Kinetics of plasma assisted pyrolysis and oxidation of ethylene. Part 2: Kinetic modeling studies

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The kinetics of plasma-assisted pyrolysis and oxidation of ethylene have been numerically investigated. Combining plasma chemistry processes including electron-impact reactions, and reactions of electronically excited species with a comprehensive combustion mechanism, a plasma-assisted kinetic mechanism of ethylene pyrolysis and oxidation has been constructed. To test the accuracy of the constructed mechanism, numerical results were compared to experimental data obtained in a plasma flow reactor, performed under highly diluted conditions in argon at a pressure of 1 atm for temperatures ranging from 520 K to 1250 K. Comparison of plasma-assisted pyrolysis results indicates little discrepancy between the model and experiments. Direct collisional quenching of electronically excited argon by ethylene is responsible for the low temperature enhancement of fuel consumption seen in the plasma-assisted pyrolysis experiments. Hydrocarbon radicals generally undergo addition and recombination reactions to yield several C\textsubscript{3} and C\textsubscript{4} hydrocarbon intermediates. As temperature increases, the plasma effects diminish and the reaction is overtaken by thermal pyrolysis. Comparison of experimental and modeling results for plasma-assisted oxidation of ethylene demonstrated relatively good agreement for most major and minor species. However, poor agreement was found for ethylene and acetaldehyde for T < 750 K. In the oxidation system, collisional quenching of excited argon by O\textsubscript{2} to generate the O-atom radical pool complemented the plasma-specific fuel dissociation reactions. The plasma was found to have different effects on the oxidation kinetics at different temperatures. At low temperatures, R+O\textsubscript{2} type chemistry (R being a hydrocarbon radical) facilitates the formation of oxygenated species to enhance oxidation by way of formaldehyde. At intermediate temperatures, the formation of hydrocarbon and alcohol intermediates slows the oxidation process relative to the low temperatures. Finally, at high temperatures, plasma chemical reactions are unable to compete against the high temperature chain-branching reactions of the neutral chemistry that dominate and control the overall oxidation process.

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1. Introduction

Plasma-assisted combustion (PAC) is considered a promising new technique to improve the performance and operability of practical combustion applications, with numerous examples demonstrating its potential efficacy (see Ref. [1]). However, an understanding of the chemical kinetics leading to these observed enhancements remains unclear. For the most part, fundamental studies examining PAC kinetics have used kinetic models to elucidate the dominant and rate-controlling chemistry, while simultaneously attempting to develop validated plasma-specific combustion mechanisms. When attempting to construct such mechanisms several challenges exist. Firstly, the chemical system cannot be described by a single temperature due to the involvement of electron-impact processes. Depending on the characteristics of the plasma (e.g., reduced electric field, reactive mixture composition), several sub-mechanisms may need to be incorporated to account for the various constituent particles that may exist in the system, including ions and excited states (electronic and vibrational). Following this, the interaction of these plasma generated species with ground state neutral chemical species becomes a cumbersome consideration due to the scarcity of available data describing such reactions, particularly when considering hydrocarbon fuels. Lastly, the relevance of most combustion mechanisms and their validation are at elevated temperatures for practical purposes (i.e., at or near autoignition or flame temperatures), whereas plasma chemistry reactions are typically studied at room temperature conditions, and the importance of their temperature dependence has yet to be fully determined.

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In the present paper, a reaction mechanism for plasma-assisted pyrolysis and oxidation of ethylene is reported. Ethylene is a dominant intermediate species formed during the oxidation of alkane hydrocarbon fuels. An understanding of its kinetic behavior is necessary to facilitate the collective hierarchical mechanism development efforts of PAC-specific kinetic mechanisms for hydrocarbon fuels.

The kinetics of ethylene PAC have been studied both experimentally and numerically in the past, using preheated \((T < 500 \, \text{K})\) non-dilute ethylene-air mixtures at low pressures \((P < 70 \, \text{Torr})\) [2–6]. Mechanistic data were derived from a combination of ex situ and in situ techniques to measure stable product [2–4] (e.g., \(\text{C}_2\text{H}_2, \text{CH}_2\text{O}, \text{CO}, \text{CO}_2, \text{and} \text{H}_2\text{O}\)) and radical species densities [5–6] (e.g., \(O, \text{OH}\)) induced by plasma reactions. From here, modeling studies involved the creation of a plasma-specific mechanism, combining air plasma processes based on the mechanism of Kossyi et al. [7] with hydrocarbon oxidation mechanisms, either GRI Mech 3.0 [8] or USC Mech II [9]. The two mechanisms were then linked together by considering ethylene and oxygen dissociation reactions by electron-impact and quenching reactions involving electronically excited states of nitrogen (e.g., \(N_2(^2\Sigma_u^+), N_2(^2\Pi_g), N_2(^2\Sigma_u^-)\)). Based on these studies, the ability to extend the combustion limit towards lower temperatures was found due to chemical heat release as a result of enhanced fuel oxidation from plasma chemical reactions, producing super equilibrium concentrations of \(O\)-atoms and \(OH\) radicals. As such, these radicals would then induce chain-branching and propagating reactions with ethylene [3], accelerating the overall reaction rate and allowing for further exothermicity and temperature rise. This sequence was corroborated by observing that direct plasma effects (i.e., direct dissociation of fuel by electron impact and/or quenching with excited nitrogen) leading to fuel consumption had minimal effect in fuel-nitrogen containing mixtures [2–4]. In certain instances, heat release would cause significant temperature rise \((\Delta T \sim 600 \, \text{K})\) and instigate early ignition. From a kinetics perspective, this behavior reflects a transition through several different kinetic regimes, moving from a slow chain-propagating reaction to a fast chain-branching reaction, which is consequentially system pressure and temperature dependent. The comparison of numerical and experimental results displayed some level of agreement, with most of the disagreement lying below the self-ignition temperature. Ultimately, the efforts to resolve and identify the deficiencies in the mechanism were limited due to the lack of experimental data of intermediate and product species, along with the inapplicability of the combustion mechanisms employed.

In this study, model predictions are compared to experimental data obtained from a plasma flow reactor (PFR) operated under dilute conditions at 1 atm pressure over a combined temperature range of 420 K to 1250 K. Decoupling the heat release effects that influence the reaction chemistry by operating under dilute conditions is useful when trying to elucidate the kinetic enhancement characteristics that plasmas have on the basic combustion phenomena. As such, large temperature changes can dictate the dynamics of the reacting system, resulting in a few select reactions and associated rate parameters dominating the entire system, thus concealing much of the underlying chemistry. Furthermore, the ability to compare many species concentrations between model predictions and experimental measurements enables greater constraints to be placed on the chemical mechanism, thereby improving the model and mechanistic understanding. Details regarding the experimental methodology can be found in a companion paper by Tsolas et al. [10]. In the current mechanism, the plasma chemistry is combined with a relatively recent comprehensive combustion mechanism well suited to consider low temperature oxidation kinetics of hydrocarbon and oxygenated fuels. In doing so, the present study hopes to alleviate inapplicability and constraints presented in past studies using other combustion mechanisms. The kinetics of the mechanism are tested over three temperature regimes, low, intermediate, and high, where it is expected that the chemistry governing the plasma-assisted pyrolysis and oxidation of ethylene would differ. Finally, major kinetic pathways leading to the production of experimentally derived intermediate and product species are presented to elucidate the kinetic enhancement characteristics under the effects of a non-equilibrium plasma.

2. Kinetic model

The plasma-assisted fuel kinetic model implemented in this study has its origin from earlier studies [2–4], and has been under active development ever since its inception [5–6,11–16]. In brief, the model consists of a set of nonlinear ordinary differential equations describing the spatial evolution of the number density of each species (e.g., neutral, excited and charged), the energy equation to predict the mixture temperature, as well as quasi-1D flow equations for conservation of mass and momentum. The species concentration equations are coupled together with the steady, two-term expansion of the Boltzmann equation to determine the electron energy distribution function (EEDF) of the plasma electrons [17]. Using experimental cross-sections for electron impact processes as inputs, the Boltzmann equation solver solves the EEDF to yield rate constants for electron impact excitation, dissociation, and ionization processes as functions of the reduced electric field \((E/N)\). These equations are solved using a stiff ODE solver (LSODE) to compute the evolution of species mole fractions as the extent of reaction progresses through the flow reactor, due to electron impact processes, plasma chemical reactions among excited species, and chemical reactions among the ground state neutral species. The full mathematical description of the numerical model can be found in Ref. [18].

Accurate prediction of \(E/N\) in the quasi-neutral plasma is non-trivial, since the effect of plasma self-shielding (due to charge separation near the dielectric-covered electrodes during nanosecond pulse breakdown) needs to be considered. To circumvent this, the present kinetic model incorporates \(E/N\) values representative of the experimental conditions \((P=1 \, \text{atm}, T=420–1250 \, \text{K})\) and gas mixture \((X/Ar > 0.99)\) predicted by an analytic model of a nanosecond pulse breakdown between two dielectric-covered plane electrodes [19] (from herein referred to as the OSU plasma model). Previously, this model was used to analyze the time-dependent behavior of \(E/N\) in dry-air plasmas generated by a nanosecond pulse discharge in a plane-to-plane geometry with dielectric covered electrodes, and to predict the energy coupled to the plasma during the discharge pulse, which was found to be in good agreement with experimental data [20]. The same approach was used in the present work. For this, the experimental voltage pulse waveform was approximated using a Gaussian fit with an appropriate full width at half maximum (FWHM) (see Fig. 1a). The model predicted the breakdown voltage \(U_{\text{br}}\), the time-dependent reduced electric field, and the ionization fraction in the plasma after breakdown. Breakdown occurs when the electric field reaches its maximum. After breakdown, the electric field in the plasma rapidly drops due to strong shielding by the sheath (a space charge region where the ion density exceeds the electron density) and charge accumulation of the dielectric surfaces (i.e., quartz channel walls), which results in termination of the ionization process and limits the energy coupled to the plasma during the discharge pulse [19]. Neglecting this effect would considerably overestimate \(E/N\) in the plasma, since the combined voltage drop across the plasma sheaths and dielectric layers can be quite significant [19]. For the discharge geometry and experimental conditions of this study, breakdown voltage predicted by the OSU plasma model scales approximately as a square
Fig. 1. Single-pulse time-dependent calculations of (a) ionization fraction, and (b) reduced electric field in the plasma (E/N) and coupled energy, based on the nanosecond pulse breakdown model of Ref. [19]. Modeling conditions: $T=600\,K$, $P=1\,atm$, $X(Ar)=1$, using a Gaussian fit for the applied voltage pulse, with peak voltage of 9.8 kV and FWHM of 50 ns.

root of the number density, and is approximated as follows:

$$U_{br} = U_{\text{applied}} \left[ \frac{500\,K}{T} \right] \left( \frac{P}{760\,\text{torr}} \right)^{1/2}$$

Eq. (1) is incorporated into the present kinetic model, and the upper limit of E/N taken at breakdown (when voltage peaks) is computed based on the number density of the reactive mixture (see Fig. 2). These E/N values are used as inputs into the Boltzmann solver to obtain the EEDF, electron swarm parameters, and rate coefficients of electron impact processes, and discharge input energy partition among different inelastic processes (such as electronic excitation, dissociation, and ionization).

The energy coupled to the plasma during the applied voltage pulse also depends on the electron density in the plasma. From the analysis of the OSU plasma model, both the electron density and the coupled energy are primarily controlled by (i) electron impact ionization, and (ii) sheath development and accumulation of charges on the dielectric surfaces, which limits the electric field in the plasma during the pulse. Note that surface charge layers formed on the inside of the dielectric channel walls next to the electrodes, and the electrodes themselves form capacitors storing energy during the discharge pulse, some of which is reflected to the pulse generator as the voltage is reduced. Time-resolved energy coupled to the plasma, as well as the sum of coupled energy and energy stored in the surface charge layer capacitors are plotted in Fig. 1b. At the conditions of Fig. 1 (argon at $P=1\,atm$ and $T=600\,K$), the peak value of $E/N$ predicted by the model is $94\,Td$, and couple pulse energy is $0.31\,mj/pulse$ ($0.051\,meV/molecule/pulse$). The model also predicts the coupled energy to scale linearly with the number density (i.e., inversely proportional to the temperature) [20], such that the energy coupled per molecule remains nearly constant.

Since the OSU plasma model of [19] is one-dimensional, it does not take into account the axial electric field nonuniformity near the electrode edges, as well as the possibility of corona discharge formation near electrode surfaces outside of the discharge channel. Both of these effects would change the energy coupled to the plasma inside the reactor. Therefore in the present work the model prediction for the total energy coupled ($Q_{\text{net}}$) to the flow during its residence time in the plasma between the electrodes, at near isothermal conditions, was validated by measuring the amount of fuel (ethylene) consumed during the plasma-assisted pyrolysis experiments in dilute ethylene-argon mixtures, over a wide range of temperatures. For this, the electron density in the plasma predicted by the model was varied (i.e., adjusting the discharge pulse current) to match the amount of decomposed fuel in the model to the experimental values. The results of this coupled energy calibration are summarized in Fig. 3. It can be seen that the model correctly reproduces the trend of total coupled energy reduction with temperature. The energy coupled per pulse inferred from the experiment is somewhat higher compared to the predictions obtained by the OSU plasma model ($Q_{\text{net}}=0.043-0.057\,meV/molecule/pulse$ for $T=520-1250\,K$), with a maximum difference of approximately a factor of two. The results also indicate a transition in coupled energy at $T=910\,K$ experiencing a maximum reduction of about 20% from $T=910-1250\,K$. The temperature-averaged value derived from the experimental results is $Q_{\text{net}}=0.083\,meV/molecule/pulse$.

The same calibration was performed in dilute ethylene-oxygen-argon mixtures, for $T<910\,K$ (at higher temperatures all the fuel is consumed), showing similar results (within 30% of the results from the ethylene–argon mixtures). Thus, in all present calculations, the specific energy coupled to the plasma was inferred based on the ethylene consumption calibration. Finally, to reduce the computational time, the 1 kHz repetitively pulsed current waveform used to
Fig. 3. Comparison of total energy coupled to the plasma \( (Q_{\text{pl}}, \text{in meV/molecule/pulse}) \) and specific energy per pulse \( (Q_{\text{sp}}, \text{in meV/molecule/pulse}) \), inferred from the plasma-assisted ethylene pyrolysis experiments (circles – Modeling conditions: \( \text{Uapplied}=9.8 \text{ kV}, \text{pulse repetition rate of } 1 \text{ kHz, } P=1 \text{ atm, } X(\text{C}_2\text{H}_4)=800 \text{ ppm, } X(\text{Ar})=0.9992 \) and predicted by the nanosecond pulse breakdown model of Ref. [19] (squares – Modeling conditions: \( \text{Uapplied}=9.8 \text{ kV}, \text{pulse repetition rate of } 1 \text{ kHz, } P=1 \text{ atm, } X(\text{Ar})=1 \)).

Fig. 4. Comparison of experimental (solid data points) and prescribed (solid lines) temperature profiles in the reactor. Hatched region denotes the electric discharge section at the beginning of the quasi-isothermal temperature reaction zone region.

reproduce discharge pulses exciting the flow in the reactor (45–110 pulses corresponding to the temperature range of 1250 K to 520 K) was replaced by a constant-in-time excitation source, with the discharge current rescaled to couple the same amount of energy to the reacting flow as defined by the pyrolysis calibration.

To reproduce the experimental behavior of the PFR and its influence on the chemical kinetics, prescribed temperature profiles are implemented in the model such to replicate similar heating and cooling ramps as observed in the experimental temperature profiles (see Fig. 4). These profiles are produced by adjusting the heat-transfer coefficient along the reactor length to match the experimentally measured axial temperature distributions. The resultant temperature profiles are delimited by a quasi-isothermal reaction zone \( (T) \), where the reactive mixture enters the reactor at a predetermined inlet temperature \( (T_{\text{inlet}}=300 \text{ K}) \) and exits at approximately the same temperature. Since specific energy loading in the discharge at the present conditions is fairly low \( (4–7 \text{ meV/molecule}) \), combined with the highly dilute nature of the reactive mixture, the flow temperature rise due to plasma Joule heating and chemical heat release in the discharge section is insignificant, \( \sim 30–60 \text{ K} \).

Fig. 5. Electron energy loss fractions in ethylene–oxygen–argon mixture versus E/N predicted by the Boltzmann equation solver: (1) \( \text{O}_2 \), vibrational excitation, (2) \( \text{O}_2 \) electronic excitation, (3) \( \text{O}_2 \) dissociation, (4) Ar electronic excitation, (5) Ar ionization, (6) hydrocarbon dissociation. Hatched region denotes the range of E/N values corresponding to the present experimental conditions. Modeling conditions: \( P=1 \text{ atm, } X(\text{C}_2\text{H}_4)=800 \text{ ppm, } X(\text{O}_2)=3000 \text{ ppm, } X(\text{Ar})=0.9962 \).

The full list of reactions incorporated into the present kinetic mechanism and their rate coefficients can be found in the supplemental material, along with the references detailing their source of origin. Based on previous modeling studies [21], under the present experimental conditions, electron–ion recombination, ion–ion neutralization, electron attachment/detachment reactions, and ion–molecule reactions have almost no effect on the electron and ion densities since they occur on time scales much longer compared to the voltage pulse duration \( (\sim 50 \text{ ns}) \). As discussed above, at the present conditions the two dominant processes controlling the electron density are the electron impact ionization and plasma self-shielding due to charge separation. Thus, in the present work ion chemistry is neglected.

The present kinetic mechanism incorporates electron impact processes with all major constituent species in the reactive mixture, including \( \text{Ar, O}_2 \) and hydrocarbon fuels, \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_2, \) and \( \text{CH}_4 \). For molecular \( \text{O}_2 \), excitation of the two low-lying metastable electronic states are considered, \( \text{O}_2(\text{A}^1\Delta_u, \text{B}^1\Sigma_u^+) \), as well as excitation of higher electronic states leading to dissociation. This includes \( \text{O}_2(\text{A}^3\Sigma_u^+, \text{C}^3\Delta_u, \text{C}^1\Sigma_u^-) \) (considered to be a single effective state) forming two \( \text{O}(\text{3P}) \) atoms, and \( \text{O}_2(\text{B}^3\Sigma_u^-) \) forming \( \text{O}(\text{3P}) \) and \( \text{O}(\text{1D}) \) atoms. Note that at the present conditions, reactions of \( \text{O}_2(\text{A}^1\Delta_u, \text{B}^1\Sigma_u^+) \) molecules have almost no effect on the plasma chemistry since the discharge energy fraction going into their generation is very low (see Fig. 5). For \( \text{Ar} \), a single excited state (denoted as \( \text{Ar}^* \)) is considered to represent the two metastable states of \( \text{Ar}(\text{2P}_0, \text{2P}_2) \). From Fig. 5, it can be seen that \( \text{Ar}^* \) reactions are likely to have a significant effect on the plasma chemistry since electronic excitation of \( \text{Ar} \) is the dominant electron impact process at the present conditions (discharge energy fraction of \( \sim 70–90\% \)). The only ionization reaction included in the mechanism is that of \( \text{Ar} \), since it is the dominant species in the reactive mixtures. \( \text{Ar}^* \) quenching rate coefficients by major constituent species, such as \( \text{O}_2 \) and \( \text{CH}_4 \), as well as the branching ratios, are available in the literature. However, for \( \text{C}_2\text{H}_4 \) and higher order hydrocarbons only the quenching rate, but not the branching ratio could be found. Therefore, in the present work the branching ratio for \( \text{Ar}^* \) quenching by \( \text{C}_2\text{H}_4 \) is inferred from the \( \text{C}_2\text{H}_4–\text{Ar} \) plasma-assisted pyrolysis experiments. Finally, electron impact excitation processes of hydrocarbon species are assumed to result in their dissociation and
formation of radicals and smaller hydrocarbons. However, these processes are expected to have a relatively minor effect on the plasma chemistry due to a very low mole fraction of the fuel in the mixture, less than 1000 ppm.

Lastly, the plasma chemical reactions are coupled to a comprehensive combustion chemistry mechanism, AramcoMech 1.3 [22], validated across several different experimental platforms and a wide range of conditions. Developed through a hierarchical approach, the mechanism includes sub-mechanisms to describe the kinetics of hydrocarbons ranging from C$_1$ to C$_4$, as well as oxygenated species. Figure 6 shows examples of predicted species mole fraction profiles for two sets of experimental conditions at different reaction zone temperatures, $T = 620$ K and $T = 862$ K. The reactive mixture enters the reactor at the inlet (reactor length = 0 m), where almost no chemical reactions occur while the flow is being preheated in the heating ramp zone. Once preheated to the desired reaction zone temperature, the extent of reaction is mainly confined to the plasma discharge region (hatched region in Fig. 6), with the mixture reacting thermally for the remainder of the reaction zone, the extent of which depends upon $T$. As the reacting mixture progresses through the cooling ramp zone, any remaining reaction is rapidly terminated prior to the flow exit.
ing at the reactor outlet (reactor length = 1.2 m). The experimental data are compared to the modeling predictions at the exit of the reactor. For T < 520 K, comparison of experimental data and the model predictions was not performed due to the presence of some nonuniformity in the plasma at these temperatures (see Tsolas et al. [10]).

3. Results

3.1. Thermal reactions

Figure 7 presents a comparison between the experimental and modeling results for the thermal pyrolysis of ethylene. The model displays approximately 8% deviation from the experiments at the maximum point of reactivity, with acetylene (C2H2) being the only measured product of ethylene consumption at temperatures greater than 1100 K. Kinetically, this behavior can be described by the following chain-propagating reactions, where the entire H-atom yield comes from the thermal decomposition of the vinyl radical (C2H3):

\[
\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_3 + \text{H}_2 \quad \text{(R1)}
\]

\[
\text{C}_2\text{H}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_2 + \text{H}(+\text{M}) \quad \text{(R2)}
\]

In Fig. 8, the comparison of the experimental and modeling results for the thermal oxidation of ethylene is presented. For the major species, namely C2H4, CO, and CO2, the model has relatively good agreement with the experimental data for T > 860 K, while the model predicts a slightly lower hot-ignition temperature, by approximately 50 K. For methane (CH4) and ethane (C2H6), the model overpredicts the mole fraction of both these species, by approximately a factor of two at the conditions of their maximum extent of formation. Also, while C2H2 was not observed in the experiments, the model predicts its formation in appreciable amounts for T=900–1000 K.

The primary pathways leading to C2H4 consumption at T=960 K are H-atom abstraction by OH (R3) and H-atom addition (R4), with the O-atom reaction (R5) being of secondary importance:

\[
\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{C}_2\text{H}_3 + \text{H}_2\text{O} \quad \text{(R3)}
\]

\[
\text{C}_2\text{H}_4 + \text{H}(+\text{M}) \rightarrow \text{C}_2\text{H}_2(+\text{M}) \quad \text{(R4)}
\]

\[
\text{C}_2\text{H}_4 + \text{O} \rightarrow \text{CH}_3 + \text{HCO} \quad \text{(R5)}
\]

Reaction (R4) forms significant amounts of the ethyl radical (C2H5) early on during the reaction process, with more than 90% of it reacting with molecular oxygen to reform C2H4 (R6). This reaction sequence consumes most of the H-atoms in the system, producing large amounts of the hydroperoxyl radical (HO2). The remaining C2H2 radicals react with H-atoms to form methyl (CH3) radicals (R7), which further react to form mostly CH4 and C2H6:

\[
\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2 \quad \text{(R6)}
\]

\[
\text{C}_2\text{H}_5 + \text{H} \rightarrow \text{CH}_3 + \text{CH}_3 \quad \text{(R7)}
\]

The extent of CO formation is dictated by the fate of the vinyl radicals, controlled by reaction (R3) and (R8), which yield formaldehyde and formyl radicals (HCO). Close to 60% of the formyl radicals are formed directly through reactions (R5) and (R8), while about 40% results from further reactions of CH2O ((R9), (R10)):

\[
\text{CH}_2\text{O} + \text{H} \rightarrow \text{HCO} + \text{H}_2 \quad \text{(R9)}
\]

\[
\text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O} \quad \text{(R10)}
\]

The alternative route to CO formation occurs through conversion of C2H3 to C2H2 (R2), in which acetylene subsequently reacts with O-atoms to form the HCCO intermediate (R11). This route effectively leads to CO and CO2 formation and accounts for approximately 5% of the CO formation in the system:

\[
\text{C}_2\text{H}_2 + \text{O} \rightarrow \text{HCCO} + \text{H} \quad \text{(R11)}
\]

\[
\text{HCCO} + \text{O}_2 \rightarrow \text{CO} + \text{CO}_2 + \text{H} \quad \text{(R12)}
\]

The kinetics associated with this route are expected to lead to the mishandling of C2H2 prediction in the model. Firstly, under the present experimental conditions, both HCO formation and consumption pathways are comparatively faster than the C2H2→HCCO consumption pathways. Secondly, in the experimental data of Refs. [23–24], C2H2 was not a reported intermediate, since it was conclusively demonstrated that reaction (R8) dominates the destructive pathways of C2H3 under high-pressure conditions over C2H2.
3.2. Plasma-assisted pyrolysis reactions

Figure 9 presents the comparison of experimental and modeling results for the plasma-assisted pyrolysis of ethylene. Considering the coupled energy calibration was performed during these experiments, as discussed in Section 2, the model predicts the C2H4 profile versus temperature with very little discrepancy. The model has also been used to investigate the kinetics associated with the formation of secondary species. The total carbon conservation predicted by the model indicates that the experiments have accounted for all the secondary species due to the plasma-assisted pyrolysis reactions, with the model displaying the same kinetic trends for all species with respect to temperature. For C2H2, C2H6, and propane (C3H8), the model demonstrates good agreement, with less than 18% deviation from the experimental data for all temperatures con-
**Fig. 9.** Comparison of experimental results and modeling predictions for ethylene plasma-assisted pyrolysis. Modeling conditions: $X(C_2H_4)=800$ ppm, $X(Ar)=0.9992$, $P=1$ atm, residence time $=311.4 s \cdot K/T$, where $T$ is the temperature of the isothermal reaction zone in the reactor, and $Q_{dis}=0.083$ meV/molecule/pulse. Hollow symbols are experimental data; solid symbols are model predictions.
sidered. As for the remaining species, subtle differences exist. For
C₄ species (e.g., butane–C₄H₁₀ and butene–C₄H₆) and T < 800 K,
the model overpredicts the experiments by up to 35%, while mi-
nor C₃ species (e.g., propene–C₃H₆, propyne–C₃H₄) are consistently
underpredicted, up to roughly 60% at their maximum extent of for-
mation. Lastly, CH₄ is overpredicted for T > 900 K by up to 40% at
its maximum extent of formation.

3.3. Plasma-assisted oxidation reactions

Figure 10 presents a comparison of experimental and model-
ing results for the plasma-assisted oxidation of ethylene. For these
results, the coupled energy calibration obtained from the plasma-
asisted pyrolysis experiments, as discussed in Section 2, has been
used to predict the plasma-assisted fuel oxidation. Using this pro-
cedure, the model predicts greater fuel consumption than in the
experiments, particularly for temperatures less than 800 K. More-
over, the model also displays the appearance of a negative tem-
perature coefficient (NTC) regime, where reactivity of ethylene de-
creases as temperature increases from 520 K to 750 K, a kinetic
trend not seen in the experimental results. Similar to the thermal
reaction, the model predicts the hot-ignition temperature approx-
imately 50 K lower than the experimental results. The predictions of
major and minor species are in relatively good agreement, with
CO, CO₂, C₂H₆, C₂H₅, and C₂H₄ exhibiting correct kinetic trends and
minimal absolute discrepancies over a wide range of tempera-
ture. For CH₄, the model overpredicts its formation by up to 40%
between temperatures of 850 to 1000 K. Similarly, C₂H₂ is under-
predicted for T < 900 K consistently by a factor of two, whereas
acetaldehyde (CH₃CHO) is in poor agreement for T < 700 K. Based
on the total carbon conservation, the model also predicts several
product species for T < 800 K in appreciable amounts, not mea-
sured in the experiments, including CH₃O, formic acid (HOCHO),
permformic acid (HO₂CHO), several alcohols, and hydroperoxides.
The formation of these species is consistent with the enhanced
fuel consumption predicted by the model for temperatures below
800 K. To better resolve and confirm the existence of these species,
the experimental GC system would require further optimization to
enhance the detection of oxygenated species. In addition, more di-
rect and explicit experimental methods could be viable options to
tailor the detection of a specific species (e.g., CH₂O LIF).

4. Discussion

The formation of the plasma is caused by electric breakdown of
the reacting mixture, by electron impact ionization of argon atoms
(ionization potential 15.8 eV) to form electrons and Ar⁺ ions. Elec-
trons formed during this process also result in electronic excita-
tion and dissociation of neutral species in the reactive mixture,
by electron impact processes. Apart from ionization, a significant
portion of the discharge input energy goes into excitation of el-
ectedronic states of argon, forming metastable Ar⁺ atoms (see Fig. 6).
Due to the highly dilute nature of the reactive system, this is the
dominant electron impact process. Direct electron impact excita-
tion and dissociation of fuel (ethylene) and oxygen are negligible,
since these species constitute less than 1% mole fraction of the
mixture. Thus, the dominant role of the plasma at the present con-
ditions is to generate Ar⁺.

4.1. Kinetics of plasma-assisted ethylene pyrolysis

Under the influence of the plasma, Ar⁺ collisional quenching re-
actions leading to the dissociation of ethylene dominate the kinetic
routes, thus enhancing fuel decomposition. Table 1 summarizes the
fuel dissociative pathways with Ar⁺ that are employed in the cur-
rent mechanism (see (R13)–(R16)) compared to reactions used in
past studies.

To derive these following ratios, a brute force sensitivity analy-
ysis was performed, where the total rate of (R13)–(R16) was kept
constant. Each branching ratio represents a separate reaction, and
hence has a different sensitivity towards a particular measured
species. Thus the branching ratios were adjusted and determined
by a best-fit analysis that replicated the product species distribu-
tion in the experimental data with the greatest degree of agree-
ment. Hence, the substantial increase in the decomposition of ethylene is expected, as these reactions provide new dissociative
pathways independent of temperature, with no kinetic equiva-
 lent in the thermal reaction. Considering that 80% of the product
branching ratios of these reactions result in C₂H₂, the model
does its formation as the major by-product of fuel decompo-
sition. In this case, reaction (R14) is equivalent to the electron-
impact reaction (c) and quenching reaction (b), contributing to
the enhancement of C₂H₂ in the non-dilute studies with air of Ref.
[3]. However, unlike Ref. [3] an additional reaction was also im-
plemented herein to increase the branching factor of this reaction
by producing two H-atoms (R13). Thus, reactions (R13) and
(R15) contribute to more than 90% of the plasma chemical H-
atom yield and are a major source of enhancing the H-atom radical
pool.

Figure 11 provides a summary of the path flux analysis de-
rived to elucidate the main kinetic routes involved in the plasma-
asisted ethylene pyrolysis process as a function of temperature.
At low (T = 620 K) and intermediate (T = 862 K) temperatures, di-
dition reactions dominate the kinetic behavior of the system, where
more than 60% of the H-atoms produced at these temperatures
to increase the hydrocarbon growth characteristics of
the system. Firstly, the plasma-specific reactions, (R13)–(R16), con-
tribute to only half of the total fuel consumption in the system,
with the remaining consumption coming from the neutral chem-
istry due to the abundance of H-atoms (see reaction R4). The C₂H₃
radical is present in the largest quantity of all the hydrocarbon
radicals at low temperatures. Even though reactions (R15) and (R16)
contribute about 20% to the product branching ratio, C₂H₃ and
methylene (CH₂) radicals are present in the established hydro-
carbon radical pool, albeit at smaller concentrations. From here,
recombination reactions involving C₂H₂ lead to the formation of
C₄H₁₀, C₄H₈, and C₂H₆. As a secondary effect, the enhancement of
H-atoms drive reaction (R7) to facilitate the formation of CH₃
radicals, which leads to the observed formation of C₃H₈ and C₂H₄.
As temperature increases (towards intermediate temperatures),
the stabilization of the C₂H₂ radical becomes increasingly difficult to
sustain, and the C₂H₃ and CH₂ radical chemistry becomes compe-
titive through reactions (R15) and (R7). The product species formed

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Comparison of quenching reactions and branching ratios of ethylene employed in the current study compared to past investigations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
<td>Rate constant [cm³/s]</td>
</tr>
<tr>
<td>(R13) Ar⁺ + C₂H₂ → Ar + C₂H₂ + H + H⁺</td>
<td>0.52</td>
</tr>
<tr>
<td>(R14) Ar⁺ + C₂H₂ → Ar + C₂H₂ + H₂</td>
<td>0.28</td>
</tr>
<tr>
<td>(R15) Ar⁺ + C₂H₂ → Ar + C₂H₂ + H + H⁺</td>
<td>0.10</td>
</tr>
<tr>
<td>(R16) Ar⁺ + C₂H₂ → Ar + C₂H₂ + CH₂</td>
<td>0.10</td>
</tr>
</tbody>
</table>

| Note: | In Ref. [3] individual excited states were considered, where N₂⁺ denotes electronically excited N₂(aΣ⁺), N₂(b²Π), and N₂(c²Π), each with a different rate constant when reacting with C₂H₂. Refer to Ref. [3] for actual rate constant values and σ denotes rate constants calculated by Boltzmann equation. |

*Note: See Table 1 for more details.*
Fig. 10. Comparison of experimental data and modeling predictions for ethylene plasma-assisted oxidation. Modeling conditions: $X(C_2H_4)=800$ ppm, $X(O_2)=3000$ ppm, $X(Ar) = 0.9962$, $P = 1$ atm, residence time $= 311.4 \times K/T$, where $T$ is the temperature of the isothermal reaction zone in the reactor, and $Q_{dis} = 0.083$ meV/molecule/pulse. Hollow symbols are experimental data; solid symbols are model predictions.
from these radicals then reach their maximum extent of formation, namely CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{3}H\textsubscript{6}. In the work of Ref. [29] (P=60 Torr), CH\textsubscript{4} was detected as a significant product in both their pyrolysis and oxidation studies at their low temperature (T < 500 K) experimental conditions. The fact that methane peaks towards higher temperatures (T > 800 K) in this work is the main motivation behind the exclusion of reaction (a). The appearance of C\textsubscript{3}H\textsubscript{4} is entirely due to the CH\textsubscript{2} route (R16), which reacts with the abundant C\textsubscript{2}H\textsubscript{2} to form the propargyl radical (C\textsubscript{3}H\textsubscript{3}), followed by H-atom addition.

At the highest temperature examined (T=1153 K), the contribution of the plasma to the overall reaction begins to dimin-
ish, since only 27% of the fuel consumption comes from reactions (R13) through (R16), while nearly 70% comes from reaction (R1). At this point, the hydrocarbon radical pool mainly consists of C₂H₃ radicals, and pathways leading to secondary hydrocarbon species formation, other than C₂H₂, cease. However, H-atoms formed from the plasma reactions (R13) and (R14) provide a secondary source to drive reaction (R1), which leads to an enhancement of both C₂H₄ consumption and C₂H₂ formation compared to the thermal reaction alone under the same high temperature conditions.

4.2. Kinetics of plasma-assisted ethylene oxidation

Similar to the collisional quenching reactions of Ar⁺ by ethylene, (R13)–(R16), Ar⁺ also provides two new dissociative pathways for molecular oxygen, which have no parallel in a thermal system until relatively high-temperatures (close to the self-ignition temperature).

\[ \text{Ar}^+ + \text{O}_2 \rightarrow \text{O} + \text{O} + \text{Ar} \quad (R17) \]

\[ \text{Ar}^+ + \text{O}_2 \rightarrow \text{O} + \text{O}(^{1}\text{D}) + \text{Ar} \quad (R18) \]

The excited O(1D) is a highly reactive species that can enhance the reactivity of the system. However, due to the relatively large proportion of Ar in the system, the fate of O(1D) primarily results in its collisional quenching with Ar to form a ground state O-atom.

4.2.1. Characteristics of low temperature kinetics

The path flux analysis for the low temperature \( (T=620 \, \text{K}) \) plasma-assisted oxidation reaction is shown in Fig. 12, where the major fuel consumption pathways are shown to fall into three major categories. The first is the direct collisional quenching of Ar⁺, identical to the pyrolysis reactions (R13)–(R16). Under oxidative conditions, these plasma-initiated reactions have considerably less influence on the reactivity of the system as they only account for 12% of the total fuel consumption. The second pathway is through radical attack, namely O-atoms and H-atoms, which are formed as a consequence of the plasma (see reaction R5). More than 90% of the O-atoms are generated by reactions (R17) and (R18), with reaction (R13) providing nearly 20% of the total H-atom yield in the system. These channels provide close to 59% of the total fuel consumption, resulting in the formation of C₂H₃ (~33% of the total fuel consumption), C₂H₂ (~14% of the total fuel consumption) and vinyl (CH₂=CHO) radicals (~12% of the total fuel consumption). The C₂H₂ and CH₂=C=O react predominately with O₂ to form RO₂, which are the main source of hydroperoxides (C₂H₃OOH, C₂H₄OOH) produced in the system by way of reactions with OH₂. To clarify, these routes are not associated with internal isomerization kinetics as found in low temperature oxidation reactions of large molecular weight hydrocarbons (see Ref. [26]). For small molecular sized hydrocarbons, a chain-branching feature is achieved by a simpler sequence through the formation and decomposition of a peroxide and hydroperoxide [27–28]:

\[ \text{C}_2\text{H}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{O}_2 \quad (R19) \]

\[ \text{C}_2\text{H}_5\text{O} + \text{HO}_2 \quad (R20) \]

\[ \text{C}_2\text{H}_5\text{OOH} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{OH} \quad (R21) \]

At 620 K, reactions (R19) and (R20) are more than 6 orders of magnitude faster than the decomposition reaction (R21). For this reason, the model predicts that C₂H₅OOH remains relatively stable at these conditions and is probably not the likely source for enhanced low temperature reaction. Considering that CH₃CHO was a minor intermediate species observed experimentally in the low temperature regime, the inability of the model to predict its formation potentially suggests that the kinetics associated with the above scheme requires further study. An indicative feature of high pressure and low temperature oxidation systems is R+O₂ = RO₂ chemistry (R being an alkyl radical), the applicability, and for that matter, the product channels that these reactions experience at lower pressures can contain considerable uncertainty. Formation of the ethoxy radical (C₂H₃O) through reaction (R21), followed by reactions (R22) and (R23) are viable routes for CH₃CHO formation:

\[ \text{C}_2\text{H}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 \quad (R22) \]

\[ \text{C}_2\text{H}_3\text{O} \rightarrow \text{CH}_3\text{CHO} + \text{H} \quad (R23) \]

Other possible routes for CH₃CHO formation are reactions (R24) and (R25). Reaction (R25) is of considerable interest because it has already been discussed that the plasma has the capacity to enhance both C₂H₂ radicals and O-atoms at low temperature conditions:

\[ \text{C}_2\text{H}_5\text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{OH} \quad (R24) \]

\[ \text{C}_2\text{H}_5 + \text{O} \rightarrow \text{CH}_3\text{CHO} + \text{H} \quad (R25) \]

The CH₃ and CH₃CHO radicals formed by O-atom reactions with C₂H₂ continue to react to form a series of oxygenated species that decompose to provide nearly 20% of the total OH yield along with CH₂O. The last major fuel consuming pathway (~29% of the total fuel consumption) is through an addition reaction with the OH radical to form C₂H₅OH, which subsequently reacts with molecular oxygen to form a peroxy intermediate that further decomposes to form CH₂O and OH, contributing another 40% to the total OH radical yield. The molecular oxygen addition pathways are the main reason why low temperature plasma-assisted oxidation does not yield C₂ or C₃ hydrocarbon intermediates, since they are favored over pyrolysis radical recombination reactions.

A major intermediate is the formation of CH₂O, where more than 62% of the CH₂O consumption results in HCO (~69% of the HCO produced is through radical abstraction reactions with CH₂O versus ~7% through the reaction of C₂H₂ with O₂), which leads to the dominant route for low temperature CO formation. The second CH₂O route provides another major source of H-atoms through HOCH₂O decomposition (~34% of the total H-atom yield). Both CH₂O consumption routes are major sinks for OH radicals, accounting for more than 50% of all the OH consumed in the system. A major by-product of CO formation is HO₂, where ~77% of the total HO₂ is produced through the HCO+O₂ reaction. At low temperatures, because of the plasma enhancement of H-atoms, HO₂ effectively reacts with H-atoms to propagate the radical pool, providing some 20% of the total OH yield:

\[ \text{HO}_2 + \text{H} \rightarrow \text{OH} + \text{OH} \quad (R26) \]

This is the same kinetic feature found in the hydrogen oxidation system of Ref. [21], where a relatively unreactive species is converted into a more reactive radical to facilitate the oxidation process. Despite the plasma being able to produce C₂H₂ with relative ease, the C₂H₂–HCO route to CO formation is of little importance at these low temperature conditions, but rather acts as a low temperature route for CO₂ formation. The remaining CO₂ is equally formed through HOCH₂O decomposition or OH-attack on CO.

4.2.2. Characteristics of intermediate temperature kinetics

The path flux analysis for the intermediate temperature \( (T=862 \, \text{K}) \) plasma-assisted oxidation reaction is shown in Fig. 13.
The plasma specific fuel decomposition reactions (R13)-(R16) still play a minor role in contributing to the total fuel consumption (~8%), with reactions (R17) and (R18) providing more than 80% of the O-atom yield. Approximately 29% of the total fuel consumption comes directly from these O-atom channels due to their enhancement by the plasma. This leads to the production of CH₃ and CH₂CHO radicals, with the latter route providing 18% of the total H-atoms in the system. The influence of reaction (R13) has also decreased compared to the low temperature reaction, since this reaction now only provides 12% of the total H-atom yield.

The greatest kinetic difference between this intermediate temperature reaction and the previously discussed low temperature reaction comes from the enhancement of the C₂H₂ production route, which has the greatest effect on consuming the fuel (~45%). The fate of C₂H₂, CH₃, and CH₂CHO then dictates the various kinetic features of the intermediate temperature reaction. The formation of peroxy radicals is non-existent at this temperature, rather the system reverts to forming stable hydrocarbon intermediate species, including C₃H₆, C₄H₆, C₂H₆, and CH₄ through recombination reactions similar to the pyrolysis system. Hydroxyl radical addition reactions become competitive and lead to the enhancement of alcohol species, namely ethanol (C₂H₅OH), ethenol (C₂H₂OH) and methanol (CH₃OH). The formation of these more stable by-products is responsible for the observed inhibition in the rate of oxidation for T=520–750 K, since they do not actively participate in contributing to the oxidation process. Another major source for inhibition comes from the C₂H₂ reforming reaction (R6), which accounts for 45% of the consumption of the C₂H₂ radical and provides one of two major sources for the production of HO₂ (~34% of the total HO₂ yield). Unlike the low temperature reaction, HO₂ plays a more active role in the oxidation process at intermediate temperatures. Reaction (R26) contributes to more than 50% of the OH-radical yield in the system, but R+HO₂ reactions lead to the formation of methoxy (CH₃O) and ethoxy (C₂H₂O) radicals. The consequences of these channels are twofold; first, they account for more than 50% of CH₂O formation and second, they also account for another major source of OH production in the system (~43% of the total OH yield). The established formation of OH radicals.

Fig. 12. Path flux analysis of the dominant species consumption routes for plasma-assisted oxidation of ethylene at low temperatures, T=620 K and P=1 atm.
Fig. 13. Path flux analysis of the dominant species consumption routes in plasma-assisted oxidation of ethylene at intermediate temperatures, $T=862$ K and $P=1$ atm.
Fig. 14. Path flux analysis of the dominant species consumption routes in plasma-assisted oxidation of ethylene at high temperatures, $T=1153$ K and $P=1$ atm.
leads to the last major fuel consumption route to enhance the formation of the C$_2$H$_3$ radical, which goes on to produce 22% of the total CH$_2$O. Similar to the low temperature reaction, CH$_2$O is a major source of HCO (∼50% of the total CH$_2$O consumed yields HCO), with nearly 40% coming from both the C$_2$H$_4$+O, and C$_2$H$_3$+O$_2$ reactions. HCO is once again the dominant species leading to CO production, with the thermal decomposition reaction now accounting for ∼38% of the total CO.

4.2.3. Characteristics of high temperature kinetics

The path flux analysis for the high temperature (T = 1153 K) plasma-assisted oxidation reaction is shown in Fig. 14. At this relatively high temperature (above the self-ignition temperature), the plasma specific reactions have little effect on the overall oxidation process. Rather, the high-temperature chain-branching processes dictate the oxidation process, where H$_2$O=O+OH provides more than 95% and 70% of both the O-atoms and OH radicals in the system. From here, more than 85% of the fuel consumption channels occur through either C$_2$H$_4$+O or C$_2$H$_4$+OH reactions, mainly resulting in the formation of CH$_3$ and C$_2$H$_3$ radicals. Although these radicals can form hydrocarbon intermediates, they are consumed immediately to form CH$_3$ fragments. All CH$_3$ channels end up falling into the CH$_2$O-HCO-CO pathway and are immediately oxidized. The CO+OH route accounts for 84% of the CO$_2$ produced in the system, with the remaining 14% provided by the C$_2$H$_2$=HCO route.

5. Conclusions

A plasma-enhanced reaction mechanism was developed and tested to study the kinetics associated with the plasma-assisted pyrolysis and oxidation of ethylene. The constructed mechanism includes several sub-mechanisms tailored to describe the pertinent chemistry governing plasma-assisted combustion (PAC), including electron-impact processes, and reactions of excited species, combined with a relatively recent comprehensive combustion mechanism (neutral chemistry) suited for low temperature combustion up to C4 and oxygenated species. For the plasma-assisted ethylene pyrolysis experiments, the kinetic trends were appropriately captured, both for major and minor species, based on the branching ratio for the Ar$^+$+C$_2$H$_4$ quenching reaction inferred from the experimental data. This ratio differs from past studies [3,29], firstly because it assumes that more than one potential dissociative pathway exists for C$_2$H$_4$, and also 80% of this reaction leads to the direct formation of C$_2$H$_2$, and 62% leads to the generation of H-atoms. Enhanced fuel consumption is attributed to collisional quenching reactions between excited states of argon generated in the plasma with ethylene. The different product channels of this reaction lead to the generation of both hydrocarbon (e.g., C$_2$H$_3$, C$_2$H$_4$) and H-atom radicals, with acetylene being the major by-product of immediate ethylene decomposition. At low temperatures, addition reactions are favored, leading to a considerable enhancement of the ethyl radical, where recombination reactions dictate the permutation of hydrocarbon intermediates formed. As temperature increases, the growth characteristics of the system become less effective, and fuel fragments predominantly result in smaller order hydrocarbons, with the methyl radicals mainly dominating the formation of intermediate species. In the oxidation system, the overall comparison of the modeling predictions with the experimental results was satisfactory. Good agreement was achieved for most major and minor species, but the lack of agreement with certain species and the prediction of several species not currently measured in the experiments highlight the deficiencies in the current mechanism. Quenching of excited argon by oxygen molecules leads to the generation of the O-atom radical pool and enhances the reactivity of the neutral kinetics. Since the rates of these quenching reactions are essentially temperature independent, these plasma specific reactions provide PAC systems their enhancing capabilities, of which there is no equivalent in thermally constrained systems. Through a path flux analysis, the inhibition in the rate of oxidation from low to intermediate temperatures is due to the competition between R+O$_2$ and pyrolysis reactions (R being a hydrocarbon radical), with the former chemistry leading to oxygenated intermediates that readily decompose to form branching products and enhance the oxidation process. The ability of the plasma to enhance the production of OH, H-atom and O-atom radicals leads to initiating the high temperature chain-branching process to improve ignition. At relatively high temperatures beyond the self-ignition point, the chain-branching kinetics are comparatively faster than any advantage the plasma is capable of providing, and the thermal neutral kinetic effects dominate the system.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2016.10.023.

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