

3D phenomenological modeling of plasma-assisted methane reforming

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Natural gas contains a significant fraction of methane, a strong greenhouse gas besides being a potent hydrogen carrier. Thus, reforming methane to a more reactive gas mixture could potentially abate the associated greenhouse heating by depleting methane and provide a pathway to generate hydrogen. The present study investigates the non-equilibrium plasma-assisted reforming of methane to produce hydrogen and reactive alkenes using repetitive nanosecond pulse discharges. A detailed gas-phase chemical kinetics mechanism along with plasma reforming kinetics derived from our previous work are used to perform 0D calculations to obtain the energy fractions for various plasma processes. A phenomenological model for the plasma-assisted reforming of methane/nitrogen mixtures is developed by considering the vibrational energy transport equations of both methane and nitrogen separately. The energy fractions involved in various plasma processes, such as ultra-fast gas heating and ultra-fast gas dissociation due to the electron excitation reactions, and slow gas heating due to the relaxation of vibrational excitation modes of methane and nitrogen, are accounted for in our new phenomenological model using energy fractions derived earlier. The newly developed phenomenological model is then used to perform 3D direct numerical simulation (DNS) of methane reforming diluted with 60% nitrogen in a pin-to-pin electrode configuration with a discharge gap of 1 mm. The effect of pulsing on the evolution of reformed mixture kernels is investigated by comparing two cases: a single-pulsed case with a pulse energy of 0.8 mJ, and another case using 4 pulses at 200 kHz, with a per pulse energy of 0.2 mJ. The single-pulsed case was observed to promote kernel separation and higher fractions of reformed products, while the multiple-pulsed case resulted in a more diffused kernel.

I. Nomenclature

u_i	=	i^{th} velocity component
ρ	=	gas density
p	=	gas pressure
τ_{ij}	=	viscous stress tensor
Y_k	=	mass fraction of species k
$V_{k,i}$	=	i^{th} component of the mixture-averaged diffusion velocity of species k
W_k	=	molar mass of species k
$\dot{\omega}_k^c$	=	net molar production rate of species k due to combustion
H	=	total non-chemical enthalpy per unit mass
q_i	=	i^{th} component of heat flux vector
h_s	=	sensible enthalpy per unit mass
$\dot{Q}_{react}$	=	heat release rate due to combustion reactions
D_{CH_4}	=	diffusion coefficient of CH_4
τ_{VT}	=	time-scale of vibrational-to-translational relaxation

II. Introduction

METHANE (CH_4), a widely available gas is among the primary constituent in natural gas mixtures [1] from petrochemical industries and is also one of the major products in various biological and physical processes [2].

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Though high in hydrogen content per carbon basis compared to other hydrocarbon gases, the separation of CH_4 from petrochemical extraction sites and its transport to distant locations for consumer utility poses economical and logistical challenges [3]. To safely discard the CH_4 uneconomical to extract and transport, routine activities such as venting or flaring of natural gas are often performed at the extraction sites [4]. Venting and flaring the natural gas into the atmosphere results in a considerable greenhouse effect owing to the 80 times more pronounced greenhouse effect of CH_4 when compared to CO_2 [5–7] owing to the incomplete destruction of CH_4 by flaring. Thus, it is paramount to explore techniques to improve CH_4 destruction by improving the reactivity of natural gas mixtures. Of all the different methods to improve the reactivity of natural gas, reforming of CH_4 to produce H_2 and other reactive hydrocarbons is investigated extensively [8–11]. Nevertheless, challenges exist associated with the reforming of CH_4 to useful products owing to a completely symmetrical tetrahedral structure and a high C-H bond energy of 438.8 kJ/mol [3]. Thus, the strong and weakly polarised C-H bond dissociation requires highly energetic reactants and extreme conditions like high pressure and temperature, which are enabled by energy-intensive processes. Therefore it is critical to explore reformation techniques that are less energy-intensive, yet capable of efficient C-H bond cleavage.

One way to enhance the cleavage of the C-H bond and formation of reactive species efficiently in the gas mixture is to perform a plasma-assisted reforming (PAR), where, the gas mixture can be reformed to a more reactive mixture by treating it with nanosecond repetitively pulsed (NRP) non-equilibrium plasma discharges [12, 13]. The application of the gas mixture with NRP discharges results in the production of electrons and ions, along with excited species [14, 15]. In addition, PAR gives rise to several reactive radicals such as H and CH_3 due to the proceeding of electron impact dissociation reactions involving CH_4 ($\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_x + (4 - x)\text{H}$) as observed in our recent 0D study [16]. These reactions, along with the subsequent H-abstraction and recombination reactions result in the production of H_2 and reactive alkene species [16] in the natural gas mixture. Regardless of these findings from 0D investigation, practical plasma systems often involve non-plane electrode geometries like pin-to-pin configuration resulting in a spatially-dependent plasma [17]. Consequently, detailed 2D/3D plasma modeling is required to encompass the spatiotemporal effects of NRP discharges on the reforming of the gas mixture. Several modeling approaches exist varying from the high-fidelity and computationally expensive particle-in-cell/Monte Carlo collision (PIC/MCC) simulations to lesser expensive fluid-based simulations [18, 19]. Despite their availability, such methods are computationally complex and are nonviable to be used to simulate practical PAR systems involving complex chemical species. To abate the computational complexity of plasma calculations, recent studies [20–22] incorporated the prime effects of NRP discharges such as ultra-fast and slow gas heating and ultra-fast dissociation of O_2 from 0D calculations into 3D DNS ignition studies. As such, these studies [20–22] observed the development of an ignition kernel and the subsequent spatiotemporal propagation/quenching of the kernel at different conditions without directly computing the plasma kinetics. Therefore, a similar implementation of the phenomenological plasma model for PAR of CH_4/N_2 mixtures, is therefore, considered to enable practical computations for PAR of CH_4 .

The aim of the present study is twofold: i) Firstly, the present study aims to extend the phenomenological NRP discharge model of Castela et al. [20] by accounting for the dissociation of CH_4 to the major radicals along with fast-gas heating and vibrational energy transport, followed by ii) investigating the formation and propagation of the reformation kernel in a CH_4/N_2 mixture and the influence the pulsed discharges over a single pulse discharge. The present article is organized as follows: Section III discusses the numerical methodology and the phenomenological plasma-assisted CH_4 reforming model used to simulate the PAR of CH_4/N_2 mixtures. The numerical results of CH_4 reforming and the effects of different conditions are presented in Sec. IV, following which, the conclusions are summarized in Sec. V.

III. Methodology

A. Numerical methodology

A quarter section of the pin-to-pin geometry in a cylindrical domain of radius 8 mm and length 5 mm as shown in Fig. 1 is used in the present work. A gap distance of 1 mm is maintained at the center of the domain and the pin-pin electrode geometry is considered in mesh generation. The mesh contains 18.18 million cells with the smallest cell size of $5\ \mu\text{m}$ (along the radial direction) at the discharge center, and a maximum cell size of $35\ \mu\text{m}$ at the boundaries in the radial direction. Along the axial direction, the cell size varies between $6\ \mu\text{m}$ near the electrodes to $33\ \mu\text{m}$ at the boundary. The outflow boundaries of the cylinder are maintained using wave transmissive boundary conditions to permit the propagation of the reforming kernel without being reflected back. Second-order, total variation diminishing central difference schemes were used for the gradient, divergence, and Laplacian terms of all the governing equations.

The temperature is fixed to 300 K everywhere and the calculations are performed at atmospheric pressure. The

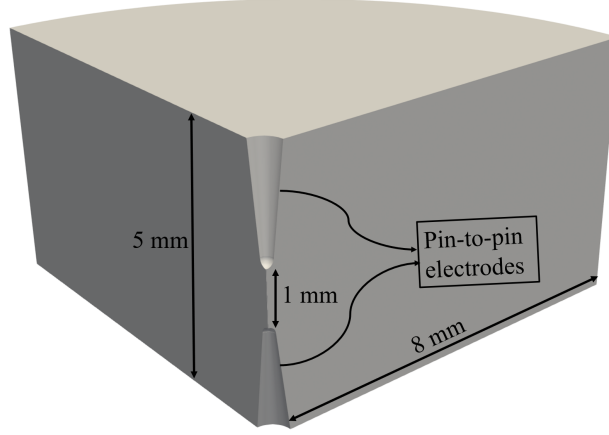


Fig. 1 The computational domain used for numerical calculations in the present work.

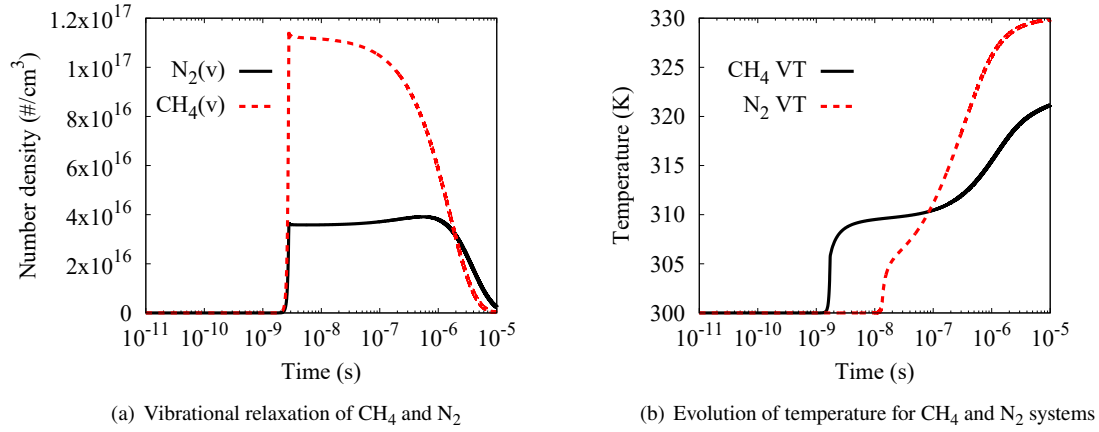


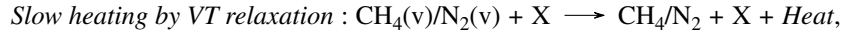
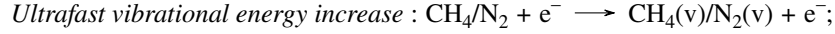
Fig. 2 Evolution of (a) the number densities of N₂(v) and CH₄(v), along with (b) the temperature evolution due to vibrational-translational (VT) relaxation for a discharge in pure CH₄ and N₂.

gas-phase chemistry model used for methane reforming is a reduced version of the GRI mechanism [23] containing 30 species and 184 reactions. For the NRP discharges, the pulse width is fixed to 20 ns, and the time step is fixed to 0.5 ns during the pulses and is allowed to vary in the gap based on the CFL number.

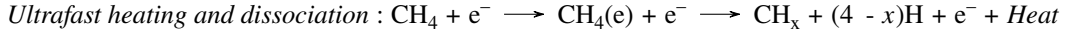
B. Reformation kinetics and PAR model

The phenomenological NRP plasma ignition model proposed by Castella et al. [20] has been adapted in the present work to model plasma-assisted reforming (PAR) of CH₄/N₂ mixtures. The model discussed herein has been implemented in-house [21, 22] on the OpenFOAM [24] platform. When the NRP discharges are characterized by a reduced electric field (E/N) ranging from 100 to 400 Td (1 Td = 10^{-17} V cm^2), about 90% of the deposited pulse energy $\dot{E}_p$ is found to be stored in vibrational and electronic modes of CH₄ and N₂. The vibrational excitation of CH₄ and N₂ occurs in a few 10's of nanoseconds and the corresponding de-excitation occurs in much longer microsecond time scales as seen in Fig. 2(a). The number densities of vibrationally excited CH₄ (CH₄(v)) is found to be significant (~ 3 times higher) when compared to that of N₂ (N₂(v)). Moreover, the relaxation of CH₄(v) is found to happen significantly earlier when compared to N₂(v). Similar observations can be made from the temperature rise due to the vibrational-translational (VT) relaxations as shown in Fig. 2(b), where the early temperature rise due to VT relaxation ($< 1 \times 10^{-7}$ s) of CH₄(v) is higher compared to that of N₂(v). Post 1×10^{-7} s, the contribution of VT relaxation of ceN₂(v) dominates as observed in Fig. 2(b). To account for these complexities in VT relaxation in the CH₄/N₂ gas mixture, it is essential to accommodate the vibrational energy transport due to both CH₄ and N₂. Thus, the two-step phenomena of slow gas heating due to the

vibrational energy transport can then be depicted by:



where $\text{CH}_4(\text{v})$ and $\text{N}_2(\text{v})$ represents a general vibrational state of CH_4 and N_2 respectively and X being any species. Unlike vibrational relaxation, the electronic excitation of CH_4 and N_2 and subsequent dissociation of CH_4 to radicals occur in a few 10's nanoseconds, thereby resulting in ultrafast dissociation of CH_4 and ultrafast gas heating as shown by the following reaction:



where, $\text{N}_2(\text{e})$ and $\text{CH}_4(\text{e})$ represents a general electronic excited state of N_2 and CH_4 respectively.

Thus, the energy deposited in the pulse $\dot{E}_p$ is divided into three components contributing to ultrafast gas heating ($\dot{E}_{p,\text{heat}}$), ultrafast CH_4 dissociation ($\dot{E}_{p,\text{diss}}$), and ultrafast increase in the vibrational energy of the gas ($\dot{E}_{p,\text{vib}}$), in addition to electron kinetic energy ($\dot{E}_{p,\text{elec}}$) as given by Eq. 1:

$$\dot{E}_p = \dot{E}_{p,\text{heat}} + \dot{E}_{p,\text{diss}} + \dot{E}_{p,\text{vib}} + \dot{E}_{p,\text{elec}} \quad (1)$$

In Eq. 5, $\dot{E}_{p,\text{vib}}$ is comprised of the vibrational energy contributions from both CH_4 ($\dot{E}_{p,\text{vib},\text{CH}_4}$) and N_2 ($\dot{E}_{p,\text{vib},\text{N}_2}$), such that $\dot{E}_{p,\text{vib}} = \dot{E}_{p,\text{vib},\text{CH}_4} + \dot{E}_{p,\text{vib},\text{N}_2}$. The set of equations solved by accounting for the three major effects of NRP discharges in CH_4 reforming is then given below:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u_i)}{\partial x_i} = 0 \quad (2)$$

$$\frac{\partial(\rho u_j)}{\partial t} + \frac{\partial(\rho u_i u_j)}{\partial x_i} = -\frac{\partial p}{\partial x_j} + \frac{\partial \tau_{ij}}{\partial x_i} \quad (3)$$

$$\frac{\partial(\rho Y_k)}{\partial t} + \frac{\partial(\rho u_i Y_k)}{\partial x_i} = -\frac{\partial}{\partial x_j}(\rho V_{k,i} Y_k) + W_k \dot{\omega}_k^c + W_k \dot{\omega}_k^p \quad (4)$$

$$\frac{\partial(\rho H)}{\partial t} + \frac{\partial(\rho u_i H)}{\partial x_i} = -\frac{\partial q_i}{\partial x_j} + \frac{\partial(\tau_{ij} u_i)}{\partial x_i} + \frac{\partial p}{\partial t} - \frac{\partial}{\partial x_i} \left(\rho \sum_{k=1}^{N_{sp}} h_{s,k} Y_k V_{k,i} \right) + \dot{Q}_{\text{react}} + \dot{E}_{p,\text{heat}} + \dot{R}_{VT,\text{CH}_4}^p + \dot{R}_{VT,\text{N}_2}^p \quad (5)$$

Eqs. 2, 3, 4, and 5 represent the continuity, momentum, species, and energy conservation equations with appropriate additional source terms to accommodate the effects of plasma. In Eq. 4, $\dot{\omega}_k^p$ ($\dot{\omega}_{\text{CH}_4}^p$, $\dot{\omega}_{\text{CH}_3}^p$, $\dot{\omega}_{\text{CH}_2}^p$, and $\dot{\omega}_{\text{H}}^p$ in this study) denotes the molar production rate to model the production of species by ultra-fast dissociation of gas species (CH_4 in the present work). In Eq. 5, H denotes the total non-chemical enthalpy per unit mass and is given by $h_s + \frac{1}{2} u_i u_i$. The slow gas heating due to VT relaxation of $\text{CH}_4(\text{v})$ and $\text{N}_2(\text{v})$ is accounted for by adding vibrational energy relaxation rates for $\text{CH}_4(\text{v})$ and $\text{N}_2(\text{v})$ ($\dot{R}_{VT,\text{CH}_4}^p$ and $\dot{R}_{VT,\text{N}_2}^p$) to the energy equation (see Eq. 5). In order to balance the vibrational energy $\dot{E}_{p,\text{vib}}$ and the corresponding VT relaxation rates $\dot{R}_{VT,\text{CH}_4}^p$ and $\dot{R}_{VT,\text{N}_2}^p$, two additional conservation equations (see Eq. 6 and 7) for the specific vibrational energy carried by CH_4 ($e_{\text{vib},\text{CH}_4}$) and N_2 molecules ($e_{\text{vib},\text{N}_2}$) are added to the system of equations:

$$\frac{\partial(\rho e_{\text{vib},\text{CH}_4})}{\partial t} + \frac{\partial(\rho u_i e_{\text{vib},\text{CH}_4})}{\partial x_i} = -\frac{\partial}{\partial x_j} \left(\rho D_{\text{CH}_4} \frac{\partial e_{\text{vib},\text{CH}_4}}{\partial x_i} \right) + \dot{E}_{p,\text{vib},\text{CH}_4} - \dot{R}_{VT,\text{CH}_4}^p \quad (6)$$

$$\frac{\partial(\rho e_{\text{vib},\text{N}_2})}{\partial t} + \frac{\partial(\rho u_i e_{\text{vib},\text{N}_2})}{\partial x_i} = -\frac{\partial}{\partial x_j} \left(\rho D_{\text{N}_2} \frac{\partial e_{\text{vib},\text{N}_2}}{\partial x_i} \right) + \dot{E}_{p,\text{vib},\text{N}_2} - \dot{R}_{VT,\text{N}_2}^p \quad (7)$$

To close this model, we assume a fractions α , β_k for the k^{th} dissociation product of CH_4 (β_{H} , β_{CH_2} , and β_{CH_3} in the present study), and γ_j for the j^{th} species contributing towards vibrational energy of the system (γ_{CH_4} and γ_{N_2} in

this study). An additional fraction η is also considered to account for the kinetic energy of electrons. Thus the energy deposited by the pulse $\dot{E}_p$ can then be distributed into four parts:

$$\dot{E}_p = \alpha \dot{E}_p + \sum_k \beta_k \dot{E}_p + \sum_j \gamma_j \dot{E}_p + \eta \dot{E}_p \quad (8)$$

The fractions β_k and γ_j can be directly obtained using 0D calculations, where, β_k corresponding to the k^{th} radical can be calculated using:

$$\beta_k = \frac{N_k \Delta H_k^\#}{E_{p,0D}} \quad (9)$$

$$\gamma_j = \frac{N_j E_{th,j}}{E_{p,0D}} \quad (10)$$

In Eq. 9, N_k denotes the number density (cm^{-3}) of the k^{th} dissociation product, $\Delta H_k^\#$ denotes the formation enthalpy in J/molecule for k , and $E_{p,0D}$ represents the energy deposited in the 0D calculations (J/cm^3). A similar approach could be utilized to calculate the fractions γ_j for the j^{th} species contributing to the vibrational energy increase of the system, with $\Delta H^\#$ replaced by the threshold energy ($E_{th,j}$) for the vibrational excitation of j (J/molecule) as shown in Eq. 10. The fraction η can also be obtained from the 0D calculation by utilizing the expression for electron kinetic energy as given in literature [25]. Now, fraction of energy for fast-gas heating α can be simply calculated using:

$$\alpha = 1 - \sum_k \beta_k - \sum_j \gamma_j - \eta \quad (11)$$

These fractions α and γ_j can now be utilized to calculate $\dot{E}_{p,heat}$, $\dot{E}_{p,vib,CH_4}$, and $\dot{E}_{p,vib,N_2}$. To calculate the species production source terms in Eq. 4, $\dot{E}_{p,diss}$ can be expressed as:

$$\dot{E}_{p,diss} = g_{diss} \dot{E}_p, \quad (12)$$

where g_{diss} denotes the fraction of $\dot{E}_p$ used for ultra-fast dissociation. If $h_{f,k}$ is the specific formation enthalpy of the species k , then $\dot{E}_{p,diss}$ can also be given by

$$\dot{E}_{p,diss} = \sum_{k=1}^{N_{sp}} h_{f,k} \dot{\omega}_k^p = \sum_{k=1}^{N_{sp}} g_{diss}^k \dot{E}_p, \quad (13)$$

where, g_{diss}^k denotes the fraction of $\dot{E}_p$ expend to produce species k . Therefore, the species production rate by plasma $\dot{\omega}_k^p$ for a species k is given by Eq. 14. g_{diss}^k is assumed to be proportional to $\frac{Y_{CH_4}}{Y_{CH_4}^f}$ where $Y_{CH_4}^f$ is the mass fraction of CH_4 in the fresh mixture. If β_k is the fraction of $\dot{E}_p$ leading to CH_4 dissociation, g_{diss}^k can then be written as given in Eq. 15.

$$\dot{\omega}_k^p = g_{diss}^k \frac{\dot{E}_p}{h_{f,k}}; \quad (14)$$

$$g_{diss}^k = \beta_k \frac{Y_{CH_4}}{Y_{CH_4}^f}. \quad (15)$$

Since the present work considers the dissociation of CH_4 to H , CH_3 , and CH_2 , the conservation of mass involving plasma reactions give

$$\dot{\omega}_{CH_4}^p = -(\dot{\omega}_{CH_3}^p + \dot{\omega}_{CH_2}^p + \dot{\omega}_H^p) = -\frac{Y_{CH_4} \dot{E}_p}{Y_{CH_4}^f} \left(\frac{\beta_{CH_3}}{h_{f,CH_3}} + \frac{\beta_{CH_2}}{h_{f,CH_2}} + \frac{\beta_H}{h_{f,H}} \right). \quad (16)$$

In Eq. 5, 6, and 7, $\dot{R}_{VT,j}^p$ for the j^{th} species is calculated using the Landau-Teller harmonic oscillator approach as given by

$$\dot{R}_{VT,j}^p = \rho \frac{e_{vib,j} - e_{vib,j}^{eq}(T)}{\tau_{VT,j}} \quad (17)$$

where $e_{vib,j}^{eq}(T)$ denotes the equilibrium vibrational energy of the j^{th} species at a given temperature T and is given by:

$$e_{vib,j}^{eq}(T) = \frac{r_j \Theta_{1,j}}{e^{\frac{\Theta_{1,j}}{T}} - 1}, \quad (18)$$

where $\Theta_{1,j}$ is the vibrational temperature of the j^{th} species corresponding to its first quantum vibrational state and $r_j = \frac{R_u}{W_j}$ (R_u being the universal gas constant). The present study utilizes $\Theta_{1,N_2} = 3396$ K [20] and $\Theta_{1,CH_4} = 1880$ K [26]. In Eq. 17, $\tau_{VT,j}$ is given by:

$$\tau_{VT,j} = \left(\sum_M \frac{1}{\tau_{VT,j}^M} \right)^{-1}, \quad (19)$$

where M denotes the collisional partners of j . The relaxation times τ_{VT,CH_4} and τ_{VT,N_2} are calculated from the rate coefficients in the literature [27] as stated elsewhere [28].

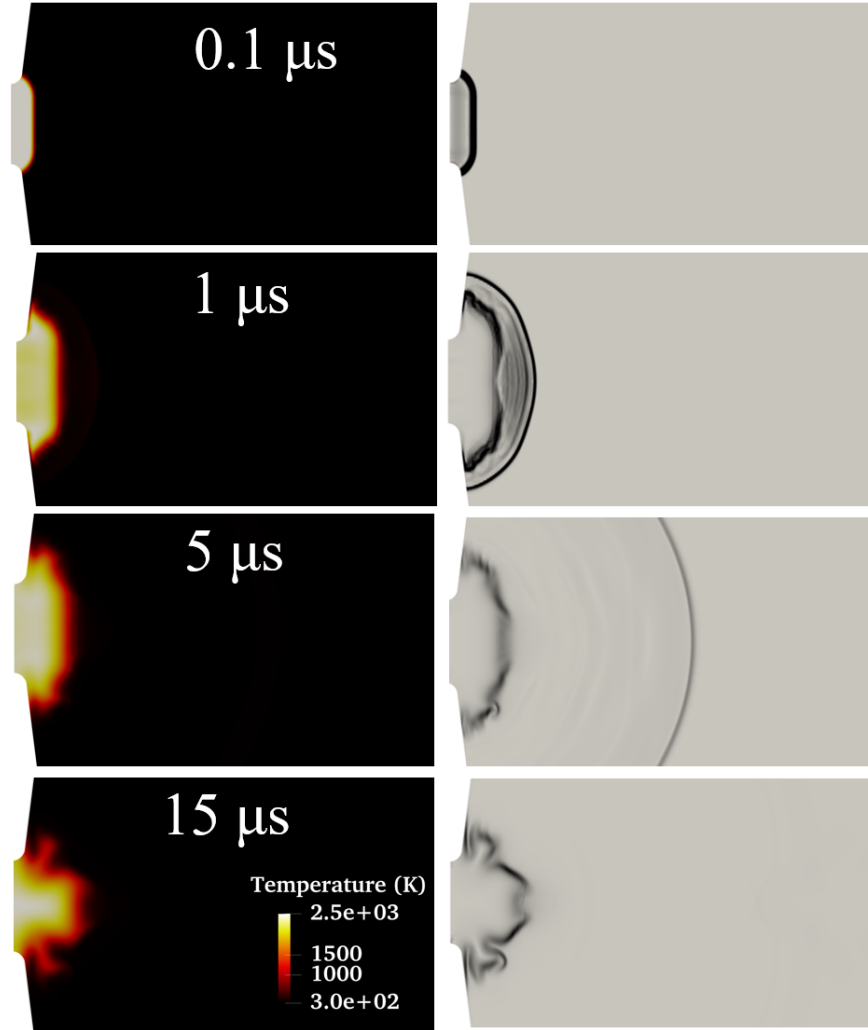


Fig. 3 Evolution of temperature and density gradient (i.e., numerical schlieren) at different time instances after the discharge pulse.

IV. Results and Discussion

An in-house 0D NRP discharge code [25] is utilized to perform 0D plasma discharges in a CH_4/N_2 mixture at 300 K and atmospheric pressure using a recently derived detailed plasma reforming mechanism for small alkanes [16]. The

simulations are performed for a single pulse, with the pulse energy fixed to 0.05 J/cm^3 and a reduced electric field (E/N) of 200 Td ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$). This value of E/N corresponds to an applied voltage of 4.8 kV in a pin-to-pin setup with a gap distance of 1 mm. The fractions obtained from the 0D calculations are shown in Table 1 and will be utilized for subsequent PAR computations.

Table 1 Energy fractions for various plasma effects obtained using 0D modeling of PAR of CH_4/N_2 mixtures.

β_{CH_3}	β_{CH_2}	β_{H}	γ_{CH_4}	γ_{N_2}	η
0.0532	0.0479	0.1565	0.0903	0.0885	0.06

A. Evolution of the reforming core

The phenomenological model introduced in the present study is utilized to simulate a single discharge of non-equilibrium plasma in CH_4 , diluted with 40% N_2 . The pulse energy is set to 0.8 mJ and the plasma energy fractions shown in Table 1 are used to account for various effects of plasma discharge. Fig. 3 shows the evolution of temperature and the gradient of density post-discharge for various instances. It can be observed that the temperature peaks around $\sim 2500 \text{ K}$ at $0.1 \mu\text{s}$, and the hot core is limited within the electrode gap with a cylindrical shape. As time progresses, the

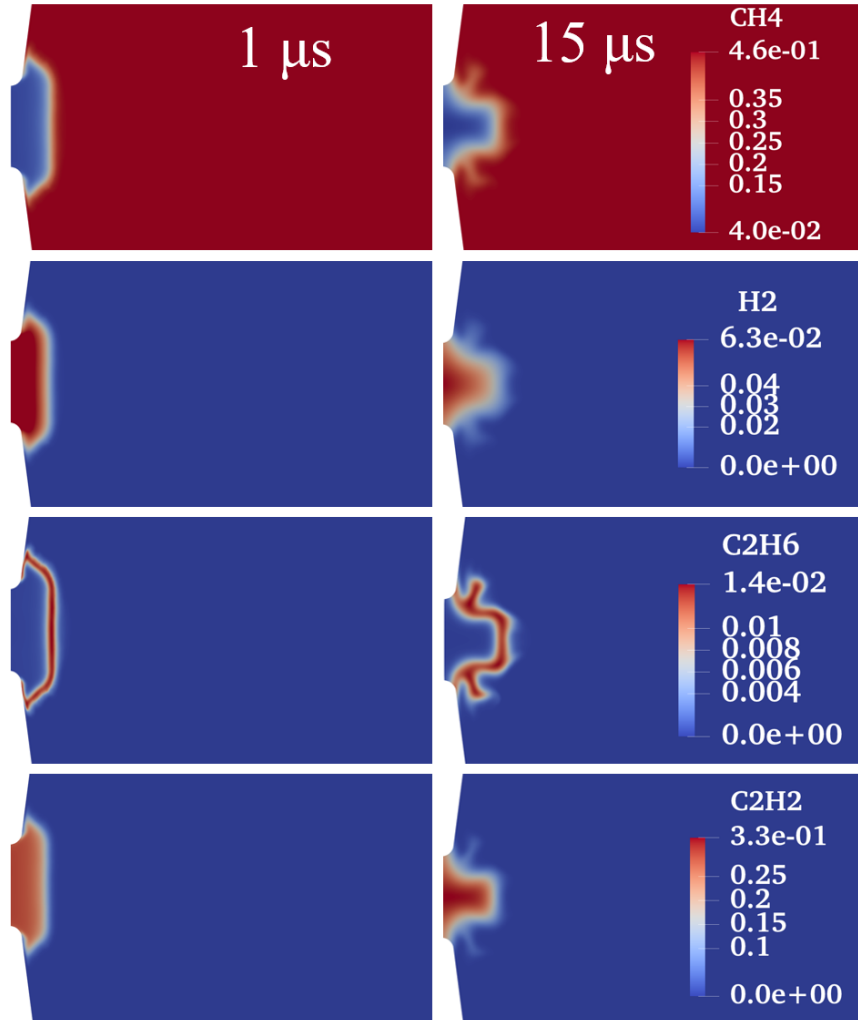


Fig. 4 Evolution of CH_4 , H_2 , C_2H_6 , and C_2H_2 at $1 \mu\text{s}$ and $15 \mu\text{s}$ after the discharge pulse.

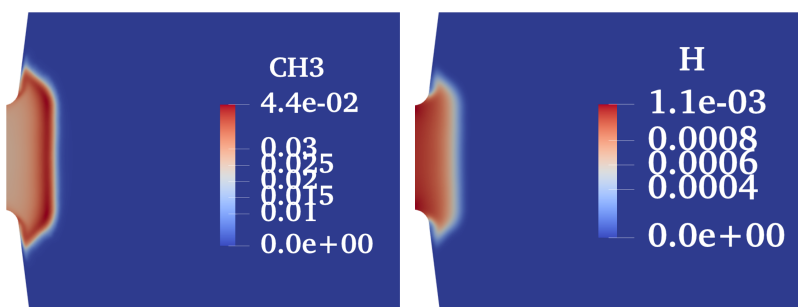


Fig. 5 Contours of CH_3 and H at $1 \mu\text{s}$ after the discharge pulse.

hot core proceeds to expand outside the gap, with the hot kernel moving around the electrode tip, and further at $15 \mu\text{s}$, the cylindrical kernel collapses to form a toroidal kernel. Similar observations can be found from the evolution of the density gradient. Fig. 4 portrays the evolution of CH_4 , along with the different reformed products such as H_2 , C_2H_6 , and C_2H_2 for two different instances. The discharge gap is found to be significantly CH_4 -depleted, whereas, the same region is found to be occupied with reformed H_2 and C_2H_2 (see Fig. 4). Despite the production of H_2 and C_2H_2 , the hot (reforming) kernel did not accommodate the production of C_2H_6 (see Fig. 4) and C_2H_4 . The production of the aforementioned species were, however, limited to the thin outer region of the reforming kernel at all time instances. To better understand the accumulation of C_2H_6 and C_2H_4 at the kernel boundaries, the contours of CH_3 and H are shown in Fig. 5, which depicts an accumulation of CH_3 and depletion of H at the kernel boundaries. The accumulated CH_3 proceed to recombine and form C_2H_6 as the temperature in the outer region is in the range between 700-1300 K. When compared to the kernel boundary, the hot core of the reforming kernel maintains a significantly higher temperature ($\sim 2500 \text{ K}$), thereby dissociating any recombined C_2H_6 and C_2H_4 . In contrast, C_2H_2 contains a strong C-C triple bond in comparison to C_2H_4 and C_2H_6 . In addition, higher temperature facilitates multiple C-H bond scissions thereby promoting an increased presence of H and CH radicals, whereas, CH_3 and CH_2 are reduced. This is evident from Fig. 5, where the hot core is found to contain lesser CH_3 and more H radicals as compared to the kernel boundary.

B. Effect of multiple pulses on reforming

To understand the effect of multiple pulses on reformed product evolution, the phenomenological model was utilized to simulate NRP discharges in CH_4/N_2 mixtures at a repetition frequency of 200 kHz. The number of pulses was limited to four with the energy per pulse set to 0.2 mJ to match the total energy deposition in the single-pulse discharge presented earlier. Figure 6 shows the contours of C_2H_4 and H_2 at $20 \mu\text{s}$ after the last plasma discharge. It can be observed that the reforming kernel in the single-pulse case (on the left in Fig. 6) proceeds to eject radially outwards with a decreased thickness of the preceding hot core, betraying a subsequent separation of the reforming kernel to form a toroidal structure. However, the 4-pulse case tends to have a more diffuse reforming core with the kernel boundaries attaching to the outer electrode regions. Thus unlike the single-pulse case, the 4-pulse case does not tend toward a toroidal separation. Moreover, the mass fractions of C_2H_4 - a clear indicator of the reforming kernel boundary as per the previous discussion - are observed to be comparatively lower for the 4-pulsed case. This suggests a more diffused core region, which could be a consequence of the pulse energy distributed across four pulses, thereby leading to a diffused plasma.

Since the energy deposited in each pulse in the 4-pulse scenario is lower by a factor of 4, the CH_4 decomposition and the temperatures are also found to be significantly lower for the 4-pulse case immediately after the first pulse (around 2% of CH_4 is decomposed) in comparison to the single-pulse scenario where about 80% of the CH_4 in the discharge gap is found to be decomposed. Nevertheless, around $0.1\text{-}1 \mu\text{s}$, the former is found to have much higher temperatures (around 4000 K), despite the energy per pulse being lower by a factor of 4. This can be attributed to the pronounced presence of CH_4 molecules after the first pulse (in the 4-pulse case) compared to the single-pulse case. The presence CH_4 introduces an early VT relaxation in times lesser than 10^{-7} s , whereas, the VT relaxation in the single pulse case comes into effect only at a later time (after 10^{-7} s). The difference in VT time scales between CH_4 and N_2 can be observed in Fig. 2. The effect of early VT relaxation on the kernel evolution in the 4-pulse case and the effect of subsequent heating due to the VT relaxation of N_2 is unresolved at the time of submission of this manuscript. More information on the interplay between VT relaxation timescales of CH_4 and N_2 and their effect on the reforming kernel evolution will be discussed in

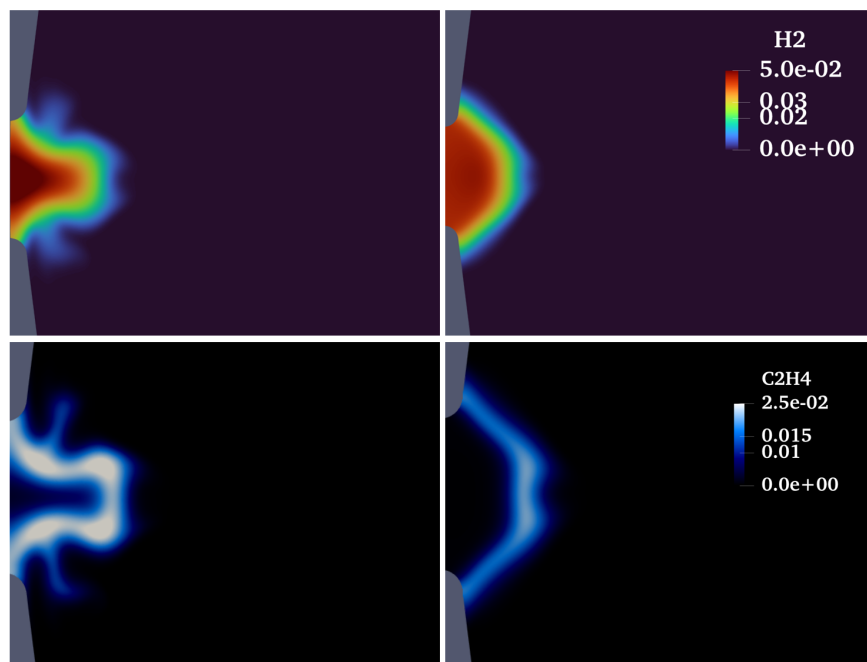


Fig. 6 Contours of C_2H_4 and H_2 for the single-pulse discharge (left) and the 4-pulse discharge (right) at $20\ \mu s$ after the discharges.

the future.

V. Conclusion

A phenomenological model to simulate the nanosecond repetitively pulsed (NRP) plasma-assisted reforming (PAR) of CH_4/N_2 mixtures is developed in the present work based on plasma-assisted combustion (PAC) models available in the literature [20, 22]. The model has been developed by considering energy fractions for various plasma processes: ultra-fast gas heating and CH_4 dissociation due to electronic excitation, and slow gas heating due to vibrational-translational (VT) relaxation of CH_4 and N_2 . The vibrational energy transport was accounted for using separate transport equations of vibrational energy for both CH_4 and N_2 . The application of the newly developed phenomenological model to CH_4 reforming in a pin-to-pin electrode configuration separated by 1 mm depicted the propagation of reforming kernel and H_2 production along with other higher hydrocarbons. H_2 and C_2H_2 were found to occupy the discharge gap, while the accumulation of C_2H_6 and C_2H_4 were limited to the reforming kernel boundaries. A single discharge case with a pulse energy of 0.8 mJ was found to promote kernel separation and higher reformed fractions over the 4-pulse case with each pulse depositing 0.2 mJ, and the latter was observed to produce a diffused reaction kernel.

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