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Experimental and Modelling Study of the Impacts of n-Butanol Blending on the Auto-Ignition Behaviour of Gasoline and its Surrogate at Low Temperatures

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Figure 3: (56.6mm+10mm)*(2.2 words/mm)*2 + words in caption=293+ 47=340 words

Tables: 0 words

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Abstract

The study investigates the impacts of n-butanol addition to a reference gasoline (RON 95, MON 86.6) and a gasoline surrogate on ignition delay times at various blending ratios (10%, 20%, 40% and 85% vol n-butanol) in a Rapid Compression Machine, through experimental measurements and numerical modelling (T = 678-916 K, P = 2 MPa, stoichiometric conditions). The surrogate measurements are used to evaluate a recent chemical mechanism describing the combustion of the blends. The TRF (toluene reference fuel) surrogate showed adequate performance in replicating the ignition response of gasoline for all conditions tested, with closest agreement for the 85% blends. Some discrepancies existed within the NTC (negative temperature coefficient) region, suggesting that better matching of both MON and RON or additional surrogate components may be required. At low temperatures, increasing n-butanol concentration led to increases in ignition delay times. Here, n-butanol acted as an octane enhancer even at low concentrations, with marginal additional effects for blends above 40%. A brute force sensitivity analysis of the surrogate model suggested that the main reaction inhibiting ignition at low temperatures is H abstraction from the α-site of n-butanol, even for the 10% blend. At higher temperatures, the chain branching routes from H abstraction by OH from the γ-site of n-butanol, and from the α-site by HO_2, become more dominant, promoting ignition. For the lower blends, the largest discrepancies between simulations and experiment were seen in the NTC region where a larger number of reactions contributed to the uncertainty in predicting $\tau_{ign.}$ For the higher blends, the largest discrepancies were noted at low temperatures, indicating that uncertainties within the low temperature n-butanol chemistry need to be resolved. Accurate, temperature and pressure dependent reaction rates for site specific H abstraction by OH and HO_2 for each of the fuel blend components are necessary to improve agreement between simulations and experimental data.

Keywords: Ignition delay times, n-Butanol, Blending, Rapid Compression Machine, Sensitivity analysis

1. Introduction

The similar physical and thermodynamic properties of alcohols compared to fossil fuels, as well as their feasible production pathways from biomass, make them viable lower carbon fuel components in spark ignition (SI) engines with little or no engine modifications required at low blending ratios, as well as facilitating the use of existing re-fuelling and distribution infrastructures [1-3].

Bio-ethanol is, at present, the most widely produced liquid bio-fuel accounting for more than 90% of the world's total bio-fuel usage [4]. As well as reducing well to tank greenhouse gas emissions, the use of ethanol can also result in efficiency improvements in spark ignition engines because of improved knock resistance, higher laminar burning velocity and benefits from charge cooling [5-7].

Butanol is also a promising bio-fuel with a higher volumetric energy content than ethanol, and with a reduced tendency to increase the vapour pressure of the fuel when blended with gasoline, although it has a poorer octane quality than ethanol [8]. These properties, as well as higher heating values and higher stoichiometric air-fuel ratios offer the scope to potentially blend bio-butanol to higher ratios than ethanol using existing infrastructure [9, 10]. Currently in the US, blends of up to 16% vol butanol in gasoline (Bu16) are permitted as an equivalent to 10% vol ethanol in gasoline (E10) [9, 11].

There are several butanol isomers with viable production pathways from biomass with n-butanol being the most prominent to date. The corollary of a lower octane number than ethanol is a higher cetane number, suggesting that n-butanol could be a possible blending component for diesel as well as for gasoline. Nevertheless , when blended with gasoline it is important to determine its impact on the potential knocking characteristics of the blend, particularly since, although it has a similar Research Octane Number (RON) to gasoline, it has a lower Motor Octane Number (MON), which means it has a higher octane sensitivity, which could be beneficial in modern downsized boosted engines [12, 13]. Relevant conditions relating to the anti-knock quality of fuel blends within engines are the temperature and pressure conditions experienced by the unburnt end gas, which in modern engines tends to be at lower temperatures than those in the RON test. Hence, the most appropriate way to describe the octane appetite is neither RON nor MON, but an extrapolation of RON/MON values to cooler conditions [14].

Several experimental and modelling investigations have been carried out to assess the effects of using n-butanol as a fuel component on combustion characteristics, performance and exhaust emissions [3, 9-11, 15-20]. Generally, the studies have shown better combustion performance of n-butanol fuel blends, while the exhaust emissions of HC, CO, NO_x and CO_2 may decrease or increase for fuel blends depending on operating conditions, when compared to neat gasoline or diesel. Dernotte et al. [15] have demonstrated that n-butanol has the capability to enhance combustion stability. Deng et al. [16] performed experiments with 0, 30 and 35% vol n-butanol blended in gasoline and observed that fuel blends are capable of providing more efficient combustion by advancing ignition timing due to the knocking resistance.

The anti-knock quality or auto-ignition resistance of fuels and fuel blends is also important with respect to the development of new technologies such as Homogeneous Charge Compression Ignition (HCCI), Reactivity Controlled Compression Ignition (RCCI) and Gasoline Compression Ignition (GCI) engines where ignition is largely controlled by the auto-ignition kinetics of the fuel. The goal of this study is therefore to provide an improved understanding of the impacts of n-butanol addition to gasoline (RON 95 and MON 86.6) on its auto-ignition properties at various blending ratios (10%, 20%, 40% and 85% vol n-butanol, referred to as B10, B20, B40 and B85 respectively here), as well as to a gasoline surrogate mixture, in order to facilitate the evaluation of a recent chemical mechanism describing the combustion of the blends. In particular, the study investigates the ignition delay times (τ_{ign}) in a Rapid Compression Machine (RCM), through experimental measurements and numerical modelling for the low temperature region 678-916 K at a pressure of 2 MPa under stoichiometric conditions.

Since the kinetics of gasoline combustion is extremely complex due to the large number of hydrocarbon components present, typical kinetic models attempting to represent gasoline combustion comprise simpler surrogate mixtures which are developed to mimic the important properties of the gasoline under investigation. In this study, a 3-component toluene reference fuel (TRF) surrogate has been employed, comprising toluene (22.97% vol), iso-octane (65.64% vol) and n-heptane (11.4% vol) as detailed in Agbro et al. [20]. The performance of this TRF surrogate in representing the ignition delay behaviour of the reference gasoline on its own, and when blended with n-butanol, is investigated first experimentally, and subsequently used to assess the ability of an existing model representing n-butanol/TRF blends to predict τ_{ign} in the RCM for the temperature range under investigation. Furthermore, through the use of brute force sensitivity analysis, the chemistry controlling the auto-ignition of the n-butanol/TRF blends was investigated to determine the main reactions which influence τ_{ign} at selected conditions and blending ratios.

2. Methodology

2.1. Experimental Specifications

Ignition delay measurements were performed in the Leeds RCM, which is used to simulate an ideal single compression stroke of an internal combustion engine. The machine is based on one half of a dual opposed, pneumatically driven and hydraulically damped piston design, where the twin piston is simultaneously triggered to decrease the compression time and achieve mechanical balance. The initial temperature, pressure and composition of diluent gases (N_2, CO_2, Ar) were adjusted to vary the compressed temperature (T_c) of the premixed fuel and oxidiser gas mixture at a constant compressed pressure. Further details of the design and operation are detailed in [20].

The gaseous test mixture was prepared by injecting liquid fuels and gases into a preheated evacuated mixing tank, where the mixture composition was determined by measurements of the relative partial pressure of each mixture component. To enable complete vapourisation of the fuel, it was ensured that the partial pressure of each major component was less than its saturation pressure corresponding to the set initial preheat temperature. The reference gasoline, iso-octane (UN1262), n-heptane (UN1206) and toluene (UN1294) were supplied by Shell Global Solutions, and high purity n-butanol by Fischer Scientific. Details on the composition and properties of the reference gasoline and surrogate mixture are provided in Supplementary Material.

Auto-ignition measurements were conducted for 10%, 40% and 85% by liquid volume of n-butanol mixed with gasoline or the surrogate fuel for temperatures of 678-916 K at 2 MPa pressure and an equivalence ratio (φ) of 1. Reported τ_{ign} are the averages of 4-6 runs made at each test condition with a standard deviation of less than 10% of the mean in every case, as an indication of reproducibility (see Supplementary Material). Similar to Zhang et al. [21], three pure dry air experiments were performed after each run, in order to limit the effect of soot deposits, and to enable good repeatability. For each reactive experiment, the corresponding non-reactive run was conducted by replacing oxygen with nitrogen while maintaining the same mixture concentration. The volume profiles calculated from pressure traces obtained in these inert experiments were used for variable volume simulations to better account for heat losses and any reactions taking place during compression. The compressed temperatures (T_c) were taken as the reference for presenting ignition delay data, and were obtained using an adiabatic core hypothesis [20], using the experimentally measured pressure at the end of compression (P_c).

From the pressure traces, the ignition delay time, τ_{ign}, is defined as the time difference between the point of ignition, where the maximum rate of pressure rise is observed (max dP/dt), and the end of the compression at top dead centre (TDC), where the piston displacement is zero, as illustrated in Fig. S2 in the Supplementary Material.

2.2.Chemical Kinetic Modelling

Simulations of τ_{ign} for all fuels and conditions tested were conducted using Cantera for a single-zone, zero-dimensional variable volume reactor model with imposed specific volume histories determined from measured pressure traces of the non-reactive counterparts to account for RCM facility effects such as heat losses and reactions taking place during compression. Consistent with the experiments, the computed τ_{ign} were defined as the time from the end of compression, determined from experimentally non-reactive runs, to the point of the maximum pressure derivative and reported at T_c determined from experimentally measured P_c as described above. The detailed chemical kinetic mechanism employed here comprises the LLNL gasoline surrogate mechanism of Mehl et al. [22] combined with the n-butanol scheme of Sarathy et al. [2] with several updated rate constants. Firstly, rates for the H-abstraction from n-butanol by OH were updated according to the study of McGillen et al. [23] as used in [20]. In addition, based on the sensitivity analysis conducted in [20] which highlighted the importance of the reaction: phenol+CH_3⇔toluene+OH, this rate has been updated according to Seta et al.[24] which was the source of other toluene+OH rate coefficients within the mechanism. The mechanism comprises 529 species and 4439 reactions and is provided in the Supplementary Material.

A brute-force sensitivity analysis was executed using predicted τ_{ign} as the target output for all fuel blends tested at $\varphi = 1$, $P = 2$ MPa and various temperatures using constant volume simulations. Constant volume conditions were used in order to achieve the shortest run times since thousands of simulations are required for a brute-force study where the sensitivity of the output to each reaction in the mechanism was computed by increasing each reaction rate A-factor by 50% from its nominal value in turn. As shown in Tables S2-S4, T_c predicted by adiabatic core relations and temperature dependent mixture specific heat ratios, have uncertainties in temperature estimation of ~9 K compared to T_c calculated using measured P_c. However, it was confirmed that the constant volume simulations did not deviate significantly from those using variable volume histories, with examples shown in the Supplementary Material. The small differences were shown to not affect the sensitivities greatly. The τ_{ign} sensitivity to each reaction in the kinetic mechanism was calculated as

$S_i = (\tau_0 - \tau_1)/\tau_0$, where S_i is the sensitivity coefficient, τ_0 is the ignition delay simulated with the original kinetic model and τ_1 the ignition delay computed when one of reaction rates has been perturbed. Consequently, a positive S_i signifies a reaction which promotes reactivity thus decreasing τ_{ign}, whilst a negative S_i signifies a reaction which inhibits reactivity thus increasing τ_{ign}. The S_i values for each blend were normalised by the maximum sensitivity at each temperature, thus the reaction with the highest effect on the predicted τ_{ign} has a sensitivity index of 1.

3. Results and Discussion

Figure 1 shows the comparisons of τ_{ign} measured in the current RCM experiments, in addition to those reported in [20] for 20% blends in order to cover a wide range of blending conditions for n-butanol with TRF and gasoline. Also shown are simulations for the pure fuels (n-butanol, TRF) and blends of 10%, 20%, 40% and 85% by volume of n-butanol with TRF as a function of inverse temperature. The results show that for the pure fuels, TRF exhibits similar temperature dependent behaviour to gasoline with both showing a shallow NTC (negative temperature coefficient) regime at intermediate temperatures. In contrast, n-butanol demonstrates a more Arrhenius like behaviour with a slight drop in slope in the lower temperature region. The lack of NTC for n-butanol means that over the whole temperature region studied, it shows a higher slope than the gasoline or TRF.

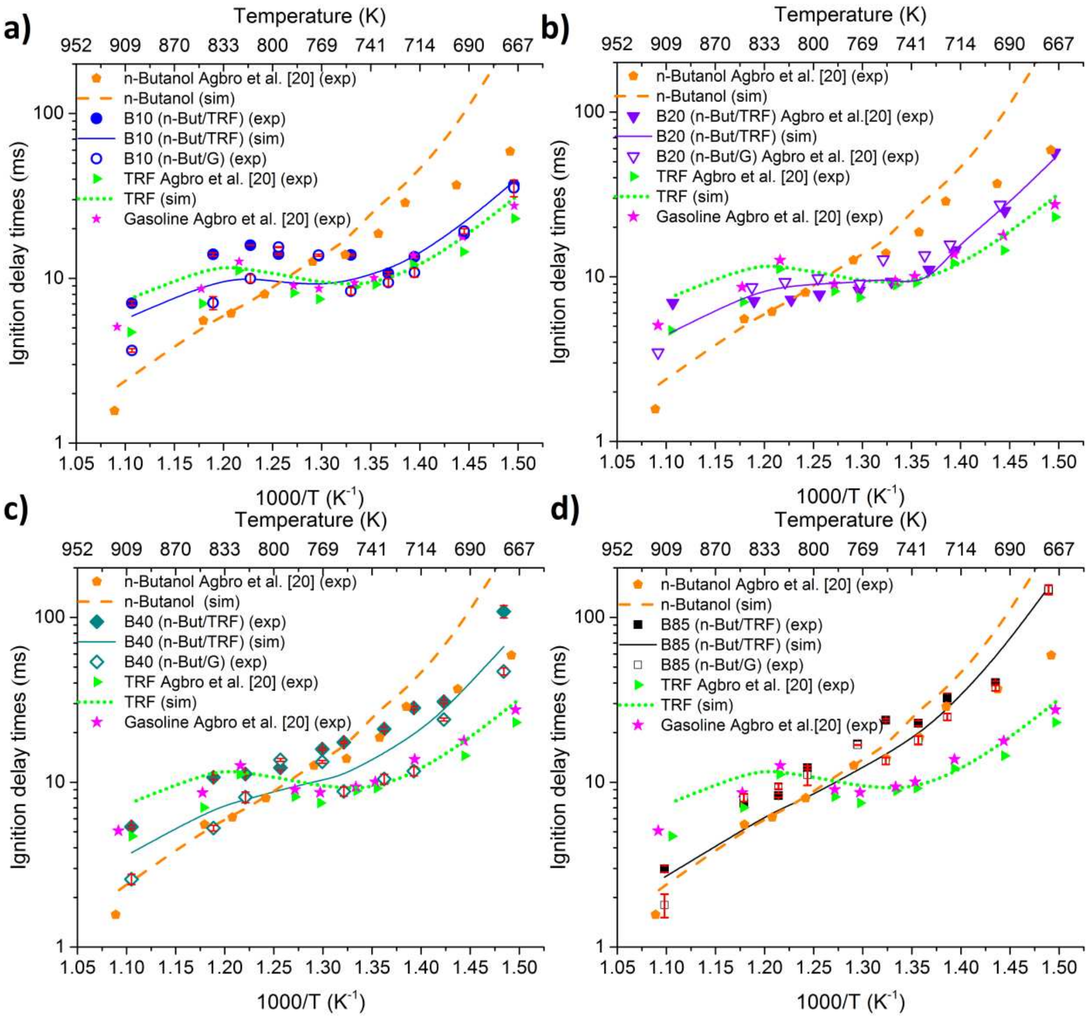

Figure 1: Comparison of simulated, and experimental ignition delays from this study and that reported in Agbro et al. [20] for a) 10% b) 20% c) 40% and d) 85% vol blends with TRF and gasoline, as well as neat fuels, at stoichiometric conditions and a pressure of 2 MPa.

In general, at lower temperatures, the agreement between experimentally measured delays using TRF and gasoline are in good agreement for all of the blends except for B40 at the lowest temperature. However, for B10, where a significant NTC still exists, the agreement between the TRF and gasoline blend is poorer in the NTC regime than at lower temperatures, showing a higher degree of non-linear blending behaviour of mixtures. During the study, additional repeats for these conditions (including 6 sequential runs, as well as repeats on separate days) were performed, which showed consistency and reproducibility. Table S2 in Supplementary Material indicates a standard error between repeats for these conditions of < 0.3 ms. These results highlight the kinetic complexities as well as the need for further research into the formulation of appropriate surrogates.

The agreement improves with blending ratio and at 85% the good agreement between the TRF and gasoline blends can be attributed to the large alcohol concentration within these blends. Whilst intuitively, we might expect the gasoline or surrogate chemistry to dominate for B10 and the n-butanol chemistry to dominate at B85, this will be explored via the sensitivity analysis in the following sections.

Using three components, two of the gasoline properties can be matched and the surrogate used here was based on matching the RON (95) and H/C ratio (1.934) of the reference gasoline with slight differences in MON and octane sensitivity (S) noted in [20]. These differences contribute to small discrepancies in the NTC slope between the n-butanol/TRF and n-butanol/gasoline blends, as illustrated in Fig. 1. Better representation may be obtained by matching both RON and MON or by increasing the number of surrogate components, using for example naphthenes and olefins, in the formulation of the model. Additional components would allow both octane numbers and the H/C to be matched and further investigation of other surrogate formulations under blending is desirable.

For the pure fuels, Fig. 1 shows that the simulations provide a reasonable representation of the temperature dependent behaviour, except for some discrepancies for the n-butanol predictions at the very lowest temperatures and for TRF at the highest temperatures. On blending, the agreement actually improves and the mechanism captures the general trend of the ignition delay times across the whole temperature range quite well, with some underestimation of τ_{ign} in the NTC region.

From Fig. 1 it can be noted that there is a cross-over of τ_{ign} for n-butanol and its blends when compared to the reference gasoline and TRF i.e. at lower temperatures the addition of butanol increases τ_{ign}, whereas at higher temperatures it tends to decrease τ_{ign}. The effects of n-butanol addition at different blending ratios to TRF and gasoline on ignition delay times are directly compared in Figs. 2a and 2b, respectively. The NTC response is seen to flatten with increasing n-butanol for both TRF and gasoline blends, almost disappearing at the highest blend tested of 85% which exhibits a more Arrhenius like temperature dependency. For the gasoline, each of the blends exhibits a shorter τ_{ign} at the higher temperatures and a longer τ_{ign} at the lower temperatures than the reference gasoline, although the temperature at which the curves cross varies with the blending ratio with a range of 792-812 K. For the TRF, only the highest blends exhibit shorter τ_{ign} than the TRF, with a range of cross over temperatures from 780-849 K, and in this sense the surrogate fails to capture the intricacies of the impact of blending on the NTC region. This would have consequences for engine simulations where a wide temperature regime would be accessed, and hence whilst the surrogate used captures the general trends when compared to the gasoline, small discrepancies in predicted τ_{ign} could be significant when trying to predict knocking regimes for different spark timings for example.

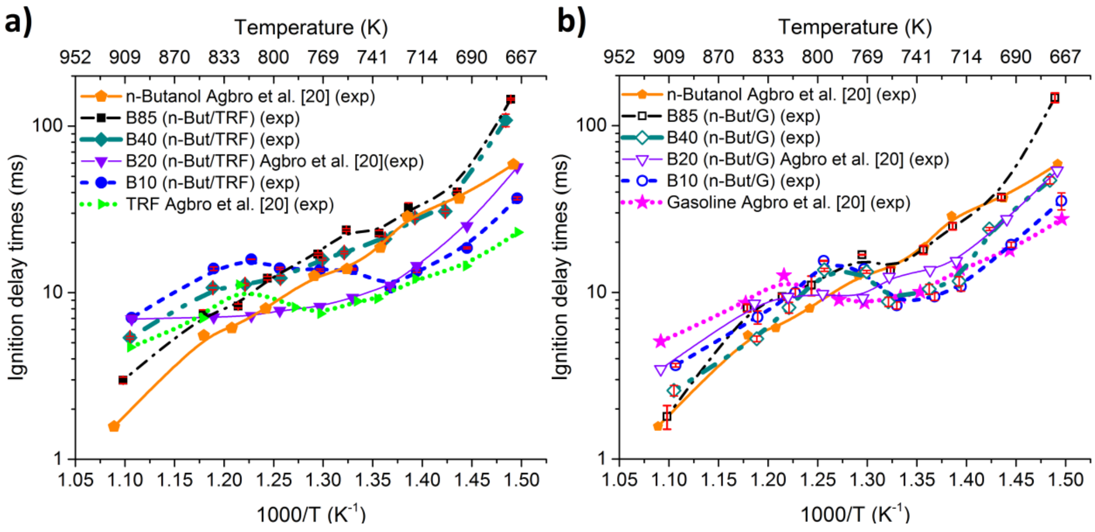

Figure 2: The effects on auto-ignition response of n-butanol addition at different blending ratios of 10%, 20%, 40% and 85% by volume with a) TRF and b) gasoline compared to pure fuels under stoichiometric conditions and at a pressure of 2 MPa.

In general within the lower temperature region, the addition of n-butanol supresses the reactivity of the blend and therefore the n-butanol is acting as an octane booster by delaying ignition. This feature is more pronounced for the TRF surrogate than for the reference gasoline, because it has a more pronounced Low Temperature Heat Release. Differences in the octane sensitivity (S) and MON of the surrogate (S=5.2 and MON=89.8) compared to the gasoline (S=8.4 and MON=86.6), will affect changes in the fuel reactivity due to changes in pressure and temperature [20, 25]. These effects may amplify with the addition of n-butanol and can be an indication of different octane number response when blended with alcohol fuels as previously reported in AlRamadan et al. [26].

For the n-butanol/TRF blends of B10 and B40, the ignition delay times lie outside the bounds of the unblended fuels in the higher temperature region (765-916 K) with the lowest blend ratio of B10 acting as more of octane booster compared to any other blend ratios tested in this temperature region. The highest blend tested of B85 also shows enhanced octane boosting characteristics compared to n-butanol in the lower temperature region (678-765 K) for both TRF and gasoline blends. According to a linear blending law, both of these blends would be expected to lie between the trends of the pure fuels. Also, in the lower temperature region, the B40/TRF blend exhibits very similar auto-ignition behaviour to the B85/TRF blend, suggesting little influence of increased concentration of n-butanol above 40% blends. The results indicate that linear blending rules based on volume would fail to capture the true temperature sensitivity of ignition delays for fuels when an alcohol compound, in this case n-butanol, is added to the test mixture. Surrogates are more commonly developed using linear-by-mole blending rules [20, 27, 28] and Anderson et al. also suggest that such an approach can be used for blending ethanol and methanol with gasoline [28]. However, the cross over of measured ignition delays for the n-butanol blends with those for pure n-butanol at the lowest temperatures suggests non-linear effects do exist for the blends studied here, even when considered on a molar basis.

Figure 3 depicts the results of the normalised brute force sensitivity analysis for the 10 most dominant reaction sensitivities at each of the three temperatures studied for the lowest and highest blends of B10 and B85 in order to assess the dominant chemistry at the chosen blending ratios.

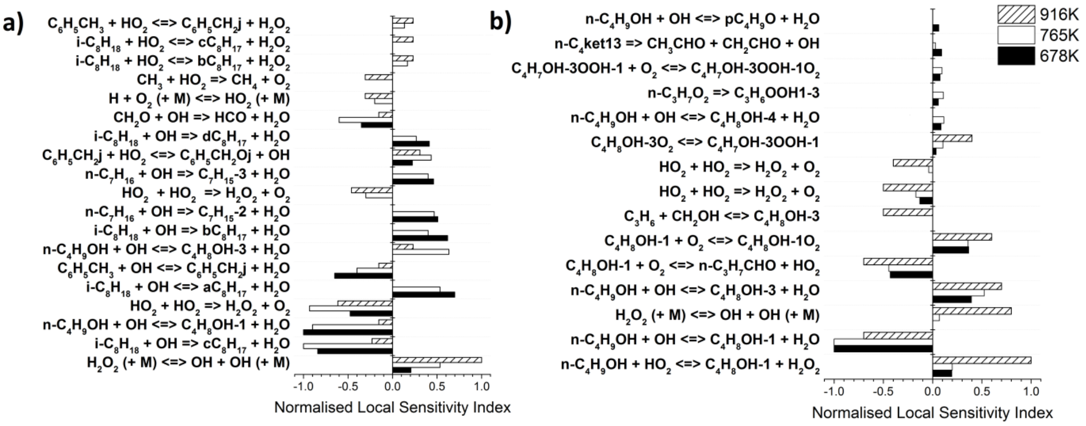

Figure 3: Normalised brute force local sensitivity indices for ignition delay time for a) 10% vol n-butanol +TRF blend and b) 85% vol n-butanol +TRF blends at 3 temperatures, $\varphi=1$ and P=2 MPa. Duplicate entries for the reaction HO_2+HO_2 indicate a double Arrhenius expression for this reaction.

Perhaps the most striking feature of the sensitivity indices in Fig. 3a is that, at the lowest temperature, it is an n-butanol reaction that ranks the highest in terms of its impact on predicted τ_{ign} despite butanol forming only 10% of the mixture by volume. H abstraction via OH from the α-carbon site ($nC_4H_9OH+OH \Leftrightarrow C_4H_8OH\text{-}1+H_2O$) has an inhibiting role, leading primarily to the direct elimination of HO_2 forming butanal as discussed in Welz et al. [29]. Other reactions inhibiting ignition at low temperatures include H abstraction from toluene ($C_6H_5CH_3+OH \Leftrightarrow C_6H_5CH_2j+H_2O$) as well as from the tertiary site of iso-octane. A Rate of Production (ROP) analysis showed that for this blend, the toluene reaction had the highest rate throughout the ignition, although τ_{ign} was not as sensitive to changes in its rate. The main reactions promoting ignition at this low temperature relate to H abstraction from n-heptane and from the primary and secondary sites of iso-octane. Therefore at low temperatures, the inhibiting role of $nC_4H_9OH+OH \Leftrightarrow C_4H_8OH\text{-}1+H_2O$ is in competition with chain branching reactions from the surrogate gasoline, and in fact for B10, only a small increase in τ_{ign} was observed compared to pure gasoline/TRF as shown in Figs. 1 and 2.

As the n-butanol increases to 85% by volume, the OH from the α-carbon site dominates the sensitivities at both the low and intermediate temperatures, and in this case is competing against the alkane-like chain branching route initiated by abstraction from the γ-site of n-butanol as also discussed for pure n-butanol in [10] and for B20 in [11]. The importance of H abstraction by OH from the α-site at low temperatures leads to the octane enhancing influence of n-butanol under these conditions as seen in Figs. 1 and 2. This differs from previous studies for ethanol/PRF blends where H abstraction by HO_2 (rather than by OH as seen here) leading to acetaldehyde and H_2O_2 was suggested to be a factor in slowing the production of reactive radicals [30]. However, at higher temperatures, abstraction from the α-site by HO_2 is the dominant reaction for the 85% blend studied here, and in this case promotes reactivity since at these temperatures the H_2O_2 formed, reacts to form 2 OH radicals. Thus at these higher temperatures, high blends of n-butanol reduce ignition delay times and butanol does not act as an octane enhancer in this situation.

The mechanism fails to properly capture the slope of ignition delays at the lowest temperatures, although as shown in tables S2-S4, this is where the largest experimental uncertainties lie. This may possibly be due to the over dominance of H abstraction from the α-channel in this temperature region. As noted in [10], the prediction of τ_{ign} is not highly sensitive to the overall rate of OH+n-butanol, but rather to the branching ratios for the different abstraction sites. McGillen et al. [23] suggest higher uncertainties for the site specific channel for the γ-site compared to the α-site and there are no site specific experimental data for temperatures of relevance in combustion. A second possible source of discrepancy is the lack of inclusion in the mechanism of possible cross reactions between the blend components. Cross reactions used in other schemes include different product channels for benzyl+n-butanol, benzyl+butanal or benzyl+1-butene. Sensitivity of ignition delay predictions to their inclusion was therefore tested here using rate coefficients and thermodynamic properties from the mechanism discussed in Pelucchi et al. [11]. Insignificant differences in simulated ignition delay times of less than 0.1 ms across the whole temperature range tested were found (see Supplementary Material for details).

At the highest temperature of 916 K, for both blends, $H_2O_2(+M) \Leftrightarrow OH+OH(+M)$ plays a key role in forming OH radicals and promoting ignition [31, 32], with the reaction of HO_2 with itself playing an inhibiting role. For B10, abstraction from the γ site, which promotes reactivity has a low sensitivity. Hence even at high temperatures, this blend shows longer ignition delay times than TRF despite a small promoting role for H abstraction from toluene and iso-octane by HO_2. For B85, H abstraction by OH from the γ-site becomes more important in promoting ignition and the ignition delay times become shorter than for TRF.

The intermediate temperatures in the NTC region for gasoline posed the largest challenges in terms of the ability of the surrogate to mimic gasoline under blending, as well as for the chemical mechanism employed. At the intermediate temperature of 765 K, we see a mixture of reactions contributing to the sensitivities, particularly for B10, including H abstraction by both OH and HO_2 from the primary fuel molecules, as well as the reactions of HO_2 and H_2O_2. The contribution of a higher number of reactions to the overall uncertainty in predicting ignition delays creates challenges for the chemical mechanism within the NTC region where there is a low gradient of τ_{ign} with respect to temperature. The main inhibiting reactions eventually leading to HO_2 formation are $iC8H_{18}+OH \Leftrightarrow cC_8H_{17}+H_2O$ and $nC_4H_9OH+OH \Leftrightarrow C_4H_8OH\text{-}1+H_2O$ [32] but these are competing against a larger number of significant chain branching routes than at lower and higher temperatures. This feature, of larger uncertainties within the NTC region, was also noted by Hébrard et al. [33] for n-butane oxidation, and suggests the need for highly accurate estimates of site specific abstraction rates by both OH and HO_2 for the main fuel molecules.

Conclusions

Today, ethanol is the most common biofuel component for the use in gasoline, and although n-butanol has a lower octane quality than ethanol, it is a bio-component in which there is interest. Ignition delay times from an RCM were reported for 10%, 20%, 40% and 85% vol n-butanol blends with a TRF surrogate and reference gasoline for temperatures of 678-916 K and a pressure of 2MPa under stoichiometric conditions. The TRF surrogate showed adequate performance in replicating the ignition response of gasoline for all conditions tested, with the closest agreement for the 85% blends. However, some discrepancies existed within the NTC region, suggesting that additional components within the surrogate may be required in order to adequately represent the chosen gasoline. However, the sensitivity analysis suggested that a larger number of reactions control the ignition within the NTC region, and hence the addition of further surrogate components may also increase the level of uncertainty within the chemical mechanism representing the surrogate within numerical simulations.

At low temperatures, increasing the n-butanol concentration led to increases in ignition delay times, showing that n-butanol acts as an octane enhancer in this region even at low concentrations, with marginal additional effects for blends above 40%. At higher temperatures, the behaviour reverses as the chain branching routes from H abstraction from the γ-site of n-butanol becomes more dominant. For the lower blends, the largest discrepancies between the simulations and experiment were seen in the NTC region where a large number of reactions contribute to the uncertainty in predicting $\tau_{ign.}$ For the higher blends, the largest discrepancies were noted in the low temperature region, indicating that uncertainties within the low temperature n-butanol chemistry need to be resolved. Accurate, temperature dependent reaction rates for site specific H abstraction by both OH and HO_2 for each of the fuel blend components are necessary in order to improve the agreement between numerical simulations and experimental data.

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List of Supplementary Material

1. Table S1: Summary of the composition and combustion characteristics of the reference gasoline and formulated Toluene Reference Fuel (TRF) surrogate.

2. Figure S1: Comparisons between typical experimental and modelled pressure traces for reactive and non-reactive cases. 40% vol n-butanol blend with TRF at T=831 K, P=2 MPa and φ=1.

3. Figure S2: Typical experimental pressure trace defining the ignition delay presented in this study. 40% vol n-butanol blend with TRF at T=831 K, P=2 MPa and φ=1.

4. Table S2: Summary of experimental and simulated ignition delay times for 10% vol n-butanol blend in TRF or gasoline and their initial and compressed conditions.

5. Table S3: Summary of experimental and simulated ignition delay times for 40% vol n-butanol blend in TRF or gasoline and their initial and compressed conditions.

6. Table S4: Summary of experimental and simulated ignition delay times for 85% vol n-butanol blend in TRF or gasoline and their initial and compressed conditions.

7. Figure S3: Comparisons of experimental and simulated ignition delay times using constant and variable volume reactor for a) 10%, b) 40% and c) 85% vol n-butanol blend with TRF. P=2 MPa , φ=1.0.

8. Figure S4: Effects on the simulated ignition delay times of benzyl + n-butanol, benzyl + butanal or benzyl + 1-butene cross reactions addition to the mechanism for a) 10% and b) 85% vol n-butanol blend with TRF. P=2 MPa , φ=1.0.

9. Kinetic reaction mechanism used in this study.

10. The zipped file encompassing the non-reactive pressure traces and the volume histories computed from the non-reactive pressure traces measured in the Leeds Rapid Compression Machine for 10%, 40% and 85% by liquid volume of n-butanol in TRF.