Low temperature auto-ignition characteristics of methylcyclohexane/ethanol blend fuels: Ignition delay time measurement and kinetic analysis

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1. Introduction

Biofuels are of increasing interests as alternatives for petroleum-based transportation fuel substitution because they offer the long-term promise of carbon neutral and reduce climatic impact. Ethanol is one of the most common biofuels and has been widely used in gasoline and diesel engines [1,2]. Because ethanol contains 35% oxygen, adding ethanol to transportation fuel results in more complete combustion and investigations have showed that ethanol addition reduces the soot precursor emission [3–5]. Besides, ethanol is also used in homogeneous charge compression ignition (HCCI) and reactivity controlled compression ignition (RCCI) combustion engines because of its high octane number, which makes the regulation of the strong pressure gradient and optimization of the two-stage heat release possible [6–8]. The addition of ethanol to fuels affects certain key properties that affect their use in engines such as the blend stability, viscosity, and lubricity. In addition, the flammability of blended fuel and the unregulated emission products such as aldehydes limit the ethanol content of blend. As a consequence, the effect of ethanol addition on the fundamental combustion parameters and the oxidation kinetics of the fuel blend need to be thoroughly understood for its application in practical engines. An accurate chemical kinetic model can be used to predict important engine combustion parameters such as pressure rise rate, heat release rate and intermediate species profiles and these parameters are helpful, in terms of chamber design, fuel injection and flow field organization. It is also important for the development of clean-burning and energy-efficient combustion techniques. As a consequence, extensive investigations have been conducted to understand the effect of ethanol addition on the global combustion parameters and oxidation kinetics of gasoline, diesel or kerosene surrogates, such as n-heptane and iso-octane, which respectively represents the main straight chain and branched chain surrogates. Specifically, Lipzig and co-workers [9] measured the laminar flame speeds of n-heptane, iso-octane, ethanol and their binary and tertiary mixtures. They showed that the laminar flame speeds of the n-heptane/iso-octane mixture (50/50, Vol. %) equals to the average of the laminar flame speeds of n-
heptane and iso-octane at the same condition. However, blending 50% ethanol into either n-heptane or iso-octane does not lead to the average of the laminar flame speed of ethanol and n-heptane or ethanol and iso-octane. Similar trends were also presented by Broustail et al. [10,11] for different conditions. Sai sirirat et al. [12] conducted jet-stirred reactor (JSR) experiments for the ethanol/n-heptane (50/50, mole %) fuel mixture oxidation and found that addition of ethanol in the fuel reduces the fuel consumption rates. For the auto-ignition characteristic studies of ethanol/iso-octane blends, Bogin and co-workers [13] used the Ignition Quality Tester (IQT) to investigate the effect of ethanol addition on the ignition delay behavior of iso-octane at low temperatures with emphasis on the negative temperature (NTC) regime. They showed that if the ethanol is more than 50%, NTC behavior vanishes. Recently, Barraza-Botet and Wooldridge [14] used their rapid compression facility (RCF) and gas chromatography (GC) to measure the ignition delay time (IDT) of the blends and to identify the intermediate species formed during the ignition delay periods, and their results indicate that the ethanol and iso-octane are consumed in a parallel reaction pathway and have no significant fuel-to-fuel chemistry interactions. Li et al. [15] investigated the auto-ignition temperature and IDT of n-heptane/ethanol in a constant volume combustion bomb.

Besides straight and branched chain alkanes, cyclic alkanes are another component in jet fuels, gasoline, and diesel with a mass fraction of around 20%, 10% and 40%, respectively [16–18]. Methylcyclohexane (MCH) is selected as the cyclic alkane representative in transportation fuel surrogates [19,20]. There have been several kinetic modeling efforts on MCH oxidation chemistry. Orme et al. [21] proposed a detailed high temperature mechanism for the oxidation of MCH and validated this kinetic scheme against IDTs obtained in their shock tube experiments. Pitz et al. [22] developed a low temperature kinetic model based on that of Orme et al. [21] by adding the low temperature reaction pathways of MCH oxidation. Subsequently, this model was updated respectively by Narayanaswamy et al. [23] and Weber et al. [24] to get better agreements with more experimental data [25]. Recently, Bissoonauth et al. [26] built a model of MCH based on the n-heptane oxidation mechanism [29] with incorporated the high temperature chemistry of MCH developed by Wang et al. [21] and the low temperature chemistry developed by Weber et al. [25] and referred to the low temperature classes for alkanes proposed by Sarathy et al. [30]. Because the model prediction for MCH oxidation in jet stirred reactor (JSR) and IDT in rapid compression machine shows a higher reactivity than the experimental measurements, they proposed that additional data of MCH especially at low temperatures are necessary for further model improvement.

As MCH is an important component in the transportation fuel surrogate formulation, and the effect of ethanol addition into MCH on ignition characteristics has not been reported yet. The

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<th>Table 1 Compositions of the tested mixtures.</th>
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Fig. 1. Schematic of the XJTU-RCM.

Fig. 2. Experimental repeatability verification and definition of measured IDT.
motivations of this work are as follows. Firstly, we will report new ignition data for blends of ethanol and MCH obtained from a rapid compression machine. These experimental data provides intuitive insights into the effect of temperature, pressure, equivalence ratio and ethanol blending ratio on IDT. Besides, these data will be used to validate the newest mechanism developed by Bissoonauth et al. [26]. In addition, the intermediate species and the consumption path during ignition process will be scrutinized with the mechanism. Through this method, key species and reactions will be identified to clarify the negative temperature coefficient (NTC) behavior and the effect of NTC regime shift due to ethanol chemistry. Finally, because the effect of ethanol blending on the low temperature ignition behaviors of the C7 hydrocarbons with different fuel structures will be compared to see if there is any generalized effect of ethanol chemistry. This study will be helpful for understanding the auto-ignition kinetics of binary fuels that contain ethanol and their possible application in engines.

2. Experimental apparatus and procedures

2.1. Rapid compression machine

IDTs can be determined by several types of devices, among which rapid compression machine (RCM) are widely adopted for low-to-intermediate temperatures measurements. In this study, a pneumatically driven and hydraulically stopped rapid compression machine was used. The schematic of this RCM is shown in Fig. 1. A high pressure gas tank is charged with compressed air to provide 0.1–0.5 MPa driving gas. The hydraulic chamber is filled with high pressure oil to hold the pistons at their resting positions before the compression. To restrain the in-cylinder roll-up vortices and ensure the homogeneous temperature distribution in the combustion chamber, a creviced piston like other RCMs [27,28] is adopted. The compression chamber of this RCM has a bore of 50.8 mm and a stroke length of 332 mm. By adjusting the length of the reaction chamber from 10 to 100 mm with different filling plates, the compression ratio can vary from 4 to 15, so that the compressed temperature at the end of compression (EOC) is changeable. When the computer releases the signal of opening the oil discharge valve, the high pressure air drives the piston to compress the gas phase mixture. The chamber pressure is measured by the pressure transducer (Kistler 6125C) and the charge amplifier (5018A), and it is recorded by a National Instrument USB-6361 data collecting card which runs at a frequency of 100 kHz. Further details and the validation of this RCM are available in Ref. [29].

2.2. Definition and reproducibility of measured ignition delay times

Pressure and temperature at the EOC ($P_c$ and $T_c$) are used to define the thermodynamic conditions for IDT determination. Some typical pressure-time ($p$-$t$) traces of MCH are shown in Fig. 2. $T_c$ is calculated according to the adiabatic compression relation, $\ln\left(\frac{P_c}{P_i}\right) = \frac{R}{\gamma - 1} \left(\frac{T_c}{T_i}\right)$, in which $T_i$ and $P_i$ are the initial pressure and temperature before the compression starts, and $\gamma$ is a temperature dependent mixture specific heat ratio. $P_i$ and the length of the combustion chamber are altered to make the comparison of different mixtures.

Fig. 3. Comparisons of the measured and simulated pressure traces for MCH/O2/N2/Ar mixtures at 20 bar. (a) $\phi = 0.5$, $T_c = 722$ K; (b) $\phi = 1.0$, $T_c = 840$ K.

Fig. 4. Comparison between measured and simulated IDTs for neat MCH at $P_c = 20$ bar: (a) Total IDTs; (b) First-stage IDTs.
is possible under the same pressure condition. And the uncertainty in $T_r$ is estimated to be less than 10 K by using the independent parameters methodology [30,31]. All experiments have been repeated with enough times and good repeatability was achieved.

Fig. 1 shows the typical pressure evolution histories with three repeating compressions at identical test conditions. The IDT at this condition is determined as the time interval between the EOC and the time of peak pressure rise rate. It is noted that the pressure slightly falls down after EOC and this indicates that there are certain extent of heat loss from the core gases to the wall of the reaction chamber after the piston is locked at EOC. To account for these heat losses in zero-dimensional simulations of the ignition process, non-reactive pressure traces are also collected by replacing the oxygen content with nitrogen, as shown by the dash line in Fig. 2. The initial conditions of reactive and non-reactive tests are identical, so the non-reactive pressure trace follows the reactive pressure trace. After the EOC, the non-reactive trace drops faster than the reactive trace as no reactions happened to release heat.

2.3. Preparation of mixture and experimental conditions

The mixtures were prepared in a stainless-steel cylinder with a volume of 20 L, which contains sufficient test mixture to minimize the uncertainty in mixture preparation. Since MCH and ethanol are liquid fuels at room temperature, they were injected via an injection port on top of the cylinder using a gas-tight syringe. Purities of nitrogen, argon and oxygen used in this study are higher than 99.999%. MCH and ethanol were purchased from Energy Chemical (Shanghai, China) with purities of more than 99% and 99.5% by volume, respectively. No further purification was carried out in this study. Different fuel mixtures are prepared according to the partial pressure of ethanol and MCH and E25 represents that the fuel contains 25% ethanol and 75% MCH in mole fraction. The equivalence ratio is calculated with considering the oxygen contained in ethanol. The experimental region of $P_c$ and $T_c$ are listed in Table 1. For each mixture, nitrogen and argon are used as the buffer gas with a 85% mole fraction and the specific components and proportions can be found in Supplementary materials.

3. Results and discussion

3.1. Mechanisms validation against new RCM data of pure MCH

Numerical simulation of ignition process is conducted using Chemkin-Pro 15131 software and the volume history tabulation is adopted, where the volume history of non-reactive mixtures is transformed from the pressure trace at corresponding condition to account for facility effect during the compression. And the kinetic model of Bissoonauth et al. [26] is used for the simulation, thus the simulated pressure history from compression to ignition is obtained. Typical simulation cases of single-stage and two-stage ignition are shown in Fig. 3 for further illustration. The non-reactive pressure traces overlap with the reactive pressure traces before the EOC at the same condition, indicating that the heat release caused by reactions before EOC is negligible. Similarly, the
moments of the maximum pressure rise in simulated pressure traces are defined as the ignition onsets. Thus, the simulated IDTs are the interval time between the EOC and the ignition onsets. In Fig. 3a, the measured and simulated pressure traces both show a two-stage pressure rise behavior, indicating the typical two stage ignition for this mixture. The measured first stage IDT and total IDT were respectively 15.4 and 19.6 ms, while the simulated first stage IDT and total IDT were 10.5 and 26.0 ms. For higher temperature case as shown in Fig. 3b, the two-stage ignition phenomenon disappears and the prediction of total IDT is longer than the measured value.

The IDTs of MCH/O2/N2/Ar mixtures at $\phi = 0.5$ and 1.0, $P_c = 20$ bar were measured over the $T_c$ range between 690 and 950 K. The total IDTs are plotted against $1000/T_c$ as shown in Fig. 4a. The total IDT shows a clear NTC behavior, and the mixture reactivity increases with the equivalence ratio increases. This tendency is consistent with the observation by Weber et al. [24]. We note that in this study, the inert concentration is fixed and the fuel concentration is fixed in the experiments conducted by Weber et al. [24]. The NTC regime, within which the total IDT increases with increasing $T_c$, is bounded by two turnover temperatures, i.e., $T_{upper}$ and $T_{lower}$ as defined in Refs [32,33]. In this NTC regime, increasing temperature actually reduces the overall reactivity. For this pure MCH fuel, the first-stage IDTs are also presented, as shown in Fig. 4b. With the increase of $\phi$, the first-stage IDT decreases, though this effect becomes progressively weakened as the temperature is reduced.

The numerical prediction with the model of Bissoonauth et al. [26] shows a shorter first-stage IDT and longer total IDT, compared with the experimental data. The max deviation happens at the temperature regime where the first-stage IDTs are relatively short. Generally, the model well captures the two-stage ignition behavior with reasonable agreement between its prediction of the total IDT, though the model slightly under-estimate the first stage IDT.

### 3.2. The effect of ethanol blending ratio

To investigate the effects of blending ethanol to MCH, the pressure traces of different MCH/ethanol mixtures at $P_c = 20$ bar and $T_c$ from 680 to 930 K are measured. The comparison between the model prediction and experimental data for $\phi = 0.5$ and 1.0 are shown respectively in Fig. 5 and Fig. 6. Symbols represent the experimental data while lines represent the simulation, error bars are omitted for concision, and different ethanol blend conditions are performed in different colors. It is noted that blending ethanol into MCH prolongs the total IDTs of the mixture significantly at both fuel lean and stoichiometric conditions. This is reasonable because the ignitability of the binary blending mainly depends on the reactive fuel with low octane number [15]. The more reactive species ignites first and releases heat which results in the increasing of temperature and pressure, and then accelerates the ignition of the less reactive species. As such, for high ethanol blending ratio mixture like E75, it cannot ignite at lower temperatures thus neither experimental nor simulation data are shown for these fuel blends. Literature indicate that there is no NTC behavior for pure ethanol [34,35] while pure MCH has NTC behavior [24,25], which is consistent with the present observation. In addition, we
observed that the NTC regime shifts to lower temperatures and narrows down along with the increase of ethanol content in Figs. 5a and 6a. When the ethanol content reaches a certain extent, the NTC regime disappears, as shown by the data of E75 in Fig. 5a and E100 in Fig. 6a. For the model simulation, the simulated total IDTs are slightly longer than the measured data around $T_{\text{lower}}$ and slightly shorter than the measured data around $T_{\text{upper}}$. We also note that the first-stage ignition phenomenon disappears when the temperature reaches to a certain extent as in Figs. 5b and 6b, and that temperature limit becomes lower as ethanol fraction increases. For the first-stage ignition simulation, the model underestimated the first-stage IDT values and failed to precisely predict whether the first-stage ignition will happen. For example, the experiments show two-stage ignition phenomenon whereas the simulations shows only one stage ignition for the mixture E75. As such further improvements for this mechanism will be needed in the future.

3.3. The effect of pressure

Fig. 7 shows the comparison of IDTs for the stoichiometric mixture of E50 at $P_i = 10$, 20, and 30 bar. Higher $P_i$ accelerates the ignition significantly: the total IDT at $P_i = 20$ bar is almost an order of magnitude higher than that at 30 bar. This is straightforward because higher temperature and pressure accelerate the speed of molecules and number density of the molecules thus enhancing the collision frequency which results in higher rate of chemical reaction. It is noted that the mixture can ignite at lower temperatures but fails to ignite when the temperature is higher than 790 K at $P_i = 10$ bar. It could be explained from the tendency that the total IDT increases with $T_i$ as far as the temperature is in the NTC regime. As a result, no ignition is observed in experiments for temperature higher than 790 K. In addition, the temperature limit where the first-stage ignition disappears is shifted to high temperatures as $P_i$ increases, as shown in Fig. 7b. For the mixture E50, good agreements between measured and simulated data for the total IDTs, while simulations for the first-stage IDTs are still slightly shorter than the experimental data.

4. Chemical kinetic analysis of binary fuel ignition

4.1. Species profiles of binary mixture

To understand the effect of ethanol addition on the ignition kinetics of MCH, the model of Bissoonauth et al. [26] is used to compute the species and temperature evolution during the ignition process of the binary fuel mixtures. The species profiles for stoichiometric mixture E50 at initial pressure ($P_i$) of 20 bar, and initial temperature ($T_i$) of 725 and 875 K are computed with Chemkin-Pro 15131. The species selected for kinetic analysis include the fuels, OH radical and H$_2$O$_2$ radicals as they are generally the ignition indicators [15,36]. Fig. 8a and b shows the typical two-stage ignition and single-stage ignition phenomenon, respectively. The initial mole fraction of MCH and ethanol are the same in mixture E50, but the mole fraction of MCH drops apparently faster than ethanol which indicates that MCH plays a leading role in competition of small radicals such as O, H and OH radicals which consumes the fuel through H-abstraction reactions. The first-stage ignition in Fig. 8a happens when the consumption rate of MCH and ethanol reach the first peak, the H$_2$O$_2$ molecule also reaches the first maximum formation rate at this time. It is found that the first-stage ignition occurs at a relative lower system temperature compared to the second-stage ignition, and the second-stage ignition starts at the moment when the OH radical concentration begins to soar. During the first-stage ignition, the OH radical concentration changes little but the model fraction of H$_2$O$_2$ molecule increase rapidly, and the H$_2$O$_2$ starts to dissociate rapidly only until the system temperature approaches approximately 1000 K [37]. The produced OH radicals will consume the remaining fuels by H-abstraction reactions which further elevate the system temperature significantly through releasing the heat. That is to say, the temperature limit of H$_2$O$_2$ decomposition can be regarded as a threshold for the ignition process, so the total IDT is actually the time spent for the system to reach that temperature threshold. To validate this assumption, the temperature histories of different mixtures at identical conditions were conducted as shown in Fig. 9. Neat MCH (E0) ignites first since its first-stage ignition occurs first and provides the largest temperature increase, and the heat release during the first-stage ignition decreases as more ethanol is blended in. The lower temperature rise in the first-stage ignition directly causes the longer second-stage IDT. All the mixtures ignite when the system temperature reaches about 1000 K under which condition H$_2$O$_2$ begins to decompose rapidly, and this indicates that the final ignition is independent of other factors but only related to the system temperature.

4.2. Reaction fluxes of neat MCH and binary fuels

With the basic understanding of ignition process, we then try to elucidate the NTC regime shift phenomenon by analyzing the reaction flux during ignition. This analysis is conducted using a constant-volume and adiabatic type simulation for mixture E0 and E50 at $P_i = 20$ bar, and three different $T_i$ (725, 800, and 875 K). Since the NTC behavior occurs for MCH species, we mainly focus on the consumption path of MCH. The path analysis presented in Fig. 10 is an integrated analysis where the rate of production of each species by each reaction has been integrated with respect to time up to 20% consumption, so the percentages represent the percent of the given reactant that is consumed to form the given product by all reactions that can form that particular product. Note that not all the possible reaction pathways are shown in Fig. 10 for simplicity.

For the primary step of fuel consumption, Narayanaswamy et al. [23] presented the reaction fluxes at $T_i = 1160$ K and found that MCH mainly undergoes unimolecular decomposition reactions. However, this is not observed in the present analysis. This indicates that the favored consumption channel in low temperatures (<1000 K) is changed from unimolecular decomposition reactions to H-abstraction reactions. There are five different sites for H-atom abstraction due to the symmetry of MCH, thus five methylcyclohexyl radicals are formed through bimolecular reactions with OH and H$_2$O$_2$.

![Fig. 9. Computed temperature histories for different mixtures at $T_i = 725$ K and $P_i = 20$ bar.](image-url)
Because nearly all the fuel radicals are oxidized to the alkylperoxy radical (ROO), and there are three main reaction classes that participate in the subsequent reactions of ROO radicals. The first class is the intramolecular isomerization to form hydroperoxyalkyl radical (QOOH). The second class is the elimination reaction to form hydroperoxyl (HO2) and methylcyclohexene molecule, and the third class is the H-abstraction by ROO to form ROOH. Take MCH2OO as a specific example. For the reactions among MCH2OO radicals to produce MCH2OJ, they consume 3.9% of MCH2OO at 700 K and less than 0.1% for the other temperatures, so this pathway is not shown in Fig. 9. The majority of MCH2OJ radical is produced through the third class reactions. Specifically, H-abstraction reactions from HO2 by MCH2OO produce MCH2OOH and an oxygen molecule, the former of which then decomposes to MCH2OJ and OH radical. The MCH2OJ subsequently undergoes ring open reactions and β-scission to produce small olefins and aldehydes with no more than 5 carbon atoms. This channel increases the mixture reactivity because OH radical is produced. However, its contribution for MCH2OO consumption quickly decreases from 21.8% to less than 5% as the Ti increases from 700 K to 800 K. This reveals that the formation of ROOH becomes substantially less important and the competition of MCH2OO consumption mainly happens between the first and second class reactions at low temperatures (<1000 K). The first class reactions produce QOOH which then faces second oxygen addition or decomposition. The former pathway produces hydroperoxyalkylperoxy (OOQOOH) radical.
which is then consumed by concerted elimination to olefinic hydroperoxides (C7H12O2) and HO2 radical or decomposition to ketohydroperoxides (C7H12O3) and OH radical. This is a typical chain branching reaction which is more favored at lower temperatures and leads to the two-stage ignition phenomenon. The competing channel, decomposition of QOOH to form a heptenone and OH radical, becomes more and more important as \( T_i \) increases. On the other hand, the second class reaction also contributes increased consumption for ROO as \( T_i \) increases, and the increase in production of methylcyclohexene and HO2 plays a crucial role in the NTC regime. The reason is that HO2 attacks H-atom from the fuel to form H2O2 which is relatively stable in the low temperature regime (<1000 K) and this channel prolongs the overall ignition as described above.

The OOQOOH formation channel plays the dominating role in ROO consumption at low temperatures (<725 K), and the large heat release results in first-stage ignition phenomenon behavior. With the increase of \( T_i \), the ROO consumption in first and third class reaction reduces and the second class reaction consumes more ROO to compensate, and the HO2 elimination of ROOH takes the leading role compared to the OOQOOH formation channel at a certain temperature which is named the "ceiling temperature" by Benson et al. [38]. When \( T_i \) is higher than this ceiling temperature, the alkyl fuel radical mainly undergoes \( \beta \)-decomposition to produce olefin and HO2 which restrains the reactivity and causes the disappearance of two-stage ignition behavior and NTC regime of total IDT. Though more H2O2 are produced as \( T_i \) increases, the gap between the system initial temperature and H2O2 decomposition temperature becomes narrowed. Finally, when \( T_i \) exceeds a certain value, H2O2 decomposes immediately as they are produced. As a consequence, the overall IDT decreases again as the \( T_i \) rises.

The original reason of NTC behavior is all related to the formation of ROO and QOOH, and these species are not formed in the ethanol oxidation [34]. This is the primary reason that ethanol does not exhibit NTC behavior. It is also found in Fig. 10 that ethanol blending changes the consumption of MCH slightly. However, in this study, the mole fraction of dilution is fixed at 85%, so the ethanol blending results the decrease of MCH mole fraction. Fig. 11 shows the effect of ethanol addition on the radical mole fractions at \( T_i = 725 \text{ K}, P_i = 20 \text{ bar}, \) and \( \phi = 1.0 \). (a) ROO radicals; (b) QOOH radicals.

Fig. 12. Total IDT as a function of the temperature for stoichiometric fuel/ethanol/O2/Ar mixtures under various ethanol blending ratios. (a) MCH; (b) n-heptane; (c) 1-heptene.
shows the computed mole fraction time-histories of ROO and QOOH for different blending ratio at the same initial condition. The ROO radicals include MCH1OO, MCH2OO, MCH3OO, MCH4OO, and CHXH2OO, while the QOOH radicals include 11 species such as MCH1QJ2, MCH1QJ3, MCH1QJ4, MCHXQJ3, etc. It is noted that the mole fraction time-histories of both ROO and QOOH decreases rapidly as the ethanol is present in the system, and the reduction of their peak value indicates fewer oxygen addition reactions happen during low temperatures. This reveals that the NTC behavior becomes less apparent as ethanol is added, which is consistent with the experimental observation as in Figs. 5 and 6. For the effect of pressure, the overall ignition threshold reaction: 
\[ \text{H}_2\text{O}_2 (\text{M}) \rightarrow 2\text{OH} (\text{M}) \] is a typical pressure-dependent reaction whose rate increases with increasing pressure, this results the NTC regime shifts to higher temperature as the pressure increases [32].

4.3. Effect of ethanol blending ratio on the turnover temperatures

Ji et al. [32,33] quantified the temperature range and slope of the NTC regime, and found that the total IDTs shows Arrhenius like temperature dependence for different alkanes with the turnover temperatures under various pressures for different alkanes. We now investigate whether this relationship still holds under different ethanol blending ratios. MCH, n-heptane, and 1-heptene are selected because all of them perform NTC behavior in previous experiments [24,30,39] and are included in the mechanism of Bissoonauth et al. [26]. The computed total IDTs as a function of temperature for a stoichiometric mixture of fuel/ethanol/O$_2$/Ar with different ethanol blending ratios were shown in Fig. 12. The concentration of fuel is fixed at 1.0% and $P_i$ is fixed at 20 bar in all the mixtures. It is seen that for each ethanol blending ratio less than 80%, the total IDTs decrease with increasing the initial temperature except the NTC regime. Both the $T_{lower}$ and $T_{upper}$ shift to lower values as ethanol blending ratio is increased, and the NTC regime shrinks accordingly. It is noted that the total IDTs does not show NTC behavior when the ethanol blending ratio reaches 80%. And the IDTs at turnover temperatures, marked by the triangle symbols in Fig. 12, show Arrhenius like temperature dependence when ethanol blending ratios is no more than 60%.

We next note that the total IDTs exhibit special dependence on the ethanol blending ratio at the turnover temperatures. Fig. 13 suggests a parabolic curve fitting, namely, 
\[ \text{IDT} = a R_e^2 + b R_e + c, \] where $R_e$ is the ethanol blending ratio. To further investigate the effect of ethanol blending ratio on total IDTs at turnover temperatures, we normalized the total IDTs according to the total IDT without ethanol blending as shown in Fig. 14. It is noted that the variation of normalized total IDTs at turnover temperatures is very similar for MCH and n-heptane, especially at upper turnover temperature. And the total IDTs of 1-heptene increase slower than the other two fuels at turnover temperatures with ethanol blending.

We finally investigate the relationship between turnover temperatures...
temperature and ethanol blending ratio as shown in Fig. 15. It is noted that as the ethanol blending ratio increases to 60%, the \( T_{\text{upper}} \) and \( T_{\text{lower}} \) of three fuels all decrease about 70 K and 30 K, respectively. Previous works \[14,15\] indicate that there are no fuel-to-fuel interactions (ethanol to n-heptane or iso-octane), and the reduced reactivity and the shrink and shift of NTC regime by ethanol addition is attributed to the decreased n-heptane and iso-octane concentration, which leads to reduced production of ROO and QOOH as ethanol fraction increases. The similar ethanol addition effect on IDT and NTC regime behavior of MCH and n-heptene with that reported in Refs. \[14,15\] indicate that for a general binary ethanol/hydrocarbon fuel system, it is unlikely to have fuel to fuel interaction, and the presence of ethanol just simply reduces the concentration of the hydrocarbon.

5. Conclusions

In this study, experimental measurements of low temperature IDT of MCH and ethanol binary fuels have been conducted over wide range of test conditions. Measurements show that pure MCH exhibits typical two-stage ignition and the negative temperature behavior (NTC). With the increase of ethanol blending ratio, the overall reactivity of the fuel blends decreases. In addition, the NTC regime which is bounded by two turnover temperatures \( (T_{\text{upper}} \) and \( T_{\text{lower}}) \) is shifted to lower temperatures and the difference between the two turnover temperatures decreases. These new IDT data were then used to validate the most updated mechanism of MCH \[26\].

Good agreements were observed with the measured and simulated total IDTs, while the model still show an underestimated the first-stage IDT.

To understand the kinetic effect of ethanol addition on the IDTs and the NTC behavior, species evolution process and reaction flux analysis were conducted. The results showed that the final ignition occurs only when the system temperature reaches the decomposition temperature of \( \text{H}_2\text{O}_2 \), and the nature of NTC behavior is the competition between chain branching and chain determination reactions under different temperatures. The main chain branching reactions and chain determination reactions are the oxygen addition reactions and the \( \text{HO}_2 \) elimination reactions, respectively. Although no significant change on MCH consumption path was observed as ethanol is blended in, the mole fraction of ROO and QOOH decrease rapidly due to the reduction of MCH initial concentration. Therefore, the MCH/ethanol blend acts as a super-position of the reaction chemistry of the two individuals, and consequently the NTC behavior becomes less apparent as ethanol is blended in.

Further comparison among the ignition kinetics of the different binary fuels including, MCH, n-heptane, and 1-heptene have been conducted to access the different structure effect. The NTC regime shrink and shift phenomenon with increasing ethanol blending ratio are observed for all the three binary fuels investigated. In addition, both total IDTs and turnover temperatures show similar variation tendency as the ethanol blending ratio increases. This similarity indicates that for a general binary ethanol/hydrocarbon system, fuel-to-fuel interactions are absent and the presence of ethanol just simply reduces the hydrocarbon concentration. However, further experimental examination of the intermediate species during the oxidation of binary ethanol/hydrocarbon fuels is of merit for kinetic mechanism validation.

Acknowledgments

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Appendix A. Supplementary data

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References


