) product
<i>k</i>	Condensed/deposited product
LHV	Lower heating value (kJ mol ⁻¹)
meas	Measured
μ	Stoichiometric coefficient
\dot{n}	Molar flow (mol min ⁻¹)
N_A	Avogadro's constant (molecule mol ⁻¹)
η	Energy efficiency
out	At reactor outlet/after reactor
<i>p</i>	Pressure (bar, atm)
<i>P</i>	Power (kW)
RE	Relative error
reac	Reaction
rep	Reported
<i>s</i>	Diluting agent/standard component
<i>S</i>	Selectivity
SEI	Specific energy input (kJ mol ⁻¹ , kJ L ⁻¹ , eV molecule ⁻¹)
<i>T</i>	Temperature (K, °C)
tot	Total

\dot{V}	Volume flow (L min ⁻¹)
V_m	Molar volume (L mol ⁻¹)
χ	Conversion
y	Molar/volume fraction
Y	Product yield