A radical index for the determination of the chemical kinetic contribution to diffusion flame extinction of large hydrocarbon fuels

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ABSTRACT

The extinction limits of diffusion flames have been measured experimentally and computed numerically for fuels of three different molecular structures pertinent to surrogate fuel formulation: n-alkanes, alkyl benzenes, and iso-octane. The focus of this study is to isolate the thermal and mass transport effects from chemical kinetic contributions to diffusion flame extinction, allowing for a universal correlation of extinction limit to molecular structure. A scaling analysis has been performed and reveals that the thermal and mass transport effects on the extinction limit can be normalized by consideration of the enthalpy flux to the flame via the diffusion process. The *transport-weighted enthalpy* is defined as the product of the enthalpy of combustion per unit mole of fuel and the inverse of the square root of fuel molecular weight. The chemical kinetic contribution provided by the specific fuel chemistry has thus been elucidated for tested individual component and multi-component surrogate fuels. A chemical kinetic flux analysis for n-decane flames shows that the production/consumption rates of the hydroxyl (OH) radical govern the heat release rate in these flames and therefore play significant roles in defining the extinction limit. The rate of OH formation has been defined by considering the OH concentration, flame thickness, and flow strain rate. A fuel-specific radical index has been introduced as a concept to represent and quantify the kinetic contribution to the extinction limit owing to the fuel-specific chemistry. A relative radical index scale, centered on the radical index of a series of n-alkanes which are observed and fundamentally explained to be common, is established. A universal correlation of the observed extinction limits of all tested fuels has been obtained through a combined metric of radical index and transport-weighted enthalpy. Finally, evidence as to the validity of the fundamental arguments presented is provided by the success of the universal correlation in predicting the extinction limits of the multi-component mixtures typical of surrogate fuels.

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1. Introduction

Extinction limits of diffusion flames in the counterflow configuration have been rigorously studied for various fuel classes from hydrocarbon to oxygenated fuels [1–18]. Since the extinction limit of diffusion flames is not only governed by chemical kinetics but also by thermal and mass transport in a coupled manner, it has been utilized as a fundamental target by which to validate kinetic and transport models for a particular fuel [7–18]. This rich coupling effect of chemical kinetics and mass transport has also resulted in the utilization of diffusion flames to evaluate the performance of surrogate fuel mixtures in emulating the behavior of real fuels [11–18]. As the diffusion flame extinction limit is affected simultaneously by many parameters such as fuel mass fraction, flame temperature, mass transport, and fuel chemistry, little progress has been made in

understanding the role of fuel chemistry in dictating diffusion flame phenomena, despite extensive experimental study. This lack of fundamental knowledge of the relation between diffusion flame extinction limit and fuel chemistry limits an understanding of the impact of molecular structure on flame extinction. Thus the fundamental design of surrogate fuel models of targeted real fuels has been impeded.

From asymptotic analysis with one-step global chemistry, the extinction limit or the extinction Damköhler number of a diffusion flame has been elucidated to be governed by the ratio of chemical heat release from the reaction zone to heat losses to the fuel and oxidizer sides [1–6]. Extinction occurs when this ratio is below a critical value as is the case when the flame temperature becomes so low that the rate of chemical heat release is not sufficient to overcome the rate of heat loss. Consequently, chemical reaction may not be sustained [1–6]. However in a detailed chemistry analysis, the chemical heat release rate is not only governed by the flame temperature but also by fuel chemistry. Recent studies of the kinetic coupling between alkanes and aromatics demonstrated

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Nomenclature

T	temperature
$\widetilde{T}$	nondimensional temperature, $\widetilde{T} = T/(\Delta H_c/C_p)$
$\widetilde{T}_a$	nondimensional activation temperature
ΔH_c	heat of combustion
C_p	heat capacity
η	nondimensional axial coordinate, $\eta = x/(\alpha k a)^{1/2}$
x	axial distance from stagnation plane
α	thermal diffusivity, $\alpha = \lambda/\rho C_p$
λ	thermal conductivity
ρ	density
k	configuration factor, 1 for planar geometry and 2 for axisymmetric
Le	Lewis number
Y	mass fraction
$\widetilde{Y}$	nondimensional mass fraction, $\widetilde{Y}_F = Y_F/Y_{F,-\infty}$, $\widetilde{Y}_O = Y_O/\gamma$

γ	stoichiometric oxidizer to fuel mass ratio
Da	Damköhler number
B	pre-exponential factor
MW	molecular weight
a	strain rate
D	mass diffusion coefficient

Subscripts

F	fuel
O	oxidizer
E	extinction
f	flame
$-\infty$	boundary of fuel side
∞	boundary of oxidizer side

that at the same flame temperature, the extinction limit is strongly governed by the balance between radical chain branching and propagation/termination reactions [8,9]. Thus, it is important to understand how the respective rates of heat release and heat loss are controlled by chemical kinetics so that the effect of fuel molecular structure/functional group as well as their interactions with mass and thermal transport can be separated and understood. In order to make a parametric study of the effect of each term on flame reactivity, it is a prerequisite to develop metrics for the respective contributions of thermal transport, mass transport, and chemical kinetics such that the respective effects on flame phenomena may be quantified and fully understood.

Recently, it has been demonstrated that a simple surrogate mixture for a specific target real fuel can be successfully formulated through the sharing of physical and chemical kinetic parameters that are important to a wide range of key fundamental combustion phenomena [13]. Dooley et al. [13] have reported on the *a priori* formulation of a mixture of n-decane, iso-octane, and toluene, to emulate the global combustion behavior of complex real fuel sample, Jet-A POSF 4658. This mixture is referred to as the "*first generation (POSF 4658) surrogate*". The successful performance of this surrogate fuel in emulating the combustion kinetics exhibited by the much more complex real fuel was demonstrated by a wide range of experimental comparisons, including diffusion flame extinction as measured with a counterflow burner [13].

More specifically, this first generation POSF 4658 surrogate mixture was observed to emulate the real fuel diffusive extinction limits when compared on a molar basis. However, it was not able to reproduce diffusive extinction limits when compared on a mass basis, apparently due to a lower average molecular weight for the surrogate fuel mixture in comparison to the real fuel (120 g/mol versus ~142 g/mol), leading to a mismatch in the rate of fuel diffusion. A second surrogate mixture formulated by the same methodology using n-dodecane, iso-octane, n-propyl benzene, and 1,3,5-trimethyl benzene was also able to emulate the same real fuel diffusive properties (average molecular weights are common) in addition to the chemical kinetic potential [17]. This *second generation POSF 4658 surrogate* is observed to reproduce the diffusive extinction behavior of the target real fuel by both molar and mass metrics.

The success of these examples in comparing surrogate and a real fuel target in a diffusion flame environment presents an important and interesting question. In addition to the apparent importance of fuel diffusivity to diffusion flame extinction, what is the relative importance of chemical kinetics in comparison to

thermal and mass transport processes? Moreover, when the contribution of chemical kinetics to the diffusive extinction is understood, can the extinction limit be predicted based on fuel chemistry characteristics for fuels of similar molecular structure?

Motivated by the above discussions of surrogate fuels and the questions to quantitatively scale the impact of fuel chemistry on diffusion flame extinction, the objective of this study is to investigate and characterize the importance of fuel chemical kinetics for structurally distinct hydrocarbon classes of normal-alkanes, isomerised-alkanes and alkyl benzenes. Extinction limits are measured for n-decane, n-nonane, n-heptane, iso-octane, toluene, n-propyl benzene, 1,2,4-trimethyl benzene and 1,3,5-trimethyl benzene diffusion flames. Where working kinetic models are available, OH radical concentrations are computed and compared to measurements made by planar laser induced fluorescence (LIF). A methodology which decouples the respective contributions of thermal, transport, and chemical kinetic potential on the overall process of diffusion flame extinction is presented theoretically, and later numerically analyzed and justified. Finally, a *transport weighted enthalpy* and a *radical index* are introduced as concepts to respectively assess and quantify the impacts of mass transport and chemical kinetics on diffusion flame extinction of the tested fuels. A universal correlation between diffusion flame extinction limit and a combined metric of transport weighted enthalpy and the radical index is obtained. The usefulness of the universal correlation is tested by the prediction of the extinction limit of surrogate fuel mixtures.

2. Experiments

The extinction limits of n-decane (nC10), n-nonane (nC9), n-heptane (nC7), iso-octane (iC8), n-propyl benzene (nPB), toluene, 1,2,4-trimethyl benzene (124TMB) and 1,3,5-trimethyl benzene (135TMB) are measured by dilution in nitrogen and in counterflow against dry air. The experimental apparatus for the measurement of diffusion flame extinction limits consists of a counterflow burner integrated with a liquid fuel vaporization system and flow controllers as described in detail previously [8–10]. A schematic of the apparatus is shown in Fig. 1. The burner separation distance is maintained at 9 mm for most of the reported measurements. The counterflow burner is of 13 mm inner diameter at the exit of the converged nozzle, resulting in a uniform velocity profile at the nozzle exit. The uniformity of velocity distribution was confirmed by using a PIV system and found to be uniform within 3% deviation between maximum and minimum values from the centerline to the edge of the nozzle tip. Extinction strain rates are measured