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

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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.

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

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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

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 CH_4 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 H_2–O_2 flames by assuming that the result of a discharge is singlet-delta, $O_2(a^1\Delta_g)$, and singlet-sigma, $(O_2(b^1\Sigma_g^+)$ 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 H_2–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.

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].

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

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