Influence of gas expansion on process parameters in non-thermal plasma plug-flow reactors: A study applied to dry reforming of methane

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Abstract

The chemical reactions that take place in non-thermal plasma plug-flow type reactors can change the number of particles, the volumetric flow rate and the concentration of species, even if they do not take part in chemical reactions themselves. These changes, however, are frequently neglected in the computation of parameters characterizing the chemical process thus introducing a systematic error in parameters such as conversion, selectivity, yield, efficiency, residence time, carbon balance and energy efficiency. We discuss errors arising from this neglect, the methods currently used to take these factors into account and propose a simple procedure to obtain correct values, based on an internal standard. This procedure is applied on methane conversion with CH_4/CO_2 or $He/CH_4/CO_2$ mixtures where we found that neglecting the volumetric flux change introduces errors of up to 20 % on process parameters.

Keywords: DBD reactor, conversion, selectivity, energy efficiency, methane dry reforming

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1. Introduction

Non-thermal plasmas (NTP), frequently in association with a catalyst, have the capacity to enhance specific reaction channels in gas-phase and in gas-surface interactions. They have been used on problems ranging from the destruction of small amounts of diluted gases, as in air-pollution control, odor removal and degradation of VOCs [1] to ozonizers [2] and the search for alternative

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technologies for processing of gases, as in the dry reforming of methane [3, 4] or CO_2 conversion [5, 6].

Most NTP reactors are plug-flow type reactors where the reactions, taking place in quasi-isobaric conditions, determine a change in the total number of particles, the gas volume and the volumetric flow rate, Φ, along the reactor. While the processing of small amounts of diluted gases results in a negligible change in the total number of particles, in other cases the change in concentration of the gas mixture components can be significant, even if a given gas component does not take part in the reactions itself. Process parameters depending on Φ are also affected. In these cases, neglecting the effect of reactions on concentrations and on gas flux introduces a systematic error in the computation of process parameters. Depending on the overall reaction stoichiometry, this error can have a very significant value.

A review of the literature on methane or CO_2 conversion, however, shows that many authors do not take into account the effect of the change of the number of particles in reactions, either in experimental work or in numerical models [7, 8]. The few articles measuring the change in the effluent gas flow use either of two techniques: a direct measurement with a bubble flow meter [9–13] or addition of an internal standard to the feed gas [14–16]. A variation of the latter is when a component itself of the feed gas is used as internal standard. We have used this variation of the technique to obtain the expansion ratio α discussed below, in a previous study [17].

Even if some authors measure the inlet and effluent gas fluxes, it is not always clear if they use these values to compute the parameters characterizing the materials and energy balances as most of them indicate expressions for conversion and selectivity based on number of moles instead of fluxes. From the cited authors, only three show expressions for process parameters based on fluxes [13, 15] or on the concentrations and a correction factor [17].

Expressions for process parameters including the gas expansion, are shown in [18] where the discussion is extended to energy balance parameters. The author, however, continues to use definitions of energy parameters that do not account for the change in the gas flow. In the present work we generalize the discussion of the effect of flow variations due either to chemical reactions or gas heating, on parameters characterizing the process in plug-flow reactors, in particular, in DBD reactors. We discuss a simple method to measure the change in flux, the limitations in difficulties in presence of condensables or solid deposition and apply the method to study the dry reforming of methane.

The paper is organized as follows: section 2 discusses the effect of gas expansion; in section 3 the process parameters are written including the fluxes; section 4 estimates the errors in these parameters if the gas expansion is neglect. Section 5 analyses the advantages and limitations of the available methods to measure the change in gas flux. Section 6 discusses a simple procedure to measure this change applied to obtaining accurate results for the process parameters on different mixtures. Section 7 concludes.

2. Changes of Gas Flux in Plug-flow Feactors

Several authors use definitions for process parameters characterizing the material and energy balances (conversion, selectivity, yield, specific input energy) based on the total number of moles of reactant and product species in the reactor [12, 19–21]. For plug-flow reactors, however, the process parameters should be based on the amounts of species i entering or exiting the reactor per unit time, $\dot{N}_i$.

While at the entrance of a plug-flow reactor where the fluxes of reactants are well defined, these time rates are known, at the exit of the reactor this information is not easily obtained. Available methods such as gas chromatography, FTIR, mass spectrometry or GC-MS to name just the most common, sample the gas flow and provide the concentrations of species, c_i, but not the time rates for the number of a given species. Process parameters are computed from these concentration values. We should be careful, however, in replacing the time rates with the concentration values. The relation between them can be easily obtained: If Φ is the volumetric flow rate through a surface S, i.e., $\Phi = \int_S \vec{v} \cdot d\vec{S}$, where $\vec{v}$ is the gas velocity, we can write

$$\dot{N}_i = c_i n \Phi \tag{1}$$

with n the gas density. $\dot{N}_i$, changes with concentration and also with the gas density and volumetric flow rate. For an isobaric process, n depends on temperature while c_i and Φ depend on volume and surface reactions.

2.1. Flux Ratio

In practice, as most process parameters involve the ratios between the time rate of species before and after reactions, the only value required, aside from the concentrations, is the ratio between the particle fluxes at the entrance, $(n\Phi)_e$, and exit, $(n\Phi)_x$, of the reactor, where the index e and x refer to the entrance and exit, respectively,

$$\alpha = \frac{(n\Phi)_x}{(n\Phi)_e} \,. \tag{2}$$

The particle flux ratio, α, together with the concentrations, are the only values required to compute the process parameters[1].

A few process parameters depend on the change of particle flux along the reactor. In this case we need to define a space dependent flux ratio. To simplify the discussion, we consider the particular case of a dielectric barrier discharge (DBD) reactor operating in steady conditions, with constant section, S, length, L, volume, $V = SL$, and oriented along z. In this case we define the space dependent flux ratio, $\alpha(z)$, as

$$\alpha(z) = \frac{n(z)\Phi(z)}{(n\Phi)_e}. \tag{3}$$

To estimate $\alpha(z)$ we start from the steady-state continuity equation for each gas component, assuming a common axial velocity, v,

$$\nabla \vec{J} = Q, \tag{4}$$

where $\vec{J}$ is the total flux and Q is the net volume rate of production (or desappearing) of new particles. In general, Q changes along the reactor with the gas mixture composition. If the stoichiometry of reactants and products, however, is not very different or the conversion rates small, Q can be approximated by a constant value along the reactor. In this case, integrating (4), using (3) and the definition of Φ, we obtain

$$\alpha(z) = 1 + \frac{QS}{(n\Phi)_r} z$$

or,

$$\alpha(z) = 1 + (\alpha - 1)\frac{z}{L} \tag{5}$$

We can write α as a function of the conversion values and the stoichiometry of reactions in the reactor. Using X_i for the conversion of reactant i, and writing a general equilibrium equation for the overall sum of the reactions in the reactor as

$$\sum_r \nu_i R_i \rightarrow \sum_p \nu_j P_j$$

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[1] For the residence time and the average energy density, the ratio of gas temperatures at the input and exit of the discharge volume of the reactor is also necessary. The effect of the temperature is, however, small.

where R_i and P_j represent reactant and products, respectively, and the ν are stoichiometric coefficients. The particle fluxes entering and leaving the reactor are,

$$(n\Phi)_e = \sum_r \dot{N}_i,$$

and

$$(n\Phi)_x = \sum_r (1 - X_i)\,\dot{N}_i + \Delta\dot{N}$$

where the first term on the right side represents the time rate of the fraction of gases that have not reacted and $\Delta\dot{N}$ is the time rate of formation of molecules from reactants and has the value

$$\Delta\dot{N} = \frac{\sum_p \nu_j}{\sum_r \nu_i} \sum_r X_i \dot{N}_i.$$

From these relations, and equations (1) and (2) we obtain

$$\alpha = 1 + \left(\frac{\sum_p \nu_j}{\sum_r \nu_i} - 1 \right) \sum_r X_i c_i \,. \tag{6}$$

Thus the measurement of α and the concentrations, c_i, provide information on the stoichiometric ratio, $\sum_p \nu_j / \sum_r \nu_i$.

2.2. Condensation and Deposition

A final aspect to consider is the effect of deposition on the reactor and the condensation of products between the reactor and the point on measurement of concentrations (as frequently happens with the use of a trap for water vapor to protect a GC column). In isobaric processes, the condensation and deposition reduces the volumetric flow rate to a value $\tilde{\Phi}_x$ and increases the concentration of the remaining species. The flux ratio decreases to $\tilde{\alpha}$, with $\tilde{\alpha} \leq \alpha$. If $\sum' c_k$ is the sum of concentrations of condensable components at the exit of the reactor and before the trap, we have

$$\tilde{\Phi}_x = \left(1 - \sum\nolimits' c_k\right) \Phi_x \tag{7}$$

$$\tilde{c}_i = \frac{c_i}{1 - \sum' c_k} \tag{8}$$

$$\tilde{\alpha} = \left(1 - \sum\nolimits' c_k\right) \alpha \tag{9}$$

where i is any non-condensable product.

3. Process Parameters for Plug-flow Reactors

3.1. Residence Time

The first parameter we consider is the residence time, τ. For a DBD reactor with section S, without plasma, we have

$$\tau_0 = \frac{V}{\Phi_e}.$$

In the presence of plasma, the flux changes along the length, z. In this case the residence time is computed from the integral,

$$\tau = S\int_0^L \frac{dz}{\Phi(z)}. \tag{10}$$

Considering the gas ideal and using (3), we can write (10) as

$$\tau = \tau_0 \frac{T_e}{L}\int_0^L \frac{dz}{T(z)\alpha(z)}. \tag{11}$$

where T_e is the input gas temperature and $T(z)$ the values at z. To progress further we need to make assumptions on the dependency of $T(z)$ and $\alpha(z)$ on z. In dielectric barrier discharges, it is usually assumed [22, 23] that, after a short distance from the entrance, the gas temperature is constant along the reactor. In these conditions $T(z) \lesssim T_x$ where T_x is the temperature at the end of the discharge. As for $\alpha(z)$, we use the approximation (5). Using these values in (11) we obtain the approximate result

$$\tau \geq \tau_0 \frac{T_e}{T_x}\frac{\log(\alpha)}{\alpha - 1}\,. \tag{12}$$

Note that this equation defines a lower limit for τ as we have neglected the lower T values at the entrance.

3.2. Material Balance Parameters

Material balance parameters rely on measurements of concentrations with and without plasma. These measurements usually take place sufficiently distant from the reactor such that the samples are at the same temperature. In this case α depends only on the ratio of volumetric flow rates, $\alpha = \Phi_x/\Phi_e$. If condensations occur, what is measured are the concentrations $\tilde{c}_i$ and $\tilde{\alpha}$. In terms of concentration and flux ratio, the most common material balance parameters are

Conversion:

$$X_i = 1 - \tilde{\alpha}\frac{\tilde{c}_{i,x}}{c_{i,e}}, \tag{13}$$

where X_i is the fraction of reactant i that is converted to products;

Selectivity:

$$S_{j,a} = \frac{\tilde{\alpha}\, \mu_{j,a}\tilde{c}_{j,x}}{\sum_i \mu_{i,a}(c_{i,e} - \tilde{\alpha}\, \tilde{c}_{i,x})}, \tag{14}$$

where $\mu_{i,a}$ is the number of a-atoms in reactant species i, and $S_{j,a}$ measures the contribution of reactants to the formation of product j, counted in terms of a-atoms. While equation (14) is a general expression, in the case of production of hydrocarbons, a is usually carbon or, in the case of H_2 production, hydrogen;

Yield:

$$Y_{j,a} = \frac{\tilde{\alpha}\mu_{j,a}\tilde{c}_{j,x}}{\sum_i \mu_{i,a}c_{i,e}}, \tag{15}$$

where $Y_{j,a}$ describes the actual amount of j produced in comparison to the maximum possible if the reactants involved were fully converted. Again, for hydrocarbons, the yield is usually calculated on the basis of available carbon or, for H_2, of hydrogen atoms;

Atom balance: In this case we have to distinguish between the non-condensable and condensable products:

$$b_a = \frac{\tilde{\alpha} \sum_j \mu_{j,a}\tilde{c}_{j,x} + \alpha \sum_k' \mu_{k,a}c_{k,x}}{\sum_i \mu_{i,a}c_{i,e}}, \tag{16}$$

where b_a is the ratio of the total a-atoms in the products to the a-atoms in the reactants. The sums on the upper term refer to the non-condensable and condensable components, respectively, including the non-converted fraction of reactants. Again for hydrocarbons, a is usually carbon and this balance can be used to estimate the carbon deposited.

As, for any a, $b_a = 1$, we can write

$$\alpha {\sum_k}' \mu_{k,a}c_{k,x} = \sum_i \mu_{i,a}c_{i,e} - \tilde{\alpha} \sum_j \mu_{j,a}\tilde{c}_{j,x} \tag{17}$$

where the right side depends only on measurable values. For simple mixtures, the corresponding set of equations for all a-atoms can be used to estimate the fraction of condensable and deposited components and α.

3.3. Energy Balance Parameters

Regarding the energy balance parameters, the most commonly used is the specific energy input (SEI) defined as the ratio between the electric power supplied to the reactor, p, to produce the plasma and the input volume flux of reactants,

$$\mathrm{SEI} = \frac{p}{\Phi_e}.$$

Although this parameter is useful, as it does not account for the change in flux along the reactor, it is not able to provide an accurate indication of the energy density (energy per unit volume) deposited in the gas. This is one important process parameter that is used in numerical models [8].

We can define the average energy density deposited on the plasma, U, as

$$U = \int_0^L \frac{dp/dz}{\Phi(z)} dz\,. \tag{18}$$

Assuming a uniform power deposition along the reactor, i.e. $dp/dz = p/L$, using the same approximations used to solve (10), we obtain the result

$$U = [\mathrm{SEI}] \frac{T_e}{T_x} \frac{\log(\alpha)}{\alpha - 1}\,. \tag{19}$$

Different definitions for the energy efficiency are found in literature [18]. E.g.[24] list two definitions, a chemical energy efficiency, η_c, based on the change of standard enthalpy, H_f, and a fuel efficiency, η_f, based on the lower heating values (LHV) and useful in oil industry. In terms of concentrations these definitions, corrected for the gas expansion, are

$$\eta_c = \frac{\tilde{\alpha} \sum_p \tilde{c}_{j,x} H_{f,j} + \alpha {\sum}'_k c_{k,x} H_{f,k} - \sum_r X_i c_{i,e} H_{f,i}}{U} \tag{20}$$

$$\eta_f = \frac{\tilde{\alpha} \sum_p \tilde{c}_{j,x} [\mathrm{LHV}]_j + \alpha {\sum}'_k c_{k,x} [\mathrm{LHV}]_k}{U + \sum_r c_{i,e} [\mathrm{LHV}]_i}\,, \tag{21}$$

where [LHV] is in units of energy/volume and, as in (16), the sums on the upper term refer to the non-condensable, condensable components and reactants, respectively.

The residence time, τ, average energy density, U, and energy efficiencies, η_c and η_f, require knowing α, while all other parameters can be computed from $\tilde{\alpha}$ and $\tilde{c}_i$. Note that, from equations (8) and (9), we have $\tilde{\alpha}\tilde{c}_i = \alpha c_i$. Thus, although equations (13-15) are written using values of concentration after condensation, $\tilde{c}_j$, they provide correct values, i.e. the process parameters that measure material balances of a single gas component (conversion, selectivity or yield) are not affected by condensation or deposition.

4. Errors in the Process Parameters from Neglecting α

The importance of the systematic error in these parameters when the change of the number of particles and the temperature increase in the reactor are neglected, can be estimated looking at the relative error, $r_x = (x_0 - x(\alpha))/x(\alpha)$, where x_0 is the value neglecting α. In this section we neglect the effect of condensation. Using the definitions (12–21) we obtain,

$$r_{X_i} = \frac{\tilde{\alpha} - 1}{\tilde{\alpha}} \left(\frac{1 - X_i}{X_i} \right) \tag{22}$$

$$r_{S_a} = -\frac{\tilde{\alpha} - 1}{\tilde{\alpha}} \frac{\sum_p \mu_{j,a} c_{j,x}}{\sum_r \mu_{i,a}(c_{i,e} - c_{i,x})}\,, \quad \forall j_{\text{prod}} \tag{23}$$

$$r_\beta = -\frac{\tilde{\alpha} - 1}{\tilde{\alpha}}\,, \quad \beta = Y_{j,a},\, b_a \tag{24}$$

$$r_\gamma = \frac{T_x}{T_e} \frac{\alpha - 1}{\log(\alpha)} - 1\,, \quad \gamma = \tau, U \tag{25}$$

$$r_{\eta_c} = \frac{\sum_p c_{j,x} H_{f,j} - \sum_r X_i c_{i,e} H_{f,i}}{\tilde{\alpha} \sum_p c_{j,x} H_{f,j} - \sum_r X_i c_{i,e} H_{f,i}} \frac{T_e}{T_x} \frac{\log(\alpha)}{\alpha - 1} - 1 \tag{26}$$

These equations deserve a few remarks:

1. For $\alpha > 1$, neglecting α underestimates selectivity, yield and atom balance and overestimates conversion, residence time, average energy density and chemical energy efficiency. For $0 < \alpha < 1$ the opposite is true;
2. The relative error in selectivity (23) is the same for all products;
3. The relative errors in yield, atom balance, residence time and average energy density (24, 25), only depend on $\tilde{\alpha}$ or α and the ratio of gas temperatures.

To estimate the errors in actual reactions, we use the ideal *syngas* production reaction from methane and carbon dioxide,

$$\mathrm{CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2}\,,$$

and, for a [1:1] mixture, assume the same value of conversion for CH_4 and CO_2, X. In this case $\alpha = 1 + X$, and the relative errors can be computed as a function of X. As for the effect of temperature on τ and U, we take $T_r = 300\,\mathrm{K}$ and consider the cases of $\Delta T = (0,\ 20 \text{ and } 45)\,\mathrm{K}$, the last two corresponding to the average temperature increase measured in DBD in CH_4[25] and $CH_4 + CO_2$[26], respectively.

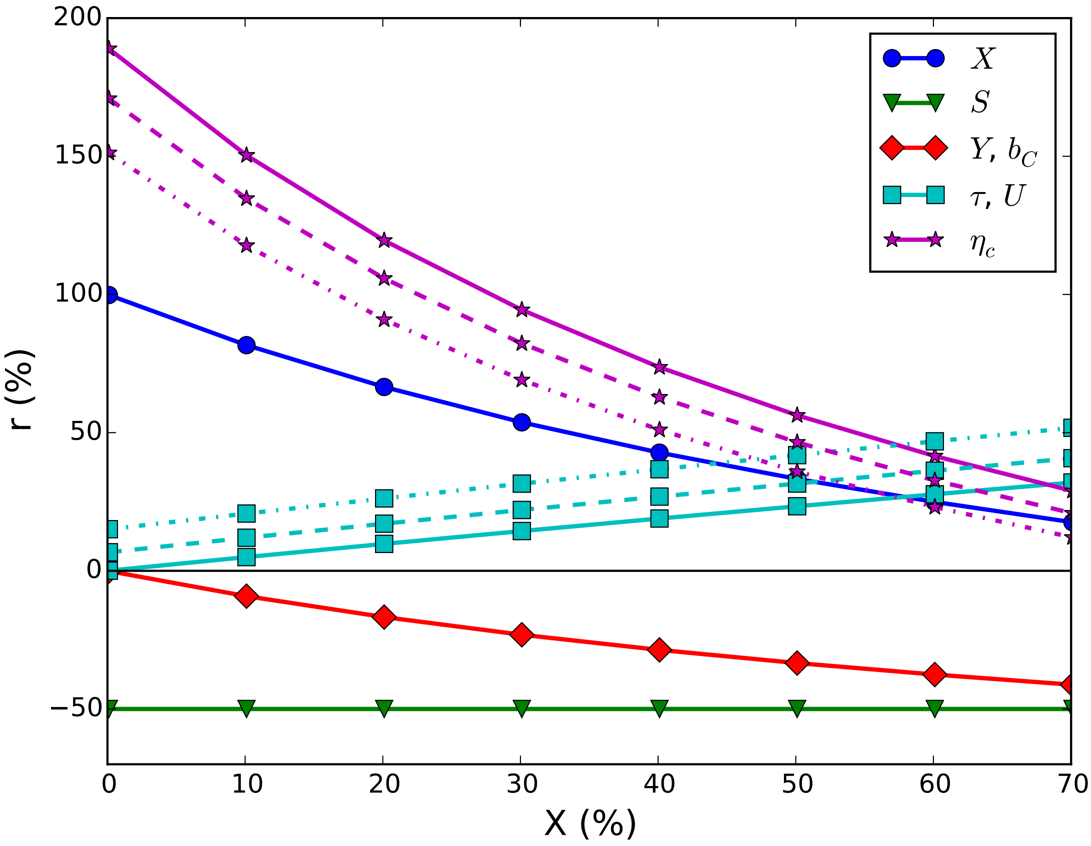

Figure 1: (color online) Ideal CH_4/CO_2 mixture: Relative errors in process parameters when the gas expansion and gas temperature increase are neglected, as a function of conversion. For the meaning of symbols, see equations (12-20). The solid, dash and dash-dot lines correspond to gas temperature increases of $\Delta T = (0,\ 20 \text{ and } 45)\,\mathrm{K}$, respectively.

As the results of figure 1 show, in these conditions, the systematic errors in process parameters when the gas expansion is neglected are large. Regarding the effect of temperature, even if it is assumed that the gas temperature increase in DBD systems is negligible for the plasma chemistry, a modest increase is sufficient to introduce non-negligible errors in the residence time, τ, and average energy density, U and chemical energy efficiency, η_c.

5. Analysis of Available Methods

As discussed in section 1, we found two methods, with variants, to correct for the gas expansion due to reactions. In this section we briefly discuss the advantages or disadvantages of these methods and variants. Note that these methods only measure $\tilde{\alpha}$. As noted in the end of section 3, the evaluation of the residence time, average energy density and energy efficiency, require knowing α, the temperatures at the beginning and end of the discharge and the amount of condensables.

5.1. Measurement of the Exhaust Flux using a Bubble Flow Meter

The first method [13] is the direct measurement of the flux with a bubble flow meter. This method is straightforward, reliable, reach accuracies of 0.5 % in semi-automatic models and the equipment is inexpensive. They do not, however, provide a continuous reading, the measurement usually require a good amount of manual work and is tedious. Digital semi-automatic models have simplified operation but are meant to be used as calibrators to other instruments as thermal conduction flow meters. Precision work requires the control of environment conditions, in particular the temperature of the flowing gas, which can be a problem in the presence of condensables.

5.2. Adding an Internal Standard to the Process Gas

The second method relies on using an internal standard in the process gas. The concentration of this internal standard at the exhaust, measured with and without plasma, is assumed to be proportional to the fluxes. Variations of the method depend on how this standard is incorporated.

5.2.1. Addition of the Internal Standard to the Feed Gas

This addition can be done at the entrance of the reactor and gases like Ar or N_2 have been used [18] for this purpose. In order to obtain valid results it is necessary that the internal standard gas does not react or interfere with the plasma in any way. This condition, however, is difficult to fulfill, for two reasons:

- In a plasma, electron collisions are responsible for the dissociation of molecules and formation of radicals that take part in further reactions, contributing to the change in the number of particles. For this reason, N_2 (or any molecular gas) is not appropriate as internal standard gas;
- In a plasma, electron collisions are the primary processes initiating the chain of reactions. The rate coefficients for these reactions depends on the electron energy distribution which, in a non-thermal plasma, is not Maxwellian and depends on the balance between the energy gained from the electric field and the elastic and inelastic collisions in the gas. Any change in gas composition, such as the introduction of an internal standard, alters this balance.

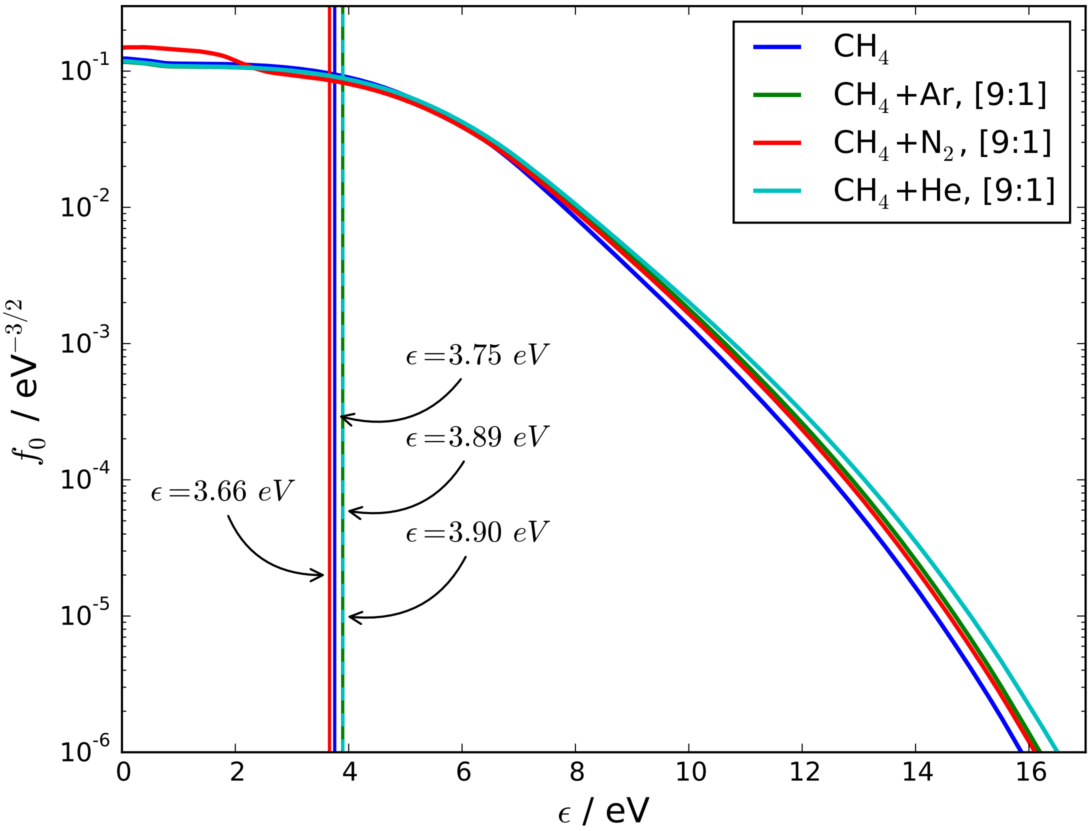

Figure 2: (color online) Isotropic component of the electron energy distribution function in pure CH_4 and mixtures of CH_4 with 10 % of Ar, He or N_2, for a reduced electric field of $E/N = 7 \times 10^{-16}\,\mathrm{V\,cm^2}$. The vertical lines indicate the mean electron energy for each mixture.

To illustrate this point, figures 2 and 3, obtained with a multi-term electron Boltzmann equation solver [27], show the effect of adding 10 % of Ar, He or N_2 to a CH_4 plasma. Figure 2 shows the isotropic component of the electron energy distribution function at a reduced electric field value of $E/N_o = 7 \times 10^{-16}\,\mathrm{V\,cm^2}$, while figure 3 shows the electron collision rate coefficient for the reaction $e + CH_4 \rightarrow e + CH_3 + H$, which is the main methane dissociation reaction in electron collisions. For the above value, E/N_o, the increase of this collision rate with the addition of the internal standard is above (80, 50 and 30) %, respectively for He, Ar and N_2.

In order to assess the actual error introduced by the addition of the internal standard, we measured the conversion of CH_4 and CO_2 in mixtures with and without 10 % of He in the conditions described in subsection 6.1. The results in figure 4 show a significant increase in conversion with

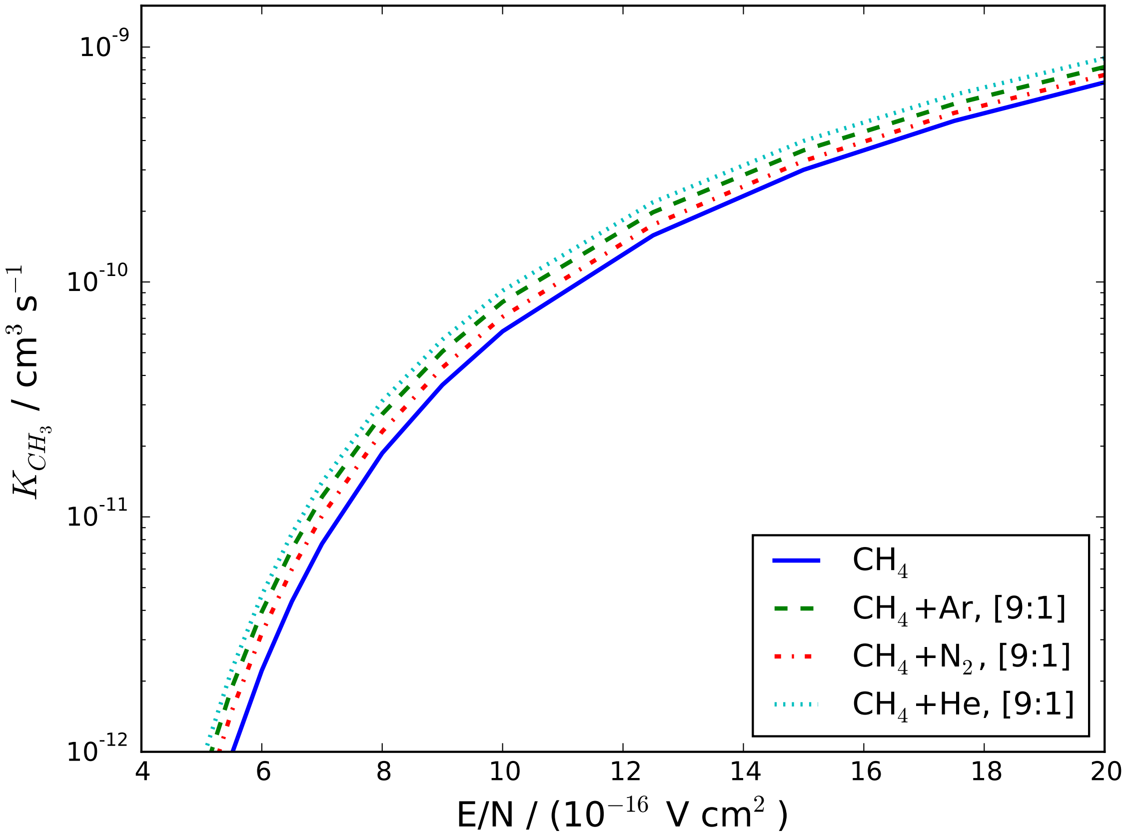

Figure 3: (color online) Electron-methane collision rate coefficient for the formation of CH_3, as a function of the reduced electric field, E/N, for pure CH_4 and mixtures of CH_4 with 10 % of Ar, He or N_2.

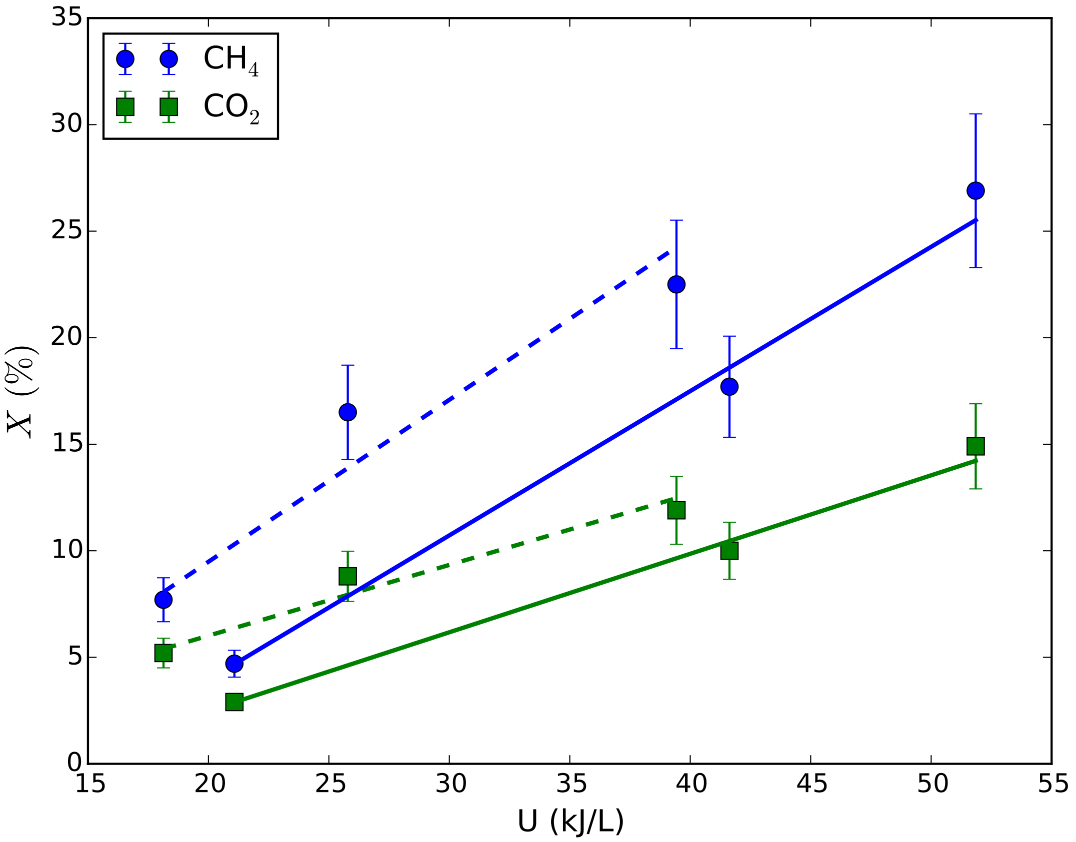

Figure 4: (color online) Conversion as a function of the average energy density, U, in He/CH_4/CO_2 mixtures with [CH_4]:[CO_2] = 1, in a DBD reactor powered by an AC power supply. a) solid line: pure CH_4/CO_2 mixture, b) dashed line: mixture with 10 % of He. The lines are the weighted least-sqare fit of the results.

helium. From the discussion above we can expect that the effect of argon or nitrogen would be smaller but nevertheless measurable.

In summary, the addition of an internal standard to the feed gas at the entrance of the reactor interferes with the discharge and should be avoided in the case of plasmas.

5.2.2. Using a Gas Mixture Component as Internal Standard

A particular case where this method provides correct results is when the gas mixture studied includes a non-reacting component (e.g. a rare gas) that can be used as internal standard. This was the case in our first attempt to address the effect of gas expansion. We studied the mixtures He/CH_4/CO_2 and He/CH_4/O_2 and were able to obtain an accurate value for $\tilde{\alpha}$ based on the He concentration.[17] In these measurements, however, the concentration of helium was indirectly obtained from the concentration of all other gases, leading to a low precision of the final value.

5.2.3. Addition of the Internal Standard to the Effluent Gas

In order to overcome the limitations of methods 5.2.1 and 5.2.2 when working with plasmas, the internal reference gas should simply be introduced between the exhaust of the reactor and the point of measurement of concentrations. In an extensive review of plasma reforming of methane, however, we have not found any reference to this procedure. We have used this procedure in our measurements on CH_4/CO_2 mixtures and found significant differences in the values of process parameters.

6. Measurement of $\tilde{\alpha}$

Let Φ_{st} represent the flux of the internal standard gas. As a result of the mixing of Φ_{st} with the process gas, the measured concentrations, $\tilde{c}_m$, have to be corrected for the value without mixing. Without plasma, the relationship is

$$c^o = c^o_m(1+\beta) \tag{27}$$

where $\beta = \Phi_{st}/\Phi_e$ and the index ^{o} indicates the values without plasma. With plasma, the relationship is

$$\tilde{c} = \tilde{c}_m\left(1+\frac{\beta}{\tilde{\alpha}}\right) . \tag{28}$$

The value of $\tilde{\alpha}$ can be obtained from the ratio of standard gas signals without, A^o_{st}, and with plasma, A_{st}. This signal is proportional to the dilution of this gas in the total flux, i.e.,

$$A_{st} \propto \frac{\Phi_{st}}{\Phi+\Phi_{st}} .$$

Keeping the flux Φ_{st} constant, we have

$$\frac{A^o_{st}}{A_{st}} = \frac{\tilde{\Phi}_x+\Phi_{st}}{\Phi_e+\Phi_{st}}$$

or

$$\frac{A^o_{st}}{A_{st}} = \frac{\tilde{\alpha}+\beta}{1+\beta},$$

from which we obtain

$$\tilde{\alpha} = \frac{A^o_{st}}{A_{st}}(1+\beta)-\beta\,. \tag{29}$$

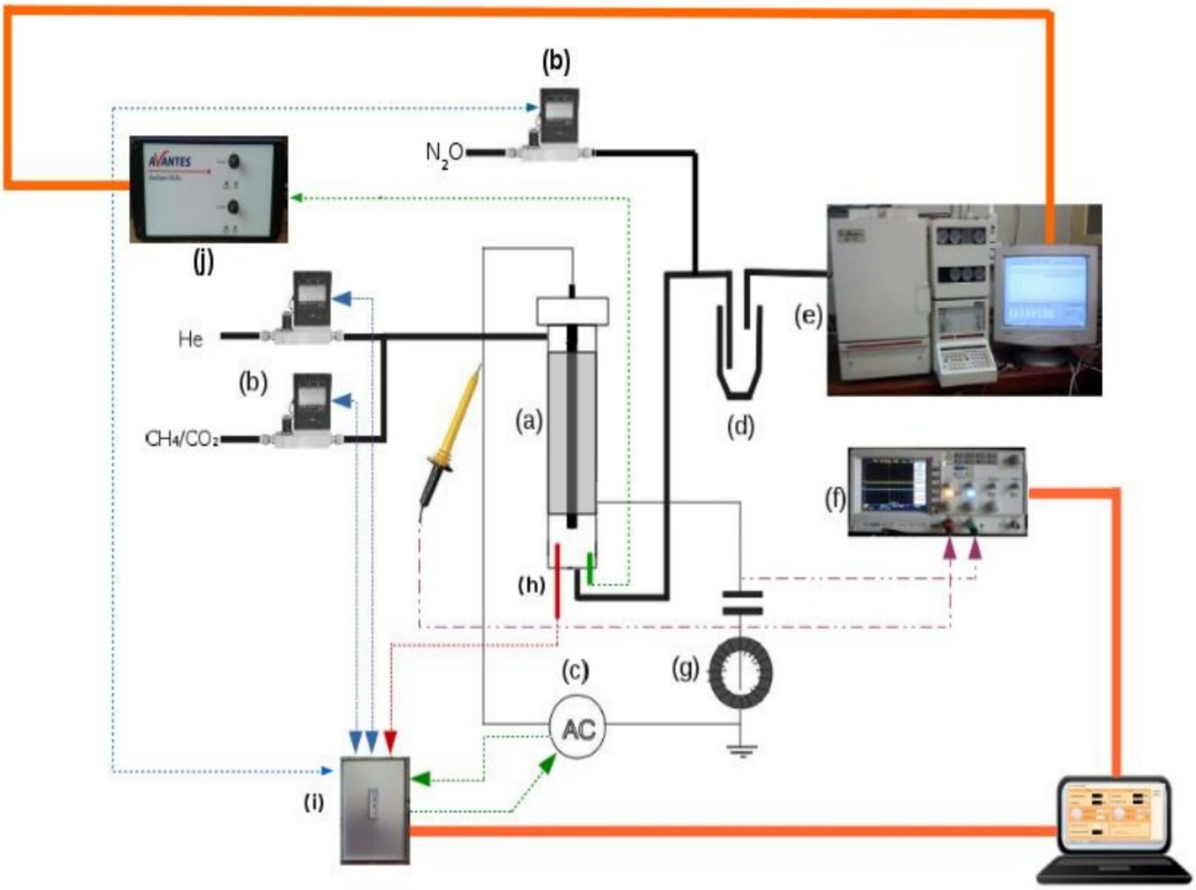

Figure 5: (color online) Schematics of the experimental system: (a) DBD reactor; (b) mass flow controllers; (c) power supply; (d) trap; (e) GC; (f) oscilloscope; (g) Rogowsky coil; (h) thermocouple; (i) DAQ; (j) UV-Vis spectrometer.

If $\Phi_{st} \ll \Phi_e$ then $c^o \approx c^o_m$, $\tilde{c} \approx \tilde{c}_m$, and $\tilde{\alpha} \approx A^o_{st}/A_{st}$. Note that in order to obtain $\tilde{\alpha}$ we only need to know the signal of the standard gas and not its actual concentration, i.e. a calibration for the standard gas is not needed.

Comparing with method 5.1 the measurement of $\tilde{\alpha}$ is easier to implement as the required signals A^o_{st} and A_{st} are obtained simultaneously with the concentration measurements.

6.1. Experimental System

We applied this method, adding the internal standard gas to the exit of the reactor, to study the dry reforming of methane in a DBD reactor using CH_4/CO_2 mixtures. As our interest lies in the discussion of the measurement of $\tilde{\alpha}$, we describe in detail only the relevant components for this study. The experimental system (Fig. 5) comprises (a) a cylindrical DBD reactor, (b) mass flow controllers for He, CH_4/CO_2 mixture (with $c_{CH_4}/c_{CO_2} = 1$) and the internal standard gas. The flux Φ_r was on the range $\Phi_r = (25 \text{ to } 50)\,\mathrm{ml\,min^{-1}}$. N_2O with a flux of $1\,\mathrm{ml\,min^{-1}}$ was chosen as internal standard because it does not overlap with other gases in the chromatogram. The reactor is powered by (c) AC or pulsed power supplies. At the exit of the reactor a (d) trap cooled at 0 °C collects the liquid products. The output gas composition was analyzed online by (e) gas chromatography using a Restek$^{\mathrm{TM}}$ ShinCarbon ST column (L = 2.0 m, f = 1/8 r, ID = 1 mm, 100/200 mesh) and a Shimadzu$^{\mathrm{TM}}$ 9A GC equipped with a thermal conductivity detector (TCD) and a 6-port gas sampling valve with a 0.25 µl loop. The (1σ) uncertainty on species mole fraction is lower than one percentage point. A (f) GDS-2000A oscilloscope and (g) Rogowsky coil were used to obtain the plasma voltage, current and power from V-Q diagrams (for AC power supply) or direct integration (for pulsed power). The exhaust gas temperature was monitored with (h) a thermocouple and (j) from the emission of the CH ($A\,^2\Delta \rightarrow X\,^2\Pi$) band. The experiment was controlled by a local-made software interfaced with a (i) data acquisition board. The gases were supplied by AirLiquide$^{\mathrm{TM}}$ and of "research grade" purity (Alphagas 2).

6.2. Results

A preliminary analysis of the results for $\tilde{\alpha}$ was shown in [28]. Here we extend the discussion by estimating α. We started by testing the composition of the CH_4/CO_2 mixture and found a ratio of $c_{\mathrm{CH_4}}/c_{\mathrm{CO_2}} = 1.09(3)$, ($2\sigma$) for the concentrations.

6.2.1. He/CH_4/CO_2 mixture

The first tests were conducted in He/CH_4/CO_2 mixtures similar to those used in [17]. In order to test the sensitivity of the method, we choose mixtures with helium concentrations of (85, 80 and 75) %. Previous results [17] have shown that with these concentrations, the products of the rate of conversion and concentration for each reactant, show a maximum. The carbon, oxygen and hydrogen balance, calculated from equation (16) neglecting condensation, were $b_C = 1.00(2)$, $b_O = 0.99(2)$ and $b_H = 0.95(2)$. From these results we cannot exclude a small formation of water vapor and subsequent condensation. Applying equation (17) to the O- and H-balances, we could estimate a water vapor concentration at the exit of the reactor between 0.01(5) % and 0.80(2) %, increasing with SEI. Overall, in our conditions and within the experimental uncertainty, we can assume that, $\alpha \approx \tilde{\alpha}$.

Figure 6 shows the results for $\tilde{\alpha}$ for these three values of helium concentration. The error bars are the (2σ) uncertainties and the lines the least-square fit results. The relative uncertainties are

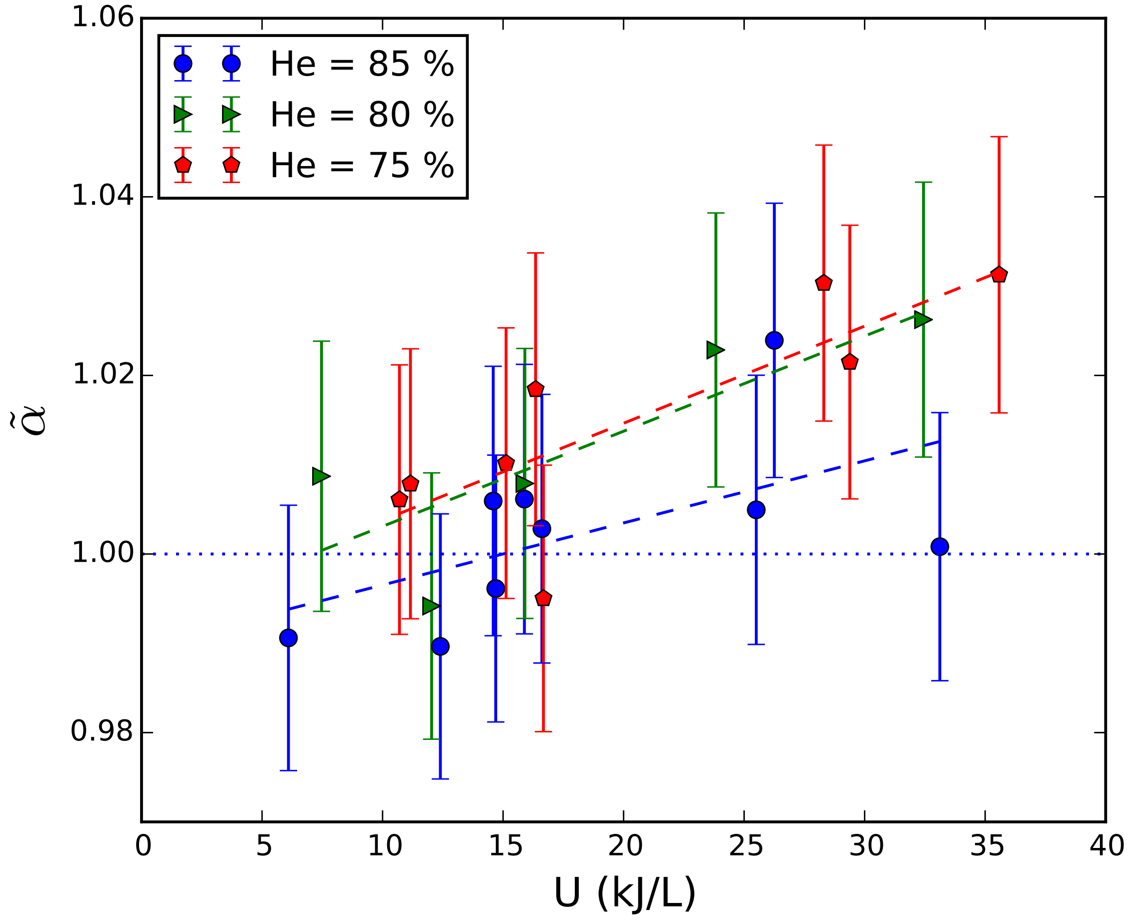

Figure 6: (color online) Dry reforming of He/CH_4/CO_2 mixtures, with [CH_4]:[CO_2] = 1, in a DBD reactor powered by a pulsed power supply: Ratio between the effluent and inlet gas fluxes as a function of the specific energy input, measured after a cold trap.

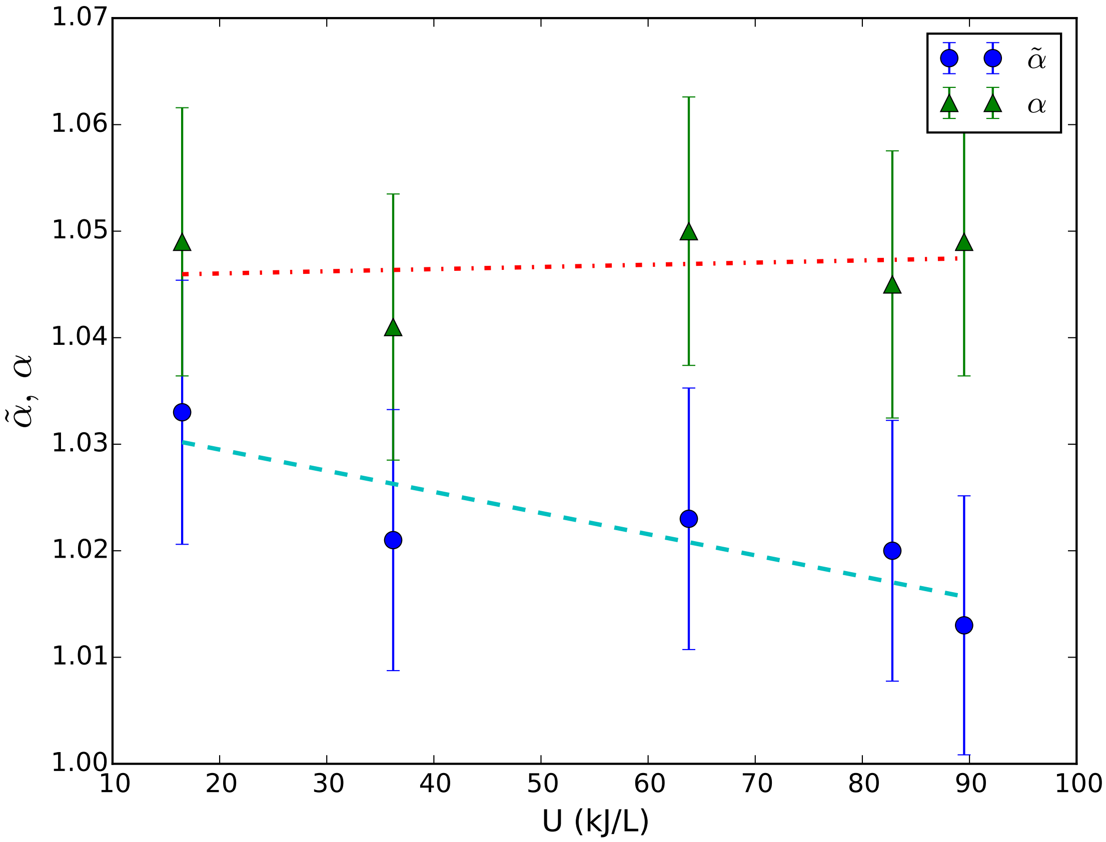

Figure 7: (color online) Flux ratios in a CH_4/CO_2 mixture with $[CH_4]$:$[CO_2] = 1$ on a DBD reactor powered by an AC power supply. $\tilde{\alpha}$ is obtained from equation (29) while α is estimated from equations (9) and (17).

high and the variation in the flux ratio is small but, at least for two mixtures (with 75 % and 80 % helium), we can conclude that there is linear increase of $\tilde{\alpha}$ with SEI. In case of the mixture with 85 % helium, although the results seem to increase with SEI, the values are not statisticaly different from one.

The results show that, even with a high concentration of neutral gas where we expect a small variation in flux, the method is sufficiently sensitive.

6.2.2. CH_4/CO_2 mixture

We measured an average increase of temperature of the effluent gas with the discharge of $\Delta T = 10\,\mathrm{K}$. The carbon, oxygen and hydrogen balances decrease with U. While the variation of the former two are small and within the experimental uncertainty, the decrease in the hydrogen balance indicates the formation of condensable products. After several hours of functioning we observed a thin carbon layer and liquid drops on the reactor walls. In the cold trap, however, we did not observe any condensation. We weighted the reactor and measured an increase of approximately 40 mg but were unable to identify the composition of the deposits or to calculate a reaction yield. Previous studies, however, have identified the main condensables as water or different types of oxygenate containing one oxygen atom in their structure (e.g. alcohols)[29, 30].

The results for $\tilde{\alpha}$ are shown in figure 7. Despite an increase of conversion with U, the values of $\tilde{\alpha}$ decrease. This can be explained by an increase in the production of condensable products with U, which is consistent with the observed decrease of the carbon, oxygen and hydrogen balances. Considering the small variation in carbon balance, we have used equation (17) for oxygen to estimate the sum of condensables, ${\sum_k}' c_{k,p}$, and then equation (9) to obtain α. We found a variation in the total concentration of condensables with U in the range (1.6 to 3.6) %. The results for α are also shown in figure 7. In this case α is slightly increasing with U. Using equation (6) we could estimate the stoichiometric ratio and found a variation with U between 1.32 and 1.13, an indication that an increase in the energy density deposited favours the formation of more complex products.

6.3. Process Parameters on the CH_4/CO_2 mixture

We started by comparing the values obtained for conversion, with previous results obtained in DBD reactors with AC power supplies [31–36]. The results shown on figure 8, were computed without including $\tilde{\alpha}$. The curved lines represent the best fit of functions of type $X(\mathrm{SEI}) = X_M(1 - \exp(-k[\mathrm{SEI}])$ to the results. The agreement between the present results and previous results is satisfactory, in particular with the results of references [31, 36].

These results, however, should be corrected to include the effect of gas expansion. The effect of $\tilde{\alpha}$ or α on different process parameters can be seen in figure 9 where the correct values are compared with expressions neglecting $\tilde{\alpha}$ or α. As for τ and U, with the measured temperature increase, ΔT, we obtain $\tau/\tau_0 = U/[\mathrm{SEI}] \approx 0.88$. The relative errors from neglecting $\tilde{\alpha}$ on X_{CH_4} decrease from (26 to 2) % with U, with the remaining parameters following the same trend. Comparing with figure 1 for the same conversion, these values are much lower indicating that the set of reactions in a plasma is more complex than assumed in that figure. Of special note are the results for the chemical energy efficiency, showing that the correct values are even smaller than usually assumed.

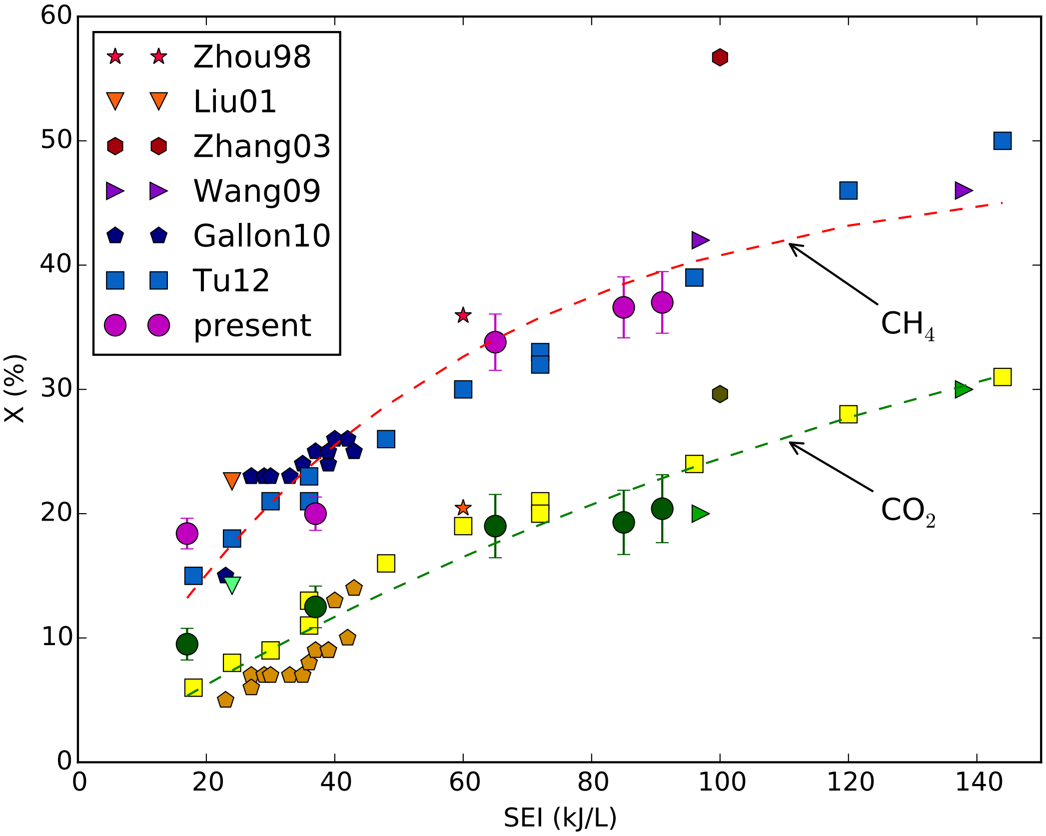

Figure 8: (color online) Conversion of CH_4 and CO_2 as a function of SEI, obtained in CH_4/CO_2 mixtures with $[CH_4]:[CO_2] = 1$ on a DBD reactor powered by an AC power supply. Comparison of the present results with previous results [31–36].

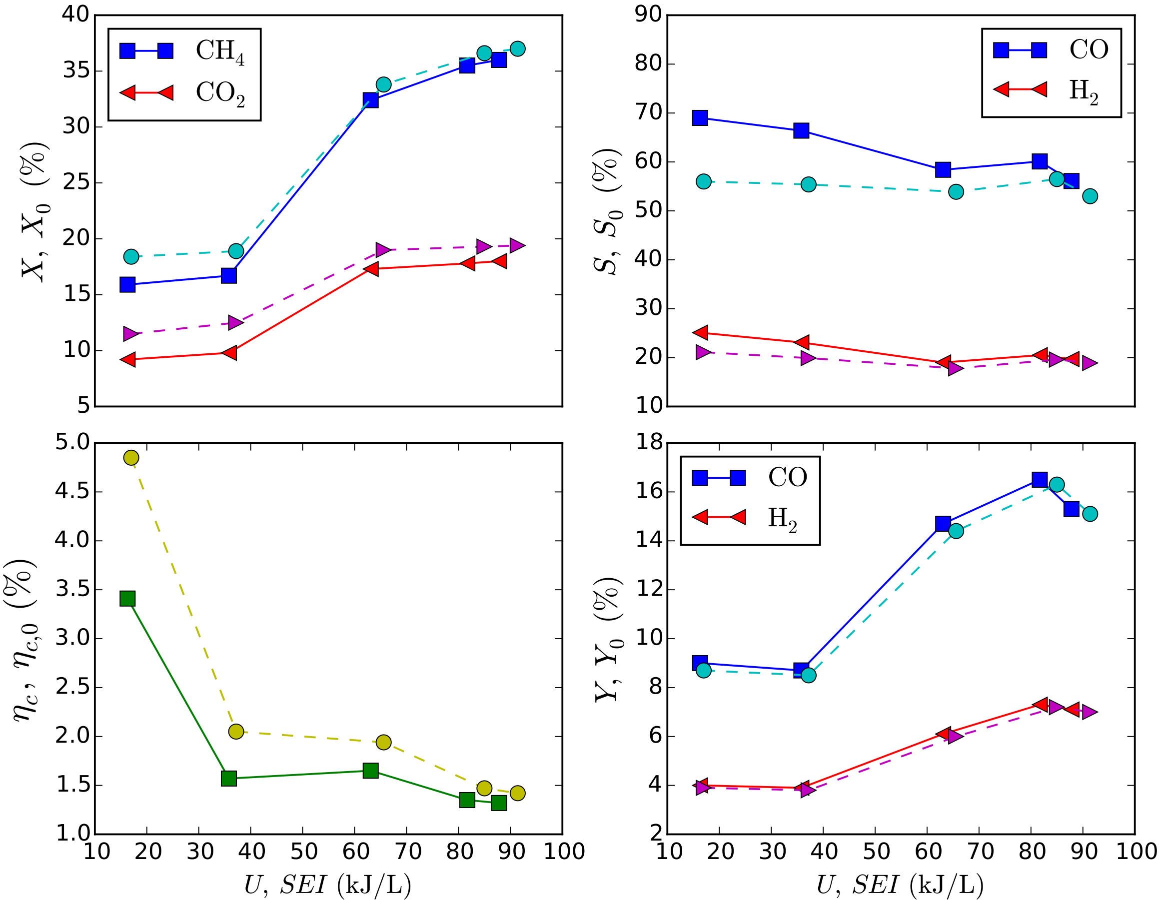

Figure 9: (color online) Process parameters as a function of the energy density. Same conditions as in figure 7. Clockwise, from left: conversion, selectivity, yield and chemical energy efficiency. The full lines are the correct values plotted against U while the dashed lines are plotted against SEI neglecting $\tilde{\alpha}$.

7. Conclusions

The computation of process parameters in plug-flow reactors should take into account the change in gas flux along the reactor resulting from reactions and the change in gas temperature. Neglecting this change introduces a systematic error on these parameters, that can reach very significant values.

Process parameters can be written as functions of concentrations and the ratio between the inlet and effluent gas fluxes. This ratio can be obtained from direct measurement of the fluxes or, indirectly, from a quantity proportional to the flux.

We discuss the addition of an internal standard to the effluent gas from the reactor to measure this flux ratio. Compared with other available methods, this has the following advantages: (i) easy to implement; (ii) does not require preliminary calibrations; (iii) does not interfere with the reactor processes and, (iv) can be used with any gas mixture.

The measurement of the flux ratio also allows the overall stoichiometric ratio and, in favourable conditions, the amount of condensables to be estimated.

In test mixtures, the proposed method allowed obtaining the flux ratio $\tilde{\alpha}$ with sufficient precision and to improve the accuracy of process parameters, to quantify the systematic error if the changes in particle flux are neglected, and to estimate the fraction of condensables.

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