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Effect of ethanol addition on the laminar burning velocities of gasoline surrogates

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ABSTRACT

Laminar burning velocities (LBV) and Markstein lengths of spherical flames of n-heptane (H), iso-octane (O), and ethanol (E) and their binary and ternary mixtures (in equal volume fractions) at elevated pressures and temperatures are experimentally investigated. Measurements are performed in a constant volume combustion vessel using two distinct techniques: flame front imaging and pressure rise rate. For pure components, ethanol shows a higher LBV compared to n-heptane and iso-octane at same conditions. A pressure dependence on LBV of each pure component is observed where ethanol is found to have the strongest pressure dependence. This is also indicated by the higher negative coefficients in three-body termination reactions through a sensitivity analysis. For binary mixtures, the EH mixture was found to have the highest LBVs compared to other blends. The pressure dependence on LBV of ethanol is also present in binary mixtures where at a higher pressures the EO blend is found to have a lower LBV compared to the OH blend due to competing reactions against the H radical pool. Non-linear behaviour of the EH mixture's LBV was observed and verified through the chemical kinetics suggesting the widely used mixing rules for blends might need additional improvements, especially at higher temperatures. An equal volume EHO ternary mixture shows the LBV to be similar to the OH mixture at 380 K. At 450 K, the LBVs differ by 7% at atmospheric pressure, but due to ethanol's pressure dependence, this difference decreases to zero as the pressure increases to 4 bar.

1. Introduction

As the engine community pushes the operating conditions of modern engines to new limits, numerical simulations of engine behaviours at these extreme conditions remains a challenge [1]. Although numerical models exist that can handle detailed chemistry while using less prior combustion regime assumptions, most widely used turbulent premixed combustion models are based on a flamelet regime assumption, where the turbulent flame is considered asymptotically thin and locally laminar. This makes the laminar burning velocity (LBV) a crucial factor in most practical engine simulations. Although LBV depends on (amongst other things) equivalence ratio, pressure, temperature, and any diluent gases in the mixture, its value is basically a characteristic strictly of the fuel itself. Therefore, to evaluate potential alternative fuels and/or suitable surrogates, the acquisition of a complete LBV database is needed. However, a major difficulty in determining LBV is that a planar and adiabatic flames can rarely be achieved. Instead, most practical flames are wrinkled, unsteady, and exist in flow fields that are themselves non uniform and unsteady. In such a situation, the

laminar flame is stretched which necessitates the definition of another fundamental mixture parameter known as the Markstein length, which quantifies the response of the flame to stretch rate. The laminar burning velocity and Markstein length, are crucial validation tools in the development of chemistry and transport models and are necessary inputs for flamelet calculations, sub grid and turbulence models.

Ethanol is regarded as one of the most promising drop-in renewable fuels, particularly for spark ignition engines as it may be produced from renewable biomass [2]. The use of ethanol in SI engines has led to observed reductions in pollutant emissions including carbon monoxide, unburned hydrocarbons, and particulate matter from the exhaust [3–5]. However, further exploration of the benefits of this phenomenon through fundamental experimental and numerical investigations of the detailed combustion chemistry has been proven to be difficult. This is due to the significant complexity of commercial gasoline which contains hundreds of individual hydrocarbon species [6]. Therefore, to emulate the physical and chemical properties of gasoline and to promote repeatability in experiments and simulations, researchers have

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adopted well-defined compositions of iso-octane (2,2,4 trimethylpentane) and n-heptane, commonly referred to as primary reference fuels (PRFs), as surrogates.

Noteworthy efforts towards the measurement of LBVs of individual PRF components and ethanol have been made covering a wide range of compositions and pressure, temperature, and equivalence ratio conditions. The LBVs of these pure components have been investigated through measurements from spherical flame (SF), counter flow (CF), and heat flux (HF) methods, primarily under the conditions of atmospheric pressure and temperatures of 298–400 K [7]. Among the three pure fuel components, Van Lipzig et al. [8] and Sileghem et al. [9] showed that the laminar burning velocity (S_L) of ethanol was the fastest whilst iso-octane was the slowest at atmospheric pressure and in the temperature range 298–338 K. While these studies provide crucial validation of detailed kinetic mechanisms, significant scatter was found even at low mixture temperature due to the inherent disadvantages of each of the techniques used. Moreover, significantly less data is available in the literature at elevated pressures and temperatures (>400 K) and they show even higher discrepancies [7]. Recently, Meng et al. [10] and Matveev et al. [11] measured the LBV of ethanol using spherical flame and heat flux methods for temperatures up to 450 K, whereas Kumar et al. [12] and Katoch et al. [13] presented iso-octane at the temperature range 300–640 K using externally heated diverging channels. However, direct comparisons between these studies for these three components would create additional errors rising from various sources, for example the selection of extrapolation techniques. Therefore, measurements of individual components using the same technique at elevated temperature and pressure are necessary to provide fair validation to the development of chemical kinetic models.

The addition of ethanol to PRF components, at low pressures, has been shown to enhance a blend's LBV [8]. While PRF blends without ethanol have been found to display a predictable variation in LBV under increased unburned temperature and pressure conditions, different behaviours are observed in ethanol/n-heptane (EH) and ethanol/iso-octane (EO) mixtures. For example, Lavadera et al. found that an EH mixture's LBV increased disproportionately with ethanol content at atmospheric pressure and 338 K [14]. For EO blends, Broustail et al. reported that LBV increased linearly with ethanol content [15] whereas Rau et al. demonstrated that the increase was a function of preheat temperature [16]. Direct comparisons of these binary blends at the same conditions are found in Van Lipzig et al.'s study where the three binary mixtures' LBVs (EH, OH, EO) are measured at atmospheric pressure and initial temperatures of 298 K and 338 K [8]. OH laminar burning velocities are found to be the average values of those of n-heptane and iso-octane within the accuracy of their measurements. However, although the burning velocities of ethanol and n-heptane are close to each other, it is found that the burning velocities of the mixture EH are not average values. The same trend was also found in EO mixtures. At similar conditions, Sileghem et al. [9] validated simple mixing rules that consider the energy fraction of the blend's components and are shown to predict the experimentally determined LBV of the mixtures at tested conditions. This was further confirmed by a recent study by some of this work's authors for EO mixtures at elevated pressure [17]. However, as pointed out by Sileghem et al. [9], the mixing rules are untested for binary mixtures especially at higher temperature. The addition of ethanol to PRF mixtures to form ethanol, n-heptane, and iso-octane (EHO) blends has been minimally studied [8]. Liao et al. observed that EHO mixtures consistently exhibited higher flame speeds than OH mixtures [18]. The study from Dirrenberger et al. [19], perhaps one of the most used experimental works for the validation of ethanol/PRF blend chemical mechanisms, is conducted at 358 K and atmospheric pressure with the addition of ethanol capped at 15% (vol). As highlighted by Sarathy et al. [20], experimental measurements on complex mixtures comprising two or more surrogate molecules especially at elevated temperature and pressure are much needed for the development of kinetic models and understanding mixing effects.

The objective of this paper, therefore, is to provide new data on unstretched laminar burning velocities of pure n-heptane, iso-octane, ethanol and their binary and ternary mixtures. These are experimentally determined by using a spherically expanding flame methodology, in a constant volume vessel at pressures of 1, 2, and 4 bar and temperatures of 380 and 450 K. Focus is given to the effect on LBV of ethanol addition to PRF components under these conditions. The insights obtained by the new measurements will help the development of kinetic models and the validation of mixing rules for gasoline–ethanol mixtures involving multiple surrogate components. LBVs for pure components of EHO are first extrapolated from a previously developed empirical correlation and compared with the numerical simulation and data from the literature. Additional experiments are conducted for pure components of EHO at conditions corresponding to binary and ternary study to improve these comparisons. The LBVs of stoichiometric mixtures of equal volume binary and ternary ethanol blends are given for the first time at the above mentioned elevated temperatures and pressures. Chemical kinetics modelling is adopted to further understand the effects on LBV of ethanol addition on the two PRF components highlighting the reactions the LBV is sensitive to, and how the fuel composition and operating condition affects this.

2. Measurement of burning velocity

Experiments were carried out in a constant volume combustion vessel shown in Fig. 1. The spherical vessel used in this study has a diameter of 160 mm with a pair of 40 mm quartz windows for optical access. Reactants were prepared in the combustion vessel using Dalton's law of partial pressures, assuming an ideal gas. The calculations for the mole fraction of fuel, air, and diluent at a given pressure and temperature are detailed in a previous study [21]. The fuel is injected into the heated air stream using a syringe and actuator where a pair of electrodes forms the spark gap at the centre of the vessel, with ignition driven by a conventional automotive inductive ignition system. Further details of the experimental set up are outlined in earlier studies [22].

The constant volume vessel used in this study is versatile as it allows two distinct techniques of determining laminar burning velocities: imaging of the flame front propagation at conditions of constant pressure, and measurement of the pressure rise combined with a constant volume combustion model. The flame front imaging method takes the images of the initial stages of flame propagation where the flame speed can be considered as the rate of change of flame radius given by the schlieren images. The schlieren radius is then related to the flame radius as defined by Bradley et al. [23]. The radius considered for flame front imaging post-processing is between 8 mm and 20 mm as previous studies have suggested beyond the critical radius of 6.5 mm, the spherical flames are no longer affected by the ignition source [24]. Due to the small radius of curvature of the flame at initial conditions, the flames are highly stretched, so a linear extrapolation of the flame speed to conditions of zero stretch is used. The use of flame front imaging allows the inclusion of ignition and flame stretch effects on laminar burning velocities where Markstein lengths are determined for all pure components and mixtures in this study. For the pressure rise method, constant pressure analysis during combustion is performed to determine the flame speed. The minimum and maximum flame radius used for post processing is determined as the radius at 20% pressure rise and 78 mm, respectively. While the maximum flame radius is restricted by the combustion chamber geometry, the minimum flame radius is identified by low stretch rate regime from previous studies [24]. The burning velocity is calculated as the pressure rises using thermodynamic data from the multi-zone BOMB program [25] where schlieren imaging was used to detect the onset of cellularity. The reason for detecting the onset of cellularity is that when the cellular structure forms in a spherically expanding flame, the area of the flame is increased, which leads to faster burning velocity even if the local flame speed at the surface is not affected by stretch. The models for

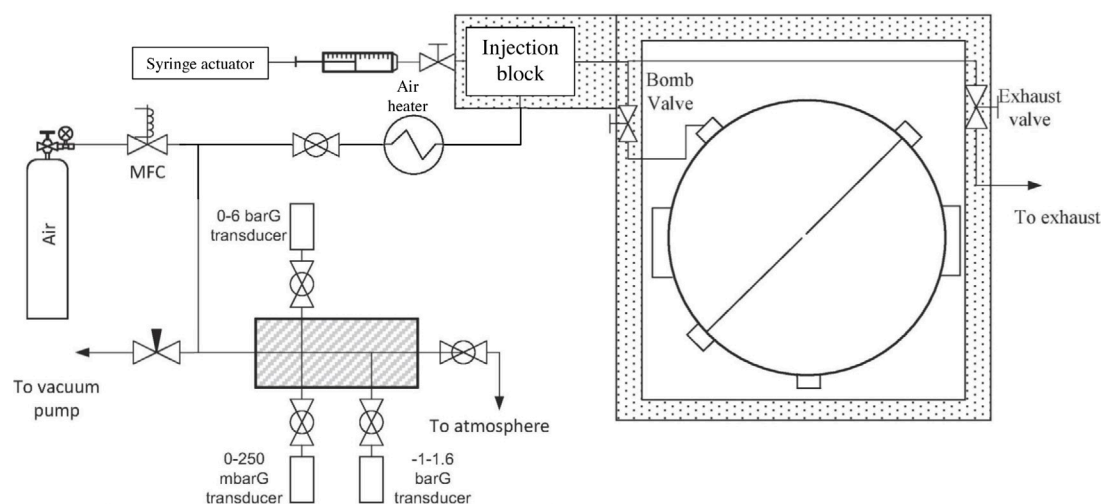


Fig. 1. Schematic diagram of the liquid fuel mixture preparation system adapted from Hinton et al. [21].

Table 1

Test conditions of the pure components, binary and ternary blends.

Fuel (pure components)	iso-octane, n-heptane, ethanol
Fuel (binary components 50/50%vol)	EH, EO, OH
Fuel (ternary components 33.3/33.3/33.3%vol)	EHO
Initial pressure (bar)	1, 2, 4
Initial temperature (K)	380, 450

constant pressure and constant volume propagation assume a smooth spherical surface, therefore, once cellularity has occurred, the value calculated based upon these models will be erroneous. The detailed processes of extracting burning velocities by both methods are included in Hinton et al. [21]. The use of pressure rise method enables the collection of burning velocities over an increased range of temperatures and pressures making it possible to obtain a large number of data points from a single experiment. The reconciliation of the above mentioned two methods have also been reported in Hinton's previous work [24] where detailed sources of errors are identified including three categories: type (1) those associated with mixture preparation, type (2) combustion measurements and type (3) data analysis. In summary, the likely error range in mixture preparation is +0.5 to -0.4%. With flame speed measurements, the only significant error is that associated with extrapolation to zero stretch, and this is estimated to be about 3%.

Previously, the same apparatus has been used to characterise pure components of EHO over a range of high pressures and temperatures. Detailed correlations for each pure fuel components were also established over more than 400 experiments [22,24]. As the focus of this work is to study the impact of ethanol on individual PRFs, the test conditions (shown in Table 1) are selected to measure the LBV of equal volume binary and ternary mixtures of ethanol, n-heptane, and iso-octane.

Equal volume blends of binary and ternary fuel are specifically chosen to enable clear distinction on the impact of each of the components on laminar burning velocities. This approach contrasts with prior works in the literature where PRF blend compositions are typically chosen to match the octane number of commercial fuels, resulting in blends with a substantially greater quantity of iso-octane than n-heptane, see [26] for example. For the same reason, most studies on ternary EHO mixtures have focused on blends containing unequal proportions of iso-octane, n-heptane, and ethanol [27]. EH blends do not have comparable properties to a commercial fuel and therefore are not well documented in the combustion literature, however they are presented in this work as an aid to understanding of chemical kinetics.

Table 2

Summary of reaction mechanisms used in the present work.

Ref	Authors	Fuels	Species-Reactions	Origin
M1	Li et al. [36]	ETPRF	59–270	KAUST [29]
M2	Wu et al. [34]	ETPRF	165–839	LLNL [35]

3. Modelling details

For all experimental conditions investigated, corresponding laminar burning velocities were computed using the PREMIX module of ChemkinPro 19.0. The equations governing the steady, isobaric, quasi-one-dimensional flame propagation can be found in the manual [28]. The burning velocity model involves a freely propagating flame. This configuration is used to determine the LBV of the gas mixture at a specified pressure and inlet unburned temperature. An assumption is made that there are no heat losses and the temperatures are computed from the energy equation. The model also assumes one-dimensional flow with uniform inlet conditions when determining the transport of heat. To ensure grid convergence, grid parameters CURV and GRAD were set to 0.01 and 0.05, respectively. The solver was set up for maximum and adaptive grid points at 5000 and 500, respectively.

Computationally, flame instabilities are usually avoided by the assumption of a one-dimensional, planar flame. Thus, the accuracy of the predicted burning velocities depends on the accuracy of the molecular transport coefficients, the realism of the chemical kinetic reaction scheme, and the accuracy of the rate constants [29]. Therefore, it is important to select a suitable chemical kinetic mechanism that are designed for the compositions in this study and are updated recently. While it is possible to use large chemical mechanisms for the simulation of laboratory flames [30,31], for high-fidelity simulations or full-cycle engine simulations reduced/skeletal mechanisms are most often adopted [32,33]. Therefore, in this study two commercially available chemical mechanisms with different origins and reduction methods were considered [29,34–36] (see Table 2).

The first mechanism, referred to as M1, is a reduced four-component, toluene/n-heptane/ethanol/iso-octane (THEO), gasoline surrogate kinetics mechanism developed by Li et al. [36]. The model was validated against various experimental data (ignition delays and LBVs) for different ethanol concentrations. The results obtained with THEO mixtures containing 27.5%/20%/8.2%/44.3% by liquid volume, respectively, suggested that the model can qualitatively predict the experimental trends. The second mechanism, referred to as M2, is based on the work of Wu et al. where three different reduction techniques

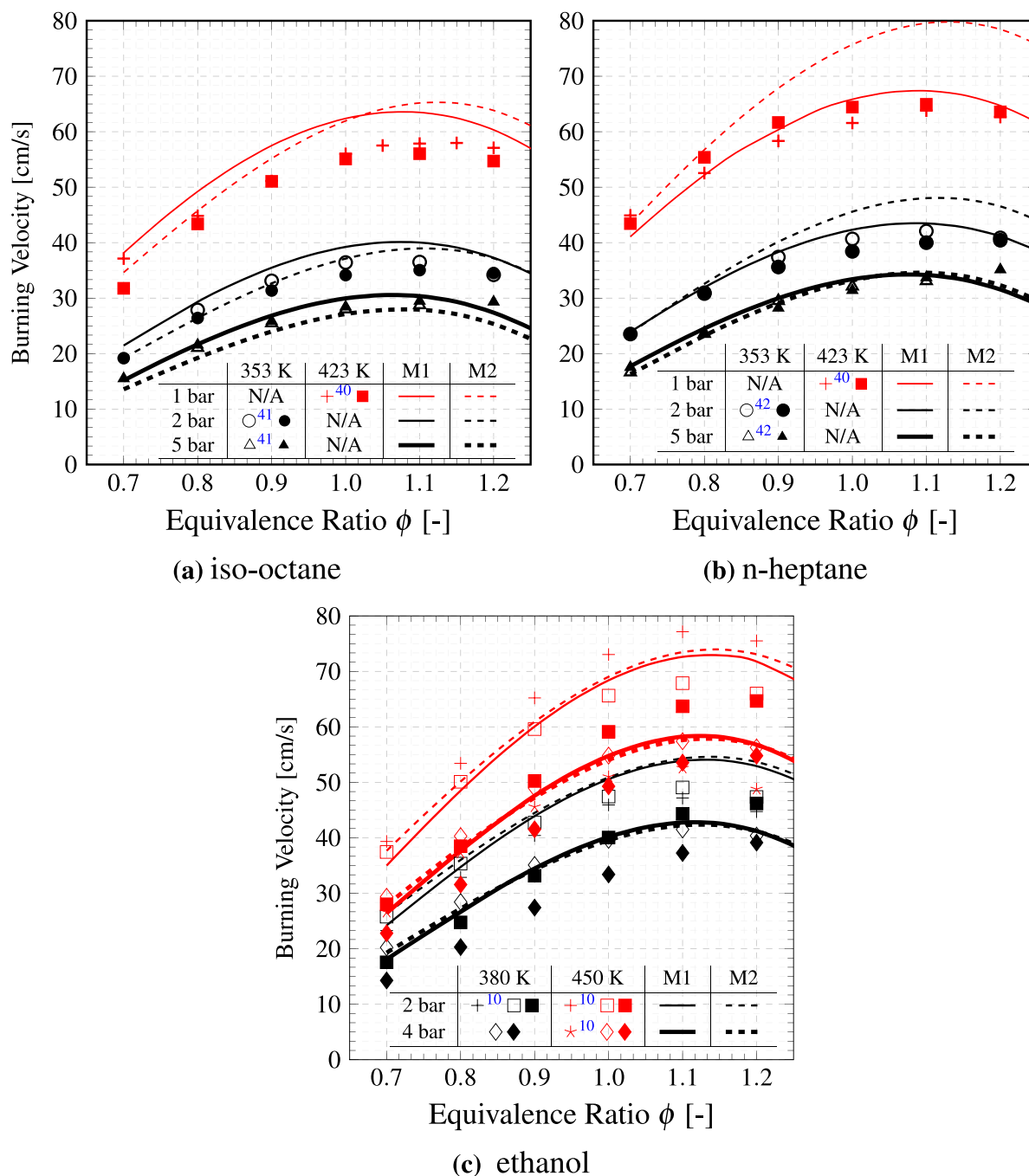


Fig. 2. Comparison of M1 [36] and M2 [34] across equivalence ratio range for pure components. All solid filled scatter data marks are derived from Marshall et al. [22]. Additional experimental data (hollow marks) include (a) iso-octane at 2 and 5 bar at 353 K [37] and at 1 bar and 423 K [38], (b) n-heptane at 2 and 5 bar at 353 K [39] and at 1 bar and 423 K [38], and (c) ethanol at 2 and 4 bar at 380 K and 450 K from present work (squares and diamonds) and Meng et al. [10].

including isomer lumping were employed under a wide range of temperature, pressure, and equivalence ratio conditions relevant to modern internal combustion engines [34]. For THEO mixtures, experimental data by Cancino et al. on ignition delay times was employed [40]. Similarly, experimental measurements on LBVs of a THEO blend with 15%vol of ethanol from Dirrenberger et al. was included [41]. This skeletal mechanism was shown to be within the experimental error limits for both ignition delay times and LBVs in comparison to experimental data and the detailed mechanism on which it is based.

To interpret the chemical effect of the different fuel components in this study, a sensitivity analysis is performed using ChemkinPro 19.0. The sensitivity of the LBV with respect to each reaction is computed;

therefore, the reactions that affect the flame speed the most are identified and compared for different compositions, initial conditions, and mechanisms. It has previously been seen that for heavier fuels (such as n-heptane/iso-octane/ethanol), the sensitivity to pre-exponential factors is nearly one order higher than to fuel mass diffusivities, which indicates the chemical effect is dominant in heavy-molecule fuels [42].

4. Results and discussion

In this section, results from experiments are represented by data markers and results from kinetic models are represented by solid or dashed lines. Correlation coefficients from the pressure rise method are detailed in [Appendix](#).

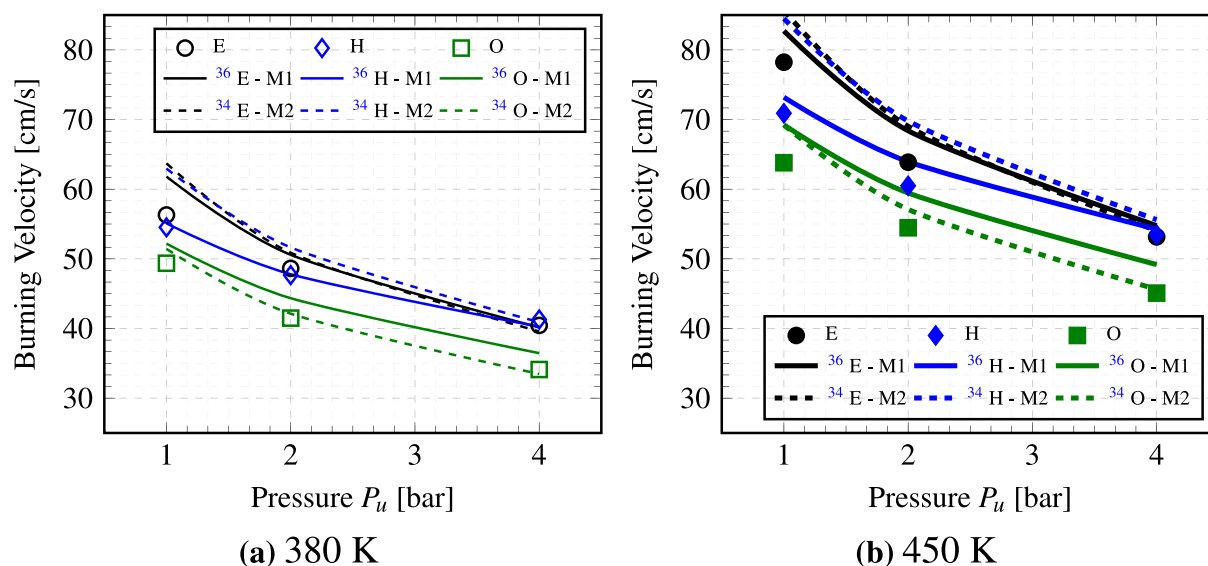


Fig. 3. LBVs at 1, 2, and 4 bar at (a) 380 K (hollow) and (b) 450 K (filled) for ethanol (circle), n-heptane (diamond) and iso-octane (square). Results from both mechanisms are presented as lines, M1 [36] (solid) and M2 [34] (dashed), at 380 K (thin) and 450 K (thick).

4.1. Pure components

Fig. 2 shows the prediction capabilities of M1 and M2 for each of the pure components (iso-octane, n-heptane, and ethanol) at different initial conditions. Looking at Fig. 2(a) (iso-octane) it is seen that the simulation results from both mechanisms closely follow the experimental data trend at the higher pressure conditions across the equivalence ratio range. At 1 bar and 423 K, the experiments, despite using different measurement techniques, show a close match across the equivalence ratio. A systematic overprediction at same conditions, however, is shown for both mechanisms. This is likely due to the overprediction of the original mechanism's temperature exponents as detailed by Konnov et al. [7]

Looking at Fig. 2(b) (n-heptane) it can be seen that the predictions of n-heptane's LBV at lower pressures and higher temperatures illustrate a significant discrepancy in M2's capability. This may be because the original detailed mechanism used to reduce to form M2 was not validated for propagating flames due to the mechanism's large size as observed by Jerzembeck et al. [26] Furthermore, Wu et al. have noticed similar over-predicting behaviour for their skeletal kinetic mechanism [34]. They observed that the detailed model used for constructing the skeletal mechanism was over-predicting the LBV values of EHO blends at atmospheric pressure and stoichiometric conditions [35]. Therefore, when comparing the skeletal mechanism (M2) to flame experiments for n-heptane, a consistent trend is observed for all data at low pressure and 298 K, in which the simulated burning velocities are much higher than the experimental values. On the other hand, data at higher pressures and temperatures are either predicted correctly or slightly under-predicted by the skeletal mechanism.

For pure ethanol (Fig. 2(c)), while the pressure and temperature effects are captured by both the mechanisms and experiments, significant lower measurements were recorded by Marshall et al.'s pressure rise method. It is worth noting that the preliminary work of Marshall et al. assumed zero stretch when applying the density ratio to obtain the burning velocities. While the mean stretch rate reported for iso-octane for the tested conditions was only 40.8 s^{-1} making it reasonable to assume no stretch, using the same arguments for the higher temperature conditions of ethanol might be erroneous [24]. Identification of these errors and their causes has enabled further development of the experimental techniques allowing flame speed and burned gas

Markstein length data measured at the same time. Hinton et al. collected additional stretch corrected experimental data using the same combustion bomb facility with both flame front imaging and pressure technique [24] where the reconciliation of these two techniques are reported for the first time in the open literature. As shown in Fig. 2(a), the stretch corrected ethanol data is found to be consistent with the literature using the same technique. However, similar to iso-octane, the predictions at higher pressures present a closer match the experimental data, where at lower pressures and higher temperatures, 423 K, both the mechanisms over-predict LBV. M2's LBV predictions are shifted towards richer equivalence ratios, compared to M1.

In order to account for the effect of stretch and provide a baseline comparison for the binary mixtures and ternary mixtures, Fig. 3 shows additional pure component LBVs collected at elevated temperatures and pressures using both flame front imaging and pressure rise methods. It is clearly seen that ethanol has the highest LBV followed by n-heptane and then iso-octane under all conditions examined (this hierarchy of pure component burning velocities is consistent with previous measurements reported in the literature [8,38,41]). The results show that the difference in the LBVs for each of the components is greater at 450 K than it is at 380 K. This is particularly noticeable between ethanol and n-heptane and at lower pressures. Moreover, the current results suggest that ethanol is more strongly affected by increases in temperature and pressure than n-heptane and iso-octane. This differential behaviour is predicted with both mechanisms, albeit with a significantly greater difference in pressure dependence predicted by M1 than M2. Considering the relative performances of the two mechanisms for iso-octane, M1 and M2 both predict similar LBVs at both temperatures and atmospheric pressure; however, the results presented in Fig. 3 clearly demonstrate that M2 is better able to capture the pressure dependence of iso-octane, which is noted to be greater than that of n-heptane at lower temperature.

In summary, both ethanol and iso-octane's LBVs display a stronger negative pressure dependence than n-heptane. The results further show that the greatest difference in the experimentally determined LBVs for the pure components occurs 450 K. It is notable therefore that, whereas M1 predicts a distinct difference in LBV between ethanol and n-heptane at this condition, M2 does not.

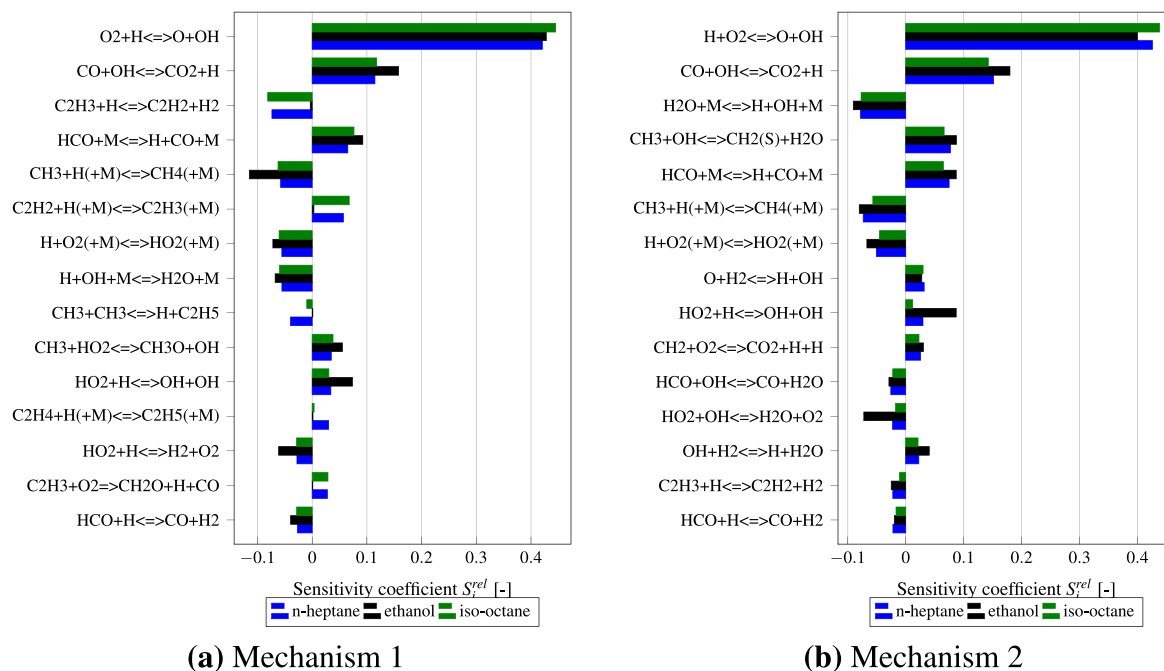


Fig. 4. Sensitivity analysis comparing the 15 most (absolute) sensitivity coefficients S_i of (a) Mechanism 1 [36] and (b) Mechanism 2 [34] on the predictions of the pure component's LBV at 2 bar and 450 K.

4.1.1. Sensitivity analysis

Because of these differences between mechanisms observed, a sensitivity study was performed at 2 bar and 450 K to highlight key differences between the mechanisms, M1 and M2. The results of these sensitivity analyses are shown in Figs. 4(a) and 4(b), where a positive sensitivity coefficient shows the reaction's influence in increasing the LBV and a negative sensitivity coefficient shows the opposite.

While fuel-specific reactions can affect the LBV to some extent, based on the sensitivity analysis for different fuels [43], reactions directly related to H radical is found to have the largest impact on LBV. The key chain branching reaction in any hydrogen containing system is R1:



Any reaction that produces the H radicals needed by R1 can increase the overall fuel oxidation rate and thereby promote the combustion process. Ethanol's greater LBV can be, therefore, partly attributed to increased production of CO which reacts with the OH radical to form CO_2 and H radicals (R2). The CO is formed through the chain carrying reaction, R3, from the formyl radical, HCO, as shown below.



For the above mentioned two reactions, ethanol displays a greater positive sensitivity using both mechanisms as seen in Fig. 4, which in turn helps accurate prediction of ethanol LBV at the conditions tested. Moreover, Reaction (R4) shows acetaldehyde's (CH_3CHO) decomposition to formyl radicals, inferring a direct link between ethanol and the increased production of HCO.



The acetaldehyde itself has its origins in the H-atom abstraction of ethanol which leads to one of three isomeric $\text{C}_2\text{H}_5\text{O}$ radicals that undergo secondary H-atom abstraction to form α -hydroxyethyl radical ($\text{CH}_3\text{C}\cdot\text{HOH}$). This unimolecularly decomposes to yield a radical and acetaldehyde [44].

For the study of n-heptane and iso-octane LBVs, both mechanisms predict similar values for iso-octane across various equivalence ratios, temperatures and pressures, however, significant differences are observed in pure n-heptane component for all data at low pressure. Previous chemical kinetics studies have suggested the oxidation of a linear alkane, such as n-heptane, produces a greater quantity of ethylene (C_2H_4), whereas the primary intermediates for a branched alkane, such as iso-octane, include propene, iso-butene, and methyl radicals [45]. These decompose to allyl radicals (CH_2CHCH_2), whereas ethylene oxidises to the vinyl radical (C_2H_3) which is more reactive, leading to a comparatively faster LBV for n-heptane. As shown in Fig. 4, these reactions are better emphasised in M1 than M2. This could again be related to the original mechanism not being validated for propagating flames due to its large size. In order to reach a better agreement between simulated and experimental pure n-heptane LBVs at low temperature (less than 1000 K) for mechanisms of this origin, Jerzembeck et al. suggested those reaction rates most sensitive to flame propagation, but fairly insensitive to homogeneous cases need to be updated [46]. While M2 retains both the high and low temperature chemistry, which are extremely different in the case of large molecules such as n-heptane and iso-octane and important for engine relevant turbulent flame simulations, for the study of propagating flame, additional adjustment might be needed. Therefore, for the following sections sensitivity analysis relevant to pure n-heptane and its respective binary/ternary mixtures is conducted using M1 only.

4.2. Binary mixtures

Fig. 5 shows LBVs from both the pressure rise (correlation) and flame front imaging (circle scatter data) techniques for a 50/50%vol/vol EO mixture at varying temperatures and pressures. Good agreement between the flame front imaging and pressure rise techniques is observed across the temperature and pressure range. The data is also seen to be both consistent with prior results at 1 bar and is now extended to a higher temperature range. Beeckmann et al. [47] showed that, for lean mixtures with 10% ethanol, the blend resulted in higher burning velocities than either pure component. Although only stoichiometric blends are tested here, such behaviour is not apparent at the conditions

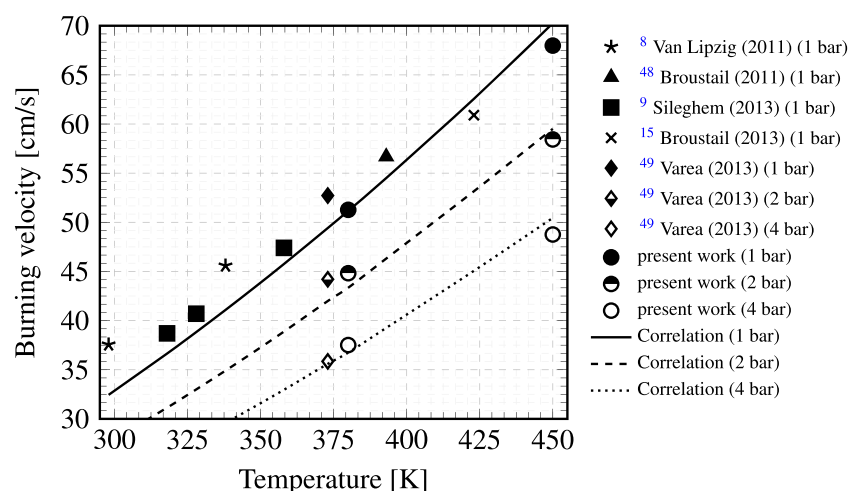


Fig. 5. Comparison of ethanol/iso-octane-air mixtures (50/50 vol/vol) across a temperature range from 298 K to 450 K and a pressure range of 1 to 4 bar at an equivalence ratio of 1. Correlation lines are derived from the pressure rise method. Additional experimental data from the literature is included for comparison [8,9,15,48,49].

tested. While a direct comparison of the pure and binary mixtures of ethanol and iso-octane is not presented separately here, the blend's burning velocity observed from Fig. 5 is found to be bounded by that of the pure components from Fig. 3, advocating the use of a simple mixing rule for EO mixtures. Previous studies have investigated the performance of using different mixing rules suggesting the modified Le Châtelier rule can be used to predict the laminar burning of the EO mixture well [17].

LBVs of n-heptane and its equal volume blends with iso-octane and ethanol are shown in Fig. 6. The results show the OH mixture LBV to be bounded by pure n-heptane and iso-octane LBV and close to the average of pure components, consistent with the M1 predictions. In contrast, the EH mixture's burning velocities, shown in Fig. 6(d), are not, with the experimental data showing EH has the lowest LBV at 380 K but both of the mechanisms showing H should. While direct comparison of the current study with the literature is not possible as a large discrepancy of EH mixture data is found likely due to the high value of temperature exponent of EH mixture when extrapolating to low temperature, the same non-linear behaviour for EH blends is seen at lower temperature and ambient pressure by Van Lipzig et al. [8]. The non-linearity can be attributed to the different stoichiometric coefficients for oxidation of the binary fuel components. Perhaps more interestingly, both the experiments and numerical simulations (M1 & M2) show that at higher pressure the binary mixture is giving lower LBVs compared to any of the pure components. This suggests that whilst simple mixing rules are suitable for mixtures such as EO, they might not be able to represent mixtures such as EH especially at elevated pressures and temperatures.

A direct comparison of the three binary mixtures is shown in Fig. 7. It can be seen that the EH mixture's LBV is greater than the LBVs of the EO and OH mixtures and the difference is greater at low pressure and high temperature conditions. Perhaps, this is to be expected as both pure ethanol and n-heptane have high LBVs. As the pressure increases, the LBV of the OH blend becomes slightly greater than EO. Whilst this change appears insignificant at 380 K, it is just visible at 450 K. As seen previously, the presence of ethanol increases the pressure sensitivity of the EO mixture's LBV. While the numerical simulations from both mechanisms were able to capture the pressure dependencies for all binary fuels, a significant discrepancy is found with M2 predictions for binary mixtures including n-heptane, which is consistent with the pure component section.

4.2.1. Sensitivity analysis

In order to review critical radicals and reactions relevant to the LBVs of n-heptane binary mixtures (EH and OH), sensitivity analysis

is performed using M1. H radical generation and consumption reactions play an important role in accelerating and suppressing the flame propagation. Figs. 8(a) and 8(b) shows the H radical distribution in the quasi-one-dimensional propagating flame for the EH and OH binary mixtures at 380 K and 450 K, respectively. The highest concentration is seen at 1 bar, and the lowest at 4 bar. Interestingly, at 450 K, as the pressure increases, the peak in H radical concentration of EH mixture becomes lower than OH mixture. This may be because ethanol has a greater suppressing effect on n-heptane's low temperature heat release (LTHR) than iso-octane. The flame speed inhibiting reactions that affect the small molecule radical pool, such as the consumption reaction (R5) of OH shown below, is also reviewed.



Fig. 9 shows the sensitivity of R5 for ethanol, n-heptane, and their binary mixture at 450 K and at 2 and 4 bar. Although the magnitude is significantly lower, it can be seen that the EH mixture's sensitivity to consuming the OH radical and inhibiting the flame speed is greater than its constituents of ethanol and n-heptane. Furthermore, in line with the trend observed in Fig. 8, this effect is greater at the higher pressure condition.

Fig. 10 presents a sensitivity analysis of all three binary blends at 1 and 4 bar for both temperatures of 380 K and 450 K using mechanism M1. The results show the sensitivity of three-body termination reactions such as R6 increases with the pressure:



The literature shows that R6 does not compete effectively with R1 under sub-atmospheric pressure conditions for pure components [43], and that under these conditions any LBV decrease due to R6 is readily compensated by a rise in temperature such that there is only a very small reduction in the flame speed. However as the pressure increases, the reduction in the flame speed from these reaction becomes more pronounced. As the kinetic trend with pressure exists for all hydrocarbons, the same pressure effects on the laminar flame speed are observed in the binary fuels analysed in this study. For all binary fuels, the three-body reaction R6 is found to compete more effectively with the two-body reaction R1 above 1 bar, resulting in a steeper decline in the flame speed. Moreover, Fig. 10 also indicates that EO, compared with OH, presents a higher negative coefficient for R2 — suggesting further consumption of H radicals to form stable radicals leading to lower LBV. This corresponds well with the experimental data where the LBV of the OH blend becomes higher than EO for the same temperature at high pressure.

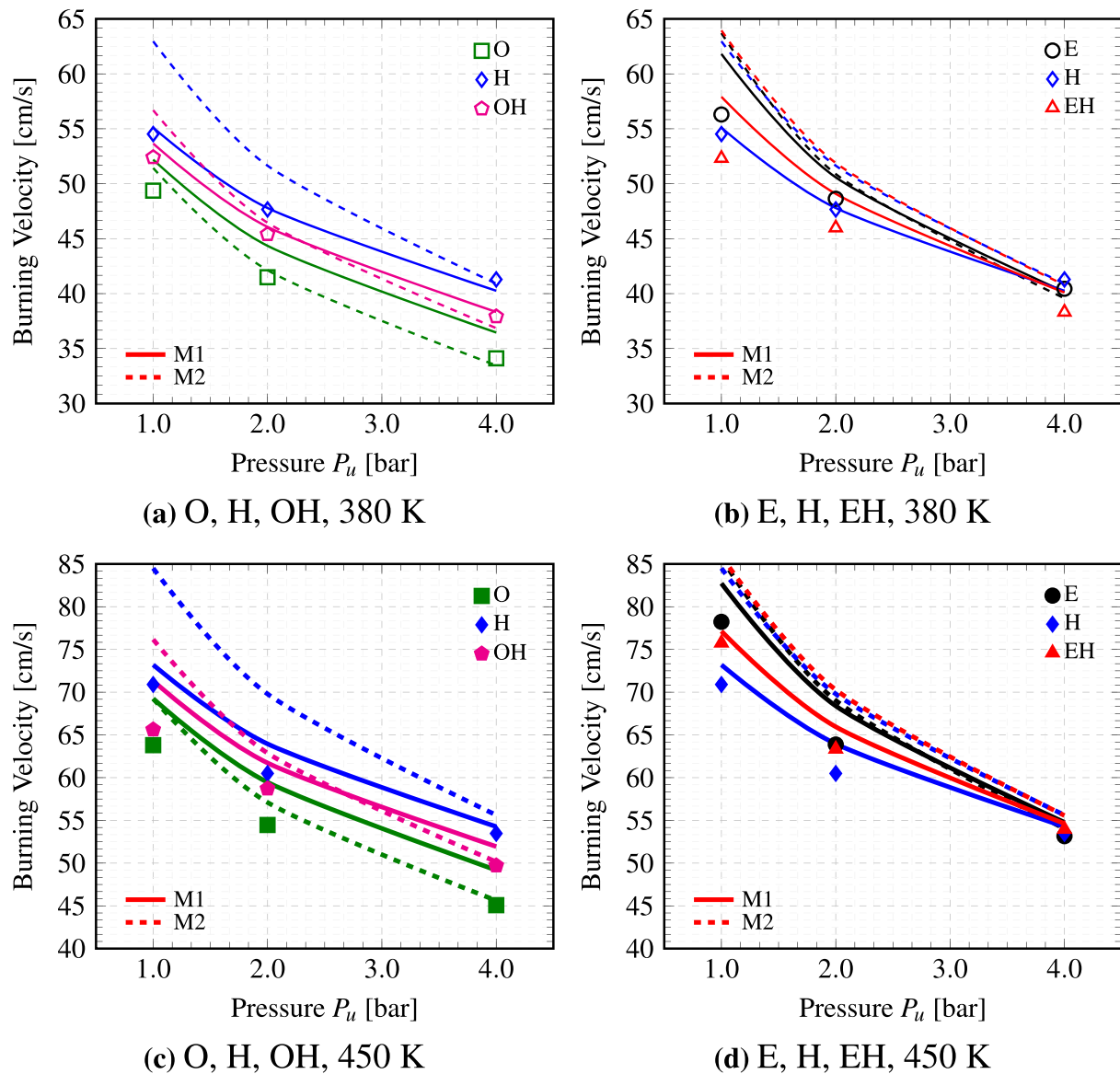


Fig. 6. Pure components versus binary mixtures for: ethanol (E) (circle), iso-octane (O) (square), n-heptane (H) (diamond), OH (pentagon) and EH (triangle) at 380 K (hollow) and 450 K (filled) at pressures of 1, 2, and 4 bar at an equivalence ratio of 1. Results from both mechanisms are presented as lines, M1 (solid) and M2 (dashed).

4.3. Ternary mixtures

Fig. 11 shows the LBVs for an equal volume fraction ternary mixture (EHO) in comparison with the PRF binary mixture (OH), which has already been presented. The experimental observations show only minor differences between the OH (PRF) blend and the EHO (EPRF) blend LBVs at 380 K at all pressures considered. While the differences between EHO and HO is observed at 450 K, as the pressure increases further drop of EHO is found. This confirms the observations previously made in binary mixtures highlighting the strong pressure dependence of ethanol and the resulting implication of ethanol addition. At 450 K, the experimental results indicate that the addition of ethanol to an OH mixture to produce an equal volume fraction mixture results in a $\sim 6\%$ increase in LBV at 1 bar. As the pressure increases, EHO mixture's LBV decreases at a greater rate than does the OH LBV resulting in less than 1% difference between the LBVs of the two blends at 4 bar. This demonstrates the significance of ethanol on the pressure dependence of the blend's LBV at higher temperatures. The results shown in Fig. 11 demonstrate that the reactivity of iso-octane is independent of ethanol as the comparison between EH and EHO shows an uniform reduction

in LBV at 450 K. On the other hand, comparing EO and EHO, the ternary mixture displays greater LBVs as both ethanol and n-heptane are reactive. Finally, the data presented in Figs. 3 to 11 shows that in all cases, even when the burning velocities of the neat fuels and their mixture are very close the hierarchy of LBVs is never biased by the experimental uncertainty rising from either pressure rise or flame front imaging techniques. This indicates, in turn, the efficacy of the evaluated accuracy of the measurements and the consistency of different series of experiments with neat fuels and their mixtures.

5. Further properties

For all fuels conditions presented in this study, trends in Markstein lengths were also investigated. Burned gas Markstein lengths are obtained from the gradient of the linear extrapolation of flame speed data. Figs. 12(a) and 12(b) shows the burned gas Markstein lengths for the pure and binary mixtures at 380 K and 450 K, respectively. It can be seen that the burned gas Markstein lengths are positive for all stoichiometric mixtures and pure components. Whilst the same general trends with pressure are seen for all the fuel components and blends,

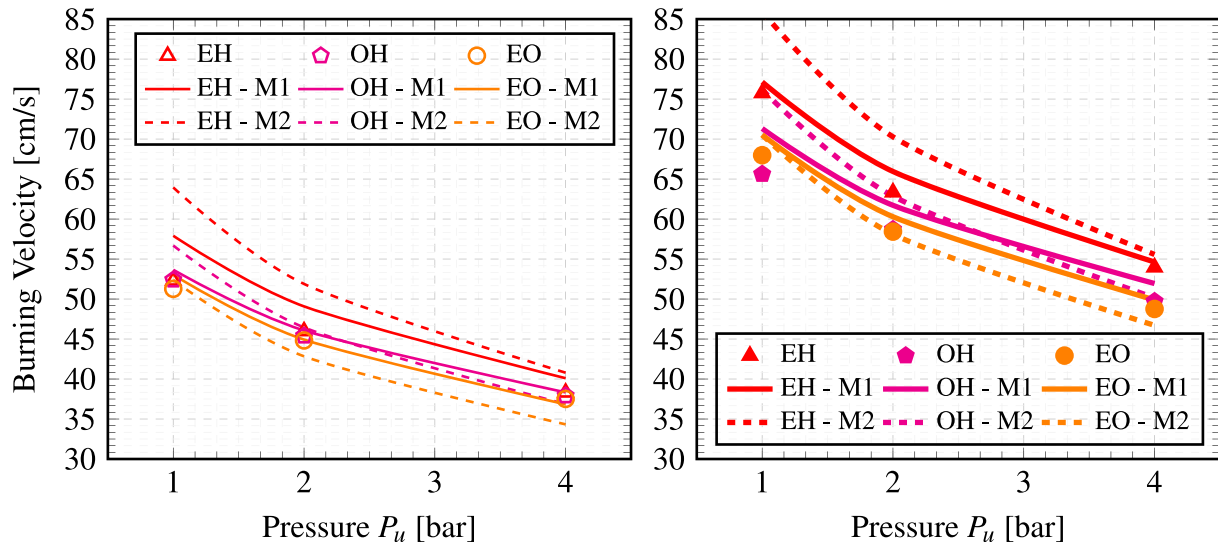


Fig. 7. Experimental results comparing equal volume binary (EH, OH, EO) mixtures. Conditions presented are at (a) 380 K (hollow) and (b) 450 K (filled) at pressures of 1, 2, and 4 bar at an equivalence ratio of 1. These results are from the current work.

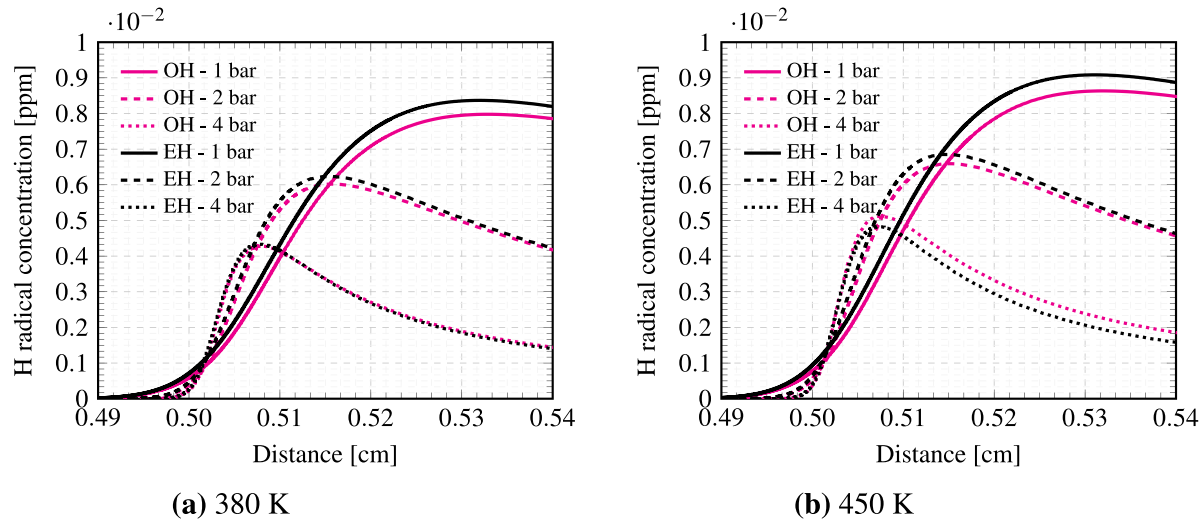


Fig. 8. Simulation results comparing H radical concentrations for OH and EH binary mixtures at (a) 380 K (b) 450 K.

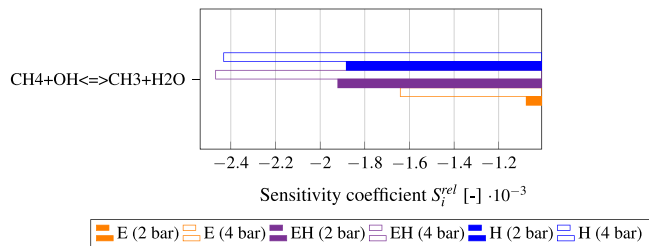


Fig. 9. Sensitivity analysis of reaction R5 at 450 K, 2 and 4 bar, for ethanol, n-heptane, and their binary mixture. These results are generated using M1 [36].

there is no consistent trend with regards to the relative Markstein lengths of the blends. Indeed, it does not appear that the Markstein lengths of blends can be represented by mixing rules in the same way as burning velocities have been even for mixtures such as ethanol and iso-octane. Previously Broustail et al. [48] presented burned gas Markstein lengths for their blends of iso-octane and ethanol, and generally found that the value for the blend would be bounded by the pure

components, however inconsistencies are observed from their studies. The difficulties in determining Markstein lengths experimentally with the spherically expanding flames and the results observed in this study suggest additional studies might be needed for these fuel components and their mixtures.

6. Summary and conclusions

In this work, experimental LBV results of pure, binary, and ternary mixtures of iso-octane, n-heptane, and ethanol obtained using the constant volume combustion bomb with a schlieren imaging system are presented. Both flame front imaging and pressure rise techniques are used to determine LBV. These experimental results are compared to two chemical kinetics mechanisms.

The results show that:

1. For pure components, the hierarchy of LBVs from the highest to the lowest is as follows: $E > H > O$.
2. Reconciliation between two distinct techniques (flame front imaging and pressure rise rate) is demonstrated for ethanol/iso-octane mixtures at all tested conditions highlighting the accuracy of the measurements.

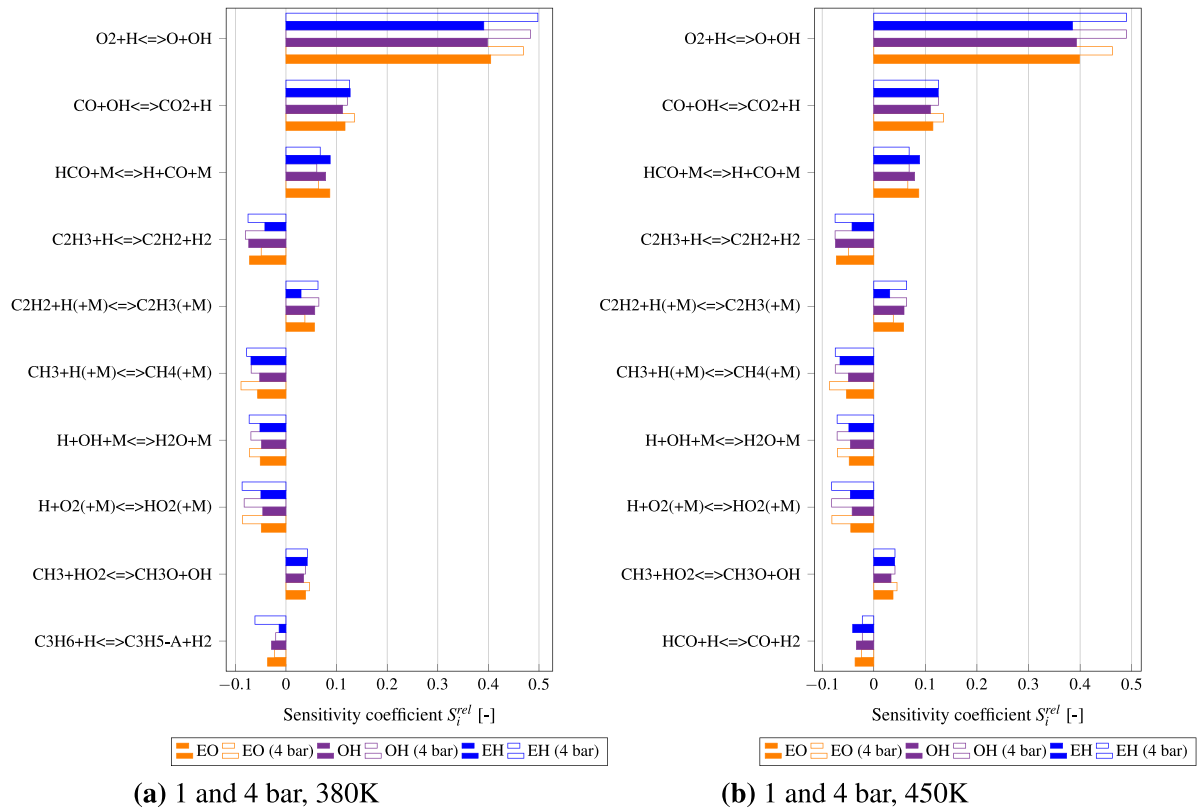


Fig. 10. Sensitivity analysis showing the top 10 reactions that affect the LBV based on absolute sensitivity coefficients S_i for the binary mixtures at 1 (filled) and 4 (hollow) bar at: (a) 380 K; and (b) 450 K. These results are generated using M1 [36].

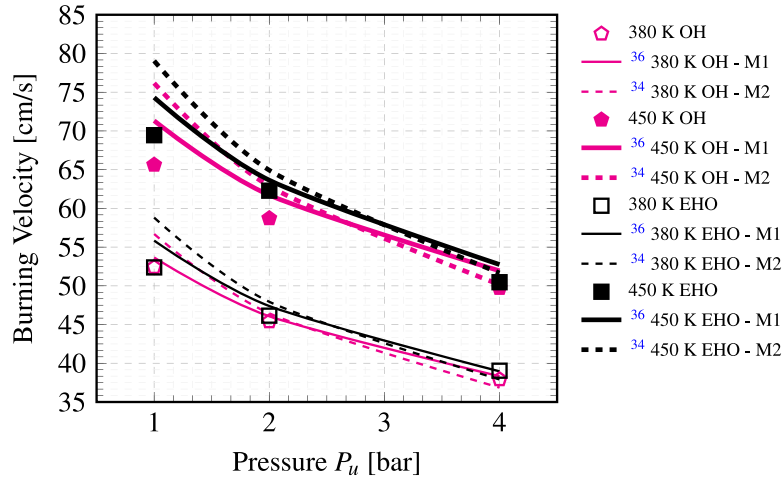


Fig. 11. Experimental results comparing equal volume binary OH (PRF) versus ternary EHO (EPRF) mixtures. Conditions presented are at 380 K (hollow) and 450 K (filled) at pressures of 1, 2, and 4 bar and at stoichiometric conditions.

3. The LBV of ethanol displays a strong pressure dependence particularly at higher temperatures, particularly in the ternary mixture (EHO).
4. Previous studies have suggested mean stretch rate for the tested iso-octane using the same experimental setup is small, making a no stretch assumption reasonable. However, higher temperature conditions involving ethanol show that the effect of stretch is significant. Therefore, linear extrapolation is applied to the spherical flames studied.
5. While both chemical kinetics models were able to capture temperature and pressure dependence of pure components, significant discrepancy is found for n-heptane LBV predictions between

mechanisms suggesting reaction rates most sensitive to flame propagation need to be updated.

6. The chemical kinetics study helped understand the LBV pressure shown by ethanol, demonstrating that, for an H-radical abstraction process, a stronger competition in OH radical consumption exists between n-heptane and ethanol at higher pressure resulting in an overall lower mixture LBV.
7. Positive burned gas Markstein lengths are observed for all stoichiometric mixtures and pure components. The Markstein length of the blends does not appear to follow either the mixing rule or be bounded by the pure components at the conditions tested.

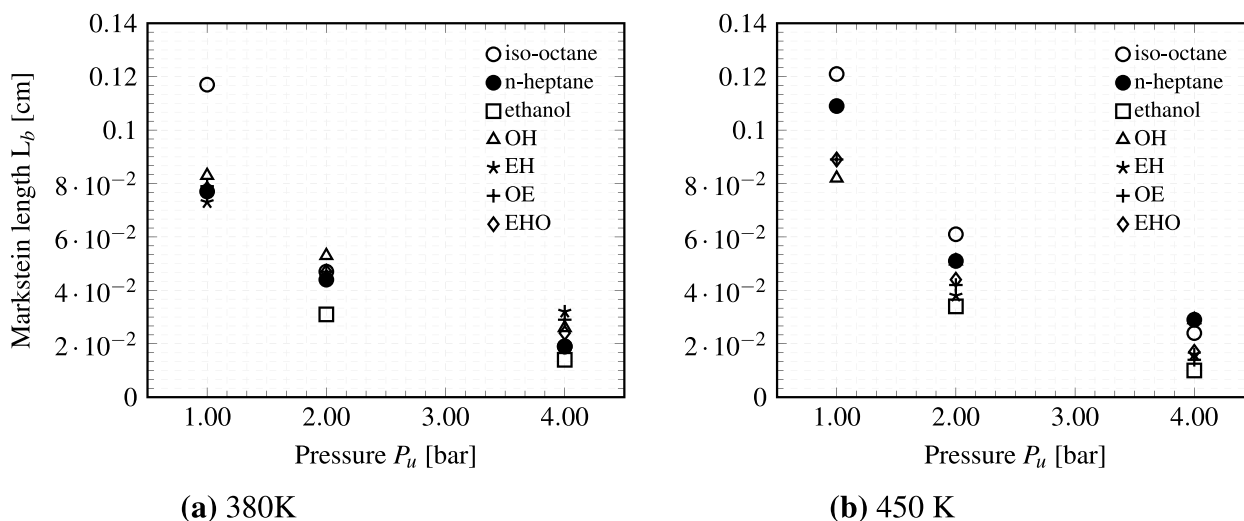


Fig. 12. Burned gas Markstein lengths for EHO components and blends at unburned temperatures of 380 K and 450 K at stoichiometry and across the pressure range from 1 to 4 bar.

Table 3

Iso-octane/air and ethanol/air measurement ranges given respectively by Marshall et al. [22] and Hinton et al. [21].

Fuel mixture	ethanol (E)		n-heptane (H)		iso-octane (O)	
	%vol	%mol	%vol	%mol	%vol	%mol
EH	0.50	0.71	0.50	0.29	0.00	0.00
OH	0.00	0.00	0.50	0.53	0.50	0.47
EO	0.50	0.74	0.50	0.26	0.00	0.00
EHO	0.33	0.57	0.33	0.23	0.33	0.20

Table 4

Manufacturer and minimum purity of fuels tested (iso-octane, n-heptane, and ethanol).

Fuel mixture	Minimum purity (%)	Manufacturer
iso-octane	99.75	Chevron Phillips
n-heptane	99.00	Fisher Scientific
ethanol	99.86	Hayman

- When comparing the binary mixtures and their constituent pure components, the LBV of the EH and EO is found to follow mixing rules while EH does not.

This last point leaves the following question unanswered: whether mixing rules are suitable for the evaluation of LBVs of different binary mixtures especially when the constituent components present similar LBVs.

Definitions/abbreviations

LBV	Laminar burning velocity
SI	Spark ignition
E	Ethanol
H	N-heptane
O	Iso-octane
EH	Ethanol/n-heptane mixture
OH	Iso-octane/n-heptane mixture
EO	Ethanol/iso-octane mixture
EHO	Ethanol/iso-octane/iso-octane mixture
ON	Octane number
SF	Spherical flame
PRF	Primary Reference Fuel
CF	Counter flow

HF	Heat flux
THEO	Toluene/n-heptane/ethanol/iso-octane mixture
LLNL	Lawrence Livermore National Laboratories
KAUST	King Abdullah University of Science and Technology
S_l	Laminar burning velocity
S_l^{rel}	Relative (normalised) sensitivity coefficient
A	Pre-exponential factor
T_u	Unburned temperature
P_u	Unburned pressure
ϕ	Equivalence ratio
M1	Mechanism 1
M2	Mechanism 2
ARC	Advanced Research Computing

CRediT authorship contribution statement

V. Shankar: Investigation, Formal analysis, Writing – original draft. **X.H. Fang:** Conceptualisation, Investigation, Writing – original draft. **N. Hinton:** Reviewing, Data collection. **M. Davy:** Methodology, Reviewing and editing, Funding acquisition. **F.C.P. Leach:** Methodology, Reviewing and editing, Funding acquisition.

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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Table 5

Coefficient values to calculate burning velocities for Eq. (1), valid for both fuels within the range of $340 \leq T_u \leq 640$ K, $0.7 \leq P_u \leq 6$ bar and $0.7 \leq \phi \leq 1.3$.

Fuels	$S_{u,0}$	$S_{u,1}$	$S_{u,2}$	$S_{u,3}$	$S_{u,4}$	α_0	α_1
Ethanol (E) (Marshall) et al. [22]	27.47	46.80	-81.89	-71.44	374.6	2.301	-1.548
Ethanol (E) (Current)	35.616	21.159	-130.38	-38.952	79.839	1.9195	-0.2463
Iso-octane (O)	28.48	13.11	-80.05	56.59	57.73	1.889	-0.08456
N-heptane (H)	31.76	12.99	-52.45	56.58	-161.2	2.026	-1.548
EH	31.021					2.0797	
OH	33.505					1.8612	
EO	32.530					1.8746	
EHO	32.924					1.8975	
	α_2	β_0	β_1	β_2	μ_1	μ_2	μ_3
Ethanol (Marshall) et al. [22]	0	-0.2625	0.1186	0	1.813	0.7961	-0.3401
Ethanol (Current)	2.3624	-0.2596	0.2100	-0.3089	1.4380	1.4111	0.20056
Iso-octane	0	-0.1997	0.1074	0	2.081	0.8283	0.02103
Heptane	0	-0.2201	0.3305	0	1.990	0.8337	0.2552
EH		-0.24068					
OH		-0.26054					
EO		-0.2383					
EHO		-0.23078					

Note: (i) the LBV correlation for pure ethanol has not been extended to include the residual mole fraction. (ii) the LBV correlation for binary mixtures is only applicable to equivalence = 1.

Appendix

Volumetric conversion for tested fuels

The volume to molar fraction conversion for each of the blends tested can be found in Table 3.

Fuel purity

The manufacturer and purity of the fuels can be found in Table 4:

Laminar burning velocities correlations

LBV correlations from the pressure rise method for neat ethanol, iso-octane and n-heptane are characterised by 14 coefficient terms, defined as follows:

$$S_u = \left[S_{u,0} + S_{u,1}(\phi - 1) + S_{u,2}(\phi - 1)^2 + S_{u,3}(\phi - 1)^3 + S_{u,4}(\phi - 1)^4 \right] \times T^\alpha \times P^\beta \times \left[1 - \mu_1 x_r^{(\mu_2 + (\phi - 1)\mu_3)} \right] \quad (1)$$

with,

$$\alpha = \alpha_0 + \alpha_1(\phi - 1) + \alpha_2(\phi - 1)^2 \quad (2)$$

$$\beta = \beta_0 + \beta_1(\phi - 1) + \beta_2(\phi - 1)^2 \quad (3)$$

$$P = \frac{P_u}{1.0} \quad T = \frac{T_u}{298} \quad (4)$$

where x_r is the mole fraction of the residual gases. The LBV correlation coefficients for each fuel component are given in Table 5.

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