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## Effect of Ethanol Addition on the Laminar Burning Velocity of Gasoline Surrogates with Toluene

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### ABSTRACT

*Laminar burning velocity (LBV) is a crucial parameter in many practical combustion simulations, and the acquisition of LBVs is a critical step for evaluating potential alternative fuels and/or suitable surrogates. Ethanol is regarded as one of the most promising alternative fuels, particularly for spark ignition engines, as it may be produced from renewable biomass. While there exists data showing the pressure dependence on ethanol's LBV compared to iso-octane and n-heptane (primary reference fuels (PRFs)), the relative magnitude of the pressure dependence of LBV between ethanol and toluene has not been established. The inclusion of toluene is important because commercial gasoline has significant levels of aromatics. In this work, common gasoline surrogate components of iso-octane, n-heptane, toluene, and ethanol were studied as pure compounds and in equal volume binary, ternary, and quaternary mixtures. Experiments are conducted in a spherical combustion bomb at elevated temperatures (380 K and 450 K) and pressures (1 to 4 bar). Under these conditions, ethanol and n-heptane present faster LBVs than iso-octane and toluene, particularly at 450 K. Ethanol and iso-octane present strong pressure dependence, with this effect accentuated at higher temperature conditions. As equal volume mixtures were studied, the effect of these distinct behaviours was examined in comparison to chemical kinetic predictions and widely used mixing rules.*

### INTRODUCTION

As internal combustion engines (ICEs) will remain an essential powertrain for the near future, researchers are pushing the operating limits of modern engines to achieve greater efficiency and further reduce emissions [1]. While there exist various combustion models catering to both detailed chemistry and turbulent chemistry interactions, for most practical engine simulations, flamelet models are used. When using flamelet assumptions, turbulent flames can be considered as an ensemble of laminar-like flame fronts propagating locally through the turbulent fields. Therefore, accurate determination of the Laminar Burning Velocity (LBV) is essential in developing more capable combustion models and validating chemical kinetic mechanisms. As the LBV is fundamentally a characteristic of the fuel of interest, despite its dependence on equivalence ratio, temperature, pressure, and diluent gases in the mixture, chemical kinetics modelling requires a correct representation of the fuel. However, as typical gasoline consists of hundreds of hydrocarbon molecules, it is difficult to study gasoline's basic combustion characteristics directly from experiments and numerical simulations. Therefore, simplified surrogate fuels which can emulate the physical and chemical properties of real gasoline are desired for repeatability in experiments and enabling faster and simpler numerical simulations.

A mixture of iso-octane and n-heptane (OH), commonly referred to as a primary reference fuel (PRF), is a widely used surrogate in the engine community. However, gasoline often

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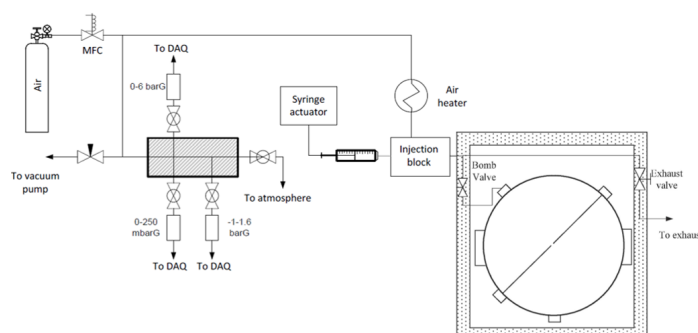
contains aromatic components that propagate at different speeds compared to alkanes, suggesting that using OH mixtures to model gasoline might introduce errors [2]. Toluene can be included to form a ternary mixture of iso-octane, n-heptane, and toluene (OHT in this study, also referred to as toluene reference fuel (TRF) or toluene primary reference fuel (TPRF)), which represents the combustion properties of aromatics [3, 4]. However, compared to alkanes, toluene has a more complicated and diverse set of reaction pathways due to its structure; these involve more species and elementary reactions [5]. Chemical kinetics studies have also highlighted that toluene only ignites in a relatively high-temperature range ( $> 1000$  K); therefore, the high-temperature behaviour of toluene oxidation can have a much greater influence on its ignition and flame propagation compared to alkanes [6]. Whilst the LBVs of individual components of the OHT blend have been extensively studied at atmospheric pressure for the development, validation, and optimisation of reaction mechanisms, binary, and ternary mixtures of these components are much less covered in the literature, particularly at elevated pressures and temperatures. Specifically, the interactions of toluene with the other components have been minimally studied, and experimental LBV data could be critical in developing and validating chemical kinetic mechanisms.

Recently, ethanol has gained significant interest as an alternative fuel [7–9]. Researchers such as Foong *et al.* [10] have studied the influence of ethanol concentration on the octane rating of ethanol blended with a TPRF and found non-monotonic effects of ethanol blending on gasoline octane rating. For LBV, the addition of ethanol to individual PRF components has been found to enhance the blend's LBV between 298 K and 358 K, particularly at low pressures [11, 12]. Liao *et al.* [13] were able to show that this phenomenon also applied to ethanol addition to the PRF mixture at ambient conditions. They also concluded that ethanol primary reference fuels (EPRFs) exhibit comparable flame speeds to TPRF mixtures where there is a similar composition of the PRF mixture. Few LBV measurements of ethanol addition to TPRF fuels exist in the literature. Di Lorenzo *et al.* [14] validated the TPRF with 5% (in volume) ethanol as a suitable surrogate of commercial gasoline at temperatures of 373 K to 473 K, pressures of 0.1 to 0.5 MPa, and equivalence ratio range from 0.8 to 1.3. They observed a divergence ( $< 15\%$  in LBV) between the behaviours of the two fuels caused by the pressure increase, and for lean mixtures, these differences were accentuated. Dirrenberger *et al.* also showed how the combination of these components was representative of conventional gasoline fuel at atmospheric pressure and 358 K. Their work reported that the influence of 15% (in volume) ethanol addition to their gasoline surrogate was negligible, and the difference was slightly accentuated ( $< 6\%$  in LBV) for lean mixtures. More recently, Fan *et al.* [15] studied different ethanol blending ratios in a TPRF

blend to form ethanol toluene primary reference fuels (ETPRF) mixtures, where they concluded that ethanol had a stronger pressure dependence of flame speed than toluene in the blend. Their work provided the relative magnitude of flame speed's pressure dependence between ethanol and toluene; however, the flame speed measurements obtained through a rapid compression machine can be significantly different from laminar burning velocities.

While it is possible to develop dedicated empirical correlations for every fuel blend of interest, the amount of experiments needed to cover relevant engine conditions makes it more attractive to use mixing rules or detailed chemical mechanisms. Previous work from Sekularac *et al.* [16] has developed correlations based on mixing rules for ethanol/iso-octane blends and showed good agreement at elevated temperatures and pressures with experimental results. With limited data available for LBV measurements at elevated temperature and pressure, especially for mixtures with more than three components, additional laminar burning velocities measurements are needed for the development of chemical mechanisms and the validation of widely adopted mixing rules.

The objective of this paper, therefore, is to provide novel data on the laminar burning velocities of ethanol-gasoline surrogates at elevated temperatures (380 K and 450 K) and pressures (1 to 4 bar). Components of surrogate fuels used in the current study are n-heptane, iso-octane, toluene, and ethanol. The impact of toluene on OH (PRF) components and ethanol is assessed in various binary and ternary compositions under the same conditions. Additionally, a chemical kinetic mechanism and mixing rules validity are also examined for the various blends. All measurements are determined by using a spherically expanding flame methodology in a constant volume vessel where laminar burning velocities are determined through both flame front imaging and pressure rise techniques.



**FIGURE 1:** Schematic diagram of the liquid fuel mixture preparation system and combustion bomb adapted from Hinton *et al.* [17]

## EXPERIMENTAL APPARATUS AND DATA ANALYSIS

A constant volume combustion vessel with liquid fuel mixture preparation system, shown in Figure 1, was used to investigate the combustion residual effects on the LBV of pure ethanol (E), iso-octane (O), toluene (T), and n-heptane (H), and their binary, ternary, and quaternary mixtures of equal volume under the test conditions shown in Table 1. Blends are denoted by the initials of the components, e.g., OH is a binary blend of iso-octane and n-heptane at 50% by volume. The blends tested for this study include: ethanol/toluene (ET), n-heptane/toluene (HT), iso-octane/toluene (OT), ethanol/n-heptane/toluene (EHT), iso-octane/ethanol/toluene (OET), iso-octane/n-heptane/toluene (OHT), and toluene/n-heptane/ethanol/iso-octane (THEO). The combustion bomb is constructed using two stainless steel halves with an inner radius of 150 mm. Dalton's law of partial pressures, assuming an ideal gas, is applied for mixture preparation. One pair of windows (40 mm usable diameter) is fitted along an optical axis to allow imaging of the flame front through a folded pin-hole schlieren system. The images are recorded using a Photron 1024 PCI high speed camera with 512 x 512 pixel resolution and a frame rate of 3000 fps. The LBV measurements of the blends together with the pure component constituents were made using a spherically expanding flame. The LBV was determined through the analysis of the early flame front propagation imaging at conditions of constant pressure and the pressure rise data in the vessel. The former method includes the ignition and flame stretch effects, whereas, in the latter method, the thermodynamic data from the multi-zone BOMB program [18] is used to calculate the burning velocity and schlieren imaging was used to detect the onset of cellularity. Details of the constant volume combustion bomb and implementation of the two methods can be found in [16, 19] where a schematic of the data processing procedure is shown in 2. The major sources of error were identified by previous studies using the same set up which are from mixture preparation and extrapolation to zero stretch [17]. The errors from these sources are considered minimal as a good agreement is found between the individual measurements of the laminar burning velocity from the flame imaging and values derived from the pressure data.

## NUMERICAL SETUP

In this section, both the chemical kinetics modeling details and the mixing rules are briefly described. The ChemkinPro 19.0 PREMIX module was used to compute the corresponding LBVs for all experimental conditions investigated in the present work. The characteristic burning velocities of the gas mixtures at specific pressures and unburned temperatures in this configuration are determined assuming one-dimensional flow with uniform inlet conditions and no heat losses. The grid parameters CURV and GRAD were set to 0.01 and 0.05,

**TABLE 1:** Test conditions of the pure components, binary and ternary blends

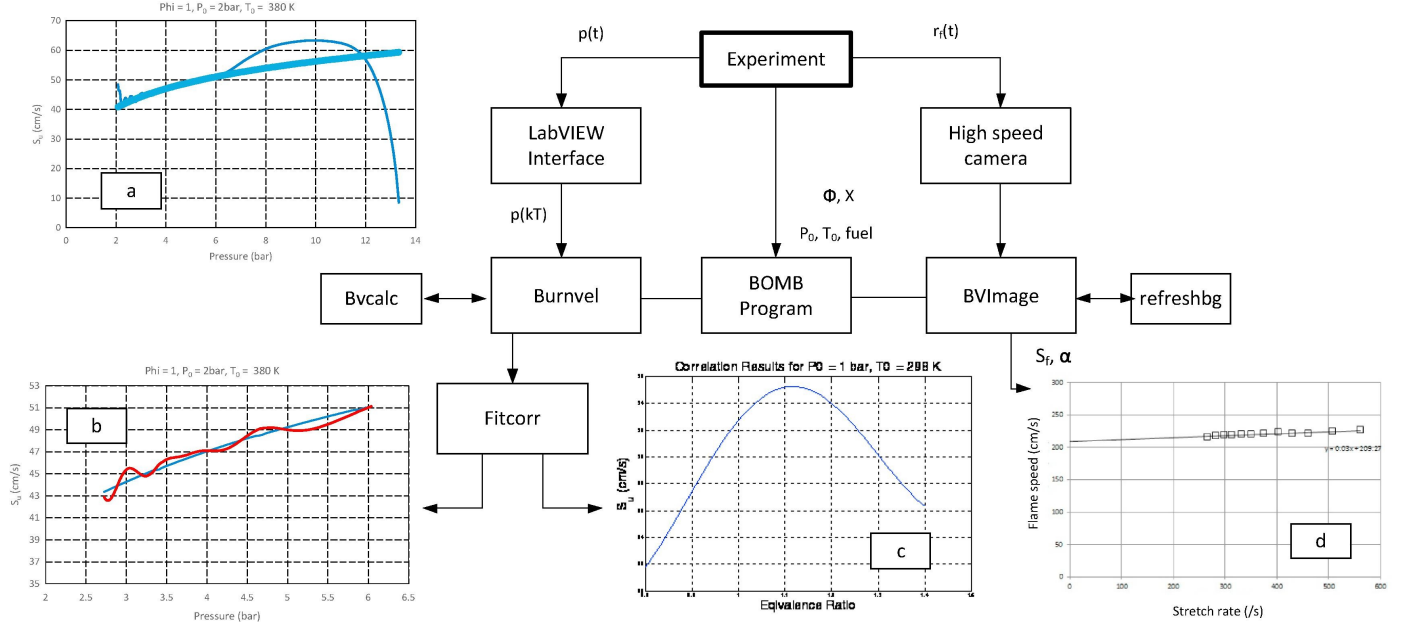
Fuel (pure components)	iso-octane (O), n-heptane (H), ethanol (E), toluene (T)
Fuel (binary components)	ET, HT, OT
Fuel (ternary components)	EHT, OHT, OET
Fuel (quaternary components)	THEO
Initial pressure (bar)	1, 2, 4
Initial temperature (K)	380, 450

respectively, to ensure grid convergence. The adaptive and maximum grid points for the solver were set at 500 and 5000, respectively. The accuracy of the burning velocity is dependent on the realism of the chemical kinetic reactions scheme and the accuracy of its respective rate constants and molecular transport coefficients. While large chemical mechanisms can be used for numerical studies, [20, 21], reduced mechanisms are often adopted for high-fidelity engine simulations [22]. Therefore, in this study, the mechanism used is a reduced four-component, toluene/n-heptane/ethanol/iso-octane (THEO), gasoline surrogate kinetics mechanism developed by Li *et al.* [23] which originated from a detailed chemical kinetic model developed at King Abdullah University of Science and Technology (KAUST) [24]. Li *et al.* [23] used ignition delay times (IDTs) and LBVs from experimental literature data of mixtures with different compositions and ethanol concentrations to validate their reduced model. In addition, Li *et al.* [23] formulated a THEO mixture containing 27.5%, 20%, 8.2%, and 44.3% by liquid volume, respectively, as a gasoline representative to further validate the accuracy of their reduced mechanism predictions in various simulations.

Sensitivity analyses were used to understand the chemical effect of the pure components, particularly toluene and ethanol, on the LBV for the different operating conditions tested. The chemical effects were also assessed in the mixtures containing these components. This analysis can quantify the impact on the output by perturbing a certain input parameter and observing the changes in the system outcomes [25]. The relative sensitivity coefficient  $S_i^{rel}$  is calculated by:

$$S_i^{rel} = \frac{\ln(S_l)}{\ln(A)} = \frac{A}{S_l} \frac{\partial S_l}{\partial A} \approx \frac{A}{S_l} \frac{\Delta S_l}{\Delta A} \quad (1)$$

Where the laminar burning velocity ( $S_l$ ) and the pre-exponential factor ( $A$ ), unique to each reaction, are the system outcome quantity and input parameter of interest, respectively.



**FIGURE 2:** Schematic diagram of data analysis procedures for both flame front imaging and pressure rise analysis techniques (a) burning velocity calculated as the pressure rises, (b) fit of the global correlation to the data selected from a single experiment, (c) a sample plot from the resulting correlation and (d) extrapolation of flame speed to zero stretch from the flame imaging. Figure adapted from Hinton *et al.* [17]

Therefore, the sensitivity of the LBV with respect to each reaction is computed and the reactions that affect the flame speed the most are identified and compared for different compositions and initial conditions.

While complex mixing rules based on non-linear expressions exist for estimating a blend's burning velocity [26, 27], additional information for the inputs, such as the adiabatic flame temperature of each of the pure constituents and the mixture, is needed for these approaches. Therefore, two simpler yet widely used mixing rules in the literature are examined in this study. The first mixing rule studied is derived from Le Châtelier's [28] work on predicting lean flammability limits of fuel blends, where the burning velocity of the blend is:

$$S_{u,blend} = \frac{1}{\sum_{i=1}^{n=N} \frac{x_i}{S_{u,i}}} \quad (2)$$

where  $x_i$  is the mole fraction of the each component in the mixture. Additional mixing rule studied is given by the work of Sileghem *et al.* [29], where they proposed a modified version of the Le Châtelier's rule whereby the energy-fraction,  $\alpha_i$  is used to replace the mole fraction,  $x_i$ , in Equation 2:

$$\alpha_i = \frac{\Delta H_i^0 x_i}{\sum_{i=1}^{n=N} \Delta H_i^0 x_i} \quad (3)$$

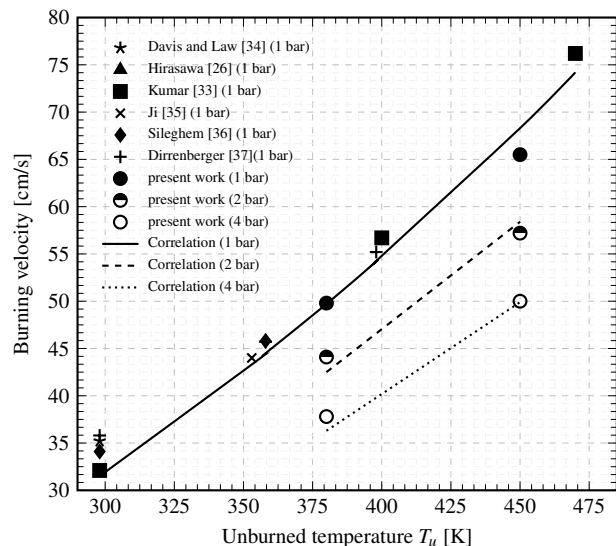
where  $\Delta H_i^0$  and  $x_i$  are respectively the heat of combustion and the mole fraction of the fuel component  $i$  within the blends. For various gasoline/alcohol blends, such as iso-octane/ethanol, the modified Le Châtelier mixing rule has presented a noticeable improvement in comparison to the conventional Le Châtelier rule [30,31].

## RESULTS AND DISCUSSION

The pure components, binary, ternary, and quaternary mixtures of the THEO components have been tested at elevated temperatures (380 K and 450 K) and pressures (1 to 4 bar) with an equal volume of each component. Note that throughout this paper, the experimental data are represented by data markers, and the correlation and chemical kinetic model predictions are represented by solid and dashed lines.

### Pure components

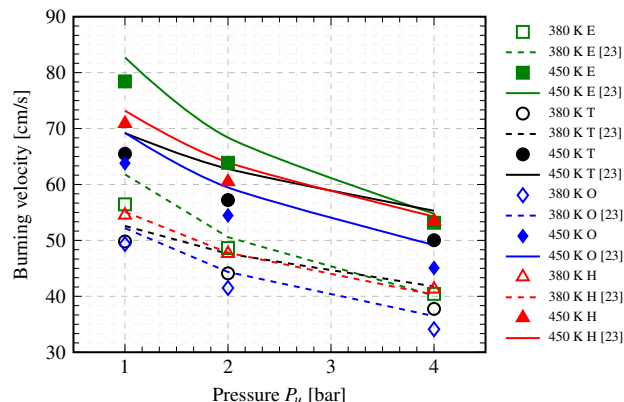
Whilst the results of iso-octane, ethanol, and n-heptane have been presented previously by the group [16, 19,32], the results of



**FIGURE 3:** Comparison of experimentally determined toluene-air mixtures from both flame front imaging (circles) and pressure rise analysis (lines) with available literature data (markers) across a temperature range from 298 K to 470 K at stoichiometric conditions.

toluene are presented for the first time in open literature. Figure 3, shows the available literature data of toluene at atmospheric pressure with varying temperatures compared with both the flame front imaging (circle marks) and pressure rise method (correlation lines) experiments. First, it is observed that at all temperatures and pressures studied, the reconciliation of two distinct methods is confirmed highlighting the precision of the current experimental setup. Compared with literature data at atmospheric pressure, a close match is found between the data extracted from the pressure rise measurements and the values obtained from other studies. As seen from Figure 3, most of the available data for toluene studied in the literature is given at 298 K. While the current study is seen to be best following Kumar *et al.*'s [33] measurements using counterflow twin-flame technique, a scatter is also observed from studies using different techniques. This further highlights the importance of using the same technique and experimental setup for the study of fuel addition in mixtures as well as the efficacy of various mixing rules.

Figure 4 presents the novel toluene data at the elevated pressures and temperatures in comparison with the other pure component constituents of a THEO mixture obtained by the same apparatus. Whilst iso-octane and toluene represent the lower LBVs at atmospheric pressure, the impact of pressure rise on the LBV of toluene is less than that of iso-octane and this phenomenon is accentuated at the higher temperature condition. Similar pressure independent behaviour is observed for n-

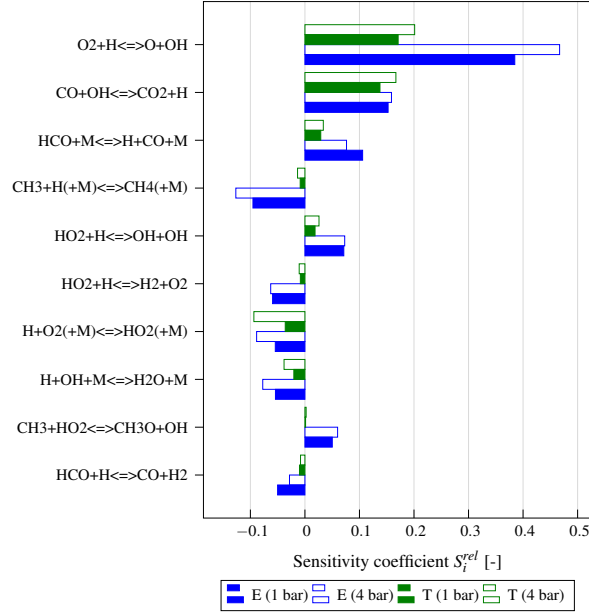


**FIGURE 4:** LBVs at 1, 2, and 4 bar at 380 K (hollow) and 450 K (filled) for ethanol (square), toluene (circle), iso-octane (diamond) and n-heptane (triangle). Mechanism [23] prediction results are presented as lines at 380 K (dashed) and 450 K (solid).

heptane, whilst the contrary is observed with ethanol. Chemical kinetic LBV predictions using the Li *et al.* mechanism are also presented. The effectiveness of these predictions for ethanol, iso-octane, and n-heptane are discussed in previous publications [16, 32]. Whilst Li *et al.*'s mechanism is able to capture the trend of toluene's LBV, the predictions are consistently higher than the experimental data for both temperatures and across the pressure range. This behaviour is likely due to the complex molecular structure and reaction process of toluene involving significant number of elementary reactions, which is difficult to synthesise in a reduced mechanism. Metcalfe *et al.* [5] found that even for existing detailed mechanisms of toluene, the predictions can display discrepancies. Li *et al.*'s mechanism was reduced from Sarathy *et al.*'s [24] mechanism, which had its toluene sub model derived from Liu *et al.* [6] whom found a 20% discrepancy between experimental and their predicted data at low pressures (1 - 3 bar).

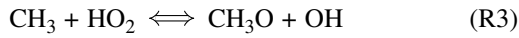
As ethanol and toluene present contrasting LBVs across the pressure range, a sensitivity analysis was performed to assess the impact of the different component's reactions on the LBV with the mechanism of Li *et al.* [23]. Figure 5 presents these results at 450 K with pressures of 1 and 4 bar. The top 10 reactivity promoting (positive sensitivity coefficient) / reactivity inhibiting (negative sensitivity coefficient) reactions for ethanol and toluene are presented. It can be seen that the flames are mainly sensitive to the reactions including small molecules (i.e., H, OH, and O). Based on Ranzi *et al.*'s [38] sensitivity analysis for different fuels, reactions directly related to H radical have the greatest impact on the LBV. The key chain branching reaction is R1:



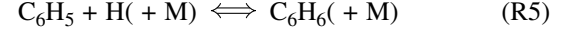
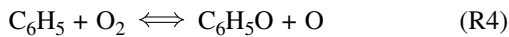


**FIGURE 5:** Sensitivity analysis comparing the 10 top (absolute) sensitivity coefficients  $S_i^{rel}$  of ethanol and toluene at 450 K with pressures of 1 and 4 bar.

Any reaction that produces the H radicals needed by R1 can increase the overall fuel oxidation rate and thus promote the LBV. A greater sensitivity for these reactions is observed with ethanol when compared to toluene as seen in Figure 5. Nevertheless, fuel-specific reactions play an important role too. For ethanol, radicals formed as part of its direct oxidation (e.g.,  $\text{CH}_3$ ,  $\text{CH}_3\text{O}$ ) affect the concentration of H and OH and thus the LBV as shown by reactions R2 and R3.



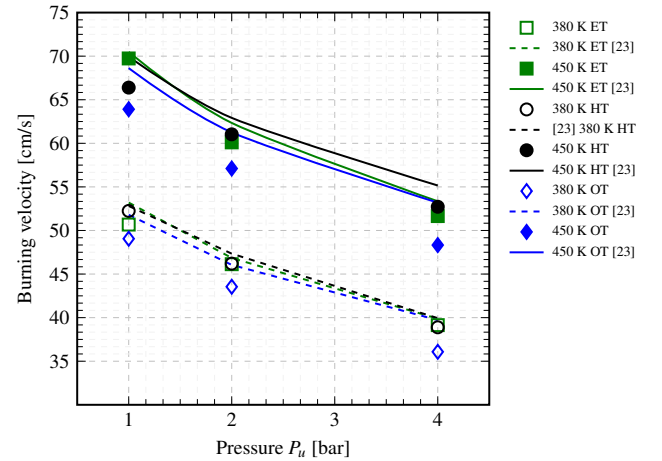
For toluene, given its aromatic structure, the radicals are associated with the phenyl group (e.g.  $\text{C}_6\text{H}_5$ ), which can affect the production or consumption of H and OH radicals. As this sensitivity analysis represents the top 10 reactions relative to ethanol, the toluene specific reactions (e.g., R4 and R5) are not highlighted in Figure 5. However, when considering toluene's incorporation in blends such as OHT or THEO, the influence of these reactions is shown. More sensitivity analysis on the toluene mixtures will be given in later sections.



## Binary mixtures

The results of binary mixture from the image analysis and correlation as well as predictions from Li *et al.*'s mechanism are presented in Figure 6. The results show that at 380 K, there is minimal difference between ethanol and toluene (ET) and n-heptane and toluene (HT) mixtures across the pressure range. The iso-octane and toluene (OT) mixture is distinctly slower and this difference increases with the pressure. This trend corresponds well with the pure components results where iso-octane and toluene display slower LBVs with iso-octane having a negative pressure dependency. At 450 K, the behaviour of OT is similar to 380 K in comparison to the other binary mixtures. However, at atmospheric pressure, there is a greater difference between ET and HT. As toluene's reactivity is greater at higher temperatures, its influence on the LBV at 450 K is more pronounced than at 380 K.

At 450 K, as the pressure increases, the ET mixture's LBV decreases and drops below HT due to ethanol's pressure dependence. Although not shown in another LBV study at same conditions, this pressure dependence was indicated in the flame speed data collected by Fan *et al.* [15] through an optical rapid compression machine. At ambient pressure, Van Lipzig *et al.* [11] does present LBV results for 50% (by volume) blends composed of either ethanol, n-heptane, or iso-octane. Their results are consistently 2-3  $\text{cm s}^{-1}$  higher than elsewhere in the literature and this study, although similar trends in terms of temperature effect is seen for the tested components. Furthermore, whilst Li *et al.*'s mechanism is able to capture



**FIGURE 6:** LBVs at 1, 2, and 4 bar at 380 K (hollow) and 450 K (filled) for equal volume binary mixtures of ET (square), HT (circle), and OT (diamond). Mechanism [23] prediction results are presented as lines at 380 K (dashed) and 450 K (solid).



these trends, particularly that of ethanol's pronounced pressure dependence at the higher temperature condition, there is a discrepancy observed between experimental and simulated data. Therefore, experimental measurements of equal volume binary mixtures of gasoline surrogate components with toluene is vital step in validating newly developed chemical kinetic mechanisms for gasoline surrogates.

### Ternary mixtures

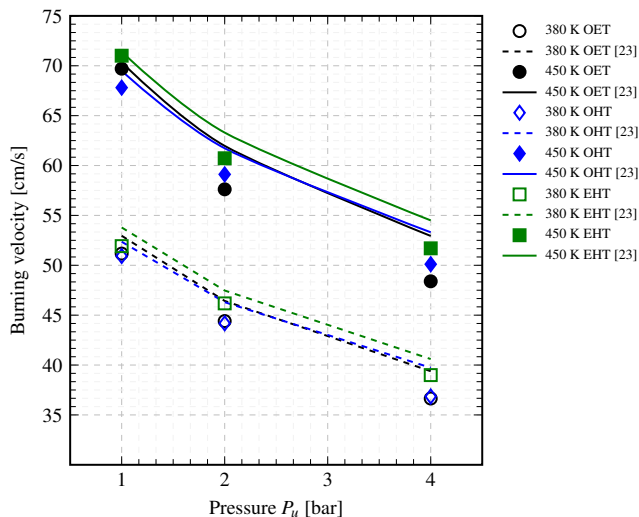
Ternary blends were also mixed on the basis of equal volume and tested at the same conditions of temperature and pressure as the binary blends. Relative burning velocities of the ternary blends are shown in Figure 7. The differences in burning velocities are found to be the greatest at higher temperatures. The blends including both iso-octane and toluene have the lowest burning velocities, whereas those with both n-heptane and ethanol are fastest, consistent with the findings from binary mixtures.

One of the few studies in the literature covering equal volume ternary blends is given by Van Lipzig *et al.* [11] showing results for a mixture of ethanol, n-heptane, and iso-octane (EHO). As mentioned before, their results (including pure and binary mixtures) are shown to be higher compared to the literature. At same conditions, the discrepancy is found to be larger for the ternary blend than binary blends compared to this study. Dirrenberger *et al.* [37] proposed a surrogate gasoline in the form of a OHT (TRF) blended (42.9% iso-octane, 13.7% n-heptane, and 43.4% toluene by volume) in order to match

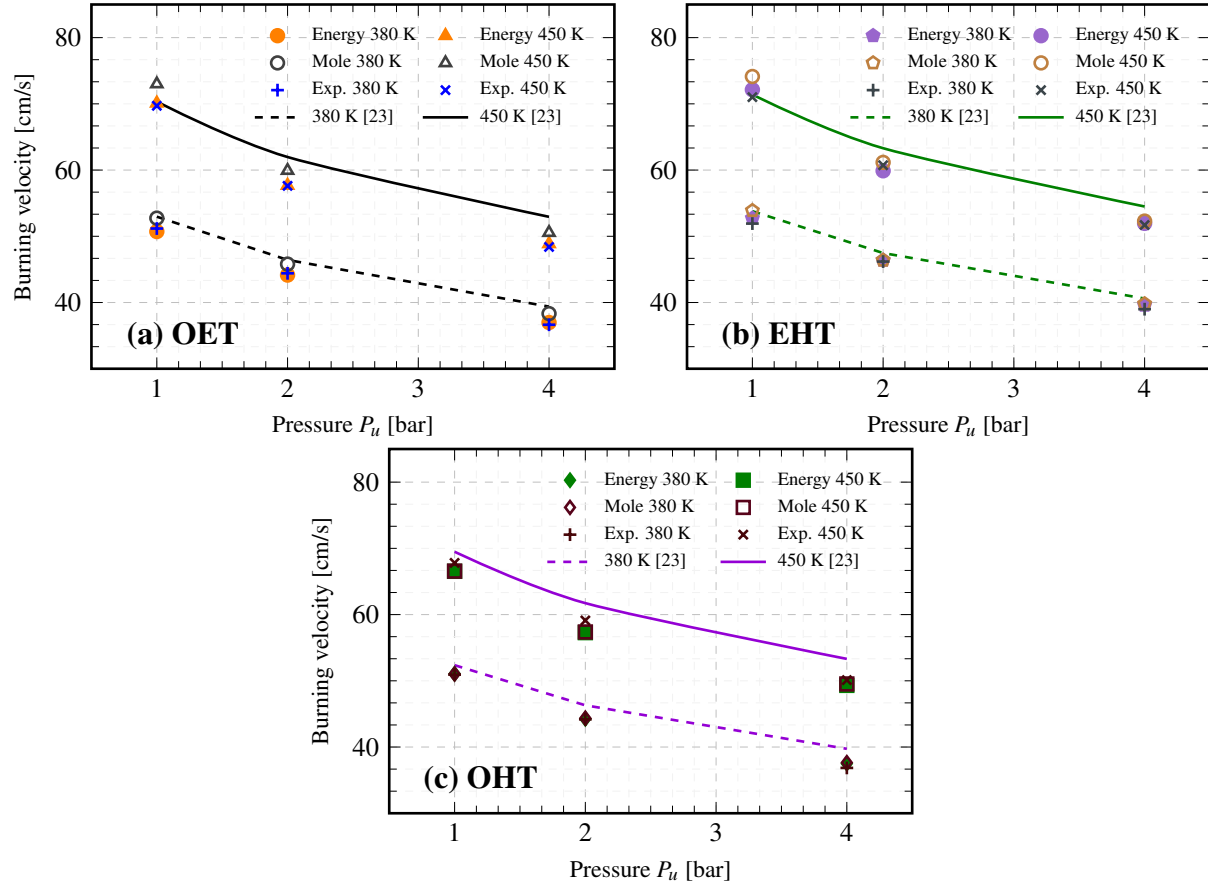
the burning velocities of the commercial gasoline TAE7000 at 1 bar, 358 K. Whilst the composition of the surrogate differs from the OHT blend studied here, in both cases there is close agreement between the burning velocity of the blend and that of toluene, particularly at 380 K. At 450 K, the OHT blend flame front image results are above that of toluene, which could be due to the increased fraction of n-heptane elevating the result. Compared with experiments, numerical simulations follow the same hierarchy where blends with ethanol and n-heptane have the greatest burning velocities.

At both temperatures, the EHT blend is significantly faster at 1 bar, however, the blend's LBV drops rapidly to match that of OET as the pressure increases. This supports previous observations on ethanol enhancing the mixture's LBV at atmospheric pressure and ethanol's pressure dependence affecting the mixture's LBV. As iso-octane's LBV is also pressure dependent, particularly at higher temperatures, the OET mixture is most affected by the pressure increases, shown clearly at 450 K. The mechanism by Li *et al.* [23] is able to predict these trends, however, as the pressure increases, there is a greater discrepancy between the experimental and simulated data. This highlights the importance of studying less common equal volume mixtures such as OET or EHT.

While there are kinetics models in the literature for fuel blends, these models are relatively large, complex, and more computationally expensive to use, as a result, mixing rules that can determine the laminar burning velocity of fuel blends out of the pure fuel components can be attractive [29]. Figure 8 shows the comparison between results from two mixing rules compared with both numerical simulations and experiments for ternary mixtures. The comparison of the mixing rules for binary and quaternary mixtures have been previously discussed by Sekularac *et al.* [16] and Hinton [39], respectively. The two variations of Le Châtelier mixing rules (mole fraction based and energy fraction based) are performed using the experimentally determined pure THEO components' laminar burning velocities. Results from mixing rules show a better match with the experiments compared to kinetic simulations across all mixtures especially at higher pressure. Comparing the two mixing rules, the mole fraction based mixing rule gives a slightly higher laminar burning velocities of multi-component fuels particularly at 450 K for ternary mixtures with ethanol (i.e., OET and EHT). While not presented in a separate figure, the hierarchy of different ternary mixture blends are also given by the energy based Le Châtelier rule. A close match from the energy based Le Châtelier rule indicates mixing rules are not expected to be linear in the fuel blend composition. The better results from energy based mixing rule also suggest the flame temperature can be the dominant factor for laminar burning velocity of the blends used in this study.



**FIGURE 7:** LBVs at 1, 2, and 4 bar at 380 K (hollow) and 450 K (filled) for equal volume ternary mixtures of EHT (square), OET (circle), and OHT (diamond). Mechanism [23] prediction results are presented as lines at 380 K (dashed) and 450 K (solid).



**FIGURE 8:** Le Chatelier mixing rules: energy based (solid fill marks) and mole fraction based (hollow marks) for equal volume ternary mixtures: (a) OET, (b) EHT (c) OHT compared with experimental results at 380 K (+) and 450 K (x). Chemical kinetics simulations [23] are presented with 380 K (dashed) and 450 K (solid).

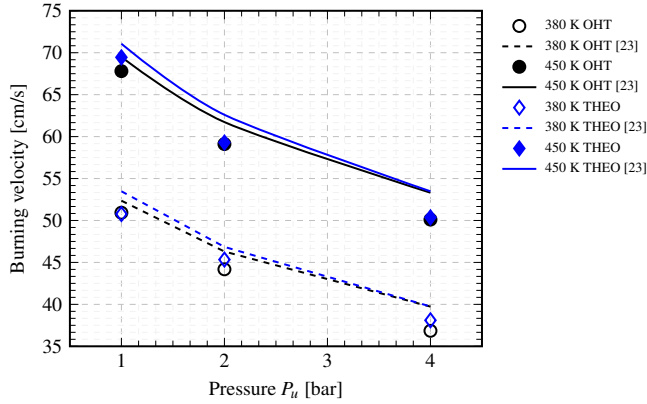
### Quaternary mixture

The THEO blend covered in this study is an equal by volume mixture of the four components of toluene, n-heptane, ethanol, and iso-octane, respectively. The results of the image analysis are shown in Figure 9. Although other blends have been studied, to the authors' knowledge, no study on equal volume quaternary blend can be found in the literature. Dirrenberger *et al.* [37] explored the addition of 15 % ethanol by volume to TAE7000 and their TPRF described in previous section, forming the new blend with 11.6 % n-heptane, 36.5% iso-octane, 36.9% toluene, and 15% ethanol. The addition of ethanol was found to have negligible effect on the burning velocities of both the surrogate and the TAE7000 fuel. More recently, Di Lorenzo *et al.* compared THEO blend with 36 % toluene, 15 % n-heptane, 5 % ethanol, and 44 % iso-octane with Euro 5 gasoline and found that greatest difference of 15% was at 473 K and 0.5 MPa. This trend is partly reflected in the current results where the THEO blend is found to have only a slightly higher burning velocity

than the OHT blend.

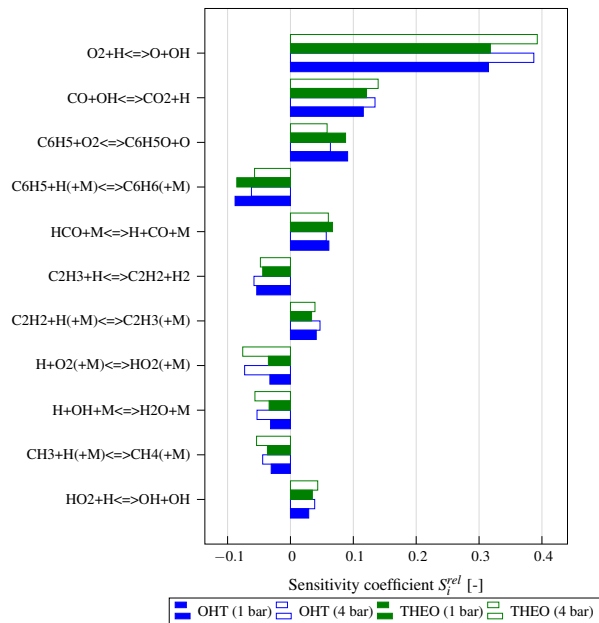
Given the high content of ethanol and toluene in this study's THEO blend compared to conventional ETPRF blends, a sensitivity analysis was performed to identify the impact of ethanol addition at 1 and 4 bar at 450 K as shown in Figure 10. At atmospheric pressure, ethanol enhances the LBV of the OHT blend, however, in line with the findings in the previous sections, as the pressure increases, there is negligible difference between OHT and THEO. Figure 10 shows that at the higher pressure condition, the sensitivity of the influential smaller radical (H, OH, and  $\text{HO}_2$ ) reactions are more similar than they are at atmospheric pressure. This is particularly visible for reactions related to ethanol, such as R2. Whilst for mixture involving toluene, previous chemical kinetics studies have suggested the H atoms on the methyl group on toluene can be abstractable and thus act as a radical scavenger depressing the reactivity of the system [40]. Using the Li *et al.* mechanism from this study, the radicals associated with the phenyl group (e.g.,  $\text{C}_6\text{H}_5$ ) are





**FIGURE 9:** LBVs at 1, 2, and 4 bar at 380 K (hollow) and 450 K (filled) comparing equal volume ternary OHT / TPRF (circle) versus quaternary THEO / ETPRF (diamond) mixtures. Mechanism [23] prediction results are presented as lines at 380 K (dashed) and 450 K (solid).

also found to affect the production or consumption of H and OH radicals. Whilst THEO blends have been studied in compositions that are designed to match commercial gasoline, these results present an opportunity to analyse the individual influence of each of the pure component constituents at elevated pressures and temperatures.



**FIGURE 10:** Sensitivity analysis comparing the 10 top (absolute) sensitivity coefficients  $S_i^{\text{rel}}$  of OHT and THEO at 450 K with pressures of 1 and 4 bar.

## CONCLUSIONS

In this work, experimental LBV results of pure, binary, ternary, and quaternary mixtures of iso-octane, n-heptane, ethanol, and toluene obtained using the constant volume combustion bomb are presented. Both flame front imaging and pressure rise techniques are used to determine LBV. These experimental results are compared to chemical kinetics modelling based on mechanism from Li *et al* [23].

The current work first extends the existing literature available for toluene at elevated pressures and temperatures. For all pure components, iso-octane and toluene represent the lower LBVs, whereas ethanol and n-heptane represent the faster LBVs at atmospheric pressure. The impact of pressure increase on iso-octane and ethanol is greater than that of toluene and n-heptane, and this phenomenon is accentuated at the higher temperature conditions. While Li *et al.*'s reduced mechanism predictions capture the trends of the pure components, there is a discrepancy in the values of absolute LBV compared to the experimental data. This discrepancy is most visible with the toluene predictions suggesting toluene's complex and greater number of elementary reactions need to be accounted for during the mechanism reduction to give accurate LBV predictions.

In the binary mixtures, toluene's radical scavenging effect (due to the easily abstractable H atoms on the methyl group which depresses the reactivity of the mixture) lowers the LBV. At all conditions the OT displays the slowest LBV in agreement with this is constituents' behaviour. At 450 K and atmospheric pressure, a distinct difference between the three binary mixtures are seen. As the pressure increases, the pressure dependence of ethanol is clearly seen in both the experimental and simulated data to affect the ET mixture. For the ternary mixtures, it was observed that blends with ethanol and n-heptane had the fastest LBV at atmospheric pressure. Ethanol's strong pressure dependence still affects the overall mixture's LBV as the pressure increases and this behaviour is pronounced at 450 K. An energy based Le Chatelier mixing rule is found to give closer match with the experiments compared with molar based mixing rule. The better results from energy based mixing rule also suggest the flame temperature can be the dominant factor for laminar burning velocity of the blends.

Finally, the THEO blend is presented as an equal volume mixture. Whilst this blend's properties may not be representative of a gasoline, this works present valuable novel experimental data at elevated temperatures and pressures that can be used for chemical kinetic mechanism validation. Furthermore, when comparing OHT (TPRF) and THEO (ETPRF), the effect of ethanol addition is accentuated at atmospheric pressure and the higher temperature condition.

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## APPENDIX

### Mass and molar fractions of fuel blends tested

The fuel densities were established at ambient conditions of 298 K and atmospheric pressure. The respective mass and molar fractions of the equal volume mixtures tested in this study can be found in Table 2.

**TABLE 2:** Mass and molar fractions of the equal volume binary, ternary, and quaternary mixtures tested in this study.

Fuel mixture	ethanol (E)		n-heptane (H)		iso-octane (O)		toluene (T)	
Percentages	mass	mol	mass	mol	mass	mol	mass	mol
ET	0.475	0.645	0.000	0.000	0.000	0.000	0.525	0.355
OT	0.000	0.000	0.000	0.000	0.444	0.392	0.556	0.608
HT	0.000	0.000	0.441	0.420	0.000	0.000	0.559	0.580
OHT	0.000	0.000	0.305	0.306	0.309	0.272	0.387	0.422
EHT	0.336	0.512	0.293	0.205	0.000	0.000	0.371	0.283
OET	0.335	0.524	0.000	0.000	0.295	0.186	0.370	0.289
THEO	0.259	0.434	0.226	0.173	0.228	0.154	0.286	0.239

### Laminar burning velocities for tested fuels

Laminar burning velocities obtained from the flame front imaging is given by the Table 3.

**TABLE 3:** Burning velocities, obtained by flame front imaging technique, of stoichiometric equal volume binary, ternary, and quaternary blends of the THEO components.

	380 K		450 K			
	1 bar	2 bar	4 bar	1 bar	2 bar	4 bar
Fuel	LBV (cm/s)					
ET	50.679	46.131	39.140	69.737	60.107	51.652
OT	49.055	43.545	36.080	63.909	57.108	48.325
HT	52.242	46.195	38.890	66.392	61.031	52.721
OHT	50.926	44.181	38.172	67.806	59.113	50.107
EHT	56.006	46.182	39.193	76.617	60.728	51.700
OET	51.171	44.411	36.875	63.169	57.615	48.393
THEO	50.771	45.337	38.100	69.448	59.289	50.366

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

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

with,

$$\alpha = \alpha_0 + \alpha_1(\phi - 1) + \alpha_2(\phi - 1)^2 \quad (5)$$

$$\beta = \beta_0 + \beta_1(\phi - 1) + \beta_2(\phi - 1)^2 \quad (6)$$

$$P = \frac{P_u}{1.0} \quad T = \frac{T_u}{298} \quad (7)$$

where  $x_r$  is the mole fraction of the residual gases.

The LBV correlation coefficients for each fuel component are given in Table 4. Mixture LBV correlations are also presented in 4. Due to the complex procedure of measuring the LBV, the mixture burning velocities are only conducted at equivalence ratio  $\phi=1$ . Correspondingly the 14 terms correlations are reduced to only three terms.

**TABLE 4:** Coefficient values to calculate burning velocities for Equation 4, valid for fuels within the range of  $340 \leq T_u \leq 640$  K and  $0.7 \leq P_u \leq 6$  bar

Fuels	$S_{u,0}$	$S_{u,1}$	$S_{u,2}$	$S_{u,3}$	$S_{u,4}$	$\alpha_0$	$\alpha_1$
Toluene (T)	29.528	20.126	-89.019	1.2224	73.252	1.9159	-0.42356
Ethanol (E)	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
ET	32.931					1.8920	
HT	32.982					1.8694	
OT	31.077					1.9000	
OHT	31.411					1.9064	
EHT	33.110					1.8512	
OET	32.039					1.8860	
THEO	32.407					1.8882	
	$\alpha_2$	$\beta_0$	$\beta_1$	$\beta_2$	$\mu_1$	$\mu_2$	$\mu_3$
Toluene (T)	0	-0.21046	0.14415	0	2.2543	0.90195	-0.048952
Ethanol (E)	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
ET		-0.23235					
OT		-0.24356					
HT		-0.21921					
OHT		-0.21911					
EHT		-0.20664					
OET		-0.23384					
THEO		-0.23211					

### Minimum fuel purity

The purity and manufacturer of fuels tested are presented in Table 5.

**TABLE 5:** Manufacturer and minimum purity of fuels tested (iso-octane, n-heptane, toluene, and ethanol)

Fuel mixture	Minimum purity (%)	Manufacturer
iso-octane	99.75	Chevron Phillips
n-heptane	99.00	Fisher Scientific
toluene	99.80	Fisher Scientific
ethanol	99.86	Hayman