Modeling plasma-assisted methane-air ignition using pre-calculated electron impact reaction rates

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Full Length Article

Abstract

Development of practical combustion applications implementing plasma-assisted ignition technology for improved efficiency or fuel versatility will benefit from computationally-feasible models which include the plasma processes governing experimentally-observed combustion enhancement. A detailed chemical kinetic reaction mechanism for methane combustion with relevant plasma reactions has been compiled, including a set of electron impact cross sections for elastic and inelastic collisions with reactants, intermediate species, and products of methane combustion. In addition to electron impact reactions, the present mechanism includes reactions involving vibrationally- and electronically-excited species, dissociative recombination reactions, three-body recombination reactions, charge transfer reactions, and relaxation reactions, taken from the literature where available, and otherwise calculated using published correlations. While many past mechanisms have made assumptions limiting their use to specific regimes such as nanosecond discharges or microwave-enhanced flames, the present mechanism is generalized to include kinetics relating to both high- and low-energy excitation. The chemical kinetic mechanism is designed for use in a two-temperature chemical kinetics solver that tracks the electron temperature in addition to the gas temperature, as non-thermal plasma regimes characteristic to plasma-assisted combustion will typically have electron energies out of equilibrium with the energy of the heavier gas particles. Analysis considers the effects of initial temperature, mixture composition, electron concentration, and electric field strength on plasma ignition effectiveness. As commonly practiced, costly calculation of the Boltzmann equation at every time step is avoided by pre-calculating electron impact reaction rate coefficients using a Boltzmann equation solver. Here we evaluate the pre-calculated rates assumption, showing that ignition predictions depend on the gas composition at which the electron impact reaction rates are generated, but that induced errors are acceptable given the uncertainty in other model parameters such as impact cross sections. Finally, chemical kinetic sensitivity analysis highlights the importance of reactions governing free charge balance and nitrogen vibrational excitation when plasma effects on combustion enhancement are strong.

Keywords: Plasma-assisted Combustion, Electron Impact, Kinetic Modeling

1 Introduction

The critical need for reductions in greenhouse gas emissions requires improved energy conversion technology, and one technological area with potential for improving efficiency is plasma-assisted combustion. Thermal equilibrium plasmas, in which electron energy is in

equilibrium with that of gas molecules, have long been used to initiate combustion in spark-ignited engines. Combustion initiation and control utilizing non-equilibrium plasma, whereby high-energy electrons influence combustion processes without directly creating large increases in gas temperatures, is a less-mature field, though much progress has been made in the 21st century (e.g. [1–4]). Commercialization of plasma technology in combustion systems will be accelerated by the development of efficient, accurate numerical models describing the chemistry and physics relevant to plasma-assisted ignition and combustion.

Plasma effects on combustion can be broadly described as being through thermal, kinetic, or transport pathways, with kinetic pathway models requiring proper description of charged species, radicals, excited species, and fuel fragments produced by the plasma [4]. The series of kinetic processes affecting plasma-assisted combustion begins when electrons, which have received additional energy through some sort of discharge, collide with gas phase components of the mixture, exciting the various degrees of freedom of the target molecules. The probable outcome of an electron collision with a molecule depends on the energy of the incident electron and the cross section of the collisional process. In non-equilibrium plasma, the distribution of electron energies depends on the applied electric field, the gas density, the ionization degree, and the gas composition.

Past modeling of plasma-assisted combustion has considered many of the kinetic processes responsible for combustion enhancement. Konstantinovskii et al. compiled a detailed mechanism for hydrogen-oxygen ignition, including treatment of electronically-excited species, with electron impact reaction rates fit to an Arrhenius form dependent on electron temperature [5]. The Starik group at the Central Institute for Aviation Motors has published several papers with chemical kinetic models that include combustion enhancement pathways in methane, syngas, ethane, and hydrogen through pathways involving electronically- and vibrationally- excited species [6–10]. Uddi couples a Boltzmann equation solver [11] with a set of gas-phase reactions and impact cross sections for modeling low-pressure ignition in methane-air and ethylene-air diffusion flames subject to nanosecond discharge, with reduced electric field being an adjustable parameter so that oxygen atom concentrations match measurements [12]. Sun extends the model of Uddi, including additional reactions between electrons and noble gases Ar and He, and adjusts the reduced electric field so that CH₄ compositions match measurements when modeling the effects of nanosecond discharges on low-pressure methane diffusion flames [13].

Flame modeling including plasma processes presents the challenge of resolving the spatial effects of the flame and electric discharge, which can take place over significantly larger time and length scales than the relevant kinetic processes. Bourig et al. simulated the effects of plasma-assisted H₂-O₂ flames by assuming that the result of a discharge is singlet-delta, O₂(*a*¹Δ_g), and singlet-sigma, (O₂(*b*¹Σ_g⁺)) electronically-excited oxygen states, and then modeled the flame using a standard one-dimensional laminar premixed flame solver with the excited species added to the oxidizer [14]. Bisetti studies electron and ion transport in methane-air flames, presenting a computationally-inexpensive method of calculating charged-species transport properties in flames [15]. Nagaraja couples a one-dimensional plasma-fluid model to a reduced chemical kinetic model of relevant plasma and combustion processes in studying ignition of H₂-air mixtures ignited by nanosecond dielectric barrier discharge [16,17]. Electron impact reaction rate coefficients in the model are calculated using BOLSIG+ and interpolated based on local electron energy, which is conserved through an equation for electron energy density, the average electron energy times electron number density. A recent study by

Adamovich identifies the areas necessary for improved predictive models of plasma-assisted combustion, highlighting the need for improved measurements of discharge characteristics and species compositions for model validation [18]. Additionally, the study declares the need for sensitivity analysis of plasma-ignition models containing relevant excited species interactions so that computationally-efficient reduced models can be developed.

While several previous works have modeled plasma-assisted combustion of methane as listed in Table 1, this study presents a detailed mechanism applicable to a range of conditions not solely focusing on nanosecond discharge or microwave-assisted combustion and provides the reaction mechanism in a format usable in commercial software. This paper documents the development of a chemical kinetic mechanism for the plasma-assisted combustion processes relevant to plasma-assisted combustion over a range of operating regimes. The mechanism supplements an existing mechanism for gas-phase methane oxidation with electron impact reactions, cation and anion chemical reactions, and reactions involving vibrationally-excited and electronically-excited species. This paper has three main goals: 1) Present a detailed compilation of chemical kinetic reactions relevant to plasma-assisted ignition and combustion over a range of conditions. 2) Validate the reaction mechanism against available experimental data and compare calculations to experimental observations. 3) Examine the limits of the assumption of calculating electron impact reaction rates using a pre-calculated electron energy distribution function at a fixed gas composition and temperature when modeling plasma-assisted ignition.

Table 1: Previous works have modeled plasma effects on methane-air mixtures, though most have chosen to focus on specific applications, eliminating certain pathways that may affect combustion under other regimes. The present model includes kinetics of both high- and low-energy excitation in a format readily accessible to modelers.

Reference	Description	Validation	Notes
Kosarev 2008	Kinetics of CH ₄ :O ₂ :Ar (n = 1–5) mixtures subject to ns discharge	Shock tube with ns discharge, CH ₄ -Ar-O ₂	Ignores vibrational and low-energy electronic excitation
Aleksandrov 2009 [19]	Mechanism for ignition of methane-air mixture	Shock tube with ns discharge, CH ₄ -N ₂ -Ar-O ₂	Ignores anions, low-energy excitation of O ₂
Uddi 2009 [12]	Kinetic model of air plasma combined coupled to BOLSIG+ solver with gas phase combustion mechanism and methane electron impact	Time-resolved O atom measurements	No treatment of vibrational kinetics
Starik 2010 [20]	Methane-air combustion mechanism including singlet oxygen kinetics	Shock tube without discharge, CH ₄ -Ar-O ₂	No discharge or vibrational species modeling
Bisetti 2012 [15]	Calculation and analysis of electron and ion transport in flames	Validation of mobility	Transport only, no kinetics mechanism
Adamovich 2015 [21]	Kinetic mechanism of coupled molecular energy transfer and chemical reactions in air, H ₂ -air, and hydrocarbon-air plasmas	Time-resolved vibration, temperature, and OH in ns discharges in air, H ₂ -air, hydrocarbon-air	Developed concurrently with present mechanism

2 Plasma-Assisted Ignition Model

2.1 Two-Temperature Well-Mixed Reactor Model

The present numerical model solves time evolution of a constant pressure well-mixed reactor. A modified version of CHEMKIN II includes Eq. (1) for electron temperature, T_e , in addition to the equation for gas temperature, T [22].

$$\frac{dT_e}{dt} = \frac{1}{\rho Y_e c_{v,e}} \left(-\rho \frac{R}{W_e} T_e \frac{dY_e}{dt} + \dot{\omega}_e \frac{5}{2} R W_e (T - T_e) - \dot{Q}_{elastic} - \dot{Q}_{inelastic} + \dot{Q}_{source,e} \right) \quad (1)$$

ρ is the gas density, Y_e is the electron mass fraction, $c_{v,e}$ the electron heat capacity at constant volume, R is the universal gas constant, W_e is the molecular weight of electrons, and $\dot{\omega}_e$ is the chemical source term for electrons. The first term on the RHS of Eq. (1) accounts for work done by electrons, and the second term the energy to change the temperature of a newly liberated electron from the gas temperature to the electron temperature. $\dot{Q}_{elastic}$ and $\dot{Q}_{inelastic}$ account for energy transfer from electrons to heavier gas molecules through elastic and inelastic collisions. $\dot{Q}_{source,e}$ is a source term for energy to the electrons,

using equations for ohmic heating of plasma [23]. Ohmic power input is proportional to the square of the absolute value of the electric field, $|\tilde{E}|^2$, the DC conductivity, σ_{dc} , and a ratio including the electron-neutral collision frequency, ν_m , and the driving frequency of the source, ω , as in Eq. (2)

$$\dot{Q}_{source,e} = \frac{1}{2} |\tilde{E}|^2 \sigma_{dc} \frac{\nu_m^2}{\omega^2 + \nu_m^2} = \frac{1}{2} |\tilde{E}|^2 \frac{e^2 n_0}{m_e \nu_m} \frac{\nu_m^2}{\omega^2 + \nu_m^2} \sim \frac{W}{m^3} \quad (2)$$

DC conductivity, σ_{dc} , depends on the electron concentration per unit volume, n_0 , the electron neutral-collision frequency, ν_m , as well as e , the charge of an electron and m_e , the electron mass. The ohmic-style heating model for the electron energy source can also apply to energy input through electromagnetic wave absorption by plasmas as in the Bouguer law expression for attenuation of an electromagnetic wave with energy flux S (W/m^2) proportional to plasma conductivity and the ratio of collision frequency to the sum of the squares of collision frequency and driving frequency [24]. The present energy input specification methods do not include stochastic heating methods through which electrons gain energy through reflection off sheaths, but for the relatively high pressures of interest in combustion applications, stochastic heating will typically be small relative to ohmic heating since electron collision frequencies are high and mean free paths are short relative to discharge dimensions.

Concentrations of chemical species and electrons in the modeled zero-dimensional homogeneous mixture evolve based upon their concentrations and the specified reaction rate coefficients, which can depend on either gas temperature or electron temperature. Time advancement of the species equation is solved using the DASAC stiff implicit ODE solver [25].

2.2 Chemical Reaction Mechanism

A set of chemical reactions is compiled for modeling methane combustion subject to the effects of high-energy electrons. The base combustion model, GRI-MECH 3.0 [26] models gas-phase oxidation of methane and is supplemented with reactions describing ozone (O_3) formation and destruction [27]. Additional reactions are compiled for describing the evolution of a plasma combustion system, including electron impact reactions, reactions involving vibrationally- and electronically-excited species, dissociative recombination reactions, three-body recombination reactions, charge transfer reactions for positive and negative ions, and relaxation reactions, taken from the literature where available, and otherwise calculated using published correlations. Thermodynamic data comes from GRI-MECH 3.0 [26] and Professor Burcat's thermodynamic database [28]. In cases of excited species whose thermodynamic data is not available in the literature, thermodynamic data for the ground-state species with the enthalpy of formation increased by the energy of excitation is used. The assumption of unchanged heat capacity after excitation is not completely accurate, as the vibrational constants of excited species may differ from those of the ground state. However, since excited species constitute a relatively small fraction of the total mixture, overall mixture heat capacity prediction will not change significantly. Table 2 lists the reaction types included in the mechanism and the methods and sources for determining their reaction rates. Excited species are denoted with the excited state in parenthesis following the ground state species. For example, $O_2(vib1)$ is the first vibrational excitation level of O_2 , and $O_2(a1)$ is the singlet delta, $O_2(a^1\Delta_g)$, state of O_2 . The reaction mechanism in its entirety and thermodynamic data are available in the supplementary data. Additionally, further details regarding the development of the various parts of the plasma-

assisted combustion mechanism are in the supplementary data, while the following subsection discusses the electron impact treatment due to the fundamental importance to the present study.

Table 2: Reaction types compiled into the present model and their sources

Reaction type	Sample Reaction	Methods employed	References
Gas phase methane-air combustion	$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	Rates provided by literature	[26]
O_3 formation and destruction	$\text{O}_3 + \text{H} = \text{OH} + \text{O}_2$	Rates provided by literature	[27]
Vibrational relaxation and energy transfer	$\text{N}_2 + \text{O}_2(\text{vib1}) \rightarrow \text{N}_2 + \text{O}_2$	Calculated using Lifshitz correlation of Landau-Teller Model; Energy transfer rates provided by literature	[29,30]
Reactions with vibrationally-excited species	$\text{H} + \text{O}_2(\text{vib1}) \rightarrow \text{OH} + \text{O}$	Calculated with Fridman-Macheret model	[24]
Collisional quenching of electronically-excited species	$\text{O}_2(\text{b1}) + \text{N}_2 \rightarrow \text{O}_2(\text{a1}) + \text{N}_2$	Rates provided by literature	[9,27,30]
Radiative relaxation of electronically-excited species	$\text{O}_2(\text{a1}) \rightarrow \text{O}_2$	Rates provided by literature	[24,30,31]
Reactions with electronically-excited species	$\text{H} + \text{O}_2(\text{a1}) \rightarrow \text{OH} + \text{O}$	Rates provided by literature, calculated by MMVT correlation	[7,8,20,27,30,32,33]
Dissociative Recombination	$\text{O}_2^+ + \text{E} \rightarrow \text{O} + \text{O}$	Rates provided by literature	[24,34–39]
Associative Detachment	$\text{O}^- + \text{C} \rightarrow \text{CO} + \text{E}$	Rates provided by literature	[40–43].
Three-Body Attachment	$\text{O}_2 + \text{E} + \text{O} \rightarrow \text{O}_2^- + \text{O}$	Rates provided by literature	[40]
Three-Body Recombination	$\text{O}_2^+ + 2\text{E} \rightarrow \text{O}_2 + \text{E}$	Thermodynamic balance method	[24]
Collisional Detachment	$\text{O}_2^- + \text{N}_2 \rightarrow \text{O}_2 + \text{E} + \text{N}_2$	Provided by literature, estimated based on electron affinities and particle excitation energy	[24,30,44,45]
Charge Transfer	$\text{H}^- + \text{N}_2\text{O} = \text{OH}^- + \text{N}_2$	Rates provided by literature	[40,41]
Electron Impact	$\text{E} + \text{O}_2 \rightarrow \text{E} + \text{O}_2(\text{a1})$	Cross sections compiled from literature, rates calculated in BOLSIG+/ZDPlasKin	[11,46–53]

2.2.1 Electron impact reaction treatment

High-energy electrons influence combustion through electron impact reactions, so determining rates of such reactions is essential for modeling plasma-assisted combustion. The rate of an electron impact reaction depends on the available electron energy and the collisional cross section of interaction, with the electron energy distribution function (EEDF), $f(\epsilon)$, containing information on the probability that an electron in the system will have energy between ϵ and $\epsilon + d\epsilon$. Integration of the product of the EEDF and the electron energy over all possible electron energies gives the average energy of the electrons, $\langle\epsilon\rangle$, in the system as in Eq. (3). The average energy can be converted to temperature units through the Boltzmann constant, k_B . The electron temperature, T_e , is used as a measure of overall electron energy in the present model.

$$\int_0^{\infty} \epsilon \cdot f(\epsilon) d\epsilon = \langle\epsilon\rangle = \frac{3}{2} k_B T_e \quad (3)$$

The present model neglects electron-electron collisions due to the low-ionization degree of the flame plasmas of interest. Solution of the energy distribution function requires information on the cross section of interaction for relevant electron impact processes.

Electron-energy-dependent impact cross sections for each reaction, $\sigma_i(\epsilon)$, have units of area, and are here compiled and modified from the literature for many of the fuel, oxidizer, intermediate, and product species relevant to hydrogen and methane ignition. Electron impact reaction rate at a given electron temperature, $k_i(T_e)$, can be calculated by integrating an electron impact cross section times the electron velocity and the electron energy distribution function at that electron temperature, $f(\epsilon)|_{T_e}$, over all possible values of electron energy ϵ as in Eq. (4).

$$k_i(T_e) = \int_0^{\infty} f(\epsilon)|_{T_e} \left(\frac{2\epsilon}{m_e}\right)^{\frac{1}{2}} \sigma_i(\epsilon) d\epsilon \quad (4)$$

As an engineering approximation in the present analysis, the electron-temperature-dependent rate coefficients are calculated before the main combustion calculation for a specified initial mixture composition as in [54]. The approximation of a time-invariant EEDF is here made since the timescale of electron energy input is often short compared to the timescale of combustion over which the mixture composition, temperature, and pressure significantly change. For improved accuracy at increased computational cost, the electron energy distribution function can be repeatedly calculated as the simulation progresses and the mixture composition and resulting shape of the EEDF changes [55]. Section 3.3 considers the limits of the pre-calculated rate approach.

Electron impact rate coefficients for the present model are calculated using ZDPlasKin [52], a Fortran 90 implementation of BOLSIG+, a two-term Boltzmann equation solver [11]. Rate coefficients can be tabulated into a look-up table or rates can be fit to a nine-coefficient ($b_{1-9,i}$) polynomial, in CHEMKIN-compatible format with the rate coefficient given by Eq. (5). Tabulated rate coefficients are more accurate than curve fits, as rate coefficients do not always follow smooth trends with temperature, however the mechanism provided in the supplemental data uses curve fits for convenience and portability.

$$k_i(T_e) = A_0 \cdot \exp \left(\sum_{n=1}^9 b_{ni} (\ln T_e)^n \right) \quad (5)$$

In the present model, rotationally-excited molecules are not tracked as a separate species from ground-state species, as the quantum of rotational energy is so small that reliable data for rotational excitation is limited [50], and rotational-translational relaxation is relatively fast. It is thus modeled that all rotational excitation simply leads to an increase in the gas-phase temperature of the impacted species. By combining rotational excitation reactions with the momentum transfer reactions into an effective rate, the total rate of collisional energy transfer from electrons to gas particles is approximately the same as it would be if rotational excitation and momentum transfer reactions were specified independently. Matching energy loss requires that the “effective reaction” has the same stopping cross section, $S(E)$, Eq. (6), as the combination of the momentum transfer reaction and the rotational excitation reaction [56].

$$S(E) = \Delta E \cdot \sigma(E) \quad [cm^2 \cdot eV] \quad (6)$$

Here ΔE is the energy transfer from the electron to the target molecule during the collision, and $\sigma(E)$ is the energy-dependent collisional cross section. For a quantized inelastic process such as a rotational excitation, the energy transferred, ΔE equals the difference in energy between the initial and final quantum states, e.g. for the N_2 $J=0 \rightarrow 2$ rotational transition $\Delta E = 1.48 \times 10^{-3} eV$. For an elastic momentum transfer collision in the laboratory frame where the target particle is at rest, the energy transferred from the electron in an elastic collision, ΔE , is proportional to the energy of the electron, E , the mass of an electron, m_e , and the mass of the target particle, M , as in Eq. (7).

$$\Delta E_{elastic} = 2 \frac{m_e}{M} E \quad [eV] \quad (7)$$

In the two-temperature kinetics solver, electron-impact reactions can be flagged as momentum transfer reactions using the keyword MOME, in which case the elastic energy loss rate of a reaction, k , $Q_{elastic,k}$, is calculated using Eq. (8). $Q_{elastic,k}$ is proportional to the mass ratio of the electron and collisional partner just as in (7). However, in the well-mixed reactor code, the assumption of a resting target is no longer made, and the energy transfer is instead proportional to the difference between average electron temperature and average gas temperature, $T_e - T$. Equation (8) additionally depends upon the electron heat capacity at constant pressure, $C_{p,e}$, and the reaction rate of the momentum transfer reaction k per unit volume, $\dot{\omega}_k$.

$$Q_{elastic,k} = 2 \dot{\omega}_k \frac{m_e}{M} C_{p,e} (T_e - T) \quad \left[\frac{W}{cc} \right] \quad (8)$$

2.2.2 Electron impact cross section compilation

The cross sections used in the present work come from a range of sources, with special attention paid to ensure that complete cross section sets are used for major gas species when available, i.e., sets with swarm parameters verified against experimentally-measured drift and diffusion data. A recent series of papers by the Itikawa research group provide well-referenced compilations of measured cross sections for electron impact processes of oxygen, nitrogen, H_2O , CO_2 , and hydrogen [50,57–60]. The Itikawa cross sections were not published as “complete” sets calibrated for discharge calculations, so the calibrated cross section compilations of A.V. Phelps

are used as a framework for cross section sets of oxygen [46] and nitrogen [47], and the cross section set of Hayashi [48] is used for methane (CH_4). Cross sections for CH_{1-3} were generated using the formulas of Janev and Reiter [61]. Cross sections for CO and H_2 come from the database assembled over the course of 30 years by W.L. Morgan, retrieved from LXCat.net [49].

The oxygen cross section sets of Phelps are modified to include information on dissociation from Itikawa [50] and Ionin [51] while preserving the calibrated total energy loss of the complete cross sections. Excitation to 6 eV is assumed to result in dissociation to ground-state neutrals wherever the Phelps 6.0 eV excitation curve and the Ionin neutral dissociation curve overlap. Excitation to 6.0 eV not resulting in dissociation is considered an energy loss. The remaining dissociation to ground-state products is then presumed to occur through the 8.4 eV threshold reaction of Phelps. Additionally, all dissociation to an excited product is assumed to occur through the 8.4 eV excitation from Phelps, as the remaining cross section for total dissociation not already included in the 6.0 eV dissociation is at all points smaller than the cross section for 8.4 eV excitation provided by Phelps. After subtracting all cross sections for dissociation from the 8.4 eV excitation cross section, the remaining excitation is once again treated as energy loss. The final results of the oxygen cross section transformations are shown in Figure 1. The cross sections are also provided in BOLSIG+ format in the supplementary data.

Electron impact with excited species can lead to stepwise processes such as ionization or dissociation. Here the approach of Ionin [51] approximates cross sections for electron impact with excited species by shifting cross sections by the amount of excitation to lower electron energies relative to the ground-state cross section. Such an approach does not apply to resonant processes such as vibrational excitation, so in the present model, vibrational excitations of electronically-excited species are ignored.

Figure 1: Transformation of the cross sections for O_2 electronic excitation of A.V. Phelps [46] at 6.0 eV and 8.4 eV preserves total electron energy loss while incorporating cross sections for

dissociation to ground-state, $O + O$, and excited-state, $O + O(1D)$, oxygen atoms from Ionin [51] and Itikawa [50]. Curves are labeled either with reaction products or as “Energy Loss” reactions, and labels include the energy threshold for the impact process.

3 Plasma-Assisted Ignition Model Calculations

With the present analysis focusing on methods for determining reaction rates relevant to plasma-assisted ignition without the implementation of electron transport calculations or the spatial solution of electric fields necessary for calculating flame speeds, present calculations focus on “zero-dimensional” well-mixed reactor (WMR) calculations. Nonetheless, as will be shown, the WMR model provides insight into the parameters impacting the effectiveness of plasma discharge on enhancing combustion reactivity. Mixture composition is presented as normalized fuel-air ratio, denoted by equivalence ratio, ϕ , with m_{fuel}/m_{air} normalized by the stoichiometric fuel-air ratio. The reduced electric field (E/N), defined as electric field divided by gas number density, has units of Townsend, $1 Td = 10^{-21} V \cdot m^2$. Reduced electric field scales electric field strength to average electron energy, with E/N decreasing as pressure increases at constant electric field strength. For all calculations, the reported electric field strengths correspond to the electric field in the bulk flame since the model presently lacks spatial modeling of electric field.

3.1 Validation of ignition delay calculations

The present model calculates transient behavior of mixtures subject to varied initial conditions and energy input rates, and can thus calculate ignition delay as the time interval required for combustion to initiate. Published experimental data for homogenous plasma-assisted methane ignition is relatively limited compared to the amount of data available for normal combustion systems. A series of papers from the Moscow Institute of Physics and Technology provide measurements of methane ignition subject to nanosecond discharge in a shock tube [62,63]. The datasets only include “typical” waveforms of discharge voltage, but in a few cases, time-resolved energy input is given, allowing a constraint so that ignition kinetics can be better-compared to experiments.

Table 3: Shock tube data used as validation for plasma-assisted methane ignition in the present study

Gas Mixture	Temperature Range	Pressure Range	Reference
$CH_4-O_2-N_2-Ar$	1156 K – 1921 K	0.27 atm – 1.99 atm	Starikovskaia [62] Aleksandrov [19]
CH_4-O_2-Ar	1233 K – 1719 K	0.41 bar – 1.18 bar	Kosarev [63]

The validation case considered in Figure 2 compares calculations with shock tube data from Starikovskaia, with ignition of 1% CH_4 , 4% O_2 , 15% N_2 , 80% Ar subject to 20 ns pulse with peak electric field strength of 100 kV/m -160 kV/m [62]. Since the present work specifically concerns the performance of the plasma-assisted combustion model, all ignition delays, τ (model and measurements,) are normalized by ignition delay calculations using the mechanism at gas conditions of the case but without an applied electric field, here denoted as $\tau_{unenhanced}$. The normalized ignition delays are plotted in terms of gas density, as the shock tube data mostly collapses to a single tendency, with the model calculations following the trend well. Without knowledge of all of the discharge behavior, the present calculations

extrapolate the waveforms of electric field profiles across the dataset and assume constant initial electron concentration, $X_{e,0}$, for all calculations. It is not expected that agreement will be perfect between model and experiment over all cases, as specifics of the discharge are unknown for most cases. Additionally, at high pressures, discharge inhomogeneity from the formation of a streamer corona diminishes the validity of the zero-dimensionality of the present calculations. For the three cases with time histories of energy input available, listed in Table 4, the initial electron fraction could be tuned to match experimental energy input, and a comparison of ignition delay could be used to evaluate the kinetics. Ignition delay in Table 4 is defined as the onset of OH production in the ignition phase, here defined as when OH mole fraction exceeds 10^{-3} .

Figure 2: Measured (Starikovskaia, 2004) and calculated (squares) ignition normalized by calculated unenhanced ignition of 1% CH₄, 4% O₂, 15% N₂, 80% Ar subject to 20 ns pulse with peak electric field strength of 100 kV/m -160 kV/m. Initial electron fraction assumed to be 10^{-5} and delay is considered to occur upon 200 K temperature rise.

Table 4: Comparison of present model against the two cases of ignition 1% CH₄, 4% O₂, 15% N₂, 80% Ar from Starikovskaia [62] with energy input data taken from [19]. Initial electron fraction is adjusted so that energy input profile matches measurements, allowing comparison of calculated ignition delay to shock tube ignition delay.

T_0 (K)	1330	1880	1282
P_0 (atm)	0.45	1.85	0.5
Total Energy Input (mJ/cc)	14	7	12
$X_{e,0}$ (-) present model	1.5×10^{-7}	1.7×10^{-5}	6.0×10^{-7}

$\tau_{ignition}$ measured (μ s)	376	100	141
$\tau_{ignition}$ present model (μ s)	140	55	270

Another validation case compares calculations to shock tube data from Kosarev (2008) for ignition of 3.3% CH₄, 6.7% O₂, 90% Ar subject to a nanosecond pulse [63]. While the reference provides ignition delays over a range of conditions, information on the energy input is only provided for two cases (Case 8 and Case 12 in the paper) along with a single measured voltage waveform (Case 12.) Using the measured voltage waveform from Case 12, the present model predicts the current and specific deposited energy consistent with the calculations and measurements of the same paper, as in Figs. 3 and 4 for a temperature of 1450 K and pressure of 1.2 bar. From the two cases, it is clear that the discharge waveform varies from case to case and thus cannot be assumed constant over all cases. The voltage waveform for Case 8 is derived iteratively from the provided energy input for the present calculations. For the two cases, initial electron fraction is varied until total energy input matches experiments, and for both cases, ignition delay compares well with experiments when ignition is considered to occur when OH mole fraction exceeds 10^{-3} . Results are compared in Table 5. A comparison between present model predictions of O, H, and CH₃ radical concentrations after the discharge show that prediction of O atoms is lower than in the Kosarev model, likely due in part to the fact that the mechanism from that paper was designed specifically to model oxygen dissociation and did not include many of the intermediate plasma-created species included in the present model.

Figure 3: Specific deposited energy calculated for the conditions of Case 12 (1450 K, 1.2 bar) of [63] compared to measurements and calculations from the same paper.

Figure 4: Current calculated for the conditions of Case 12 (1450 K, 1.2 bar) of [63] compared to calculations from the same paper.

Table 5: Comparison of present model against the two cases of ignition in 3.3% CH₄, 6.7% O₂, 90% Ar from Kosarev, 2008 [63] that include energy input data. Initial electron fraction is adjusted so that energy input profile matches measurements, allowing comparison of calculated ignition delay to shock tube ignition delay. Calculated radical mole fractions after the discharge are given at 1000 ns for Case 8 and 200 ns for Case 12 to compare with numerical model results of [63].

	Case 8	Case 12
T_0 (K)	1649	1447
P_0 (bar)	0.69	1.18
Total Energy Input (mJ/cc)	34	14
$X_{e,0}$ (-) present model	7.2×10^{-7}	3.42×10^{-5}
τ_{ignition} measured (μs)	4	250
τ_{ignition} present model (μs)	13	221
X_O calculated in [63]	0.012	0.00142
X_H calculated in [63]	0.00507	7.1×10^{-4}
X_{CH_3} calculated in [63]	0.00427	5.79×10^{-4}
X_O present calculation	0.00107	2.82×10^{-4}

X_H present calculation	0.00105	2.30×10^{-4}
X_{CH_3} present calculation	0.00273	2.76×10^{-4}

In addition to shock tube validation, a qualitative analysis ensures that model trends are consistent with trends reported in other plasma systems. When temperature varies with normalized fuel-air ratio, as is the case in typical flames, the model reproduces the trend of decreased reactivity with air. Applying electric fields over a range of normalized fuel air ratios, Figure 5 models the effect of electric fields on the reactivity of premixed flames at varying compositions. The model replicates the experimentally-observed trend of increased ignition enhancement at excess air conditions in methane-air flames [64]. In the calculations of Figure 5, excess air conditions have a smaller reduced electric due to the inverse relation between gas density and temperature, but still plasma ignition is more effective at excess air conditions. Some of the relative plasma effectiveness at excess-air conditions is due to lower gas-phase reactivity at lower temperatures, but even when temperature (and thus reduced electric field) is held constant with fuel-air ratio, present calculations show higher relative plasma effectiveness at excess-air conditions than stoichiometric, despite the fact that gas-phase ignition is slightly faster at excess-air conditions when temperature is held constant due to the radical-scavenging nature of CH_4 [65]. For example, with $T=1500$ K, $P=1$ atm, $X_{e,0}=10^{-7}$, applying a 200 kV/m (40.9 Td) for 0.1 ms electric field enhances ignition by 64% at $\phi = 0.6$ ($\tau_{enhanced} = 0.362$ ms, $\tau_{unenhanced} = 1.01$ ms) as compared to 62% enhancement at $\phi = 1.0$ ($\tau_{enhanced} = 0.451$ ms, $\tau_{unenhanced} = 1.19$ ms).

Figure 5: Calculation of ignition delay as a function of electric field strength and normalized fuel-air ratio, ϕ , where initial temperature varies with gas mixture such that $T_0 = 0.7 \cdot (T_{adiabatic}(\phi) - 300 K) + 300 K$ and $X_{e,0} = 10^{-7}$. Consistent with measurements, relative enhancement is greater at off-stoichiometric compositions.

3.2 Initial electron fraction and electric field strength effects

The amount that a plasma discharge enhances combustion depends on both the electric field strength, which affects the total amount of energy deposited to the electrons, and the concentration of free electrons available for absorbing energy. Figure 6 plots ignition delay for calculations with varied initial electron mole fraction, $X_{e,0}$ (and consequently varied initial electron number density, N_{e0}) and varied strength of the applied 2.45 GHz electric field, E . For all calculations in the parameter sweep, initial mixture pressure and temperature are $P = 1$ atm, $\phi = 1$ and $T_0 = 1500$ K. Enhancement of ignition delay by energy input is studied by considering the ratio of ignition delay time with plasma enhancement to unenhanced ignition delay time, as in Eq. (9), with ignition considered to occur upon 200 K temperature rise.

$$\tau_{ignition}/\tau_{ignition,unenhanced} \quad (9)$$

When reduced electric field is less than about 5 Td the effect on the ignition delay time becomes insignificant, as gas-phase combustion processes dominate the combustion-enhancing plasma processes. Additionally, when electron mole fraction is less than 10^{-9} ($N_{e0} = 5 \cdot 10^9 \text{ cm}^{-3}$), an applied electric field does not affect ignition until it is strong enough to induce breakdown, as there are insufficient electrons for absorbing incident energy. Near the low-ionization threshold, the ignition delay is sensitive to electron attachment reactions, flattening the enhancement contours at intermediate field strengths. At high initial ionization levels, $X_{e,0} > 10^{-6}$ ($N_{e0} = 5 \cdot 10^{12} \text{ cm}^{-3}$), the energy released by electron-ion recombination slightly enhances combustion even without applied electric fields. When both electric field strength and initial electron fraction are sufficiently high, $E/N > 10 \text{ Td}$ and $X_{e,0} > 10^{-9}$ ($N_{e0} = 5 \cdot 10^9 \text{ cm}^{-3}$), ignition delay is reduced compared to the unenhanced ignition case as mixture reactivity is enhanced through plasma processes, and ignition delay reduces with both increasing electric field and increasing initial ionization degree. When electric field and initial electron concentration reach higher values, calculated ignition approaches zero, indicating that the electric field has sufficient strength to sustain ionization reactions.

Figure 6: Varying initial electron concentration and electric field of 0.1 ms discharge at $T_0 = 1500\text{ K}$, $P = 1\text{ atm}$, $\phi = 1.0$, identifies regimes of effective ignition enhancement by plasma. Contours show percent enhancement of ignition delay relative to unenhanced ignition as in Eq. (9). With low initial electron concentration or weak electric field, ignition is unaffected. When initial electron concentration and electric field are sufficiently high, applied electric fields enhance mixture reactivity. At high electric fields with sufficient initial electron concentration, ignition is practically instant as electrical breakdown occurs.

The regimes shown in Figure 6 may explain experimental observations of microwave-assisted spark plug limitations. Wolk measured that delaying the start of microwave enhancement relative to spark timing in a constant-volume chamber diminishes microwave enhancement of early flame kernel growth even in slow-burning mixtures that remain near the electrodes over long timescales [64]. The time delay in the experiment allows more time for free electron recombination, reducing the concentration of free electrons available to accept microwave energy enhancement such that they perhaps fall below the threshold for effective plasma enhancement of reactivity. Fialkov [66] reports typical ambient flame electron mole fraction in flames of about $X_{e,flame} \approx 3 \times 10^{-9}$ (10^{10} cm^{-3}), which is approximately the ionization threshold below which reactivity enhancement is negligible in the present model. If ionization levels in the flame kernel after the spark relax to the ionization level of a typical flame before the microwave turns on, then microwaves may not contribute significantly to flame development.

3.3 Exploration of the limits of the pre-calculated electron impact rate coefficients assumption

The computational cost of repeatedly calculating the Boltzmann transport equation during plasma-assisted combustion modeling can be avoided by pre-calculating electron impact rates as a function of electron energy. The use of electron impact reaction rates calculated at a single gas condition may adversely affect simulation accuracy since the electron energy distribution function varies with gas temperature and composition. The validity of such an approach is

examined by comparing ignition delay calculations over a range of temperatures and fuel-air ratios using electron impact reaction rates pre-calculated at a fixed gas temperature and composition, τ_{fixed} in Eq. (10), (1500 K, stoichiometric fuel/air ratio) ignition delay calculations with electron impact rates calculated specifically for the temperature and composition of interest, $\tau_{specific}$ in Eq. (10). Equation (10) gives the error resulting from using electron impact reactions with rates calculated at the incorrect gas composition or temperature.

$$Error\left(T_0, \phi_0, \frac{E}{N}\right) = 100\% \cdot \frac{|\tau_{fixed} - \tau_{specific}|}{\tau_{specific}} \quad (10)$$

Figure 7 reveals that plasma-assisted ignition calculations are much more sensitive to gas composition than gas temperature, which is expected since temperature only affects BOLSIG+ predictions of electron energy distribution functions when electric field is so low that electrons gain significant energy through elastic collisions [11]. Variations in error with temperature seen in Figure 7 can be attributed to the variation of plasma effectiveness with initial conditions such that the error induced by using electron impact reactions with rates calculated at distinct air fuel ratio will have greater effects under conditions where ignition is specifically sensitive to the reactions with affected rates.

Figure 7: Contour showing the error as calculated by Eq. (10) induced in methane-air ignition delay calculations with electron impact rates pre-calculated at 1500 K and $\phi = 1$ under a reduced electric field of 51 Td for 0.1 ms while the initial conditions vary as on the horizontal and vertical axes. Deviations in composition induce larger error than deviations in initial temperature.

With the knowledge that errors in ignition delay are only induced when impact reaction rates are tabulated at incorrect initial mixture conditions, it can be then helpful to see how the error induced by changing mixture composition varies with electric field strength. Figure 8 shows a contour of errors induced when ignition delay calculations at off-stoichiometric conditions are conducted using impact reaction rates pre-calculated at stoichiometric conditions. At sufficiently low field strength, results are insensitive to the air-fuel ratio at which rates are calculated, and at higher field strength, maximum error is induced between 50 and 55 Td.

Figure 8: Contour of error as calculated by Eq. (10) in methane-air ignition delay calculations with electron impact rates pre-calculated at 1500 K and $\phi = 1$ when initial normalized fuel-air ratio, ϕ , changes. Error increases as mixture initial conditions become farther from the composition at which the rates were calculated. At low electric fields, results are insensitive to the mechanism conditions. Discharge duration is 0.1 ms. Maximum error is induced between 50 Td and 55 Td.

3.4 Exploration of phenomena governing calculations

Sensitivity analysis reveals the reactions governing predictions of plasma ignition enhancement. Normalized sensitivity measures the impact of a reaction rate or set of reaction rates towards influencing ignition delay under a specified set of conditions and is given by Eq. (11) for a reaction with rate coefficient k_i .

$$\text{Normalized sensitivity } (k_i) = \frac{\tau(k_i \cdot 150\%) - \tau(k_i \cdot 50\%)}{(150\% - 50\%) \cdot \tau(k_i, \text{unchanged})} \quad (11)$$

It is clear from Figure 9, which plots the reactions to which the mechanism is sensitive from 0 to 41 Td at 1 atm, 1500 K, and stoichiometric fuel-air ratio, that model results are especially sensitive to reactions affecting the free electron balance as well as vibrational excitation of nitrogen, which serves as an important electron energy sink. At increased reduced electric fields, when average electron energy is sufficient to initiate significant ionization, oxygen and methane ionization reactions enhance ignition. On the other hand, the associative detachment reaction $E + O_2 \rightarrow O + O^-$ delays ignition by reducing the number of free electrons available to receive energy from electromagnetic waves, while the reaction $O^- + CH_2O \leftrightarrow CHO_2^- + H$ delays ignition by transferring negative charge to an anion with higher electron affinity that is more difficult to release through collisional detachment reactions. Apart from the importance of charge balance and electron energy balance, sensitivity analysis reveals how an increasing electric field affects the ignition pathways. For example, the reactions $CH_3 + O_2 \leftrightarrow O + CH_3O$ and $CH_3 + O_2 \leftrightarrow OH + CH_2O$ enhance ignition at $E/N < 40$ Td, but at sufficiently high reduced electric field, the same reactions slightly hinder ignition. One notable reaction, which has been

experimentally shown to enhance combustion [67], is the collision reaction to form singlet oxygen $E + O_2 \rightarrow E + O_2(a1)$, to which the ignition exhibits a decreasing sensitivity with increased reduced electric field.

Figure 9: Sensitivity analysis identifies reactions most affecting ignition. Bars pointing to the left indicate reactions which enhance ignition when their rates increase, and the length of the bar corresponds to the sensitivity of calculated ignition delay to the length of the bar. Conversely, bars pointing to the right indicate reactions that slow ignition when their rates are increased. Initial conditions are $T = 1500$ K, $P = 1$ atm, $X_{e,0} = 10^{-7}$, stoichiometric fuel-air ratio, with reduced electric field strength ranging from 0 Td to 41 Td.

One difference between the presently-developed mechanism and several preceding mechanisms in the literature is the present explicit treatment of vibrationally-excited species. Some example calculations show the relative importance of such reactions. At 1500 K, $\phi = 0.6$, $P = 1$ atm with a 0.1 ms discharge at 100 kV/m and an initial electron fraction $X_{e,0} = 10^{-7}$, the model predicts ignition delay of 605 ms. If oxygen vibrational excitation through electron impact is instead treated as an energy loss that directly increases the gas temperature, ignition is predicted to be just 0.7% slower. An analysis of the rates of production of vibrationally-excited oxygen reveals that the majority of the $O_2(\text{vib}^*)$ is consumed through collisional vibrational-translational relaxation, with N_2 collisions consuming about 65% of the $O_2(\text{vib}1)$ during the discharge and just 0.3% of $O_2(\text{vib}1)$ participating in the chain branching reaction with H to form OH and O. The explicit treatment of vibrationally-excited nitrogen is more important than that of vibrationally-excited oxygen at this same condition. Treating all electron impact vibrational excitation of nitrogen as electron energy loss that directly heats the gas results in ignition delay predictions that are 8% faster, a result of the fact that in the current model, energy is stored in the vibrational quanta of nitrogen and relaxation times are long enough that that energy is temporarily unavailable to enhance reactions. At higher electric fields, explicit treatment of N_2 vibration can have the opposite effect. At 300 kV/m under the same conditions, the model predicts a delay of 24.5 ms, whereas removing explicit treatment of vibrationally-excited N_2 slows ignition to 61.7

ms. The primary reason for such a strong effect on ignition prediction is the importance of vibrationally-excited N_2 in collisional detachment reactions which release electrons from negative ions such as O^- , resulting in a larger pool of free electrons and increasing the energy absorbed by the discharge.

4 Conclusions and opportunities for further study

A chemical kinetic mechanism for combustion calculations in systems with enhanced electron energies is developed and validated. The reactions are designed for use in a two-temperature solver which solves conservation equations for both gas-phase energy and electron energy. The base combustion model is an existing gas-phase mechanism for methane oxidation in air. Electron impact reaction rate coefficients are calculated from a set of impact cross sections compiled from the literature and modified for the present analysis. Rate coefficients for electron impact reactions are calculated using a freely-available solver for the two-term expansion of the Boltzmann transport equation and curve-fits for reaction rates are calculated as functions of electron temperature. Reactions describing interactions of excited species and ions relevant to plasma-assisted ignition are included in the mechanism, with rates taken from the literature when available or calculated using published empirical correlations when necessary.

The present numerical model is verified quantitatively against shock tube data, with calculations agreeing well with data given the limited availability of data on discharge conditions, and qualitatively against measured ignition trends with a microwave-assisted spark plug. Modeled trends in reactivity enhancement against fuel-air ratio follow experimental observations of improved effectiveness when the reacting mixture is diluted with excess air. A predicted diminished ignition enhancement at low initial electron concentrations correlates to the experimental observation that microwave-assisted spark plug effectiveness diminishes when microwave input is delayed relative to dc spark breakdown.

Analysis of sensitivity of plasma-assisted ignition delay calculations to the temperature and gas composition at which tabulated electron impact reaction rates are calculated shows that variations in initial mixture can induce errors when gas compositions vary from those at which the rates are pre-calculated, but that error is not induced by variations in temperature at which rates are calculated. When conducting ignition delay calculations at off-stoichiometric mixtures using reactions pre-calculated at stoichiometric conditions have overall errors of around 20%, which is acceptable given the other uncertainties in many reaction rates and electron impact cross sections. Sensitivity analysis of model predictions to individual reaction rates highlights the increased importance of charge balance reactions (both ionization and negative ion attachment/detachment reactions) as well as energy loss to nitrogen vibrational excitation.

Future model development will benefit from addition of the capability for spatial modeling of flames subject to electromagnetic discharge and reduced and skeletal mechanisms to accelerate calculations. Challenges to implementing spatial simulation will include the numerical treatment of electron transport and quantitative modeling of charge near electrodes. Additional model fidelity may be gained by coupling the two-temperature Boltzmann solver to the gas-phase combustion code, but a potentially-improved accuracy comes with added computational cost, making the pre-calculated rates approach a suitable engineering approximation for numerical study of plasma-assisted combustion processes. On the other hand, reduced chemical kinetic

mechanisms derived from the present detailed mechanism will allow efficient simulation of practical combustion systems.

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