An experimental and numerical analysis of the HCCI auto-ignition process of Primary Reference Fuels, Toluene Reference Fuels and Diesel Fuel in an engine, varying the engine parameters

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Abstract

For a future HCCI engine to operate under conditions that adhere to environmental restrictions, reducing fuel consumption and maintaining or increasing at the same time the engine efficiency, the choice of the fuel is crucial. For this purpose, this paper presents an auto-ignition investigation concerning the primary reference fuels, toluene reference fuels and diesel fuel, in order to study the effect of linear alkanes, branched alkanes and aromatics on the auto-ignition. The auto-ignition of these fuels has been studied at inlet temperatures from 25 to 120 °C, at equivalence ratios from 0.18 to 0.53 and at compression ratios from 6 to 13.5, in order to extend the range of investigation and to assess the usability of these parameters to control the auto-ignition. It appeared that both iso-octane and toluene delayed the ignition with respect to n-heptane, while toluene has the strongest effect. This means that aromatics have higher inhibiting effects than branched alkanes. In an increasing order, the inlet temperature, equivalence ratio and compression ratio had a promoting effect on the ignition delays. A previously experimentally validated reduced surrogate mechanism, for mixtures of n-heptane, iso-octane and toluene, has been used to explain observations of the auto-ignition process.

Key words: auto-ignition, diesel fuel, primary reference fuels, toluene reference fuels, HCCI, engine, inlet temperature, equivalence ratio, compression ratio

1 Introduction

The choice of the fuel plays an important role on the combustion process in an engine. For Spark Ignition engines, gasoline is preferred for its high octane rating, being relatively resisting for auto-ignition. For Compression Ignition engines, however, diesel is preferred for its high cetane rating, being suitable for auto-ignition. The kind of fuel or the kind of combustion mode influences also the kind and quantity of gases that are emitted by internal combustion engines. It seems very likely that the number of vehicles will increase. This makes it urgent to either improve the current combustion modes or find an alternative. The Homogeneous Charged Compression Ignition (HCCI) seems to be promising. This combustion mode has gained much interest lately **[1-10]**. Depending on the fuel, the auto-ignition can proceed in one-stage, two-stage or multi-stage ignitions **[11-17]**. This confirms that the fuel chosen is crucial for the combustion process, since the chemical kinetic pathways can be considerably different. It is very likely that only one type of fuel is used for an engine at the same time, perhaps two. So, the purpose of investigating the fuel composition is to have a better insight into the effect of the fuel on the auto-ignition process, so that the most interesting compositions can be chosen for the application in an HCCI engine. The investigation of the auto-ignition of several fuels has lead to general trends, including a rough dependence (though not explicit) of the auto-ignition delay on the octane number of the fuel. For instance, the ignition characteristics in a Rapid Compression Machine for low alkylbenzenes are measured by **[8]**, finding that compositions with a low Research Octane Number (RON), like ethyltoluene and n-butylbenzene, had a low delay time and vice versa, like toluene and m-xylene. It is also stated **[18]** that iso-octane (which has a higher RON) has a lower reactivity than n-heptane. Another study **[3]** about the auto-ignition of several pure fuels in a rapid compression machine, presenting the ignition delays and the burn rates (dP/dt) for some pure fuels (ϕ = 0,4, ε = 16, T_{inlet} = 318 K and P_{inlet} = 1 bar), shows that both the ignition delays and the burn rates are strongly affected by fuel structure.

In principle, a wide variety of fuels can be used with this mode of combustion. It is therefore of interest to investigate the behaviour of the auto-ignition as a function of several fuels. In order to obtain preliminary information about this behaviour, standard fuels are chosen. For this purpose, this paper intends to investigate the auto-ignition of two different types of fuel: n-heptane/iso-octane mixtures (PRF's) and n-heptane/toluene mixtures (TRF's). Since, in some cases, diesel surrogates are composed out of mixtures of n-heptane/toluene, the auto-ignition of diesel is also presented. A previously validated kinetic mechanism for mixtures of n-heptane/iso-octane/toluene is used for the explanation of the observed phenomena. The inlet temperature is set either on 70 or on 120 °C and the compression ratio either on 10.2 or on 13.5. The equivalence ratio is changed from 0.13 to 0.53. The first aim of this paper is to study the behavior of the auto-ignition of the aforementioned fuels at different operating conditions. The second aim is to study the effects of engine parameters on the auto-ignition delay for their suitability to control the auto-ignition. For this purpose, the inlet temperatures are varied from 25 to 70 °C, the equivalence ratios from 0.18 to 0.41 and the compression ratios from 6 to 13.5.

2 HCCI chemistry

The chemical kinetics of the auto-ignition of n-heptane, iso-octane and toluene is elaborately discussed in the literature **[6,8,9,17-20]**, though not much is known about toluene. A short reminder of the auto-ignition of these fuels is presented in the form of three schemes, using the cited literature. Figures 1, 2 and 3 present respectively the chemical reaction paths of n-heptane, iso-octane and toluene. The differences between the n-heptane and iso-octane reaction pathways are discussed in section 4.1. These compounds are immiscible in water, colourless, highly flammable and volatile and when their vapour is mixed with air they are explosive. Toluene is also toxic. Great care should be taken and any physical contact should be avoided.

3 Experimental

The experimental set-up, the characteristics of the HCCI engine and the error assessment have been discussed in previous work **[21]**. Some essential configurations, assumptions, error estimations and calculations will be recalled in this section. Table 1 shows the engine characteristics. The experimental set-up comprises an HCCI engine, equipped with an air inlet system and a fuel nozzle injection system, being assisted by pressurized air. A mixture tank serves to mix the fuel as homogeneously as possible, measuring the air flow, the fuel flow, the inlet pressure and the inlet temperature (confidence interval +/- 1 °C). This allows calculating the equivalence ratio, with a confidence interval of +/- 0.005. The HCCI engine has a variable compression ratio (confidence interval +/- 0.5), being defined as the volumetric ratio of the total volume (clearance volume and displacement volume) and the clearance volume. The fuel is composed by measuring the volumetric quantity (confidence interval +/- 1 vol%) of each constituent of the fuel and mixing these together. For the post treatment of the experiments, the cylinder pressure is measured by a pressure sensor, exhibiting a standard deviation of the maximum pressure of around 0.12 % for a motored pressure, but this can go up to about 1.5 % at combustion and 3 % for unstable combustion. This pressure allows investigating the behaviour of the auto-ignition process as a function of the aforementioned parameters. Another tool for this analysis is the ignition delay. As said before, PRF's exhibit two-stage ignitions, translated into a heat release with two maxima, the latter being higher than the former. The ignition delays are defined identically, the cool flame delay being the Crank Angle Degrees (CAD) interval from Bottom Dead Center (BDC) until the first heat release maximum and the final ignition delay being the CAD interval from BDC until the second heat release maximum. The heat release shows a confidence interval of 10 % for the maximum and the ignition delays show a confidence interval of +/- 0.5 CAD. These ignition delays are calculated, by using a 0 D engine model, calculating the heat release. The heat release, $dQ_{release}/d\theta$ is calculated, using the following equation:

$$\frac{dQ_{release}}{d\theta} = \frac{dQ_{wall}}{d\theta} + \frac{\gamma}{\gamma - 1} P \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dP}{d\theta} \tag{1}$$

Here θ is the crank angle degree, while $dQ_{wall}/d\theta$ is the heat loss to the wall. The volume, V, is determined from the engine geometry and γ is the isentropic constant (C_p/C_v). The heat loss is calculated at each point in time according to:

$$Q_{wall} = hA(T - T_{wall}) \tag{2}$$

where the temperature T is estimated by using the gas temperature, calculated from the ideal gas law. A is the surface of the cylinder. The wall temperature T_{wall}, is estimated by measuring the heat loss to the cooling water and using the standard heat convection and conduction correlations. A heat transfer correlation that is adjusted for HCCI application **[14]** has been used in order to estimate the overall heat transfer correlation to the wall. Furthermore, for the use of the reduced kinetic model as explanation of the experimental findings, an estimation of the residual gas fraction and temperature has been performed in order to estimate more realistically the temperature at inlet valve closing. More detail about the heat transfer, the estimation of the wall temperature and the estimation of the residual gas fraction and temperature, according to the experimental configuration of this paper, can be found in previous work **[21]**. The fuels, next to commercial diesel fuel, used in this paper are composed out of three compounds: n-heptane, iso-octane and toluene. Table 2 shows the fuels that are used for this work. The fuel composition measured a volumetric confidence interval of +/- 1 vol%.

4 Results and discussion:

4.1 The auto-ignition of PRF's and TRF's

This section discusses the effect of the fuel composition of Primary Reference Fuels (n-heptane/iso-octane) and Toluene Reference Fuels (n-heptane/toluene) on the auto-ignition delays. Figure 4 shows the effect of the fuel composition of the PRF's on the auto-ignition delays. Since the fuels PRF80 and iso-octane did not ignite at the same conditions, figure 5 presents the results for these two fuels as a function of the equivalence ratio at a different compression ratio of 13.5. Figures 4 and 5 show clear trends. Generally speaking, a mixture containing more n-heptane will ignite easier than a mixture containing more iso-octane, since n-heptane, having a higher burn rate, is easier to ignite than iso-octane. The addition of iso-octane to n-heptane seems to delay the cool flame and the final ignition delay. The iso-octane oxidation scheme is very similar to that for n-heptane. The main difference lies in the distribution of the mass flows through the different reaction branches. Dagaut et al. **[22]** write that the sum of secondary and tertiary H atoms (which are more reactive than primary H atoms) is much lower in the case of iso-octane. So the H-abstractions and isomerization reactions are less likely to occur. Therefore the initiation reaction of iso-octane and oxygen has a lower rate than that of n-heptane and oxygen and also the formation of the peroxides and the isomerisations. So the pathway to the cool flame is longer for iso-octane, increasing the cool flame delay. It was said that for iso-octane the H-abstractions and isomerization reactions are less likely to occur. A consequence of this is that, once entered into the cool flame, the propagation sequence from hydroperoxy alkyl radicals to cyclic ethers and olefins is favored more for iso-octane than it is for n-heptane, the latter of which favors the formation of oxygenated species from the hydroperoxy alkyl radicals. Therefore, mostly stable species such as olefins and cyclic ethers are produced during low-temperature oxidation of iso-octane, while the rate of oxygenated species formation is low. This causes the longer NTC-region for fuels with higher iso-octane content. In this discussion the focus will be on the formation of either olefins or oxygenate species, the former of which is favored by iso-octane and the latter of which is favored by n-heptane.

Let's represent the olefins by ethene and the oxygenated species by formaldehyde, since these are known to be the ones that are mostly formed. Two pathways can then be observed for both iso-octane and n-heptane. The first pathway (pathway 1) results into the formation of ethene producing the relatively stable HO_2 radical and the second pathway (pathway 2) results into the formation of formaldehyde producing the reactive radical OH. Pathway 1 decreases the overall reactivity, thus increasing the NTC-period and delaying the final ignition, while pathway 2 does the inverse. Both pathways are represented by n-heptane and iso-octane, except that the one favors a certain pathway and the other another pathway. The mechanism is used to calculate the concentration profiles of ethene, representing the preference for pathway 1, and formaldehyde, representing the preference for pathway 2. This is presented in figure 6. Figure 6 shows clearly that formaldehyde formation (pathway 2) is preferred by n-heptane and ethene formation (pathway 1) is preferred by iso-octane. This means that the NTC-period for iso-octane is longer, illustrated by more ethene production and less formaldehyde formation. This implies less OH radicals, which lowers the overall reactivity and delays the final ignition. This can also be seen by the build up profile of H_2O_2 in figure 6 (a typical species of the NTC-region **[22,23]**). The case for n-heptane is the opposite. It can be clearly seen, in figure 6, that H_2O_2 is formed much later for iso-octane and to a lesser extent, showing the late decomposition of H_2O_2 into OH for iso-octane, indicating a later final ignition. Furthermore, for iso-octane the existence of H_2O_2 is longer, indicating also a longer NTC-period. This longer NTC-period for a fuel containing more iso-octane, is also confirmed by looking to the heat release curves in figure 7 as a function of the n-heptane/iso-octane composition. There, it can be seen that the distance between the two heat release maxima is higher for the PRF60 than for the PRF20 (indicated by double arrows). This coincides with the lower overall reactivity of iso-octane and the higher ignition delays.

The fuel toluene is much different than n-heptane and/or iso-octane. The influence of the fuel composition of the TRF's on the auto-ignition delays is presented in figure 8. The results in figure 8 show that toluene delays both the cool flame and the final ignition. Also toluene seems to have a bigger impact on the auto-ignition of n-heptane than on iso-octane. Contrary to paraffins, the oxidation of aromatics does not show the NTC behavior typical for aliphatic hydrocarbons such as n-heptane and iso-octane. Furthermore, toluene is more resistant to auto-ignition than iso-octane and n-heptane, as also indicated by its high blending RON index (124). This is thought to be caused by the inhibitory effect of certain intermediary species which act as radical sinks, especially the benzyl radical. The consummation of toluene involves a replacement of a very reactive radical (OH• or H•) by the unreactive benzyl radical $C_6H_5CH_2$•. Thus, the controlling step in the reaction system is not the direct oxidation of the fuel but oxidation of intermediary species such as the benzyl radical. This causes the overall OH radical concentration to be lowered, delaying therefore both the cool flame and the final ignition of n-heptane mixture more than iso-octane does. The reason, for which toluene's impact on delaying the final ignition is stronger than that of iso-octane, is the fact that while iso-octane produces less OH radicals, toluene has reactions that function as a sink for OH radicals. Therefore it reduces the OH concentration and delays the auto-ignition. In the mean time, the produced HO_2 radicals build up H_2O_2. As soon as the temperature is high enough so that the H_2O_2 decomposition is important enough to overcome the consummation of OH by toluene, the final ignition takes place. Figure 9 shows adiabatic calculations were the H_2O_2 and OH concentrations are compared for the fuels 60 vol% n-heptane / 40 vol% iso-octane and 60 vol% n-heptane / 40 vol% toluene at a compression ratio of 10.2, an equivalence ratio of 0.4 and an inlet temperature of 70 °C. Figure 9 shows indeed that the H_2O_2 and OH concentrations of the n-heptane/iso-octane fuel are higher than those for the n-heptane/toluene fuel, just before they are consumed (final ignition). This calculation confirms that therefore the ignition reactivity for toluene is lower, for it contains less OH radicals. Furthermore, it shows that the fuel containing toluene ignites later than the fuel containing iso-octane and has a longer NTC-period, for the presence of H_2O_2 is longer.

The higher reactivity of the n-heptane/iso-octane mixture with respect to the n-heptane/toluene mixtures is also expressed in the relative total heat release, illustrated in figure 10. The total heat release, presented in figure 10, seems to decrease when increasing the iso-octane content in the fuel. The stronger effect of toluene is confirmed by the total heat release, which decreases faster for the addition of toluene than for the addition of iso-octane to n-heptane. Figure 11 shows the ratio of the heat release at the final ignition and the heat release at the cool flame for both the PRF's and TRF's. Figure 11 shows extra information with respect to figure 10. The ratio of the heat release at the final ignition and the heat release at the cool flame increases when adding iso-octane or toluene to n-heptane: the heat release distribution disfavors the cool flame more than the final ignition. This seems to confirm the findings in the literature, discussed in the introduction, that adding iso-octane or toluene to n-heptane makes the cool flame weaker. Toluene, as said earlier in this subsection, has indeed a stronger effect than iso-octane, which is confirmed by figure 11.

4.2 The auto-ignition of diesel fuel

The fuel diesel and the improvement of Diesel Compression Ignition engines have been subject to many studies **[24-29]**. Linear alkanes seem to auto-ignite more easily than branched alkanes or aromatics. Diesel is known to have more linear alkanes than gasoline, less branched alkanes and about the same amount of aromatics. So, one would say that diesel is much easier to auto-ignite than gasoline. True, but to investigate diesel, an additional problem has to be considered. Diesel shows an inhibitive physical aspect that makes it not that easy to auto-ignite at first instance. Diesel has a higher viscosity and density than gasoline, for instance. So the injection of diesel, in the fuel/air inlet system of the experimental set-up of this work, would result into drops that are too big. Furthermore, the boiling point of diesel is higher than that of the PRF's and TRF's, so that at the same inlet temperature as the PRF's (70 °C), a part of the diesel will not evaporate and will rest in the inlet system, not entering into the cylinder. In order to prevent this, the diesel fuel has to be injected with a higher injection pressure and inlet temperature. A relative injection pressure of 2.5 bar as well as an inlet temperature of 120 °C seemed to improve significantly the physical properties of the injected fuel. The behaviour of the auto-ignition of diesel can be studied numerically. This, however, would request kinetic mechanisms representing dozens and dozens of compounds, which would make kinetic mechanisms too large for the computing time to be realistic. A suitable surrogate that has the same auto-ignition characteristics can be used. Corcione et al. **[30]**, in their study of multiple injections and auto-ignition of diesel sprays in a constant volume vessel, propose a diesel surrogate, composed out of 70 mole% n-heptane and 30 mole% toluene. This composition can, according to them, sufficiently represent the cetane number as well as the other properties of the real diesel fuel. In volumetric units, this corresponds to 76 vol% n-heptane and 24 vol% toluene. The compounds n-heptane and toluene are present in the surrogate mechanism. The n-heptane/toluene mixtures are discussed in the previous subsection. Validating experimentally the diesel surrogate with respect to the diesel fuel, would mean that the results of the diesel surrogate (n-heptane/toluene mixture) can be used to analyze the auto-ignition of the diesel fuel by the surrogate mechanism. This can be done by comparing the auto-ignition delays. Figure 12 presents the cool flame and final ignition delays as a function of the equivalence ratio and the compression ratio for diesel and its surrogate at an inlet temperature of 120 °C. The influence of the compression ratio and the equivalence ratio are merely shown in order to compare diesel and its surrogate over a range of parameters. The interesting point is the relatively low ignition delays, except at equivalence ratios lower than 0.2, where the final ignition delay approaches TDC. This confirms the suggestion that, once the majority of the diesel fuel is evaporated and the drops are fine enough, the auto-ignition is rather easy and a relatively low fuel/air ratio is enough. The results in figure 12 show that the auto-ignition delays of the diesel fuel compare satisfactorily with those of the diesel surrogate. This does not mean that the whole combustion analysis of diesel fuel can be replaced by the mere analysis of its surrogate. This does, however, mean that the surrogate mechanism and all the results in the previous subsections can be used to analyze the global auto-ignition process of the diesel fuel.

4.3 The effect of engine parameters on the auto-ignition process of the PRF’s

Having studied the auto-ignition behaviour of the PRF’s, TRF’s and diesel fuel, it is the aim to investigate the influence of the inlet temperature, equivalence ratio and the compression ratio on the auto-ignition delays of the PRF’s, which should show their suitability for the control of the auto-ignition process in HCCI engines. The qualitative effect should be the same on the other fuels.

To begin with, the effect of the inlet temperature on the auto-ignition process is discussed. Figure 13 shows that a higher inlet temperature decreases the cool flame delay, in the same way as it decreases the final ignition delay. A higher inlet temperature accelerates the overall kinetics and thus makes both the ignition delays advance. The influence of the inlet temperature on the auto-ignition process can be seen in a different manner, showing the ratio of the heat release at the final ignition and the heat release at the cool flame as a function of the inlet temperature. The ratio A_f / A_c represents thus the ratio of the fuel burned at the final ignition and at the cool flame. Figure 14 shows that the “A_f / A_c ratio” remains about constant even for different equivalence ratios and that the inlet temperature does not effect the distribution (over the cool flame and the final ignition) of the consumed fuel. This is important if such a parameter is used for the control of the auto-ignition delay.

The effect on the experimental ignition delay is presented in figure 15. Figure 15 shows that the equivalence ratio seems to decrease both the cool flame delay and the final ignition delay, though more pronouncedly the latter. A higher equivalence ratio adds more fuel to the inlet mixture, thereby increasing the rate of reaction between the hydroxyl radical and the fuel. This leads to more fuel consumption and advancement of the ignition delays. This is confirmed by the heat release. Figure 16 shows the relative total heat release as a function of the equivalence ratio. The relative total heat release is with respect to the total heat release at an equivalence ratio of 0.23. Figure 16 shows indeed that an increasing equivalence ratio increases the total amount of heat release. Figure 15 shows furthermore that it seems that at higher equivalence ratios the influence of the equivalence ratio becomes less for the cool flame. There is another aspect to be taken into account, besides the energy supply by the fuel. More fuel decreases the heat capacity of the mixture. A decreasing heat capacity means an increase of the poly-entropic constant. This means that during the compression, due to the compressional heating, the gas temperature is lower already before the cool flame. The compressional heating is easily overcome when the burn rate of the fuel is high enough. Most of the fuels studied contain enough n-heptane, which has a relatively high burn rate. Therefore most of the fuels show a decreasing tendency of the cool flame on increasing the equivalence ratio. However, beyond a certain equivalence ratio, depending on amongst others the burn rate of the fuel, this is no longer overcome and a further increase of the fuel quantity will delay even the final ignition. Figure 17 illustrates this effect, using the surrogate mechanism. The inlet temperature is 70 °C, the compression ratio is 10.2 and the fuel is n-heptane. At an equivalence ratio around 1.0, it can be seen that the final ignition begins to increase on increasing the equivalence ratio, while the cool flame increases significantly from an equivalence ratio of around 0.4. Before an equivalence ratio of 0.4, the cool flame delay is nearly constant on increasing the equivalence ratio, except between an equivalence ratio of 0.2 and 0.3. The cool flame delay seems to be much more influenced by the compressional heating than the final ignition. The simulation shows also that at an equivalence ratio of around 0.9, it seems that the two-stage combustion turns into a one-stage combustion. This means that the conditions are such that the NTC region does not has the time to be present at equivalence ratios higher than 0.9. The relative sensitivity of the ignition delays and heat release to a small change in the equivalence ratio make this parameter suitable for the control of the auto-ignition, though a compromise should be made with fuel consumption.

The influence of the compression ratio has been studied for two fuels: n-heptane and "60 vol% n-heptane / 40 vol% iso-octane". Figure 18 shows the influence of the compression ratio on the ignition delays for these two fuels at an equivalence ratio of 0.40 and an inlet temperature of 70 °C. From figure 18, it appears that the compression ratio has a large influence on the cool flame delays and on the final ignition delays. The compression ratio seems to have two effects. On one hand, a higher compression ratio increases the concentration of all the species and increases also the peak temperature and the overall reactivity. This causes the ignition delays to advance. On the other hand, another effect of the compression ratio plays an important role: the fraction of the residual gases. The residual gases can have two important effects. The fraction of the residual gas (*f*) is a reciprocal function of the compression ratio (ε), expressed by the following approximation **[21]**:

$$f=\frac{T_{inlet}}{\left(\frac{P_{IVC}r_E}{P_E r_{IVC}}\varepsilon-\frac{C_{p,R}}{C_{p,IVC}}\left(\frac{P_{IVC}}{P_E}\right)^{\left(\frac{\bar{T}-1}{\bar{T}}\right)}\right)T_E+\left(\frac{C_{p,R}}{C_{p,IVC}}-1\right)T_0+T_{inlet}} \qquad (3)$$

This equation results from mass and energy balances made at Inlet Valve Closing (IVC) at the Exhaust (E) and for the Residual gases (R). The residual gas has a higher temperature than the inlet temperature and therefore the overall kinetics are higher than would be the case if no residual gases were present. A higher compression ratio results into a lower residual gas fraction. Therefore the effect of the residual gas temperature is less at higher compression ratios. So, on increasing the compression ratio, the overall reactivity does increase, but more slowly every time the compression ratio increases. This effect can be seen in figure 18, where the ignition delays decrease at a slower rate on increasing the compression ratio. The second effect of the residual gases is its composition. True, at a higher compression ratio, the residual gas fraction is smaller. However, due to the higher compression ratio, the overall concentrations are higher and also those of the residual gas. It could be that the residual gas contains chemically active species, of which the concentration increases at a higher compression ratio. Depending on the competition between this concentration increase and the decrease of the residual gas fraction, these chemically active species can affect the auto-ignition process in a way that might compensate or reinforce the increasing overall reactivity of the auto-ignition. For the control of the auto-ignition, the compression ratio is a suitable parameter that can be used to choose optimal operating conditions.

5 Conclusions

This paper presents an auto-ignition investigation concerning the primary reference fuels, toluene reference fuels and diesel fuel, in order to study the effect of linear alkanes, branched alkanes and aromatics on the auto-ignition. The influence of the addition of respectively iso-octane and toluene to n-heptane on the auto-ignition delays seemed to be similar, though the chemical reasons are quite different. The more difficult H-abstraction for iso-octane delays the cool flame. Iso-octane addition delays the final-ignition, since it extends the NTC-region by its propagation reactions, forming relatively stable olefins and ethers. This decreases the overall reactivity at that moment.

The addition of toluene also plays a role in decreasing the overall reactivity, at the NTC-region of n-heptane (toluene auto-ignition is a one-stage ignition), but by a different set of reactions. The initiation reactions of toluene are inhibitive, since they consume OH radicals, while forming relatively stable species. So less OH radicals are available for n-heptane, disfavoring the cool flame and delaying the final ignition. Both additions of iso-octane and toluene decrease the overall reactivity, while iso-octane seems to favor the NTC region and toluene the opposite. Both additions of iso-octane and toluene delay the final ignition. The total heat releases confirm these findings as well as the results obtained from the surrogate mechanism. It has appeared that the diesel surrogate (and thus the surrogate mechanism) can be used to analyze globally the auto-ignition process of the diesel fuel.

The inlet temperature, the equivalence ratio and the compression ratio were varied and their influence on the auto-ignition process of the PRF40 and n-heptane were analyzed. The inlet temperature was changed from 25 to 70 °C and the equivalence ratio from 0.18 to 0.41, while the compression ratio varied from 6 to 13.5. The influence of the inlet temperature has shown a clear promoting effect on the ignition delays. The heat release distribution did not seem to be affected by the inlet temperature. This could imply that the inlet temperature is a parameter than can be used to influence the auto-ignition process, without altering the energetic content. The influence of the equivalence ratio has shown two distinct effects. One effect is the promoting effect on the ignition delay, due to the higher energy supply. The other effect is the compressional heating due to the increase of the heat capacity of the mixture. These two effects compete with each other and it seemed that as long as the burn rate of the fuel is high enough, the effect of the compressional heating is overcome. The heat release seemed to be affected quite clearly by the equivalence ratio, showing that on increasing the equivalence ratio, the heat release increases as well. Generally speaking, it can be said that the equivalence ratio can be used to decrease the ignition delays at HCCI conditions, having a great influence on the heat release. This makes the equivalence ratio a suitable candidate for the HCCI control. The compression ratio also appears to have two effects. The obvious effect is advancing the ignition delay, due to higher overall reactivity, pressure, temperature and overall concentrations. The other effect is the residual gas fraction. A higher compression ratio results into a lower residual gas fraction and thus a lower thermal effect of the residual gas. This effect seems to slow done the increasing overall reactivity. On increasing the compression ratio, the residual gas can have another indirect effect. The higher compression ratio causes the overall concentrations to increase, including the species that are present in the residual gas, which can interact with the fuel. These findings and observations have provided an overall insight of the auto-ignition process influenced by important engine parameters. Furthermore, the use of the kinetic mechanism has provided deeper insight of the influence of the parameters on the auto-ignition process, which can be used for auto-ignition control purposes.

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Figure captions

Figure 1: The major reaction branches of n-heptane oxidation

Figure 2: The major reaction branches of iso-octane oxidation

Figure 3: The major reaction branches of toluene oxidation **[20]**

Figure 4: Ignition delays as a function of the equivalence ratio and the fuel composition of n-heptane/iso-octane at a compression ratio of 10.2 and an inlet temperature of 70 °C

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Figure 10: Relative total heat release (with respect to the total heat release for n-heptane) at an equivalence ratio of 0.41 and 0.29, a compression ratio of 10.2 and an inlet temperature of 70 °C, varying the fuel composition of both n-heptane/iso-octane and n-heptane/toluene mixtures

Figure 11: Heat release ratio of the final ignition (A_f) and the cool flame (A_c) at an equivalence ratio of 0.41 and 0.29, a compression ratio of 10.2 and an inlet temperature of 70 °C, varying the fuel composition of both n-heptane/iso-octane and n-heptane/toluene mixtures

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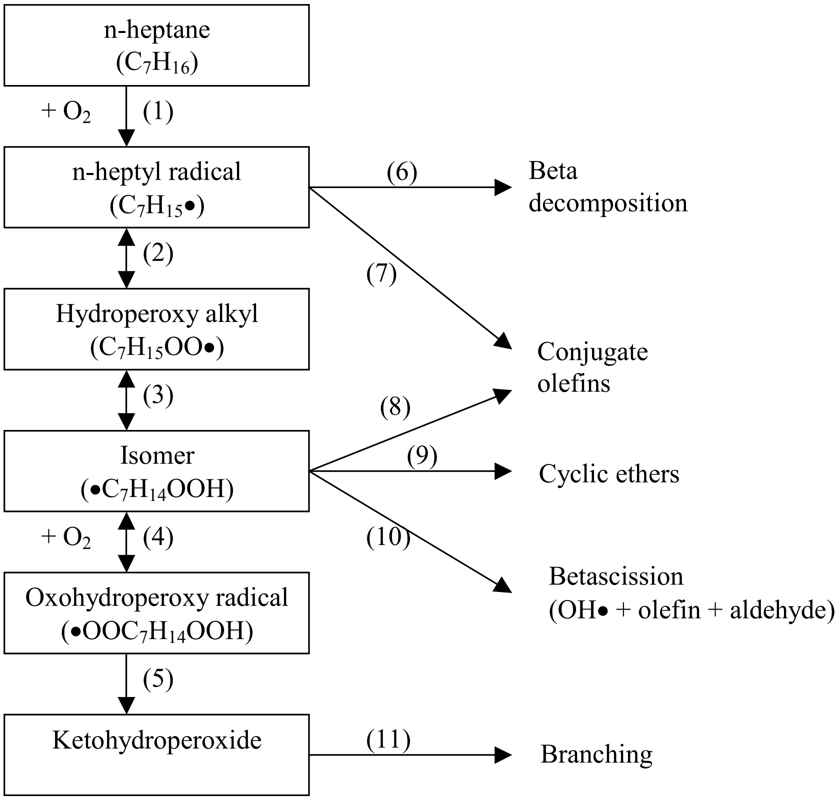
Figure 18: Influence compression ratio on the ignition delays at an inlet temperature of 70 °C, an equivalence ratio of 0.40 comparing the fuels n-heptane and PRF40

Figures



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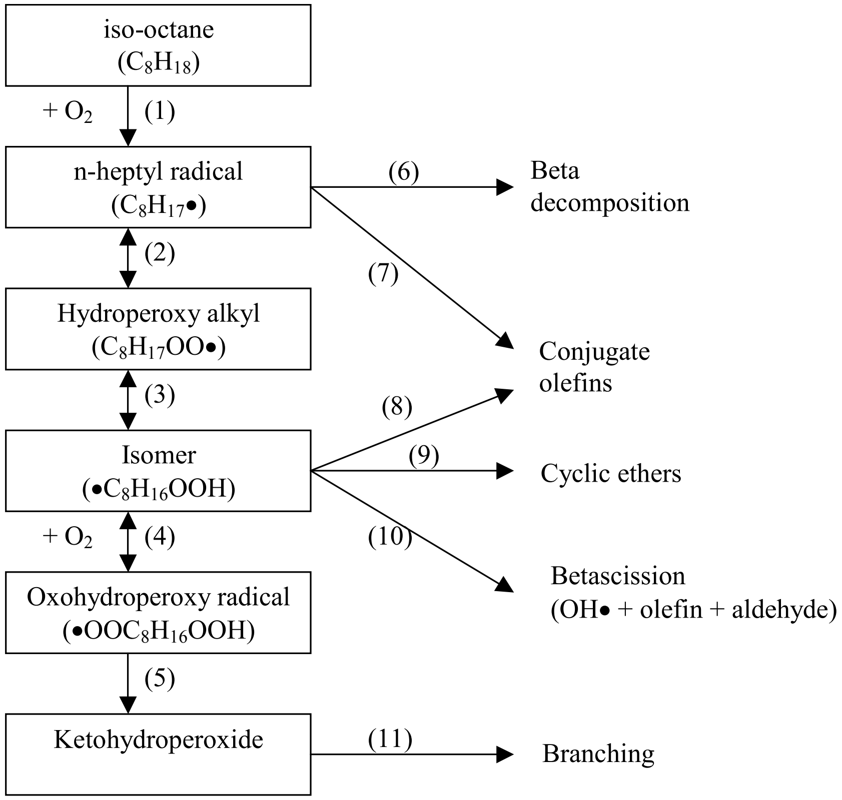
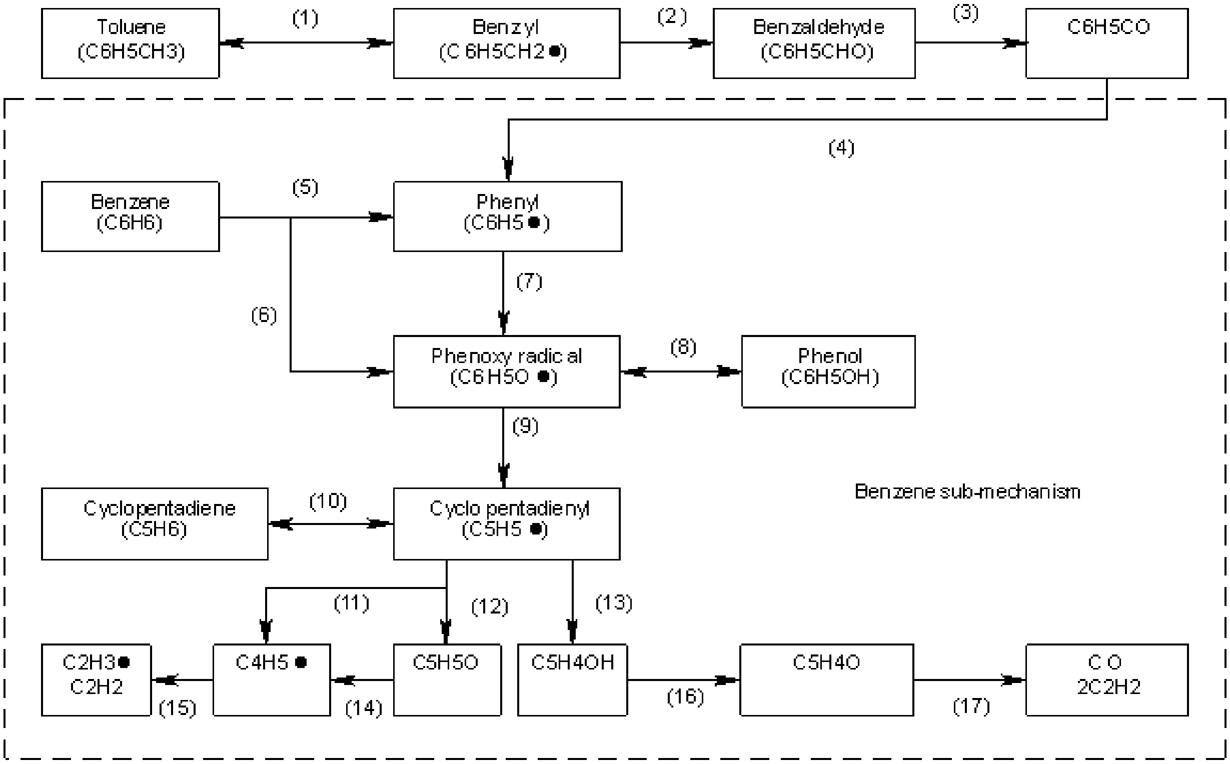


Figure 2: The major reaction branches of iso-octane oxidation



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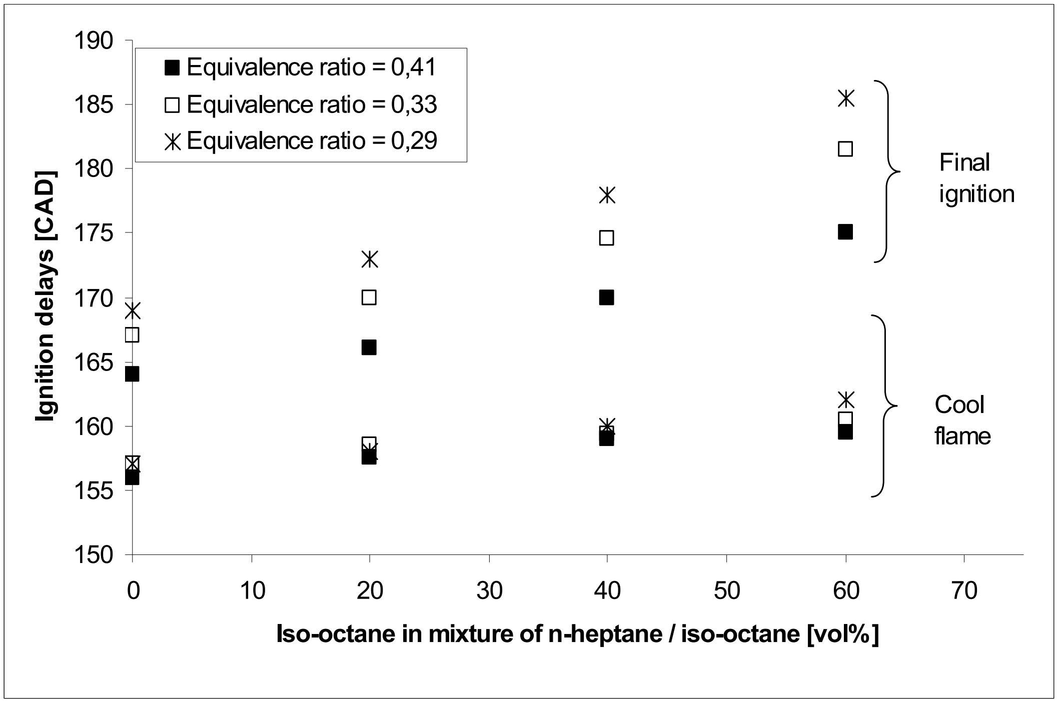

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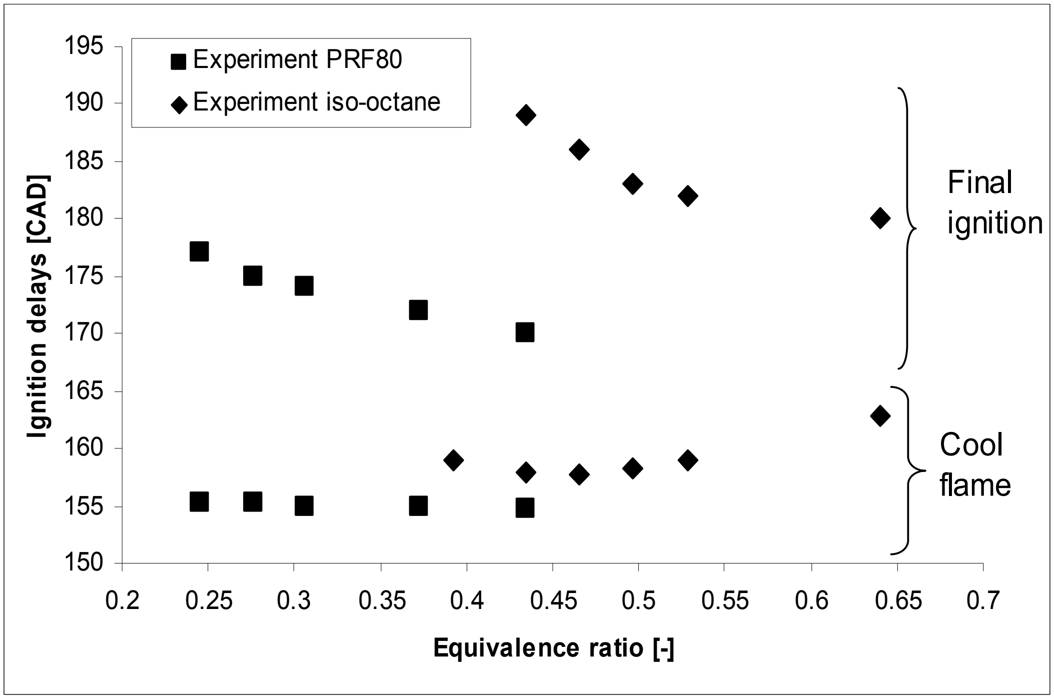

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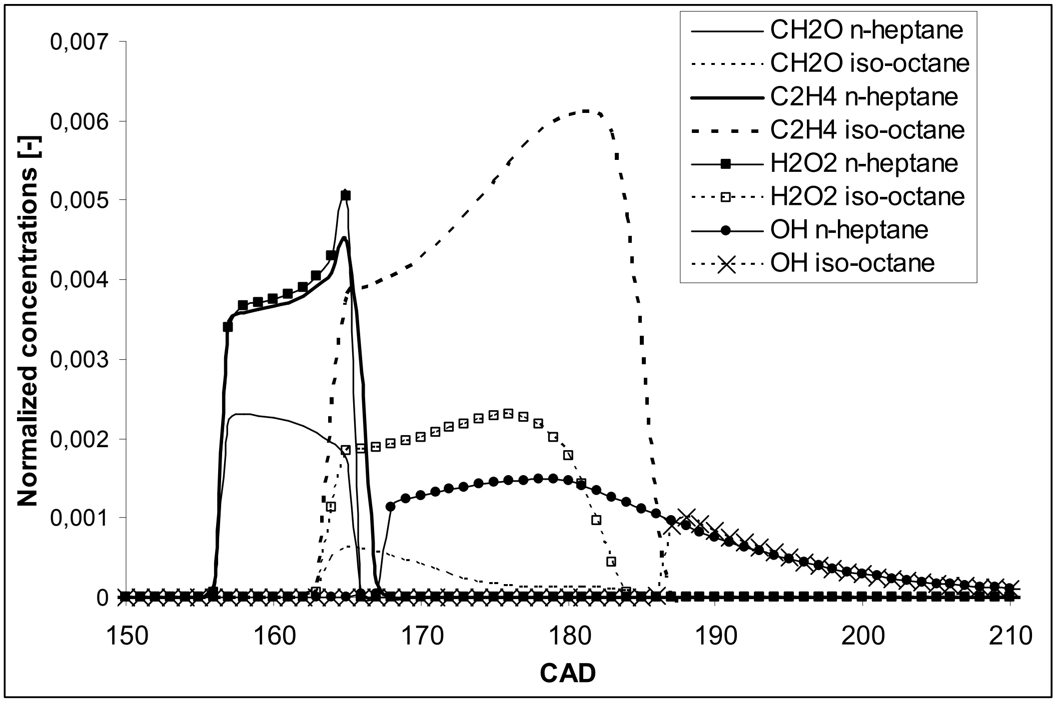

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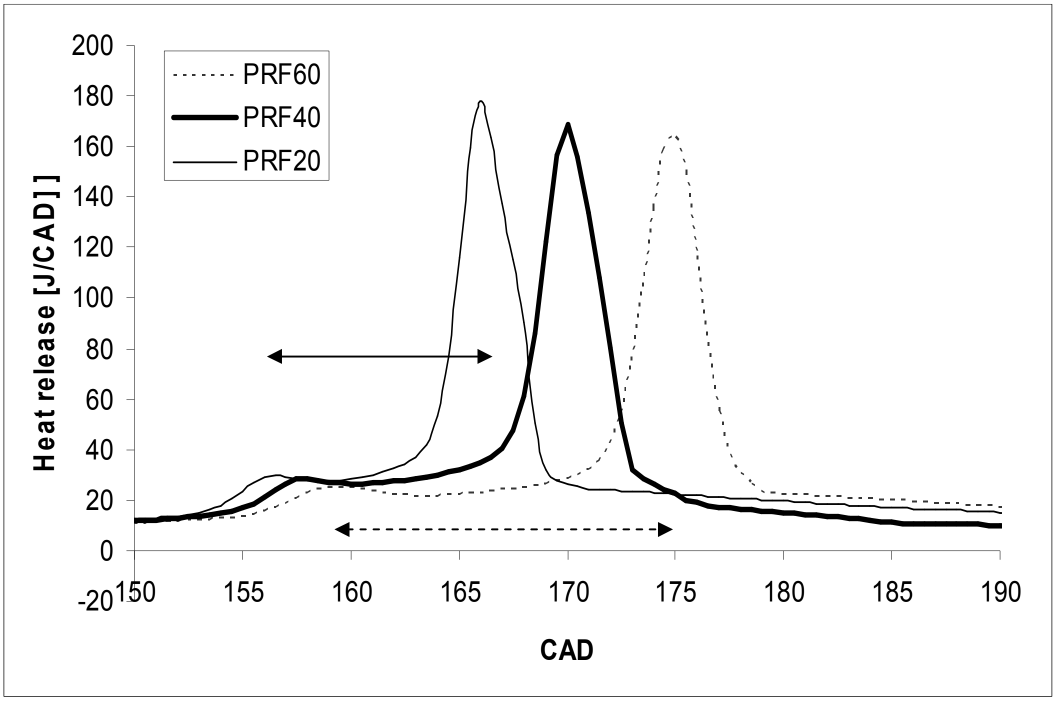

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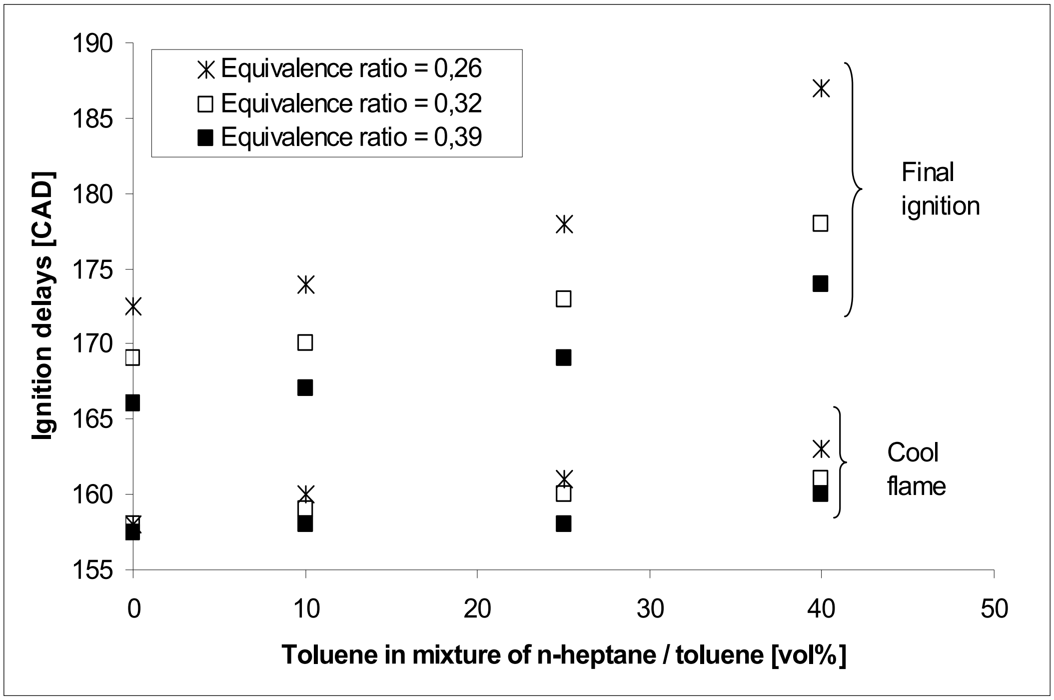

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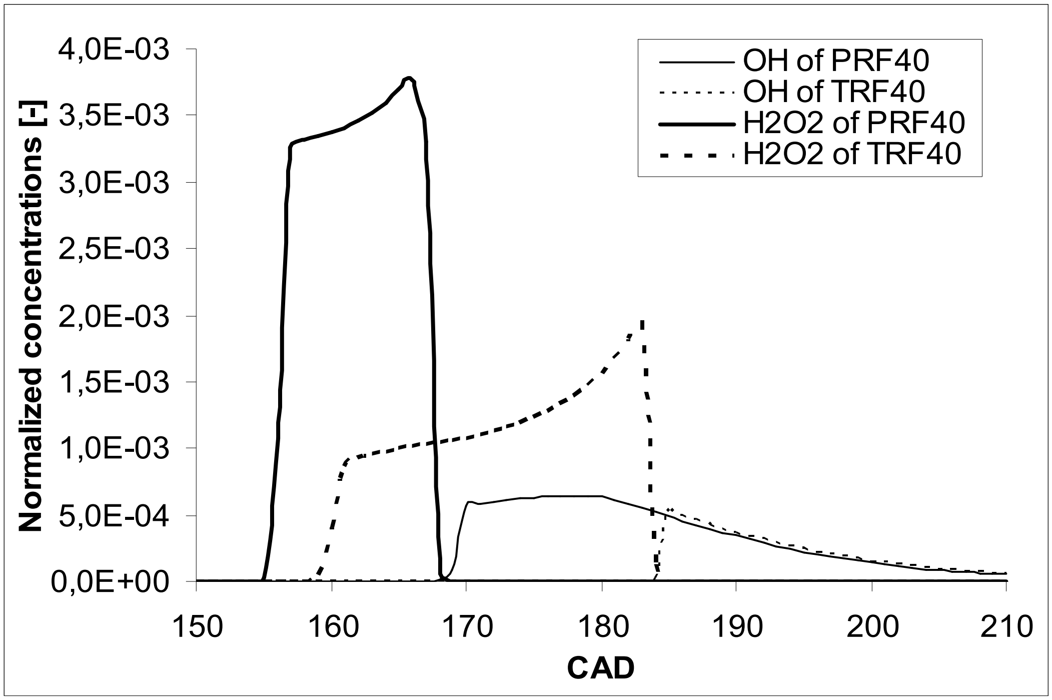

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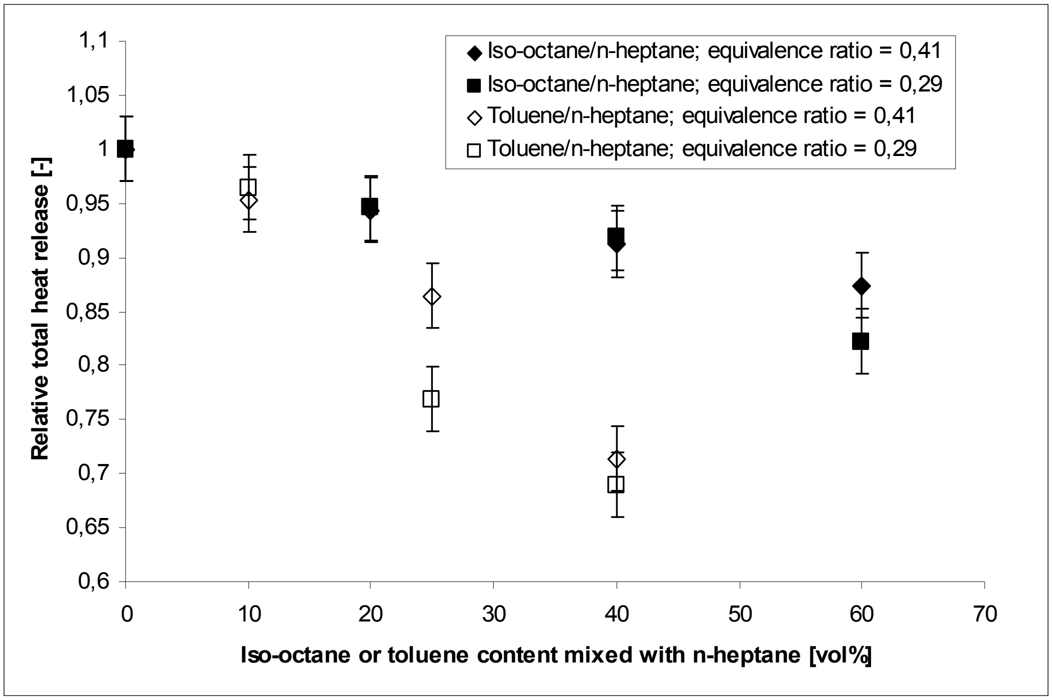

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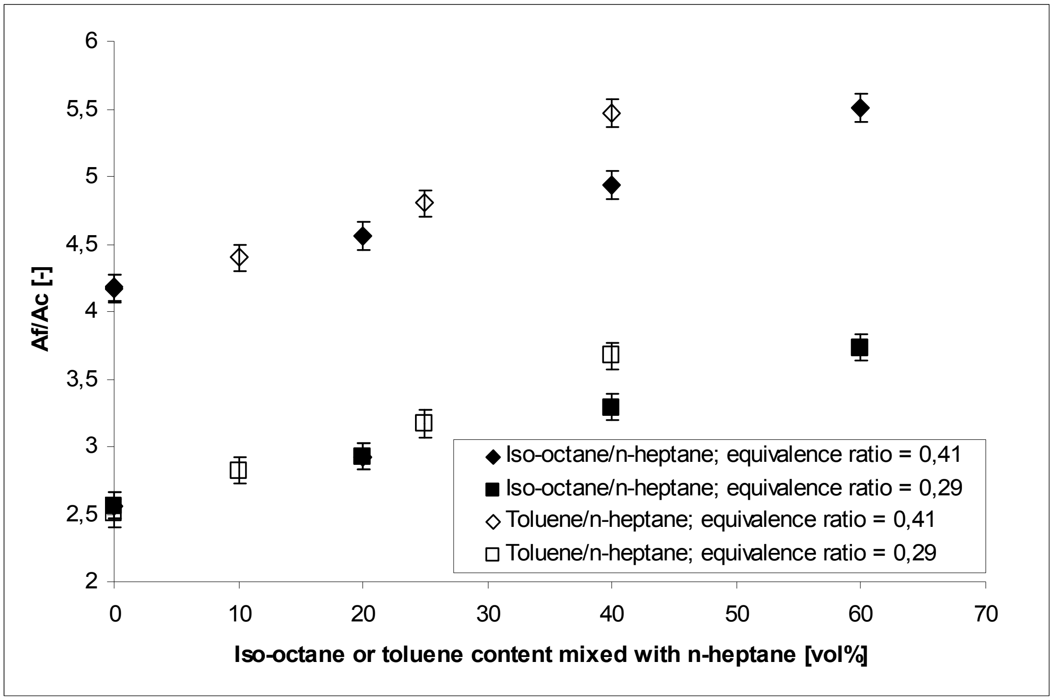

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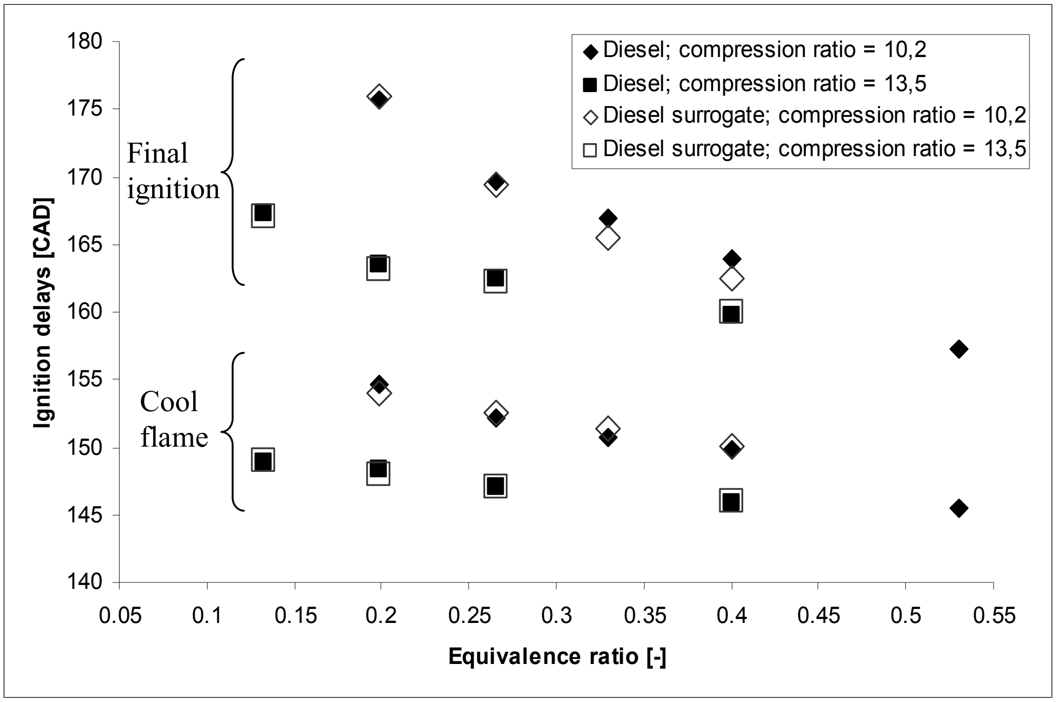

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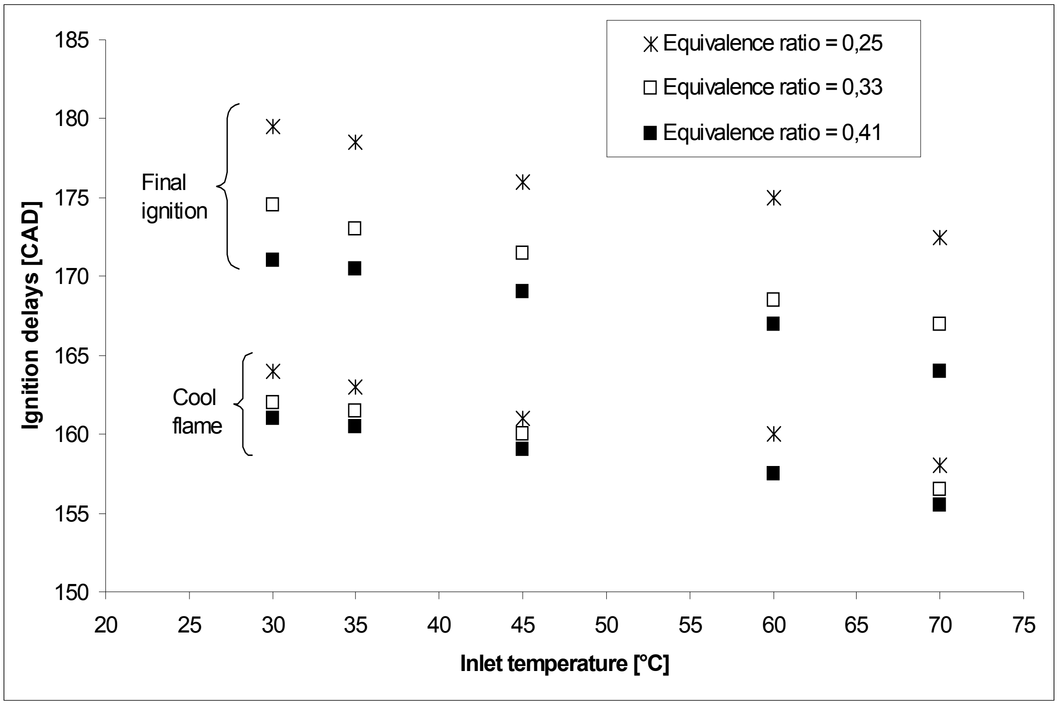

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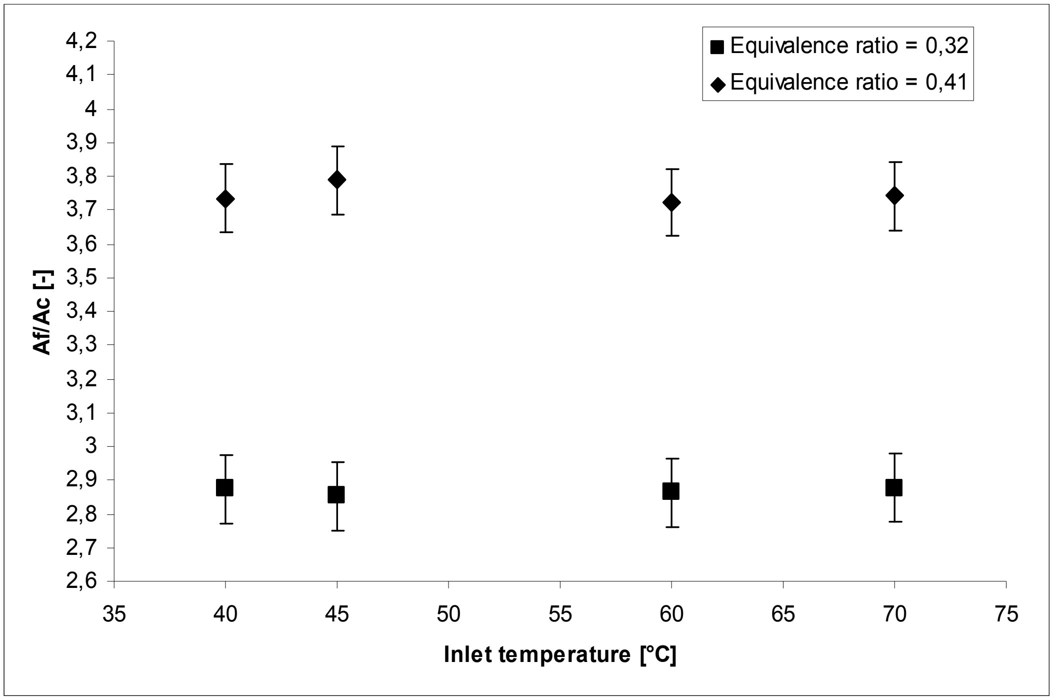

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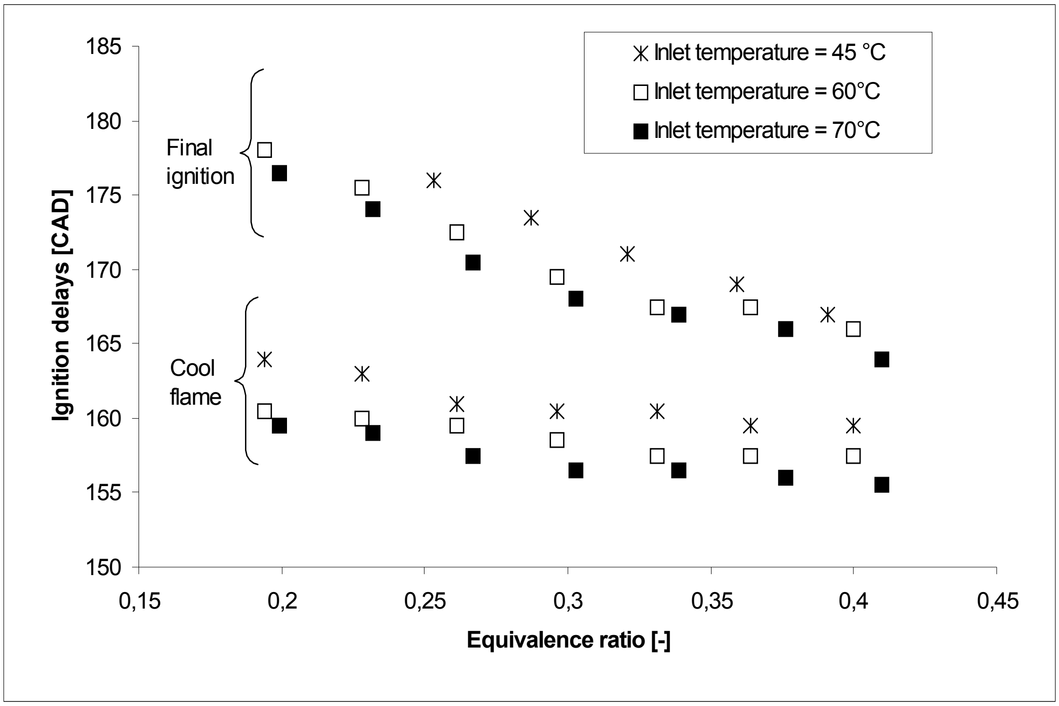

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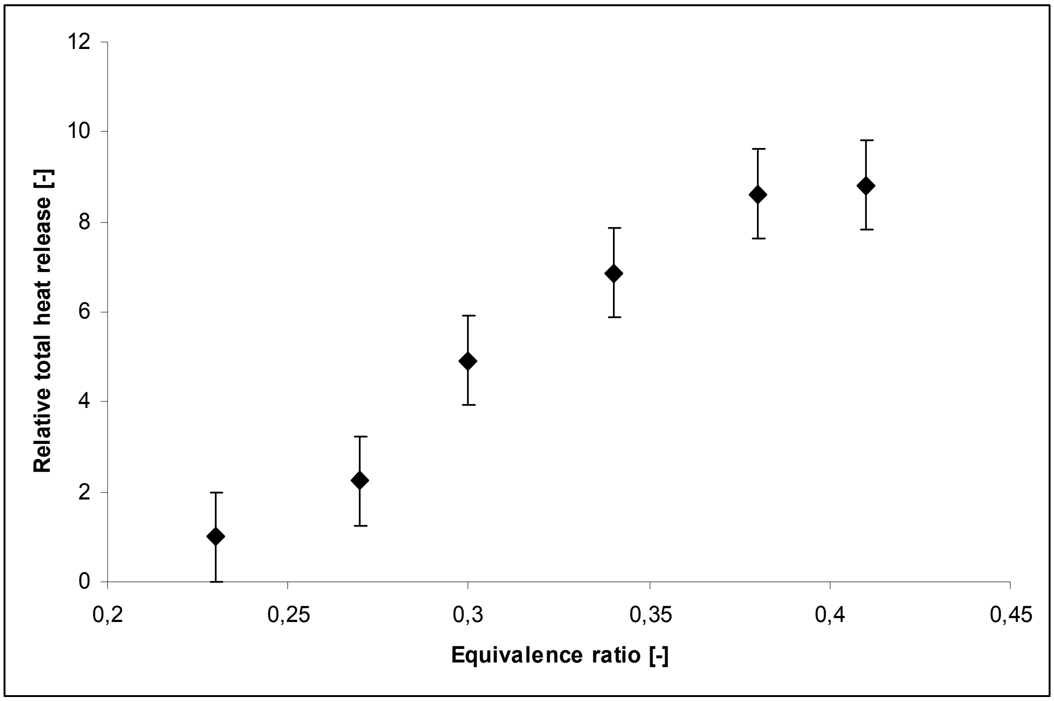

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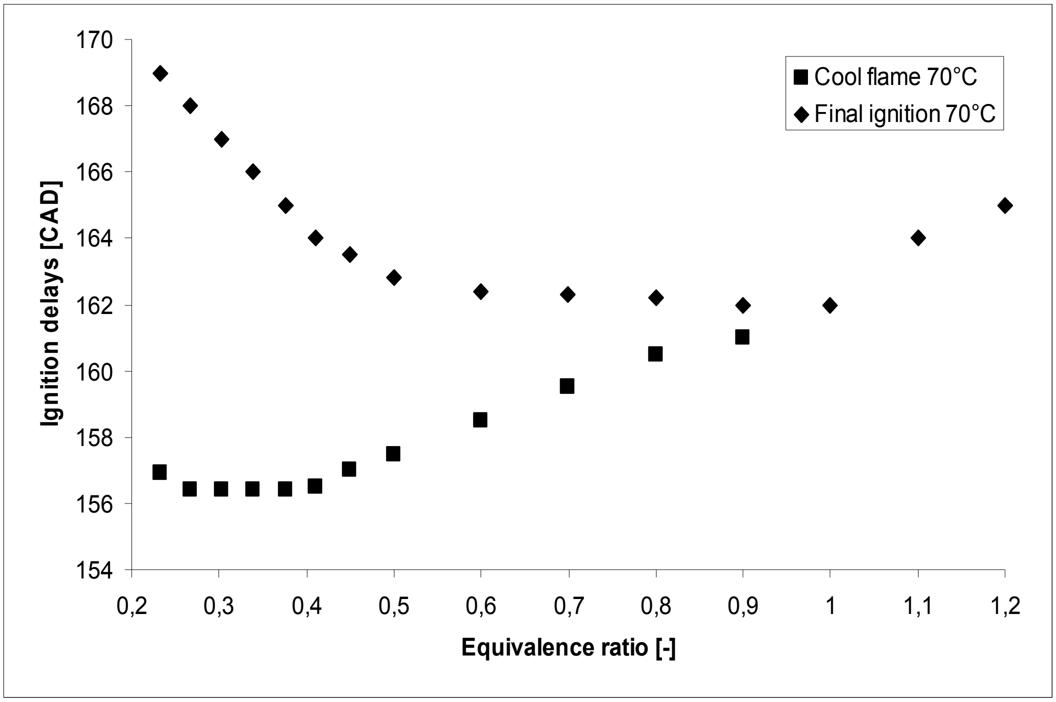

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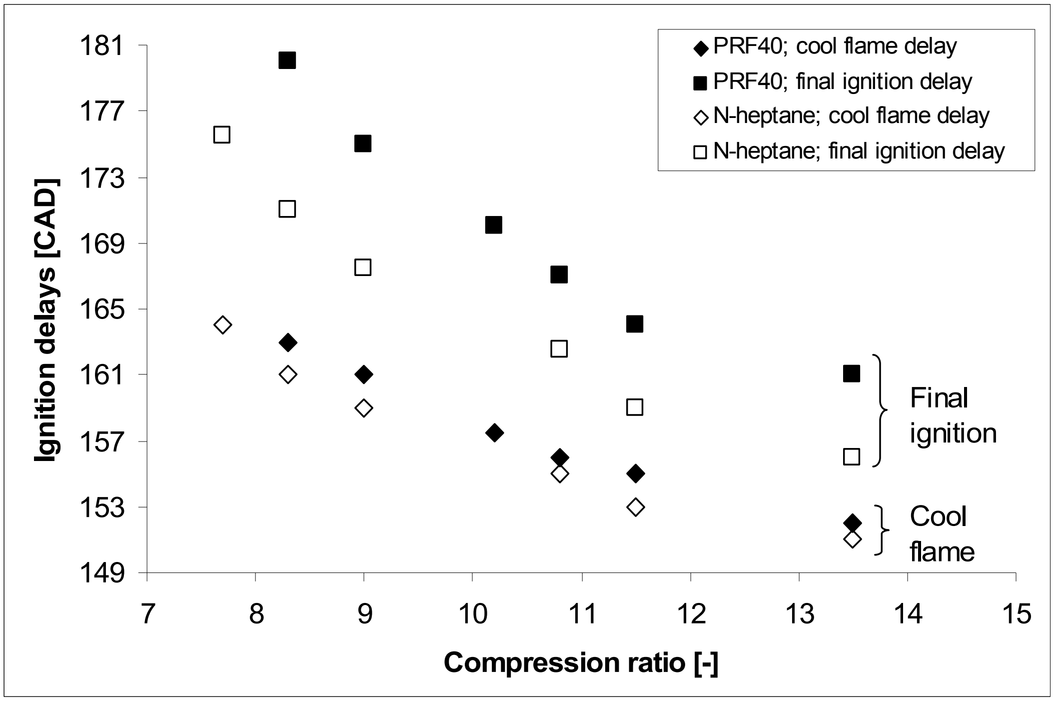

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Table

Table 1: CFR engine characteristics

Compression ratio	4 ~14
Bore	82.55 mm
Stroke	114.5 mm
Displacement volume	611 cm3
Engine connecting rod to crank radius ratio	4.44
Exhaust valve open	140 °ATDC
Exhaust valve close	15 °ATDC
Intake valve open	10 °ATDC
Intake valve close	146 °BTDC

Table 2: The fuels that are used for the auto-ignition in the HCCI engine

Fuel	N-heptane [vol%]	Iso-octane [vol%]	Toluene [vol%]
PRF's	0-20-40-60-80-100	100-80-60-40-20-0	0
TRF's	60-75-90-100	0	40-25-10-0
Diesel fuel	**Commercial diesel fuel**		