



Kinetic development of low-temperature propane oxidation in a repetitively-pulsed nanosecond discharge

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ABSTRACT

The kinetics of plasma assisted low temperature oxidation of $C_3H_8/O_2/Ar$ mixtures have been studied in a wide specific deposited energy with the help of nanosecond repetitively pulsed discharge. Two types of nanosecond pulsed plasma sources, the nanosecond capillary discharge (nCD) and dielectric barrier discharge (DBD) combined with the synchrotron photoionization mass spectrometry are investigated. The electron impact reaction rate of propane dissociation and some combustion chemical reactions rate constants are updated according to the nCD and DBD experiment results, and uncertainty of the reactions are analyzed in detail. Compared to the existing model, the updated model's prediction accuracy has great improvement in species H_2O , CO_2 , CH_4 , CH_2O , CH_3OH , C_2H_2 , C_2H_6 , C_2H_5OH , C_2H_5OOH , C_3H_4-A , C_3H_4-P , C_2H_5CHO , $i-C_3H_7OH$ and C_3H_7OOH . The propane oxidation processes assisted by DBD and nCD were compared under different single pulse deposited energy (SPDE) conditions while maintaining the same total deposited energy. The reduced electric field in nCD is concentrated at 150–200 Td and 450–500 Td, whereas in DBD it ranges from 1–100 Td and 260–380 Td. Notably, for nCD at different voltages with a similar reduced electric field distribution, SPDE shows minimal influence on the C_3H_8 oxidation process, which is primarily governed by total deposited energy. nCD is more effective discharge form for contribute to C_3H_8 dissociation compared to DBD.

Novelty and significance statement

The study of plasma assisted fuel conversion and efficient combustion requires precise data on plasma chemistry and combustion chemical reaction kinetics. However, the computational complexity of excited state reaction kinetics data based on first principles is enormous, resulting in a scarcity of relevant basic data. Propane, as a relatively large molecule, is an important object for studying its low-temperature oxidation pathway in plasma ignition and combustion assistance. The research that was lacking in the early stage mainly used analogy estimation and limited experimental research on a few reactions. In this work we revised the reaction kinetics mechanism of propane low-temperature oxidation reaction by constructing two independent experiments, and discussed the general effects of energy deposition and electric field (which are the key parameters of a plasma system) on propane plasma low-temperature oxidation. This study can serve as a foundation and reference for studying plasma pyrolysis of macromolecular fuels.

1. Introduction

Non-equilibrium plasma-assisted combustion (PAC) offers an effective approach for controlling ignition in internal combustion engines, industrial burners, and aviation engines, thereby enhancing flame stability, reducing pollutant emissions, and expanding ignition limits [1–3]. Understanding the detailed mechanism of PAC requires studying the kinetic pathways of PAC and quantifying their reaction rates. Many studies have been carried out to understand the role of plasma

generated species on ignition, flame speed, and flame stabilization of small molecular fuels such as hydrogen [4,5], methane [6–10], ammonia [11–14], ethylene [15,16]. Particularly, the kinetics of non-equilibrium plasma-assisted small molecules like hydrogen, methane have been extensively studied.

Propane, as the smallest n-alkane with low-temperature reactivity, serves as a typical molecule for studying the kinetics of large alkanes [17,18], attracting significant attention from researchers.

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Adamovich et al. [19] proposed a plasma-assisted propane-air combustion kinetic model, which showed good agreement with experimental temperature and time-resolved OH density measurements. They further studied the plasma-assisted propane oxidation kinetics in $C_3H_8/O_2/Ar$ mixtures [20], validated the kinetic model with experiments on alkane small molecule density at different temperatures, and found large discrepancies for C_2H_2 and CH_3CHO . Chen et al. [21] employed molecular beam mass spectrometry with tunable synchrotron vacuum ultraviolet photoionization (SVUV-PIMS) to measure hydrocarbons and oxygenated intermediates during plasma-assisted $C_3H_8/O_2/Ar$ processes, reporting numerous oxygenated intermediates and establishing a kinetic model. However, significant discrepancies existed between the model predictions and experimental measurements for certain hydrocarbons and intermediates. Ban et al. [22] developed a propane-air plasma combustion mechanism and validated it against OH density measurements from experiments [23] that lacked sufficient validation. Based on the above analysis, current kinetic models still exhibit significant discrepancies with experimental measurements in predicting certain hydrocarbons and oxygenated intermediates. Furthermore, current kinetic models are validated under specific single pulse deposited energies, necessitating further validation under larger deposited energy scales.

To validate the kinetics of the plasma-assisted oxidation process in $C_3H_8/O_2/Ar$ mixtures under large deposited energy scales, stable discharge characteristics and spatiotemporal uniformity are required in experiments. Fast ionization wave (FIW), a nanosecond capillary discharge at moderate pressures, is characterized by spatiotemporal uniformity of discharge, high reduced electric field, high electron energy, and fast propagation speed [24]. FIW serves as an ideal platform for investigating fundamental plasma processes under various discharge parameters and energy deposited conditions [24–30]. Due to its uniformity and high energy deposited, FIW is suitable for investigating plasma-assisted fuel cracking and oxidation. FIW has two discharge types depending on the presence or absence of a metal screen. In the absence of a metal screen (referred to as nanosecond capillary discharge, nCD), the discharge propagation pattern shifts from single-direction to dual-direction propagation, improving discharge channel uniformity. Consequently, nCD is particularly suitable for validating the accuracy of $C_3H_8/O_2/Ar$ plasma combustion mechanisms under varying energy deposited conditions.

In this study, we investigate the mechanism of plasma-assisted low-temperature oxidation of propane using numerical simulations and capillary discharge experiments. Section 2 outlines the numerical model, the kinetic schemes, and the experimental setups. The validation of the kinetic schemes against capillary discharge experiments and DBD experiments [21] is detailed in Section 3. An uncertain analysis of the kinetic schemes is performed using path analysis in Section 4.1. Section 4.2 compares the differences between nCD and DBD in the process of propane oxidation. Finally, we provide conclusions in Section 5.

2. Experiment and modeling method

2.1. The experiment settings

The experimental setup of the nCD-assisted propane oxidation is depicted in Fig. 1. This setup primarily comprises a gas supply and control system, a plasma discharge system, and a gas collection and analysis system. The discharge system includes a high-voltage electrode, a ground electrode, a cylindrical quartz tube, and insulating rubber gaskets. The cross-sectional diameter and length of the discharge region are 4.5 mm and 50 mm, and the distance between the two electrodes is 44 mm.

The gas mixture in the cylinder consists of Ar, O_2 , and C_3H_8 in a ratio of 92.46:6.33:1.21. Gas flow is controlled using a flowmeter (ASERT AST10-ALC 100 sccm) set at 30 sccm, and pressure is maintained at 3000 Pa by a rotary vane pump, monitored by a vacuum gauge

(AILEIKE TT&C Equipment Co., Ltd., ALKC400HJ, 0–1 atm absolute pressure gauge, 0.05%FS). As shown in Fig. 2, valve 3 is adjusted to stabilize the gas pressure before collecting the gas. During collection, valves 3 and 2 are closed, and a compression tank with variable volume stabilizes and stores the low-pressure gas, which is later pressurized to atmospheric pressure and analyzed using a gas chromatograph (GC) (Agilent 7890B) for species concentrations.

The discharge is powered by a nanosecond pulse discharge power supply (Xi'an Lingfengyuan Electronic Technology Co., Ltd., HVP-20P), providing continuous pulse outputs for steady-state gas collection. Each pulse has triangular wave shape with 50 ns rise and fall times, operating at a frequency of 1 kHz and a voltage range of 4.2 kV to 5 kV. Discharge voltage is monitored with a high-voltage probe (Tektronix, P6015A), and discharge current is measured with a current coil (Pearson 6585). Both voltage and current data are recorded using an oscilloscope (Siglent SDS2354X 350 MHz).

2.2. Modeling methods

A new coupled plasma and combustion chemistry solver, CPCC, has been developed by integrating the ZDPlasKin code [31] with a custom-built combustion code in F90 format. CPCC supports sensitivity and path flux analysis and interfaces with popular post-processing software such as QtPlasKin [32] and PumpKin [33]. Detailed descriptions of CPCC can be found in [13]. The electron impact process is solved using the Boltzmann equation solver BOLSIG+ [34], which is integrated within ZDPlasKin. The plasma kinetic mechanism and ground state kinetic mechanism are alternately solved using the splitting method. For efficient solution of large combustion kinetic mechanisms, CPCC utilizes the semi-implicit ODE solver VODPK [35] and the fifth-order implicit Runge–Kutta ODE solver, RADAU5 [36].

The key parameter of the reduced electric field (E/N) is derived from experimental current data using the following equation:

$$I = n_e \mu \left(\frac{E}{N} \right) E e S \quad (1)$$

where n_e is the electron density (initially set to $1.0 \times 10^9 \text{ cm}^{-3}$), I is the discharge current, μ is the electron mobility dependent on the reduced electric field, calculated by a Boltzmann equation solver (BOLSIG+) [34], N is the natural particle density of last time, E is the electric field, e is the elementary charge, and S is the cross-sectional area of the plasma. E is iteratively obtained using Eq. (1) through the Newton iteration method. The initial electron density is given a empirical value, because E is insensitive to the initial electron density, which will iterate consistently to a reasonable value in the first few time steps without affecting the result of the calculation. Then E/N is obtained by dividing E by N .

In present model, as the Poisson equation is not solved, the deposited energy is assumed to be an adjustable parameter and controls the discharge duration [7]. For DBD experiment, the present model's deposited energy stands at $2.35 \times 10^{-5} \text{ J/cm}^{-3}$, significantly lower than the experimentally measured value. For nCD experiment, To ensure good agreement with the experimental results, the model utilized 40% of the experimental deposited energy to regulate the discharge time.

To account for primary energy loss due to conduction to the quartz channel walls, similar to the approach in Ref. [9], the model includes surface heat transfer between the plasma and the quartz wall. In the energy equation for the nCD experiment, an additional energy loss term is introduced:

$$\rho C_v \frac{dT_{\text{gas}}}{dt} = - \sum_{i=1}^{i_{\text{max}}} H_i \omega_i - \frac{T_{\text{gas}} - T_{\text{wall}}}{\left(\frac{1}{A_1 h_1} + \frac{\ln(r_2/r_1)}{2\pi \lambda L} \right) V_p} \quad (2)$$

where ρ is the gas density, C_v is the specific heat capacity at constant volume of the gas, H_i and ω_i represent the enthalpy of formation and production/loss rate of component i , respectively. T_{wall} is the outer wall temperature of the quartz tube (set to 300 K), A_1 is the contact area

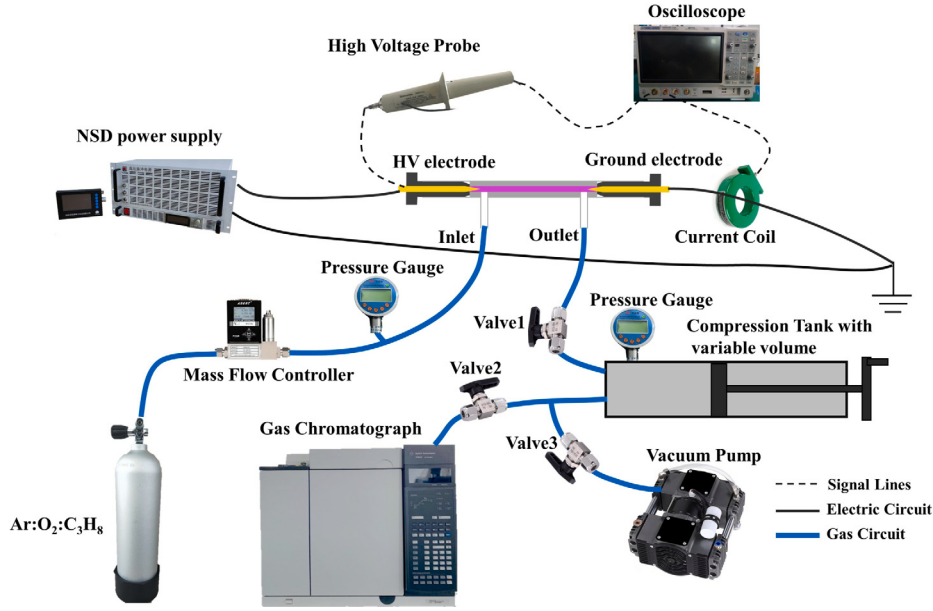


Fig. 1. The schematic of the nCD assisted propane oxidation experiment.

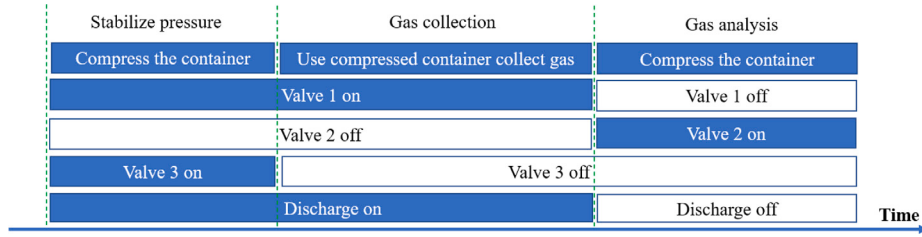


Fig. 2. The nCD experimental operation sequence diagram on the process of gas collection.

between the plasma and the inner wall of the quartz tube, h_1 is the heat transfer coefficient between the plasma and the inner wall of the quartz tube (which has been adjusted to $10 \text{ W}/(\text{m}^2 \text{ K})$ based on experimental results due to the cylindrical shape and small diameter of this structure, making empirical formulas unsuitable for estimating the heat transfer coefficient), r_2 and r_1 are the outer and inner radius of the quartz tube, λ is the thermal conductivity of quartz (which is $1.09 \text{ W}/(\text{m K})$), L is the length of the discharge region, and V_p is the volume of the plasma.

For a DBD configuration where the discharge region is rectangular, the energy loss term in the gas energy equation is adjusted as follows:

$$\rho C_p \frac{dT_{\text{gas}}}{dt} = - \sum_{i=1}^{i_{\text{max}}} H_i \omega_i - \frac{T_{\text{gas}} - T_{\text{wall}}}{\left(\frac{1}{A_2 h_2} + \frac{\delta}{A_2 \lambda} \right) V_p} \quad (3)$$

$$h_2 = \frac{\lambda}{L N_u} \quad (4)$$

$$N_u = 0.664 R_e^{1/2} P_r^{1/3} \quad (5)$$

$$P_r = \frac{C_p \mu}{\lambda} \quad (6)$$

$$R_e = \frac{\rho v L}{\mu} \quad (7)$$

where A_2 is the contact area between the plasma and the upper and lower walls, h_2 is the surface heat transfer coefficient of the walls (calculated using Eq. (4)), and the Nusselt number N_u is calculated using Eq. (5) from the book [37]. P_r is the Prandtl number (calculated by Eq. (6)), R_e is the Reynolds number (calculated by Eq. (7)), μ is the dynamic viscosity, v is the airflow velocity, and C_p is the specific heat capacity at constant pressure of the gas.

This kinetic model includes both plasma chemistry and classical combustion chemistry. The combustion chemistry model incorporates a total of 2521 reactions, which have been updated based on the scheme proposed in Ref. [21]. Specific modifications derived from experimental data are outlined in Table 1. In addition, several combustion reactions have been added and replaced, drawing from various established mechanisms such as HP-Mech v3.3 [38], AramoMech3.0 [39], NUIGMech1.1 [40] (shown in supplementary material of Table S1). The plasma chemistry model consists of 2202 reactions, involving vibrationally excited species such as $\text{C}_3\text{H}_8(\text{v}1)\text{-C}_3\text{H}_8(\text{v}27)$, $\text{CH}_4(\text{v}2, 4)$, $\text{CH}_4(\text{v}1, 3)$, $\text{O}_2(\text{v}1)\text{-O}_2(\text{v}4)$; electronically excited species like $\text{O}_2(\text{a}^1\Delta_g)$, $\text{O}_2(\text{b}^1\Sigma_g^+)$, $\text{O}_2(4.5 \text{ eV})$ (summation of $\text{O}_2(\text{c}^1\Sigma_u^-)$, $\text{O}_2(\text{C}^3\Delta_u)$, $\text{O}_2(\text{A}^3\Sigma_u^+)$), $\text{O}(\text{D})$, $\text{O}(\text{S})$, $\text{Ar}(1s_2)$, $\text{Ar}(1s_4)$, $\text{Ar}(11.55 \text{ eV})$, $\text{Ar}(2p_1)$; ions like O^+ , O_2^+ , O^- , O_2^- , O_3^- , CH_4^+ , CH_3^+ , CH_2^+ , CH_5O^+ , $\text{C}_2\text{H}_3\text{O}^+$, CHO_3^- , CO_3^- , CHO_2^- , OH^- , C_2H_4^+ , C_2H_5^+ , C_2H^+ , C_2H_3^+ , $\text{H}_5\text{C}_2\text{O}^+$, C_3H_7^+ , C_4H_9^+ , C_3H_8^+ , and electron. The plasma chemistry model includes chemical reactions involving vibrationally excited states, vibrational relaxation reactions, charge transfer reactions, and reaction channels involving $\text{O}(\text{D})$, $\text{O}(\text{S})$, $\text{O}_2(\text{a}^1\Delta_g)$, $\text{O}_2(\text{b}^1\Sigma_g^+)$, $\text{O}_2(4.5 \text{ eV})$, $\text{Ar}(1s_2)$, $\text{Ar}(1s_4)$, $\text{Ar}(11.55 \text{ eV})$, $\text{Ar}(2p_1)$ with fuel fragments. The electron collision dissociation cross-section for C_3H_8 is sourced from Ref. [41], while reactions involving electron collision dissociation for CH_4 , including dissociation and ionization, are adopted from Ref. [8]. The plasma chemistry of Ar and O_2 are taken from Ref. [42].

The original model in Sections 3 and 4 is defined as the plasma chemistry and classical combustion chemistry in which the reaction rate coefficients are from literature without any modifications. Compared to the model of Ref. [21], the original model reconstruct the plasma chemistry and has the same combustion chemistry. As some

Table 1
Updated plasma reactions and combustion reactions in this work.

	Plasma reaction	Original rate constant	Updated rate constant
R1	$e + C_3H_8 \rightarrow e + H_2 + C_3H_6$	$f(\sigma_1)[41]$	$0.8 \times f(\sigma_1)$
R2	$e + C_3H_8 \rightarrow e + CH_2 + C_2H_6$	$f(\sigma_2)[41]$	$12 \times f(\sigma_2)$
R3	$e + C_3H_8 \rightarrow e + CH_4 + C_2H_4$	$f(\sigma_3)[41]$	$0.36 \times f(\sigma_3)$
R4	$e + C_3H_8 \rightarrow e + H_2 + H_2 + C_3H_4$	$f(\sigma_4)[41]$	$0.75 \times f(\sigma_4)$
R5	$e + C_3H_8 \rightarrow e + CH_2 + C_2H_2 + 2H_2$	0.0	$21 \times f(\sigma_2)$
	Combustion reaction	Original Arrhenius equation of A	Updated Arrhenius equation of A
R6	$CH_3OH + O_2 \leftrightarrow CH_3O + HO_2$	3.58×10^4	0.0 [43]
R7	$n-C_3H_7O_2 + HO_2 \leftrightarrow n-C_3H_7O_2H + O_2$	1.75×10^{10}	6.0×10^8
R8	$i-C_3H_7O_2 + HO_2 \leftrightarrow i-C_3H_7O_2H + O_2$	1.75×10^{10}	6.0×10^8
R9	$i-C_3H_7O_2 + C_2H_6O_2 \leftrightarrow CH_3COCH_3 + C_2H_5OH + O_2$	0.0	2.5×10^{16}
R10	$n-C_3H_7O_2 + n-C_3H_7O_2 \leftrightarrow C_2H_5CHO + n-C_3H_7OH + O_2$	1.42×10^{16}	7.0×10^{15}
R11	$n-C_3H_7O_2 + i-C_3H_7O_2 \leftrightarrow C_2H_5CHO + i-C_3H_7OH + O_2$	1.409×10^{16}	4.109×10^{16}
R12	$i-C_3H_7O_2 + n-C_3H_7O_2 \leftrightarrow CH_3COCH_3 + n-C_3H_7OH + O_2$	1.409×10^{16}	1.169×10^{15}
R13	$i-C_3H_7O_2 + i-C_3H_7O_2 \leftrightarrow CH_3COCH_3 + i-C_3H_7OH + O_2$	1.409×10^{16}	2.109×10^{16}

* σ_x indicate the cross sections for the electron-impact reaction. The rate constant values are calculated by BOLSIG+ (indicated by f) given E/N and the cross section data. The unit of cross section data is m^2 . The unit of arrhenius equation pre-exponential factor A is $cm^3 mol^{-1} s^{-1}$.

reactions are not validated with experiments or quantum chemical calculations, the original model predictions for some species have large uncertainties. So the electron impact cross sections of propane, branch ratios of self-/cross-reactions for i -/ n - $C_3H_7O_2$ and H-abstraction of i -/ n - $C_3H_7O_2$ are fitted within uncertainties according to experimental data and path flux analysis (named as updated model in Sections 3 and 4). The updated reactions are listed in Table 1. Detailed descriptions and uncertainty analysis can be found in Section 4.1. The species overall predictions of the updated model are highly improved compared to the original model in DBD experiment [21] and nCD experiment conditions. Even so, the quantum chemical calculations or fundamental kinetic experiment are still required to improve the model's prediction capacity.

3. Validation of the mechanism

3.1. Validation I: DBD assisted propane oxidation

Model validation is performed by comparing the model predicted and experimental molar fractions of species in a repetitively-pulsed nanosecond DBD [21], as shown in Fig. 3. The experimental conditions involve a deposited energy of $1.64 \times 10^{-4} J/cm^3$, at 30 Torr and a discharge region temperature of 340 K, with a $C_3H_8/O_2/Ar$ mixture (mole fraction 4:20:76). The updated model's predictions for several species, including H_2O , CH_2O , CH_3OH , C_2H_2 , C_2H_4 , C_2H_5OH , C_2H_5OOH , C_3H_4-A , C_3H_4-P , C_3H_6 , CH_3COCH_3 , C_2H_5CHO , $i-C_3H_7OH$, and C_3H_7OOH are found to be in good agreement with experimental data, falling within the range of experimental measurement errors. The updated model's predictions for species CO , CO_2 , CH_4 , C_2H_6 , CH_2CO , CH_2CHO , and $n-C_3H_7OH$ are within 5 times of the experimental measurement. However, the updated model's predictions for species CH_3 , CH_3OOH , $c-C_3H_6$, C_2H_3CHO , $C_3H_6O_{1-3}$, and $C_3H_6O_{1-2}$ are over an order of magnitude off. The updated model demonstrates noticeable improvements in prediction accuracy for many species compared to the original model and a previously published model [21].

The reasons for the lower predictions of $C_3H_6O_{1-2}$ and $C_3H_6O_{1-3}$ in the updated model are as follows: In Ref. [44,45], C_3H_6 is consumed by an O atom to form $C_3H_6O_{1-2}$ and $C_3H_6O_{1-3}$ intermediates through the addition of an O atom to the C=C bonds in the center and end carbon atoms of C_3H_6 . Then, $C_3H_6O_{1-2}$ and $C_3H_6O_{1-3}$ intermediates decompose into CH_3 , C_2H_5 , CH_2O , and H, among others. The reactions provided in Ref. [44] do not consider these intermediate products ($C_3H_6O_{1-2}$ and $C_3H_6O_{1-3}$) but instead directly provide the reactions leading to the final products. This ultimately results in the underprediction of $C_3H_6O_{1-2}$ and $C_3H_6O_{1-3}$.

3.2. Validation II: nCD assisted propane oxidation

The DBD experiment was conducted under conditions with a specific deposited energy of $1.64 \times 10^{-4} J/cm^3$. To further validate the accuracy of the mechanism, nCD experiments were conducted with specific deposited energies ranging from $1.7 \times 10^{-4} J/cm^3$ to $1.53 \times 10^{-3} J/cm^3$. The uniformity of the nCD was evaluated using images captured by a high-speed ICCD camera operated at 4.5–5.5 kV, which were processed using an Abel transformator, as shown in Fig. 4. Due to the enhanced electric field near the electrode tip, localized discharge enhancement was observed on the ground electrode. Conversely, a phenomenon of discharge weakening was noted at distances ranging from 9 to 20 mm away from the high-voltage electrode. These localized effects were considered negligible in comparison to the overall discharge characteristics. Overall, the nCD was found to exhibit relatively uniform behavior across the tested conditions.

Fig. 5 presents a comparison between experimental measurements and predictions from different kinetic schemes in the nCD conditions. The original model exhibits poor predictions for species such as CO , H_2 , CO_2 , CH_4 , C_2H_6 , C_2H_2 , C_3H_6 . In contrast, the updated model shows significant improvements across these species. However, despite these enhancements, notable discrepancies remain in the predicted mole fractions of CO_2 , C_2H_4 , and CO , which are under-predicted by 55%, 45%, and 45%, respectively.

The updated model's predictions for C_3H_8 , H_2 , CH_4 , and C_2H_6 generally fall within the experimental error range. For C_3H_6 , while it is overpredicted by 30% at low deposited energy, the agreement improves at higher deposited energies. The trend of C_2H_2 predicted by the updated model aligns with experimental data, albeit with molar fractions approximately 30% lower than measured values. This suggests that while the added reaction pathways in the updated model are correct, further research is needed to refine the cross-sectional data used.

4. Results and discussion

4.1. Uncertainty analysis in the plasma and combustion kinetic mechanism

The updated model was derived from the original model through adjustments to several reactions based on experimental findings and pathway flux analysis. Specifically, the modifications listed in Table 1 are discussed in detail as follows.

In the original model, significant over-predictions of i -/ n - C_3H_7OOH were observed during the DBD-assisted propane oxidation process, as depicted in Fig. 3. The generation rate of i -/ n - C_3H_7OOH was found to be two orders of magnitude larger than its consumption rate. Pathway flux analysis based on the original model identified that the primary

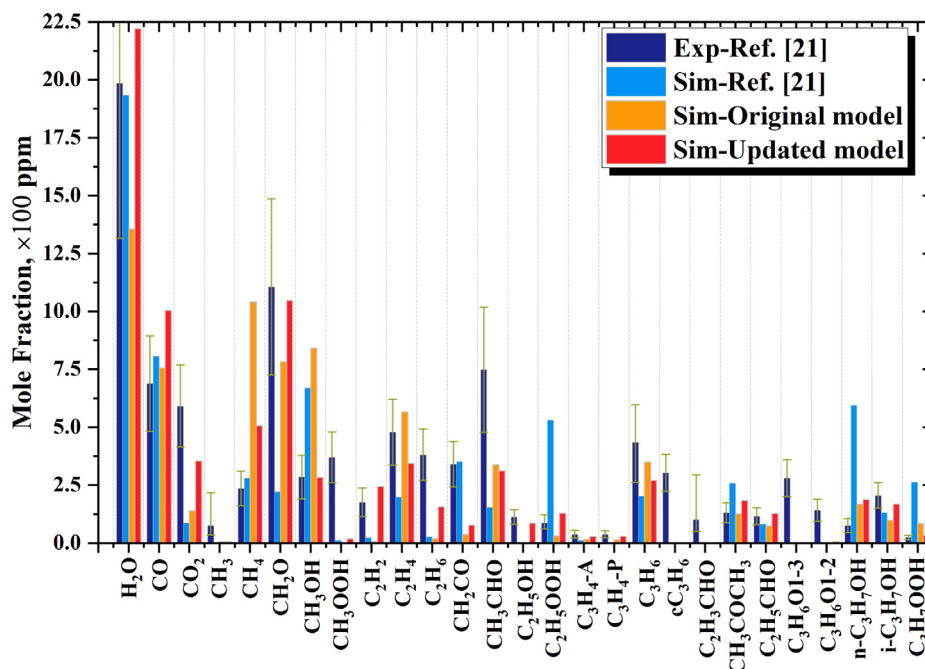


Fig. 3. Comparison between measurement and predictions from different kinetics schemes species in repetitively-pulsed nanosecond DBD. The deep blue and light blue bars represent experiment measurement and model prediction results from the Ref. [21]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

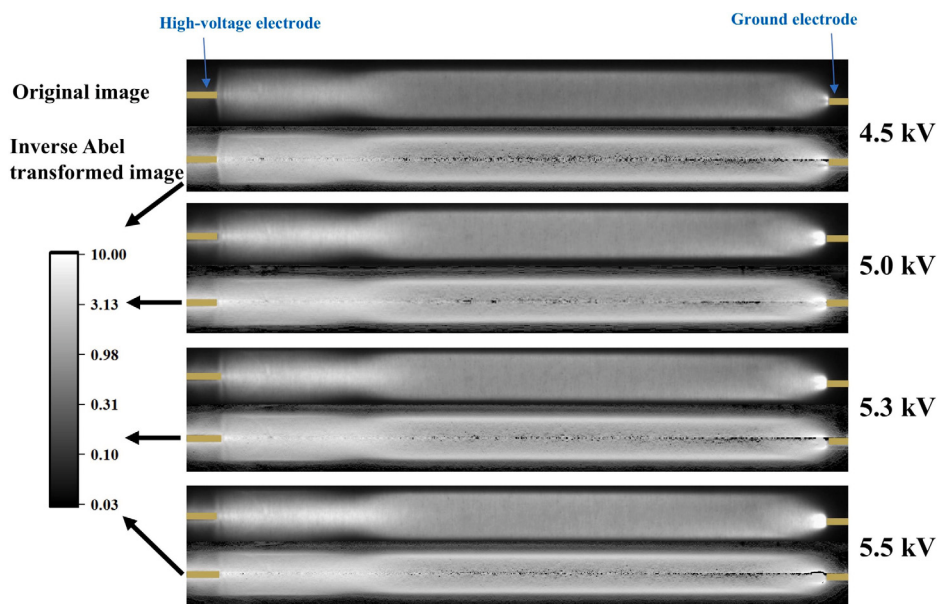


Fig. 4. The nCD image captured by high-speed ICCD camera and Abel transformed image with voltage of 4.5–5.5 kV.

generation pathways for i -/ n - C_3H_7OOH involved reactions i -/ n - $C_3H_7O_2$ with HO_2 (reactions R7 and R8, respectively), as illustrated in Fig. 6. However, the rate coefficients for R7 and R8 used in the original model were adapted from analogous reactions such as those between CH_3O_2 and HO_2 reported in Ref. [46]. These rate coefficients are valid within a temperature range below 338 K and are subject to an error of up to 5. Given the temperature range of 340–500 K in the current study and the inherent uncertainties associated with the analogy method, significant uncertainties were anticipated for R7 and R8. Besides, the removal of reaction R6 causes the increase of HO_2 density, which further contributes to the i -/ n - C_3H_7OOH density increase via reactions R7 and R8. Therefore, adjustments were made to the rate coefficients of R7 and R8, reducing them by a factor of 0.034 based on insights from

the DBD experiment [21]. The updated model now indicates that 87% of n - C_3H_7OOH is generated from the reaction of n - C_3H_7O with OH , and 88% of i - C_3H_7OOH is produced via reaction R8.

Both the model by Chen et al. [21] and the original model exhibit under-prediction of CH_2O and over-prediction of CH_3OH . As depicted in Fig. 7, pathway flux analysis of the original model indicates that 96% of CH_3OH is generated via the reaction of CH_3O with HO_2 (R6). However, it was noted that the reaction rate coefficients of R6 were sourced from Ref. [43], which states that the reaction between CH_3OH and O_2 produces CH_2OH and HO_2 , not CH_3O and HO_2 . Consequently, in the updated model, reaction R6 has been removed. The updated model's prediction for CH_3OH now aligns well with experimental measurements, with 63% of CH_3OH being produced by the self-reaction of

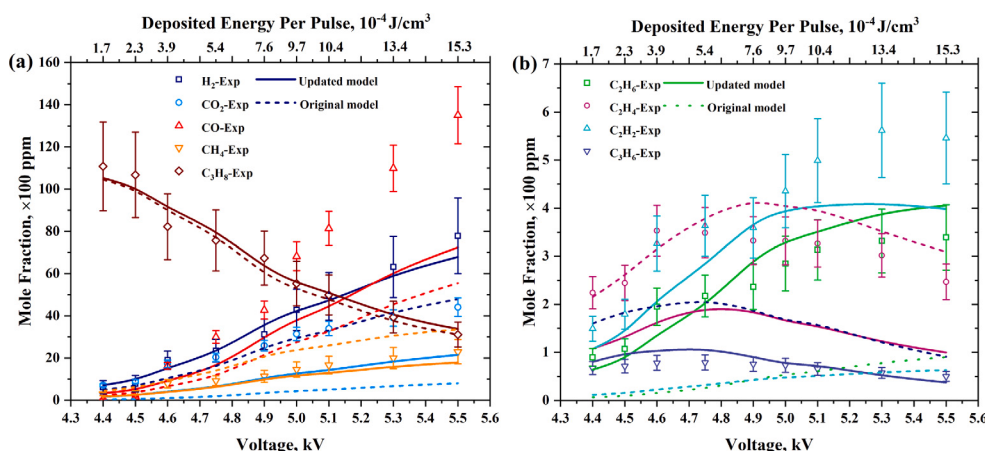


Fig. 5. Comparison between measurement and predictions from different kinetics scheme in nCD at different voltages.

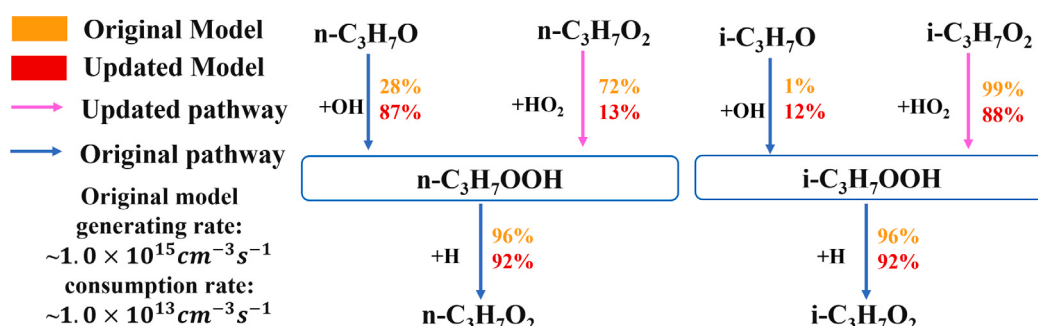


Fig. 6. The pathway analysis of i-/n-C₃H₇OOH in the updated model and the original model on the process of DBD assisted propane oxidation.

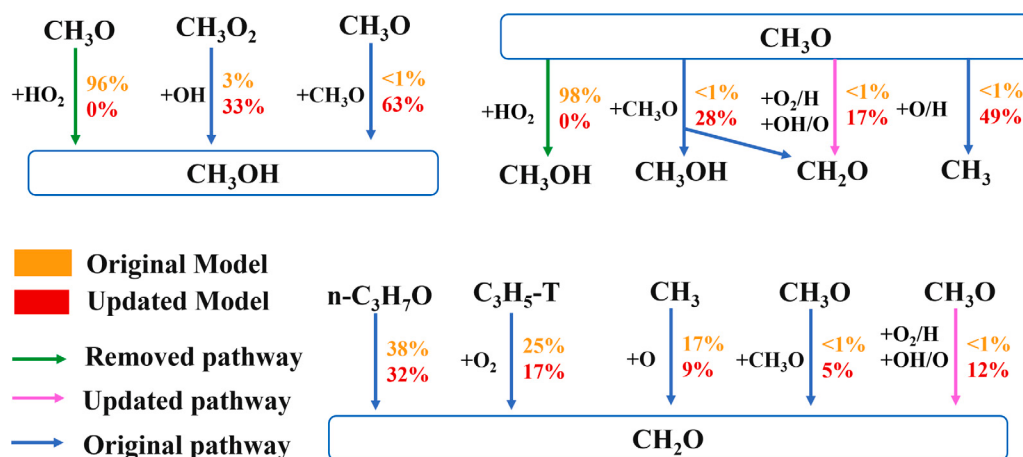


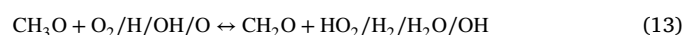
Fig. 7. The pathway analysis of CH_3OH , CH_3O and CH_3O in the updated model and the original model on the process of DBD assisted propane oxidation.

CH₃O (Reaction (8)), and 33% being generated through Reaction (9).



To address the lack of certain CH_3O consumption pathways, the CH_3O sub-mechanism was supplemented by referencing the HP-Mech v3.3 mechanism [38] (shown in Supplementary Material Table S1). The removal of R6 and the supplement of CH_3O consumption reactions led to significant changes in the CH_3O consumption pathway, as illustrated in Fig. 7. In the original model, CH_3O was almost exclusively consumed by the reverse reaction of R6. In contrast, in the updated model, half of

CH₃O is consumed to form CH₃, while the remaining CH₃O is consumed to form CH₂O and CH₃OH. Consequently, the prediction of CH₂O in the updated model has improved and now aligns well with experimental measurements due to the removal of R6 and the supplement of CH₃O consumption reactions.



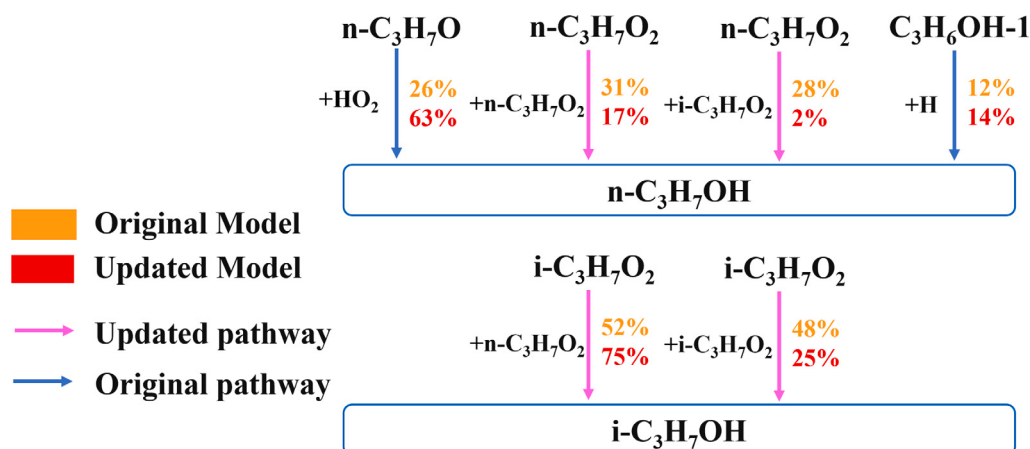


Fig. 8. The pathway analysis of $n\text{-C}_3\text{H}_7\text{OH}$ and $i\text{-C}_3\text{H}_7\text{OH}$ in the updated model and the original model on the process of DBD assisted propane oxidation.

As depicted in Fig. 3, the original model exhibited over-predictions of $n\text{-C}_3\text{H}_7\text{OH}$ and under-predictions of $i\text{-C}_3\text{H}_7\text{OH}$. It was observed that nearly all $i\text{-C}_3\text{H}_7\text{OH}$ and almost half of $n\text{-C}_3\text{H}_7\text{OH}$ were produced through self- and cross-reactions of $n\text{-}/i\text{-C}_3\text{H}_7\text{O}_2$ (Reactions R10–R13), as illustrated in Fig. 8. The inaccuracies in the branching ratios of these reactions likely contributed to the over-prediction of $n\text{-C}_3\text{H}_7\text{OH}$ and the under-prediction of $i\text{-C}_3\text{H}_7\text{OH}$. The rate coefficients for Reactions R10–R13 were originally derived from Ref. [17]. However, the temperature-dependent rate constants used in Ref. [17], sourced from Ref. [47], lacked detailed pressure and temperature dependencies. Moreover, the products of Reactions R10–R13 were not experimentally validated in Ref. [17], contributing to significant uncertainty in the branch ratios. To improve prediction accuracy, this model adjusted the branching ratios of Reactions R10–R13 based on DBD experimental results. This adjustment notably enhanced the prediction accuracy for $i\text{-C}_3\text{H}_7\text{OH}$, although a slight increase in $n\text{-C}_3\text{H}_7\text{OH}$ mole fraction compared to the original model was observed. This increase can be attributed to the enhanced reaction rate of $n\text{-C}_3\text{H}_7\text{O}$ with HO_2 , which results from the increased mole fraction of HO_2 following the deletion of Reaction R6.

Additionally, a formation pathway for $\text{C}_2\text{H}_5\text{OH}$ was introduced based on the NUIGMech1.1 mechanism [40], using rate coefficients similar to those self-/cross-reactions of $n\text{-}/i\text{-C}_3\text{H}_7\text{O}_2$. This pathway brought the model's prediction for $\text{C}_2\text{H}_5\text{OH}$ within the experimental measurement error range, as depicted in Fig. 3.

Furthermore, the original model showed under-prediction of $\text{C}_2\text{H}_5\text{OOH}$ compared to experimental measurements, with almost all $\text{C}_2\text{H}_5\text{OOH}$ formed via the reaction between $\text{C}_2\text{H}_5\text{O}_2$ and HO_2 . The increased mole fraction of HO_2 in the updated model led to an enhanced reaction rate between $\text{C}_2\text{H}_5\text{O}_2$ and HO_2 , aligning the predicted mole fraction of $\text{C}_2\text{H}_5\text{OOH}$ more closely with experimental measurements. This further supports the decision to delete Reaction R6.

The discrepancies of CH_4 , C_2H_2 , C_2H_4 , C_2H_6 and C_3H_6 between experimental measurements and the original model are observed in the DBD experiment and the nCD experiment. Given the large specific energy deposited scales of the nCD experiment, it was chosen as the primary reference for adjusting the kinetic model. A discharge peak voltage of 5.0 kV was selected for pathway flux analysis, as shown in Fig. 9. In the original model, CH_4 , C_2H_4 , C_2H_6 , and C_3H_6 are produced from the electron impact dissociation of C_3H_8 . The dissociation cross sections for C_3H_8 were obtained from Ref. [41], which provided estimates based on the total experimental dissociation cross sections for both ionized and neutral fragments ($e + \text{C}_3\text{H}_8 \rightarrow \text{A} + \text{B} + e$ and $e + \text{C}_3\text{H}_8 \rightarrow \text{A}^+ + \text{B} + 2e$). However, the cross-section branch ratios were estimated using empirical formulas, leading to significant uncertainties. Consequently, the reaction rate coefficients for C_3H_8 dissociation were

adjusted according to experimental results.

First, in the original model, Reaction (R1) is the primary production pathway for C_3H_6 , and its prediction was overestimated across all discharge voltage scales in the nCD experiment. To improve accuracy, the cross section for Reaction (R1) was reduced by a factor of 0.8, which enhanced the prediction accuracy for C_3H_6 , as shown in Fig. 5.

Second, reaction (R2) is responsible for the formation of C_2H_6 . The original model significantly under-predicted C_2H_6 in the nCD experiment. An adjustment factor of 12 was applied to the cross section for Reaction (R2), aligning the C_2H_6 predictions with the experimental results. And the C_2H_6 prediction of the updated model has also improved in DBD experiment.

Furthermore, reaction (R3) is the primary pathway for the formation of both CH_4 and C_2H_4 . The plasma sub-mechanism for CH_4 was adopted from Ref. [7,8] with experimental validation, indicating that the CH_4 consumption rates in the original model were accurate. Despite this, both CH_4 and C_2H_4 were over-predicted in the DBD experiment, and CH_4 was also over-predicted in the nCD experiment. This suggested that the cross section for Reaction (R3) was overestimated. An adjustment to the cross section for Reaction (R3) was made to achieve better agreement for CH_4 in the nCD experiment and C_2H_4 in the DBD experiment.

Besides, A discrepancy in the prediction of C_3H_4 between the original model and the DBD experiment was noted. Reaction (R4) is responsible for 93% of the formation of $\text{C}_3\text{H}_4\text{-A}$ and $\text{C}_3\text{H}_4\text{-P}$. Thus, the rate of Reaction (R4) was adjusted to better match the DBD experimental results.

Finally, the original model under-predicted C_2H_2 in both the nCD and DBD experiments, as shown in Figs. 5 and 3. In the original model, C_2H_2 is generated through reactions between excited argon and C_2H_4 and reaction between O and $\text{C}_3\text{H}_4\text{-A}$. However, with a mole fraction of C_2H_2 around 600 ppm in the nCD experiment compared to a C_2H_4 mole fraction of less than 400 ppm, C_2H_4 alone cannot account for the C_2H_2 formation. Similarly, $\text{C}_3\text{H}_4\text{-A}$ is present at too low a concentration to significantly contribute to C_2H_2 production. Therefore, electron-impact dissociation of C_3H_8 (Reaction R5) was considered as a primary source for C_2H_2 . Adding Reaction (R5) to the updated model significantly improved the accuracy of C_2H_2 predictions, with the updated model's C_2H_2 predictions closely matching experimental results from both the nCD and DBD experiments.

As stated above, the model undergoes significant updates through pathway flux analysis, informed by experiments conducted under nCD and DBD conditions. By adjusting key reaction mechanisms according to experimental data, the updated model now demonstrates markedly improved predictive accuracy. This improvement is particularly evident in its ability to more accurately replicate experimental observations in both nCD and DBD experiments.

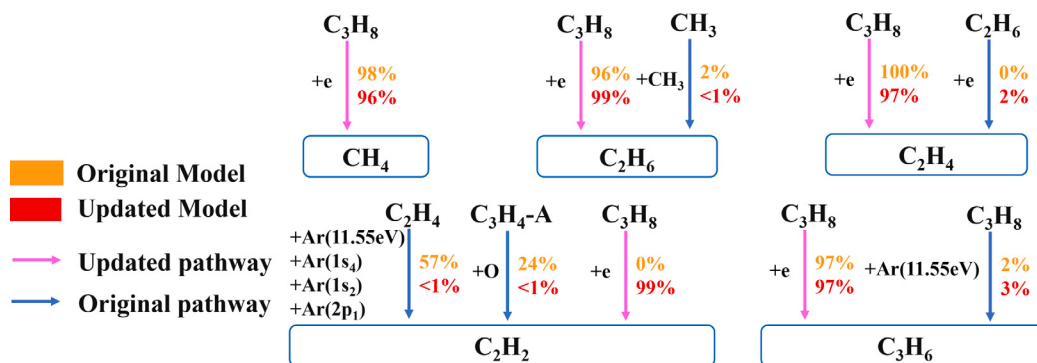


Fig. 9. The pathway analysis of CH_4 , C_2H_2 , C_2H_4 , C_2H_6 and C_3H_6 in the updated model and the original model on the process of nCD assisted propane oxidation.

Table 2

Initial parameters of simulation cases.

	Case1	Case2	Case3
Discharge type	DBD	nCD	nCD
Peak voltage, kV	9.0	4.5	5.0
Discharge time, ms	20		
Frequency, Hz	20 000	5200	1250
Pulse number	400	104	25
Single pulse deposited energy in model, J/cm^3	2.2×10^{-5}	9.04×10^{-5}	3.75×10^{-4}
Total deposited energy in model, J/cm^3	9.4×10^{-3}		
Gas temperature, K	400		
Pressure, Pa	4000		
Discharge mixture	$\text{C}_3\text{H}_8/\text{O}_2/\text{Ar}$ 4:20:76		

4.2. The comparisons of C_3H_8 oxidation process assisted by DBD and nCD

To explore the impact of the single pulse deposited energy (SPDE) on the oxidation of C_3H_8 , we have designed three distinct cases, each tailored to mimic specific energy deposited conditions. As depicted in Table 2, these cases are denoted as Case1, Case2, and Case3, with corresponding SPDE values in the model set at $2.35 \times 10^{-5} \text{ J}/\text{cm}^3$, $9.04 \times 10^{-5} \text{ J}/\text{cm}^3$, and $3.75 \times 10^{-4} \text{ J}/\text{cm}^3$, respectively. Notably, the total deposited energy in the model is standardized at $9.4 \times 10^{-3} \text{ J}/\text{cm}^3$ by adjusting the discharge frequency and pulse number, ensuring consistency across the cases. Furthermore, the gas temperature is maintained at a constant 400 K, while the discharge current values for the DBD and nCD in the models are sourced from Ref. [21] and the nCD experiment, respectively. These cases are designed to provide insights into the role of SPDE on C_3H_8 oxidation, offering valuable comparisons under varying deposited energy conditions.

In Fig. 10(a), the average reduced electric field evolution for DBD and nCD is depicted, where the reduced electric field is averaged over all discharge pulses. Notably, the average reduced electric field for nCD reaches 450–500 Td before 3 ns, followed by a dramatic decrease to 150–200 Td at 8 ns, maintaining this level until the end of the discharge. In contrast, the average reduced electric field for DBD increases from 270 Td to 380 Td, then decreases to 25 Td at 8 ns. Fig. 10(b) shows a small peak with a value of 180 Td at 10–14 ns, followed by fluctuations between 1–25 Td at 14–40 ns. As illustrated in Fig. 10(b), the reduced electric field distribution for nCD is concentrated at 150–200 Td and 450–500 Td. In comparison, the reduced electric field distribution for DBD predominantly ranges from 1–100 Td and 260–380 Td, accounting for approximately 44% and 43%, respectively, indicating a lower reduced electric field distribution compared to nCD.

Fig. 11 presents a comparison of species density in the C_3H_8 oxidation process assisted by DBD and nCD. The species density of DBD and nCD has similar distribution varying the SPDE values. However, the species density of DBD is slightly lower than that of nCD, especially in CO , CO_2 , C_2H_2 , C_2H_4 , C_2H_6 and CH_4 , despite the total deposited energy remaining the same. Fig. 12 highlights the time evolution of

C_2H_6 and CH_4 in DBD and nCD. Both C_2H_6 and CH_4 are produced during the nanosecond pulse discharge and subsequently consumed in the discharge gaps. The increase in C_2H_6 and CH_4 during a given period correlates with the rise in SPDE. However, the generation rates of C_2H_6 and CH_4 in nCD are significantly higher than those in DBD. The difference in generation rates results from the difference in the reduced electric field. Compared to nCD, the proportion of the reduced electric field in DBD is greater in the range of 1–10 Td. More deposited energy in DBD is used for vibrational excitation of C_3H_8 and O_2 , which causes less energy being deposited into dissociation of C_3H_8 and O_2 (referencing electron energy loss fraction shown in Supplementary Material). Interestingly, when the total deposited energy remains the same, the density and generation rates of C_2H_6 and CH_4 of nCD in 4.5 kV and 5.0 kV are nearly identical. This is because the nCD cases at 4.5 kV and 5.0 kV have similar reduced electric field distributions.

As depicted in Fig. 13, the consumption pathways of C_3H_8 in DBD and nCD environments were analyzed. In DBD, 58% of C_3H_8 is consumed through vibrationally excited reactions, attributed to the concentrated reduced electric field distribution of 1–20 Td, which enhances efficient vibrational excitation. Conversely, in nCD, a lower proportion of C_3H_8 is consumed via vibrationally excited reactions, with a higher contribution from species such as $\text{O}(^1\text{D})$, e, $\text{O}_2(4.5 \text{ eV})$ and OH. Consequently, compared to DBD, nCD is a more effective discharge form for contributing to C_3H_8 dissociation.

5. Conclusions

This study investigates the kinetics of plasma-assisted propane oxidation in nanosecond pulse discharge. A zero-dimensional plasma-combustion coupled solver equipped with sensitivity and pathway flux analysis modules was developed, based on the ZDPlaskin package and a custom-built combustion chemistry code. A kinetic model was proposed and validated against the nCD experiment using gas chromatography and the nanosecond DBD experiment using synchrotron photoionization mass spectrometry. The updated model demonstrates predictions for 14 species falling within the range of DBD experimental

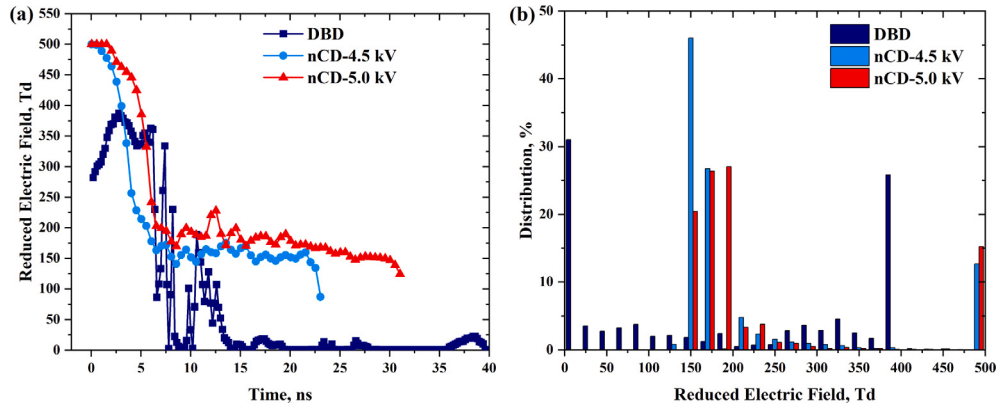


Fig. 10. The comparison of average reduced electric field and reduced electric field distribution in DBD and nCD.

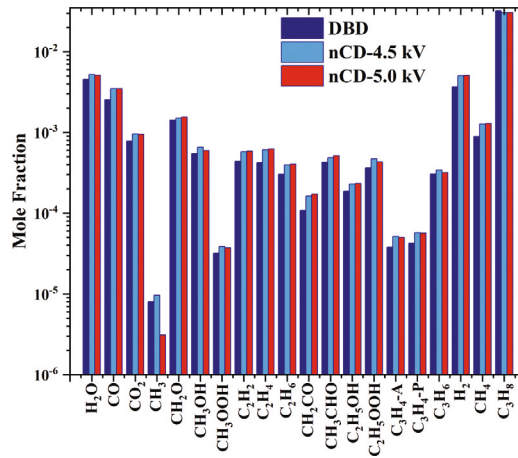


Fig. 11. Comparison of species density in C_3H_8 oxidation process assisted by DBD and nCD.

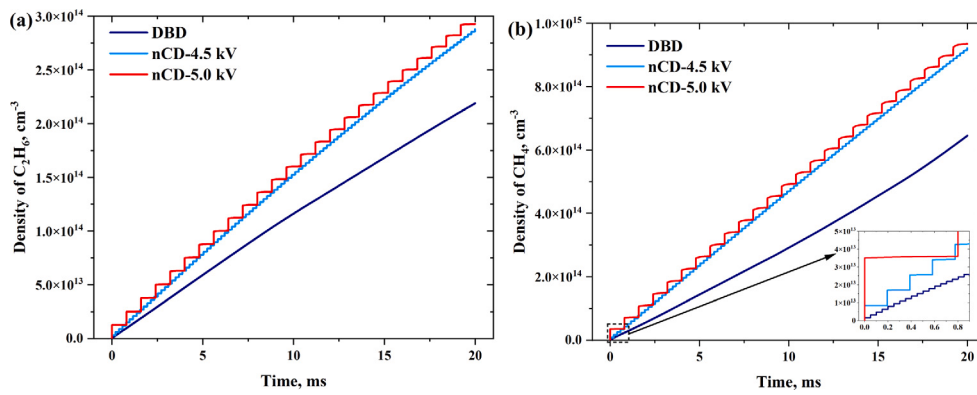


Fig. 12. C_2H_6 and CH_4 time evolutions in C_3H_8 oxidation process assisted by DBD and nCD.

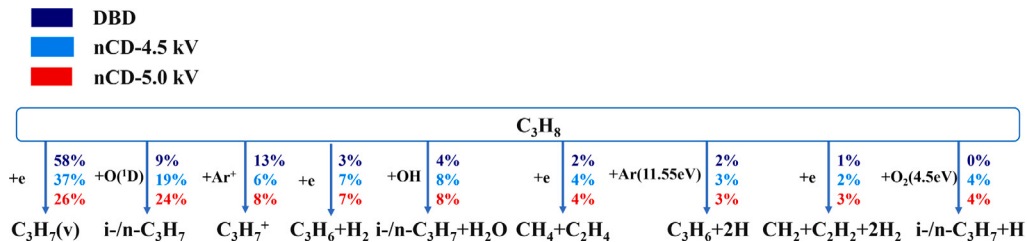


Fig. 13. C_3H_8 consumption pathways analysis in DBD and nCD.

measurement errors, with significantly improved prediction accuracy for 14 species. Notably, the updated model exhibits good prediction accuracy with the nCD experiment for C_3H_8 , H_2 , CH_4 , and C_2H_6 under large deposited energy scales. However, the model-predicted fractions of CO_2 , C_2H_4 , and CO are 55%, 45%, and 45% lower than those measured in the nCD experiment, respectively.

Several modifications to the reactions were made based on experiments and pathway flux analysis. This included fitting the reaction rate coefficients of $i\text{-}n\text{-}C_3H_7O_2$ with HO_2 (R7, R8) due to the large uncertainty of the analogy method. Additionally, the deletion of the erroneous addition reaction $CH_3OH + O_2 \leftrightarrow CH_3O + HO_2$ resulted in improved model predictions for CH_3OH . The supplementation of the CH_3O sub-mechanism from the HP-Mech v3.3 mechanism enhanced the updated model's prediction accuracy for CH_2O . Furthermore, adjustments to the C_3H_8 dissociation reaction rate coefficients, owing to large uncertainties, greatly improved the prediction accuracy for H_2 , CH_4 , C_2H_6 , C_2H_2 , and C_3H_6 .

Comparisons of C_3H_8 oxidation processes assisted by DBD and nCD were conducted under varying SPDE but with the same total deposited energy. Compared to nCD, DBD is more effective at enhancing the vibrational excitation of C_3H_8 and less effective at contributing to the dissociation of C_3H_8 , which is attributed to the larger proportion of reduced electric field in 1–10 Td range. nCD is more effective discharge form for contributing C_3H_8 dissociation compared to DBD. For nCD in different discharge voltages, the C_3H_8 process is primarily controlled by total deposited energy due to the similar reduced electric field distribution.

Overall, these findings illustrated the intricate interplay between plasma and combustion chemistry, offering valuable insights into the mechanisms of plasma-assisted propane oxidation.

CRediT authorship contribution statement

Zhenyang Li: Writing – original draft, Validation, Formal analysis, Data curation. **Bo Yin:** Investigation, Data curation. **Qifu Lin:** Supervision, Investigation. **Yifei Zhu:** Writing – review & editing, Conceptualization. **Yun Wu:** Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.combustflame.2025.114023>.

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