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Insights into the underlying reaction kinetics of gasoline–ethanol interactions and their effects on the auto-ignition characteristics of gasoline/ethanol blends

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ABSTRACT

Ethanol-blended gasolines show enhanced anti-knock behavior in spark-ignition engines. Fundamental experimental investigations on their auto-ignition behavior are however scarce in the literature. In addition, previous numerical studies present diverse explanations for the effects of ethanol blending on the ignition delay times of gasoline/ethanol blends. These factors motivate the present study, aiming to extend the knowledge on the ignition of gasoline/ethanol blends and the understanding of the underlying reaction kinetics. For this purpose, ignition delay time measurements of the mixtures of a real gasoline fuel blended with ethanol were carried out in a shock tube and a rapid compression machine for range of conditions with respect to temperature, pressure, equivalence ratio, and blending ratio. Numerical modeling of the fuel ignition was performed based on a chemical mechanism, which is proposed in this study to predict the obtained data accurately. The reported datasets, in conjunction with the numerical analyses, demonstrate the significant mitigating impact of ethanol blending on the gasoline reactivity in the low- and intermediate-temperature ranges. It is found that, while the ignition delay times at intermediate temperatures are influenced by both physical dilution and chemical kinetic effects, the retarded ignition at low temperatures below 700 K is solely attributed to the chemical interaction of gasoline surrogate and ethanol in terms of OH radical competition. The OH radical scavenging character of ethanol also leads to a non-linear blending behavior. At high temperatures, the blending of ethanol accelerates the auto-ignition slightly, owing to its moderately higher reactivity at these conditions.

1. Introduction

Ethanol is an attractive biofuel, which can be produced in a sustainable manner, and is widely used as additive to petroleum-derived gasoline to improve its performance [1]. The addition of ethanol facilitates higher knock resistance of gasoline [2] in spark-ignition (SI) engines, allowing higher compression ratio and intake pressure to increase the engine efficiency [3]. Besides, as the flame propagation speed and heat of vaporization of ethanol are higher than those of gasoline, gasoline/ethanol blends provide faster combustion and higher volumetric efficiencies [4]. Ethanol-blended gasoline can also reduce regulated emissions, in particular NO_x [5], carbon monoxide (CO) [6], and soot [7].

Ethanol-blended gasoline fuels have been investigated in fundamental experiments, such as jet-stirred reactor [8] and heat flux burner [9]. Regarding the auto-ignition behavior, a number of relevant studies have been performed. Song et al. [10] measured the ignition delays of iso-octane/ethanol mixtures in a rapid compression machine (RCM) at 750–900 K and found that the addition of 0%, 10%, and 20% ethanol by liquid volume retards the reactivity of iso-octane. But this effect was observed to become weaker as temperature increases. Ethanol was found to impose only minor influences on ignition reactivity of gasoline surrogates within the intermediate temperature regime, but significantly suppresses the low-temperature reactivity [11]. Vuilleumier et al. [12] reported that the addition of ethanol to gasoline leads to low reactivity at both low (<850 K) and intermediate (850–1050 K) temperatures. A non-monotonic impact of ethanol blending was observed by Bogin et al. [13] on the oxidation reactivity of iso-octane. Interestingly, the increase of ethanol concentration from 0% to 20% increases the ignition delay significantly, whereas the further increase to 50% leads

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to a minor increase of ignition delay. Fikri et al. [14] and Cancino et al. [15] reported ignition delay times of gasoline surrogate/ethanol mixtures measured in a shock tube (ST). Experiments of the respective gasoline surrogates without ethanol addition were, however, missing in these two studies, making a direct assessment of the blending effect infeasible. Yahyaoui et al. [16] investigated the ignition behavior of gasoline surrogate/ethanol blends at temperatures of 1220–2315 K and found a promoting effect of ethanol on the blend reactivity. Du et al. [17] measured the auto-ignition and deflagration characteristics of practical gasoline/ethanol fuel at 1100 to 1800 K, and the results show that the ignition delay period of ethanol–gasoline/air mixture is prolonged with the increase of equivalence ratio. The investigated conditions of the above literature works are summarized in Table S1 in the Supplementary Material (SM).

Even though many studies pointed out the inhibiting effect of ethanol blending on the ignition propensity of the mixtures and revealed the importance of the OH or HO_2 radical fate, their understandings are inconsistent. Saisirirat et al. [18] regarded the reduced reactivity as a result of the reduced OH production rates due to the lower initial concentration of *n*-heptane, while Frassoldati et al. [19] and Haas et al. [20] highlighted the role of ethanol as OH radical scavenger. Cheng et al. [3] reported that ethanol blending effects are dominated by the competition between the H-atom abstraction from ethanol and other fuel components by OH radicals at low temperatures, and by HO_2 radicals at intermediate temperatures. Lu et al. [21] proposed that ethanol suppresses the reactivity in the ethanol/iso-octane mixtures by reducing OH mole fractions, given that ethanol oxidation consumes more OH than iso-octane produces, even at low ethanol content. Barraza-Botet et al. [22] studied the reaction pathways of iso-octane and ethanol mixtures and found that the reaction channels of both fuels develop independently without significant fuel interactions, until common intermediates are formed and connected by a shared OH radical pool. Singh et al. [23] observed superior radical scavenging characteristics of ethanol at both low and high temperatures for various blends of ethanol with *n*-heptane/iso-octane in homogeneous simulation with batch reactor. Fan et al. [24] investigated the synergistic effects between ethanol and toluene at low-to-intermediate temperatures and ultra-lean conditions, which is attributed to the increased HO_2 production from ethanol and the consequent consumption by benzyl.

Consequently, the present study is motivated by the insufficient experimental evidence for real gasoline/ethanol fuels and the diverse interpretations of the ethanol blending effects mentioned above. Its purpose is to provide a deeper understanding of the ethanol blending effect on the ignition characteristics of gasoline/ethanol fuels. The ignition delay times of blends of a real gasoline with ethanol are determined experimentally in an RCM and in an ST, covering a temperature range of 660–1255 K at engine relevant pressures of 15, 20, and 40 bar and equivalence ratios of 0.77, 1.00, and 1.18. In particular, experiments are performed for three ethanol blending ratios of 0, 20, and 40 mol% in order to explore the influence of ethanol blending. To further explore the blending effects with respect to a wide range of conditions and to distinguish between chemical and physical influences, numerical modeling was performed by using a tailor-made surrogate mixture and a chemical mechanism [25], which was updated to predict the obtained data accurately. Moreover, results from computational analyses, such as sensitivity analysis for ignition delay times on elementary reactions, are presented providing insights into the kinetics controlling the chemical interactions between gasoline and ethanol.

2. Experimental investigation

The measurements were conducted for a characterized research grade gasoline, RON95, and its mixtures with ethanol. The RON95 was supplied by Shell Global Solutions GmbH and has research and motor octane numbers (RON and MON) of 95.1 and 85.3, respectively. Its H/C ratio, liquid density, and oxygen content are 1.88, 0.73 kg/L, and 0.71 wt%, respectively. The temperature-dependent specific heat was characterized for the calculation of compressed mixture temperatures in experiments and the distillation curve was determined for the specification of initial reactor temperatures.

Table 1
Measurement conditions.

Facility	p [bar]	T [K]	ϕ [-]	Diluent
ST	20, 40	895–1255	1.00	N_2
RCM	20	670–840	1.00	N_2
	15	660–965	0.77, 1.18	N_2, N_2/Ar

The scanned experimental conditions are summarized in Table 1. The ignition delay time is defined as the time interval between the steep pressure rise caused by the auto-ignition and the arrival of the reflected shock in ST or the end of compression in RCM experiments [26]. The tabulated experimental data are available in the Supplementary Material (SM). For all experiments, the oxidizer was composed of oxygen and diluent gas with a mole fraction of 21%/79%. As diluent gas, either pure nitrogen or a mixture of nitrogen and argon (35%/65% by mole fraction) was employed. The O_2, N_2, and Ar with purities of >99.99% were supplied by Westfalen AG. The fuel/oxidizer mixtures were prepared in heated mixing vessels and their compositions were controlled by monitoring partial pressures with static pressure sensors.

2.1. Shock tube

A shock tube [27] was applied to measure high-temperature ignition delay times. The lengths of the driven and the curved driver sections are 4.1 and 3.0 m, respectively. The driven section has an inner diameter of 63.5 mm. The two sections are separated by a double diaphragm chamber, housing up to two pre-scored aluminum diaphragms. Five uncoated PCB 113B22 pressure transducers are mounted over the last 1.0 m of the driven section to record the incident shock velocities. The pressures and temperatures behind the reflected shock were calculated using an in-house code developed based on the shock and detonation toolbox [28]. Considering uncertainties in the measurements of initial conditions and shock velocities as well as in the thermodynamics data, the uncertainties of the estimated pressure and temperature are ±1.5% and ±0.7%, respectively [26]. As it is infeasible to quantify accurately the uncertainties caused by non-ideal behaviors, such as mixture inhomogeneity, the typical experimental scatter of ignition delay times of ±20% [29] is assigned here as the total measurement uncertainty, following previous works [26], and is indicated by error bars of the reported data in the figures presented later. For the present configuration, an average pressure rise rate (dp/dt) of 7%/ms caused by the boundary layer effect was determined from the recorded pressure histories and has been incorporated in the respective kinetic simulations. The dominating facility effect in the shock tube is shock attenuation that leads to the constant pressure rise. Heat loss effects are of minor importance as discussed by Frazier et al. [30]. A detailed description of this ST can be found in [27].

2.2. Rapid compression machine

The RCM [31], applied for low- and intermediate-temperature ignition measurements, is composed of a pneumatically driven piston, a hydraulic control and braking, and a reaction chamber with the reactor piston. The internal diameters of the reactor is 50 mm, and the piston has a stroke of 250 mm. To avoid fuel condensation, the chamber is pre-heated with an external heating system. Creviced piston heads are used to suppress the formation of roll-up vortices, which ensures a homogeneous temperature field within the reactor core at the end of compression. The dynamic pressures are measured by Kistler

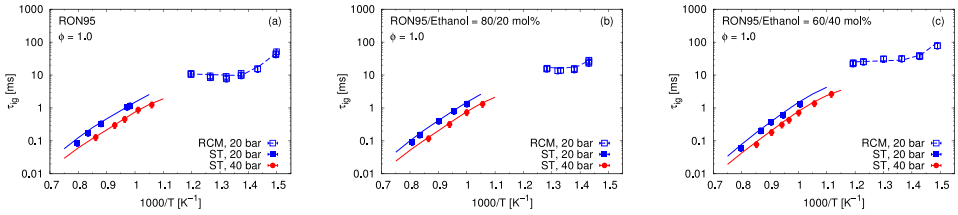

Fig. 1. Ignition delay times of RON95 and its mixtures with ethanol. Solid and open symbols denote the data from ST and RCM, respectively. Solid and dashed lines show the simulation results of ST and RCM, respectively.

6125C-U20 sensors and the initial temperatures are monitored by 13 type-T thermocouples mounted along the reactor wall. A complete description of the RCM is available in [31]. The temperatures after compression were estimated by assuming an adiabatic compression of the core gas [32]. Based on error propagation analysis, the uncertainty in temperature is estimated to be ±0.4–1.0% [33]. Similar to the ST experiment, non-ideal behaviors appear in RCM measurements and are difficult to quantify. Büttgen et al. [34] found that, concerning the facility effects, the measured ignition delay times from various RCMs lie within a range of ±21%. Following the work of Jacobs et al. [26], this experimental scatter is assigned as the measurement uncertainty of this RCM. The RCM is modeled as an adiabatic reactor with time-varying volume to account for the non-ideal behaviors, such as heat loss [32]. For this, non-reactive experiments were conducted by replacing O_2 with N_2 in the mixture in addition to the reactive ones, and their pressure traces were converted into time-resolved effective volume profiles (available in the SM) by assuming an isentropic relationship.

3. Kinetic modeling

3.1. Surrogate formulation

In this work, a surrogate mixture of *n*-heptane, iso-octane, toluene, and ethanol with the molar composition of 14.04%/44.03%/37.45%/4.48% (15.17%/ 53.59%/29.32%/1.92% by liquid volume fraction) is employed to emulate the RON95 gasoline fuel. Its composition was determined by minimizing the differences of a set of physical target properties between the real fuel and the surrogate. More details on the applied surrogate formulation methodology are described in [25]. Here, the RON, MON, H/C ratio, liquid density, and oxygen content of RON95 were considered as the target properties in the formulation. The derived surrogate mixture has a RON of 93.2 and a MON of 86.8, and the deviations of all target properties between the surrogate and the RON95 are less than 2%. Note that the RON95 does not contain ethanol with measurable quantity. The small amount of ethanol in the surrogate mixture represents the oxygenated compounds in the RON95.

3.2. Chemical mechanism

A number of chemical kinetic mechanisms of gasoline surrogate fuels [35–37] are available in the literature. The chemical mechanism [25], which was developed and validated in our previous work, is employed in the present study to simulate the ignition of gasoline/ethanol blends. This mechanism contains the oxidation chemistry of various C_0–C_8 hydrocarbons and substituted aromatics, including *n*-heptane, iso-octane, toluene, and ethanol, allowing for the description of the oxidation of the proposed surrogate fuel.

It is found that this model [25] can predict the ignition delay times of RON95 fuel with reasonable accuracy, while it fails to match the data reported here for the blends. Sensitivity analyses (shown later) reveal the large importance of the H-abstraction reaction of ethanol by OH radical, forming the α-ethanol radical (CH_3CHOH), for accurate ignition delay predictions of gasoline/ethanol mixtures with blending ratios of 20–80 mol%. Thus, its rate constant was modified by incorporating the theoretically calculated value from Sivaramakrishnan et al. [38]. The rate coefficients of the other two H-abstraction channels were revised consistently according to [38], ensuring a correct estimation of their branching ratios. Carr et al. [39] proposed rate constants for these reactions as well, based on their experiments. While the measured total rate constant of the three channels agrees with that of [38], the branching ratios and site-specific constants are different. These coefficients have not been incorporated in the present mechanism, as the model performance is not satisfactory, when using them. The mechanism [25] was revised additionally by removing redundant species and reactions, adding missing consumption reactions, and updating rate constants. The details are listed in the SM. The final mechanism (available in the SM) was also validated against the literature experiments, which have been considered as targets in our previous studies [25,35] and in the studies of neat ethanol [40–42]. Examples are shown in the SM. In the present work, numerical simulations were performed using the FlameMaster code [43].

The rate parameters from Sivaramakrishnan et al. [38] were also adapted in the mechanism of Mittal et al. [44] and used by Sarathy et al. [45], where they were modified slightly in terms of the branching ratios between different carbon sites for better prediction of jet-stirred reactor and flow reactor results. The incorporation of these modified rates into the final mechanism decreases the average calculated ignition delay times of 20% and 40% ethanol blended mixtures at temperatures below 850 K by 11.4% and 20.1%, respectively. By replacing the ethanol sub-mechanism completely with the one from Mittal et al. [44], the calculated ignition delay times of 20% and 40% ethanol blended mixtures are reduced by 12.7% and 24.5%, respectively. However, it was found that the results and conclusions of the kinetic analysis presented in later sections are barely affected by these modifications.

4. Results and discussion

4.1. Ignition delay times

The ignition delay times measured at stoichiometric conditions and pressures of 20 and 40 bar are shown in Fig. 1. The results for lean and rich mixtures are depicted in Fig. 2. For comparison, the results predicted by the updated model are shown in the respective figures. Reasonable agreement between model and data is observed at most investigated conditions. The model slightly under-predicts the ignition delay times of lean and rich mixtures below 700 K. The comparison results of the initial and final models are available in the SM. The updated model improves the ignition delay time prediction performance, especially at low temperatures, high ethanol blending ratios, and fuel-rich conditions.

4.2. Effect analysis

Fig. 3 compares the experimental results for varying blending ratios of ethanol, demonstrating both the inhibiting influence of ethanol addition on fuel reactivity at low and intermediate temperatures and the non-linear blending behavior. In the high-temperature regime, the ignition delay times are in general not highly sensitive to the ethanol content. Interestingly, the inhibiting impact of ethanol is reversed for ignition at very high temperatures. For instance, at 1255 K and 20 bar,

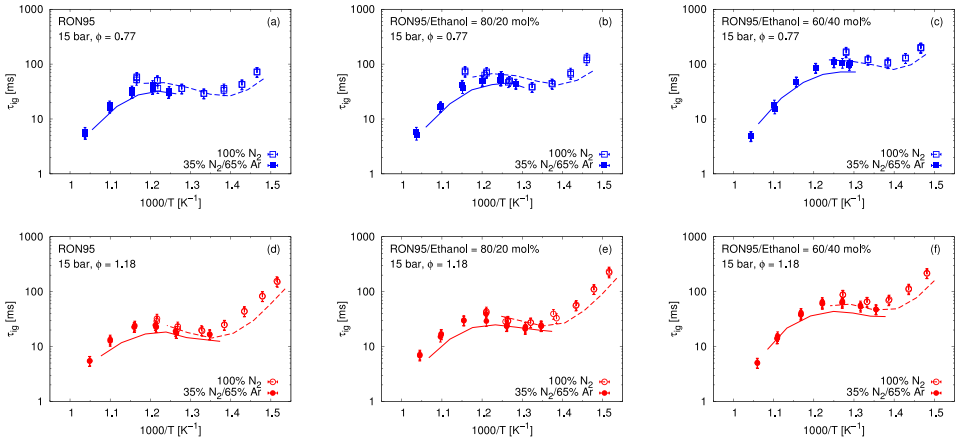

Fig. 2. Ignition delay times of RON95 and its mixtures with ethanol measured in the RCM. Closed and open symbols denote the data with diluent gases of N_2/Ar and N_2, respectively. Solid and dashed lines show the simulation results for the experiments with dilution by N_2/Ar and N_2, respectively.

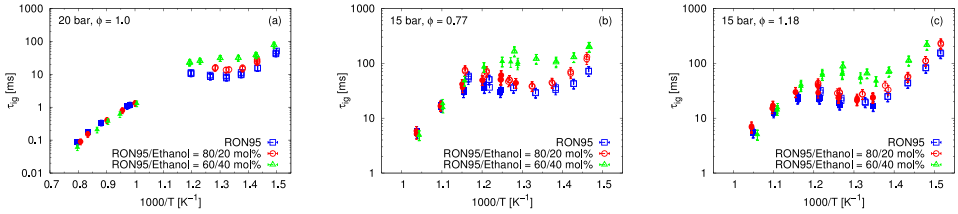

Fig. 3. Ignition delay times of RON95 and its mixtures with ethanol. Open symbols denote the RCM data with pure N_2 as diluent. Solid symbols denote the ST data in (a) and the RCM data with the N_2/Ar mixture as diluent in (b) and (c).

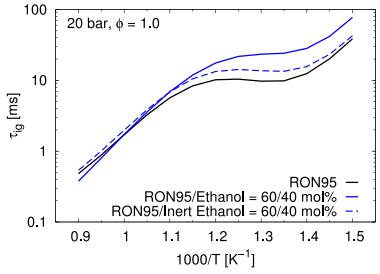

Fig. 4. Computed ignition delay times of RON95, RON95/ethanol blends, and RON95/inert ethanol blends.

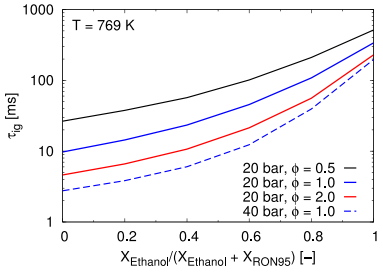

Fig. 5. Computed ignition delay times of RON95/ethanol blends at 769 K over ethanol blending ratios.

the addition of 40% ethanol decreases the ignition delay times of RON95 by more than 30%. This phenomenon was also observed by Yahyaoui et al. [16].

The blending of ethanol can influence the mixture reactivity through the dilution effect of reducing the initial concentration of gasoline components and through the chemical effect of changing reaction pathways of the blending components. To distinguish between these two factors, the calculated ignition delay times of pure RON95 and of RON95/ethanol mixtures (60/40 mol%) are compared in Fig. 4 with the results of simulations, where the blended ethanol is assumed to be inert. The inert component was added into the base mechanism in a way that it is not involved in any reaction but with the same thermodynamic properties as the reactive one. It is seen that the blending with inert ethanol, which essentially reduces the equivalence ratio of the reactive mixture, retards the auto-ignition at both high and intermediate temperatures. However, this dilution effect is of marginal importance at low temperatures. As discussed in [46], the cool-flame ignition delay time is weakly correlated with equivalence ratio. The comparison between the reactive and inert cases reveals that the fuel reactivity at low temperatures is solely influenced by the chemical effect of ethanol blending. The chemical impact vanishes nevertheless with increased temperatures. At high temperatures of above 1000 K, it is even reversed. Reactive ethanol increases the ignition propensity of the blend, as observed in the experiment as well.

Constant volume calculations were performed for RON95/ethanol mixtures with blending ratios of 0%–100% at pressures of 20 and 40 bar, and equivalence ratios of 0.5, 1.0, and 2.0, to explore the effect of ethanol blending over a wider range of conditions. The simulations were carried out at 769 K, where significant blending impact is observed in the experiments. As shown in Fig. 5, the logarithmic ignition delay times increase almost linearly with ethanol mole fraction at 20 bar and $\phi = 0.5$, while enrichment of the mixture enhances the non-linearity. Non-linearity is quantified as the change in the slope. The blending impact depends more strongly on pressure than on equivalence ratio at high ethanol loadings. This can be attributed to the fact that, at higher pressure, the condition of 769 K is shifted into the low-temperature regime, where the chemical impact is more pronounced. The highest non-linearity is found at a blending ratio of roughly 60%, for which the reason will be discussed in the next section.

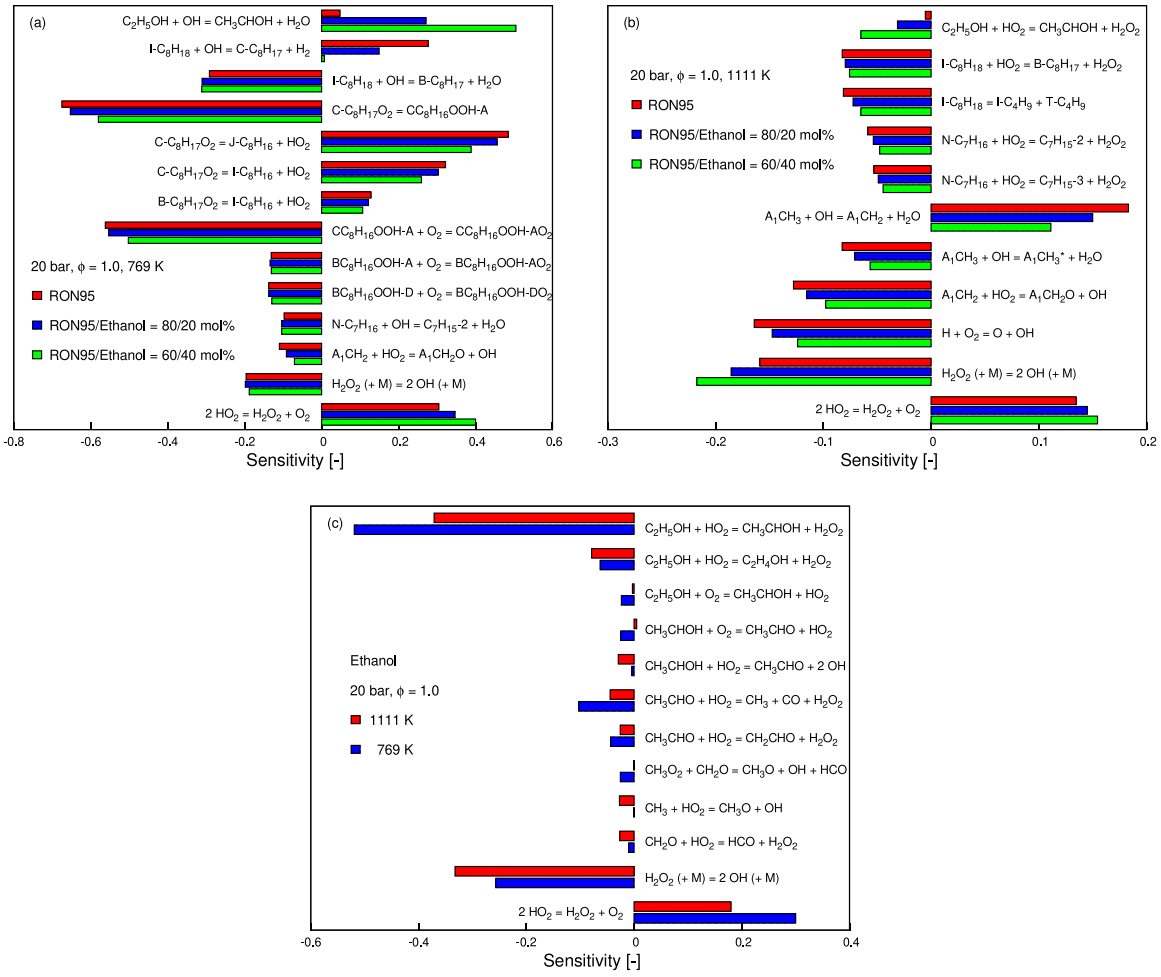

Fig. 6. Sensitivities of ignition delay times on reactions for RON95, ethanol, and RON95/ethanol mixtures at 20 bar, ϕ= 1.0, and 769 K and 1111 K.

4.3. Analysis of underlying kinetics

To explain the findings outlined above and to understand the chemical effects, the oxidation kinetics of gasoline/ethanol blends are explored in terms of sensitivity analysis. Sensitivities of ignition delay times on elementary reactions were calculated as normalized coefficients [27] and are presented in Fig. 6. Fig. 6(a) shows the sensitive reactions for stoichiometric ignition of RON95/ethanol mixtures with different blending ratios at 20 bar and 769 K. Besides the decomposition of H_2O_2 and the recombination of HO_2 radicals, the most sensitive reactions are those related to the low-temperature chemistry of iso-octane, which is the major surrogate constituent with 44 mol%. With the increase of ethanol content, the sensitivities of most reactions are changed only slightly, except for the first two reactions depicted in Fig. 6(a), namely the α-H abstraction from ethanol by OH radical and the tertiary-H abstraction from iso-octane by OH. The former has a sensitivity of roughly 4% for the ignition of RON95, whose surrogate contains 4.48 mol% ethanol. By adding 40% ethanol, its sensitivity increases significantly by more than a factor of ten. This reaction attracts the OH radicals produced by the consumption of iso-octane and *n*-heptane, initiating a slow chain-propagation channel via the reaction of CH_3CHOH with O_2 to CH_3CHO and HO_2, and simultaneously inhibiting the H-abstraction from iso-octane and *n*-heptane by OH. As the subsequent chain-branching pathways of alkane radicals cannot be initiated, the reactivity of the fuel blend is decreased.

The H-abstraction from the tertiary carbon of iso-octane by OH shows positive sensitivity for the ignition of RON95. The molecular conformation of the tertiary radical inhibits the second intramolecular H-migration in the conventional low-temperature chemistry, making its consumption less effective in OH production than that of other radicals of iso-octane. Note that, with the increase of ethanol content, the impact of this reaction does not vanish, but is in fact reversed, such that its sensitivity even exhibits a negative value of −0.1 at the blending ratio of 60% (not shown in Fig. 6(a)). The subsequent pathways of tertiary iso-octyl radical, including the newly proposed alternative isomerization reactions [25], produce more reactive radicals than the chain-propagation reactions of ethanol at low temperatures, which explains the promoting impact of its formation at high ethanol loadings.

Note that the H-abstractions from the α- and β-carbon sites of ethanol by OH were both identified by Frassoldati et al. [19] as sensitive reactions for the auto-ignition of *n*-heptane/iso-octane/ethanol mixtures. However, by using the theoretically calculated rate constants from Sivaramakrishnan et al. [38], only the α-H-abstraction is found to play a crucial role here. Due to the very high branching ratio between these two sites predicted by Sivaramakrishnan et al. [38], the sensitivity coefficient for the β-H-abstraction is estimated to be less than 0.01 at a blending ratio of 40%.

In order to confirm that the gasoline–ethanol interaction proceeds mainly through the α-H-abstraction from ethanol by OH, Fig. 7 compares the ignition delay predictions of RON95/ethanol mixture for cases of reactive and inert ethanol with those of a simulation with reactive ethanol, in which this reaction is removed from the mechanism. By artificially suspending this reaction, the results with reactive ethanol become identical to those with inert ethanol at low temperatures,

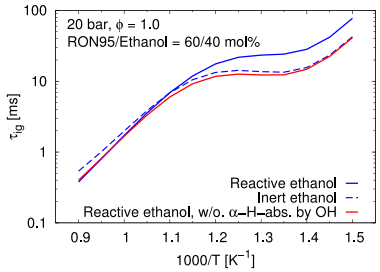

Fig. 7. Computed ignition delay times of RON95/ethanol blends for reactive ethanol, inert ethanol, and reactive ethanol without the α-H-abstraction by OH in the ethanol mechanism. w/o, without.

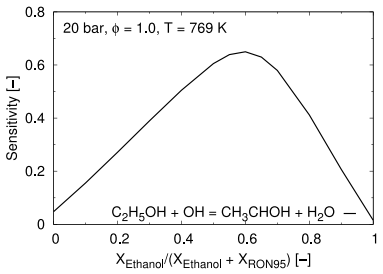

Fig. 8. Sensitivities of ignition delay times on the reaction of $C_2H_5OH + OH = CH_3CHOH + H_2O$ for RON95/ethanol blends.

demonstrating that the chemical impact is solely introduced by this reaction. At high temperatures, its absence affects the reactive simulation results negligibly.

Fig. 8 presents the sensitivity of ignition delay times on this reaction over ethanol mole fraction at 769 K. The results demonstrate its large importance in predicting the ignition delay times of gasoline/ethanol blends at low temperatures in a blending ratio range of 20%–80%, and also explains the non-linear blending behavior observed in Fig. 5. When small amounts of ethanol are in the blend, still the degenerate chain branching of long-chain components leads to the auto-ignition, even though a number of OH radicals are scavenged. With further ethanol blending, more OH radicals are consumed by ethanol. The inhibiting impact increases consequently, up to a blending ratio of 60%, where both OH and ethanol molecules are present with large quantities. For blending ratios larger than 60%, the reduced initial concentrations of *n*-heptane and iso-octane decrease the OH production rate strongly. The auto-ignition at such blending ratios is governed by the chain-propagation chemistry of ethanol, which is slower than alkane chain-branching chemistry. Thereby, as shown in Fig. 5, while blending ethanol with a ratio of 60% increases the ignition delay by about a factor of four, further enrichment of ethanol to 100% enlarges the ignition delay time additionally by about an order of magnitude.

For very low and high ethanol loadings, the importance of $C_2H_5OH + OH = CH_3CHOH + H_2O$ vanishes, due to the low concentrations of ethanol and OH, respectively. This is different from the cases, where fuels with low-temperature chemistry, such as *n*-butanol [47], are blended into gasoline. The longer chain of *n*-butanol favors its chain-branching reactions, which produce OH radicals as well. This leads to large sensitivities on H-abstraction reactions of *n*-butanol by OH regardless of the blending ratios, as discussed in [47]. While *n*-butanol still attracts the OH radicals in the system, its inhibition of reactivity is smaller than of ethanol [18].

The sensitive reactions for the auto-ignition propensity at higher temperature are depicted in Fig. 6(b). The important fuel-specific reactions are the initial reactions of the surrogate components. When adding ethanol, the sensitivities of these reactions are reduced, due to the lower initial concentrations of the surrogate components. In contrast, α-H-abstraction from ethanol by HO_2 becomes important, while the H-abstraction by OH is insensitive and thus not shown in Fig. 6(b). No strong interaction is observed between the reactions of the gasoline surrogate and ethanol through radical competition. At high temperatures, while the radicals of *n*-heptane and iso-octane mainly undergo chain-breaking β-scission reactions, the major consumption channel of CH_3CHOH is still its reaction with oxygen, yielding CH_3CHO and HO_2. This chain-propagation pathway leads to the slightly higher reactivities of ethanol and ethanol-blended gasolines at high temperatures. Fig. 6(c) shows the results of sensitivity analyses for the ignition of neat ethanol. The H-abstraction reactions of ethanol by HO_2 are the most important fuel-specific reactions at both low and high temperatures, while the H-abstraction by OH has marginal sensitivity.

5. Concluding remarks

The present work investigated the ignition characteristics of gasoline/ethanol blends and their underlying reaction kinetics. Ignition delay time measurements were performed in an ST and an RCM for blends with varying blending ratios over an extended range of conditions. It was found that the ethanol addition at low and intermediate temperatures has a non-linear inhibiting influence on fuel reactivity. In contrast, the blending of ethanol accelerates the fuel ignition slightly at high temperatures. Based on a tailor-made surrogate formulation and a chemical mechanism from the literature, a kinetic model for gasoline/ethanol blends was updated by incorporating theoretically calculated rate constants of crucial reactions and the agreement between experimental and numerical results is satisfactory.

The experimental datasets, in conjunction with the numerical results, provide a comprehensive evaluation of the impact of ethanol blending on the ignition delay times of gasoline/ethanol fuels, for which the knowledge is insufficient in the literature. Both physical and chemical effects introduced by the blending of ethanol increase the ignition delay times in the intermediate-temperature regime, while the reduced reactivity at low temperatures is almost solely attributed to the OH radical scavenging by α-H-abstraction from ethanol. With the increase of ethanol content, the inhibiting impact increases consequently, up to a blending ratio of 60%, where both OH and ethanol molecules are present at large quantities. The chemical impact vanishes nevertheless with increased temperatures and even reverses at high temperatures, owing to moderately higher reactivity of ethanol at these conditions.

CRediT authorship contribution statement

Jiaqi Zhang: Writing – original draft, Investigation. **Philipp Morsch:** Investigation, Data curation. **Heiko Minwegen:** Writing – review & editing, Investigation. **Florian vom Lehn:** Writing – review & editing, Supervision. **Xudong Wu:** Writing – review & editing. **Karl Alexander Heufer:** Writing – review & editing, Supervision. **Heinz Pitsch:** Writing – review & editing, Supervision. **Liming Cai:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jaecs.2025.100333.

Data availability

Data will be made available on request.

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