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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 validatedn 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

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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

2

26 oxidation with 68 and 62 additional reactions [16], while the second study came along withincluded 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 [197].

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 [2018]. 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 [2119], while lower temperature measurements (600–900 K) were

34 completed in a rapid compression machine (RCM) study [2022]. 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 [2321]. 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 [2422] 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 [2523–2827].

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 ($\varphi = 0.5$ 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.

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

Toluene Heptane ratio	Mole fraction (%)					
	C_7H_8	C_7H_{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 N_2 mole fraction when Argon is also used as diluent in the respective RCM cases for the intermediate temperature regime (830-1000K)						

Table 1: Detailed conditions of the experimentally investigated mixtures

2. Experimental Setup

2.1 High Pressure Shock Tube

Ignition delay times at higher temperatures (800–1400 K) were measured in the HPST facilities of NUIG. The experimental setup has been described previously [35][36], thus it will be only briefly described here. The tube consists of two separate sections; the driven section, where the mixture sample is loaded, and the driver section where He or He/N_2 is introduced. These sections are 5.73 m and 3 m long respectively, and are separated by a 3 cm long double-diaphragm (middle) section. The aluminum diaphragms are pre-scored before each experiment. After the mixture is introduced into the driven section,

the driver and middle sections are filled with the He/N$_2$ driven gas to roughly half of the driver gas pressure. The driver

section alone is finally filled to the driver pressure. The gas from the middle section is evacuated and the pressure difference

is sufficiently high to burst the diaphragms. The high-pressure driver gas expands rapidly into the driven section creating

a reflected shock wave that heats and compresses the mixture to the desirable conditions. The achieved shock velocity is

measured by interpolating the shock arrival time at PCB 113B24 pressure transducers along the driven section. A 603B

Kistler pressure transducer is used to monitor the pressure of the gas at the endwall. The ignition delay time is defined as

the time elapsed between the arrival of the shock wave at the endwall and the ignition event. The mixture was prepared by

controlling the partial pressure of each constituent species in a stainless-steel mixing tank, while ensuring that it did not

exceed a value of at least half of its vapor pressure. A heating system was installed on the mixing tank and the piping

leading to the HPST to ensure that the fuel would remain in the vapor phase.

The entire experimental apparatus as well as the manifolds, piping and mixing vessel were heated to 60°C but not higher,

to avoid overheating damage to the equipment (pressure transducers, gauges, etc.). The mixture was prepared, ensuring

that the partial pressures of each of the fuels did not exceed a value of at least half of its vapor pressure.

2.2 *Rapid Compression Machine*

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

[36][37] and later re-commissioned at NUIG [37][38]. A short description follows here. Two opposite facing pistons are pushed

forward to volumetrically compress a fuel mixture. At the end of compression (~16 ms), the pistons are locked forward

and maintain a constant reactor volume, thus allowing a constant volume reaction to take place. The motion of the pistons

is controlled pneumatically, while a chamber filled with hydraulic oil surrounding the connecting rod is used to lock and

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

Positek P100 linear inductive position sensor that is within the hollow connecting rod. The pressure inside the reaction

chamber is measured using a Kistler 6045a mounted in the reaction chamber wall. A Kistler 5018 is used to amplify the

pressure trace, while a Sigma 90 oscilloscope by Nicolet Technologies sampling at 20 kHz and 12-bit resolution is used

for recording the traces. The pressure traces are filtered by a hardware Buttersworth low-pass filter with a cut-off frequency

of 3 kHz, after amplification. The compression ratio of the RCM, defined as the ratio of the density before and after

compression is 10. The ignition delay time is defined as the time between end of compression and the maximum pressure

rise due to chemical reactions. The temperatures at the end of compression were adjusted by varying the initial temperature

of the chamber. This was achieved by the installation of an electrical heating system which has been optimized to minimize

stratification in the chamber. More detailed description of the heating system installation can be found in [38][39]. The

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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 pistonsones 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 wereas 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.

2.3 Experimental issues

115 In this study three blending ratios of high toluene content were measured. The high toluene concentration increases the

116 depositsion 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.* φ = 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 increasedresulted in higher

122 IDT compared to the initial experimentone. To solve this, the method reported in [32][33] was used, leading however, to

123 no ignition.

3. Chemical Kinetic Modeling

125 In this work, the LLNL model was adopted in its originalinitial state published in [32][33], while an updated nother 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 theas Supplementary mMaterials.

6

4. Results and Discussion

The measured ignition delay times for all conditions are~~have been~~ 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 (~~φ=0.5 in the top row, φ=1.0 in the middle and φ=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) → (c), (d) → (f) and (g) → (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 (φ=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,~~one,~~ 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~~one~~, 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.

7

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.
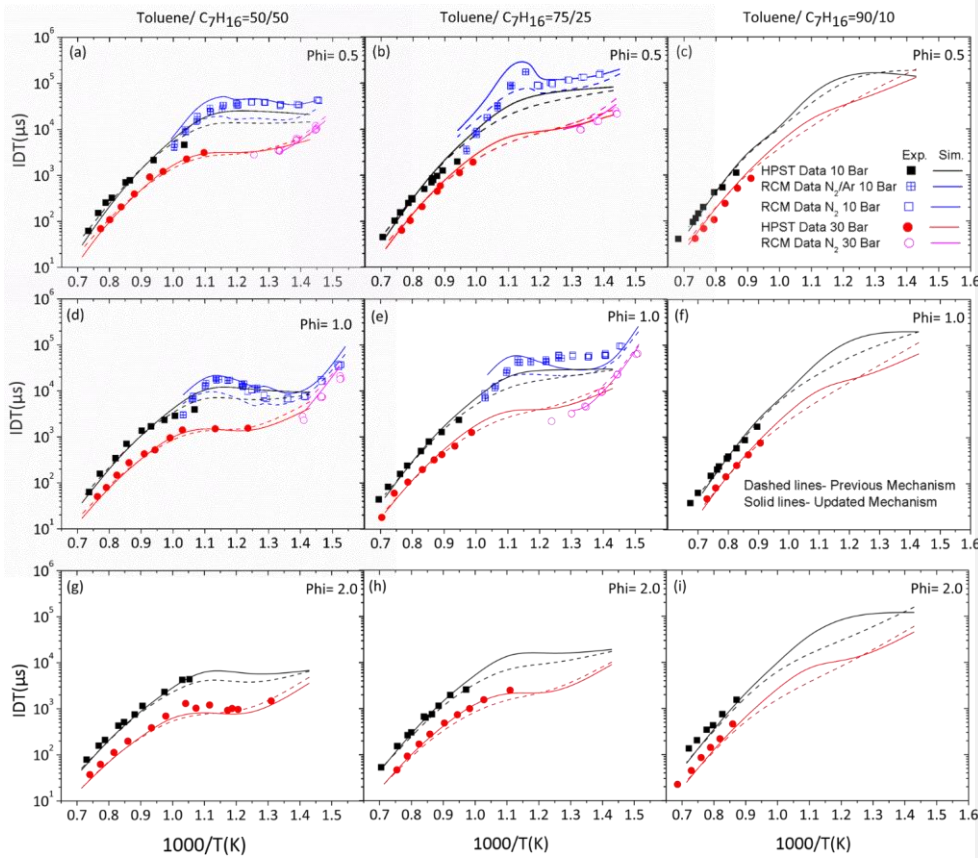
171 Figure 1: Experimentally determined HPST (closed symbols) and RCM data (open symbols) versus simulations using the

172 original LLNL TRF mechanism (dashed lines) and the current updated mechanismone (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. 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 [~~33~~26] 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 HO_2 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 HO_2 radical are enhanced and produce H_2O_2 that decomposes into OH radicals, which in turn will trigger ignition. Abstraction reactions by HO_2 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 mixture~~s~~ 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 show_n in Fig. 3, which is based on calculations for mixtures with mixing ratio 50:50, $\varphi=1.0$ 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 ($\Delta H(0)_f$=229.0±4kJ/mol ~~[42]~~[43]). The self-recombination of

9

benzyl is one of the major consumption pathways at low temperature, which is a chain terminating reaction and largely inhibits the overall reactivity (see yellow frame in figure 3). Another consumption channel of benzyl is through the reactions with HO_2 radicals, either through recombination-decomposition or chemically activated paths, which produce benzoxyl radicals and OH radicals (see green frame in figure 3). The chemically activated paths are enhanced as the temperature rises and were found to be sensitive at the current conditions (see also Fig. 2 (c), (e-g)). This also partly explains why toluene chemistry is less sensitive when the mixing ratio is 1:1. Benzyl radicals are mostly consumed in the reactions with HO_2 radicals that are largely produced from the concerted elimination of heptylperoxy radicals, and produce the more reactive OH radical. Therefore, the production of benzyl has a less inhibiting effect on the reactivity for the conditions presented in Fig. 2 (b-c) and respectively its recombination is not shown among the most sensitive reactions. However, the chain terminating reaction of benzyl and HO_2 radicals that produces toluene and oxygen is also enhanced by increasing temperature and inhibits reactivity at high temperatures. This reaction competes with the chain propagation process that produces OH radicals and thus has positive sensitivitye coefficients. It also needs to be noted that this reaction becomes sensitive only when the production of benzyl and HO_2 radicals are comparable within a certain range, as show in Fig. 2 (e–f).

Besides the toluene oxidation chemistry which is the primary topic in the present work, n-heptane oxidation is of large importance to the ignition delay time simulations, hence, a snapshot of the major chemical routes for the same conditions with that of toluene is given in Figure 4.
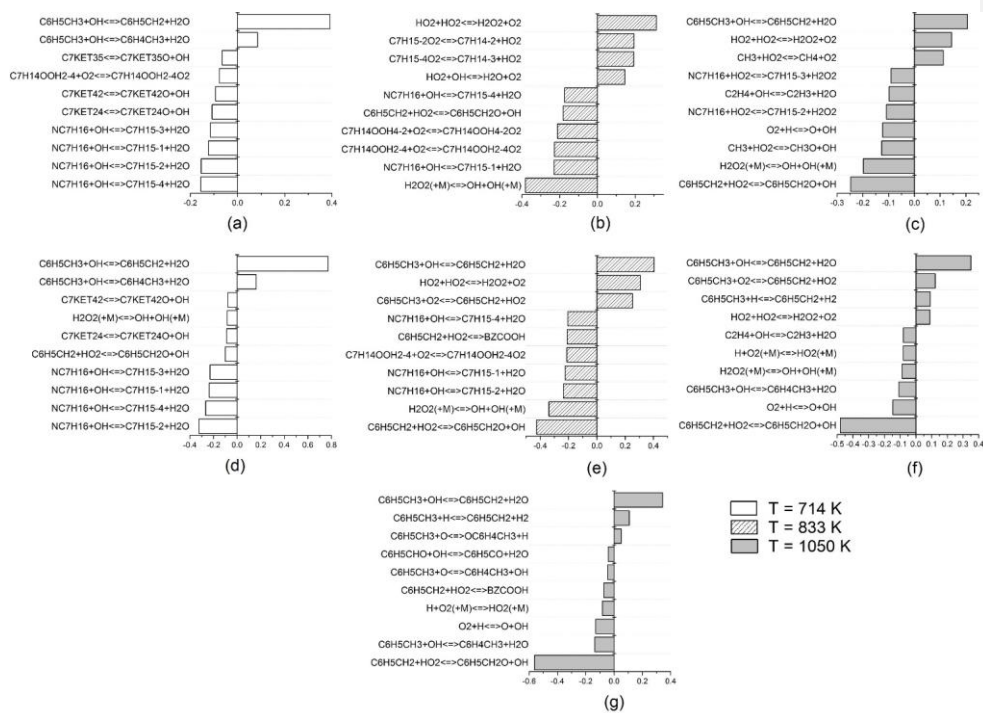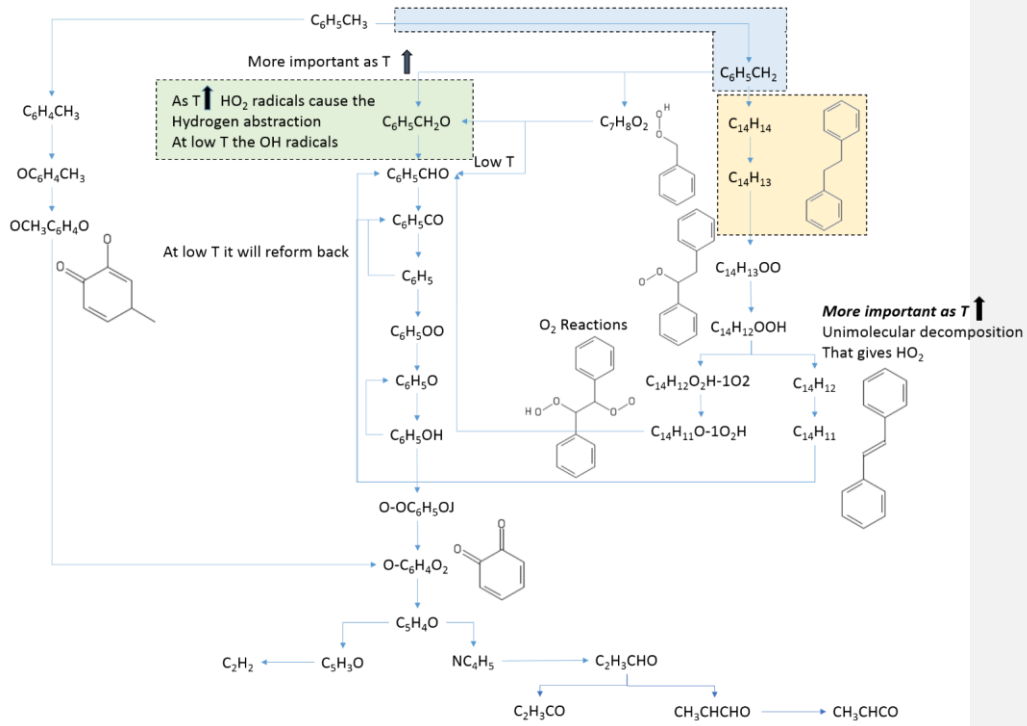
Figure 2: Sensitivity analysis for ignition delay times at different toluene/ n-heptane mixing ratios and temperatures for stoichiometric mixtures. (a-c): mixing ratio at 50:50; (d-f) mixing ratio at 75:25; (g) mixing ratio at 90:10

C₆H₅CH₃

More important as T ↑

C₆H₅CH₂

C₆H₄CH₃

As T ↑ HO₂ radicals cause the
Hydrogen abstraction
At low T the OH radicals

C₆H₅CH₂O

C₇H₈O₂

C₁₄H₁₄

OC₆H₄CH₃

C₁₄H₁₃

OCH₃C₆H₄O

Low T

C₆H₅CHO

At low T it will reform back

C₆H₅CO

C₆H₅

C₁₄H₁₃OO

C₆H₅OO

O₂ Reactions

C₁₄H₁₂OOH

More important as T ↑
Unimolecular decomposition
That gives HO₂

C₆H₅O

C₁₄H₁₂O₂H-1O2

C₁₄H₁₂

C₆H₅OH

C₁₄H₁₁O-1O₂H

C₁₄H₁₁

O-OC₆H₅OJ

O-C₆H₄O₂

C₅H₄O

C₂H₂

C₅H₃O

NC₄H₅

C₂H₃CHO

C₂H₃CO

CH₃CHCHO

CH₃CHCO

Figure 3: Toluene oxidation route as obtained by reaction path analysis at 20% of fuel consumption for mixture ratio 50:50, φ=1.0 at p = 10bar and for T = 690/870/1100/1400 K.

12

Figure 4: N-Heptane oxidation route as obtained by reaction path analysis at 20% of fuel consumption for mixture ratio 50:50, $\varphi = 1.0$ 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

13

path and sensitivity analyses have shown that toluene inhibits reactivity, since it ~~commits~~ consumes OH radicals for hydrogen abstraction reactions from its benzylic site, leading to the formation of relatively stable benzyl. This effect is less pronounced in the 1:1 mixture as the large amount of HO_2 formed from heptylperoxy decomposition reacts with benzyl yielding the more reactive OH radicals.

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