

The character and dynamics of low-temperature combustion: flames and oxidation

Omar R. Yehia[†] and Yiguang Ju[‡]

Abstract

The low-temperature combustion of hydrocarbons remains an outstanding problem in flame chemistry and theory [1]. Being fundamentally kinetic in nature, the understanding of such flames has only rapidly evolved recently owing to advancements in the understanding of peroxy kinetics [2,3], although much remains unknown regarding the role of low-temperature chemistry in both laminar and turbulent flames. Originally thought to be an unstable non-premixed mode of burning in the partial-burning regime [4,5], it is now known that low-temperature flames may be stabilized by kinetic competition, such as the negative temperature coefficient reactivity [6,7]. These low-temperature cool flames, owing to their characteristically slow peroxy branching chemistries and the leakage of reactants across the reaction zone, allow for the existence of multiple spatially-distinct oxidation layers such as those in premixed multistage double flames [8,9] that are a result of the disparity in the characteristic activation energies of the different classes of reactions that govern each oxidation zone. While such multistage character has been known to manifest in premixtures, it was not associated with the low-temperature burning modes of initially unmixed reactants. However, we have recently demonstrated that such multistage double non-premixed flames can exist [10,11] and appear to bridge the transitions between single-stage cool flames and hot flames [11,12]. The character of such non-premixed multistage flames is such that the peroxy branching sequence governs oxidation in the first oxidation layer and produces intermediates that can be consumed in a secondary layer. The intermediates are produced primarily from the decomposition of the ketohydroperoxide, which is a necessary branching step in the first oxidation stage. Our analysis further suggests that, owing to the mechanism described, the dominant mode of low-temperature burning is a multistage burning mode, whereas a single-stage low-temperature burning mode occurs only at near-limit conditions, where the near-limit flame temperatures are such that either peroxy chemistry (near extinction) or intermediate chemistry (near hot flame transition) dominate [11]. Current work is being performed regarding the nature of such flames at elevated pressure conditions, at which criticality vanishes and the different burning modes become coupled through smooth transitions owing to the acceleration of the low-temperature branching sequence due to the suppression of the radical termination routes through the scission of the fuel and hydroperoxylalkyl radicals.

There are interesting consequences of the existence of multistage premixed and non-premixed flames, particularly in turbulent environments. Owing to the spatially-distinct oxidation layers in both premixed and non-premixed flames, new flame length scales need to be introduced in order to adequately resolve flame-turbulence interactions, realizing that the spatial separation between the coupled multiple oxidation layers can exceed the nominal flame thicknesses of the cool and hot flames. Specifically, it has been recently shown [13] that different transient flame structures can exist during flame penetration by a vortex in a premixed double flame, including local quenching of the hot flame but survival of the cool flame. Current experimental and analytical

[†]Graduate student, Princeton University

[‡]Robert Porter Patterson Professor, Princeton University

work regarding the flame-vortex interactions between multistage non-premixed flames and vortices is being performed. Further, current work is also being performed on the dynamics of turbulent non-premixed flames near and at autoignition conditions in Bunsen-type configurations in order to elucidate the role of flame-turbulence interactions on the structure and stabilization of low-temperature flames.

We further consider the role of low-temperature chemistry in problems of practical interest, such as that of real fuel surrogate formulation. All petroleum-based transportation fuels (gasoline, diesel, and jet aviation) are comprised of hundreds of chemical components, the majority of which are normal alkanes, branched alkanes, cycloalkanes, aromatics, and naphthalenes. The problem of developing kinetic schemes that accurately describe the physical and combustive behavior of such fuels, to be used for computational engine design, becomes therefore intractable. A straightforward alternative is to, instead, develop and characterize a surrogate fuel that closely emulates the behavior of the real target fuel. To minimize the number of components needed to achieve acceptable kinetic fidelity of the surrogate, the intermediates that result from the initial oxidation of the parent fuel molecules should be the proper parameter of interest, and not their initial molecular structure [14]. The remainder of the problem then becomes that of determining the kinetic interactions between the distinct intermediate structures that, in turn, govern the combustive behavior of the surrogate. Therefore, we devote particular attention to the kinetic coupling between low-temperature intermediates of normal alkanes and alkylbenzenes, the two most abundant molecular classes in petroleum-based fuels. Using *n*-dodecane and *n*-propylbenzene as the components in a surrogate mixture, we demonstrate [15] the influence of the kinetic coupling between the alkyl and aromatic intermediates on mixture reactivity through flame extinction in the opposed flow configuration. We demonstrate that, owing to the low ceiling temperature for the dissociation of the benzylperoxy radical, the aromatic intermediates of *n*-propylbenzene inhibit the low-temperature peroxy branching sequence by scavenging the hydroxyl radical. Whereas, at elevated temperatures where ring-opening chemistry is facile, the aromatic intermediates act to promote the small radical branching sequence, relative to inert dilution. However, the kinetic coupling mechanism depends on the size of the aromatic ring and the length of the alkyl chain, therefore extensions to other surrogate components needs further detailed consideration. We also propose a simple scaling to isolate the thermal and kinetic effects of different components in non-premixed cool flames. We attempt to generalize our analysis in order to build a framework for the low-temperature reactivity of mixtures and of different molecular structures, through the analysis of both ignition and extinction behavior. Our analysis suggests that the extent of reactant leakage must be explicitly accounted for, unlike the framework developed for non-premixed flames in the near-equilibrium diffusion flame regime [16], in order to elucidate the influence of transport and the kinetic contribution by different fuel components. Other subtle differences include the role of the crossover temperature in dictating the cool flame temperature in the partial-burning regime, whereas the hot flame temperature in the near-equilibrium diffusion flame is determined, to leading order, simply by the enthalpy of combustion of the fuel. Current work along these lines is being performed.

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