Comparative study on the laminar flame speeds of methylcyclohexane-methanol and toluene-methanol blends at elevated temperatures

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ABSTRACT

Laminar flame speeds of methylcyclohexane (MCH)-methanol and toluene-methanol blends were experimentally determined with spherically expanding flame method in a constant volume bomb at atmospheric pressure, initial temperatures of 393 and 433 K, covering wide equivalence ratio range. The blending ratio of methanol in liquid volume varies as 0%, 20%, 40%, 60%, 80%, 100%. Nonlinear methodology was employed to remove the stretch effect in the data processing. Experimental results show that MCH-air flame propagates faster than toluene at the same condition. The addition of methanol into MCH and toluene results in acceleration of laminar flame speed especially at the rich mixtures. Since the published model suffers difficulty in reproducing experimental data, model refinements were carried out and the refined model yields better performance. Comprehensive analyses were developed regarding thermal and chemical kinetic properties. For MCH has lower adiabatic flame temperature than toluene and methanol addition into the two cyclic fuels decreases the adiabatic flame temperature, the thermal effect on laminar flame speed difference is negligible. Therefore, the effect of chemical kinetics was specifically discussed. MCH and toluene have different ring structures. The disintegration of aromatic ring plays as the limiting step in the high-temperature oxidation of toluene, resulting in low concentration of active radical pool and overall reactivity. However, the ring opening reaction of MCH occurs easily after the initial H-abstraction reaction, which favors the production of active intermediates and the enhancement of flame propagation. For the blending fuels, the analyses show that the laminar flame speed variation of the blends are primarily caused by the methanol substitution and the disturbance of reaction pathway through affecting the generation of important intermediates.

1. Introduction

Methanol is considered as potential alternative fuels since it shows competitive performance regarding the concerns of broad sources preparation, high octane number and eco-friendly [1–3]. However, there also exists problems of high specific fuel consumption and cold start when using methanol in engines due to its low energy density and high latent heat. Consequently, methanol is extensively utilized as an additive into gasoline or diesel in nowadays. Cyclic alkanes and aromatics take high proportion in traditional fuels [4,5], among which MCH and toluene are of specific interest since they are always selected to represent cyclic alkane and aromatic components in surrogate fuels [6,7]. Therefore, a comprehensive fundamental study on the combustion characteristics of MCH-methanol and toluene-methanol blends will promote the understanding of methanol blending fuels as well as their practical use.

Laminar flame speed is a representative parameter characterizing the chemical and physical properties in flame propagation. It is the basis of turbulent flame study and can be employed to evaluate the accuracy of chemical kinetic model [8,9]. Until now, a variety of work have been conducted to understand the laminar flame characteristics of methanol blending fuels. Gülder et al. [10] and Beeckmann et al. [11] both measured the laminar flame speed of methanol-isoctane blends at atmospheric pressure and elevated temperatures. However, their conclusions are inconsistent. Gülder et al. [10] found the methanol-isoctane blends yield lower laminar flame speeds than both pure methanol and isoctane, while Beeckmann et al. [11] indicated that methanol-isoctane blends exhibit lower laminar flame speeds than methanol but higher values than isoctane. Li et al. [12] developed a comprehensive laminar flame study on methanol-isoctane blends, and found the blends have higher laminar flame speeds than isoctane and lower values than methanol, which supports the result of Beeckmann et al. [11]. Besides, the data of Li et al. [12] were adopted to aid the model development of methanol-isoctane. Sileghem et al. [13]
determined the laminar flame speeds of methanol-isooctane and methanol-n-heptane blends using the heat flux method. Based on the experimental data, the mixing rules for the blends were validated. Mohamad et al. [14] measured the laminar flame speeds of the mixtures of methanol, isooctane and indolene at elevated temperature and pressure, and proposed empirical equations. It is found published work mostly concern the effect of methanol addition to chain alkanes, while limited data were reported for the blends of methanol and cyclic hydrocarbons.

MCH differs from toluene in the unsaturation degree of ring structure. The unsaturation degree of ring structure has been suggested to contribute soot formation and auto-ignition differently [15–17], and it is speculated to cause deviation on combustion behavior. Actually, Law et al. [18] conducted the effect of unsaturation degree by investigating the laminar flames of ethane, ethylene and acetylene. They found acetylene yields the fastest laminar flame speed, then ethylene, and the flame of ethane propagates the slowest. This laminar flame speed difference is found to result from both adiabatic temperature and the chemical structure. To our knowledge, limited comparable investigation has been published on laminar flames of cyclic hydrocarbons, however the effect of different unsaturation degree was rarely concerned. Very recently, Zhong et al. [19] compared three typical C7 fuels including n-heptane, MCH and toluene in terms of laminar flame speeds and found $S_{n\text{-heptane}} > S_{MCH} > S_{toluene}$ at all experimental conditions. The main reason was interpreted as the different H/C ratio and hence different chemistries of H radical production and consumption through comparing the H concentrations in three fuel flames. However, the inherent kinetic effect resulted from the unsaturation degree needs to be further discussed for detailed kinetic analyses were not provided.

Ji et al. [20] measured the laminar flame speeds of the blends of 80% n-dodecane + 20% MCH and 80% n-dodecane + 20% toluene with the counterflow configuration. This study found MCH has faster laminar flame speed than toluene but the reason was not illustrated. Most previous research focused on the comparison of MCH, toluene with their corresponding mono-alkylated derivatives respectively. Wu et al. [21] and Ji et al. [22] determined the laminar flame speeds of...
cyclohexane and mono-alkylated cyclohexane at different initial conditions, and found increasing the branching degree inhibits flame propagation. Davis et al. [23] and Wang et al. [24] compared the laminar flame speeds of benzene and toluene and found toluene propagates slower than benzene.

Present study aims to provide the experimental laminar flame speeds of MCH-methanol and toluene-methanol blends at different initial conditions and methanol volume blending ratios. These measurements allow us to identity the order of laminar flame speed of MCH and toluene, as well as the laminar flame speed variation with methanol addition into different cyclic hydrocarbons. On the basis of present data, a comprehensive kinetic model published previously was refined to achieve higher accuracy. Detailed analyses regarding thermodynamics and chemistry were performed to clarify the inherent reason leading to the laminar flame speed deviation between MCH and toluene as well as the effect of methanol addition.

2. Experimental method and numerical simulation

2.1. Experimental apparatus

In this study, laminar flame speeds were determined using a constant combustion bomb with the details described in previous literatures [25,26]. Here just a brief introduction is provided for clarity. The bomb is cylindrical with a heating-tap surrounded to heat the chamber and the inner mixture. The temperature was monitored using a K-type thermocouple with the accuracy of 2–3 K and the pressure was calibrated with the pressure transmitter and transducer. The combustible mixture was prepared based on partial pressure law. Before each experiment, the chamber was vacuumed and heated up to experimental initial temperature. When the liquid fuels were injected into the chamber, at least five mins was awaited to ensure the full evaporation. Then the air composing of 21% oxygen and 79% nitrogen was delivered into the chamber. Another five mins was awaited to achieve homogeneous mixture prior to ignition. The mixture was ignited by tungsten electrodes located in the center of the chamber and the high speed camera was utilized to record the flame propagation.

Nonlinear method developed by Frankel and Sivashinsky [27,28] was adopted to remove the stretch effect on the flame surface with the method expressed as, \( \frac{S_b}{S_b} \cdot \frac{2}{b_b b_b f} \cdot \frac{L_b}{b_b} \), where \( L_b \) is the Markstein length of the burned mixture, \( S_b \) is the stretched laminar flame speed. Finally, the laminar flame speed could be determined according to mass conservation, \( \frac{S_u}{S_u} = \frac{\rho_b}{\rho_u} \), where \( \rho_b \) and \( \rho_u \) are the density of the burned and unburned mixtures, respectively.

In the laminar flame speed measurement, uncertainty exists due to the effects of ignition, chamber confinement, flame instability, radiation, etc. Burke et al. [29] suggested that the confinement effect is negligible when the flame radius is smaller than 0.3 times of the chamber wall radius. Considering the ignition effect as well, the flame radii between 8 and 22 mm was employed to process data. Present experiments were performed at atmospheric pressure, and the effect of flame instability was not taken into account. The radiation-induced uncertainty was corrected with the correlation proposed by Yu et al. [30]. Comprehensive uncertainty analysis was estimated using the methods proposed by Moffat et al. [31], and the uncertainty was approximately ± 2–4 cm/s according to the flame conditions.

2.2. Computational methods

Laminar flame speeds were simulated using CHEMKIN PRO software [32]. The mixture-averaged model was used and the Soret effect was taken into consideration. GRAD and CURV values were set as 0.03 and 0.02, respectively, and the maximum grid points was set to be...
Three chemical kinetic models were selected to simulate the blending fuels for they include the chemical information of MCH, toluene and methanol. JetSurF2.0 [33], hereafter referred to as J-model, contains 348 species and 2163 reactions and includes the pyrolysis and high-temperature oxidation kinetics of jet-fuel surrogate. The main species in J-model are C_1–C_{12} alkanes, cycloalkanes (cyclohexane, methyl-, ethyl-, n-propyl-, and n-butyl-cyclohexane), and aromatics (benzene and toluene). N-model represents the comprehensive model developed by Narayanaswamy et al. [34] aiming at transportation fuel surrogates. It contains the low and high temperature chemistry of methylcyclohexane, n-dodecane and aromatic species. C-model indicates the diesel surrogate fuel model developed by Chang et al. [35]. This model is a skeletal model and consists of 70 species and 220 reactions.

3. Results and discussion

3.1. Validation of present experimental apparatus

To test the performance of present experimental apparatus, Fig. 1 lists present data and the literature data measured over a wide temperature range from 353 to 470 K. It is seen that all data follow the rule of temperature dependence that $S^o_u$ at higher temperature is faster, though slight differences are observed among the data at the same temperature measured by different groups. In Fig. 1a, $S^o_u$ of MCH measured by Rotavera et al. [36] at 403 K is lower than the results of Ji et al. [20] at 403 K, Kumar et al. [37] and Munzar et al. [38] at 400 K. The main reason is that Rotavera et al. [36] adopted the spherical propagation method, which is different from three other groups using the counterflow configuration. From this figure, it can also be realized that present data reach the peak around equivalence ratio of 1.1, which is consistent with the data of most groups [21,36–38] except the results of Ji et al. [20,22] which give the peak value around equivalence ratio of 1.05 both at 353 and 403 K. Fig. 1b gives present data of toluene-air mixtures along with the data published in previous researches. For the data of Wang et al. [24] were obtained with the constant-volume bomb which is the same as present study, the data derived by Wang et al. [24] at 423 K were adjusted to make direct comparison with present data at 433 K by removing the 10 K temperature difference through the empirical correlation of $S^o_u \propto T^1_{\lambda}$ [39]. The result indicates that the adjusted data is in good agreement with present data. And as expected, $S^o_u$ measured in present work at 393 K are slightly lower than those reported by Davis et al. [23], Hui et al. [40], Kumar et al. [37] at 400 K and by Dirrenberger et al. [41] at 398 K.

3.2. Model evaluation and refinement

Present data were adopted to evaluate the performance of the proposed models. Methanol is a small molecular fuel, and its model always plays as the base model of large hydrocarbons. Simulations of methanol were performed using the three models mentioned above. Fig. 2a plots the experimental and computed $S^o_u$ versus equivalence ratio at 393 K for methanol. It can be seen the simulations of N-model agree well with present data, falling within the uncertainty range of the experimental data. C-model yields satisfactory predictions at lean and rich sides, but

![Fig. 4. Ignition delay times for toluene. Symbols – experiments: Vasudevan et al. [48]; solid lines – results from the numerical simulations of NN-model; dash lines – simulations result from N-model.](image)

![Fig. 5. Comparison between present $S^o_u$ of MCH and toluene.](image)
slightly over predicts the experimental data around stoichiometric ratio. J-model yields reasonable predictions at lean mixtures, however significantly over predicts the experimental data at the equivalence ratio over 1.0. Considering the poor prediction ability of J-model, N-model and C-model were selected to do the further validation. Fig. 2b and c plot the comparison between the experimental and simulated laminar flame speeds of toluene and MCH, respectively. The simulations of N-model are indicated as solid lines and those of C-model are indicated as dash lines. For toluene in Fig. 2b, N-model reasonably predicts the experimental data at lean and rich mixture conditions but yields over-predictions around stoichiometric equivalence ratio. Similar result was also reported when the toluene sub-model was proposed by Narayanaswamy et al. [42] that the simulated laminar flame speeds of toluene are noticeably higher than the experimental data measured by Johnston and Farrel [43]. C-model over predicts the experimental data at all equivalence ratio range with the deviation especially greater at the lean and rich mixtures. For MCH in Fig. 2c, it is found that the simulations of C-model reasonably agree with the experimental data. The simulations of N-model fall within the experimental uncertainty range at the lean and rich mixtures but are beyond the uncertainty range around stoichiometric equivalence ratio. Therefore, both N-model and C-model have difficulty in accurately simulating the flames of MCH, toluene and methanol simultaneously. Considering N-model includes more detailed chemistry information than C-model, N-model is selected to be improved for further analysis.

It is obviously that the sub-model of toluene in N-model is the key

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**Fig. 6.** Reaction path analyses of (a) MCH, (b) toluene at \( \phi = 1.5, T_u = 393 \text{ K}, \) and \( P_u = 0.1 \text{ MPa}. \) The numbers indicate the branching ratios.
point to be refined. After examining N-model in details, problems are found as follows. Wang et al. [24] indicated that reactions related to fuel-specific species play important roles in laminar flame propagation except small molecule species. Methylphenyl radical (C\textsubscript{6}H\textsubscript{4}CH\textsubscript{3}) was initially generated from the initial H abstraction reactions and the rate constants of those reactions in N-model were obtained by analogy with those of benzene forming phenyl radicals. Considering the structure difference between toluene and benzene, it is more rational to reduce the A factor of analogy reactions of benzene by 1/6 to account for five abstraction sites [44,45]. Moreover, the rate constant of a dominant reaction, which is toluene (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}) converting to benzyl (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}), C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3} + O=C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2} + OH shows big uncertainty for its exact origin is unclear. Thus, the value was updated with the experimental data given by Hoffmann et al. [46]. In addition, according to the research of Yuan et al. [47] and Bounaceur et al. [45], the reactions producing stable benzoquinone (o-C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}) radicals from toluene are lost in N-model and should be included in the refined model. All modified reactions are shown in Table 1 and the refined kinetic model is named NN-model.

Fig. 3 depicts $S^0_u$ of MCH, toluene and methanol experimentally and simulated with NN-model and N-model at 0.1 MPa. It is seen that NN-model yields much better predictions than N-model for toluene, and satisfactorily predicts the experimental data of MCH and methanol as well. The accuracy of NN-model is further verified by simulating the experimental ignition delay times measured by Vasudevan et al. [48], as seen in Fig. 4. It is observed that NN-model yields better predictions on the experimental data at $\phi = 0.5$ than N-model, and comparable predictions at 1.0 and 1.5. Thus, NN-model was adopted to do further kinetic analysis.

### 3.3. Analyses on laminar flame speed variation

#### 3.3.1. Comparison between MCH and toluene

Fig. 5 gives the comparison between present experimental $S^0_u$ of MCH and toluene at 393 and 433 K. It is shown that the two fuels reach the peak value at equivalence ratio around 1.1 and MCH presents faster laminar flame speeds than toluene, especially near stoichiometric equivalence ratio. Zhong et al. indicated that the laminar flame speed deviation between MCH and toluene is dominated by kinetic effect for toluene has higher adiabatic flame temperature than MCH, but limited kinetic analyses were presented. Therefore, the reaction pathway analyses were carried out to illustrate the inherent reason, as seen in Fig. 6.

Reaction pathway analyses were carried out with NN-model for MCH and toluene, as seen in Fig. 6. At high temperature, MCH primarily undergoes H abstraction reactions to generate five isomerized methylcyclohexyl radicals differentiated by the carbon sites abstracted. Then the ring opening reaction occurs subsequently in most of these radicals, producing the straight and branched chain intermediates. These intermediates finally crack into various small radicals, including large amount of ethylene (C\textsubscript{2}H\textsubscript{4}) and vinyl radical (C\textsubscript{2}H\textsubscript{3}). These two radicals have been concluded to be active and enhance the overall...
reaction rate [18], thus their high concentrations are positive for the flame propagation of MCH. However, for toluene flame in Fig. 6b, it is seen that toluene is difficult to open the ring due to the stable chemical structure and the ring opening process is undoubtedly the limiting step in terms of toluene decomposing at high temperature. Specifically, toluene initially goes to benzene (C₆H₆), benzyl radical (C₆H₅CH₂) and methylphenyl (C₆H₄CH₃). And then almost 80% of benzene, over 10% of benzyl radical and other intermediate radicals, like benzaldehyde (C₆H₅CHO), will form phenyl radical(C₆H₅). The reaction rates of C₆H₅ related reactions are much slower when compared to those of intermediates in MCH flames, retarding the flame propagation of toluene. In addition, the chain termination reactions in toluene flame especially the reaction of C₆H₅CH₂ + H < = > C₆H₅CH₃, further decrease S⁰. Moreover, it is observed there are considerable amount of propargyl (C₃H₃) generated. This species participates in several chain terminating reactions such as C₃H₃ + H = pC₃H₄ and put an adverse impact on the flame propagation [20]. As a consequence, there are a variety of active species generated in MCH flame while relative stable species produced in toluene flame, causing significant difference of laminar flame speed between MCH and toluene.

3.3.2. Analyses on laminar flame speed variation of blending fuels

Fig. 7 gives the comparison between the measured laminar flame speeds and simulations for the MCH-methanol and toluene-methanol blends at different blending ratios. In general, the simulation results of NN-model reasonably agree with the experimental data and accurately capture the laminar flame speed variation. With the methanol addition, the laminar flame speed increases and the increment is remarkable at the equivalence ratio over 1.0 and methanol blending ratio over 40%. When the blending ratio of methanol is less than 40%, the laminar flame speed increases slightly. At the equivalence ratio smaller than 1.0, the laminar flame speed varies little and even slight decrease is observed at high methanol blending ratio for MCH-methanol blends. To investigate the reason leading to above change on laminar flame speed, the adiabatic temperature (Tₐ) of the blends were calculated. As shown in Fig. 8, for both MCH-methanol and toluene-methanol blends, Tₐ presents decreasing trend with the addition of methanol, which is different from the laminar flame speed variation, demonstrating the thermal effect is not the dominant cause.

As concluded in the previous study [12], methanol is a high-activity fuel. At high temperature, methanol primarily goes to HCO through H abstraction reactions step by step and finally release high concentration of H radical pool. With the addition of methanol, the H radical pool is

![Fig. 9. Reaction path analyses of (a) MCH-methanol, (b) methanol-toluene at ϕ = 1.5, Tₐ = 393 K, and Pₐ = 0.1 MPa at M20 (normal text), M50 (italic text) and M80 (bond text). The numbers indicate the branching ratios.](image)

enriched correspondingly. Moreover, as one important intermediate, methanol addition will exert an effect on the reaction process of MCH and toluene. Fig. 9a and b shows the reaction pathways of MCH-methanol and toluene-methanol blends respectively at $\phi = 1.5$ and different methanol volume blending ratios (M20, M50, M80). It is observed that the cracking procedures of MCH and toluene in the blends are almost the same with their pure fuel as illustrated in details above. With the increase of methanol blending ratio, the branching ratios of the initial reactions vary little. For MCH-methanol blends, the reactions producing C2 and C3 radicals are influenced with the branching ratios changed. Vinyl (C$_2$H$_3$) and ethylene (C$_2$H$_4$), as mentioned previously, exert positive effect on the propagation of flame. On the contrary, allyl (C$_3$H$_5$) and propene can participate chain terminating reactions of aC$_3$H$_5$ + H + M = C$_3$H$_6$ + M and C$_3$H$_6$ + H = aC$_3$H$_5$ + H$_2$, decreasing the concentration of H radical. As shown in Fig. 10, the concentrations of C$_2$H$_3$, C$_3$H$_5$, aC$_3$H$_5$ and C$_3$H$_6$ all decrease with the addition of methanol. The competition among those radicals related reactions finally characterizes as the concentration variation of reactive radicals like H and OH. As shown in Fig. 10c, the addition of methanol significantly increased the concentration of H and OH, demonstrating the increase of overall reactivity.

As shown in Fig. 9b, for toluene-methanol blends, the methanol addition exerts inhibiting effect on the production of 5-member ring, such as cyclopentadiene-C$_2$(C$_3$H$_4$ = O), which are regarded as the main resources of C$_3$H$_3$. As mentioned above, C$_3$H$_3$ plays negative effect on flame propagation through participating chain terminating reactions.

Fig. 11 shows the mole fractions of C$_3$H$_3$ produced in the flames of toluene-methanol blends. It is found less C$_3$H$_3$ are generated with more methanol blended, demonstrating that the addition of methanol inhibits propargyl production and prompt the overall reactivity in toluene-methanol blends. Therefore, the kinetic effect of methanol addition on the laminar flame propagation primarily results from both methanol substitution and the disturbance of chemical reaction process.

4. Conclusions

A comprehensive study was conducted experimentally and numerically on the laminar flames of MCH-methanol and toluene-methanol blends to investigate the effect of unsaturation degree and the addition of methanol on laminar flame speed. Laminar flame speeds were determined at atmospheric pressure and elevated temperatures, over a wide range of equivalence ratio. The experimental data were employed to validate and improve the accuracy of published models. And the refined model is demonstrated to yield satisfactory predictions on present data and ignition delay times published previously. With the refined model, detailed analyses were conducted to illustrate the inherent reason causing the laminar flame speed variation.
Present experimental data and simulation results all show that the laminar flame speeds of MCH are higher than toluene. With more methanol added into MCH and toluene, laminar flame speed increases especially at rich mixture side and methanol blending ratio over 40%. At the lean mixtures, laminar flame speed varies little and even slight decrease can be observed at high methanol blending ratio for MCH-methanol blends.

For toluene has higher adiabatic temperature than MCH and methanol addition into MCH and toluene will decrease the adiabatic temperature, the thermal effect is excluded as the main reason causing the laminar flame speed variation. Thus, the kinetic effect was specifically discussed. Reaction path analyses revealed that the aromatic ring in toluene is much more stable than the ring in MCH, resulting in more difficulty in opening the ring for aromatic rings. Besides, the production of phenyl radicals and other lower-activity radicals in toluene flame also exert an inhibiting effect on the flame propagation. Therefore, the chemical structure difference finally causes the laminar flame speed deviation between toluene and MCH.

The kinetic effect of methanol addition into MCH and toluene on flame propagation is primarily due to methanol substitution and the disturbance of chemical reaction process. Compared to MCH and toluene, methanol is much more active with high concentrations of H radical produced in methanol flame. With the addition of methanol, the H radical pool is enriched correspondingly. Besides, the methanol addition changes the branching ratios of reactions generating C2, C3 and the other active species, which ultimately influences the concentrations of H and OH and hence the flame propagation process.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2019.02.091.

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