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Modelling the dynamics of hydrogen synthesis from methane in nanosecond-pulsed plasmas

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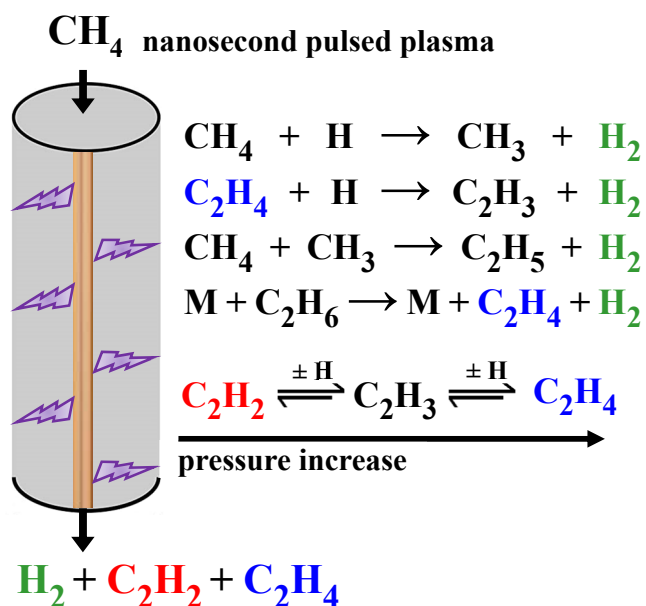
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Abstract

A chemical kinetics model was developed to characterise the gas-phase dynamics of H₂ production in nanosecond-pulsed CH₄ plasmas. Pulsed behaviour was observed in the calculated electric field, electron temperature and species densities at all pressures. The model agrees reasonably with experimental results, showing CH₄ conversion at 30% and C₂H₂ and H₂ as major products. The underlying mechanisms in CH₄ dissociation and H₂ formation were analysed, highlighting the large contribution of vibrationally excited CH₄ and H₂ to coupling energy from the plasma into gas-phase heating, and revealing that H₂ synthesis is not affected by applied pressure, with selectivity remaining unchanged at ~ 42% in the 1 to 5 bar range.



Keywords

Hydrogen; chemical kinetics model; nanosecond pulsed discharges; methane; reaction mechanism

1. Introduction

As society turns away from finite and non-renewable fossil fuel resources, hydrogen production (for numerous applications) becomes a critical research subject within the efforts to remodel the framework for energy generation. Sustainable and efficient CO₂-free H₂ production can be accomplished by plasma-based CH₄ conversion [1]–[4]. The clear advantage of employing plasma technology in this process is related with the ease to avail of the current renewable energy infrastructure (i.e. solar, hydroelectric, wind, etc.) to promote CH₄ dissociation and conversion [3]–[5]. In turn, plasma can forgo indirect CO₂ emissions from the traditional fossil-fuel-based energy sources currently applied in CH₄ reforming for reactor heating [6], resulting in a fully circular carbon process.

Even though the utilisation of plasma in CH₄ reforming is in rapid expansion, there is a gap to be bridged between plasma-assisted CH₄ conversion and conventional processes in terms of operating efficiency and stability, selectivity and addition of catalysts [3], [7]. A variety of plasma reactors (in the thermal, warm and non-thermal plasma regimes) has been tested in CH₄ reforming [2]–[4], [8], [9], each yielding significantly different CH₄ conversions and product selectivity, mainly depending on the electron and gas temperature [4], [8]. Generally, warm plasmas, such as microwave and gliding arc plasmas, are preferred for H₂ generation, as the gas temperature (in the range of a few 1000 K) favours dehydrogenation of C_xH_y species, directing the selectivity towards C_(s) and C₂H₂ (and consequently H₂) [1], [2], [10].

More recently, the utilisation of nanosecond pulsed discharges (NPD) in CH₄ conversion has been reported with considerably high CH₄ conversion (between 40 and 50%) and varying C₂H₂, C₂H₄ and C₂H₆ product distribution [11]–[13]. The versatile selectivity observed in NPD plasmas is attributed to the low degree of thermal equilibrium in pulsed plasma environments, which is ideal for applications in gas conversion, as the reactions can be driven towards specific products by changing the pulse frequency, input power and applied pressure [11], [14]–[16]. Concerning H₂ generation from CH₄ streams treated with pulsed plasmas, the mechanism of H₂ synthesis in the non-oxidative CH₄ conversion (NOMC) has not yet been elucidated and the influence of pressure on the gas-phase H₂ formation and dissociation dynamics remains unexplored [8], leaving questions about optimal operational conditions and posing difficulties to potential industrial applications [1].

This work aims to model in zero dimensions the gas-phase kinetics of an NPD CH₄ plasma to shed light on the reaction pathways of CH₄ dissociation and those of H₂ generation, consumption and (de)excitation, as well as clarify the role of applied pressure in these processes. The model also considers the vibrational excitation and relaxation kinetics of CH₄ and H₂, demonstrating how these are intimately related to gas-phase heating following the pulsed plasma discharges.

2. Description of the plasma chemical kinetics model

2.1. Numerical details

The zero-dimensional chemical kinetics model was constructed using the ZDPlasKin kinetic solver which evaluates the continuity differential equations for all chemical species p considered in the model with number density $n_p(t)$.

$$\frac{dn_p}{dt} = \sum_r C_{r,p} k_r \prod_q n_q \quad (1)$$

where $C_{r,p}$ is the stoichiometric coefficient of a given species p in reaction r , k_r is the rate coefficient of reaction r and q is the colliding species in this process. Reactions which do not involve electron collisions have their rate coefficients k_r retrieved from the literature. k_r is often given within a temperature range and written as a function of gas temperature. In the case of electron impact reactions, k_r is extracted from continuous evaluation of collisional cross sections and the electron energy distribution function (EEDF) via the BOLSIG+ solver. BOLSIG+ operates in tandem with ZDPlasKin and requires the electric field and mean electron energy (provided by the EEDF) as inputs to return rate coefficients for electron impact reactions. ZDPlasKin was also utilised to self-consistently calculate the gas temperature as a function of time via the variation in the reaction enthalpies included in the model [17]. The model assumes that T_{gas} (in Kelvin) is identical for all neutral species, solving the adiabatic isometric heat transport equation with time [18]:

$$\frac{dT_{\text{gas}}}{dt} = (P_{e,el} + \sum_j R_j \Delta H_j - P_{ext}) / (N \frac{\gamma k}{\gamma - 1}) \quad (2)$$

where $N = \sum n_i$ is the total neutral species density, γ is the specific heat ratio of the total gas mixture, k is the Boltzmann constant (in J K^{-1}), $P_{e,el}$ is the gas heating power density due to elastic electron-neutral collisions (in W m^{-3}), R_j is the rate of reaction j (in $\text{m}^{-3} \text{s}^{-1}$), ΔH_j is the heat released (or consumed when this value is negative) by reaction j (in J) and P_{ext} is the heat loss due to energy exchange with the surroundings (in W m^{-3}). The latter is given by the equation:

$$P_{ext} = \frac{8\lambda_{\text{CH}_4}}{r^2} (T_{\text{gas}} - T_{\text{gas,edge}}) \quad (3)$$

With r being the radius of the plasma zone, T_{gas} the plasma gas temperature and $T_{\text{gas,edge}}$ the gas temperature at the edge of the plasma zone, which is assumed to be the average between room temperature and the plasma temperature, according to Berthelot [19]. The gas thermal conductivity of CH_4 , λ (in $\text{W cm}^{-1} \text{K}^{-1}$), was taken from Hepburn et al.[20] and can be expressed as:

$$\lambda_{CH_4} = (1.49 \times 10^{-6}) * T_{gas} - 9.92 \times 10^{-5} \quad (4)$$

It should be noted that this model investigates the gas temperature in the plasma volume confined within the reactor (a finite element volume) by evaluating the reaction enthalpy of all the chemical reactions considered. It does not account for convective heat transfer since the gas flow is not included in the temperature calculations. Thus, the gas temperatures in the model may not reflect the gas temperature in the whole reactor body. More details about ZDPlasKin and BOLSIG+ can be found in [18], [21].

2.2. Chemistry component

The species included in the model are shown in Table 1. Electron impact and recombination reactions for all species were considered in this study. For a complete list of the reactions and corresponding rate coefficients (including interactions between vibrational levels), as well as relevant citations, we refer to our previous work [16], where we studied the generation of olefins from CH₄/H₂ NPD plasmas in experiments and via 0D modelling, highlighting the effect of pressure on C₂H₄ production.

Table 1. Species considered in the model.

Stable molecules	Radicals	Ions and electrons	Excited molecules
CH ₄ H ₂ C ₂ H ₂ C ₂ H ₄ C ₂ H ₆ C ₃ H ₆ C ₃ H ₈ C ₄ H ₁₀ C _(s)	C C ₂ C ₃ H CH ₃ CH ₂ CH C ₂ H C ₂ H ₃ C ₂ H ₅ C ₃ H ₅ C ₃ H ₇ C ₄ H ₉	H ⁺ H ₂ ⁺ H ₃ ⁺ C ⁺ C ₂ ⁺ CH ⁺ CH ₂ ⁺ CH ₃ ⁺ CH ₄ ⁺ CH ₅ ⁺ C ₂ H ⁺ C ₂ H ₂ ⁺ C ₂ H ₃ ⁺ C ₂ H ₄ ⁺ C ₂ H ₅ ⁺ C ₂ H ₆ ⁺ H ⁻ CH ⁻ CH ₂ ⁻ electrons	Vibrational: H ₂ (v = 1...14) CH ₄ (v = 1...4) Electronic: H ₂ * and CH ₄ *

2.3. Power input and number of pulses

The model was developed to investigate the results from CH₄ conversion experiments using a NPD source (n-PS, NPG-18/100k, Megaimpulse Ltd.) carried out in a coaxial configuration with a length of 25 cm and a plasma gap of 4.2 cm (the radii of the inner and outer electrode are 1.0 and 5.2 cm, respectively). The details related to reactor geometry, laboratory apparatus and experimental conditions are described in [22], [23]. In order to mimic the experimental conditions, the following parameters were applied in the model: a gas feed composition of 100% CH₄, flow rate of 200 sccm, pulse frequency of 3 kHz, residence time of 27.8 ms (i.e. time spent by the gas in the reactor) and volume of the plasma region as ~ 2% of the total reactor volume. The plasma volume was estimated considering that the diameter of an NPD streamer (taken as a column) is ~ 0.3 mm at the operating conditions [24], and the total effective reactor volume is the space defined by the NPD diameter and the plasma reactor cross-section area. Since the NPD streamer is randomly ignited around the HV electrode, the plasma volume is assumed to be equal to the total effective reactor volume occupied by each NPD event, which is approximately 2%. The number of pulses in the simulations was adjusted by multiplying the total number of pulses in the residence time by the percentage plasma

volume, which resulted in 16.7 pulses. This was then rounded to a constant number of 15 modelled pulses (i.e. molecules traversing the reactor experience one pulse every 1.9 ms, as shown in Figure 1), which is sufficient to drive this plasma system to steady state.

Power density was inserted into the model using the approach described in our previous work [16], where the power profile of pulses, and the current and voltage traces (at each studied pressure) can be found. In accordance with experimental observations [22], [25], the present work considers the pressure effect on the power density, i.e. the energy discharged by the pulses is lowered upon increasing pressure (as pulse duration is shortened), and the power pulses were constructed as asymmetrical triangles with shorter upslopes and longer downslopes.

2.4. Conversion and selectivity

The equations used to calculate experimental and modelled CH₄ conversion, and hydrocarbon and H₂ selectivity are as follows:

$$\chi_{CH_4}(\%) = 1 - \frac{n_{CH_4 f} (cm^{-3}) * v_f (cm s^{-1})}{n_{CH_4 i} (cm^{-3}) * v_i (cm s^{-1})} \times 100\% \quad (6)$$

$$S_{C_xH_y}(\%) = \frac{x n_{C_xH_y} (cm^{-3}) * v_f (cm s^{-1})}{n_{CH_4 i} (cm^{-3}) * v_i (cm s^{-1}) - n_{CH_4 f} (cm^{-3}) * v_f (cm s^{-1})} \times 100\% \quad (7)$$

$$S_{H_2}(\%) = \frac{\frac{1}{2} * n_{H_2} (cm^{-3}) * v_f (cm s^{-1})}{n_{CH_4 i} (cm^{-3}) * v_i (cm s^{-1}) - n_{CH_4 f} (cm^{-3}) * v_f (cm s^{-1})} \times 100\% \quad (8)$$

where $n_{CH_4 f}$ and v_f are the CH₄ density and velocity at steady state, $n_{CH_4 i}$ and v_i are the initial CH₄ density and velocity, and $n_{C_xH_y}$ and n_{H_2} are the densities of any hydrocarbon and H₂ in the steady state, respectively. The velocity (given by the flow rate divided by the cross sectional area of the reactor) is considered in these equations to correct the conversion and selectivity calculations, accounting for the effect of pressure changes (due to gas expansion and temperature increase) on the flow rate, which is self-consistently calculated in the model at each simulation step.

3. Results and discussion

3.1. Modelled plasma characteristics

The peak power density, pulse duration and energy per pulse implemented in the model, and the response of the calculated maximum reduced electric field, electron density and electron temperature (i.e. at the peak of the pulses) at each applied pressure are summarised in Table 2.

Table 2. Pulse characteristics in the model and calculated maximum electron density (n_e), maximum electron temperature (T_e) and maximum reduced electric field (E/N) at different pressures. The experimentally estimation maximum E/N values are shown in the last column for comparison (the value marked with * was estimated at 3.3 bar)

[22]. Experimental assessment of E/N was carried out via the capacitive probe method described in [24], determining the field (E), given by the electric potential (V) across the electrodes divided by the length of the discharge gap (l), and assuming a constant neutral species density $N = 2.66 \times 10^{19} \text{ cm}^{-3}$.

Pressure (bar)	Pulse characteristics			n_e max (cm^{-3})	T_e max (eV)	E/N max (Td)	Measured E/N max (Td)
	Peak power density (MW · cm^{-3})	Duration (ns)	Energy (mJ)				
1	183.2	18.0	19.2	1.0×10^{16}	4.4	345.6	244
2	205.3	14.2	17.1	8.2×10^{15}	4.1	280.6	163
3	213.1	12.3	15.3	7.0×10^{15}	3.9	247.0	102*
4	239.2	10.7	15.0	6.1×10^{15}	3.7	215.4	
5	270.4	9.36	14.8	4.5×10^{15}	3.6	181.9	70

As the duration of the pulses decreases with rising pressure, less energy per pulse is channelled into the reactor, despite the higher peak power density. This observation is consistent with the experimental results published by Delikonstantis et al. for NPD CH_4 plasmas in the 1 to 5 bar pressure range [22], and it is also in line with modelled trends for other pressurised NPD systems [14], [23], [26], [27]. The calculated response of the reduced electric field (and in turn that of the electron temperature) to the power pulses exhibits pulsed behaviour (top and middle plots in Figure 1), with peaks registered in the beginning of each power density pulse. This observation is as expected since the model applies the power input to compute the electric field, which is transferred to BOLSIG+ for EEDF and electron temperature calculations. The latter governs the energy of the electrons in the plasma which becomes high during the pulses, triggering electron impact dissociation of CH_4 molecules upon power application. As the reduced electric field is inversely proportional to the density of gas-phase species, the modelled maximum values of E/N are reduced as the pressure is increased. This is also observed in the experimental estimations of E/N (see last column in Table 2). The discrepancy in the absolute values of modelled versus experimental E/N is likely due to the nanoscale duration of the pulses and deposition of solid carbon on the electrodes, rendering accurate experimental assessment of the electric field very challenging and resulting in delayed (i.e. lower) measurements. On the other hand, the modelled E/N is also subject to uncertainties due to the approximation of spatial independence, inherent to the calculations in a 0D chemical kinetics model.

As illustrated in Figure 1 (bottom plot), the model shows that the electron density also peaks with the power pulses along the residence time, with the maximum varying from $4.5 \times 10^{15} \text{ cm}^{-3}$ at 5 bar to $1.0 \times 10^{16} \text{ cm}^{-3}$ at 1 bar (see Table 2). In line with the pulsed power density, these peaks are intense but short lived, hence both electron density and temperature fall to negligible levels ($1.0 \times 10^9 \text{ cm}^{-3}$ and 0.08 eV) in the absence of power between the pulses. Thus, electron impact processes are halted, and recombination reactions become dominant in the interpulse periods (i.e. in the afterglows). The large increase in the peak of electron density over the second pulse (compared to the first pulse), i.e. at 1.9 ms, is due to the increase in the

reduced electric field, as the gas temperature in the system rises, as discussed also in our previous study [16].

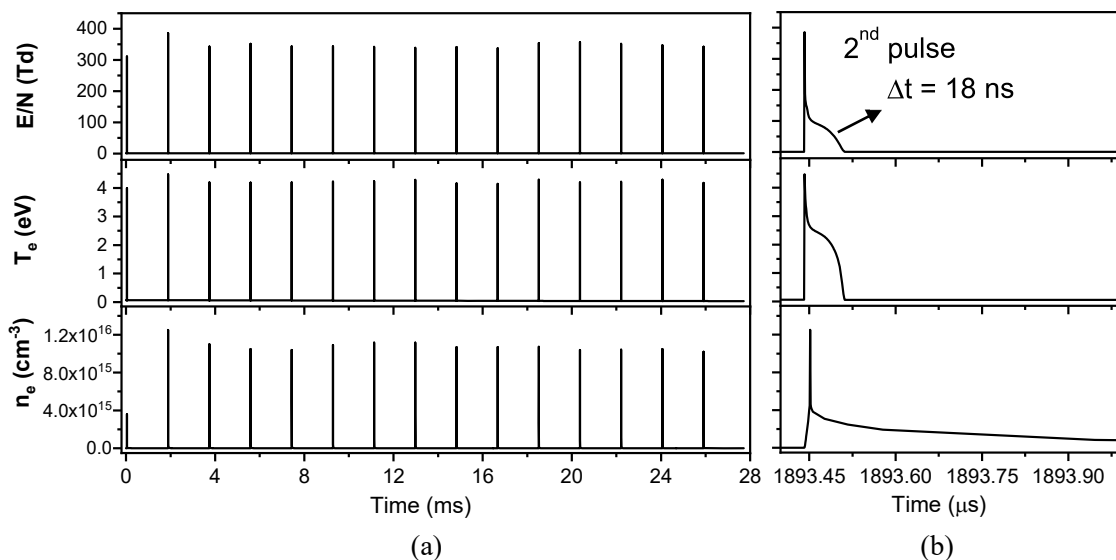


Figure 1. Calculated temporal profile of the reduced electric field E/N (top) and the ensuing responses of the electron temperature, T_e (middle) and electron density, n_e (bottom) (a) in the entire residence time (27.9 ms) and (b) over the second pulse and the beginning of the following afterglow. These calculations were performed at 1 bar.

3.2. Modelled species densities

Consistent with the calculated E/N , electron temperature and density, the density profiles of all species studied in our model also exhibit pulsed behaviour. The density profiles of the main species are plotted in Figure 2. The density of all stable molecules, i.e. CH_4 , H_2 , C_2H_2 and C_2H_4 , fall with the concomitant power pulses, while the radical and ion species pulses exhibit a sharp and rapid peak. These trends are reverted when the pulse ends, i.e. stable species see a steep density increase, whilst those of the radicals and ions sharply drop, and more gradual and slower variations are seen in the afterglows.

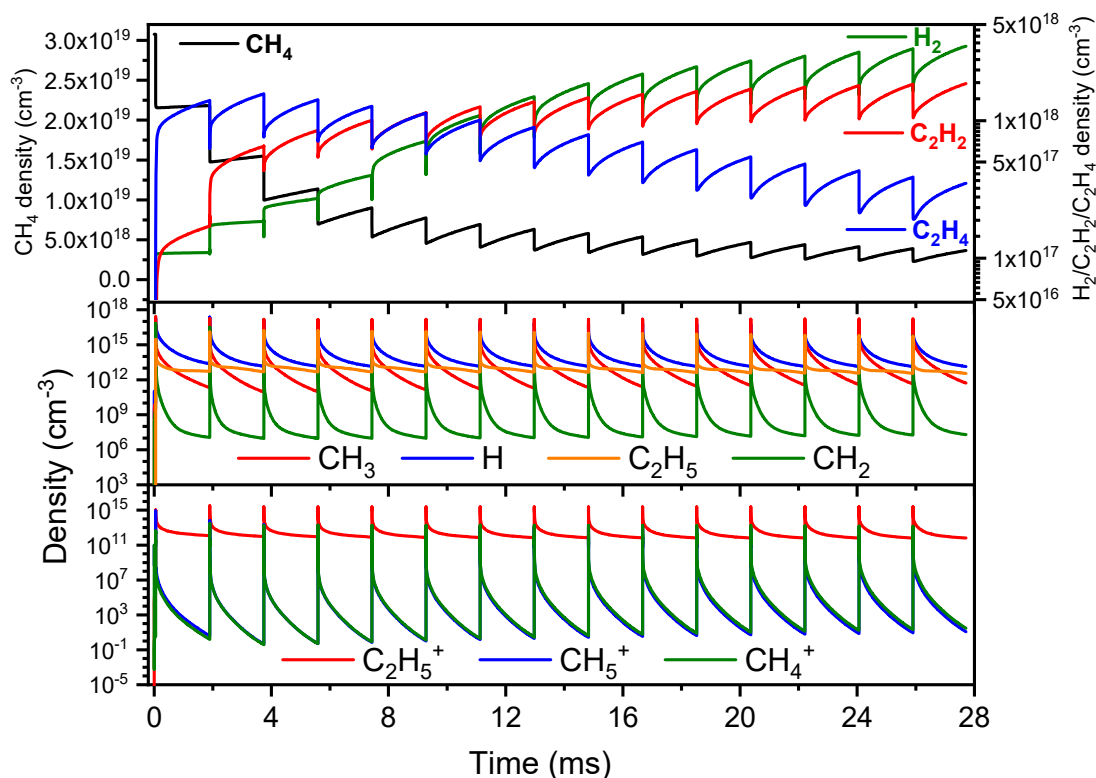


Figure 2. Modelled density profiles of stable molecules with CH₄ being the reactant and H₂, C₂H₂ and C₂H₄ the main gaseous products (top), principal radical species (middle) and main ionic species (bottom) in the simulations. These calculations were performed at 1 bar.

The profiles of the stable molecules (top plot in Figure 2) indicate an overall consumption of CH₄, as the feed molecule is dissociated through electron impact (cf. decrease in density during the pulses) and reformed in the afterglows (exhibiting steady growth) via the CH₃ + H recombination channel. H₂ is the product with highest density in this system, followed by the C₂H₂ and C₂H₄ hydrocarbons. C₂H₆ remains a minor product with much lower densities over the residence time ($\sim 5 \times 10^{16} \text{ cm}^{-3}$). These products also undergo consumption during the pulses (hence the sharp drop in their density profile), however they are reformed in the afterglows, exhibiting a continuous growing density trend as a function of the residence time. The modelled densities of the main radicals and ions (middle and bottom plots in Figure 2) reveal that the order of abundance of these species (during the pulses) is CH₃ > H > C₂H₅ > CH₂ and C₂H₅⁺ > CH₅⁺ > CH₄⁺, respectively. The density peaks are reached via a steep rise during the power pulses and are followed by a (also steep) drop to $\sim 3/4$ of the maximum density as the pulse ends. In the afterglows, the decrease decelerates, resulting in the tails seen in all profiles of the radicals and ions.

3.3. Modelled conversion, selectivity and experimental validation

Figure 3 shows the modelled and experimental trends of CH₄ conversion and product selectivity across the 1 to 5 bar pressure range. The results demonstrate that the applied pressure has an important effect on CH₄

conversion and on product selectivity (although more pronounced in the calculated selectivity trends). Both model and experiments see an increase in CH₄ conversion upon increasing pressure, with peak conversion registered at ~ 3 bar (3.3 bar in the experiments). Further pressure increases appear to have a negative impact, as reduced conversions are observed in the 4 to 5 bar range. While lesser in the experiments, this decrease is very pronounced in the modelled results, leading to considerably lower conversions than that registered at 3 bar.

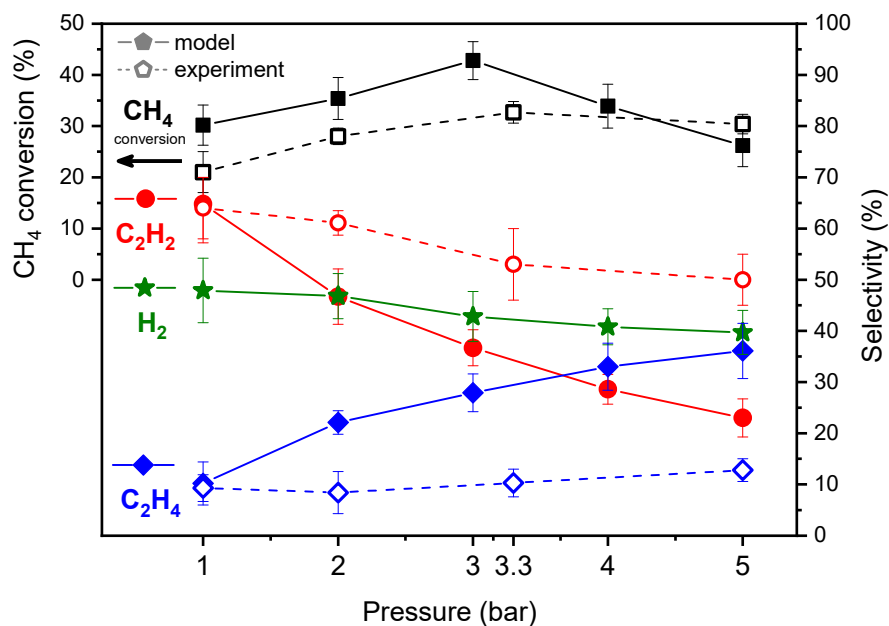


Figure 3. CH₄ conversion and selectivity of H₂, C₂H₂ and C₂H₄. Modelled and experimental results are compared across the 1 to 5 bar pressure range. H₂ selectivity was only assessed in the model. The experiments were carried out at 1, 2, 3.3 and 5 bar and are described in the study by Delikonstantis et al [22], whilst the simulations were run with 1 bar increments.

In terms of selectivity, model and experiments both show C₂H₂ as the main product at 1 bar, followed by H₂ (only modelled selectivity) and C₂H₄. In fact, a remarkably good agreement can be observed at 1 bar and these results tally well with other studies of CH₄ conversion in NPD plasmas [11], [14], [23]. As the pressure is raised, however, model and experiments begin to exhibit discrepancies in the selectivity towards C₂H₂ and C₂H₄. While the C₂H₄ production remains largely unaffected by pressure in the experiments (with selectivity fluctuating around 10%), increased pressures in the model have a strong beneficial effect on C₂H₄ formation. In fact, the model predicts ~ 10% C₂H₄ selectivity at 1 bar (in line with the experiments), growing steadily to 35% at 5 bar. Evidently, the C₂H₂ selectivity sees a concomitant decrease, which is again considerably more accentuated in the model (from 60 to 25%). This trend was also registered in our previous study in CH₄ and H₂ plasmas [16] and in later experimental works by Delikonstantis et al. [11], [23], which reported gains in C₂H₄ selectivity at higher pressures for NOMC in NPD systems. While this discrepancy may signal that the model underestimates the gas temperature at high pressures (in turn leading

to an overestimated ratio between C_2H_4/C_2H_2 selectivity), it may also be an indication that the power inputs in the experiments could have varied with pressure, influencing the average gas temperature, conversion and product distribution. This effect cannot be verified due to unavailability of voltage and current data for these experiments.

Another reason for selectivity discrepancies as a function of pressure may be the effect of soot production, which is widely reported in the experiments, especially in the conditions under study (i.e. in the absence of H_2 in the gas feed), and which is difficult to accurately capture in a 0D model. Albeit detected, the formation of solid particles was not quantified owing to challenges in collecting and measuring the mass of the solids. This model attempted to simulate $C_{(s)}$ formation via stepwise dehydrogenation reactions in the H-Abstraction C_2 -Splitting (HACS) channel, i.e. $C_2H_y \rightarrow 2 C_{(s)} + \frac{y}{2} H_2$ [28]. The results show moderate quantities of $C_{(s)}$ being formed at all pressures, with a maximum concentration of $\sim 6\%$ registered at 1 to 3 bar. The model also predicts that the $C_{(s)}$ concentration decreases above 3 bar, with a minimum of $\sim 1.5\%$ at 5 bar. This also contributes to lowering the CH_4 conversions above 3 bar. However, this trend in $C_{(s)}$ concentration remains unverified awaiting further experimental validation. Most likely, the lower $C_{(s)}$ quantities predicted upon increased pressure reflect the also lower maximum of the gas temperature attained at higher pressures (as previously shown in our CH_4/H_2 plasmas) [16], which reduces the efficiency of the HACS channels, in turn leading to less $C_{(s)}$ [29]. In future works, this approach should be expanded to account for the influence of surfaces on the HACS mechanism, and to include polymerisation via benzene and acetylene monomer additions, which are also important pathways for soot formation [30], [31].

C_2H_6 was only detected in the model as a minor product with very low selectivity across the studied pressure range, but rising from 0.8% at 1 bar to 2.6% at 5 bar. This selectivity increase is readily ascribed to the $CH_3 + CH_3 + M \rightarrow C_2H_6 + M$ recombination reaction which is enhanced by increasing the applied pressure.

Regarding H_2 , this product was not measured in the experiments, thus only the modelled values for selectivity are shown in Figure 3. The H_2 selectivity dwindles slightly as the pressure is increased, falling from 44% at 1 bar to 40% at 5 bar. The decrease is possibly reflected in the C_2H_2 selectivity drop and C_2H_4 selectivity gain (discussed above), as larger quantities of H atoms remain attached to the C_2 hydrocarbon molecules. From an indirect assessment performed via a H balance using the available experimental results [22], the H_2 selectivity does not appear to be pressure dependent in the experiments either, with estimated figures varying between 35 and 45%. Although this H_2 selectivity was obtained via an approximative method (since the experiments do not report the concentrations of C_2H_6 and C_3 species or the composition of the solids produced), this result is generally well aligned with the calculated counterparts. This H_2 selectivity trend suggests that the applied pressure does not affect the rate of H_2 production from CH_4 conversion in NPD plasmas, although direct experimental validation is required to confirm this calculation

result. To corroborate and aid the comprehension of these results, a detailed reaction pathway analysis is presented in section 3.5 below.

Overall, the CH_4 conversion and C_2 selectivity trends in Figure 3 signal reasonable alignment between the model and experiments (especially at 1 bar), which accredits the model's capability to capture the gas-phase kinetics of CH_4 conversion in NPD plasmas.

3.4. Modelled gas temperature and heating dynamics

The temporal evolution of the reaction rates, electron and gas temperatures (self-consistently calculated via the enthalpy variations induced by the processes included in the model, as described in section 2.1 above) was investigated in the 1 to 5 bar pressure range, offering insights into the interplay between temperature, pressure and chemical reactivity. This time-resolved analysis allows for (i) the assessment of the heating dynamics (see Figure 4) and (ii) the study of the CH_4 (and other molecules) dissociation and recombination pathways in this NPD plasma (presented below).

This study has found that vibrational excitation of CH_4 molecules to $\text{CH}_4(v1, 3)$ and $\text{CH}_4(v2, 4)$ does not contribute to CH_4 dissociation, in line with our previous work [16] and other reports on CH_4 conversion [12], [32]–[34], because these excited species undergo nearly instantaneous quenching (~ 50 ns) to ground-state CH_4 via vibrational-translation relaxation. However, unlike in the CH_4/H_2 plasma previously investigated [16], the present model predicts that upon VT relaxation to $\text{CH}_4(v4)$, vibrationally excited $\text{CH}_4(v1, 3)$ and $\text{CH}_4(v2)$ molecules are responsible for over 90% of the heat released into the system in the first three power pulses (see Figure 4).

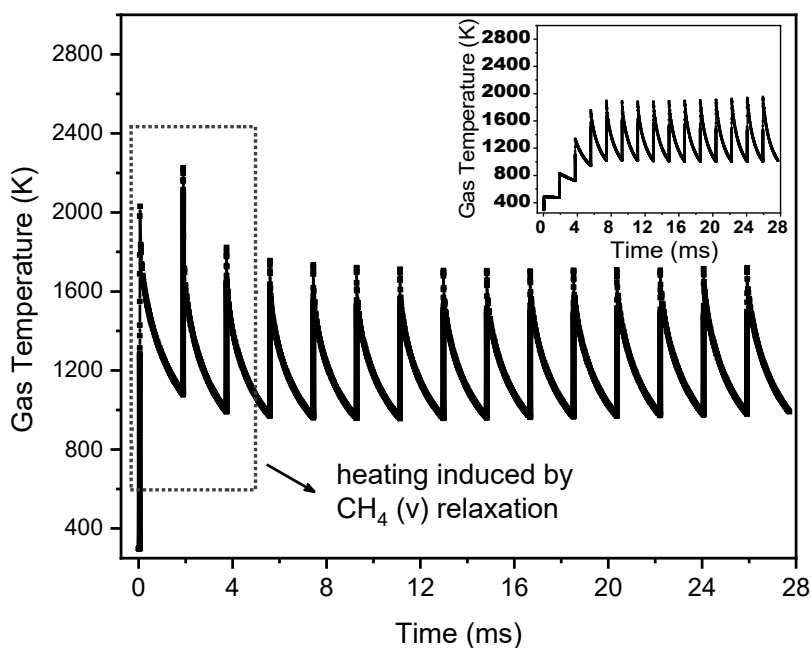


Figure 4. Calculated temperature profile at 1 bar, showing the pulsed evolution of the gas temperature as a function of the residence time. The impact of CH₄ (v) relaxation on the heating dynamics becomes clear by comparison with the inset, which displays a temperature profile calculated in the absence of CH₄ (v) kinetics, highlighting the significant difference in the gas temperature over the first three power pulses.

Four reactions have marked importance in the heat release in the first 4 ms:

- | | |
|--|---|
| 1. CH ₄ (v3) + CH ₄ → CH ₄ (v4) + CH ₄ | $\Delta H = - 20.45 \text{ (kJ mol}^{-1}\text{)}$ |
| 2. CH ₄ (v1) + CH ₄ → CH ₄ (v4) + CH ₄ | $\Delta H = - 19.30 \text{ (kJ mol}^{-1}\text{)}$ |
| 3. CH ₄ (v2) + CH ₄ → CH ₄ (v4) + CH ₄ | $\Delta H = - 2.70 \text{ (kJ mol}^{-1}\text{)}$ |
| 4. CH ₄ (v3) + CH ₄ (v4) → CH ₄ (v4) + CH ₄ (v4) | $\Delta H = - 20.45 \text{ (kJ mol}^{-1}\text{)}$ |

These results suggest that in the absence (and at low densities) of H₂ molecules during the first 4 ms of the simulation (see H₂ density evolution profile in Figure 2), there is no competition between H₂ and CH₄ for electron-impact-driven vibrational excitations, and thus the vibrational levels of CH₄ can be populated to high densities (with a maximum of $4 \times 10^{18} \text{ cm}^{-3}$); and upon relaxation, energy is released as heat. This mechanism of energy coupling into gas-phase heating seems to have low efficiency in the presence of H₂, as the model shows that vibrational excitation of H₂ to H₂ (v1) can be up to 16 times more favourable than that of CH₄ to CH₄ (v1, 3) and CH₄ (v2, 4). This is the reason why heating via CH₄ vibrational deexcitation only prevails in the first 4 ms, prior to any significant H₂ production in pure CH₄ NPD plasmas, and does not seem to occur at all when H₂ is present in the gas feed, as discussed in our previous study [16]. Generally, these results indicate that the vibrational excitation-relaxation of H₂ molecules is more important for gas heating than that of CH₄, after these 4 first pulses, with exothermic vibrational-translational (VT) relaxations of excited H₂ accounting for ~ 28% of the heat released to the gas phase at steady state. Also, the model reveals the other two major contributors to gas heating are (i) elastic momentum transfer (~ 35 %) and (ii) CH₃ + H recombination (~ 37 %).

3.5. Reaction pathway analysis

Figure 5 presents a reaction diagram network, summarising the mechanisms for H₂ (and C₂ hydrocarbon) production under the modelled conditions.

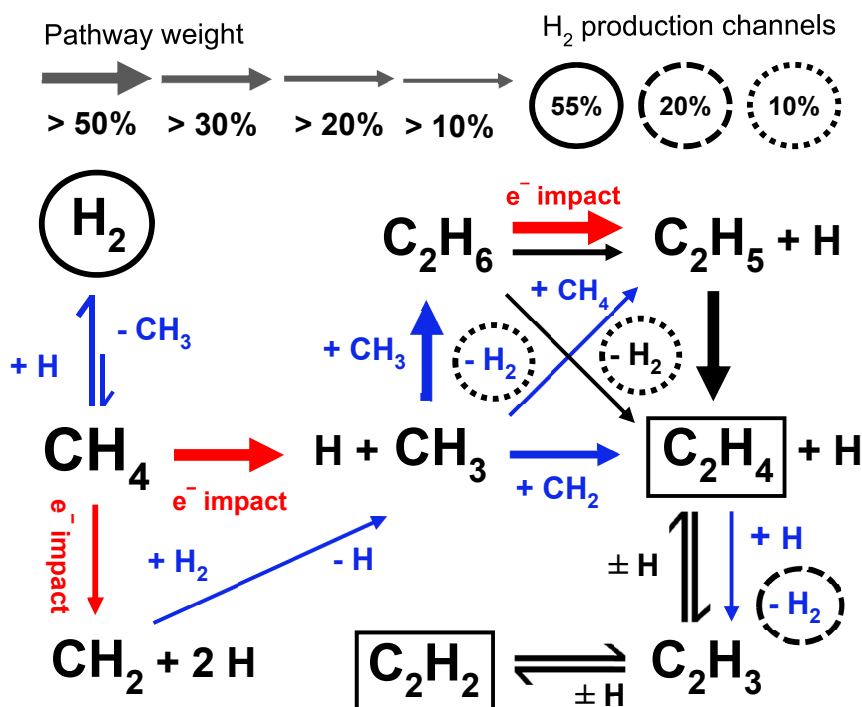


Figure 5. The main reaction pathways involved in the dissociation of CH₄ into H₂ and coupling into C₂ hydrocarbons at steady state. The other H₂ formation channels (involving C₂ hydrocarbons) are also displayed. This analysis is generally valid in the 1 to 5 bar pressure range. The respective percentage contributions are indicated by the circles and the thickness of each arrow is also related to the percentage efficiency of each process (see legend). Electron impact reactions are indicated by red arrows, heavy particle reactions by blue arrows and molecular dissociations by black arrows. The main hydrocarbon products are shown in boxes. Vibrational kinetics are not shown for clarity.

In this pure CH₄ NPD plasma, the dynamics of CH₄ dissociation and radical recombination to C₂ products largely follow the pathways described by our previously discussed CH₄/H₂ model [16]. In brief, the power pulses give rise to a high density of electrons, which collide with incoming CH₄ molecules, triggering C–H bond cleavage into CH₃ (78.4%) and CH₂ (21.0%) (and H) radicals. The principal avenue for CH₄ splitting occurs via electronic excitation through the CH₄^{*} (7.9 eV) state, which undergoes immediate dissociation, accounting for over 90% of all C₁ radical formation [35], [36]. In the afterglows, rapid vibrational relaxation and recombination reactions (the latter taking place on the μs timescale) largely govern the gas-phase chemistry, as electron impact processes are halted. CH₄ molecules are formed anew via the CH₃ + H channel, which gains traction with increasing pressure, elucidating the lower CH₄ conversions in the experiments and model at pressures greater than 3 bar.

The CH₃ and CH₂ radicals also recombine upon C–C coupling, thereby generating the first C₂H₆, C₂H₄ and C₂H₅ species in the system via the reactions: (i) CH₃ + CH₃ → C₂H₆, (ii) CH₃ + CH₂ → C₂H₄ + H and (iii) CH₃ + CH₄ → C₂H₅ + H₂, which account for 22%, 10.5% and 3% of CH₃ radical consumption, respectively, while the CH₃ + H recombination into CH₄ accounts for 64.5% of CH₃ consumption. Akin to the CH₄/H₂

plasma system [16], at the average gas temperatures in the model (> 1000 K), the above radical reactions are followed by stepwise dehydrogenation, eventually leading to C_2H_2 (see Figure 5). The equilibrium of the $C_2H_4 \rightleftharpoons C_2H_3 \pm H \rightleftharpoons C_2H_2$ reactions is regulated by the applied pressure, with C_2H_4 being favoured at pressures greater than 4 bar, whilst C_2H_2 is dominant at lower pressures.

Novel and more noteworthy here are the findings from the kinetics of H_2 production and consumption. At steady state, H_2 is predominantly formed in four reactions, which mainly occur in the afterglows (the respective relative contributions are indicated):

1. $CH_4 + H \rightarrow CH_3 + H_2$ ($\sim 55\%$)
2. $C_2H_4 + H \rightarrow C_2H_3 + H_2$ ($\sim 20\%$)
3. $CH_4 + CH_3 \rightarrow C_2H_5 + H_2$ ($\sim 10\%$)
4. $M + C_2H_6 \rightarrow M + C_2H_4 + H_2$ ($\sim 10\%$)

The relative contributions (also shown in Figure 5) amount to 95% of all H_2 produced when the gas temperature stabilises. From the remaining 5%, 4% are due to H atom recombination in the $M + H + H \rightarrow M + H_2$ reaction (where M is any gas species acting as third body). The latter reaction, alongside $M + C_2H_6 \rightarrow M + C_2H_4 + H_2$, are the only two important pressure-dependent mechanisms for H_2 formation. Since the applied pressure affects these two mechanisms in a competing manner (i.e. the dissociation of C_2H_6 is favoured at lower pressures and inhibited at high pressures, while the applied pressure has the opposite effect on H + H recombination, which is a three-body reaction), it is plausible to posit that pressure will not significantly affect H_2 production in this NPD CH_4 plasma. This is in line with the calculated H_2 selectivity (Figure 3 above), which remains mostly unaffected across the pressure range studied.

Conversely, during the power pulses, H_2 is converted, undergoing electronic and vibrational excitation via impact with hot electrons (and ensuing energy transfer to the gas phase) in the following reactions (i) $H_2 + e^- \rightarrow H_2(v1, 5) + e^-$ and (ii) $H_2 + e^- \rightarrow H_2^* + e^- \rightarrow H + H + e^-$, and ionisation via the (iii) $H_2 + e^- \rightarrow H_2^+ + 2e^-$ reaction. These constitute the three major loss pathways, accounting for 72%, 18% and 4% of the total H_2 reacting in the pulses. The vibrational promotions create an excitation-deexcitation loop (leading to rapid $H_2(v)$ relaxation to H_2 via exothermic VT interactions), which results in the steep rises seen immediately after each pulse in the H_2 density profile in Figure 2 and contributes with $\sim 28\%$ to the heat maintenance mechanism at steady state, as discussed above. While vibrational excitation does not result in H_2 dissociation, electronic excitation to H_2^* (11.83 eV) promptly induces H_2 splitting (as shown in the second reaction above) and ionisation to H_2^+ leads to ion exchange reactions with H_2 and CH_4 (producing H_3^+ , CH_3^+ and CH_5^+), ultimately also contributing to H_2 loss. Combined, these three processes are responsible for $\sim 27\%$ of the total energy consumed in the pulses at steady state. The remaining percentage in energy

consumption is composed of elastic collisions (~ 38%), CH₄ excitation, dissociation and ionisation (~ 21%), and excitations, dissociations and ionisations of other molecules (~ 14%).

4. Conclusions

In this work, a time-resolved 0D chemical kinetics model was developed to investigate an NPD plasma with a gas feed of 100% CH₄, and its conversion into H₂ and C₂ hydrocarbons. The model considered the effect of applied pressure on the pulsed power depositions and on various plasma properties, such as the reduced electric field, electron density and electron temperature at different pressures. The gas temperature was calculated self-consistently with time, based on enthalpy changes induced by the chemical reactions included in the model.

The modelled variations in CH₄ conversion and C₂ hydrocarbon product selectivity as a function of applied pressure were compared with experimental results from literature for pure CH₄ in a coaxial reactor under NPD conditions. Model and experiments are overall well aligned at 1 bar, however the modelled selectivity towards C₂H₂ and C₂H₄ begins to deviate from those measured in the experiments at higher pressures. The discrepancies can be attributed to possible underestimations of gas temperature in the model and also to the difficulties in modelling soot formation which is widely seen in the experiments.

The simulations have shed light on the gas-phase dynamics of CH₄ dissociation and reforming following a mechanistic analysis, which elucidates the reaction pathways involved in the production of H₂ and C₂ species. Analogously, the model predicts that H₂ formation is not affected by the applied pressure (with calculated selectivity around ~ 42% from 1 to 5 bar), as most reactions leading to H₂ are pressure independent, and the two pressure-dependent routes are compensatory. Further, the model also shows that vibrationally excited CH₄ and H₂ molecules play an essential role in coupling the energy from the power pulses into gas-phase heating in this CH₄ NPD plasma.

Prospective work plans to investigate an expanded approach to capture soot formation in the model by including aromatic and linear polymerisation routes and the effect of surfaces on the nucleation of solid particles from the various gas-phase reactants present in the plasma. It would also be of interest to carry out spectroscopic measurements in the plasma region to provide further experimental data for model validation.

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Tables

Table 1. Species considered in the model.

Stable molecules	Radicals	Ions and electrons	Excited molecules
CH ₄ H ₂ C ₂ H ₂ C ₂ H ₄ C ₂ H ₆ C ₃ H ₆ C ₃ H ₈ C ₄ H ₁₀ C _(s)	C C ₂ C ₃ H CH ₃ CH ₂ CH C ₂ H C ₂ H ₃ C ₂ H ₅ C ₃ H ₅ C ₃ H ₇ C ₄ H ₉	H ⁺ H ₂ ⁺ H ₃ ⁺ C ⁺ C ₂ ⁺ CH ⁺ CH ₂ ⁺ CH ₃ ⁺ CH ₄ ⁺ CH ₅ ⁺ C ₂ H ⁺ C ₂ H ₂ ⁺ C ₂ H ₃ ⁺ C ₂ H ₄ ⁺ C ₂ H ₅ ⁺ C ₂ H ₆ ⁺ H ⁻ CH ⁻ CH ₂ ⁻ electrons	Vibrational: H ₂ (v = 1...14) CH ₄ (v = 1...4) Electronic: H ₂ * and CH ₄ *

Table 2. Pulse characteristics in the model and calculated maximum electron density (n_e), maximum electron temperature (T_e) and maximum reduced electric field (E/N) at different pressures. The experimentally estimation

maximum E/N values are shown in the last column for comparison (the value marked with * was estimated at 3.3 bar) [22]. Experimental assessment of E/N was carried out via the capacitive probe method described in [24], determining the field (E), given by the electric potential (V) across the electrodes divided by the length of the discharge gap (l), and assuming a constant neutral species density $N = 2.66 \times 10^{19} \text{ cm}^{-3}$.

Pressure (bar)	Pulse characteristics			n_e max (cm^{-3})	T_e max (eV)	E/N max (Td)	Measured E/N max (Td)
	Peak power density (MW cm^{-3})	Duration (ns)	Energy (mJ)				
1	183.2	18.0	19.2	1.2×10^{16}	4.4	345.6	244
2	205.3	14.2	17.1	8.2×10^{15}	4.1	280.6	163
3	213.1	12.3	15.3	7.0×10^{15}	3.9	247.0	102*
4	239.2	10.7	15.0	6.1×10^{15}	3.7	215.4	
5	270.4	9.36	14.8	4.5×10^{15}	3.6	181.9	70

Figures

Figure 1. Calculated temporal profile of the reduced electric field E/N (top) and the ensuing responses of the electron temperature, T_e (middle) and electron density, n_e (bottom) (a) in the entire residence time (27.9 ms) and (b) over the second pulse and the beginning of the following afterglow. These calculations were performed at 1 bar.

Figure 2. Modelled density profiles of stable molecules with CH₄ being the reactant and H₂, C₂H₂ and C₂H₄ the main gaseous products (top), principal radical species (middle) and main ionic species (bottom) in the simulations. These calculations were performed at 1 bar.

Figure 3. CH₄ conversion and selectivity of H₂, C₂H₂ and C₂H₄. Modelled and experimental results are compared across the 1 to 5 bar pressure range. H₂ selectivity was only assessed in the model. The experiments were carried out at 1, 2, 3.3 and 5 bar and are described in the study by Delikonstantis et al [22], whilst the simulations were run with 1 bar increments.

Figure 4. Calculated temperature profile at 1 bar, showing the pulsed evolution of the gas temperature as a function of the residence time. The impact of CH₄ (v) relaxation on the heating dynamics becomes clear by comparison with the inset, which displays a temperature profile calculated in the absence of CH₄ (v) kinetics, highlighting the significant difference in the gas temperature over the first three power pulses.

Figure 5. The main reaction pathways involved in the dissociation of CH₄ into H₂ and coupling into C₂ hydrocarbons at steady state. The other H₂ formation channels (involving C₂ hydrocarbons) are also displayed. This analysis is generally valid in the 1 to 5 bar pressure range. The respective percentage contributions are indicated by the circles and the thickness of each arrow is also related to the percentage efficiency of each process (see legend). Electron impact reactions are indicated by red arrows, heavy particle reactions by blue arrows and molecular dissociations by black arrows. The main hydrocarbon products are shown in boxes. Vibrational kinetics are not shown for clarity.