

The three-stage auto-ignition of gasoline in an HCCI engine: an experimental and chemical kinetic modelling investigation

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Abstract

The alternative HCCI combustion mode presents a possible means for decreasing the pollution with respect to the conventional gasoline or diesel engines, while maintaining the efficiency of a diesel engine or even increasing it. This paper investigates the possibility of using gasoline in an HCCI engine and analyses the auto-ignition of gasoline in such an engine. The compression ratio that has been used is 13.5, keeping the inlet temperature at 70 °C, varying the equivalence ratio from 0.3 to 0.54 and the EGR (represented by N₂) ratio from 0 to 37 vol%. For comparison, a PRF95 and a surrogate containing 11 vol% n-heptane, 59 vol% iso-octane and 30 vol% toluene are used. A previously validated kinetic surrogate mechanism is used to analyze the experiments and to yield possible explanations to kinetic phenomena. From this work, it seems quite possible to use the high octane-rated gasoline for auto-ignition purposes, even at lean inlet conditions. Furthermore, it appeared that gasoline and its surrogate, unlike PRF95, shows a three-stage auto-ignition. Since the PRF95 does not contain toluene, it is suggested by the kinetic mechanism that the benzyl radical, issued from toluene, causes this so-defined “obstructed pre-ignition” and delaying thereby the final ignition for gasoline and its surrogate. The results of the kinetic mechanism supporting this explanation are shown in this paper.

Key words: three-stage auto-ignition of gasoline, HCCI engine, combustion, kinetic mechanism, obstructed pre-ignition

1 Introduction

The HCCI combustion has been proposed as an interesting alternative combustion technology for the reduction of the automobile pollution. This technology has not been implemented in the real market, mainly due to the lack of sufficient control of the ignition delay. For this

purpose, several physical parameters that affect the quality of the HCCI combustion and the ignition delay have been studied in the literature [1-11]: mixture homogeneity, inlet temperature of air and fuel, fuel composition and kinetics of the fuel oxidation at lower temperatures. Since the operating conditions of an HCCI engine are dependent on the fuel that is to be used, special attention is given to fuel auto-ignition research, both experimentally and numerically: primary reference fuels (PRF) [2], aliphatic hydrocarbons [4,5,12,13], aromatics [7,8], light hydrocarbons and gaseous fuels [14-17], diesel fuels [18-24] and gasoline fuels [25-27], to mention a few. Before any alternative fuels will be used, the use of conventional fuels, such as gasoline and diesel, in HCCI engines is of importance. Therefore, the auto-ignition of such fuels should be investigated. The first part of this paper intends to analyze the kinetics of the auto-ignition of gasoline in an HCCI engine with a compression ratio of 13.5, an inlet temperature of 70 °C, varying the equivalence ratio from 0.3 to 0.54 and the EGR ratio (represented by N₂) from 0 to 37 vol%.

Gasoline is a multi-component fuel. Hydrocarbon interaction during the combustion can occur, where the intermediary products of one fuel component intervene with the intermediary products of another fuel component. Some investigations [28-30] have been performed, studying such interactions between hydrocarbons. They state that interactions can take place through a radical pool of OH, H and O radicals. They also mention the possibility that chemical interactions can take place between different fuel components and their radicals. An example is presented in [28], concerning the reaction between respectively an alkyl- or alkylperoxy radical from one fuel component with an alkane from another fuel component. As such, there is a possibility that interactions between fuel components and their intermediary species can take place that can influence the auto-ignition process. This necessitates the use of chemical kinetic mechanisms for multi-component fuels for the analysis of such interactions as is done by [28-30]. The second part of this paper aims at analyzing the hydrocarbon

interaction taking place in gasoline, by the use of a surrogate fuel and a corresponding experimentally validated surrogate mechanism [31,32], included in the appendix.

2 Experimental

The experimental set-up is presented elaborately in previous work [32]. The essentials are reported in this section. The complete experimental set-up comprises an HCCI engine, the air inlet system, the fuel injection system, a pre-mixture tank for inlet mixture homogeneity purposes and an EGR installation. In the case of this paper, the EGR installation provides for the dilution by nitrogen, which is used as a parameter for the gasoline auto-ignition investigation. A pre-mixture tank serves to mix the injected fuel with the entering air and subsequently with the EGR flow. Before the fuel/air/EGR mixture enters the engine, it passes through a tube of which the geometry (several 90° bends) enhances the homogeneity of the mixture.

The HCCI engine's compression ratio is set to be 13.5 for this study. The engine has a bore of 82.55 mm, a stroke of 114.5 mm and a displacement volume of 612 cm^3 . The ratio of the connecting rod to crank radius is 4.44. The exhaust valve opens at 140° After Top Dead Center (ATDC) and closes at 15° ATDC. The intake valve opens at 10° ATDC and closes at 146° BTDC. The measurements of the equivalence ratio, measured by the flow rates of the fuel and the air, present an error of ± 0.005 , while the compression ratio shows an error of ± 0.5 . The temperatures of the cooling water (50°C) and the oil (40°C) as well as that at the inlet of the engine show an error of $\pm 1^{\circ}\text{C}$. The composition of the fuel has an error of ± 1 vol%, while that of the EGR flow exhibits an error of $\pm 2\%$.

Three fuels are used in this work: a commercial gasoline with octane number 95; a gasoline surrogate that consists of a mixture of n-heptane, iso-octane and toluene; and a primary

reference fuel (PRF), containing 95 vol% iso-octane and 5 vol% n-heptane, referred to as PRF95. In order to generalize this study and broaden the range at which it is performed, the gasoline auto-ignition process is done at different equivalence ratios and EGR ratios. These are parameters that influence considerably the energy of the system. The cylinder pressure is measured by a pressure sensor and the heat release is calculated from this measured pressure. The ignition delays are calculated from the heat release maximums. The cool flame delay is defined as the Crank Angle Degrees' (CAD) interval from Bottom Dead Center (BDC) until the first heat release maximum and the final ignition is defined as CAD interval from BDC until the last heat release maximum. The auto-ignition process is a result of various complex chemical, physical and energetic processes that take place during the auto-ignition process. The ignition delays represent the chemistry; the pressure and the heat release represent the power, work, energy and heat involved. The experimental findings are analyzed, using the same experimentally validated kinetic surrogate mechanism that is used in previous work [31,32]. This mechanism has been obtained by reducing detailed individual n-heptane, iso-octane and toluene kinetic mechanisms, using the quasi-steady-state-assumption and the partial equilibrium assumption. Furthermore, by leaving the reactions that are important to simulate the auto-ignition at HCCI operating conditions, the mechanisms were reduced even more. Finally, these mechanisms were merged into a ternary reduced kinetic mechanism for gasoline and diesel surrogates. The surrogate mechanism has been validated experimentally in a constant volume environment for temperatures between 700 and 1400 K, for pressures between 9 and 55 bar at equivalence ratios of 0.5 and 1.0 and for several fuels containing binary and ternary mixtures of n-heptane, iso-octane and toluene [31]. Moreover, it has been validated for HCCI engine applications both numerically [31] (at inlet temperatures varying from 290 to 500 K, equivalence ratios from 0.2 to 0.7 and compression ratios from 8 to 18)

and experimentally [31] (at inlet temperatures varying from 35 to 70 °C, equivalence ratios from 0.28 to 0.64, compression ratios from 7 to 14 and EGR ratios from 0 to 30 vol%).

One of the gasoline representatives is the PRF 95, which is often used as a representation of gasoline 95 in the literature, having a Research Octane Number (RON) of 95 and a Motor Octane Number (MON) of 95 and thus an octane number of 95. An octane number is a quantitative, but imprecise measure of the maximum compression ratio at which a particular fuel can be utilized in an engine without some of the fuel/air mixture "knocking" or self igniting. Directionally, as the compression ratio of the engine increases, so does the required octane number of the gasoline if engine knocking is to be avoided. Per definition, the RON and MON of n-heptane are respectively equal to 0, while the RON and MON of iso-octane are respectively equal to 100. Linear combinations of these two components are used to measure the octane number of a particular fuel. A 90%/10% blend of iso-octane/n-heptane has an octane value of 90. Any fuel knocking at the same compression ratio as this mixture is said to have an octane number of 90. The RON simulates fuel performance under low severity engine operation. The MON simulates more severe operation that might be incurred at high speed or high load. In practice the octane number of a gasoline is reported as the average of RON and MON or $(RON+MON)/2$.

The other fuel is a gasoline surrogate, consisting of n-heptane, iso-octane and toluene. When using aromatics, the blending rule is not linear. Generally, octane numbers do not blend linearly in practice. To accommodate this, complex blending calculations employing blending octane numbers as opposed to the values for pure hydrocarbons are routinely employed. As an improvement over octane numbers of pure compounds, there are tabulations of blending octane numbers for both RON and MON [33,34]. These "blending RON and MON" values are taken in order to calculate the octane number of this surrogate gasoline.

To determine a composition for this gasoline surrogate, the major components of gasoline should be known. Gauthier et al. [6] states that the following major components are present in gasoline, giving their molar concentrations: cyclo-pentane (16,8), toluene (9,7), iso-pentane (7,8), meta-xylene (4,9), 3-methyl-hexane (4,4), n-heptane (3,6), 2-methyl-hexane (3,3), ethyl-benzene (3,2), n-pentane (3) and 2,2,4-trimethyl-pentane (iso-octane) (2,5). The octane number for the gasoline they used is 87. In this study the gasoline surrogate should have an octane number of 95. Furthermore the surrogate that is used for this study should solely contain n-heptane, iso-octane and toluene, to minimize the number of constituents, whilst guarding specific characteristics of gasoline. N-heptane should then represent the linear alkanes, iso-octane the branched / cyclo alkanes and toluene the aromatics. To have an octane number of 95, it is supposed that the ratio of the major components should be the same in a gasoline of octane number 95 as a gasoline of octane number 87. Therefore, the gasoline surrogate of octane number 95, is obtained in this study, using the molar ratio as specified above, calculating the volumetric ratios and representing the mentioned major components as follows:

- **n-heptane** represents n-heptane and n-pentane,
- **iso-octane** represents cyclo-pentane, iso-pentane, 3-methylhexane, 2-methylhexane and iso-octane and
- **toluene** represents toluene, meta-xylene and ethylbenzene.

The obtained corresponding volumetric fractions, for the gasoline surrogate are, then (with an error of +/- 1 vol%): 11 vol% of n-heptane, 59 vol% of iso-octane and 30 vol% of toluene. N-heptane and iso-octane have both the RON and MON of respectively 0 and 100 (for these species the RON and MON are equal). Toluene, however, has a RON of 124 and a MON of 112. The gasoline surrogate has then a RON of 96.8 and a MON of 93.2 resulting into an octane number of 95.

3 Results and discussion

3.1 The auto-ignition process for gasoline

Figure 1 presents the auto-ignition delays (cool flame delay and the final ignition delay) for gasoline and the gasoline surrogate as a function of the dilution by N_2 and the equivalence ratio at a compression ratio of 13.5 and an inlet temperature of 70 °C. The gasoline surrogate and gasoline did not auto-ignite at all for a dilution of 37 vol% at equivalence ratios of 0.46 and lower. At equivalence ratios of 0.39 and lower, these fuels did not present a final ignition for dilutions of 10 vol% and higher, showing only cool flame activity. For gasoline, as figure 1 shows, the effects of the equivalence ratio on the final ignition delays are as expected. A higher equivalence ratio means more fuel, more energy and an increased overall reactivity. This results into a decreased final ignition delay. A higher dilution rate decreases the overall concentrations of the inlet mixture and decreases the peak temperature. This results into a decreased overall reactivity and an increased final ignition delay. The ignition delays for the gasoline surrogate show a satisfactory agreement with those of the gasoline for several dilution ratios and equivalence ratios. The effect of the dilution and the equivalence ratio is not the subject of this paper, but serves to study the gasoline auto-ignition process at different initial conditions. The used compression ratio and inlet temperature were necessary in order to have a proper auto-ignition and could not be varied as the equivalence ratio. Higher values of the compression ratio were not tested, since the engine was not built for that purpose. The effect of the inlet temperature has already been subject to numerous studies and is kept therefore constant.

The cool flame delay seems to be affected by the so-called compressive heating, since after an equivalence ratio of 0.4, the cool flame delay increases on increasing the equivalence ratio. The more fuel there is, the higher the heat capacity of the mixture becomes, and the lower the peak temperature will be. This competes with the burn rate of the fuel. The burn rate at the

final ignition is sufficient to overcome the effect of compressive heating, while the burn rate at the cool flame seems to be overtaken by this effect at equivalence ratios higher than 0.4.

The PRF's used in the literature for the simulation of gasoline are often mixtures of n-heptane and iso-octane. However, these n-heptane/iso-octane mixtures do not simulate exactly the behaviour of gasoline. For modelling investigations, it is useful to have a surrogate that behaves as gasoline does. To assess these differences, the comparison is made between gasoline95, a PRF95 (5 vol% n-heptane and 95 vol% iso-octane) and the gasoline surrogate (11 vol% n-heptane, 59 vol% iso-octane and 30 vol% toluene), all with an octane number of 95. Figures 2 and 3 give a comparison between these fuels for the pressure and the heat release at an equivalence ratio of 0.462.

Figures 2 and 3 show that for both the pressure and heat release, the gasoline surrogate and gasoline95 compare quite satisfactorily. The PRF95, however, shows a difference of 3 to 4 CAD for the final ignition and no significant error for the cool flame for an equivalence ratio of 0.462. This implies that for HCCI operating conditions, the octane number is not an optimal indication for the behaviour of the auto-ignition delays. To illustrate this, the auto-ignition delays at different octane numbers are compared using two different mixtures for each octane number, presented in figure 4. The compression ratio is 13.5, the equivalence ratio is 0.41 and the inlet temperature is 70 °C. It can be seen from figure 4 that two mixtures with the same octane number do not result into the same final ignition delay, as indicated in figure 4 by the circles. Nonetheless, a certain trend is observed. This demonstration shows that two mixtures with the same octane number do not necessarily have the same ignition delay and that the octane number can only be used as a global indication for the ignition delay.

3.2 A three-stage auto-ignition for gasoline

When looking more closely to the heat release curve for gasoline (figure 3), at an equivalence ratio of 0.462, another heat release appears to be present between the cool flame and the final ignition. The gasoline surrogate shows the same behaviour. The same is true for other equivalence ratios as is shown for three equivalence ratios (0.302, 0.396 and 0.462), in figure 5. Let us call this other heat release a pre-ignition. The experimental heat releases are obtained with a compression ratio of 13.5, an inlet temperature of 70 °C and gasoline as the fuel.

The cool flame, the pre-ignition that was observed for gasoline in figure 3 and the final ignitions are indicated in figure 5 by respectively the letters C, P and F. The equivalence ratios 0.302, 0.396 and 0.462 are indicated in the same figure by respectively 1, 2 and 3. It can be seen that on increasing the equivalence ratio from 0.302 to 0.396, the cool flame, the pre-ignition and the final ignition delays advance. This follows the usual trend and is discussed earlier in the text. On increasing the equivalence ratio further to 0.462, the final ignition delay advances again. However, the cool flame and the pre-ignition delay at that moment. This could be caused by the compressive heating (discussed earlier), which appears also to influence the pre-ignition. This suggests that the pre-ignition has a weak burn rate, like the cool flame, followed by a second Negative Temperature Coefficient (NTC).

The results that are presented so far suggest that gasoline (and its surrogate), in the experimental conditions of this work, ignites in a three stage combustion. Say that gasoline auto-ignites in a three-stage combustion, then could be defined a cool flame delay, a pre-ignition delay and a final ignition delay, each represented by a heat release maximum. This could imply that other small heat releases can take place for gasoline before the final ignition. These could be called several pre-ignitions. Two possible explanations can be suggested. A first possibility is a mixture homogeneity point of view. Then, it can be suggested that before

the final ignition occurs, some sites in the cylinder have local higher temperatures (caused by a certain inhomogeneity) and therefore already some small auto-ignitions take place before the final ignition. If this would be the case, a purely kinetic homogeneous simulation as is the case for a 0D calculation coupled with a kinetic mechanism should not show this extra heat release. For this purpose, a simulation by the surrogate mechanism is performed at the same experimental initial conditions as figure 3: an inlet temperature of 70 °C, an equivalence ratio of 0.462 and a compression ratio of 13.5 for the gasoline surrogate. A 0 D HCCI engine module, with the same geometry as the experimental engine, implemented in the Chemkin 4 code [35], is used for this calculation. The result is presented in figure 6.

The homogeneous combustion simulation shows, in figure 6, clearly that there is an extra heat release between the cool flame and the final ignition. This simulation suggests that the phenomenon is rather due to thermodynamic/kinetic interactions than to mixture homogeneity effects, though the latter is not fully excluded. Since, the result in figure 6 shows that an extra heat release occurs between the cool flame and the final ignition without any mixture effects, the explanation will be proposed from a kinetic point of view. Gaffuri et al. [12] and Ranzi et al. [13] state in their research that they found oscillatory cool flames and multi-stage ignition in their hydrocarbon kinetic modelling, which they explain to be caused by the interaction of heat release and kinetics during the combustion process. To analyse this interaction, the surrogate mechanism is used. This analysis is presented in the next section.

4 Analysis of the auto-ignition of gasoline by the surrogate mechanism

Since the phenomenon is also observed for the gasoline surrogate, the simulation is performed using the gasoline surrogate composition: 11 vol% n-heptane, 59 vol% iso-octane and 30 vol% toluene. Three stages are distinguished: the low-temperature stage, the intermediate-temperature stage and the high-temperature stage. The phenomenon to be analyzed takes

place at the intermediate-temperature stage and therefore the analysis focuses on this temperature stage. The discussion is presented with respect to species' concentrations, the rates of reaction and the interaction between the products that are formed from the gasoline surrogate's components. Figures 7 and 8 show some of the most important species that govern this second temperature range, according to the surrogate mechanism.

Just after the cool flame (156-157 CAD), the concentrations of the formed pentyl and hexyl radicals (by dissociation of ketohydroperoxides) decrease due to dissociation reactions, forming, via oxidation of iso-butyl (IC_4H_9), propyl (IC_3H_7) and ethyl (C_2H_5) radicals, respectively the species iso-butene (IC_4H_8), propene (C_3H_6) and ethene (C_2H_4). The benzyl radical is mainly formed from the reaction between OH radicals and toluene. Right after the cool flame it can also be seen that acetaldehyde is formed. This is due to the reaction of propene with OH radicals. The concentration of acetaldehyde increases steadily, while that of propene does not decrease and that of OH radicals increases. Apparently, just after the cool flame, the production of propene is more than its consumption, but enough to form acetaldehyde. When oxygen abstracts a hydrogen radical, a HO_2 radical is formed. The reaction of HO_2 radicals with n-heptane and iso-octane, at the cool flame, forms H_2O_2 . It can be seen that indeed the concentration of HO_2 increases and then decreases, while the concentration of H_2O_2 increases after the cool flame. At this same moment (157 CAD), the benzyl radical's concentration decreases, shown in figure 8, forming benzaldehyde, then the phenoxy radical and then the cyclo-pentadienyl radical, illustrated by the increasing concentrations of these species. In the mean time, a build-up of H_2O_2 takes place. A certain concentration and a state of equilibrium for H_2O_2 are attained. This and the formation of the relatively stable olefins cause the effect named the NTC and subsequently the cool flame stabilizes. The heat release decreases at increasing temperature and the pressure does not increase much further (except by compression). The importance of the benzyl radical in the

auto-ignition of toluene is also mentioned in the literature [29,36,37]. According to [29], benzaldehyde is formed via the reaction of benzyl with oxygen through reversible addition of oxygen followed by an internal H-transfer reaction and an O-O scission. This would suggest that the hydroperoxybenzyl radical is an intermediary species between the benzyl radical and benzaldehyde. Furthermore, it appears [36,37] that the rate-controlling step of toluene oxidation is not the direct fuel oxidation but the oxidation of intermediates such as benzyl radicals. This suggests that the benzyl radical is the key species in toluene auto-ignition. According to [37], the reaction of the benzyl radical with the HO₂ radical is the major reaction for the oxidation of benzyl radicals.

As the temperature increases, due to the compression, H₂O₂ reaches a certain thermodynamic and kinetic state that it gradually starts to decompose into OH radicals (158-170 CAD). After 164 CAD, the benzyl radical concentration increases, due to the reaction of OH radicals with toluene. At this moment, apparently not enough HO₂ radicals are present to react with the benzyl radical. When the temperature of around 1020 K is attained (according to the gasoline surrogate mechanism), the thermodynamic conditions are then such that H₂O₂ decomposes rapidly into OH radicals, as figure 7 shows at 171 CAD. Figure 9 illustrates this as well, presenting the rates of reaction of the formation and consumption of OH radicals. Figure 9 shows that the reaction producing OH radicals (reaction 62) reaches its maximum between 172 and 173 CAD. At the same time, more H₂O₂ is produced (reaction 53) from HO₂ radicals. The OH radicals react with the fuel components n-heptane, iso-octane, and toluene or with their intermediate products. This makes the heat release increase. The consumption of the main olefins – according to the surrogate model, these are ethene, propene and isobutene – produces the energy for this pre-ignition heat release. This is shown in figures 10 and 11. Apparently, the most important reaction, taking place for the n-heptane combustion

mechanism, is the consumption of ethene and propene by OH radicals. For iso-octane, the reactions consuming iso-butene, propene and iso-octane are important. However, this does not seem to lead to the final ignition. This can be explained by figure 9. The rest of the available OH radicals also reacts with toluene, producing the relatively stable benzyl radical. This decreases the overall reactivity.

Normally, the final ignition should have taken place at the decomposition of H_2O_2 , but this is obstructed by sharing the OH radicals by toluene, forming the relatively stable benzyl radical at this temperature range. The formation of the benzyl radical competes with the reaction of OH radicals with the other alkanes and olefins. Thus, it can be said that the benzyl radical works as a sink for the formed OH radicals. In the mean time, HO_2 radicals are formed which form again H_2O_2 . So, the pre-ignition could be perceived as a misfire of the final ignition, and a delay of the final ignition is the consequence. The reactivity and concentration of the fuel components and their intermediate products are high enough to cause a reaction with the existing OH radicals, but not high enough to cause a final ignition, because the concentration and the relative unreactivity of the benzyl radical (consuming much OH radicals) are high enough to delay the final ignition. As soon as the temperature is high enough (1240 K, according to the surrogate mechanism), HO_2 radicals are formed and attain a critical concentration (at 178 CAD in figure 7), so that the benzyl radical reacts with HO_2 into the more reactive benzaldehyde and the stability caused by this benzyl radical disappears. This causes the circle " $\text{H}_2\text{O}_2 \rightarrow \text{OH} \rightarrow \text{benzyl}, \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$ " to be broken and the formation of H_2O_2 becomes less important than its decomposition, causing the stability of the system to reduce and the overall reactivity to increase. The OH radicals then consume any fuel with no obstruction, causing the final ignition to occur. As such, the pre-ignition can be called the "obstructed pre-ignition" (OPI). Figure 12 shows a simulation of the influence of the amounts of toluene in a gasoline surrogate on the concentration of H_2O_2 .

While the volumetric ratio “n-heptane : iso-octane” is fixed at “11:59”, the ratio of n-heptane/iso-octane to toluene is varied from 70:0 (11/70 parts of n-heptane, 59/70 parts of iso-octane and 0/70 parts of toluene) to 70:50 (11/120 parts of n-heptane, 59/120 parts of iso-octane and 50/120 parts of toluene). The simulation is made by the surrogate mechanism. Figure 12 shows clearly that a two stage ignition is observed for toluene proportions of 0 and 10. A three stage ignition is observed for toluene proportions of 20, 30 and 40. It seems that at a proportion of 50 for toluene, the final ignition doesn't even occur. These simulations suggest that at low amounts of toluene present in the fuel, the stability of the benzyl radical is overcome by the reactivity of the consumption of the fuel and their intermediates by the OH radicals. No OPI occurs then. At the proportions of 20, 30 and 40, it seems though that the stability of the benzyl radical is strong enough to overcome the reactivity of the consumption reactions. An OPI can then be observed. At higher toluene amounts, the OPI does occur, but this time it is the OPI that is not overcome, since after the OPI, the H_2O_2 does not decompose, marking no final ignition.

Figure 13 shows a global summary of the auto-ignition process, illustrating the impact of the obstructed pre-ignition phenomenon with the most important reactions and species (indicated within a dashed square), as is proposed by the surrogate mechanism.

5 Conclusions

This paper investigated the auto-ignition of gasoline95 and two surrogates in an HCCI engine. The used surrogates are a PRF95 and a mixture of 11 vol% n-heptane, 59 vol% iso-octane and 30 vol% toluene. It appeared from this study that relatively high compression ratios are needed in order to auto-ignite gasoline95. Nonetheless, complete combustion is observed. The

typical cool flame and final ignition stages are observed. In addition, another small heat release seems to be observed for gasoline and its 3-component surrogate. This heat release is called here the “obstructed pre-ignition”. The fact that for the PRF95 this heat release is not observed, suggests that the kinetics of the auto-ignition of toluene play an important role. In order to understand these phenomena, an experimentally validated kinetic chemical mechanism is used. This surrogate mechanism shows that the competition between the consumption of the fuel and the formation of an at that moment relatively stable benzyl radical from toluene, cause the so-defined “obstructed pre-ignition” and delay the actual final ignition. For the conventional fuel, gasoline95, the same three-stage ignition is observed. The results obtained from the auto-ignition of the 3-component surrogate would then suggest that the aromatics that are present in gasoline95 have the same impact as toluene, causing the so-called “obstructed pre-ignition”, followed by a delayed final ignition.

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Appendix

Reduced chemical kinetic reaction scheme representing surrogates of n-heptane, iso-octane and toluene and the interaction of NO with the surrogates

$k = A T^b \exp(-E_a/RT)$				
Reaction number	Reaction	A [mole-cm-s-K]	b [-]	Ea [J/mole]
Reactions	N-heptane initiation reactions			
1	<chem>C7H16+O2=>C7H15-2+HO2</chem>	2,80E+14	0	197212,4
2	<chem>C7H16+OH=>C7H15-2+H2O</chem>	4,80E+09	1,3	2886,29
3	<chem>C7H16+HO2=>C7H15-2+H2O2</chem>	1,00E+13	0	70851
4	<chem>C7H15-2+O2=C7H15O2</chem>	2,00E+12	0	0
5	<chem>C7H15O2=C7H14O2H</chem>	6,00E+11	0	85188,4
6	<chem>C7H14O2H+O2=C7H14O2HO2</chem>	2,34E+11	0	0
7	<chem>C7H14O2HO2=>C7KET21+OH</chem>	2,97E+13	0	111606
8	<chem>C7KET21=>C5H11+CO+CH2O+OH</chem>	1,00E+16	0	177232
9	<chem>C5H11=>C2H5+C3H6</chem>	3,20E+13	0	118294
10	<chem>C3H6+OH=>CH3CHO+CH3</chem>	3,50E+11	0	0
Reactions	Iso-octane initiation reactions			
11	<chem>IC8H18+O2+O2=>R2C8H17OO+HO2</chem>	2,10E+17	0	204820
12	<chem>IC8H18+OH=>CC8H17+H2O</chem>	2,48E+13	0	1839,2
13	<chem>IC8H18+HO2=CC8H17+H2O2</chem>	2,02E+12	0	60192
14	<chem>CC8H17+O2=R2C8H17OO</chem>	2,50E+19	-2,5	0
	Reverse reaction	1,79E+13	0	103747,6
15	<chem>R2C8H17OO=C8H16OOH</chem>	3,28E+12	0	119130
	Reverse reaction	1,80E+11	0	84018
16	<chem>C8H16OOH+O2=R2C8H16OOHOO</chem>	3,52E+19	-2,5	0
	Reverse reaction	7,00E+12	0	91040,4
17	<chem>R2C8H16OOHOO=>OH+C7H14CHO(OOH)</chem>	4,80E+12	0	119130
18	<chem>C7H14CHO(OOH)=>CO+IC6H13+CH2O+OH</chem>	2,05E+15	0	173052
19	<chem>CC8H17+HO2=>IC6H13+C2H3+H2O2</chem>	2,00E+12	0	0
20	<chem>CC8H17=>IC4H8+IC4H9</chem>	4,28E+12	0	115368
21	<chem>IC6H13=>IC3H7+C3H6</chem>	2,51E+13	0	117876
22	<chem>IC4H9+O2=>IC4H8+HO2</chem>	1,00E+12	0	20900
23	<chem>IC4H8+OH=>IC3H7+CH2O</chem>	1,51E+12	0	0
24	<chem>IC3H7+O2=>C3H6+HO2</chem>	1,00E+12	0	20900
25	<chem>C3H6+OH=>C2H5+CH2O</chem>	1,00E+12	0	0
Reactions	Toluene initiation reactions			
26	<chem>C6H5CH3+O2=C6H5CH2+HO2</chem>	3,00E+14	0	179706,56
27	<chem>C6H5CH3+OH=>C6H5CH2+H2O</chem>	5,27E+13	0	10796,94
28	<chem>C6H5CH2+HO2=>C6H5CHO+H+OH</chem>	5,00E+12	0	0
29	<chem>C6H5CHO+OH=>C6H5CO+H2O</chem>	2,25E+10	1,18	-1868,46
30	<chem>C6H5CO=>C6H5+CO</chem>	3,98E+14	0	122892
31	<chem>C6H5+O2=>C6H5O+O</chem>	2,60E+13	0	25581,6
32	<chem>C6H5O=>CO+C5H5</chem>	3,76E+54	-12,06	310574
33	<chem>C5H5+O2=>C5H4O+OH</chem>	1,80E+12	0,08	75240
34	<chem>C5H4O+O+2O2=>3CO+2HCO+H2O</chem>	3,60E+16	1,45	-3586,44
Reactions	C2 reactions			
35	<chem>C2H5+O2=>C2H4+HO2</chem>	2,00E+10	0	-9196
36	<chem>C2H4+OH=>CH2O+CH3</chem>	6,00E+13	0	4012,8
37	<chem>C2H4+H=>C2H3+H2</chem>	1,51E+07	2	25080
38	<chem>C2H3+O2=>CH2O+HCO</chem>	3,98E+12	0	-1045
39	<chem>CH3CHO+OH+M=>CH3+CO+M+H2O</chem>	1,80E+17	0	60192
Reactions	C1 reactions			
40	<chem>CH3+HO2=>CH3O+OH</chem>	4,30E+13	0	0

41	CH3O(+M)=CH2O+H(+M)	2,00E+13	0	114615,6
	Low pressure limit	2,34E+25	-2,7	127908
42	CH2O+OH+O2=>H2O+HO2+CO	6,69E+14	1,18	-1868,46
43	CH2O+O2+M=>H+CO+M+HO2	6,20E+16	0	154660
44	CH2O+HO2=>HCO+H2O2	2,17E+11	0	33440
45	HCO+O2=>CO+HO2	3,98E+12	0	0
46	HCO+M=H+CO+M	2,50E+14	0	70232,36
47	CO+HO2=>CO2+OH	1,51E+14	0	98857
48	CO+O=CO2	1,80E+10	0	10190,84
49	CO+O+M=CO2+M	5,89E+15	0	17138
50	CO+OH=CO2+H	3,09E+11	0	3072,3
51	CO2+O=CO+O2	2,75E+12	0	183209,4
	Reverse reaction	3,25E+11	0	153280,6
Reactions	O/H reactions			
52	HO2+HO2=H2O2+O2	3,22E+15	0	-6809,22
53	H2+O=>H+OH	1,82E+10	1	37202
54	H2O2+OH=H2O+HO2	1,00E+13	0	7524
	Reverse reaction	2,03E+13	0	145798,4
55	H2O+M=H+OH+M	2,19E+16	0	438900
	Enhancement factors:	--	--	--
	H2O	21	--	--
	CO	2,0	--	--
	H2	3,3	--	--
56	H+O2+N2=>HO2+N2	2,60E+19	-1,24	0
57	H+O2=HO2	2,07E+18	-1,69	3720,2
58	OH+HO2=H2O+O2	1,91E+16	-1	0
59	H+O2=OH+O	2,10E+15	-0,3	84436
60	OH+OH=O+H2O	1,50E+09	1,14	415,492
61	OH+OH=H2O2	1,00E+25	-5,452	12832,6
62	OH+OH(+M)=H2O2(+M)	7,60E+13	-0,37	-8151
	Low pressure limit	4,30E+18	-0,9	-7106
	TROE coefficients 0,7346; 94; 1756; 5182	--	--	--
	Enhancement factors:	--	--	--
	H2	2,0	--	--
	H2O	6,0	--	--
	CH4	2,0	--	--
	CO	1,5	--	--
	CO2	2,0	--	--
	N2	0,7	--	--

Figure captions

Figure 1: Ignition delays as a function of the equivalence ratio and the dilution by N_2 at an inlet temperature of $70\text{ }^\circ\text{C}$, a compression ratio of 13.5 using gasoline 95 and its surrogate as fuel

Figure 2: Comparison of the pressure profiles using three fuels with an octane number of 95, at an inlet temperature of $70\text{ }^\circ\text{C}$, a compression ratio of 13.5 and an equivalence ratio of 0.462

Figure 3: Comparison of the heat release profiles using three fuels with an octane number of 95, at an inlet temperature of $70\text{ }^\circ\text{C}$, a compression ratio of 13.5 and an equivalence ratio of 0.462

Figure 4: Influence octane number on ignition delays at an inlet temperature of $70\text{ }^\circ\text{C}$, a compression ratio of 13.5 and an equivalence ratio of 0.41

Figure 5: Comparison of the heat release profiles using three equivalence ratios for gasoline 95 as the fuel at an inlet temperature of $70\text{ }^\circ\text{C}$ and a compression ratio of 13.5

Figure 6: Modelling result of the heat release for the gasoline surrogate, at an inlet temperature of $70\text{ }^\circ\text{C}$, a compression ratio of 13.5 and an equivalence ratio of 0.462

Figure 7: Comparison between the heat release and the intermediate small radical species, formed during the intermediate temperature range for the gasoline surrogate, with an inlet temperature of 385, an equivalence ratio of 0.6, a compression ratio of 14

Figure 8: Comparison between the heat release and the intermediate large radical species, formed during the intermediate temperature range for the gasoline surrogate, with an inlet temperature of 385, an equivalence ratio of 0.6, a compression ratio of 14

Figure 9: Rates of reaction of the reactions between the cool flame and the final ignition of the formation and consumption of H_2O_2 in the gasoline surrogate, with an inlet temperature of 385, an equivalence ratio of 0.6 and a compression ratio of 14

Figure 10: Rates of reaction of the consumption of n-heptane and its intermediates ethene and propene in the gasoline surrogate together with the heat release, with an inlet temperature of 385, an equivalence ratio of 0.6, a compression ratio of 14

Figure 11: Rates of reaction of the consumption of iso-octane and its intermediates propene and iso-butene in the gasoline surrogate together with the heat release, with an inlet temperature of 385, an equivalence ratio of 0.6, a compression ratio of 14

Figure 12: The normalized concentrations of H_2O_2 in a fixed mixture of n-heptane/iso-octane (11:59) which are mixed with toluene at different proportions (0 to 50) at an inlet temperature of 70 °C, an equivalence ratio of 0.6 and a compression ratio of 14

Figure 13: A global summary of the reaction pathway showing the interaction of the “obstructed pre-ignition” phenomenon proposed by the surrogate mechanism

Figures

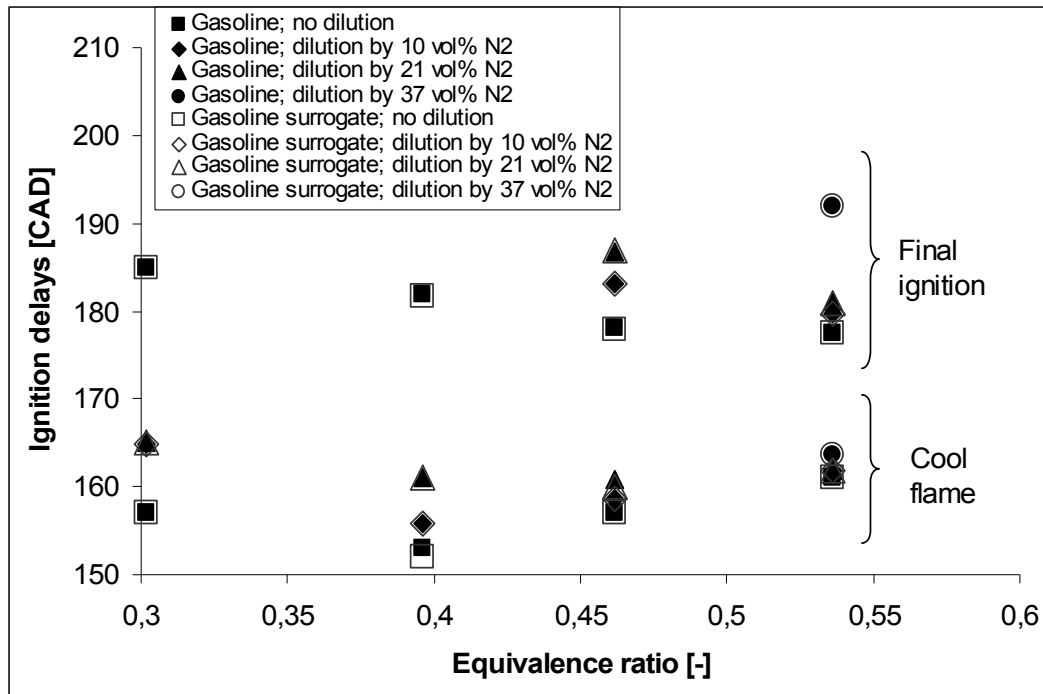


Figure 1: Ignition delays as a function of the equivalence ratio and the dilution by N_2 at an inlet temperature of $70\text{ }^\circ\text{C}$, a compression ratio of 13.5 using gasoline 95 and its surrogate as fuel

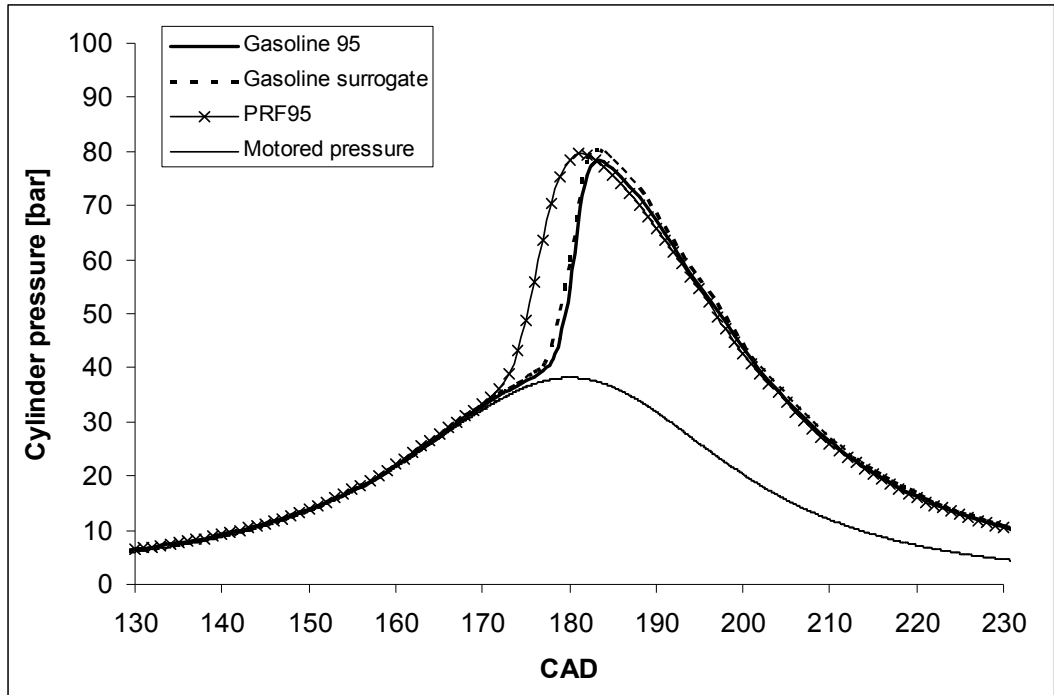


Figure 2: Comparison of the pressure profiles using three fuels with an octane number of 95, at an inlet temperature of 70 °C, a compression ratio of 13.5 and an equivalence ratio of 0.462

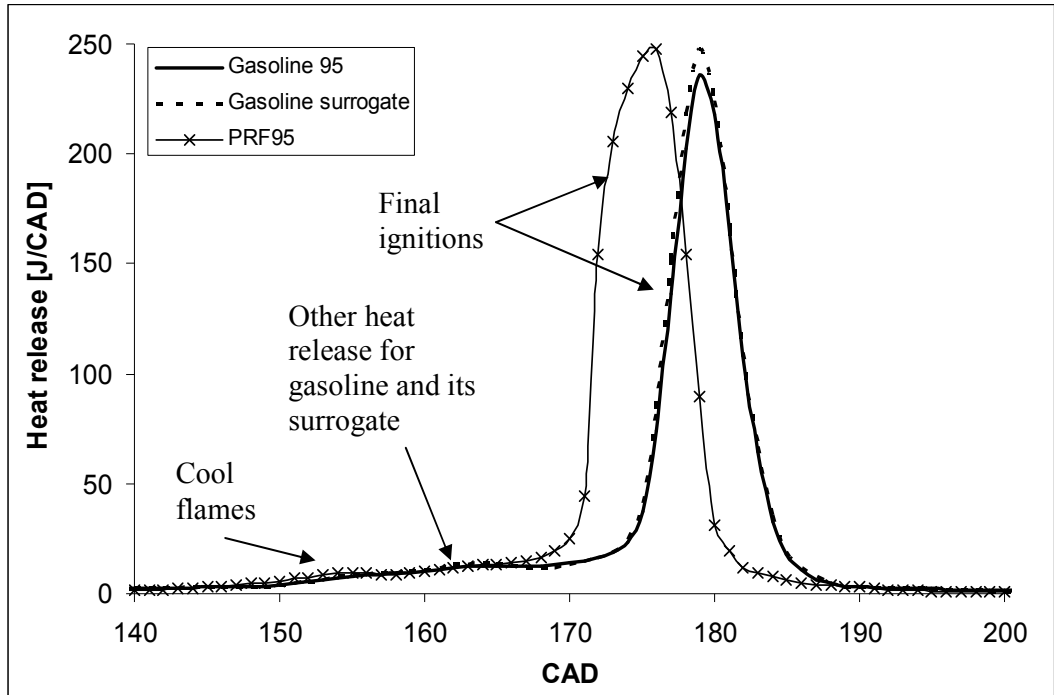


Figure 3: Comparison of the heat release profiles using three fuels with an octane number of 95, at an inlet temperature of 70 °C, a compression ratio of 13.5 and an equivalence ratio of 0.462

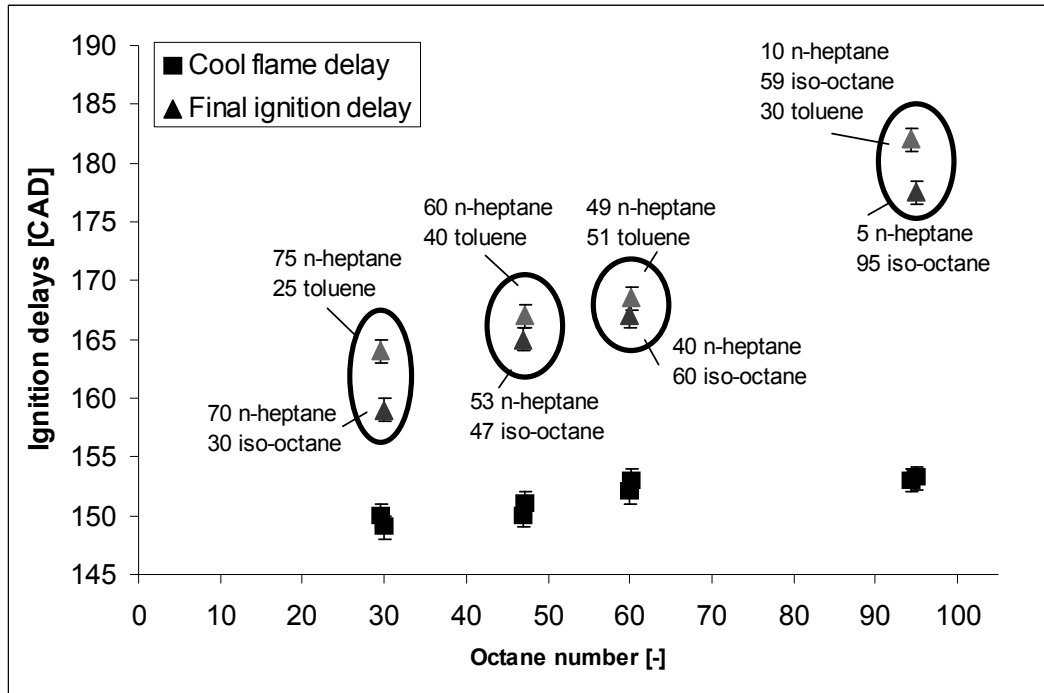


Figure 4: Influence octane number on ignition delays at an inlet temperature of 70 °C, a compression ratio of 13.5 and an equivalence ratio of 0.41

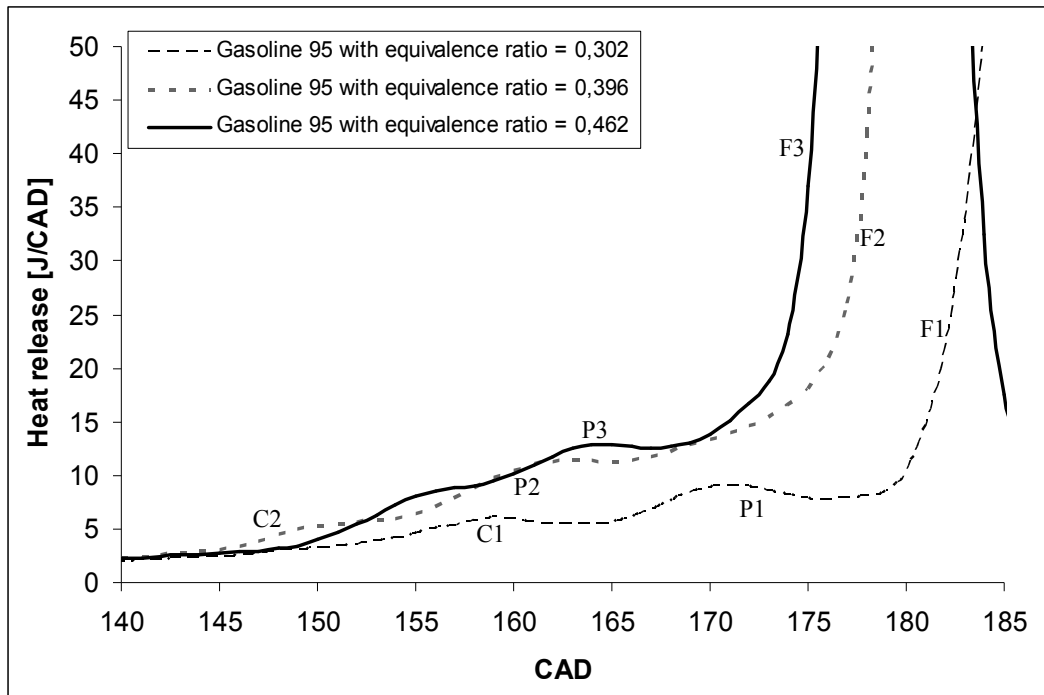


Figure 5: Comparison of the heat release profiles using three equivalence ratios for gasoline 95 as the fuel at an inlet temperature of 70 °C and a compression ratio of 13.5

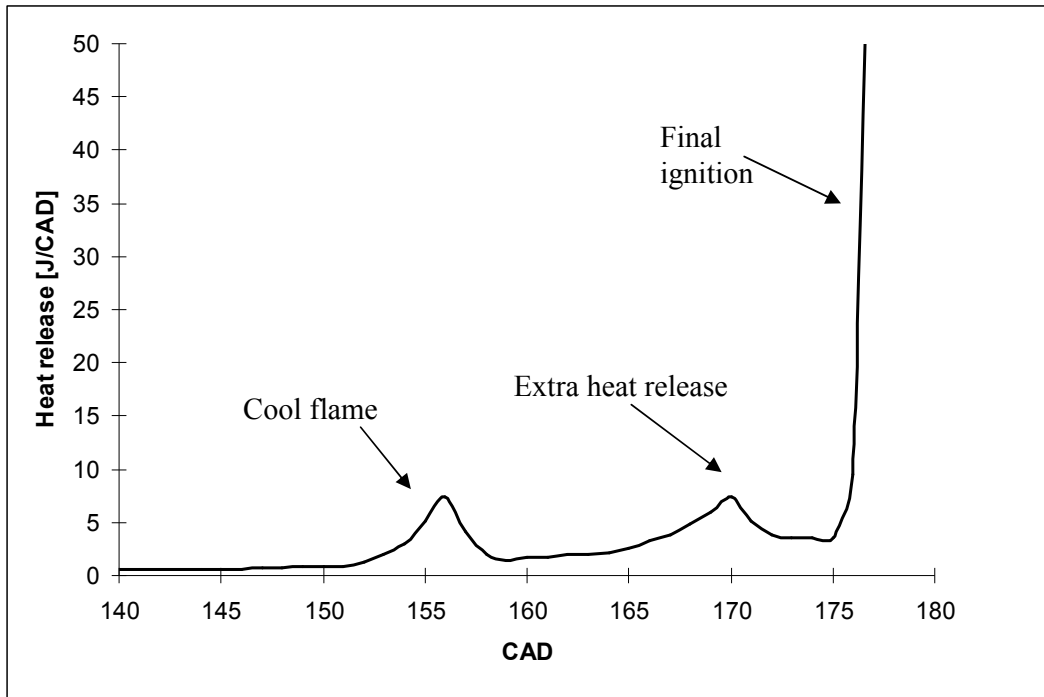


Figure 6: Modelling result of the heat release for the gasoline surrogate, at an inlet temperature of 70 °C, a compression ratio of 13.5 and an equivalence ratio of 0.462

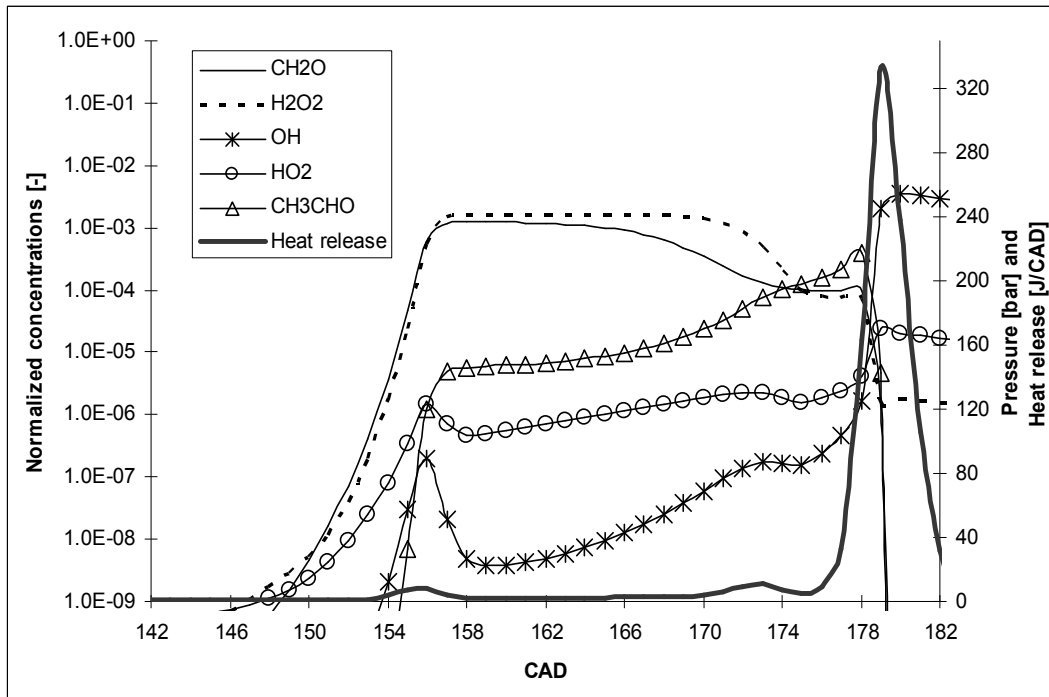


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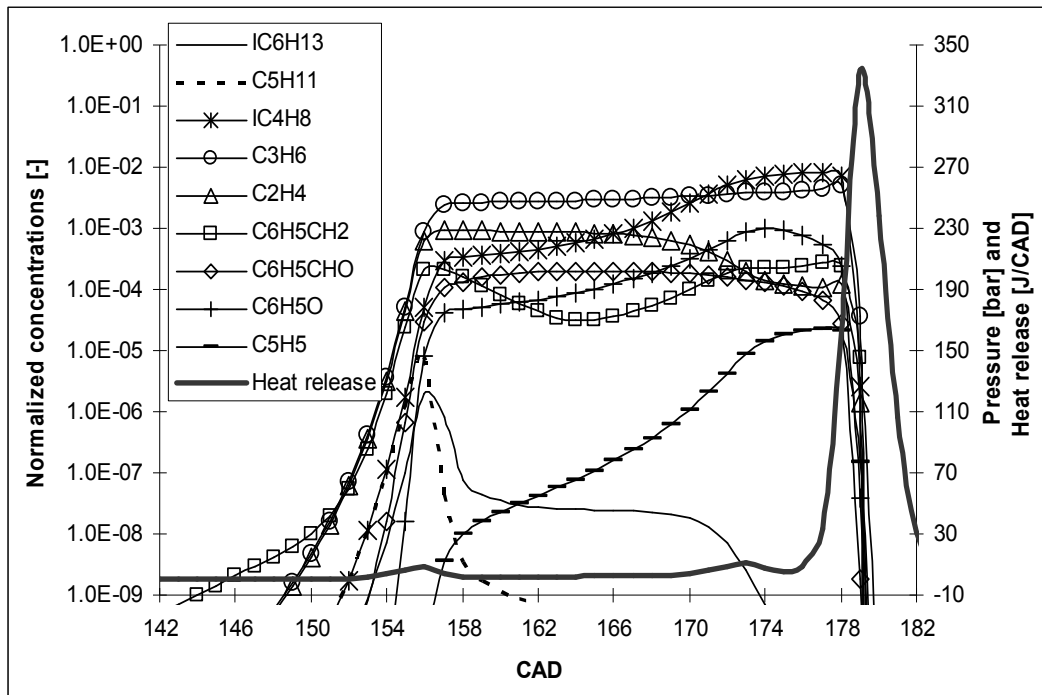


Figure 8: Comparison between the heat release and the intermediate large radical species, formed during the intermediate temperature range for the gasoline surrogate, with an inlet temperature of 385, an equivalence ratio of 0.6, a compression ratio of 14

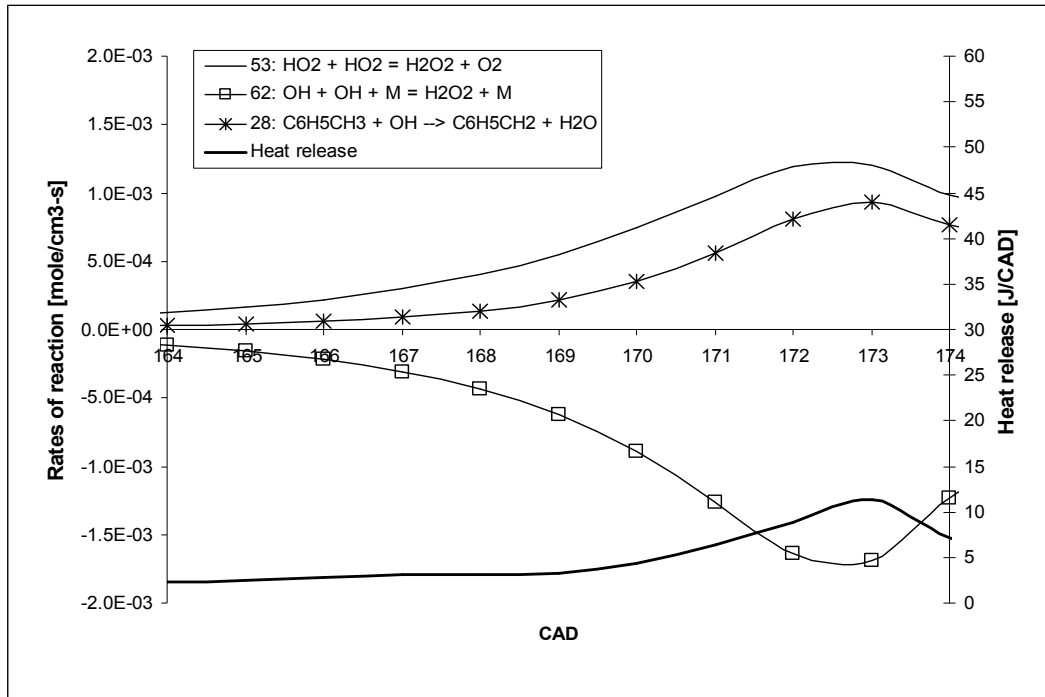


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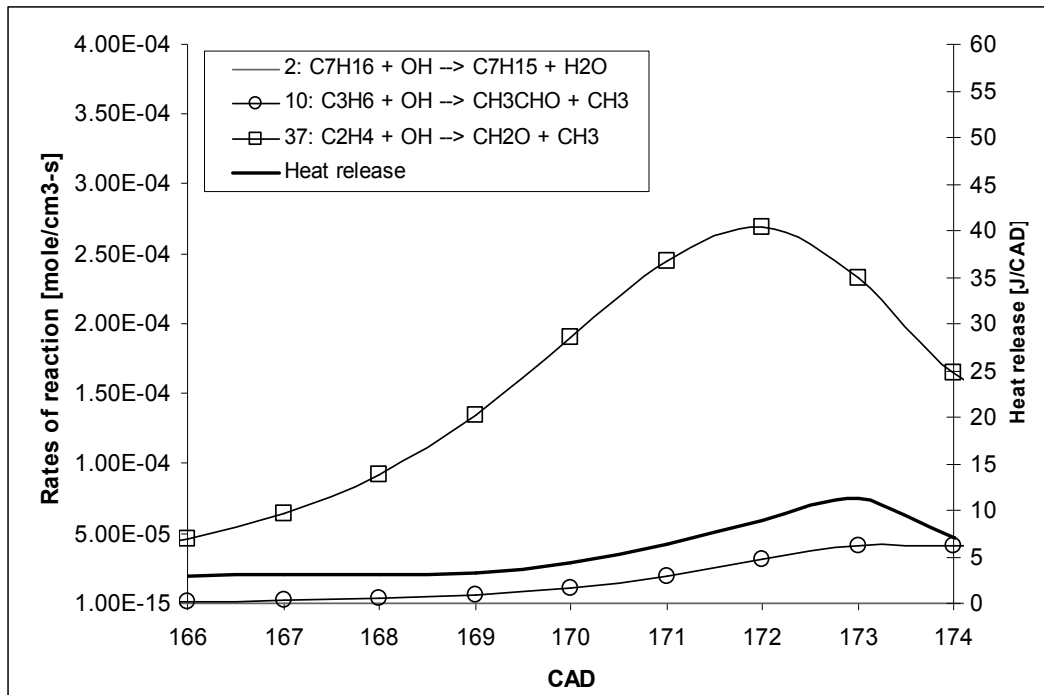


Figure 10: Rates of reaction of the consumption of *n*-heptane and its intermediates ethene and propene in the gasoline surrogate together with the heat release, with an inlet temperature of 385, an equivalence ratio of 0.6, a compression ratio of 14

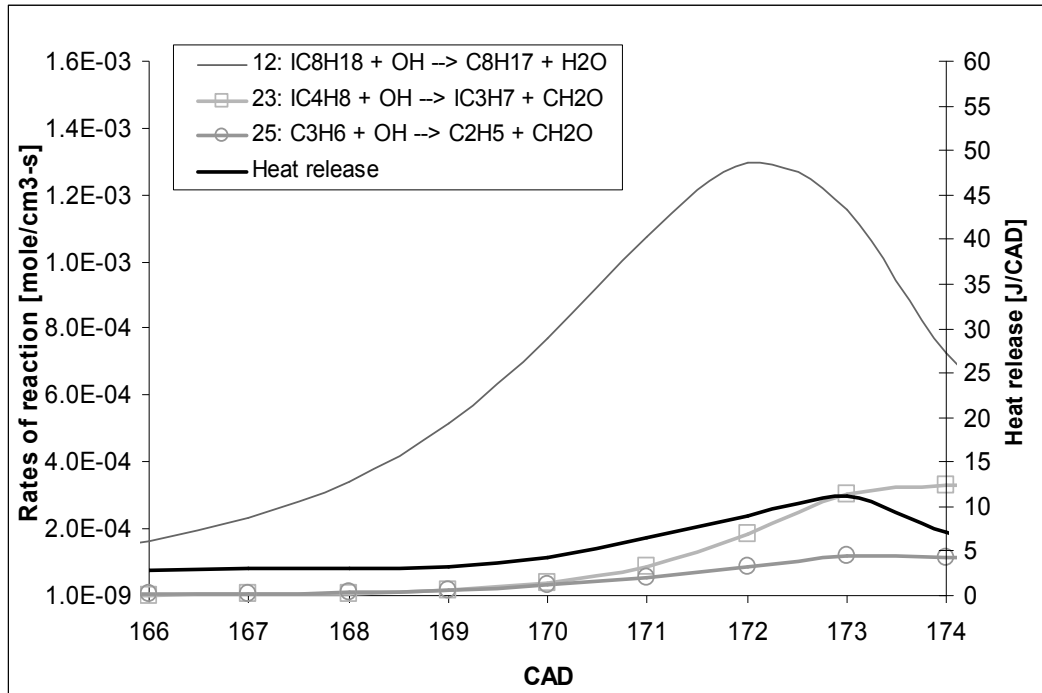


Figure 11: Rates of reaction of the consumption of iso-octane and its intermediates propene and iso-butene in the gasoline surrogate together with the heat release, with an inlet temperature of 385, an equivalence ratio of 0.6, a compression ratio of 14

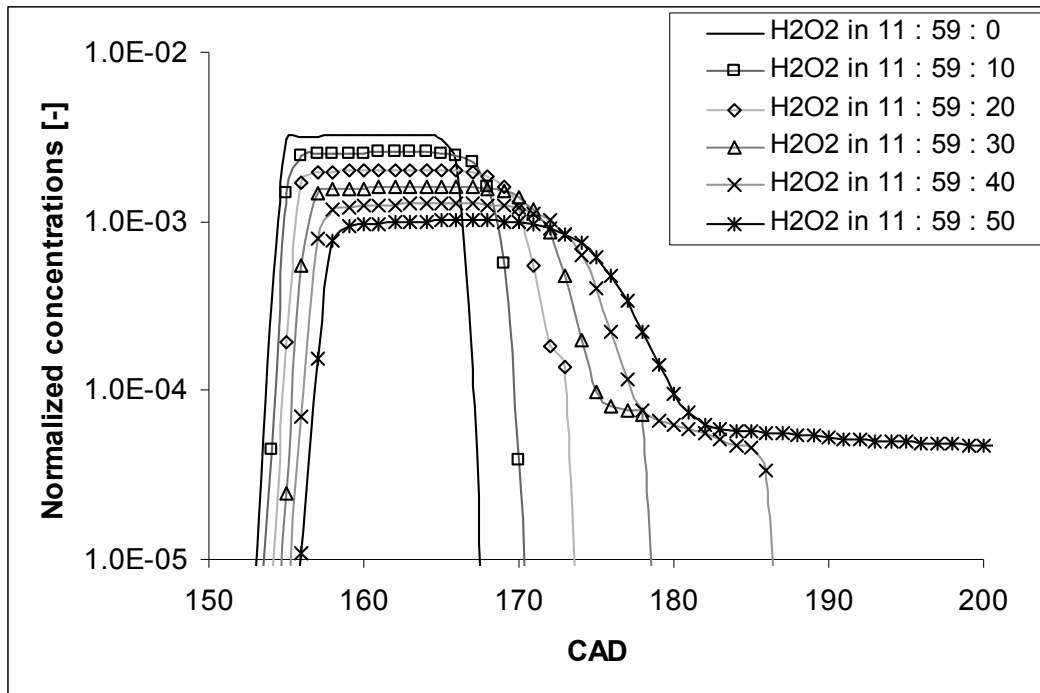


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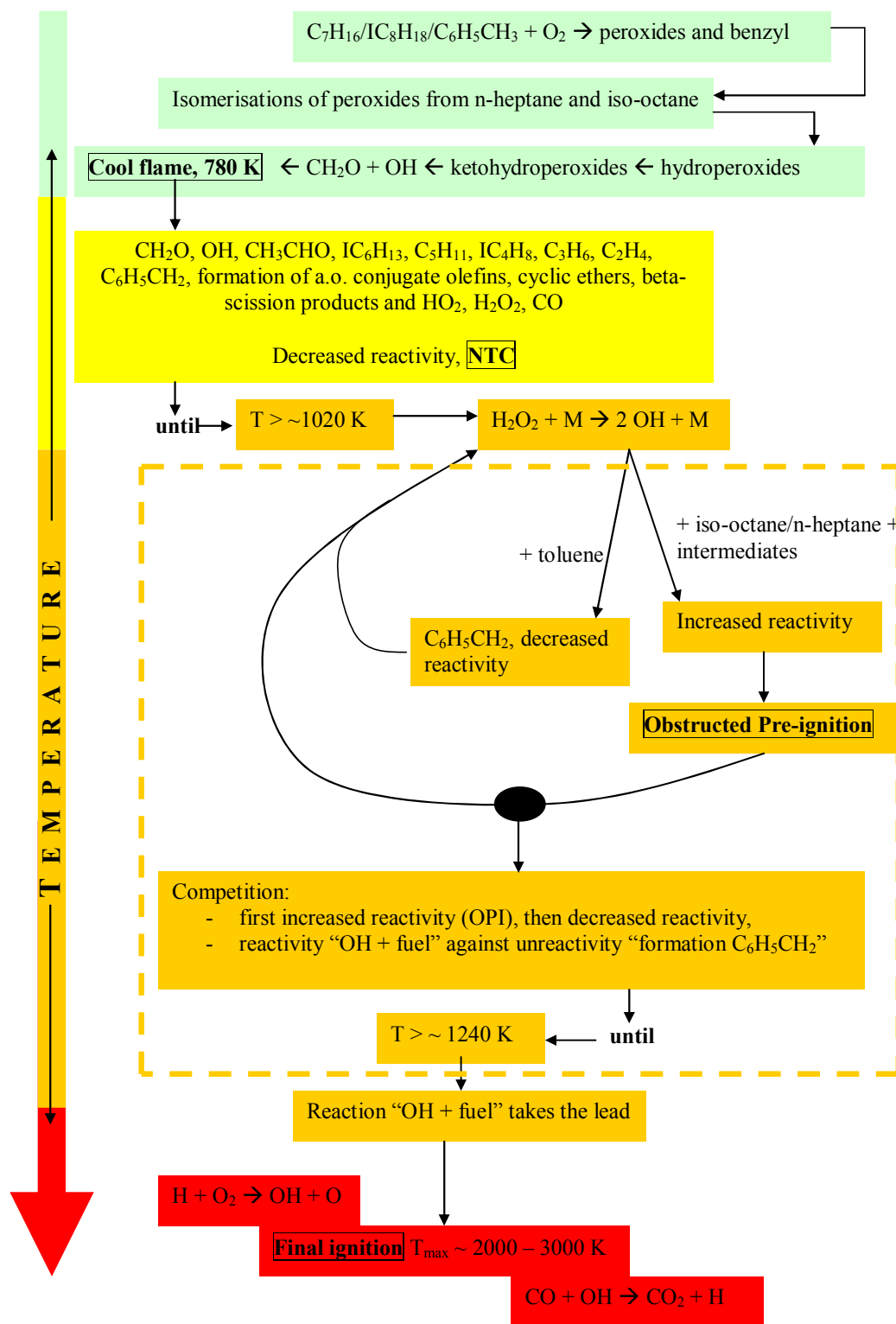


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