Ignition Delay Measurements of Iso-octane/Ethanol Blend Fuel in a Rapid Compression Machine

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Abstract

Ignition delays of gasoline surrogate fuel containing iso-octane and ethanol were measured by a rapid compression machine over a temperature range of 750–900 K to compare the chemical reactivity of fuels with different ethanol contents and dilution levels. By experimenting the higher dilution level, it was found that the chemical and the thermal effects of the low temperature chemistry could be effectively separated. Results show that even a small amount of ethanol added to iso-octane can be very effective in suppressing the reactivity, especially under the negative temperature coefficient (NTC) temperature region. A computational study with detailed chemical kinetics mechanism was also performed to understand the experimental results, where it reasonably reproduced the experimental observations. By comparing species-time histories for both non-dilution and dilution cases near NTC region, it was shown that the chemical effect of low temperature chemistry could be effectively de-coupled from the thermal effect.

Introduction

Recently, many researchers focus on developing more efficient and less polluting internal combustion engines by introducing bio-fuels, such as biodiesel or bioethanol from agricultural feedstock or algae. New standards mandating the use of automotive bio-fuels are being implemented throughout the world, e.g. Low Carbon Fuel Standard of State of California [1], Renewable Fuel Standard of the U.S. [2], and Renewables Directive of the European Union [3]. As a result, number of countries around the world adopt various types of blend fuels. For example, several states in the U.S. mandate the use of E10 blend (which stands for the mixture of 10% ethanol and 90% gasoline in volume fraction). Some countries had already introduced bio-fuels to the market before these legislations were activated e.g. Brazil, the largest ethanol-consuming country in Latin America, has supplied wide range of blends to the market from the lower limit of E18–E25 to the higher extent of E85 or even E100, i.e. neat ethanol.

Along with these renewable fuels, government regulations on the fuel economy have been continuously reinforced; for example, the U.S. Department of Transportation mandates the average fuel consumption of fleet to reach 54.6 miles per gallon (or about 23 km/l) by year 2025. [4]. In case of spark-ignition (SI) engines, these regulations promote 'downsizing' of the engine displacement volume with intake boosting device such as a turbocharger, which eventually requires a severe engine operating condition caused by elevated mean effective pressure (MEP) in the range of 1250–1700 kPa, as compared to the typical values of naturally aspirated SI engine between 850–1050 kPa [5]. This may stimulate undesirable and abnormal combustion phenomenon inside the cylinder, i.e. knock, which is generally induced by the autoignition of fuel-air mixture before the flame arrives, causing instantaneous pressure unbalance followed by pressure wave formation. This knock phenomenon is responsible for noise, vibration, and potential damage to the engine components, and hence strong demand for an appropriate fuel, which endures severe operating conditions and suppresses knock propensity in the downsized, boosted engine, arises recently.

Ethanol is one of the well-known knock inhibitors with higher octane number (ON) as well as a renewable fuel source from carbon life-cycle chain, making it a promising component for future gasoline. Generally higher ON assures better anti-knock behavior which suggests that autoignition chemistry of certain fuel is a key factor in rating ON. Several studies [6–8] reported the anti-knock benefits of gasoline-ethanol blend fuel, where both research octane number (RON) and motor octane number (MON) were measured respectively by the prescribed test methods [9,10]. Since gasoline itself is a mixture of hydrocarbon components, pure chemical substances such as iso-octane (2,2,4–trimethylpentane) and n-heptane are designated as surrogate components for ON rating. Studies regarding iso-octane and n-heptane as major surrogate components in gasoline-ethanol blend fuel were also performed by a group of researchers, e.g. Haas et al. [11] measured major intermediate species with the help of flow reactor and suggested that major reaction pathway of n-heptane could be affected by the presence of ethanol in blend. Cancino et al. [12] investigated autoignition chemistry of iso-octane/ethanol blend by shock tube experiments and detailed kinetics modeling. Yahyaoui et al. [13] also performed shock tube experiments for high temperature region over 1200 K. Foong et al. [14] measured RONs of various ethanol blends by engine test and explained that the charge cooling effect of the ethanol fuel should be considered when rating ON of high-ethanol content fuels.

Most of these previous studies were focused on autoignition characteristics of blend fuels in relatively high temperature region, which are not closely relevant to the knocking conditions in an SI engine. In this study, we focus on relatively lower temperature region, i.e. low

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temperature chemistry and the thermal and chemical effects of it on the autoignition propensity of a tested fuel. In the experiments, by using a rapid compression machine (RCM), autoignition characteristics of iso-octane/ethanol blend over a temperature range of 750–900 K and pressure of 27 bar are investigated by measuring ignition delays of fuel-air mixture. Temperature and pressure conditions are selected to represent the possible unburned zone conditions of a downsized SI engine where the low temperature chemistry is generally observed. Pressure histories of mixtures are compared with respect to blending ratio, and the role of ethanol in the autoignition characteristics of blend fuel is discussed. Reactants are prepared in both non-diluted and diluted conditions, so that the chemical and thermal effects of low temperature chemistry can be handled separately. Chemical kinetics simulations with detailed mechanism were also performed to interpret the experimental results.

Experimental Setup

The experiments were performed with hydraulically-driven RCM, which takes about 30 ms to complete the compression process. The compression ratio can be adjusted from 5 to 20 and the test chamber can be preheated up to 140 °C, both of which enable various post–compression temperature and pressure conditions. Reactant mixture is prepared in a separate 12.3 L, preheated mixing chamber in which liquid substances are injected first by a syringe after vacuum condition is reached, thereby leading to instantaneous vaporization. Here, the amount of liquid-phase chemical substances such as iso-octane (99.8%, Sigma-Aldrich) or ethanol (≥99.5%, Sigma-Aldrich) are not to exceed the vapor pressure for a given mixing temperature of 60 °C. The rest of gaseous components are mixed by using their partial pressures to achieve the desired composition. The pressure profile of the mixture in the test chamber is logged by Kistler 6052C31 piezoelectric pressure transducer along with Kistler 5073A charge amplifier.

Reactant mole fractions for various blends are given in Table 1. Here the amount of oxygen is decided to maintain the equivalence ratio of unity for all cases since SI engine is generally operated under stoichiometric condition. However, the non-diluted and the diluted conditions contain different amount of nitrogen, i.e. the former has 3.76 times moles of nitrogen than those of oxygen, leading to the engineering air composition, while

Table 1 Mole fractions of reactants for non-diluted and diluted conditions

| Non–diluted	$x_{O_2}:x_{N_2} = 1:3.76$			
	$x_{iC_8H_{18}}$	$x_{C_2H_5OH}$	x_{O_2}	x_{N_2}
E0	0.0165	-	0.2066	0.7769
E10	0.0153	0.0048	0.2059	0.7740
E20	0.0140	0.0099	0.2051	0.7710
Diluted	$x_{O_2}:x_{N_2} = 1:5.64$			
	$x_{iC_8H_{18}}$	$x_{C_2H_5OH}$	x_{O_2}	x_{N_2}
E0	0.0119	-	0.1488	0.8393
E10	0.0110	0.0035	0.1484	0.8371

the latter has 5.64 times moles of nitrogen, resulting in 1.5 times of nitrogen to oxygen ratio than in the engineering air.

Results and Discussion

1. RCM characteristics and data processing

First of all, repeatability of the RCM operation was verified by comparing pressure profiles of three independent test runs with pure nitrogen in Fig. 1. There is observed slightly damped oscillation of pressure profile immediately after the end of compression, which is caused by collision between the driving piston and the hydraulic oil. The maximum amplitude of pressure fluctuation was observed to be less than 4% of the peak pressure, which corresponds to the temperature fluctuation to be less than 2% of the peak temperature.

Typical pressure profile of a reacting case is shown in Fig. 2, where start of compression, end of compression, pressure rise from the ignition, and ignition delay period are all noted. In this study ignition delay is defined as a time lapse from the end of compression to the moment when the pressure rise rate has its maximum value, which is adopted by many researchers [15–17].
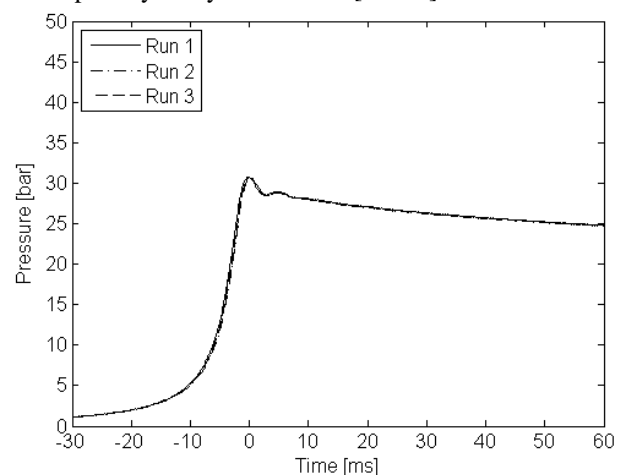
Fig. 1 Nitrogen compression test results. Runs 1, 2 and 3 are plotted together which demonstrates the repeatability of RCM experiments.
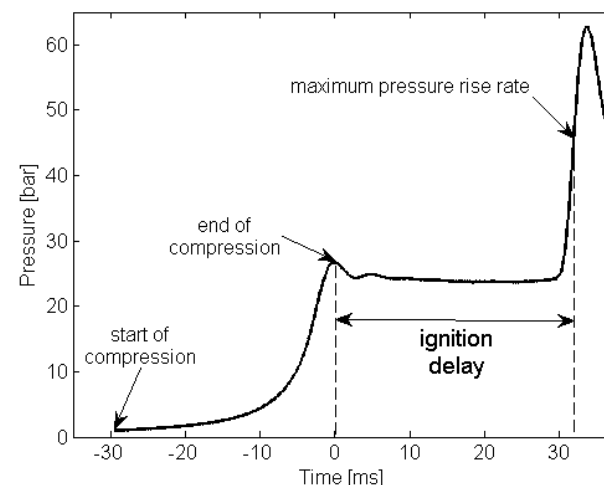
Fig. 2 Typical pressure profile of a reacting case. E0, φ=1, diluted, Tc=758 K, Pc=26.72 bar.

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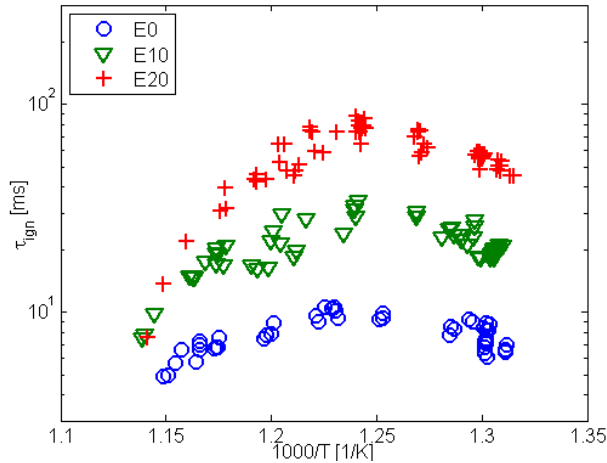
Fig. 3 Ignition delays of various iso-octane/ethanol blends in non-diluted condition.

2. Ignition delay measurement of non-diluted mixtures

Ignition delays of E0, E10, and E20 blends for non-diluted condition are plotted in Fig. 3. As ethanol content increases, ignition delay becomes longer in the tested temperature range. Similar negative temperature coefficient (NTC) behavior is observed for all the fuels below 800 K, although considerable gap between ignition delays of E0 and the others still exists. On the other hand, as temperature increases, the gap in ignition delays diminishes among the mixtures. In the following subsections, these ignition trends of three blends under higher and lower temperature regions are investigated in details, especially from the aspect of the low temperature chemistry or cool flame.

2.1 Higher temperature region (above 800 K)

In this region, there is no NTC behavior observed, while the ignition delay increases with higher ethanol content, mainly by the following reasons. Initiation reactions of iso-octane oxidation are directly affected by concentration decrease when ethanol is present in the blend which results in slower radical formation and fuel break-up, followed by decreased reaction rates of major
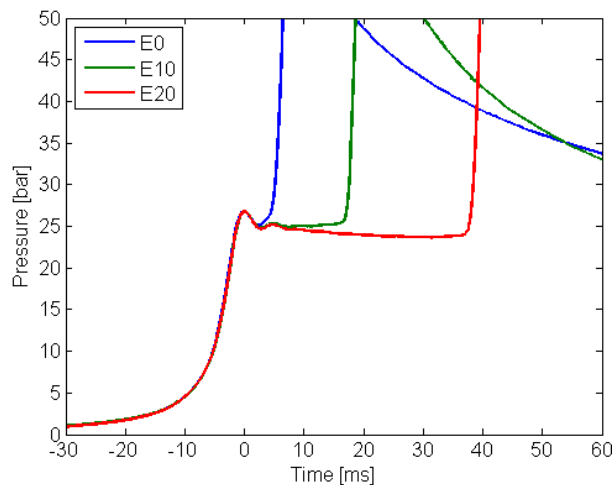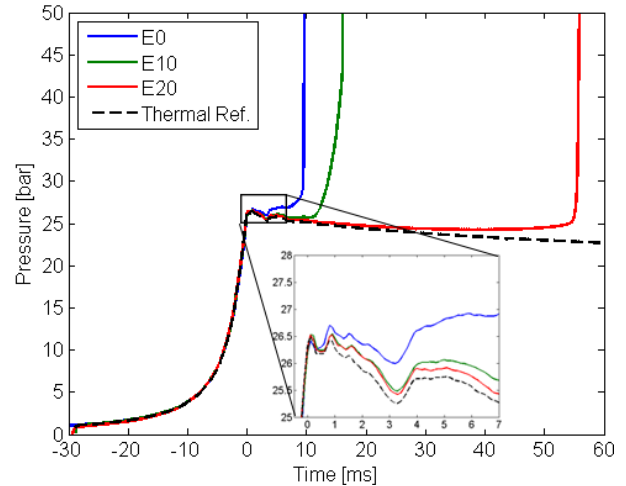

Fig. 4 Pressure histories for 850 K, non-diluted condition. There is no observable cool flame behavior in all the cases.

pathway. Additionally, some of the combustion radicals, e.g. OH or HO_2, produced from iso-octane chemistry may contribute to initiate ethanol reaction pathways, which are relatively slow, thereby limiting iso-octane oxidation progress by certain extent.

Pressure histories for the mixtures at 850 K are presented in Fig. 4, where the initial progresses right after the end of compression are similar in shape, and there is no significant exothermicity observed until the main ignition occurs. The overall combustion reaction demonstrates a typical single-stage ignition behavior, without cool flame exothermicity. Therefore, in this relatively high temperature range, the aforementioned chemical effect from reduced iso-octane concentration or radical consumption in the ethanol reaction pathways are mainly responsible for longer ignition delays of ethanol-containing blend fuels.

2.2 Lower temperature region (800 K or below)

Pressure profiles for various fuel blends at 800 K and 770 K are plotted in Figs. 5 and 6, respectively. For comparison, pressure history ('dotted line') of non-


Fig. 5 Pressure histories for 800 K, non-diluted condition. Magnified plot inside shows a slight pressure rise after the end of compression.
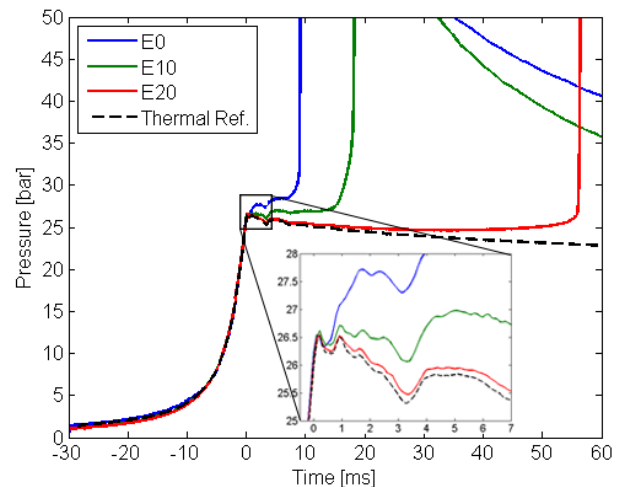

Fig. 6 Pressure histories for 770 K, non-diluted condition. Degree of the first pressure jump is relatively large, implying higher cool flame exothermicity.

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reacting mixture with similar heat capacity was included as a reference profile. When neglecting the pressure fluctuations from the physical oscillation of the RCM piston, which can be represented by the non-reacting profile, the degree of the first pressure jump around at 1 ms and the continuing pressure increase for E0 case are clearly distinguished from the other blends, especially at 770 K. These initial pressure jumps are the evidence of low temperature chemistry and associated exothermicity in the two-stage ignition of fuels. To clearly see the exothermicity regarding low temperature chemistry, the normalized pressure difference with respect to non-reacting reference profile is shown in Figs. 7 and 8 for 800 K and 770 K, respectively. Here, the value is normalized by using the test condition, i.e. 27 bar. It is clear that the exothermicity from the low temperature chemistry can increase the reactant pressure and temperature, and thus promote faster reactions, which is more prominent in 770 K than in 800 K, as expected. It is also noted that the higher ethanol content suppresses the low temperature chemistry of iso-octane, mainly by
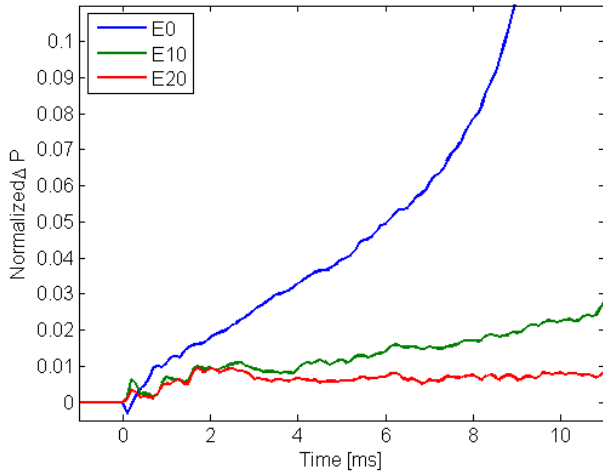
Fig. 7 Normalized pressure difference for 800 K, non-diluted condition. Slight initial pressure jump is observed for E0 case, while almost none shown for the others.
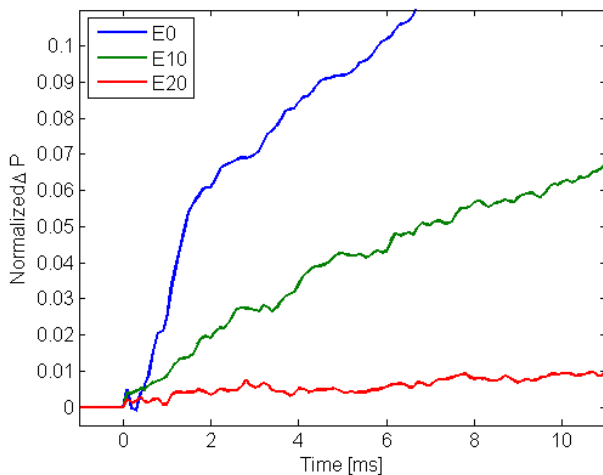
Fig. 8 Normalized pressure difference for 770 K, non-diluted condition. Strong initial pressure jump is observed for E0, while moderate, continuous pressure rise for E10 and no significant change for E20 are shown.

reduced iso-octane concentration and altered reaction pathways.

3. Ignition delay measurement of diluted mixtures

To effectively isolate the chemical effect of the low temperature chemistry from the thermal effect, ignition delay measurement was carried out by increasing the amount of inert gas, i.e. nitrogen, without changes in total pressure and stoichiometric ratio of fuel and oxygen. It is expected that this additional inert gas will limit the temperature increase of the mixture from the exothermicity of the low temperature chemistry.

The ignition delay measurements of diluted E0 and E10 mixtures are depicted in Fig. 9. Although there is no direct comparison possible between ignition delays of non-diluted and diluted mixtures due to different partial pressures of fuel and oxygen as well as buffer gas concentration, it is very interesting to note that the NTC behavior is significantly reduced with dilution in the tested temperature range for both E0 and E10.

Pressure histories of diluted E0 and E10 cases for different temperature conditions are plotted in Figs. 10 and 11, respectively. E0 case still shows small cool flame exothermicity, increasingly so with lower temperature condition, while E10 case has a little pressure increase only at the lowest temperature condition. It is worth mentioning that the ignition delays remain at the similar level even with lowered temperature below 800 K, which can be mainly attributed to the chemical consequence or compositional change from the low temperature chemistry, without its associated exothermicity. It is well known that the major reaction pathway of iso-octane oxidation in low temperature region is,

$$R + O_2 \leftrightarrow RO_2 \qquad (R1)$$

where R represent alkyl radicals e.g. AC8H17, DC8H17, or TC4H9, etc. (R1) in forward direction is typically treated as temperature independent while the reverse direction shows strong temperature dependency [18,20], which can explain the NTC behavior. However, in the diluted operation, we effectively reduce the reactant (or alkyl radicals) concentration in (R1), by limiting the temperature rise from the low temperature chemistry,
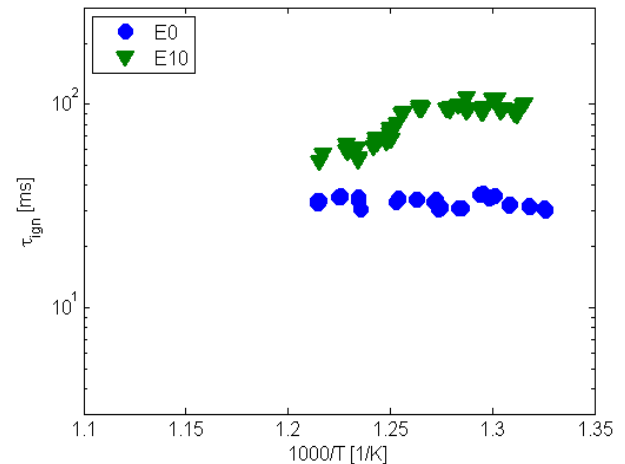
Fig. 9 Ignition delays of E0 and E10 blends for diluted conditions.

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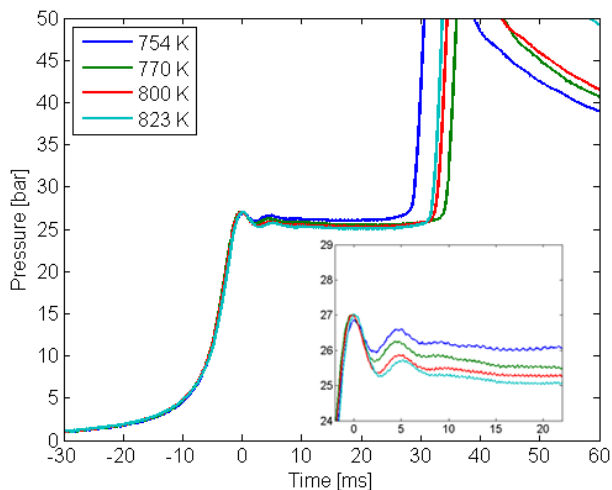
Fig. 10 Pressure profiles of diluted E0 case. The initial pressure rise from the low temperature chemistry is well suppressed, compared to non-diluted E0 case.
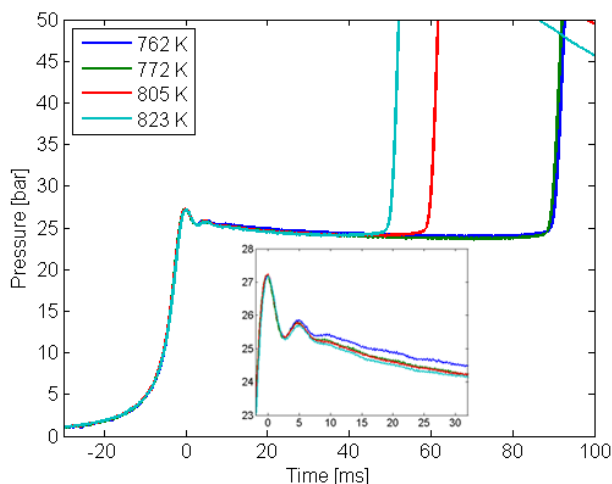

Fig. 11 Pressure profiles of diluted E10 case. Low temperature exothermicity is almost not observed and ignition delay monotonically changes with temperature.

which thus leads to the limited NTC behavior, as shown in Fig. 9.

4. Chemical kinetics modeling results

The modeling was performed by using MATLAB and Cantera toolbox for thermo-chemical calculation. LLNL iso-octane mechanism including ethanol submechanism [18,19] was adopted for validation and interpretation of experimental results. The mechanism consists of 874 species and 6864 reactions. The model was designed to effectively reproduce the compression stroke of the RCM, while the post-compression stage was assumed as an constant volume reactor. Figure 12 shows ignition delays of diluted cases, as compared to the experimental results. Modeling shows overall similar trends with experiment, while there is a discrepancy in the ignition delays for E10. However, the degree of NTC behavior is somewhat over-predicted for E0, while more similar for E10.

Modeling results of species-time histories of E10 blend at 770 K for both non-diluted and diluted conditions are presented in Fig. 13. It should be noted that
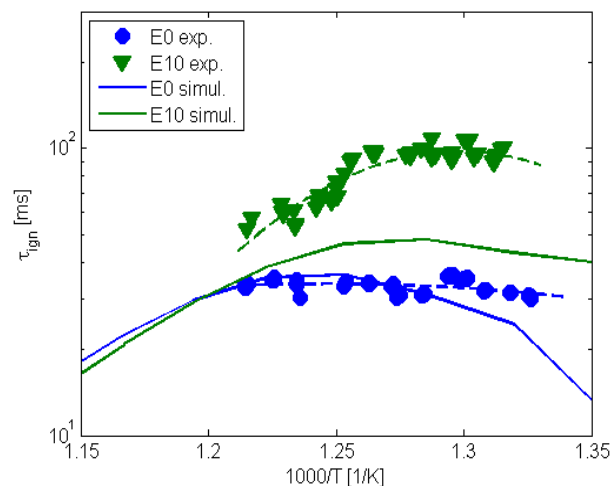
Fig. 12 Ignition delays for diluted condition, both from experiments and simulations. The NTC behavior at lower temperature region is reasonably reproduced.

overall species profiles are similar in both cases, even though the low temperature exothermicity is present for the former and vice versa. This modeling results suggest that the chemical and thermal effects of the low temperature chemistry can be effectively de-coupled.

Conclusions

Reactivity of various iso-octane/ethanol blend fuels was compared by measuring ignition delays in a rapid compression machine under similar conditions (750–900 K, 27 bar) to the unburned zone during combustion in an SI engine. At 800 K or below, it was demonstrated that the low temperature chemistry and associated exothermicity were suppressed to cause longer ignition delay with increased ethanol content. On the other hand, at higher temperature than 800 K, no significant low-temperature-exothermicity was observed, and the reduced iso-octane concentration and the radical consumption through ethanol reaction pathways were the main causes of longer ignition delay with ethanol addition.

Ignition delays of diluted iso-octane/ethanol blend fuels were also measured under the same conditions and compared with non-dilution cases, which was to isolate the chemical effect of the low temperature chemistry from the thermal effect or exothermicity. It was found out that the NTC behavior was reduced for all the tested blends. It was speculated that the reduction of alkyl radicals, one of the major reactant species in the low temperature chemistry, by limiting the temperature rise from the low temperature exothermicity, should be a main reason for this reduced NTC behavior.

Finally, chemical kinetics simulation was performed to understand the experimental results. The ignition delay for diluted operation showed decent agreement with those in experiments, but there was some discrepancy in the prediction of NTC behavior reduction. From the speciation results, it was shown that the chemical and thermal consequences of low temperature chemistry could be effectively de-coupled by adopting dilution method.

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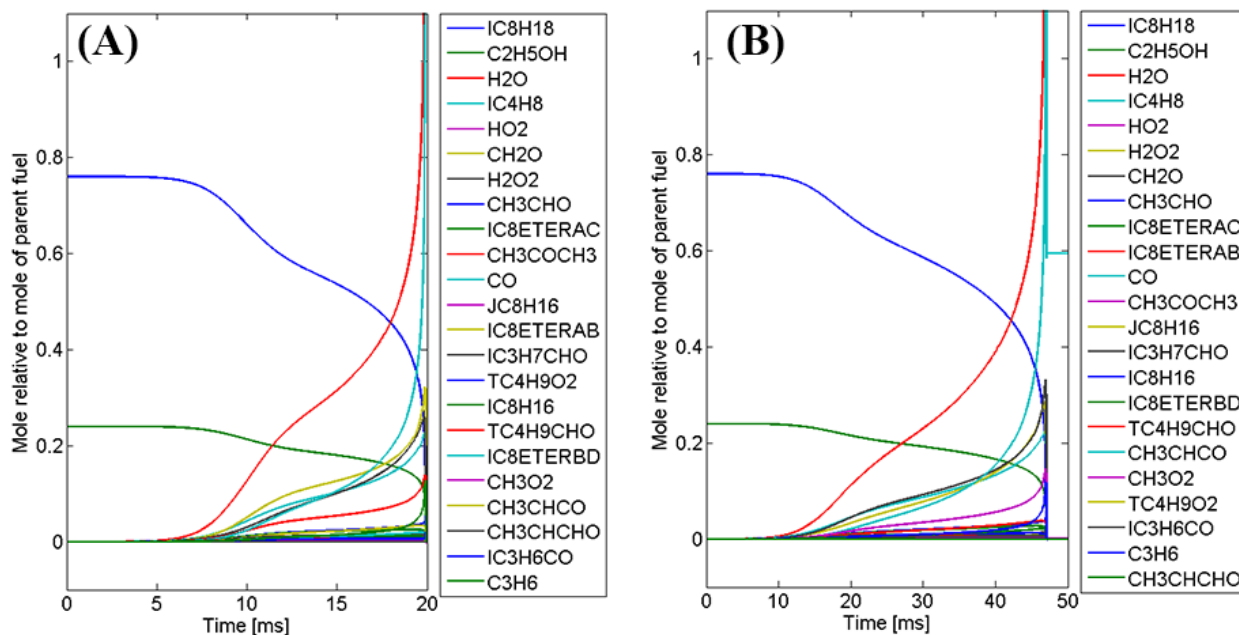
Fig. 13 Species-time histories of E10 blend at 770 K for (A) non-diluted, and (B) diluted conditions. Although ignition delay times are different, both cases show similar reaction progress.

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