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A comparative experimental kinetic study of spontaneous and plasma-assisted cool flames in a rapid compression machine

G. Vanhove [a,*], M.-A. Boumehdi [a], S. Shcherbanev [b], Y. Fenard [a], P. Desgroux [a], S.M. Starikovskaia [b]

[a] *Univ. Lille, CNRS, UMR 8522 - PC2A - Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France*

[b] *Laboratory of Plasma Physics (CNRS, Ecole Polytechnique, Sorbonne Universities, University of Pierre and Marie Curie – Paris 6, University Paris-Sud), Ecole Polytechnique, Route de Saclay, 91128 Palaiseau, France*

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Abstract

Plasma-assisted cool flames of *n*-heptane were generated in the combustion chamber of a rapid compression machine coupled with a nanosecond dielectric barrier discharge, at a pressure of 1.5 bar and temperature $T_C = 650$ K. Increasing of the voltage pulse amplitude at the electrode resulted in a transition from no reactivity to induced cool flame and then to fast ignition. Sampling of the reacting mixture was performed at selected times during the experiments to draw mole fraction profiles of the fuel and major low temperature stable intermediates, showing a gradual increase in the mole fraction of these species after the discharge. Comparison with a spontaneous cool flame case at a slightly higher pressure shows that no new species are formed in the plasma-assisted case, and that after the initiation of reactivity by the discharge at the nanosecond timescale, the distribution and relative importance of the main reaction pathways is conserved at the millisecond timescale. Differences in the shape of the mole fraction and light emission profiles however suggest that the plasma-assisted cool flame is propagative.

Keywords: Plasma-assisted ignition; Low temperature combustion; Cool flame; Rapid compression machine; Kinetics

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1. Introduction

In new engine technologies, such as PPCI (Partially Premixed Compression Ignition) or HCCI (Homogeneous Charge Compression Ignition) configurations [1], the initiation of combustion is highly dependent on the chemical kinetics associated with Low Temperature Combustion (LTC). This combustion regime is associated with degenerate chemical branching through the formation of highly unstable peroxidic species, the formation of such being constrained by the structure of the initial fuel [2]. This chemical branching

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[*] Corresponding author.
E-mail address: guillaume.vanhove@univ-lille1.fr (G. Vanhove).

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results in cool flames, i.e. faint light emission around 400 nm, usually attributed to the formation of excited formaldehyde, as well as a moderate temperature increase. Difficulties in ensuring reproducible ignition timing in such engine configurations have triggered interest in plasma-assisted ignition in the LTC regime [3–5].

Among the fuels that have been studied in such conditions, *n*-heptane is a good example, as it shows high LTC reactivity, is one of the Primary Reference Fuels for octane number measurement, and is often used as a surrogate for diesel fuel. Its LTC chemical kinetics have been studied in several reactors, including jet-stirred reactors [6,7], shock tubes [8] or rapid compression machines [9,10]. It is well established that the chain branching mechanism responsible for its LTC reactivity proceeds through the following steps:

- Initiation by hydrogen abstraction by O_2, $\dot{O}H$ or $HO\dot{O}$, yielding an *n*-heptyl radical and $HO\dot{O}$, H_2O or H_2O_2, respectively.
- Addition of the *n*-heptyl radical to O_2 molecules to form a $RO_2\cdot$ radical.
- Internal isomerization of this $RO_2\cdot$ into a $\cdot QO_2H$ radical.
- Addition of the $\cdot QO_2H$ radical to O_2 molecules.
- Formation and decomposition of ketohydroperoxides, yielding two $\dot{O}H$ radicals.

The thereby formed $\dot{O}H$ radicals will take part in the initiation reactions and accelerate the global reactivity, resulting in chemical branching. In the reaction sequence that follows initiation, internal isomerization reactions are rate-limiting, making it more likely for species with a long alkyl chain. Other LTC chemistry pathways consist in propagation reactions and yield stable intermediates, for example by decomposition of $\cdot QO_2H$ radicals into alkenes, carbonyls and cyclic ethers, depending on the positions of the initial H abstraction and the internal isomerization.

The possibility to induce ignition of methane or *n*-butane in high pressure conditions in a Rapid Compression Machine (RCM), by means of local production of excited species and radicals by a Dielectric Barrier Discharge (DBD), has been demonstrated in a recent paper [11]. This work focuses on using the same tools to stimulate the LTC reactivity of *n*_heptane.

2. Experimental

The coupling of the Lille University RCM [12] and the Laboratoire de Physique des Plasmas (LPP) DBD electrode system [13] has been described previously [11], so only the major elements will be reminded here. The RCM has right-angle geometry to ensure constant volume at Top Dead Center (TDC). During a classical experiment, the piston position, pressure and light emission are recorded, using respectively a Honeywell HOA 20001-001 optocoupler, a Kistler 6052 piezoelectric transducer coupled to a Kistler 5017 charge amplifier, and a RCA 1P21 photomultiplier. The initial temperature of the combustion chamber is fixed with a ±1 K accuracy along the RCM axis. The temperature of the adiabatic core is calculated following the isentropic law from the initial temperature, initial and compressed pressures following the adiabatic core assumption [12]. The RCM is equipped with a creviced piston following the design suggested in [14] to limit mixing of the boundary layer with the adiabatic core. 99.8% grade *n*-heptane from Sigma-Aldrich and oxygen and nitrogen with 99.99% purity from Air Liquide were used to prepare gas mixtures in a separated facility, where they were left to homogenize overnight.

The DBD electrode system was installed in the place of the end plate of the RCM. It consists of a central coaxial high voltage (HV) electrode which is ended by a brass convex segment of a radius of a curvature of 50 mm. The outer diameter of the segment is 20 mm and equal to the inner diameter of the low voltage grounded electrode. The low voltage electrode is made of aluminum. The high and low voltage electrodes are separated with a thin, 0.3 mm, dielectric PVC layer. A FID Technology FPG20-03NM high voltage generator delivered single pulses of negative or positive polarity, 12–55 kV in amplitude, 2 ns pulse front rise time and 20 ns pulse duration on the half-height to the electrode through a 30 m coaxial high-frequency RG213 cable. Two calibrated custom-made back current shunts (BCS) were installed in the cable shield break at half the length of this cable and 1 m before the electrode. The first BCS was used to measure the waveforms of the incident pulse of electrical current/voltage and of the pulse reflected from the electrode system. The second was used for synchronization of RCM and the high-voltage generator. A LeCroy Wave Runner 600 MHz oscilloscope was used to monitor the signals, which can later be used to extract the energy deposited in the discharge. The absence of spark formation was controlled from current waveforms for all the experiments presented here.

To probe the formation of stable oxidation intermediates during the experiments, the whole contents of the reaction chamber were extracted in a separate vessel, as applied previously in autoignition experiments [15], the pressure drop being fast enough to quench the reactivity in less than a millisecond. Acquired samples were analyzed offline in a Bruker Scion Gas Chromatograph equipped with mass spectrometry and FID/TCD detection. The detected intermediates were identified on the basis of their mass spectra. Calibration of the detectors was performed for the species that are readily

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