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Testing the validity of a mechanism describing the oxidation of binary n-heptane/toluene mixtures at engine operating conditions

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Abstract

The aim of the work is to evaluate the influence of the n-heptane/toluene ratio on the reactivity of ~~binary toluene-Toluene~~ ~~reference-Reference fuels-Fuels (TRF)(TRF)~~, through a combined experimental and numerical work. Novel experimental ignition delay time (IDT) data of three binary TRFs of varying n-heptane/toluene ratios are obtained in a high-pressure shock tube (HPST) and a rapid compression machine (RCM) at conditions relevant to novel engine operation. Measurements have been performed at two pressures (10 and 30 bar), and three fuel/air equivalence ratios (0.5, 1.0 and 2.0) for TRF mixtures of 50%, 75% and 90% vol. toluene concentration, ~~over the temperature range of 650–1450 K~~. It was found that, increasing the n-heptane content, an increase in the reactivity and shorter IDTs occur. Reduced sensitivity to the equivalence ratio was observed at high temperatures, especially for high toluene content mixtures. A ~~well validated#~~ ~~accredited~~ detailed kinetic mechanism for TRF oxidation was utilized to provide further insight into the experimental evidence. The mechanism, which has recently been updated, was also assessed in terms of its validity, contributing thus to its continuous development. Reaction path analysis was performed to delineate critical aspects of toluene oxidation under

the considered conditions. Further, sensitivity analysis highlighted the interactions between the chemistry of the two TRF components, revealing toluene's character as a reactivity inhibitor mainly through the consumption of OH radicals.

Keywords

Ignition Delay Time, HPST, RCM, toluene, n-heptane, detailed kinetics

1. Introduction

Efficient and clean combustion of hydrocarbons has always attracted the attention of the scientific community. The two most common types of Internal Combustion Engines (ICEs) namely Spark Ignition (SI) and Compression Ignition (CI) make use of real (i.e. being the outcome of a distillation process in a refinery) gasoline and diesel fuels, respectively. These fuels are complex mixtures of several hydrocarbon families [1] and hence, simplified mixtures, denoted as fuel surrogates, are used to emulate their properties. The most common fuel surrogates for the combustion of real gasoline and diesel fuels consist mainly of the so-called primary reference fuels (PRFs), i.e. mixtures of iso-octane and n-heptane, which mark the 100 and 0 in the octane rating scale, respectively. Matching the octane numbers (RON and MON [2]) of the actual fuel is a measure of a fuel's resistance to auto-ignite under a compression ignition engine environment [3]. As engine development has moved towards unconventional low-temperature combustion (LTC) operating modes, PRF blends proved to be inadequate to describe the actual fuel's behavior e.g. [4]. This has also been attributed to the fact that the utilized PRF blends exhibited zero sensitivity i.e. RON=MON [5]. Sensitivity, defined as the difference between RON and MON values was found to be more important than the sole values of RON and MON as it described the auto-ignition performance throughout a wide temperature regime and not only at the temperatures of interest for conventional gasoline and diesel engines e.g. [6], [7]. In an effort to capture the behavior of real transportation fuels in engines operating under LTC modes, PRF fuels were blended with toluene, the simplest methylated aromatic species, creating the so-called Toluene Reference Fuels (TRF) [8, 9]. [TRF is a generic term frequently used to define binary or ternary mixtures of toluene with either or both n-heptane and iso-octane, in the present study used to denote binary toluene and n-heptane mixtures. It is further noted that](#) Toluene has often been used as an anti-knock measure since it exhibits very high RON and MON numbers, between 116-120 and 103-110, respectively [8, 10-12].

Toluene oxidation has attracted a lot of attention [as a single component](#) which has yielded a large amount of studies, both numerical and experimental. A detailed list of the toluene related work has been reported previously by Metcalfe et al. [13]. Speciation data at atmospheric pressure for fuel-lean and fuel-rich mixtures, were measured in a flow- [14] and a jet-stirred reactor [15]. These two studies have served as validation targets and were subsequently used for modelling development purposes. The former dataset was utilized for the development of a sub-model for benzene and toluene

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26 oxidation with 68 and 62 additional reactions [16], while the second study ~~came along with~~ included a developed model of
27 120 species and 920 reactions [15]. [Flow reactor measurements and model development were also carried out by Bounaceur](#)
28 [et al. \[17\]. The mechanism developed was based on a previously published benzene model \[18\].](#) Ignition delay times (IDT)
29 were also measured in shock tube studies for various equivalence ratios at pressures varying from 1.95 to 8.85 atm [19].
30 IDTs, defined as the time interval between the initiation of a combustion process and the first energy release, belong to the
31 global reactivity measurements, provide modeling targets and are used for engine optimization [20]. These studies
32 focused at temperatures above 1400 K. A more recent study expanded the available data to temperatures lower than 900
33 K, measuring at a pressure range between 14–59 atm [21], while lower temperature measurements (600–900 K) were
34 completed in a rapid compression machine (RCM) study [22]. Similarly, IDT data were measured at temperatures close
35 to 1000 K for pressures in the range 25–45 atm, for lean and rich mixtures [23]. In addition to the models mentioned
36 previously, which were focused on ideal reactors, another detailed toluene mechanism of 141 species and 743 reactions
37 was developed [24] utilizing experimental data from premixed and counter-flow flames as well. The two initial models
38 reported above [15, 16], have been, and still are subjected to optimization by studies that followed [25–28].
39 Toluene's IDT has also been widely studied as a fuel component and not solely as a neat fuel. The first of these numerous
40 studies investigated stoichiometric blends of 1:1 toluene/n-heptane and toluene/iso-octane mixtures in an RCM at 4 and 12
41 bar, reaching temperatures as low as 650 K [28][29]. Subsequently, the concentration of toluene was increased to 72%
42 (vol.) against 28% of n-heptane in a High Pressure Shock Tube (HPST) study [29][30] that focused on both fuel-lean and
43 stoichiometric mixtures at various pressures, offering six sets of IDT data in the intermediate temperature regime. This
44 work was published with an accompanying study that utilized the experimental data for modeling purposes, developing a
45 model for a binary TRF mixtures [30][31]. Moreover, mixtures of toluene/iso-octane and toluene/n-heptane (10/90 and
46 40/60% vol.) were measured in a shock tube study at 40 bar at two equivalence ratios ($\phi = 0.5$ and 1.0) [31][32]. Recently,
47 toluene/dimethyl ether (DME) mixtures were investigated at several blending ratios ranging from 100% toluene to 100%
48 DME, in both a HPST and in an RCM, using DME as a radical initiator [32][33].
49 Despite the systematic effort and the wide range of studies available, accurate predictions of toluene oxidation remains
50 challenging. The issue is manifested in that most literature models are unable to reproduce experimental data at lower
51 temperatures. In this context, the present study, like others before [27–31], focuses on blending toluene with a very reactive
52 and well characterized fuel as is n-heptane, to increase mixture's reactivity and to extend the available experimental data
53 to a wider range of conditions.

54 This study provides novel experimental ignition delay time data at conditions that have not been investigated yet, measuring
 55 both at low temperatures and high toluene concentrations, in an attempt to fill the observed gap in the literature.
 56 Measurements include three mixtures (50%, 75% and 90% vol. by toluene concentration, [balance n-heptane](#)) at lean
 57 ($\phi=0.5$), stoichiometric ($\phi=1.0$) and rich ($\phi=2.0$) conditions at 10 and 30 bar over the temperature range of 650–1450 K.
 58 [Detailed conditions of the investigated mixtures are listed in Table 1](#). The experiments were carried out in the high-pressure
 59 shock tube (HPST) and rapid compression machine (RCM) at the National University of Ireland, Galway (NUIG). The
 60 devices have been used in a complementary way in order to cover the desired temperature range. Further, in order to
 61 investigate the synergies of toluene and n-heptane in the reactivity of the TRF mixtures and to provide a detailed kinetics
 62 insight to the observed trends, the LLNL TRF detailed kinetic mechanism is utilized. Mechanism performance against the
 63 herein obtained data is assessed for both the original version of the mechanism [\[32\]\[33\]](#) as well as for the recently updated
 64 [versionone](#) [\[33, 34\]](#), and the latter is found to yield improved and an overall good agreement. Sensitivity and reaction path
 65 analysis have been performed to delineate the key kinetic processes which control the oxidation of the considered mixtures
 66 under the reported conditions.

Toluene Heptane ratio	Mole fraction (%)					
	C ₇ H ₈	C ₇ H ₁₆	O ₂	N ₂	Ar	Phi
50:50	1.03	1.03	20.57	77.37 (15.47)	(61.9)	1
50:50	0.52	0.52	20.8	78.17 (23.45)	(54.72)	0.5
50:50	2.01	2.01	20.16	75.82	-	2
75:25	1.62	0.54	20.55	77.30 (17.77)	(59.53)	1
75:25	0.82	0.27	20.77	78.14 (24.23)	(53.91)	0.5
75:25	3.18	1.06	20.11	75.66	-	2
90:10	2.01	0.22	20.53	77.24	-	1
90:10	1.02	0.11	20.76	78.11	-	0.5
90:10	3.93	0.44	20.08	75.55	-	2

*Numbers in parenthesis correspond to N₂ mole fraction when Argon is also used as diluent in the respective RCM cases for the intermediate temperature regime (830-1000K)

67 [Table 1: Detailed conditions of the experimentally investigated mixtures](#)

68

69 2. Experimental Setup

70 2.1 High Pressure Shock Tube

71 Ignition delay times at higher temperatures (800–1400 K) were measured in the HPST facilities of NUIG. The experimental
 72 setup has been described previously [\[35\]\[36\]](#), thus it will be only briefly described here. The tube consists of two separate
 73 sections; the driven section, where the mixture sample is loaded, and the driver section where He or He/N₂ is introduced.
 74 These sections are 5.73 m and 3 m long respectively, and are separated by a 3 cm long double-diaphragm (middle) section.
 75 The aluminum diaphragms are pre-scored before each experiment. After the mixture is introduced into the driven section,

76 the driver and middle sections are filled with the [He/N₂ driven gas](#) to roughly half of the driver gas pressure. The driver
77 section [alone is finally](#) filled to the driver pressure. The gas from the middle section is evacuated and the pressure difference
78 is sufficiently high to burst the diaphragms. The high-pressure driver gas expands rapidly into the driven section creating
79 a reflected shock wave that heats and compresses the mixture to the desirable conditions. The achieved shock velocity is
80 measured by interpolating the shock arrival time at PCB 113B24 pressure transducers along the driven section. A 603B
81 Kistler pressure transducer is used to monitor the pressure of the gas at the endwall. The ignition delay time is defined as
82 the time elapsed between the arrival of the shock wave at the endwall and the ignition event. The mixture was prepared by
83 controlling the partial pressure of each constituent species in a stainless-steel mixing tank, [while ensuring that it did not](#)
84 [exceed a value of at least half of its vapor pressure](#). A heating system was installed on the mixing tank and the piping
85 leading to the HPST to ensure that the fuel would remain in the vapor phase.

86 The entire experimental apparatus as well as the manifolds, piping and mixing vessel were heated to 60°C but not higher,
87 to avoid overheating damage to the equipment (pressure transducers, gauges, etc.). ~~The mixture was prepared, ensuring~~
88 ~~that the partial pressures of each of the fuels did not exceed a value of at least half of its vapor pressure.~~

89 2.2 Rapid Compression Machine

90 The ~~(red)~~ RCM used in this study is one of the twin RCMs currently in operation at NUIG. It is the original RCM built at Shell
91 [\[36\]\[37\]](#) and later re-commissioned at NUIG [\[37\]\[38\]](#). A short description follows here. Two opposite facing pistons are pushed
92 forward to volumetrically compress a fuel mixture. At the end of compression (~16 ms), the pistons are locked forward
93 and maintain a constant reactor volume, thus allowing a constant volume reaction to take place. The motion of the pistons
94 is controlled pneumatically, while a chamber filled with hydraulic oil surrounding the connecting rod is used to lock and
95 release the pistons. The RCM has a 168 mm stroke and a 38.2 mm bore. The position of the pistons is monitored with a
96 Positek P100 linear inductive position sensor that is within the hollow connecting rod. The pressure inside the reaction
97 chamber is measured using a Kistler 6045a mounted in the reaction chamber wall. A Kistler 5018 is used to amplify the
98 pressure trace, while a Sigma 90 oscilloscope by Nicolet Technologies sampling at 20 kHz and 12-bit resolution is used
99 for recording the traces. The pressure traces are filtered by a hardware Buttersworth low-pass filter with a cut-off frequency
100 of 3 kHz, after amplification. [The compression ratio of the RCM, defined as the ratio of the density before and after](#)
101 [compression is 10.](#) The ignition delay time is defined as the time between end of compression and the maximum pressure
102 rise due to chemical reactions. The temperatures at the end of compression were adjusted by varying the initial temperature
103 of the chamber. This was achieved by the installation of an electrical heating system which has been optimized to minimize
104 stratification in the chamber. More detailed description of the heating system installation can be found in [\[38\]\[39\]](#). The

105 maximum initial temperature used was 105°C, to avoid degradation of the seals inside the machine. Nitrogen was used as
106 a sole diluent for the low-temperature measurements (650–830 K), while argon was added in the mixtures to proceed to
107 the higher temperature regime (830–1000 K) and couple the RCM data with the ones obtained in the HPST. Throughout
108 the measurements the deviation from the desired compressed pressure was maintained below 1%. The pistons used in this
109 study are creviced leading to a suppression of the roll-up vortices that otherwise form within the boundary layer gas,
110 offering higher homogeneity in the mixture. They are a modified version of the [pistons](#) proposed by [\[39\]\[40\]](#). Heptane was
111 supplied by TCI UK with a purity of 99%. Toluene was supplied by Sigma Aldrich ~~and came~~ with a purity of 99.9%. None of the
112 fuels ~~were~~ subjected to any further purification process. The blended samples were made by mass on a high precision scale.
113 Nitrogen, argon and oxygen were provided by BOC Ireland.

114 2.3 Experimental issues

115 In this study three blending ratios of high toluene content were measured. The high toluene concentration increases the
116 ~~deposition~~ of soot and other residues in the experimental facility, *e.g.* in the RCM reaction chamber. Previous studies have
117 reported an early heat release and the occurrence of pre-ignition due to the presence of such depositions [21], while some
118 works [\[32\]\[33\]](#) dealt with this issue by performing three consecutive oxygen shots after each experiment in the RCM. This
119 proved to be a good method to clean the chamber and to obtain repeatability. In the present work the fuel-rich mixtures
120 (*i.e.* $\phi = 2.0$) and ~~the ones with~~ high (*i.e.* 90%) toluene content ~~mixtures~~ were not studied, due to similar difficulties. In
121 particular it was found that the consecutive repeated shots for these cases ~~would pose a very increased~~ ~~resulted in higher~~
122 IDT compared to the initial ~~experiment~~. To solve this, the method reported in [\[32\]\[33\]](#) was used, leading however, to
123 no ignition.

124 3. Chemical Kinetic Modeling

125 In this work, the LLNL model was adopted in its ~~original~~ ~~initial~~ state published in [\[32\]\[33\]](#), while an ~~updated~~ ~~rather~~ version with
126 modifications to the n-heptane part from [\[33\]\[34\]](#) and the toluene part from [\[34\]\[35\]](#) was also utilized for comparison. The main
127 modifications on the n-heptane mechanism include updated isomerization reactions for the heptyl radicals, as well as
128 updates in the rates for cyclic ether formation. A detailed discussion on the modified parts is beyond the scope of the
129 present paper and the reader is referenced to respective studies [\[343, 354\]](#) for further insight. The model includes 1426 species
130 and 6128 reactions. Simulations were carried out utilizing the Aurora module of CHEMKIN-PRO [\[40\]\[41\]](#) with constant
131 volume conditions. Heat loss effects due to the facility for the RCM simulations as described in [\[41\]\[42\]](#) are taken into
132 consideration in simulations. Input files for RCM simulations can be found ~~in the~~ ~~as~~ Supplementary ~~m~~Materials.

4. Results and Discussion

The measured ignition delay times for all conditions are plotted in Fig. 1 allowing for a comparison of many different variables. Each row contains measurements for a certain equivalence ratio with an ascending order ($\phi=0.5$ in the top row, $\phi=1.0$ in the middle and $\phi=2.0$ in the bottom row). Accordingly, the columns present measurements for mixtures with respect to their toluene content in ascending order, i.e. toluene/n-heptane ratio of 50/50 (left), 75/25 (middle) 90/10 (right).

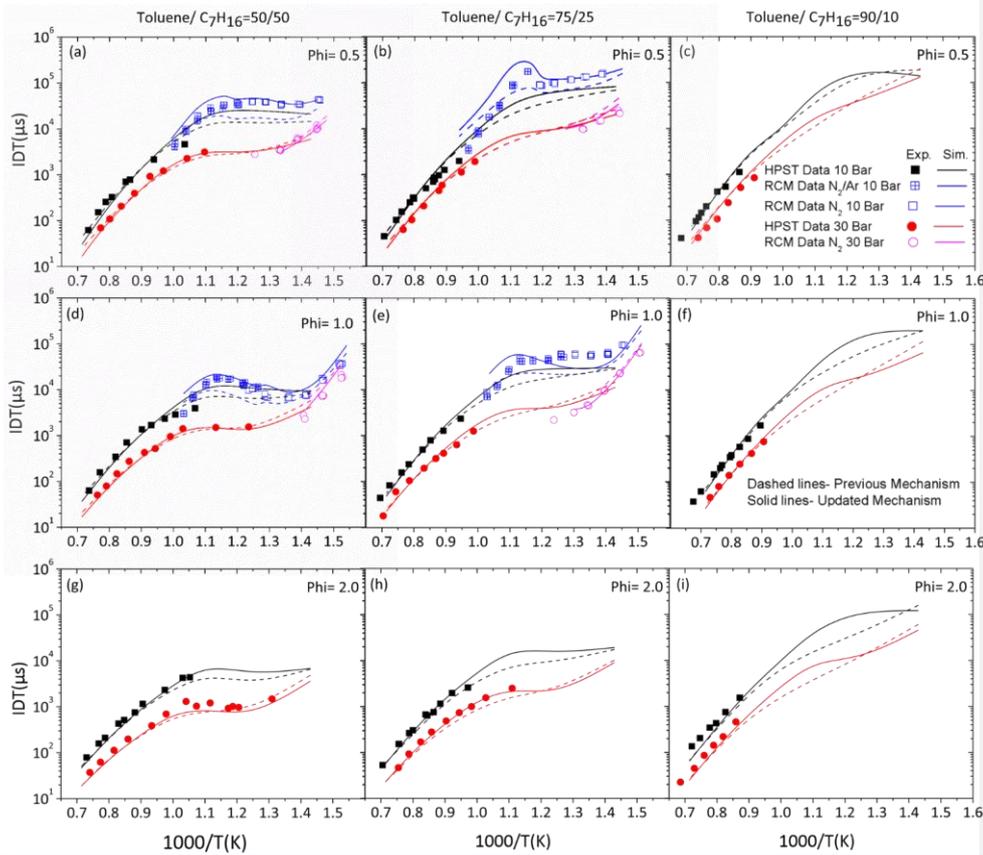
Interestingly, a comparison along the y-axis (vertically) shows that the IDTs in the 10 bar measurements are almost insensitive to variations in equivalence ratio at temperatures above 1150 K. This behavior is less pronounced as pressure increases and can be observed at temperatures only above 1250 K. Increasing the toluene concentration enhances this effect as data are sensitive to temperature for $T > 1050$ K for the low-pressure measurements. As temperatures decrease beyond these thresholds the fuel-lean cases have the longest IDTs. Another important observation can be made for the 90/10 mixture ratio at 10 bar, where the IDT for the fuel-lean and the stoichiometric cases coincide, while the fuel-rich mixtures have significantly longer IDTs at low pressures. At 30 bar, the fuel-rich and stoichiometric mixtures coincide, while the fuel-lean mixture has notably shorter IDTs.

A comparison of the results in the x-direction (horizontally (a) \rightarrow (c), (d) \rightarrow (f) and (g) \rightarrow (i)) shows an increase in IDTs with increasing toluene content. However, this increase is more pronounced at lower temperatures and as the equivalence ratio (ϕ) increases. As discussed previously, rich mixtures ($\phi=2$) and mixtures with high toluene content (90/10) were not measured in an RCM, therefore Figures 1 (c), (f), (g), (h), (i) contain no RCM data.

Regarding the performance of the mechanisms, Fig. 1(a) shows that the current updated mechanism predicts longer IDTs in the low pressure case yielding improved performance against experimental data at lower temperatures. Both the HPST and the RCM data are satisfyingly captured. The modifications made to the mechanism do not affect its performance at 30 bar. Increasing the toluene concentration in the mixture to 75% naturally leads to longer predicted IDTs, as expected, Fig. 1(b). The current updated version of the mechanism predicts longer IDTs, compared to the original mechanism, at lower temperatures and reproduces better the ignition delay time data in this regime. In the NTC region, the updates cause the model to predict longer IDT, with negative impact on the agreement. Again, modeling agreement at 30 bar is not affected by the mechanism modifications. In general, the modifications have resulted only in a small change of mechanism performance at high pressure, leading to improved predictions.

Figures 1(d)–(f) show the stoichiometric measurements for all three mixture ratios. The current updated model again predicts longer IDTs than the original mechanism, showing improved agreement against the reported data at temperatures below 1000 K. In the high temperature regime, no difference in the performance of both models is observed.

162 Both mechanisms, however, fail to capture the NTC behavior of the 75:25 mixture ratio Fig. 1(e), predicting shorter IDTs.
 163 As in the fuel-lean case, the 90:10 mixture shows only small sensitivity to [the mechanism modifications](#) ~~the changes~~, Fig.
 164 1(f).
 165 As described earlier, the 90:10 mixtures were not measured in the RCM due to repeatability issues. The same problem
 166 occurred also in the rich cases, therefore only HPST data are presented in Figs. 1(g)–(i). For the 50:50 and the 75:25
 167 mixture the agreement is very good for all measurements. The [current updated](#) mechanism captures well the IDTs at
 168 temperatures close to 900 K in the 30 bar case. Nonetheless, a small over-prediction for the 10 bar case is observed in the
 169 low temperature regime.



170
 171 Figure 1: Experimentally determined HPST (closed symbols) and RCM data (open symbols) versus simulations using the
 172 original LLNL TRF mechanism (dashed lines) and the [current updated mechanism](#) (solid lines) Square symbols refer
 173 to experiments at 10 bar and circle symbols to those at 30 bar. [Figures 1 \(c\),\(f\),\(g\),\(h\),\(i\) contain no RCM data](#)

5. Sensitivity and reaction path analysis

Sensitivity analysis was performed for the ignition delay times at several conditions for stoichiometric mixtures, with the results shown in Fig. 2, (a-c) for a toluene/heptane mixing ratio of 50:50, (d-f) a mixing ratio of 75:25 and (g) a mixing ratio of 90:10. The A factor of each reaction was increased and decreased by a factor of two (k_+ and k_-), leading to the perturbed ignition delay times (τ_+ and τ_-). The sensitivity coefficient (S) is calculated as:

$$S = \frac{\ln(\tau_+/\tau_-)}{\ln(k_+/k_-)} = \frac{\ln(\tau_+/\tau_-)}{\ln(2/0.5)}$$

Therefore, a positive sensitivity coefficient here indicates a prohibitive/inhibitive effect upon the reactivity from a specific reaction, while a negative sensitivity coefficient means this reaction promotes reactivity. In the studies of this work, n-heptane is more reactive than toluene, especially at low and intermediate temperatures. n-Heptane has low temperature chain branching channels [3326] that produce OH radicals. All the heptylperoxy radicals can undergo intramolecular hydrogen transfer via low energy transition states, and the subsequent reaction sequences eventually lead to chain branching. This has also been indicated by the appearance of hydrogen abstraction and the low temperature reactions of n-heptane among the most promoting reactions in Fig. 2 (a-b), (d-e). At intermediate temperatures, chain propagating channels such as concerted HO₂ elimination become more competitive than hydrogen abstraction reactions by OH and lead to the negative temperature coefficient (NTC) behavior. These reactions become sensitive when the relative concentration of n-heptane is higher in the fuel mixture, as shown in Fig. 2(b). At high temperatures, the hydrogen abstraction reactions by HO₂ radical are enhanced and produce H₂O₂ that decomposes into OH radicals, which in turn will trigger ignition. Abstraction reactions by HO₂ also possess negative sensitivity coefficients, but again only at the highest concentration of n-heptane in the fuel mixture (Fig. 2(c)).

In general, the chemistry of toluene dominates the reactivity of these fuel mixtures over the whole temperature range shown in Fig. 2. This is because the reactivity of the fuel mixtures not only depends on the reaction flux going through chain branching pathways that produce reactive radicals, but also depends on the branching ratio of the consumption pathways for those radicals. Under these conditions, toluene is a strong competitor for OH radicals despite being much less reactive than n-heptane. Fig. 2 shows that the hydrogen abstractions from toluene inhibit reactivity at most conditions, except for when the mixing ratio is 1:1, where the n-heptane chemistry becomes more important.

The major reaction pathways in the oxidation of toluene are shown in Fig. 3, which is based on calculations for mixtures with mixing ratio 50:50, $\phi=1.0$ at P=10 bar and for T=690/870/1100/1400 K. Toluene does not have low temperature chain branching channels. The hydrogen abstraction of toluene mainly happens on the benzylic site and produces benzyl (see blue frame in figure 3). Benzyl is a relatively stable radical ($\Delta H(0)_r=229.0\pm 4\text{kJ/mol}$ [42][43]). The self-recombination of

203 benzyl is one of the major consumption pathways at low temperature, which is a chain terminating reaction and largely
204 inhibits the overall reactivity [\(see yellow frame in figure 3\)](#). Another consumption channel of benzyl is through the
205 reactions with HO₂ radicals, either through recombination-decomposition or chemically activated paths, which produce
206 benzoyl radicals and OH radicals [\(see green frame in figure 3\)](#). The chemically activated paths are enhanced as the
207 temperature rises and were found to be sensitive at the current conditions (see also Fig. 2 (c), (e-g)). This also partly
208 explains why toluene chemistry is less sensitive when the mixing ratio is 1:1. Benzyl radicals are mostly consumed in the
209 reactions with HO₂ radicals that are largely produced from the concerted elimination of heptylperoxy radicals, and produce
210 the more reactive OH radical. Therefore, the production of benzyl has a less inhibiting effect on the reactivity for the
211 conditions presented in Fig. 2 (b-c) [and respectively its recombination is not shown among the most sensitive reactions](#).
212 However, the chain terminating reaction of benzyl and HO₂ radicals that produces toluene and oxygen is also enhanced by
213 increasing temperature and inhibits reactivity at high temperatures. This reaction competes with the chain propagation
214 process that produces OH radicals and thus has positive sensitivity coefficients. It also needs to be noted that this reaction
215 becomes sensitive only when the production of benzyl and HO₂ radicals are comparable within a certain range, as show in
216 Fig. 2-(e-f).

217 [Besides the toluene oxidation chemistry which is the primary topic in the present work, n-heptane oxidation is of large](#)
218 [importance to the ignition delay time simulations, hence, a snapshot of the major chemical routes for the same conditions](#)
219 [with that of toluene is given in Figure 4.](#)

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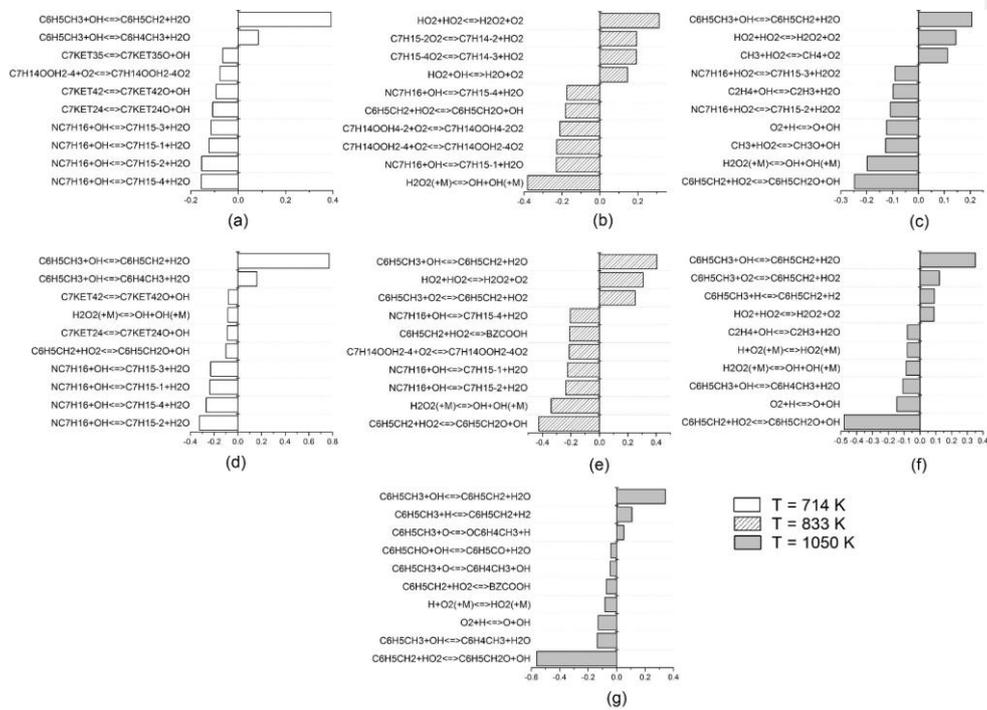
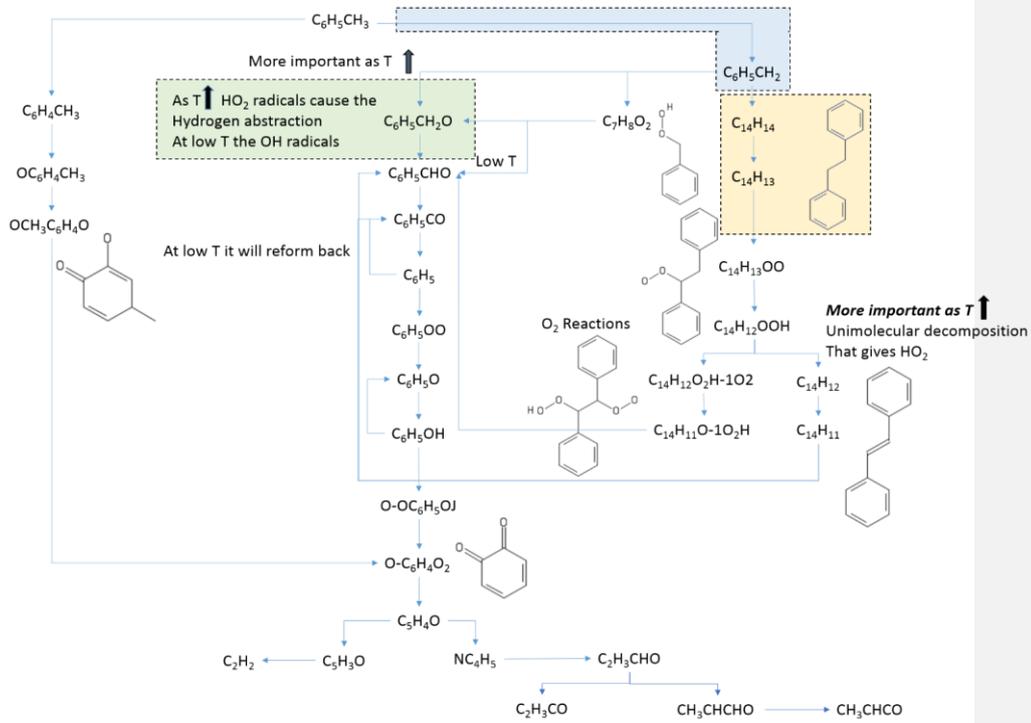


Figure 2: Sensitivity analysis for ignition delay times at different toluene/n-heptane mixing ratios and temperatures for stoichiometric mixtures. (a-c): mixing ratio at 50:50; (d-f) mixing ratio at 75:25; (g) mixing ratio at 90:10

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225

226

Figure 3: Toluene oxidation route as obtained by reaction path analysis at 20% of fuel consumption for mixture ratio

50:50, $\phi=1.0$ at $P_p=10$ bar and for $T=690/870/1100/1400$ K.

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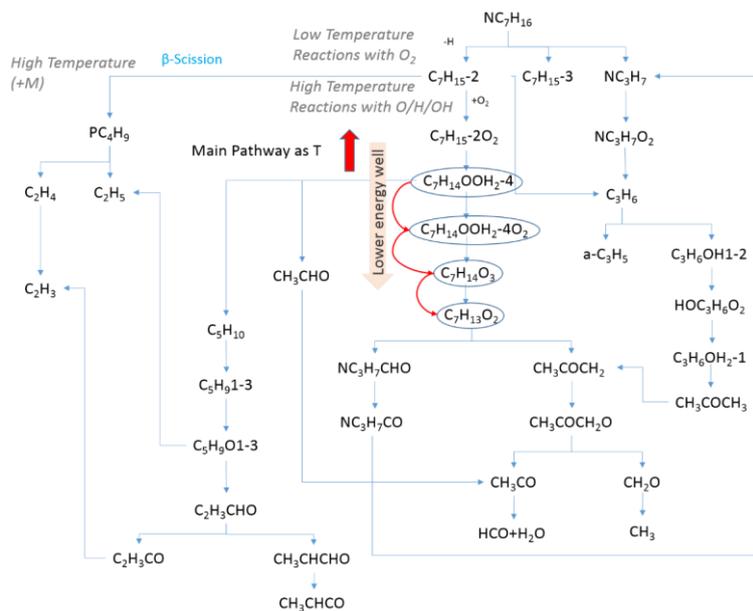


Figure 4: N-Heptane oxidation route as obtained by reaction path analysis at 20% of fuel consumption for mixture ratio 50:50, $\phi = 1.0$ at $P_p = 10$ bar and for $T = 690/870/1100/1400$ K.

Conclusions

The purpose of this work is twofold as it aims to (a) provide novel experimental ignition delay time data of toluene/n-heptane mixtures under conditions relevant to novel engine operation, which has not been reported before, and (b) to interpret the effect of the mixing ratio of toluene/n-heptane on the measured TRF IDT values, utilizing computational tools *i.e.* sensitivity and reaction flow analysis, ~~utilizing based on~~ a detailed kinetic mechanism from the literature. In particular, the LLNL TRF model is used, both under its original and its recently updated version.

Experimental data have revealed that IDTs were insensitive to changes in equivalence ratio at higher temperatures. This behavior was less pronounced at higher pressures, starting at higher temperatures, but was enhanced when the toluene content increased. At low temperatures, the fuel-lean mixtures showed the longest IDTs. The opposite was observed for higher temperatures, where the lean mixtures posed increased reactivity.

Computations ~~demonstrated~~ ~~have proved~~ the improved agreement of the updated LLNL model on the current dataset; the updated model reproduces the experimentally observed longer IDTs in the low and intermediate temperature regime, presenting an overall improved performance, while it retains the original model's good performance in the high temperature regime. Reaction

246 path and sensitivity analyses have shown that toluene inhibits reactivity, since it ~~commits~~ consumes OH radicals for hydrogen
247 abstraction reactions from its benzylic site, leading to the formation of [relatively stable](#) benzyl. This effect is less
248 pronounced in the 1:1 mixture as the large amount of HO₂ formed from heptylperoxy decomposition reacts with benzyl
249 yielding the more reactive OH radicals.

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