Kinetic effects of aromatic molecular structures on diffusion flame extinction

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Abstract

Kinetic effects of aromatic molecular structures for jet fuel surrogates on the extinction of diffusion flames have been investigated experimentally and numerically in the counterflow configuration for toluene, \( n \)-propylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. Quantitative measurement of OH concentration for aromatic fuels was conducted by directly measuring the quenching rate from the emission lifetimes of OH planar laser induced fluorescence (LIF). The kinetic models for toluene and 1,2,4-trimethylbenzene were validated against the measurements of extinction strain rates and LIF measurements. A semi-detailed \( n \)-propylbenzene kinetic model was developed and tested. The experimental results showed that the extinction limits are ranked from highest to lowest as \( n \)-propylbenzene, toluene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. The present models for toluene and \( n \)-propylbenzene agree reasonably well with the measurements, whereas the model for 1,2,4-trimethylbenzene underestimates extinction limits. Kinetic pathways of OH production and consumption were analyzed to investigate the impact of fuel fragmentation on OH formation. It was found that, for fuels with different molecular structures, the fuel decomposition pathways and their propagation into the formation of radical pool play an important role to determine the extinction limits of diffusion flames. Furthermore, OH concentrations were found to be representative of the entire radical pool concentration, the balance between chain branching and propagation/termination reactions and the balance between heat production from the reaction zone and heat losses to the fuel and oxidizer sides. Finally, a proposed “OH index,” was defined to demonstrate a linear correlation between extinction strain rate and OH index and fuel mole fraction, suggesting that the diffusion flame extinctions for the tested aromatic fuels can be determined by the capability of a fuel to establish a radical pool in a manner largely governed by molecular structure.

Keywords: Extinction limit; Jet fuel surrogate; OH index; Kinetic mechanism; OH PLIF

1. Introduction

Postulated surrogate models for realistic transportation fuels contain a mixture of a few representative fuel components [1–4]. Due to the larger molecular weight components found in jet fuels, it has become necessary to study larger individual fuel components [5–17]. In addition to the fact that jet fuels contain approximately 20% aromatics, the presence of aromatic components has a significant impact on the initiation and growth of the radical pool in a reacting flow and consequently in a surrogate mixture [16]. Compared to alkane fuels, kinetic
model development for aromatic fuels remains a challenging problem due to a lack of fundamental kinetic understanding. Nevertheless, to construct a jet fuel surrogate and develop its kinetic model, the combustion behavior of both individual aromatic fuel components and their mixtures must be investigated and validated [5–17]. Furthermore, to match the fundamental combustion properties of real transportation fuels such as ignition delay time, strained ignition/extinction behavior, and laminar flame speed, the mixing ratio of these fuel components should be carefully determined based on a firm understanding of kinetic and transport coupling effects between the fuel components [5–17].

It has been demonstrated that the extinction strain rate of n-decane/toluene diffusion flames decrease significantly with increased toluene addition [16]. This observation has been explained by a kinetic coupling effect of the n-decane/toluene blend caused by fuel fragments entering the high-temperature zone where peak radical concentrations occur. For the toluene/n-decane blended fuels, the radical concentration decreases considerably due to the consumption of radicals by reactions with toluene and its fragments, thus leading to diffusion flame extinction at lower strain rates. In addition, it was also revealed that the extinction strain rate has a linear dependence on radical concentration, especially the OH radical. OH serves not only as an indicator of the overall radical pool concentration in diffusion flames but also as the chemical heat release rate. Analysis of OH concentrations and extinction limits demonstrated that the extinction strain rate can be linearly correlated with fuel mole fraction, the ratio of hydrogen to carbon (H/C ratio), and mean fuel molecular weight [16]. However for aromatic fuels, the molecular structure poses a new dimension in varying the OH concentration as well as burning properties. For example, n-propylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene have the same H/C ratio and molecular weight, but have different reactivity.

Recently, a three-component surrogate of n-decane, iso-octane, and toluene has been proposed by constraining the H/C ratio and Derived Cetane Number of a real jet fuel [17]. It was revealed that this three-component surrogate can emulate very well the auto-ignition behavior of the target fuel as well as the extinction limit of diffusion flames in terms of fuel mole fraction. However, this surrogate fails to reproduce extinction limits in terms of fuel mass fraction due to the mismatch with the target fuel molecular weight [17]. Consequently, larger aromatic fuels, such as n-propylbenzene, trimethylbenzene, and xylene have to be considered as aromatic components of a jet aviation fuel surrogate.

The objective of the present study is to investigate and characterize the kinetic effect of molecular structure for potential aromatic surrogate fuel components on diffusion flame extinction in the counterflow configuration. n-propylbenzene (nPB), 1,2,4-trimethylbenzene (124TMB) and 1,3,5-trimethylbenzene (135TMB) are chosen to be examined in addition to toluene. Comparison of the three C9H12 isomers allows for examination of effect of the molecular structure on extinction limits independent of molecular weight and H/C – focusing on the arrangement of the respective alkyl moieties. To quantify typical radical concentrations for each aromatic fuel, OH planar laser induced fluorescence was performed for different strain rates and initial fuel mole fractions. A kinetic model for nPB under flame conditions is developed in order to employ numerical simulations to further analyze the effect of molecular structure on flame structure. An OH index is defined to generate a correlation between fuel structure and its extinction limit.

2. Experiments and numerical simulations

To measure the extinction limits, a counterflow burner with a fuel vaporization system was used. The experimental apparatus consisted of the burner, vaporization system, flow controllers, and a Planar LIF system as shown in Fig. 1. Details of experimental setup can be found in [16]. The flow rates of toluene (>99.9% purity), nPB (>98%), 124TMB (>98%), and 135TMB (>99%) were controlled by a syringe pump (Harvard Apparatus, PHD 22/2000). A chamber of 300 cc volume for the vaporization was used to reduce the flow response time and to enhance the vaporization for low-vapor-pressure fuels. Liquid fuel and heated nitrogen were injected into the vaporization chamber through the inner nozzle (0.2 mm) and outer coflow nozzle (1 mm), respectively, to obtain the steady state atomization. The temperature at the exit of vaporization chamber was maintained at 500 K with PID control. The upper burner was also maintained at 500 ± 5 K. In our previous study, no

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Fig. 1. Schematic of experimental setup.
fuel decomposition was observed at 500 K by FTIR measurement for n-decane [16]. Aromatic fuels examined in the present study have higher temperature of thermal decomposition rather than n-decane, thus, it is not expected that fuel decomposition before the burner exit would be significant. The oxidizer temperature was 298 K. The two hydro-dynamically converging nozzles had 13 mm i.d. at the exit. The uniformity of velocity profile was confirmed with PIV measurements (the uniformity of radial velocity profile was >97% at all tested flow conditions). To investigate the effect of gas expansion due to chemical heat release on the boundary conditions at the nozzle exit, measurements were performed for different nozzle distances 9–12.7 mm, yielding extinction strain rates within 5%. The extinction strain rates were measured by increasing the flow velocities of both the fuel and oxidizer by matching the flow momentum. Global strain rate, α, was utilized to represent the flow conditions at the extinction limits [16,18]. For LIF measurements, 200 images were accumulated to obtain higher signal-to-noise ratio. The spatial resolution of the employed ICCD camera was 39 μm/pixel.

Numerical calculations were performed using the OPPDIF module of the CHEMKIN package [19] with a modified arc-length continuation method for both plug flow and potential flow conditions [20,21]. For consistency, numerical calculations with plug flow conditions and same definition of global strain rate were utilized to be compared to the measurements. Further details on calculations were described previously [16].

3. Kinetic models

The development of a kinetic model for a multi-component jet fuel surrogate requires common sub-models for small species chemistry. Accordingly, we have developed a high temperature kinetic model for nPB by considering of the efforts by Dagaut et al. [22]. The toluene kinetic model of Metcalfe et al. [23], which contains 138 species and 509 reaction steps (after reduction for high temperature kinetics [24]) is utilized for toluene and serves as base mechanism for the nPB sub-mechanism (Table S1 in Supplementary data).

Thermo-chemical properties of nPB and those of the radicals and intermediates formed from its oxidation/decomposition have been estimated using the method of group activity [25] as implemented through THERM [26]. Since the C–H and C–C bonds of the n-alkyl chain are much weaker than those of the aromatic moiety of the molecule (~86–101 vs ~112 kcal/mol), it is assumed that the vast majority of fuel consumption will take place by oxidation or decomposition of the alkyl chain (Fig. S1 in Supplementary material). Therefore, our chemical kinetic model describes nPB oxidation in a semi-detailed fashion.

Fuel decomposition channels have been considered at their high pressure limit values. As described in similar previous modeling efforts, the rate constants of these reactions have been estimated in the reverse recombination direction [27,28]. The model has been assembled by analogy to toluene oxidation where appropriate (Table S1). The rate constant describing the substitution of the alkyl chain of the fuel molecule with a hydrogen atom is assumed equal to the similar process in toluene and our description of this reaction is taken from the work of Bounaceur et al. on toluene oxidation [29]. The rate constants for hydrogen abstraction from C–H bonds of typical BDEs, i.e. primary (101 kcal/mol) and secondary (98.5 kcal/mol), have been assigned as recommended by Orme et al. [30]. The rate constants for hydrogen abstraction from the benzylic type position have been estimated from the analogous process in toluene oxidation. We make no correction for the slightly weaker C–H BDE of nPB relevant to toluene (~89 vs ~86.5 kcal/mol), only correcting for the change in degeneracy of abstraction site; three available H atoms in the case of toluene verses only two in the case of nPB.

The bimolecular processes of the benzylic type radical (c6h5ac3h6) with oxygenated radicals have been adopted from Dagaut et al. [22], as has the rate constant which describes the β-scission of the benzylic type radical to form styrene and a methyl radical. The β-scission of the radical formed by hydrogen abstraction from the secondary position, c6h5bc3h6, is assumed to behave in a similar fashion to the ethyl benzene radical. As such, our description of these processes has been described by analogy to toluene oxidation [29]. The radical formed by hydrogen abstraction from the primary position is assumed to decompose by β-scission of the labile C–C bond only, and the rate constant for this process comes from Dagaut et al. [22].

For 124TMB diffusion flames, the kinetic model for a proposed kerosene surrogate [15,31] was utilized, which includes n-decane and 124TMB chemistries in a semi-detailed description.

4. Results and discussion

Figure 2 shows experimental measurements of extinction strain rates for toluene, nPB, 124TMB, and 135TMB diffusion flames and their comparisons to the numerical calculations as a function of fuel mole fraction, Xf. It is clearly shown that the extinction limits dramatically vary according to the fuel molecular structure. Considering that the extinction limit of diffusion flames are strongly governed by the initiation of the radical pool by
to quantify the radical pool concentration for chain branching and propagation/termination reactions [16]. Thus, the extinction limit of 124TMB is 40% lower than that of toluene for fixed X_f = 0.15 and aE = 0.1, where now the ratio of signal to noise is approximately five after subtraction. The flatness of OH LIF signal also demonstrates the uniformity of the flow field, which has been validated by PIV measurements, whereas the PAH LIF signal shows non-uniformity due to the strong sensitivity on the temperature, as discussed previously [16].

Estimation of the LIF quenching rate is important to minimize the uncertainty of measurements [37,38]. In our previous work [16], the quenching rate of the LIF signal for n-decane/toluene diffusion flames was estimated by considering the major species numerically. However, greater case is required in the case of aromatic diffusion flames, since the current kinetic model does not fully describe the formation of PAHs, which have higher absorption coefficients at UV ranges as well as unknown quenching coefficients [39].

To determine the quenching effect of LIF signals, OH LIF images were sequentially taken with 2 ns gate width by varying the delay time from the laser Q-switch output at the same flow condition for all aromatic fuels. Figure 4 shows the decay trends of OH LIF signal normalized by the peak OH LIF signals. It is noteworthy that the LIF emission lifetimes are significantly different for each aromatic fuel. The LIF emission lifetime is around 8.26 ns from linear fitting for toluene diffusion flame. 124TMB, 135TMB, and nPB diffusion flames revealed 1%, 21%, and 30% reduction of LIF emission lifetime compared to that of toluene, respectively. Note that the decay of emission lifetime was not observed to be an

4.1. OH LIF measurements

Figure 3 shows the direct images of PLIF for the nPB diffusion flame at X_f = 0.15. The direct PLIF image in Fig. 3a demonstrates three distinctive signals when the Q1(6) excitation line for OH (282.930 nm) is used. Firstly, it shows the existence of PAH formation at the fuel side from the PAH LIF, which has higher intensity than that of OH LIF by a factor of five. Secondly, considerable interference from the LII signal of the soot particles located near the stagnation plane is observed. Although it is possible to suppress the LII signal by reducing the gate width [36], additional efforts are required to suppress the PAH LIF signals, since it has comparable emission lifetime with that of OH LIF signals. To remove these interferences, the wavelength of UV laser beam was slightly detuned from Q1(6) OH excitation line to 282.85 nm to obtain only PAH LIF and soot LII signals as shown in Fig. 3b. Finally, this detuned image was subtracted from the original LIF image to remove the interferences. Figure 3c shows the evaluated OH LIF images for the nPB diffusion flame at X_f = 0.15 and a = 100 s^{-1}, where now the ratio of signal to noise is approximately five after subtraction. The flatness of OH LIF signal also demonstrates the uniformity of the flow field, which has been validated by PIV measurements, whereas the PAH LIF signal shows non-uniformity due to the strong sensitivity on the temperature, as discussed previously [16].

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exponential function of time [40]. Since the measured emission lifetime is of the same order of the present laser pulse duration (\(\sim 8\) ns), the time resolution for OH excitation was not good enough to resolve the details of LIF signal decay characteristics. Nevertheless, the present method still shows the capability to observe the variation of decay time. Finally, the OH LIF intensities of different fuels have been normalized by their respective emission lifetimes to account for the different quenching effects of different fuels.

Figure 5 shows the changes of OH concentration as a function of \(a\) at \(X_f = 0.15\) for toluene, nPB, 124TMB, and 135TMB diffusion flames. Since the present measurements did not employ the standard calibration burner [37], kinetic model predictions were used to convert the present LIF signals into units of concentration. However, it has been shown that the LIF signal can be properly interpreted in terms of maximum concentration, if the kinetic model successfully predicts the extinction limits of diffusion flames [16]. Thus in the present study, toluene diffusion flame was utilized as a reference for the unit translation. Maximum OH intensities of toluene diffusion flames were traced by varying the \(X_f\) and the strain rate, and compared to the numerical calculations at the same fuel conditions. A linear correlation was obtained with the correlation coefficient of 0.95. The error bars presented on present LIF measurements in Fig. 5 are based on signal-to-noise ratio during the subtractions and quenching measurements. The inset in Fig. 5 shows the spatial profiles of OH concentration for both LIF measurements and calculations of nPB and toluene diffusion flames at \(a = 140\) s\(^{-1}\) with reasonable agreement. The deviation between
measurements and calculations can be attributed to the effect of respective temperature profiles, as demonstrated previously [41], which were not measured and evaluated in the present study. Nevertheless, the results show that the nPB kinetic model reproduces the variation of OH concentration with change of $a$ at $X_f = 0.15$ reasonably well. However, similar to the prediction of extinction limit, the 124TMB model shows significant under-prediction of OH concentrations.

It has been demonstrated that the extinction strain rate of $n$-decane/toluene diffusion flames has a linear relationship with maximum OH concentration [16]. Accordingly, it is of interest that the overall magnitudes of maximum OH concentrations for the aromatic fuels are also proportional to the extinction strain rates in the order of nPB > toluene > 124TMB > 135TMB. Therefore, to understand why the OH concentration is sensitive to molecular structure, the production and consumption pathways of OH for the toluene diffusion flame are investigated in the following section and the kinetic impact of fuel fragmentation pathway on the formation of OH will be also examined for toluene, nPB, and 124TMB diffusion flames.

4.2. Production and consumption of OH

The production and consumption pathways of OH for toluene diffusion flame have been analyzed by spatially integrating the rate of production of OH from the numerical calculation at $X_f = 0.20$ and $a = 50 \text{ s}^{-1}$. The production pathways of OH can be easily identified. The following three chain-branching reactions, (1) $\text{H} + \text{O}_2 = \text{O} + \text{OH}$, (2) $\text{O} + \text{H}_2\text{O} = 2 \text{OH}$, and (3) $\text{O} + \text{H}_2 = \text{H} + \text{OH}$, contribute to more than 75% of total OH production. Figure 6 shows the OH consumption pathways, which are mainly chain propagation and termination reactions along with the heat production by $\text{H}_2\text{O}$ and $\text{CO}_2$ formation. Analysis on the heat production pathways shows that most of heat is produced by OH consumption pathways ($\approx 40\%$). It is noteworthy that OH consumption through fuel fragments grows as $a$ increases near the extinction limit. To investigate the role of the different OH consumption pathways in terms of the spatial coordinate, the major heat production and fuel fragments reactions in Fig. 6 are respectively summed and plotted in Fig. 7. It is shown clearly that the maximum OH concentration is insensitive to $a$ below 140 $\text{s}^{-1}$, whereas a significant reduction is observed near the extinction limit of $a = 228 \text{ s}^{-1}$. At lower strain rates from 50 to 140 $\text{s}^{-1}$, OH consumption through the fuel fragments seems not to affect the balance between total production and consumption of OH. However, near the extinction limit of $a = 228 \text{ s}^{-1}$, the participation of fuel fragment reactions becomes considerable, enlarging the total OH consumption rate. As $a$ is increased, the concentration of fuel fragments grows due to the increase of fuel flux into the reaction zone. Consequently, due to the decrease of residence time, fuel fragments cannot be fully oxidized, and are instead consumed by reactions with OH. This change in character of the reacting flow has a large impact on heat production, leading to extinction as $a$ is increased further.

Figure 8 shows the total fuel consumption rate and the most dominant elementary reactions on fuel consumption with flame temperature at the fixed $X_f$ and $a$ for toluene, nPB, and 124TMB diffusion flames. The maximum consumption rate of nPB is located in the relatively lower temperature region of 1300 K, whereas 124TMB consumption is located near 1500 K and toluene at 1600 K. In particular, the most dominant elementary reaction for nPB fragmentation is the chain-branching thermal decomposition ($\text{C}_6\text{H}_5\text{C}_2\text{H}_4 = \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_2\text{H}_6$), which is dominant over H abstraction reaction by a factor of five. In case of 124TMB and toluene, the consumption pathways of these fuels are dominated by H abstraction reactions.

Fig. 6. Major OH consumption pathways for toluene diffusion flames with varied strain rate at $X_f = 0.20$. (near extinction at $a = 228 \text{ s}^{-1}$).

![Fig. 6. Major OH consumption pathways for toluene diffusion flames with varied strain rate at $X_f = 0.20$.](image_url)

Fig. 7. Spatial profiles of OH concentrations and reaction rates of major production and consumption channels of OH for toluene diffusion flames with varied strain rate at $X_f = 0.20$.

![Fig. 7. Spatial profiles of OH concentrations and reaction rates of major production and consumption channels of OH for toluene diffusion flames with varied strain rate at $X_f = 0.20$.](image_url)
4.3. Linear correlation of extinction limits

The extinction limits of n-decane/toluene diffusion flames have been found to be a linear function of the maximum OH concentration [16]. The present numerical results also revealed that extinction limits of these aromatic fuels have a linear function of maximum OH concentration near extinction limits. The present work has revealed that maximum OH concentration in aromatic diffusion flames is related to fuel fragmentation and its propagation into the formation of radical pool, especially OH, which plays a significant role on the heat production, and thus on the determination of the extinction limits of diffusion flames. Such a result suggests that diffusion flame extinction is strongly related to capability of fuel to establish a radical pool. The radical pool may be represented by the maximum OH concentration as a radical index for different aromatic fuels. Accordingly, the OH index was determined as maximum OH concentrations at the lowest $a$ among the LIF measurements shown in Fig. 5. Figure 9 shows that the extinction limits of aromatic diffusion flames correlate linearly with the OH index and $X_f$. This linear correlation indicates that the extinction limits for a given amount of fuel ($X_f$) are predominantly controlled by the radical production capability (OH index), which is determined by the molecular structure and chemical kinetics of the fuel fragmentation processes.

5. Concluding remarks

To understand the kinetic effects of molecular structure of aromatic fuels, the extinction limits of diffusion flames were investigated experimentally and numerically in the counterflow configuration for toluene, nPB, 124TMB and 135TMB. A semi-detailed nPB kinetic model has been developed. The maximum OH concentrations have been quantitatively measured with planar LIF techniques. Extinction limits of aromatic fuels are found to be dramatically changed according the molecular structure, ranked from highest to lowest as nPB, toluene, 124TMB, and 135TMB. The comparison between experiments and modeling reveals that the toluene and nPB models are able to properly reproduce the experimental results, whereas the 124TMB model under-estimates the formation of OH, thus leads to under-estimation of extinction limits. The analysis on the production and consumption pathways of OH shows production predominantly by three elementary chain-branching reactions, whereas the consumption pathways consist of chain propagation and termination reactions producing heat formation and fuel fragmentation. It was also demonstrated that at the low strain rate, OH consumption through reactions with fuel fragments are negligible compared to that of heat formation, so that the maximum OH concentration is relatively insensitive to the change of strain rate. However, the maximum OH concentration starts to decrease significantly as strain rate nears the extinction limits, since the OH is being consumed considerably by the fuel fragments. Furthermore, it was found that nPB is mainly decomposed thermally at relatively low temperatures, whereas toluene and 124TMB are decomposed by H abstraction reactions by the H, which leads to a reduction of OH concentration. The OH index determined from LIF measurements is proposed to represent the radical pool production capability for the aromatic fuels. Finally, a linear correlation of extinction strain rates with OH index and fuel mole fraction was demonstrated for all aromatic diffusion flames, allowing the kinetic effects of molecular structure on extinction of diffusion flames to be identified with OH concentration (OH index).
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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.proci.2010.05.082.

References


