A comparative study of $n$-propanol, propanal, acetone, and propane combustion in laminar flames

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Abstract

The laminar flame speeds of C₃ oxygenated fuels ($n$-propanol, propanal and acetone) and hydrocarbon (propane) were measured in a combustion bomb to compare combustion characteristics of C₃ alcohol, aldehyde, ketone, and alkane. Propanal shows the highest flame speeds while acetone gives the lowest one. The experimental observations are further interpreted with chemical kinetic models. The effects of distinctive molecular structures on the fuel consumption pathways are clarified. Propanal generates a large H atom pool that enhances the oxidation, leading to the highest flame speeds. However, acetone forms methyl radical (CH₃) and has lower flame speeds as a consequence. The calculated maximum concentrations of H, OH, and CH₃ confirm this analysis. It is found that propanal yields the highest H and OH concentrations while acetone produces the lowest H and OH concentrations among all tested fuels. Moreover, acetone presents higher CH₃ concentration, especially for fuel rich condition. $n$-Propanol and propane show comparable flame speeds and similar radical concentrations, especially H and OH. The different kinetics among hydrocarbon species with the same carbon numbers can provide a horizontal view in the hierarchical hydrocarbon chemistry.

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1. Introduction

Energy efficiency and emission reduction have become major topics of interest to the combustion community in the last few decades. Biofuels have been investigated as an alternative fuel to resolve these issues. Particularly, small alcohols have been commercialized and widely used in engines. Recently, the fermentation methods of alcohols have been well developed. This facilitates the application of alcohols and attracts more attention to the study of alcohol chemistry. Many works have been done on alcohols to clarify their combustion characteristic and chemical kinetic models were developed to predict experimental data and understand complex combustion phenomena [1–7]. The previous studies indicate that aldehydes, mainly produced from parent alcohols by the reactions at the $\alpha$-carbon or hydroxyl (OH)

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group, play an important role in the decomposition and oxidation of alcohols as key stable intermediate products [8–11]. Ketones are another important intermediate species in the combustion of hydrocarbons and oxygenates. Aside from being intermediates in combustion, aldehydes and ketones are also toxic emissions from engines that threaten environmental safety and human health. Many studies have been focused on the detection and formation of these toxic emissions [12–14]. An accurate detailed kinetic model is required not only for the control of these emissions, but also for understanding the combustion chemistry of other molecules that are formed from aldehydes and ketones in combustion systems. Most research focuses on single fuel chemistry, fuel isomers, and the hierarchical structure of fuels with the same functional group but varied carbon chain length [6,15–21]. It is found that the reactions related to the destruction of functional groups play an important role on the global reactivity of a specific fuel. In the present work, hydrocarbons with different functional groups and the same carbon number are studied to aid the development of a more accurate reaction model.

C₃ oxygenated fuels are the smallest hydrocarbons including alcohol isomers, aldehyde and acetone structures. Propanol isomers can be obtained through fermentation [22–25]. Acetone is one of the main products from the traditional ABE (Acetone–butanol–ethanol) fermentation method [26]. An early study by Norton and Dryer [11] concluded that higher concentrations of propanal enhanced the overall reactivity of n-propanol, while acetone, a product of iso-propanol oxidation, decreases overall reactivity. Li et al. [27] investigated acetone, n-propanol, and iso-propanol with tunable synchrotron photoionization and molecular beam mass spectrometry. Flame species including isomeric intermediates were identified. Veloo et al. [28] studied the flame propagation and extinction of n-propanol, iso-propanol, and propane in the counterflow configuration at atmospheric pressure. The effects of the presence and the location of hydroxyl radical were investigated. Benjamin et al. [29] investigated the ignition behavior of selected C₃ oxygenated hydrocarbons behind reflected shock waves, including propanal and acetone. Differences between isomer were revealed for ketone (acetone) and aldehyde (propanal). Burluka et al. [30] measured the laminar flame speed of propylene oxide, propanal, and acetone, but the calculated results had only qualitative agreement with the experimental results. Ranzi et al. [31] reviewed the kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels hierarchically and comparatively, including C₃ alcohol isomers, propanol and acetone. However, more experimental data and further kinetic studies are needed for more accurate predictions of the combustion characteristics of C₃ fuels. In the present study, the laminar flame speeds of n-propanol, propanal, acetone, and propane are investigated in this study using a constant volume bomb for the validation of chemical kinetic models, which are used for a comparative chemical kinetic study. The oxidation mechanisms of fuels with different functional groups are also investigated by comparing the intermediate species pools that are accumulated from the oxidation of specific molecules.

2. Experimental approach

Laminar flame speeds were measured in a cylindrical combustion bomb with a 180 mm of inner diameter and a length of 210 mm. 80 mm diameter optical windows are located on both sides of the chamber. The combustion chamber was heated up to the initial temperature of 343 K and 393 K by an electrical band heater and the temperature was monitored by a thermocouple installed in the chamber with an accuracy of ±3 K. The liquid fuels, n-propanol, acetone, and propanol, were injected into the heated chamber using micro syringes through a valve. The purities of liquid fuels used in this study are more than 99.8%. The main properties of the fuels tested are tabulated in Table 1. To reduce the uncertainty of the amount of liquid fuel, different measuring ranges of micro syringes with microscopic scales were used for each target volume. The operation of the fuel injection valve was instantaneous to avoid the possible fuel loss.

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Chemical structure</th>
<th>Heat of combustion (kcal/mol)</th>
<th>Boiling point (K)</th>
<th>Density at 20 °C (kg/m³)</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃H₇OH</td>
<td></td>
<td>483.22</td>
<td>370</td>
<td>803</td>
<td>60.1</td>
</tr>
<tr>
<td>C₂H₅CHO</td>
<td></td>
<td>455.78</td>
<td>321</td>
<td>810</td>
<td>58.08</td>
</tr>
<tr>
<td>CH₃COCH₃</td>
<td></td>
<td>423.52</td>
<td>329</td>
<td>791</td>
<td>58.08</td>
</tr>
<tr>
<td>C₃H₈</td>
<td></td>
<td>530.52</td>
<td>231</td>
<td>1.83</td>
<td>44.1</td>
</tr>
</tbody>
</table>
during the injection. The gases, propane (99.9%), oxygen (99.9%), and nitrogen (99.9%), were introduced through intake valve to the required partial pressures to meet the target equivalence ratio. The mixture was allowed to wait to ensure complete vaporization of the liquid fuels and homogeneous mixing before ignition. The mixture was ignited at the center of the chamber by an electric spark. After each experiment the burned gas in the chamber was vacuumed immediately and the chamber was flushed using fresh air at least three times to eliminate the effect of residual species on the next experiment.

During the experiments, a Redlake HG-100 K high-speed camera was employed to capture the sequential images of flame propagation at the speed of 10,000 frames/s using a schlieren system. Flame diameters up to 25 mm were used for analysis, where the pressure increase was minimal and the cylindrical confinement effects can also be neglected [32]. The flame diameter was extracted from the schlieren images using an automated edge finding program. The linear extrapolation method was used to determine the unstretched flame speed [33]. More details of this experimental setup and data post-processing can be found in the literature [34–36].

3. Simulation approach

Laminar flame speeds were calculated using the CHEMKIN PREMIX code [37]. Simulations included consideration of the Soret effect and the multicomponent transport formulations were employed. The chemical kinetic models were carefully selected and modified to achieve good agreement with experimental results. For n-propanol, the chemical kinetic model used here is based on the previous model developed by Johnson et al. [3] while C1–C4 sub-model has been updated to the newest AramcoMech 1.3 mechanism developed by Metcalfe et al. [38]. However, some oxidation paths of propanol were not included in this sub-model and lead to the absence of the formation of several oxygenated intermediates [4,10]. For completeness, these reactions were adapted from the propanol model developed by Man et al. [39]. The modified model can be found in the Supplemental material. To confirm the performance of this updated model, Fig. 1 compares n-propanol laminar flame speeds from experiments [28] against simulations. The results show that this newly updated model produces more accurate predictions of flame speeds than previous models developed by Johnson et al. [3] and Man et al. [39]. Additionally, the simulated ignition delays using this model were also compared with the previous experimental data and slight differences were observed when compared with Johnson’s model [3], as shown in the Supplemental material.

The propane sub-model in AramcoMech 1.3 [38] was used for propane flame speed calculations. The kinetic models for n-propanol and propane were reduced systemically with the Princeton Chem-RC software [40] due to memory limitations. A small threshold value of 0.2 was adapted to maintain accuracy. The reduced models were validated against the detailed ones over a wide range of temperature, pressure and equivalence ratios for ignition delays and perfectly stirred reactor simulations and differences less than 3% were observed. The kinetic models of Pichon et al. [41] and Veloo et al. [42] were used for acetone and propanal simulations without reduction, respectively.

4. Results and discussions

4.1. Comparison of experimental flame speeds

Figure 2 shows the measured laminar flame speeds of four different fuels as a function of equivalence ratio at 343 K and 1 atm. The flame speeds of acetone were measured in the present work and experimental data for n-propanol, propane, and propanal were taken from Veloo

![Fig. 1. Experimental and calculated laminar flame speeds of n-propanol at 343 K and 1 atm.](image)

![Fig. 2. Laminar flame speeds of n-propanol, propanal, propane, and acetone/air premixed flames as a function of equivalence ratio at 343 K and 1 atm. Experimental data of n-propanol, propanal, and propane are from [28,42].](image)
et al. [28,42] which were measured in counterflow configurations. For equivalence ratios less than 1.3, propanal exhibits the highest flame speed and acetone gives the lowest one among the fuels investigated here. n-Propanol has comparative flame speed with propane [28]. When the equivalence ratio is larger than 1.3, acetone presents higher flame speed than that of n-propanol and propane, leading to the order change on the fuel rich side. Nevertheless, it still can be concluded that aldehyde shows the highest reactivity, while alkane and alcohol have the similar reactivity less than aldehyde, and ketone is the slowest among the same carbon number fuels in this experimental range. The laminar flame speeds of the four fuels were also measured in the present experiment at 393 K and 1 atm, as shown in Fig. 3. The order of global reactivity is reconfirmed at the elevated temperature with different experimental configurations.

4.2. Comparison of measured laminar flame speeds and simulation

Figures 2 and 3 also show the comparison of laminar flame speeds between experiment and simulation at 343 K and 393 K, respectively. Simulation results at 343 K have reasonable agreements with measurements except a maximum over prediction of around 6 cm/s for n-propanol flame speeds for fuel rich conditions. At an initial temperature of 393 K, acetone and propanal have relatively good agreement between experiment and simulation, while the kinetic models of propane and n-propanol over predict the experimental data with the maximum percent difference of 11% at equivalence ratios of 0.9 and 1.0. Even in this case, the overall kinetic performance still captures the trend of the flame speeds of different fuels, implying that the flame oxidation chemistry of the four different fuels are appropriately described in each kinetic model. In the following section, chemical reaction path flux analyses over the entire flame zone for each fuel are utilized to interpret the uniqueness of the fuel chemistry and the distinctive nature of C3 hydrocarbon series.

4.3. Path flux analysis

Propanal shows the highest flame speed compared with the other fuels as shown in Figs. 2 and 3. Laminar flame speed is a global parameter, representing the high temperature reactivity of fuel which is mainly governed by the adiabatic flame temperature and fuel specific kinetics. Propanal exhibits the highest adiabatic flame temperature among the tested fuels as shown in Fig. 4, contributing to the highest flame speeds. To clarify the kinetic effect on flame speeds, reaction path flux analysis is performed for a stoichiometric propanal flame at 343 K and 1 atm, as shown in Fig. 5. Propanal (C3H7CHO) is mainly consumed through H abstraction by H, OH and O radicals and generates equal amount of propionyl (C2H5CO) and 2-methyl vinoxy (CH3CHCHO) for about 37% each. The remaining 19% of propanal goes to CH2=CHCHO radical through H abstraction from the terminal carbon atom (CH3). Subsequently, CH2=CHCHO decomposes to C2H4 and HCO. Propionyl (C2H5CO) mainly decomposes to ethyl radical C2H5 and CO. It is noteworthy that C2H4 is an unstable radical and rapidly decomposes to form C2H2 and an H atom. Moreover, CH3CHCHO releases an H atom to form either CH2=CHO or C2H3CHO. This fast generation of an H atom at an early stage increases the overall branching ratio. This specific kinetic effect along with the adiabatic flame temperature contributes to the highest flame speed of propanal.

On the other hand, acetone shows the lowest flame speed although the adiabatic flame temperature of acetone is comparable to that of propane and even higher than that of n-propanol as shown in Fig. 4. This means that acetone chemistry slows down the overall reactivity compared to propane and n-propanol. Reaction path flux analysis for the stoichiometric acetone flame at 343 K and
Almost identical radical concentration is observed for fuel rich conditions. Acetone presents the lowest concentration for fuel rich conditions, which is a less reactive fuel and known to produce the unstable radical CH3CHO as a chain termination radical. Large amounts of radical (CH3CO) and methyl radical (CH3) are decomposed to ketene (CH2O) and methyl radical (CH3). CH3 is a less reactive and known radical as shown in Fig. 2 (study of Veloo et al. [28]). The minimal thermal effect on the flame speed of each fuel, the calculated maximum concentrations of H, OH, and CH3 are plotted in Figs. 9(a–c). Almost identical maximum H and OH concentrations are found between n-propanol and propane over the wide range of equivalence ratio, confirming the comparable kinetic effects on flame speeds, even though propane generates higher CH3 concentration than n-propanol.

To extend and validate the previous discussions on the fuel reactivity, maximum H, OH and CH3 concentrations of propanal and acetone are also plotted in Fig. 9. Propanal shows the highest maximum H and OH concentrations and the lowest CH3 concentration. Acetone presents the lowest H and OH concentrations for fuel lean condition and the highest CH3 concentration for fuel rich condition. These qualitative results confirm that the major consumption of fuel and its intermediate species are mainly caused by H and OH. However, there are no dominant consumption pathways or notable radical production, which implies the minimal kinetic effect on flame speeds as well. Regarding the kinetic effects on the alcohols, Davis and Law [21] found that the substitution of H by OH has minor effect on ethanol compared to that on methanol. Veloo et al. [15] reported that, for primary alcohols, the effect of OH functional group diminishes with the increase of carbon chain length. Moreover, the similarity between the behavior of the alkane and straight chain alcohol can be ascribed to their similarity of radical pools. To further clarify the kinetic effect on the flame speed of each fuel, the calculated maximum concentrations of H, OH, and CH3 are plotted in Figs. 9(a–c). Almost identical maximum H and OH concentrations are found between n-propanol and propane over the wide range of equivalence ratio, confirming the comparable kinetic effects on flame speeds, even though propane generates higher CH3 concentration than n-propanol.

The flame speeds of n-propanol and propane are very similar as shown in Fig. 2 (study of Veloo et al. [28]) and Fig. 3. The minimal thermal effect is expected due to the 16 K difference in adiabatic flame temperature between n-propanol and propane at an equivalence ratio of 1.05. With respect to the effect of kinetics, Figs. 7 and 8 show the reaction path flux analysis for stoichiometric n-propanol and propane at 343 K and 1 atm, respectively. It is found that H abstraction reactions occur at different carbon positions and the
propanal has the highest flame speed due to the large amount of H atoms which accelerate the chain branching rate, while the high concentration of CH₃ leading to chain termination is responsible for the lowest flame speed of acetone. More interestingly, on the fuel rich side, the maximum H and OH concentrations of acetone give almost the same value as that of n-propanol and propane. This may explain the closer flame speeds of acetone, n-propanol, and propane in fuel rich side.

5. Conclusions

Laminar flame speeds of n-propanol, propanal, acetone, and propane were measured in a cylindrical combustion bomb at atmospheric pressure to study the effects of different functional groups. Experimental results showed that propanal has the highest flame speed among the tested fuels, while acetone gives the lowest one except for fuel rich condition at 343 K. The kinetic models were updated and the computed flame speeds agreed well with the experimental results. To identify the causes of different flame speeds among the fuels, reaction path flux analyses were performed. The simulation results showed that the concentrations of intermediate species generated from fuel consumption were the main cause of the difference in flame speeds. H atom released from the oxidation of propanal accumulates to a high concentration. This phenomenon accelerates the overall reactivity of propanal, leading to the highest flame speeds of propanal. On the other hand, the consumption of acetone is dominated by H abstraction reactions and then the β-scission reaction, CH₃COCH₃ → CH₃COCH₂ → CH₃ + CH₂CO. One channel of CH₂CO consumption produces CH₃ and carbon monoxide. As a result, abundant methyl radical (CH₃) is produced because of the unique molecular structure. The high concentration of methyl radical enhances the chain termination reaction and results in reduced reactivity of acetone. Results of maximum H, OH and CH₃ concentrations confirm these analyses, which depicts that propanal generates the highest H and OH radicals and acetone produces the highest CH₃ concentration. The comparable flame speeds of n-propanol and propane is ascribed to the similarity of the intermediate species pool, especially H and OH radical.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.proci.2014.05.066.

References
