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Abstract

The influence of blending *n*-butanol at 20% by volume on the ignition delay times for a reference gasoline was studied in a rapid compression machine (RCM) for stoichiometric fuel/air mixtures at 20 bar and 678 K-858 K. Delay times for the blend lay between those of stoichiometric gasoline and stoichiometric *n*-butanol across the temperature range studied. At lower temperatures, delays for the blend were however, much closer to those of *n*-butanol than gasoline despite *n*-butanol being only 20% of the mixture. Under these conditions *n*-butanol acted as an octane enhancer over and above what might be expected from a simple linear blending law. The ability of a gasoline surrogate, based on a toluene reference fuel (TRF), to capture the main trends of the gasoline/ *n*-butanol blending behaviour was also tested within the RCM. The 3-component TRF based on a mixture of toluene, *n*-heptane and iso-octane was able to capture the trends well across the temperature range studied. Simulations of ignition delay times were also performed using a detailed blended *n*-butanol/TRF mechanism based on the adiabatic core assumption and volume histories from the experimental data. Overall, the model captured the main features of the blending behaviour, although at the lowest temperatures, predicted ignition delays for stoichiometric *n*-butanol were longer than those observed. A brute-force local sensitivity analysis was performed to evaluate the main chemical processes driving the ignition behaviour of the TRF, *n*-butanol and blended fuels. The reactions of fuel + OH dominated the sensitivities at lower temperatures, with H abstraction from *n*-butanol from α and γ sites being key for both the *n*-butanol and the blend. At higher temperatures the decomposition of H_2O_2 and reactions of HO_2 and that of formaldehyde with OH became critical, in common with the ignition behaviour of other fuels. Remaining uncertainties in the rates of these key reactions are discussed.

Keywords: gasoline surrogates; ignition delays; *n*-butanol; blending; rapid compression machine

1. Introduction

The development of clean and efficient engine technologies like Homogeneous Compression Charge Ignition (HCCI) engines and the use of oxygenated fuels are two viable options being currently pursued for the achievement of lower carbon emissions in the transportation sector [1]. Because auto-ignition in HCCI engines and knock in spark ignition (SI) engines largely depends on the chemical kinetics of fuel oxidation, research on chemical kinetics and the effects of fuel structure on oxidation has become increasingly significant. Bio-derived alcohols are considered as viable blends for petroleum derived fuels in order to reduce their overall carbon footprint [2]. The similarity of their physical and chemical properties to those of fossil-derived fuels make them compatible with modern engines, particularly when used as blends [3, 4]. This means that fewer modifications have to be made to the existing hardware, and additional costs for infrastructure and maintenance can be lower than for other biofuels. Ethanol has been used extensively and can be used at low blending ratios with gasoline without requiring engine modifications. Butanol isomers have been less commonly used in practice but may offer the potential for higher blending ratios due to having more similar properties to gasoline than ethanol. A key property of any fuel under consideration for blending is its ability to auto-ignite. If a fuel is less able to auto-ignite under engine relevant conditions than gasoline, then higher compression ratios may be able to be used in the engine, allowing more power to be delivered efficiently and economically [3]. It is therefore important to understand the auto-ignition behaviour of proposed replacement fuels over a variety of temperatures and pressures. However, there is currently very little data on the impact of blending butanol isomers with gasolines and their surrogates on key properties such as ignition delay times. This work is thus focussed on observing the auto-ignition response of gasoline when blended with the oxygenate *n*-butanol in a rapid compression machine (RCM), including investigation of the underlying processes driving observed ignition delays via chemical kinetic modelling within a zero-dimensional framework.

The consideration of butanol isomers for blending with gasoline stems from several important features. One is that *n*-butanol can be sourced from renewable bio-energy sources. The blending of oxygenates like *n*-butanol with gasoline, also enables more complete combustion, potentially leading to reductions in pollutant emissions such as carbon monoxide and soot [5]. Mixtures of other butanol isomers (2-butanol and tert-butanol) blended with TRF mixtures have previously been studied under shock tube conditions [6] demonstrating that at lower temperatures, these butanol isomers lengthened ignition delays of the mixtures, thus acting as octane boosters. Similar studies have not yet however been performed for *n*-butanol blending with gasoline, or in the lower temperature conditions of the RCM which is the aim of the current study.

Gasoline's complexity makes it practically impossible to model its chemistry exactly, so an appropriate 3-component toluene reference fuel (TRF) surrogate is formulated in this work. Methods have recently been developed to predict the octane numbers of TRF mixtures, via correlations with homogeneous gas-phase fuel/air ignition delay times for conditions covering both the research octane number (RON) and motor octane number (MON) [7]. Hence it is important to establish that TRF mixtures can be representative of the ignition behaviour of gasoline, not only for pure gasoline, but also under blending with alternative fuels. Experimentally, we assess the ability of the TRF surrogate to represent the ignition delay behaviour of the reference gasoline at low temperatures, both alone, and when blended with *n*-butanol. If observed ignition delays can then be successfully modelled using surrogate chemical mechanisms, it allows the estimation of octane numbers over wide ranges of conditions for use in engine development and optimisation. Therefore, in addition, we evaluate a combined gasoline surrogate and *n*-butanol scheme in terms of its ability to accurately reproduce the low temperature ignition behaviour of *n*-butanol, TRF, and a TRF-*n*-butanol blend from 678K- 858K, $\phi = 1$, at 20 bar. One of the major objectives of this work is to provide understanding of the underlying chemistry responsible for the observed ignition delay behaviour of the gasoline/butanol blends. This goal is achieved through local sensitivity analysis, using the brute-force approach. It serves to highlight the important reactions driving the influence of *n*-butanol when blended with gasoline on ignition delay times at low temperatures providing useful information for kinetic studies that will improve model robustness. Finally, we provide useful data for model validation and improvement including non-reactive volume histories that can be used by other modellers and for model optimisation.

2. Methodology

2.1 Surrogate formulation

For a surrogate fuel to accurately reproduce the combustion characteristics of a target fuel, either the chemical (auto-ignition, flame speed, formation of pollutants) or/and physical characteristics (e.g. evaporation) of the target fuel must be considered in its development, depending on the target property or application [8]. Primary reference fuel (PRF) is a commonly used surrogate for gasoline and is a mixture of iso-octane and *n*-heptane. However, PRFs have the same RON and MON values and therefore cannot provide a realistic representation of the octane sensitivity exhibited by gasolines and other practical fuels [9]. Sensitivity is a measure of the deterioration in the octane quality (anti-knock property) of a fuel as the end gas temperature increases above the standard MON test condition. The addition of non-paraffinic compounds such as alkenes and aromatics to PRF provides the opportunity to formulate gasoline surrogates with non-zero sensitivities. One such commonly used surrogate is toluene reference fuel (TRF) comprising toluene, iso-octane and *n*-heptane. The suitability of TRF as a gasoline surrogate for auto-ignition applications has been demonstrated via experimental studies using shock tubes [6, 10], flow reactors [11] and rapid compression machines [1]. Predicted ignition delays based on a mechanism by Mehl et al. [12] were also evaluated in [1]. Pitz et al. [13] recommended use of such a 3-component surrogate mixture to meet immediate developmental needs. However, 4-component surrogates involving TRF/1-pentene and TRF/2-pentene have also been formulated and investigated by e.g. [14-16], as well as complex multicomponent surrogates for various non-oxygenated gasolines [17, 18]. The reasonable extent of agreement between TRF and gasoline, in addition to the availability of well validated chemical mechanisms of its oxidation pathways, makes it currently a more feasible surrogate for gasoline in terms of ignition delay modelling compared to more complex surrogates [19] and blending effects, and hence it is used in this work.

The reference gasoline, PR5801 that was modelled in this work satisfies European standards and was supplied by Shell Global Solutions. The octane number (RON+MON)/2 of the reference gasoline is

91 while the H/C ratio is 1.934. The components and properties of the reference gasoline are presented in Table 1.

Table 1 - Comparison of the composition and properties of reference gasoline and formulated 3-component surrogate

Gasoline component	**PR5801[a]** **% volume**	**TRF95** **Component**	**TRF95** **% mole**	**TRF95** **% volume**
Paraffins	47.1	Iso-octane	57.50	65.64
		n-heptane	11.25	11.40
Olefins	7.9	-	-	-
Naphthenes	8.2	-	-	-
Aromatics	26.0	Toluene	31.25	22.97
Oxygenated (ethanol)	4.7	-		
RON	95		95	
MON	86.6		89.8 ([b] calc.)	
H/C	1.934		1.934	
O/C	0.011		0.000	
S= RON-MON	8.4		5.2	
AKI =(RON+MON)/2	90.8		92.4	

[a] Values are taken from analysis supplied by Shell Global Solutions

[b] Calculated based on a linear blending law and component properties list in Table S2 of Supplementary Material

Table 2 - Calculated % composition for blended surrogate.

Gasoline-butanol component	**TRF95-B20** **% mole**	**TRF95-B20** **% volume**
iso-octane	41.21	52.51
n-heptane	8.07	9.12
toluene	22.41	18.38
n-butanol	28.32	20.00

Gasoline anti-knock performance under realistic engine conditions depends on the temperature and pressure conditions but historically has been classified as a function of the RON and MON of the fuel, or alternatively of the RON and sensitivity of the fuel. According to the model of Kalghatgi [20], the effective octane number, known as octane index (OI), is given by OI= (1-K) RON + K x MON = RON - K x S, where K is an empirical factor accounting for the influence of the engine operating conditions and S = RON - MON is the sensitivity of the fuel. As mentioned in [19], the Kalghatgi correlation suggests that a correct representation of the Research Octane Number (RON) and a proper estimation of the gasoline sensitivity are enough to formulate a surrogate that can well reproduce the auto-ignition properties of gasoline. Other important properties include the hydrogen to carbon atom ratio and the aromatic content of the fuel which affect key combustion properties such as lower heating value, density and boiling point.

The method of Pera and Knop [19, 21] was employed here for formulating the TRF surrogate. Based on this method for an *n*-component surrogate, only *n*-1 properties of the target fuel can be used to constrain the surrogate model. We chose here to match the RON and the hydrogen to carbon atom ratio of the fuel and hence other quantities such as the MON and the O/C ratio may not be matched exactly. Table 1 shows that the TRF formulation gives quite a close match to the aromatic content of the gasoline with a reasonable representation of the MON and sensitivity based on calculations using a linear blending law and MONs for the surrogate components as listed in Table 2 of Supplementary Material. The ability of the surrogate to capture the true temperature sensitivity of ignition delays for the gasoline will be studied in detail here experimentally. Hence following Pera and Knop [19, 21] the TRF formulation is based on the following constraints:

$$\sum_{i=1}^{n} x_i = 1; \ \frac{\sum_{i=1}^{n} x_i H_i}{\sum_{i=1}^{n} x_i C_i} = \frac{H}{C}; \ \sum_{i=1}^{n} RON_i \, x_i = RON \qquad (1)$$

where *n* represents the number of components in the surrogate and H, C represent the number of hydrogen, carbon atoms in each of the respective fuel components. The use of a linear blending rule based on a simple average of compound values weighted by the volume fractions for determination of ON of fuel mixtures, has been shown in various studies [22-26] to be inadequate for formulating surrogate mixtures for gasoline. The linear-by-mole blending rule for determination of ONs of TRF mixtures was demonstrated in [19, 21] to produce results that are as accurate as the complex formulations found in the literature and was therefore employed for formulating the TRF surrogate mixture in this study.

The components and composition of the surrogate formulated in this work, referred to as TRF95, are presented in Table 1 alongside those for the reference gasoline, while the composition of the TRF/*n*-butanol blend surrogate (80% TRF / 20% butanol by volume), referred to in this work as TRF95-B20 are presented in Table 2. The properties of the reference gasoline in comparison with the two surrogates investigated are given in the Supplementary Material, alongside the properties of the component compounds used in the computation for each surrogate.

2.2 Ignition delay measurements using the RCM

The Leeds RCM was used for acquiring all experimental data presented. It is a heated single piston machine driven by compressed air and stopped by a hydraulic system. Compressed air from the air reservoir is used for firing the piston which then compresses the premixed mixture of fuel and oxidant/diluents in the combustion cylinder/chamber to a pre-calculated temperature and pressure prior to combustion. The major geometric and operating parameters and details of the RCM are given in Supplementary Material.

The fuels used in this study are: reference gasoline PR5801, iso-octane (UN1262), *n*-heptane (UN1206) and toluene (UN1294), all supplied by Shell Global Solutions, and high purity (99.5+%) *n*-butanol supplied by Fischer Scientific. Oxygen was used as the oxidant while diluents including oxygen, nitrogen, carbon dioxide and argon were used depending on the desired compressed temperature and pressure conditions. Preparation of the fuel-air mixtures was carried out in a separate mixing chamber, initially purged with high pressure air to remove all residuals and heated to the pre-set temperature for 2 hours. The liquid fuels were then administered into the combustion chamber via a syringe while gases were added based on their calculated partial pressures. The prepared mixture was left for over 30 minutes to obtain homogeneous mixtures for the test. The temperature and pressure of the mixture, which determines the volume of liquid fuel injected, is chosen such that the partial pressure of each fuel component is less than the vapour pressure of the fuel to ensure full vaporisation.

Experiments were performed for gasoline and TRF for T= 678-858 K, at P=20 bar and an equivalence ratio (φ) of 1. Gasoline-*n*-butanol blends and TRF-*n*-butanol blends were then studied by mixing 20% *n*-butanol by volume to the gasoline and the surrogate mixture as defined in Table 1. Full details of the set of conditions for the blend can be found in Supplementary Material.

Non-reactive tests were also carried out for all conditions with the oxygen in each mixture replaced by nitrogen. The pressure data from the non-reactive tests were used for generating the volume histories used in the variable volume simulations in this study.

Ignition delay measurements are usually referred to the temperature and pressure conditions at the end of compression. These conditions were pre-calculated using the adiabatic core hypothesis in which compression is taken to be quick enough to assume an adiabatic core gas with heat loss occurring only at the boundary layer. The temperature of the adiabatic core gas at the end of compression T_c is given by:

$$\frac{T_c}{T_i} = \left(\frac{P_c}{P_i}\right)^{\frac{\gamma-1}{\gamma}} \quad (2)$$

where T_i and P_i are the initial temperature and pressure, T_c and P_c are the temperature and pressure conditions at the end of compression, and γ is the temperature-dependent specific heat ratio. A range of end of compression temperatures were obtained by varying T_i, P_i and γ. The specific heat ratio γ is varied by varying the type of diluents used and/or the respective concentrations of the diluents in the mixture. The thermodynamic data employed in the adiabatic compression calculations were obtained from [27]. The experimental temperature and pressure at TDC are usually slightly lower than the values predicted using the adiabatic core assumption due to heat loss across the core gas. In order to minimise the error in the use of the adiabatic core relations, the actual temperatures at the end of compression were computed using equation (2) where P_c is now the measured pressure at the end of compression, while T_i, P_i and γ are the same as in enq (2). The reported ignition delays are based on the compressed temperature conditions computed from the measured pressures. The other main factors contributing to the error or uncertainty in the calculated actual compressed temperature are the error in the measured initial pressure and temperature as well as the measured compressed pressure.

The computed ignition delay time is defined as the time from the end of compression (at TDC) to the point of maximum rate of pressure rise $\left(max\, {}^{dP}/_{dt}\right)$. The time at the end of compression is determined experimentally from the point where the piston displacement becomes zero. The ignition delay times reported in this work represent an average of 3-5 runs made for each test condition with errors between runs <10% based on one standard deviation.

Figure 1 shows a typical pressure trace for a TRF + *n*-butanol mixture at compressed conditions of 20 bar and 702 K alongside the definition of ignition delay used in this work. Additional pressure traces covering various compressed temperature conditions at 20 bar and ϕ= 1 are also presented for TRF and TRF + *n*-butanol in Figures 2 – 4. The figures show very good agreement between the measured traces for gasoline and TRF at the higher temperature and under conditions of blending. The TRF surrogate exhibits a slightly shorter ignition delay times than that for gasoline at the lower temperature as discussed further in the results section.

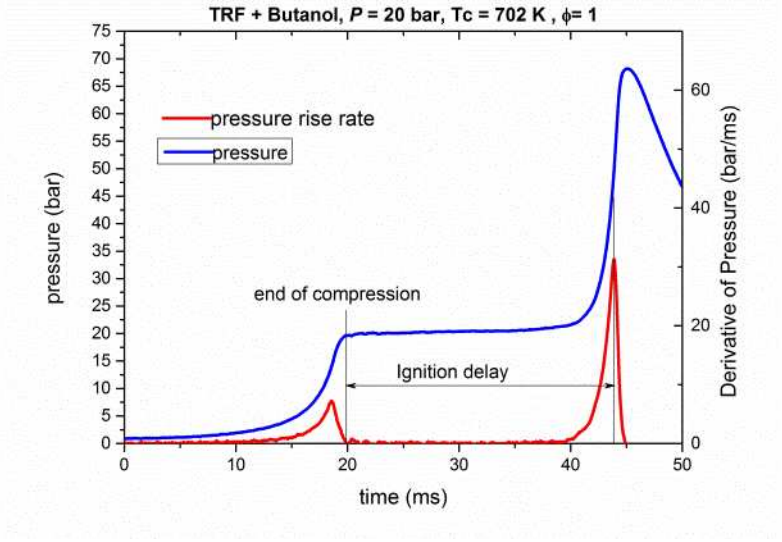


Figure 1 - Typical pressure trace illustrating the definition of ignition delay reported in this study

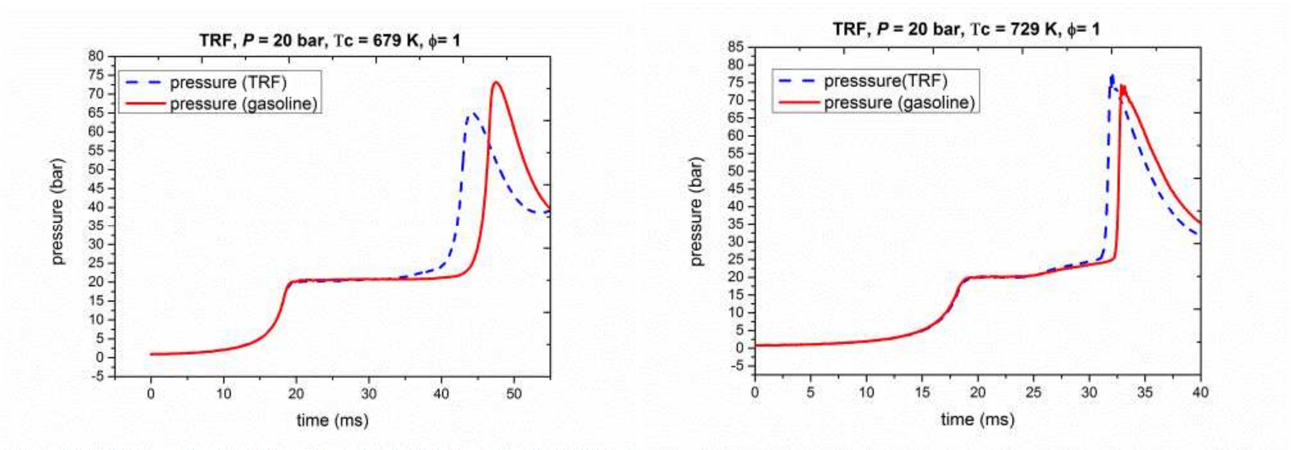


Figure 2 - Experimental pressure traces showing how TRF compares with gasoline at a) 679 K b) 729 K

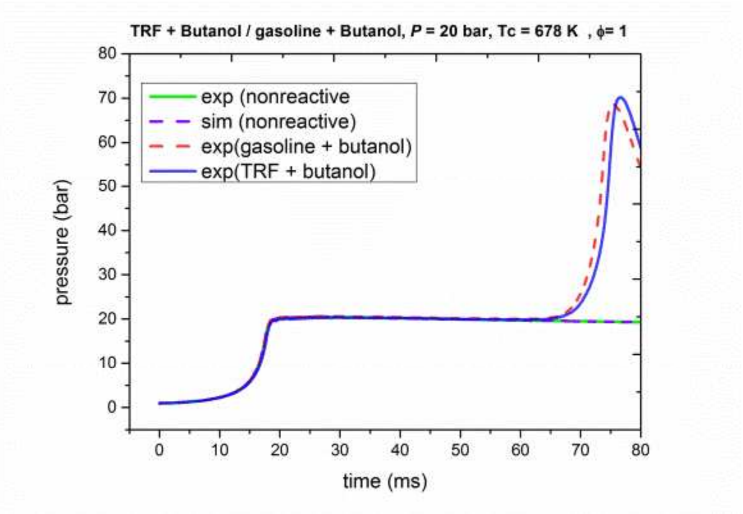


Figure 3 - Experimental pressure traces showing how gasoline + *n*-butanol compare with TRF+ *n*-butanol and how the simulated nonreactive case matches the experimental case.

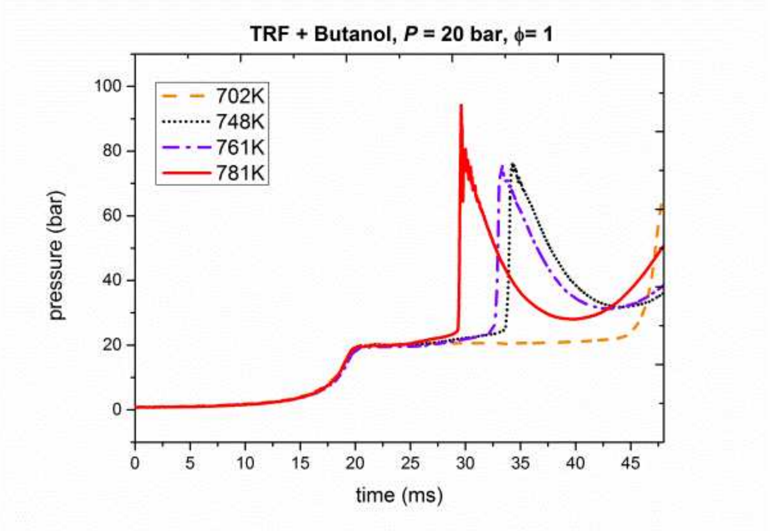


Figure 4 - Comparison of experimental pressure traces for gasoline + *n*-butanol at various temperature conditions

2.3 Simulations and sensitivity analysis

The detailed kinetic model used in this study was derived from merging previously reported mechanisms for gasoline surrogates [12] and *n*-butanol [3]. It was shown in our previous study [28] that the relative rates (branching ratios) for the hydrogen abstraction reactions of *n*-butanol by OH from the α and γ sites are critical for accurate prediction of *n*-butanol auto-ignition at low temperatures. Therefore, the mechanism of [3] was used with modifications to the rate constants for the H-abstractions of *n*-butanol by the OH radical according to rate constants suggested by McGillen et al. [29] to improve the reactivity at lower temperatures. The resulting detailed mechanism consists of 1944 species and 8231 reaction steps. The mechanism is provided as Supplementary Material to this paper. A comparison of simulated ignition delay times using the updated *n*-butanol model compared with the original model of [3] is presented in Figure 5.

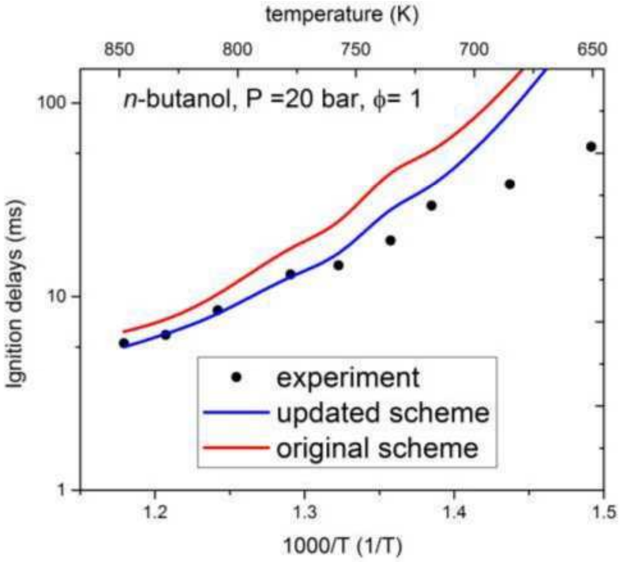


Figure 5 - Comparison of original *n*-butanol scheme with the updated scheme

Ignition delay times measured in the rapid compression machine (RCM) were simulated using CHEMKIN PRO [30] by running homogeneous variable volume history simulations accounting for heat loss in the experiments. The volume traces were determined from the measured pressure trace of the non-reactive experiment using isentropic core relations and a temperature-dependent mixture specific heat ratio [31]. Details on compositions and volume histories can be found in Supplementary Material.

In order to highlight the important reactions controlling the auto-ignition, brute-force sensitivity analyses were conducted at 20 bar and various temperature conditions using the closed homogeneous batch reactor module in CHEMKIN PRO [30] and constant volume simulations. Since brute-force analysis requires a simulation for each reaction tested, temperature sensitivities were first calculated at the time of ignition to identify the most important reactions. This method has been previously shown to identify the same reactions as a brute-force sensitivity analysis on ignition delay times and hence provides a useful screening method [32]. The brute force sensitivity coefficients were then computed for the top 20 reactions from the screening by varying the reaction rate A-factors using the formula $\sigma = \log(\tau+/\tau-)/\log(2.0/0.5)$, where $\tau+$ and $\tau-$ are the computed ignition delay times corresponding to an increase/decrease in the A-factor by a factor two [33, 34]. Therefore, negative sensitivities indicate that ignition delay times decrease when the reaction rate coefficient is increased. The values were normalized by the maximum sensitivity at each temperature and hence the most important reaction has a sensitivity index of 1.

3 Results and Discussion

3.1 The representation of the reference gasoline via the TRF surrogate

Figure 6 shows that the 3-component TRF surrogate provides a good representation of the ignition delay data in comparison to the reference gasoline for the conditions studied. Both fuels show weak negative temperature coefficient (NTC) behaviour as has been previously noted by Kukkadapu and co-workers [15, 35]. They suggested [15] that adding an additional component, 2-pentene, to *n*-heptane, iso-octane, and toluene gave a closer match to the ignition delay data for the research grade gasoline (RD387). Here however, we find that a 3-component TRF surrogate provides adequate representation of the ignition delay data for the reference gasoline, and hence the same TRF mixture will be used in the butanol blending study.

The ability of the LLNL surrogate gasoline mechanism [12] to capture the low temperature ignition delay data is also demonstrated in Fig. 6. The mechanism captures the general temperature dependence fairly well, although the NTC region predicted by the model is shallower and narrower than that seen in the experimental data. The cause of this slight discrepancy can be attributed to the model itself rather than the surrogate formulation, since the experimental data for the surrogate mixture shows a similar NTC behaviour to the gasoline. At low temperatures there is a slight over estimation of ignition delay times, although experimental uncertainties are expected to be larger for these longer delays. A brute-force sensitivity analysis was carried out (see Section 2.3) to determine the main reactions driving uncertainties in predicted ignition delays across the temperature range (Fig. 7).

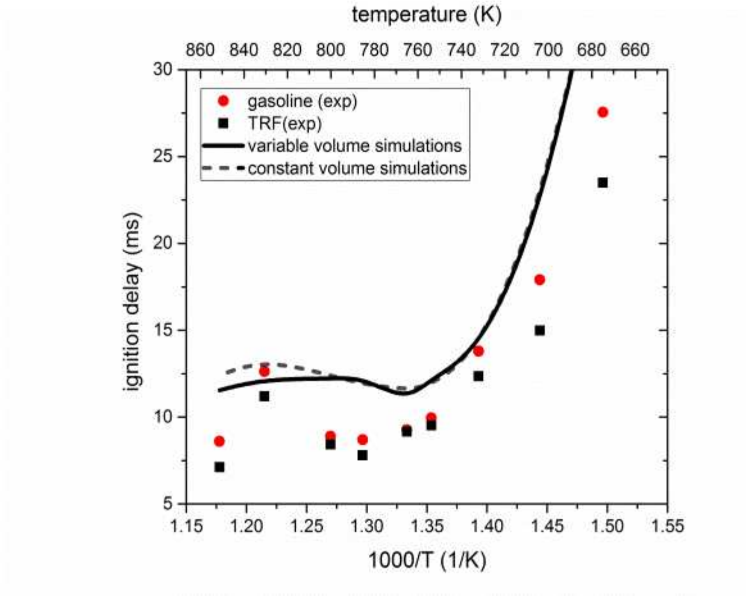


Figure 6 – Experimental and simulated ignition delays for gasoline and TRF. φ = 1, *P* = 20 bar.

The sensitivity analysis demonstrates that the most dominant reactions below temperatures of 761 K are those of OH reacting with either iso-octane, *n*-heptane or toluene with the sensitivity indices for the H abstraction reaction from *n*-heptane by OH being the lowest for these set of reactions. The absolute values of the normalized sensitivity indices for H-abstraction reactions from the α, β and γ sites are 0.739, 0.631 and 1.000 respectively for iso-octane while those for *n*-heptane are 0.389, 0.581 and 0.512 respectively. The only H abstraction reaction for toluene highlighted by the sensitivity analysis of the LLNL scheme is via HO_2 radical. The main toluene + OH route captured in the sensitivity analysis is expressed as the reverse rate constant leading to the formation of CH_3 and C_6H_5OH and its sensitivity index was estimated as 0.918. In contrast to both *n*-heptane [36] and iso-octane [37, 38], toluene does not exhibit NTC behaviour [39], and the sensitivity analysis shows the reaction of toluene + OH is almost as important as that of iso-octane at low temperatures. A high temperature shock tube study for toluene was reported in [40] where the reaction of toluene + H was noted as the most dominant abstraction channel in simulations carried out at 10 atm and 1600 K . Large discrepancies in toluene mechanisms were noted in [39] for stoichiometric toluene ignition delay data at high pressure (45 bar) and 1045 K in an RCM. Their work also showed substantial discrepancies in local sensitivities between the different mechanisms, with toluene + OH and toluene + H reaction channels ranking very highly for one of the mechanisms and then very poorly for another of the mechanisms [39]. Hence the relative importance of different product channels for these reactions could be important for the accurate prediction of the behaviour of surrogate mixtures. The main kinetic study of toluene + OH of relevance to combustion temperatures is a transition state theory study from Seta et al. [41]. There are likely to be large uncertainties in this system which will clearly impact on the robustness of TRF mechanisms. Further detailed studies on toluene would therefore be beneficial in order to elucidate on its key oxidation channels at low temperatures.

At slightly higher temperatures, iso-octane + OH is the more dominant reaction when compared to that of toluene. This reaction was also dominant in the analysis of a 4-component surrogate mixture in [15], at 780 K for stoichiometric conditions, followed by the toluene + OH pathways and to a lesser extent *n*-heptane + OH as seen here. Here, the reaction of formaldehyde + OH is important across the whole temperature range, but particularly so at the highest temperature. The sensitivity analysis also shows that the reactions of HO_2 dominate above 780 K. Nagy et al. [42] highlighted uncertainties of a factor of 2.5 in the reaction rate for $HO_2 + HO_2 = H_2O_2 + O_2$ for temperatures above 700 K. A similar level of uncertainty was suggested for OH + OH (+M) = H_2O_2 (+M) which ranks highly here for temperatures above 780 K.

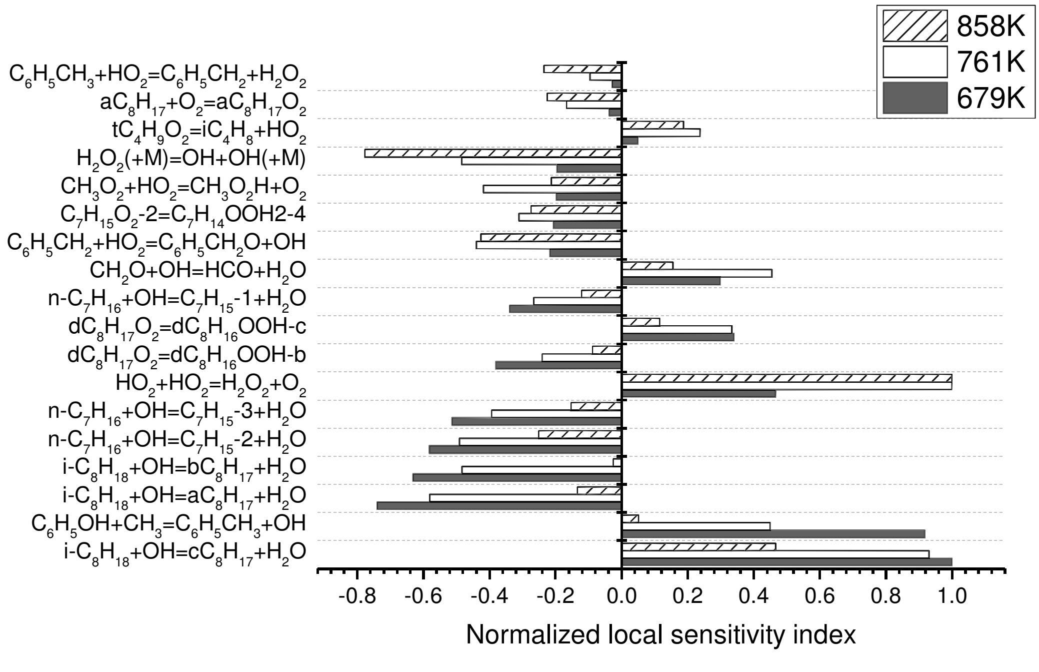
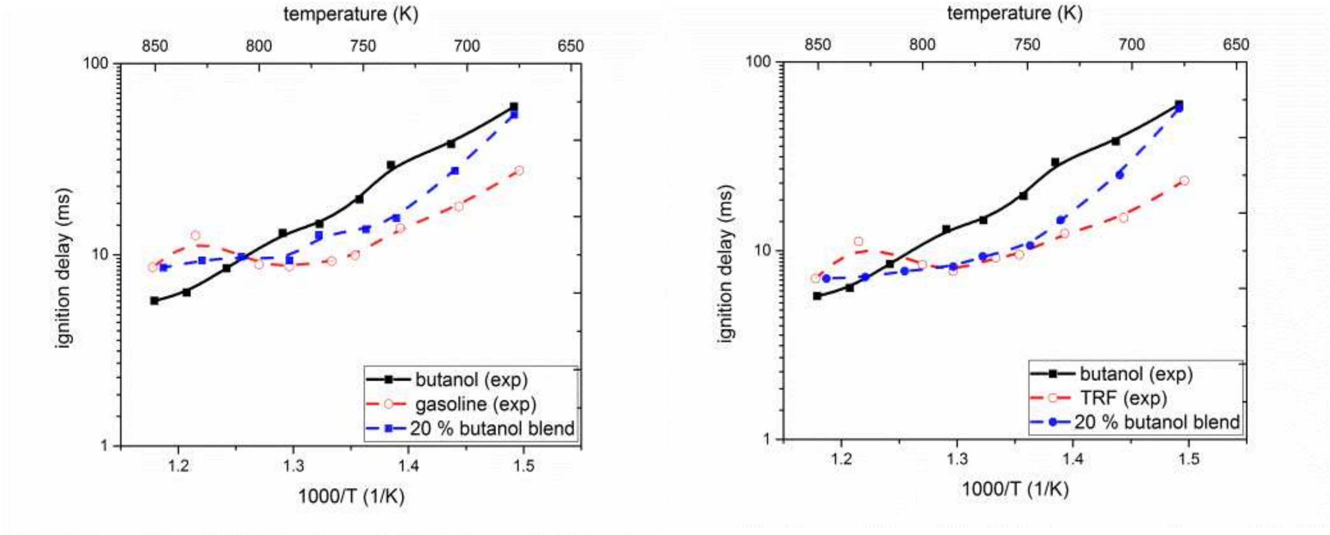


Figure 7 - Normalised local sensitivity indices for simulations of ignition delay time for TRF at 3 different temperatures. φ = 1, P = 20 bar.

The isomerisation reactions from RO_2 to QOOH are of lower importance here than fuel + OH which contrasts with the behaviour of smaller molecules [43]. However, they do feature for both iso-octane and *n*-heptane channels across the range of temperatures studied, and thus uncertainties in the temperature dependence of these reactions could affect the prediction of NTC behaviour. Nevertheless, since overall the predictions from the LLNL surrogate mechanism provide a reasonable representation of the temperature dependence of the gasoline ignition delay data we proceed to use the mechanism as the basis for modelling blending in the next section.

3.2 The influence of *n*-butanol blending

20% *n*-butanol by volume was blended with both the gasoline and TRF surrogates to determine its influence on ignition delay times. Figure 8 shows that both for the gasoline and the TRF, the ignition delays of the blend lie somewhere in between those of the unblended fuels across the temperature range. The chosen TRF formulation is seen to behave very similarly to gasoline and therefore appears to provide a reasonable representation of the effects of blending across the temperature range. However, an interesting feature emerges at the lowest temperatures studied, where the ignition delays for the blend lie very close to those of pure *n*-butanol despite it being only 20% of the mixture. At these lower temperatures the *n*-butanol clearly acts as an octane booster. The addition of *n*-butanol also has the effect of smoothing out the NTC region when compared to the gasoline/TRF behaviour. A similar effect was reported in Frassoldati et al. for ethanol, where ethanol addition to a PRF mixture was observed to result in the disappearance of the NTC region [44]. As highlighted in this work (Figure 8) and in [44], the inhibiting effect of alcohols, however, disappears at high temperatures as the observed delays are quite similar for both the gasoline and the alcohol blend. The effect of blending a single stage ignition fuel such as *n*-butanol with a two-stage fuel (i.e. *n*-heptane, PRF or gasoline) was also reported in Saisirirat et al. [45]. In their work, similar to the findings in this study, it was shown that at low to intermediate temperatures, the cool flame delay and the main combustion stage delay of *n*-heptane are increased with increasing 1-butanol addition to *n*-heptane.



(a) (b)

Figure 8 - Experimental ignition delays for (a) gasoline and (b) TRF on blending with 20% *n*-butanol by volume. P = 20 bar, ϕ= 1.

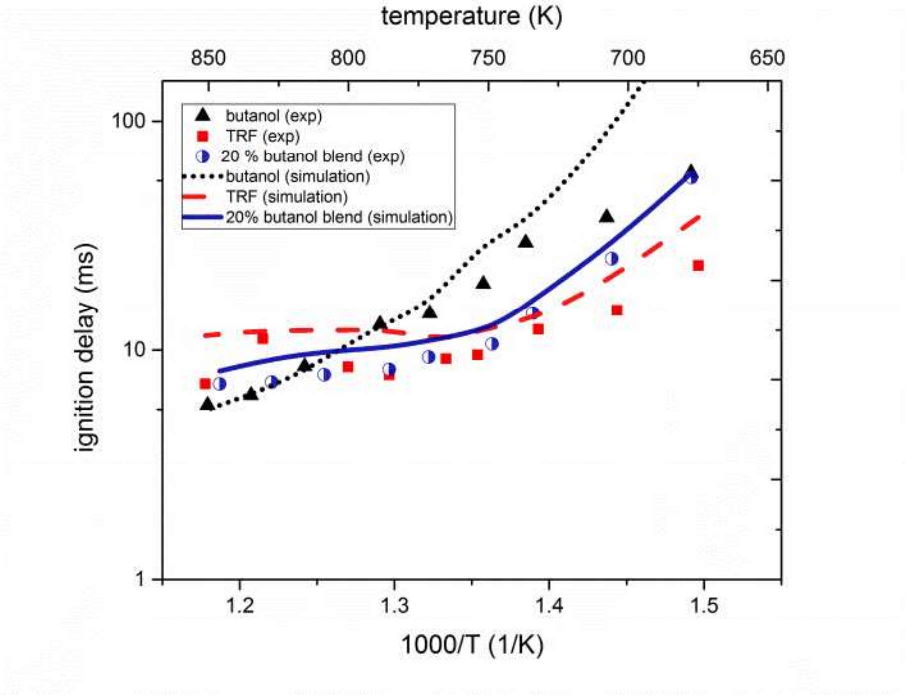


Figure 9– Comparison of simulated and experimental ignition delays for TRF on blending with 20% *n*-butanol by volume with those of stoichiometric TRF and *n*-butanol. P = 20 bar.

Simulations of the blend were achieved by combining the LLNL gasoline surrogate mechanism [12] with the *n*-butanol scheme of Sarathy et al. [3] with updates as described above. The scheme reproduces the temperature dependence of the ignition delays well for the blends, with the predicted delays lying between those for TRF and *n*-butanol across the temperature range (Fig. 9). However, at the lowest temperatures, the simulated delays for *n*-butanol are significantly longer than the measured data. (triangle symbols in Fig. 9). Hence the combined model seems to better predict the delays for the blends than for *n*-butanol. The sensitivity analyses presented in Figs. 10 and 11 highlight possible reasons for the discrepancy.

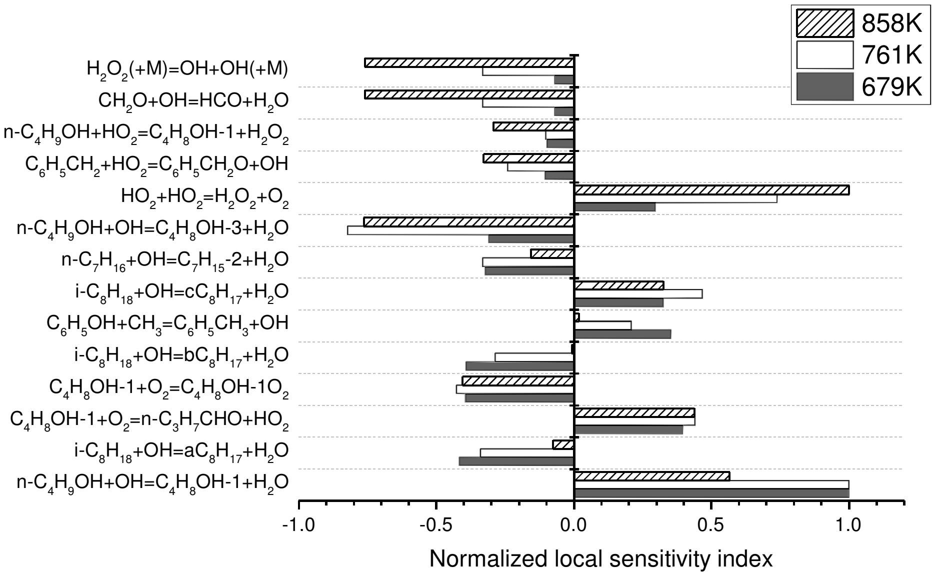


Figure 10 - Normalised local sensitivity indices for simulations of ignition delay time for TRF, *n*-butanol blend at 3 different temperatures. φ = 1, *P* = 20 bar. *n*-butanol is 20% by volume.

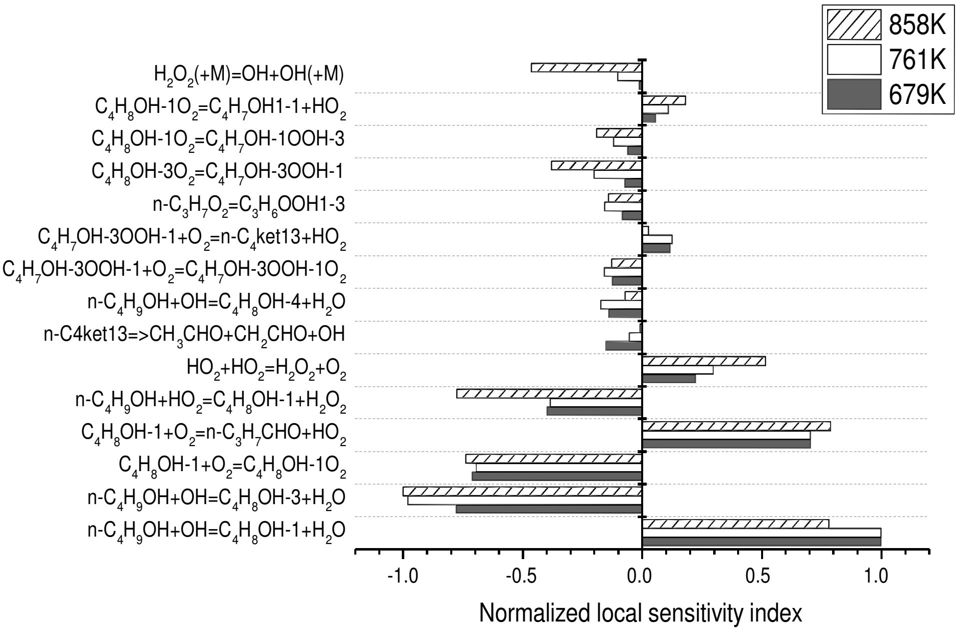


Figure 11 - Normalised local sensitivity indices for simulations of ignition delay time for *n*-butanol at 3 different temperatures. $\varphi = 1$, $P = 20$ bar.

The first interesting feature is that, despite forming only 20% of the mixture by volume, it is the *n*-butanol + OH channels that dominate the predictions for the blends across the temperature range studied (Fig. 10). Similar to the findings in Frassoldati et al. [44], the sensitivity analysis of Fig. 10 also reveals the role of *n*-butanol in scavenging OH radicals from the system particularly leading to the formation of H_2O and hydroxybutyl radicals. For the blend mixture, H abstraction from the α site dominates at the lowest temperatures. Abstraction from the γ site increases in relative importance as temperature increases. For *n*-butanol (Fig. 11), the γ pathway is relatively more important at the lowest temperature compared to the blend (Fig. 10). It is this low temperature region for *n*-butanol where the biggest discrepancies occurred between the simulated and experimental results. The temperature dependence for the overall reaction rate suggested in [29] is based on a fit to both low temperature measurements below 400 K and the high temperature shock tube measurements of [46] (888−1178 K). Thus, the uncertainty in the overall rate may be larger in the temperature region of interest here. In addition, a previous global sensitivity study of predicted ignition delays for *n*-butanol at 725 K and 15 bar [28], demonstrated that the sensitivity to the relative rates of abstractions from the α and γ sites was much higher than that to the overall rate constant. McGillen et al. suggest higher uncertainties for the site specific channel for the γ site compared to the α site [29]. Hence uncertainties in the relative rates could be significant.

The sensitivity analysis shows that the hydroxybutyl radicals produced via the main fuel hydrogen abstraction reactions from the α sites are the most dominant compared to those from the other abstraction sites both in terms of RO_2 and HO_2 formation. The α-hydroxybutyl radical are consumed via two different reaction pathways: the oxygen addition reaction (α-hydroxybutyl + O_2) leading to the formation of the peroxy radical (RO_2) that drives auto-ignition; and the competing oxygen addition reaction (α-hydroxybutyl + O_2) leading to the formation of HO_2, a termination step that inhibits auto-ignition. Although it is well known [43] that isomerisation reactions of RO_2 dominate auto-ignition chemistry in general low-temperature mechanisms for smaller fuels, the dominance of the main fuel hydrogen abstraction reactions in the blended TRF-butanol scheme may be due to its key role in determining the amount of *n*-butanol that goes to termination steps compared with how much is available for chain branching and propagation. The ability of the reaction mechanism to correctly predict the low temperature delays for both *n*-butanol and the blend requires that the balance between the two dominant abstraction channels for *n*-butanol + OH is known for a wide range of temperatures and significant uncertainty still exists requiring further study.

Conclusions

The influence of blending *n*-butanol at 20% by volume on the ignition delay times for a reference gasoline was studied in a rapid compression machine (RCM) at 20 bar from 678 K-858 K. Delay times for the blend lay between those of gasoline and *n*-butanol under stoichiometric conditions across the temperature range. At lower temperatures, delays for the blend were much closer to those of *n*-butanol than gasoline, despite *n*-butanol being only 20% of the mixture, showing that *n*-butanol acts as an octane enhancer over and above what might be expected from a simple linear blending law. Further studies employing a wider range of blending ratios and exploring potential nonlinearities in the anti-knock behaviour of *n*-butanol, TRF blends will further add to the results of this study. At higher temperatures the delay times for the blend were slightly shorter than those for gasoline and TRF within the shallow NTC region, although similar at the highest temperatures tested here. Whether the addition of *n*-butanol leads to octane enhancing qualities will therefore be highly dependent on local engine temperature conditions with a particularly sensitive region around 775-850 K. Experimentally, the 3-component TRF surrogate was able to capture the gasoline trends well across the temperature range. This was the case for both pure gasoline and on blending with *n*-butanol at 20%. The TRF formulation used therefore appears to be fairly robust but would need to be tested over wider ranges of blending conditions in future work. Based on simulations using a detailed chemical mechanism, hydrogen abstraction reactions by OH from *n*-butanol appear to be key in predicting the effect of blending. Uncertainties in the temperature dependence of relative abstraction rates from the α and γ sites may still be present within current mechanisms, and in particular may affect the ability of the mechanisms to capture the low temperature delay times for *n*-butanol. Further studies of the product channels for *n*-butanol + OH for temperatures of relevance to combustion applications could help to improve current mechanisms. At higher temperatures, the reactions of HO_2 and that of formaldehyde with OH also became critical and attempts to reduce uncertainties in the temperature dependent rates of these reactions would be useful.

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Figure Captions

Figure 1 - Typical pressure trace illustrating the definition of ignition delay reported in this study.

Figure 2a - Experimental pressure trace showing how TRF compares with gasoline at 679 K.

Figure 2b - Experimental pressure trace showing how TRF compares with gasoline at 729 K.

Figure 3 - Experimental pressure traces showing how gasoline + *n*-butanol compare with TRF+ *n*-butanol and how the simulated nonreactive case matches the experimental case.

Figure 4 - Comparison of experimental pressure trace for gasoline + *n*-butanol at some close temperature conditions.

Figure 5 - Comparison of original butanol scheme with the updated scheme.

Figure 6 – Experimental and simulated ignition delays for gasoline and TRF. $\varphi = 1$, $P = 20$ bar.

Figure 7 - Normalised local sensitivity indices for simulations of ignition delay time for TRF at 3 different temperatures. $\varphi = 1$, $P = 20$ bar.

Figure 8 - Experimental ignition delays for (a) gasoline and (b) TRF on blending with 20% *n*-butanol by volume. $P = 20$ bar.

Figure 9 – Comparison of simulated and experimental ignition delays for TRF on blending with 20% *n*-butanol by volume with those of stoichiometric TRF and *n*-butanol. $P = 20$ bar.

Figure 10 - Normalised local sensitivity indices for simulations of ignition delay time for TRF, *n*-butanol blend at 3 different temperatures. $\varphi = 1$, $P = 20$ bar. *n*-butanol is 20% by volume.

Figure 11 - Normalised local sensitivity indices for simulations of ignition delay time for *n*-butanol at 3 different temperatures. $\varphi = 1$, $P = 20$ bar.

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