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Low temperature oxidation and pyrolysis of n-heptane in nanosecond-pulsed plasma discharges

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Abstract

The present study seeks to explore the parametric effects of oxygen concentration, argon dilution and plasma discharge frequency on pyrolytic and oxidative reaction pathways of n-heptane assisted by non-equilibrium plasma discharge. Low temperature reaction pathways of n-heptane/O₂/Ar mixtures with a nanosecond repetitively pulsed plasma discharge are experimentally investigated in both *in situ* time-dependent TDLAS and steady state gas sampling diagnostics. Fuel consumption is found to be more effective in higher argon than higher oxygen concentrations, indicating higher electron number densities with argon dilution is more effective than direct electron impact dissociation of oxygen. Steady state sampling results suggest a linear trend of n-heptane dissociation and product species formation with increasing plasma frequency, with different major product species for oxidation and pyrolysis. In the time-dependent measurements, the comparison between experiments and numerical modeling show that formation of a major intermediate species, formaldehyde, is significantly under-predicted while fuel and water production are over-predicted. This discrepancy suggests missing reactions in the current model, possibly involving excited alkyl peroxide radicals.

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1. Introduction

Initiation of hydrocarbon oxidation and pyrolysis using non-equilibrium plasma discharges has

potential applications in combustion and fuel conversion processes, opening new avenues for cleaner engines or for selective production of chemical products [1,2]. Recent studies have found that sustained fuel conversion can be achieved at temperatures far below the autoignition temperature using plasma discharges [3–7], and can even lead to sustained flames far below the adiabatic flame

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temperature, termed “cool flames” [8–10]. Unfortunately, due to the non-equilibrium nature of the plasma, the chemical mechanism governing plasma-assisted hydrocarbon chemistry is poorly understood, particularly for large hydrocarbons.

The contribution of the discharge to hydrocarbon kinetics stems from electron collision reactions, which excite, dissociate, and ionize the initially ground state gas molecules. This forms an initial pool of active species which can then attack the fuel and oxygen molecules, leading to the formation of primary radicals for chain-branching and propagation. In the presence of oxygen, at low temperature, the fuel radicals will combine with O_2 to form alkyl peroxy radicals, which are involved in complex low temperature reaction processes. For large n-alkanes, the low temperature reaction pathways will lead to degenerate chain branching and are responsible for the so-called negative temperature coefficient (NTC) behavior of fuels. In the NTC region, two distinct ignition regimes exist for these fuels: a first stage ignition, in the low temperature range mentioned above, which is dominated by the low temperature oxidation process as described, and a subsequent second stage ignition, which is the traditional high-temperature oxidation pathway. Plasma produced active species accelerate the limiting chain-initiation step at low temperature and thus has the potential to significantly alter the ignition behavior of n-alkanes.

Previous studies of n-heptane plasma kinetics have been conducted, both numerically and experimentally. Tsolas et al. explored n-heptane oxidation in a nanosecond pulsed discharge at various temperatures in a plug flow reactor [11]. It was found that the plasma enabled fuel oxidation at atmospheric pressure and temperatures below 900 K, which was not observed in the absence of the plasma. The formation of CO, CO_2 and C_2H_4 was observed at temperatures starting as low as 400 K, and increased until 680 K, at which point a clear negative temperature coefficient effect was observed, indicating the interaction between plasma initiated oxidation and low temperature chain branching pathways. Nagaraja et al. [12] performed a modeling study of n-heptane ignition in a nanosecond pulsed dielectric barrier (DBD) reactor. It was found that the ignition delay time for both first and second stage ignition of n-heptane/air mixtures could be lowered with the application of only a few plasma pulses. It was found that the relative decrease in ignition time compared to the autoignition case was most pronounced for the lowest temperature conditions in the range of 550–650 K. They attributed the reduction in the first stage ignition delay time to low temperature chain branching processes, which were initiated by plasma-produced species participating in H-abstraction reactions with the fuel molecule. The reduction in the second stage ignition delay was mostly due to thermal enhancement resulting from

the relaxation of the electronically excited species produced during the discharge.

While both the experimental and modeling studies have made large strides toward understanding the reaction mechanism of large hydrocarbon oxidation in the plasma, few time-dependent species history measurements and quantitative comparisons were made between model and experiment. Thus, the understanding of the effect of plasma on n-heptane oxidation remains unclear. This study aims to take the next step in understanding the chemical kinetic effects of plasma on low temperature chemistry. This is accomplished by measuring the temperature and product or intermediate species produced in a nanosecond repetitively pulsed (NRP) discharge using both *in situ* and *ex situ* diagnostic techniques. The relative contribution of electron collision processes, excited species quenching reactions, and low temperature oxidation reactions are compared by varying the diluent concentration in the mixture. The experimental results are compared to 1-D plasma/combustion chemistry computations, and the model fidelity is assessed. Finally, path flux analysis is used to identify important reaction processes and pinpoint the reason for any model discrepancies.

2. Experimental approach

Measurements of both time dependent and steady state species and temperature profiles are performed in a nanosecond repetitively pulsed dielectric barrier discharge flow reactor coupled with a liquid fuel vaporization system. Only modifications to the experimental apparatus described in previous publications [13–15] will be outlined. Liquid n-heptane (Sigma Aldrich, >99% in purity) is injected via syringe pump (Harvard Apparatus PHD 2000) into the vaporization chamber at 800 Torr, along with a co-flow of argon diluent to enhance fuel atomization. The vaporizer is maintained at ~ 360 K by a band heater to ensure complete vaporization. Oxygen is mixed with the diluent-fuel stream just prior to injection into the reactor to prevent any possibility of reactions in the heated vaporization chamber.

The plasma reactor is housed in a vacuum chamber and maintained at a constant pressure of 60 Torr and room temperature for all experiments, with a total flow rate of 0.4 m/s. Argon is used as a diluent to study the competing processes of electron impact excitation (Ar^*) versus electron impact oxygen dissociation for radical production. Argon was also chosen due to its lower discharge threshold and improved uniformity compared to N_2 , and elimination of complicated NO_x coupling chemistry for the present investigation. Three operating conditions were explored in this study, listed in terms of percent mole fraction:

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