HCCI engine modeling and experimental investigations – Part 1: The reduction, composition and validation of a n-heptane/iso-octane mechanism

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Abstract

A certain possible approach for the control of HCCI chemistry is to use kinetic chemistry mechanisms. This opens a field of interest that lead to the composition of a validated reduced PRF chemistry mechanism. For this purpose a skeletal chemical reaction mechanism for n-heptane and for iso-octane are constructed from a detailed n-heptane and iso-octane mechanism of the Chalmers University of Technology. Subsequently these two mechanisms are forged into one reduced chemical reaction mechanism for mixtures of n-heptane and iso-octane (39 species and 47 reactions). This mechanism is numerically validated against the Chalmers mechanisms, respecting the HCCI application range. The reduced mechanism is also successfully numerically validated against another more detailed mechanism provided by LLNL. Engine experiments are performed validating this mixture mechanism with respect to the fuel composition containing n-heptane and iso-octane. The influence of the compression ratio and the equivalence ratio is also studied and used to validate the reduced PRF mechanism.

Keywords: HCCI engine application, auto ignition control, reduced mechanism kinetics, numerical and experimental validation, influence of fuel composition

Short version of the title: A reduced validated PRF mechanism for HCCI engine applications

1 Introduction

Environmental effects and strategy of the automobile industry implies developing new engines functioning with a low equivalence ratio, lower fuel consumption and consequently reducing CO_2 emission. A promising alternative to combustion in SI and Diesel engines is the Homogeneous Charge Compression Ignition (HCCI) process. The HCCI engine generally runs on a lean, diluted mixture of fuel, air and combustion products, which is not ignited by a spark but by compression auto-ignition instead. The temperature of the charge at the beginning of the compression stroke has to be increased to reach auto-ignition conditions. Due to the nature of HCCI, a fundamental control challenge exists. Concerning the emission reduction during the combustion process, HCCI appears to be a rather good solution to respect the future emission norms. Using an HCCI combustion allows for a higher thermal efficiency, less NOx emissions and less particulate-matter emissions (Huang et al., 2004) than conventional SI and Diesel engines. Whereas diesel combustion is mainly controlled by turbulence during flame diffusion and gasoline combustion with a flame front propagation, the auto-ignition phenomenon in an HCCI engine is mainly controlled by chemical kinetics. The turbulence mainly influences the level of homogeneity (thermal and concentration) during the mixture process and the end of the combustion. Much research (Curran et al., 2002, Tanaka et al., 2003a, Tanaka et al. 2003b and Griffiths et al., 2002) is performed in investigating auto-ignition for different chemical compounds, experimentally as well as numerically. A great part of the HCCI investigations use the so-called Primary Reference Fuels such as iso-octane and n-heptane (Bikas and Peters, 2001). These two compounds are the basic elementary compounds for a more complex mixture which will represent actual fuels or an advanced HCCI fuel. Kinetic models of low dimensionality allow for quick parametrical analyses to investigate the control of HCCI combustion numerically and extend conclusions

of experimental approach. Another objective of reduced chemistry modelling is to be implemented in multi-dimensional models in order to reduce computing time. The reduction of the mechanism gives a smaller kinetic mechanism that needs less CPU time to give an outcome. The reduced PRF mechanism showed a mean CPU time of 5 seconds. These 5 seconds are relatively long for a real application in an engine, but not far from the desired response time (the CPU time does not take minutes), which is expected to be about 20 times shorter. A stronger processor can easily overcome this delay, though. Such a mechanism can be used for real-time on-board calculation for the control of the auto-ignition of in a real engine. On demand of a certain acceleration the on-board computer can then alter the initial conditions, using the reduced mechanism, to respond to that demand. So, this could be one of the means to control the HCCI combustion process. The main purpose of this paper is to propose a reduced chemical kinetic reaction scheme of mixtures of n-heptane and iso-octane that can be used for the control of HCCI combustion at low inlet temperatures. Numerical and experimental investigations, using respectively Chemkin and a Cooperative Fuel Research (CFR) engine, are presented under various initial conditions, (equivalence fuel air ratio, fuel composition, initial temperature, compression ratio), which have an impact on the combustion process, accelerating or inhibiting the oxidation of the mixture.

2 HCCI chemistry overview

The HCCI chemistry process generally follows three different steps in a two-stage ignition (Curran et al., 2002, Tanaka et al., 2003a, Tanaka et al. 2003b and Glassman, 1996). An induction period after the end of the intake stroke which ends into the propagation of a cool flame (first stage heat release and delay), a period of decreasing reactivity and the main combustion with the hot ignition (second stage heat release and delay). The values of the two delays depend on the nature of the fuel and initial thermodynamic conditions of the mixture as

well as the equivalence ratio. Between the cool flame and the final flame, a specific domain is characterised as the "negative temperature coefficient" (NTC) region, where increasing temperature at constant pressure decreases the reaction rate. This can also be described as a passage from branching to non-branching mode. Therefore it is important to have an insight into the chemistry of the HCCI combustion. For this purpose the chemical mechanism of n-heptane will be discussed. The chemical mechanism of iso-octane and the n-heptane/iso-octane mixture is globally similar. The main difference lies in the distribution of the mass flows through the different reaction branches. The distribution of the products formed changes accordingly. For n-heptane at low temperatures, the most important reactions in this domain are C7H16 + O2 → C7H15• + HO2• and C7H16 + X• → C7H15• + XH. Owing to its high endothermicity, this initiation reaction is not an important way to the formation of the n-heptyl radical C7H15•. Once the reaction system has created other radicals (X•), such as OH•, O• and H•, hydrogen abstraction by such radicals is favoured more than the abstraction by molecular oxygen (Glassman, 1996). The hydroxyl radical OH• has a higher rate of attack. After the H-abstraction step, the heptyl radical can react further with molecular oxygen to form an alkylperoxy radical: C7H15• + O2 → C7H15OO•. According to Curran et al. (1998), this is the most important reaction for low-temperature oxidation. Furthermore, they state that the equilibrium constant of this reaction is very strongly temperature dependent: at higher temperatures the equilibrium of the reaction begins to shift towards dissociation, thereby indicating the switch from low- to high-temperature chemistry, via the intermediate-temperature chemistry. This reaction path continues then with an isomerization step, in which a hydroperoxy alkyl radical is formed from the alkylperoxy radical: C7H15OO• → •C7H14OOH. When a second oxygen molecule is added to the product of the isomerization step, the following reaction occurs: •C7H14OOH + O2 → •OOC7H14OOH. The hydroperoxy-alkylperoxy radical •OOC7H14OOH can then isomerize further and decompose

into a relatively stable ketohydroperoxide species and OH•. The low-temperature reactions are exothermic and can raise the system temperature by hundreds of degrees (the cool flame) (Glassman, 1996). For the intermediate-temperature range, no significant amount of heat is released and the reactions describe the conversion of •C7H14OOH radicals into conjugate olefins, cyclic ethers and beta-scission products, instead of ketohydroperoxides, formed at low temperatures (Curran et al. 1998 and Ranzi et al., 1995a). An example is •C7H14OOH → C7H14 + HO2•. This reaction is responsible for a large part of the NTC behavior (Curran et al., 1998), where the system reactivity decreases with a rising temperature. The low-temperature chain branching reactions are replaced by propagation reactions at intermediate temperatures, which do not lead to increasing numbers of reactive radicals. HO_2• can be formed by the following reaction leading to the formation of H2O2 (Curran et al., 1998), which is at this temperature-interval a relatively stable product, lowering the overall reactivity: H• + O2 + M → HO2• + M and Alkane + HO2• → Alkyl radical + H2O2. When the temperature becomes higher than the intermediate-temperature range, the high-temperature interval is reached. At high enough temperatures (higher than approximately 1000 K), the conversion reactions of heptyl radicals to beta decomposition products and conjugate olefins take place: C7H15• + O2 → C7H14 + HO2•. If the temperature rises above 1200 K, the relatively high activation energy of the reaction H• + O2 → O• + OH• is overcome and it becomes the dominant chain branching step (Curran et al., 1998 and Ranzi et al. 1995b); the reactants, including one radical, lead to two product radicals. Another important high-temperature reaction is the decomposition of H2O2 into two hydroxyl radicals. This chain branching reaction takes place at around 1000 K and it characterises the moment of ignition: H2O2 + M → OH• + OH• + M. The resulting OH• radicals rapidly consume any fuel, and a rapid increase in temperature follows.

3 Chemical kinetic mechanisms reduction

This section describes the reduction methodology of the iso-octane/n-heptane mixture mechanism. This is obtained from the union of the reduction of the detailed iso-octane and n-heptane mechanisms, containing respectively 412 reactions and 84 species and 290 reactions and 57 species, provided by the Chalmers University of Technology in Sweden. These mechanisms have previously been validated successfully in a shock tube between 600 and 1000 K and between 15 and 35 bar and subsequently successfully applied to HCCI modeling (Ogink and Golovitchev, 2001). Both a numerical and an experimental validation of this obtained reaction mechanism will be discussed. For the simulations an Aurora application is used, provided in the Chemkin code. The reduction of the Chalmers mechanism is obtained by eliminating reactions in a manner to keep the same predictability as the initial Chalmers mechanism (the obtained model must be accurate and only 2 % fluctuations on the pressure curves is allowed). The reduction is performed using a method developed by Peters (Banerjee and Ierapetritou, 2003), which comprises several steps (Soyhan et al, 2002). Firstly, using the analysis of the conversion rate of the reactant species, the redundant species were removed (Lu et al., 2001) from the Chalmers mechanisms. Secondly, by introducing the quasi-steady-state assumption (Banerjee and Ierapetritou, 2003) and, thirdly, the partial equilibrium assumption. The quasi-steady-state assumption is a classical hypothesis in the domain of combustion chemistry. It consists of assuming an equilibrium between the production and consumption of certain intermediary species that are very reactive (Lu et al., 2001) (on calculating the rate constants), with a short lifetime (Lovas et al., 2000) and in small quantities (due to the high reactivity). This approach proved to be successful for the construction of reduced chemical kinetic schemes (Banerjee and Ierapetritou, 2003, Lu et al., 2001 and Lovas et al., 2000) for the combustion of several hydrocarbons (Soyhan et al, 2002 and Simon et al., 1996). The separate mechanisms were further reduced obtaining the skeletal

mechanism of 29 reactions and 27 species for iso-octane and 21 reactions and 27 species for the n-heptane mechanism, which were both validated experimentally in previous work (Machrafi et al., 2005a and Machrafi et al., 2005b). On preserving the overall global reaction paths, for low-temperature hydrocarbon chemistry, the mechanism is further reduced. The difference between the aforementioned reduction steps is that only the most important reactions that govern the temperature and pressure profiles at low-inlet-temperature chemistry are kept (the reactions that prescribe, for instance, H-abstraction, peroxide formation, peroxide isomerization and decomposition, formation of formaldehyde, H_2O_2, OH, CO, CO_2, H_2O describing well the cool flame and the NTC-region). This means that the reactions of n-heptane and/or iso-octane decomposition that take mainly place at higher inlet temperatures are neglected, reducing considerably the mechanisms. The obtained mechanisms are thus oriented to low-inlet-temperature chemistry, preserving the intermediate- and high-temperature chemistry that takes place afterwards. After the reduction of these mechanisms, the two mechanisms were merged into one mechanism for mixtures of iso-octane and n-heptane, resulting into a mechanism for mixtures of iso-octane and n-heptane with 47 reactions and 39 species, after reducing double reactions. This mechanism is presented in table 1, regrouping the reactions following the "chronological" reaction pathways. The reactions presented in this mechanism do not represent, naturally, all the reactions that govern a n-heptane/iso-octane combustion. The reduction is obtained so that the temperature, pressure, heat release and energy profiles give the same results as the detailed ones. So, this reduced mechanism is intended to be used for HCCI engine applications and not for detailed species analysis, of which the applicability is not excluded, since it has not been studied yet. Furthermore for reduction purposes some reactions that take normally place in several reactions are grouped in one reactions with one set of Arrhenius parameters, equal the one of the slowest reactions. This is one of the principles of the Quasi-Steady-State-Approximation.

Reaction 10 is an example thereof, which summarizes the H-abstraction of iso-octane by oxygen and an oxygen addition of the octyl radical. This summary does not represent the real elementary reactions that take place, but represent rather a shortcut, preserving the same energetic effect on the auto-ignition. The same is the case for reaction 13, representing a shortcut for H-abstraction by HO_2, followed by decomposition of an octene into a hexyl radical and a ethenyl radical. Reactions 1 to 9 represent the reactions concerning the initial reactions of n-heptane alone, while 10 to 23 represent those of iso-octane. These reactions take primarily place at the lower temperature zone and cause the cool flame to occur. Reactions 24 to 36 represent the reactions at the intermediate temperature zone, leading to the so-called NTC. Reactions 37 to 43 represent the reactions (along with the fuel consumption reactions 2 and 11) that take place at the high temperature zone, causing the final ignition to occur. Reactions 44 to 47 represent the reactions that take place after the final ignition around the peak temperature. The reaction pathways are explained in section 2.

4 Modelling validation results

The numerical validation of the reduced mechanism is performed using Chemkin. The parameters that will be investigated are the inlet temperature, the equivalence ratio, the compression ratio and the fuel composition. To check the validity of the reduced mechanisms, besides a comparison to the Chalmers mechanism from which they were reduced, these are also compared to the more detailed and already validated mechanisms (3606 reactions and 857 species for iso-octane and 2539 reactions and 561 species for n-heptane), provided by LLNL (Curran et al., 2002 and Curran et al., 1998). To compare the mixture mechanism to the pure detailed n-heptane mechanisms, the mole fraction of iso-octane was set to zero and to compare the mixture mechanism to the pure detailed iso-octane mechanism, the mole fraction of n-heptane was set to zero. For readability purposes, the mechanism from the Chalmers

University will be called ‘Chalmers’, the mechanism from the LLNL ‘LLNL’, and the obtained reduced mechanism for mixtures of iso-octane and n-heptane will be called ‘Mixture’.

Figure 1 shows that the Chalmers, the LLNL and the Mixture mechanisms results are in good agreement in terms of ignition delays. The calculation of the ignition delay from modelling experiments is based on a thermodynamic model. This model is based on a simple zero dimensional model in which the cylinder was modelled as a closed system with no mass loss via blowby and with initial mass comparable with the one given in experimental conditions. The calculations were performed, using Chemkin. This model was adapted to calculate heat release from calculated and measured pressure data, including auto ignition periods. The ignition delay values given in this paper are referenced to the zero crank angle which is the bottom dead centre preceding the compression stroke. The cool flame delay is defined as the time in CAD between BDC and the first maximum of the heat release, while the final ignition delay is defined as the time in CAD between BDC and the second maximum. The similarity is obtained for a wide range of the parameters. The aim of the results in figure 2 is to verify the ability of the mixture model to reproduce the comparable results when only one fuel is considered. The comparison with the Chalmers, the LLNL and the Mixture mechanisms show a slight discrepancy more visible by the heat release curve. This discrepancy could be caused by the large elimination of several reactions that have their proper heat releases, though each one of them negligible. However, all of these eliminated heat releases sum up to cause the discrepancy, though small, as figure 2 shows. In summary, the calculations show clearly that the composed reduced mixture (for n-heptane and iso-octane) mechanism is quite well numerically validated, with respect to the cool flame delays, the final ignition delays, the pressure and the heat release.

5 Experimental validation of the reduced mixture mechanism with respect to the fuel

The goal in this section is the experimental validation of the mixture mechanism. The mono-cylinder CFR engine (Table 2), chosen for the validation, presents many advantages. The global air/fuel equivalence ratio is well controlled. To ensure a homogeneous mixture, the intake was provided with a 3-D twisted admission pipe, realizing a relatively good homogeneous mixture of the fuel and the air. This also is requested to validate the mechanism, since the internal combustion engine module in Chemkin assumes a perfectly homogeneous charged inlet mixture. This admission pipe can be heated to about 120 °C. At the entrance of the admission pipe a small tank the fuel enters with the air. The air is regulated by a flow meter and can be held at a certain desired temperature going also up to 120 °C. The fuel flow is regulated by an HPLC pump and injected into the mixing tank by a nebulizer. The CFR engine runs at two rotation speeds (600 and 900 rpm). The compression ratio can be varied in the range of 4-16. The fuel used for this study is the PRF fuel for gasoline. The effects of the residual gas in the CFR engine were compensated in the calculations by adding a mixture of N_2, CO_2 and O_2 and H_2O at a temperature in a range of 800-1000 K depending on the experimental conditions. A zero dimensional model was used to take into account the residual gas properties: mass, temperature, composition. The reference point for all of the measurements is inlet valve closing (IVC) where the in-cylinder composition and conditions can be determined. Combining the measured intake manifold flows and conditions with the known residual fraction allows IVC conditions to be calculated. Beyond the IVC point, the mean gas temperature T and the pressure P were calculated using the engine geometry (Table 2). Then P and T were used to calculate the internal energy. The heat transfer coefficient accounting for heat loss was set to match the temperature profile during the early stage of compression where no apparent heat release occurred, using the Woschni correlation. With

assumptions made above and engine calibration data, the heat release is calculated according to the first law of thermodynamics. In HCCI mode, the heat release has a characteristic shape with two maximums representing the ignition delays, demonstrating the ability of this mechanism to model HCCI combustion. This model is then calibrated once (the same model is afterwards used for every calculation without altering it) using several experiments (at several initial conditions), measuring for each experiment the pressure and temperature at IVC and at the exhaust as well as the mass flow into the cylinder. The model gives then as output the quantity and temperature (error of +/- 10 °C) of the residual gas. Using the heat capacities, quantity and temperature of respectively the residual gas and the inlet mixture, the temperature at initial conditions can then be calculated, with an error of +/- 2 °C. The composition of the residual gas results from exhaust gas analysis. The comparison of the calculated ignition delays obtained by Chemkin (designated by Chemkin modelling) and the ones obtained from the CFR experiments (designated by CFR experimental) is shown in figure 3. The ignition delays were obtained by calculating maximums of the heat release rate. The ignition delays showed an error of +/- 0,2 CAD, the equivalence ratios +/- 0,005, the compression ratio +/- 0,2 and the fuel composition +/- 0,1 vol%. The pressure curves are a mean of 50 cycles with a dispersion of 1 bar at the maximum pressure. The pressure is obtained by a pressure sensor inserted into the head of the cylinder. The pressure is subsequently post treated, using the First Law of Thermodynamics with an energy balance, obtaining a law of heat release, which depends on the ratio of the specific heats, the volume and its derivative and the pressure and its derivative. The cool flame delay is then defined as the number of crank angle degrees from BDC to the first maximum of the heat release, while the final ignition is defined as the number of crank angle degrees from BDC to the second maximum of the heat release. Figure 3 shows that the mechanism predicts well the cool flame delays and the final ignition delays at different equivalence ratios (better at higher equivalence

ratios) and fuel compositions of n-heptane and iso-octane. The observed trend that the ignition delay decreases when increasing the equivalence ratio or decreasing the octane number (of a mixture containing n-heptane and iso-octane) seems to be in good agreement with the literature (Battin-Leclerc et al., 2000, Glaude et al., 1998 and Dagaut et al., 1994). A higher equivalence ratio means more fuel added to the system, resulting into more fuel to burn, more energy released at the first stage, advancing the ignition delay. However, the ratio of the specific heats decreases, decreasing the compressional heating. This effect is, however, negligible in this case, since this effect is overcome by n-heptane. The sum of secondary and tertiary H atoms is much lower in the case of iso-octane than it is for n-heptane. So the H-abstractions and isomerization reactions are less likely to occur, favoring the propagation sequence through alkyl peroxy radicals, hydroperoxy alkyl radicals and cyclic ethers and the existence of the cool flame and a longer NTC, retarding the final ignition. Figures 4 and 5 both show that the mechanism predicts well the pressure and the heat release at different fuel compositions of n-heptane and iso-octane. The slight discrepancy that is observed could be caused by the error in the temperature of the residual gas calculated by the heat transfer model. The second point is the difficulty to calibrate the experimental heat transfer model.

6 Experimental validation of the mixture mechanism for high octane fuels

As shown in the previous section, the fuel composition has a strong influence on the auto-ignition delays. A higher iso-octane content increased the ignition delays. This was shown in figure 3. The explanation was provided in the previous section. The compression ratio that is used for the previous study is 10,2. At these conditions iso-octane as the fuel could not be studied, nor could the fuel “20 vol% n-heptane / 80 vol% iso-octane” (PRF80). For this purpose another compression ratio should be chosen. Figure 6 shows the ignition delays for the fuel PRF80 at a equivalence ratio of 0,4 as a function of the compression ratio obtained

from the experimental results. This figure shows that no combustion takes place before a compression ratio of 10,8 at an equivalence ratio of 0,4, an inlet temperature of 70 °C for the PRF80 as the fuel. At these conditions the Critical Compression Ratio (CCR) is about 10,8. The trend shown by the compression ratio is without surprise. An increasing compression ratio has a relatively smaller dead volume. At TDC, this smaller volume causes a higher overall concentration and a higher overall reactivity. At the aforementioned conditions, iso-octane did not ignite until a compression ratio of 13,3, having thus a CCR of about 13,5. Figure 7 shows the influence of the equivalence ratio on the fuel PRF80, both experimentally and numerically. Both results showed the same trend, even quantitatively. A higher equivalence ratio provides more energy to the system, increasing the overall reactivity. However, this rather simple explanation is not always valid. The so-called compressional heating can play an important role. It becomes important for fuels with relatively low burn rates and at relatively high equivalence ratios. For the fuel PRF80 it seems that the final ignition decreases on increasing the equivalence ratio, while the cool flame decreases only slightly. This difference is probably due to the higher amount of fuel at the final ignition, so that the heat release is higher at that point. A change at that point will be more visible. The same experiment and simulation are performed for pure iso-octane at the same conditions. Figure 8 presents the results. The same trend is observed for the final ignition as well as the same good agreement between the mechanism and the experimental values. The cool flame delay, however, seems to increase on increasing the equivalence ratio from about 0,46 on. Apparently, from this value, the compressional heating becomes important enough to delay the cool flame delay, even when increasing the equivalence ratio. The final ignition seems to be inaffected, probably, because the energy supply is that important that the compressional heating can be neglected. The compressional heating seems also to be neglected for the lower octane fuels, since their burn rate is high enough to overcome this effect. To preserve the

engine, the experiments with much higher equivalence ratios, could not be done to see whether also the final ignition delay will know a certain minimum. Nonetheless the mixture mechanism can give an idea. Figure 9 represents a simulation, where the equivalence ratio is increased up to 1,2 for iso-octane at a compression ratio of 15 and an inlet temperature of 70 °C. It appears that the cool flame delay starts to increase from an equivalence ratio of about 0,3 and the final ignition delay from about 1,0. Though at these conditions, the mechanism was not validated, it still shows the utility of mixture mechanisms to be used at conditions that are probably not feasible for a certain engine for estimated extrapolation, pointing out interesting trends and the direction that need to be investigated.

7 Conclusion

In this study, a reduced chemical kinetic mechanism for a n-heptane / iso-octane mixture is proposed, validated numerically as well as experimentally in certain conditions. The mixture model contains 39 species and 47 reactions and can be well used for modelisation of PRF mixtures at low inlet temperature conditions. The simulated ignition delays, pressure curves and heat release curves are in good agreement with the experimental values, validating the model. The decomposition reactions of the fuel can be neglected and are of no importance for low inlet temperature modelling. The model must integrate all the effective chemical impact which helps the understanding of the HCCI control. It is shown that the reduced mechanism can be used to predict the right initial parameters for certain ignition delays, being a possible tool for the control of HCCI combustion. The mechanism shows good agreement with the experimental values for both low and high octane fuels, suggesting that the fusion of the n-heptane and iso-octane mechanism is rather successful. The results obtained for the fuel PRF80 and for iso-octane, are performed at other compression ratios. This suggests that the mechanism can also perform under different compression ratio. Concluding, it can be said this

paper proposes a PRF mechanism that is both numerically and experimentally validated having a operating range of initial conditions, varying from pure n-heptane to pure iso-octane, from 0,25 to 0,54 for the equivalence ratio and from 10,2 to 13,5 to the compression ratio. The numerical operating range is larger extending the compression ratio from 8 to 18 and the inlet temperature from 40 to 90 °C and the equivalence ratio from 0.2 to 0.7. Table 3 represents summarizes this clearly. A larger experimental validation should be done including also EGR parameters as NO, which will be presented in a next paper.

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Table 1.

The reduced PRF chemical mechanism for n-heptane and iso-octane

$k = A\ T^b\ \exp(-E_a/RT)$				
Reaction number	Reaction	A [mole-cm-s-K]	b [-]	Ea [J/mole]
1	C7H16+O2=>C7H15-2+HO2	2,80E+14	0	197401
2	C7H16+OH=>C7H15-2+H2O	4,80E+09	1,3	2889
3	C7H16+HO2=>C7H15-2+H2O2	1,00E+13	0	70919
4	C7H15-2+O2=C7H15O2	2,00E+12	0	0
5	C7H15O2=C7H14O2H	6,00E+11	0	85270
6	C7H14O2H+O2=C7H14O2HO2	2,34E+11	0	0
7	C7H14O2HO2=>C7KET21+OH	2,97E+13	0	111713
8	C7KET21=>C5H11+CO+CH2O+OH	1,00E+16	0	177402
9	C5H11=>C2H5+C3H6	3,20E+13	0	118407
10	IC8H18+O2+O2=>R2C8H17OO+HO2	2,10E+17	0	205016
11	IC8H18+OH=>CC8H17+H2O	2,48E+13	0	1841
12	IC8H18+HO2=CC8H17+H2O2	2,02E+12	0	60250
13	CC8H17+HO2=>IC6H13+C2H3+H2O2	2,00E+12	0	0
14	CC8H17+O2=R2C8H17OO	2,50E+19	-2,5	0
	REV	1,79E+13	0	103847
15	CC8H17=>IC4H8+IC4H9	4,28E+12	0	115478
16	R2C8H17OO=C8H16OOH	3,28E+12	0	119244
	REV	1,80E+11	0	84098
17	C8H16OOH+O2=R2C8H16OOHOO	3,52E+19	-2,5	0
	REV	7,00E+12	0	91128
18	R2C8H16OOHOO=>OH+C7H14CHO(OOH)	4,80E+12	0	119244
19	C7H14CHO(OOH)=>CO+IC6H13+CH2O+OH	2,05E+15	0	173218
20	IC6H13=>IC3H7+C3H6	2,51E+13	0	117989
21	IC4H9+O2=>IC4H8+HO2	1,00E+12	0	20920
22	IC4H8+OH=>IC3H7+CH2O	1,51E+12	0	0
23	IC3H7+O2=>C3H6+HO2	1,00E+12	0	20920
24	C3H6+OH=>CH3CHO+CH3	3,50E+11	0	0
25	C3H6+OH=>C2H5+CH2O	1,00E+12	0	0
26	C2H5+O2=>C2H4+HO2	2,00E+10	0	-9205
27	C2H4+OH=>CH2O+CH3	6,00E+13	0	4017
28	C2H4+H=>C2H3+H2	1,51E+07	2	25104
29	C2H3+O2=>CH2O+HCO	3,98E+12	0	-1046
30	CH3CHO+OH+M=>CH3+CO+M+H2O	1,80E+17	0	60250
31	CH3+HO2=>CH3O+OH	4,30E+13	0	0
32	CH3O(+M)=CH2O+H(+M)	2,00E+13	0	114725
	Low pressure limit	2,34E+25	-2,7	128030
33	CH2O+OH+O2=>H2O+HO2+CO	6,69E+14	1,18	-1870
34	CH2O+HO2=>HCO+H2O2	2,17E+11	0	33472
35	CH2O+O2+M=>H+CO+M+HO2	6,20E+16	0	154808
36	HCO+O2=>CO+HO2	3,98E+12	0	0
37	O+OH=>O2+H	4,00E+14	-0,5	0
38	H+O2+N2=>HO2+N2	2,60E+19	-1,24	0
39	HO2+HO2=>H2O2+O2	2,00E+15	0	8661
40	OH+OH(+M)=H2O2(+M)	7,60E+13	-0,37	-8159
	Low pressure limit	4,30E+18	-0,9	-7113
	TROE coefficients 0.7346; 94; 1756; 5182	--	--	--
	Enhancement factors:	--	--	--
	H2 2	--	--	--

	H2O	6	--	--	--
	CH4	2	--	--	--
	CO	1.5	--	--	--
	CO2	2	--	--	--
	N2	0.7	--	--	--
41	H2+O=>H+OH		1,82E+10	1	37238
42	H2O2+OH=H2O+HO2		1,00E+13	0	7531
	REV		2,03E+13	0	145938
43	H2O+M=H+OH+M		2,19E+16	0	439320
	Enhancement factors:		--	--	--
	H2O	21	--	--	--
	CO2	5	--	--	--
	CO	2	--	--	--
	H2	3.3	--	--	--
44	CO+OH=>CO2+H		3,51E+07	1,3	-3171
45	CO+HO2=>CO2+OH		1,51E+14	0	98952
46	CO+O+M=CO2+M		5,89E+15	0	17154
47	CO2+O=CO+O2		2,75E+12	0	183385
	REV		3,25E+11	0	153427

Table 2.

CFR engine parameters

Compression ratio	4 ~16
Bore	82,55 mm
Stroke	114,3 mm
Displacement	611 cm^3
Ratio connecting rod to the crank radius	4,44
Exhaust valve open	140 °ATDC
Exhaust valve close	15 °ATDC
Intake valve open	10 °ATDC
Intake valve close	146 °BTDC

Table 3.

Validated initial conditions for the PRF mixture mechanism

Parameter	Numerically validated range	Experimentally validated range
Inlet temperature	40 – 90 °C	70 °C
Equivalence ratio	0,2 – 0,7	0,25 – 0,54
Compression ratio	8 – 18	10,2 – 13,5
Fuel composition	PRF0 to PRF100	PRF0 to PRF100

Figure captions

Figure 1: Ignition delays as function of the inlet temperature, comparing different mechanisms at different equivalence ratios (ϕ) and compression ratios (ε) with n-heptane as the fuel. o for Chalmers, □ for LLNL, ▲ for Mixture.

Figure 2: Pressures and heat releases calculated by different mechanisms at compression ratio of 13, equivalence ratio of 0,5 and an initial temperature of 365 K, with iso-octane as the fuel.

Figure 3: Comparison of ignition delays with mixture mechanism (lines) and the CFR experimental results (symbols), inlet temperature of 70 °C, a compression ratio of 10,2, varying the fuel composition.

Figure 4: The comparison of the mixture mechanism and the CFR experimental results regarding the pressure and the heat release for an inlet temperature of 70 °C, an equivalence ratio of 0,41, a compression ratio of 10 and a mixture of 80vol% n-heptane and 20 vol% iso-octane as the fuel.

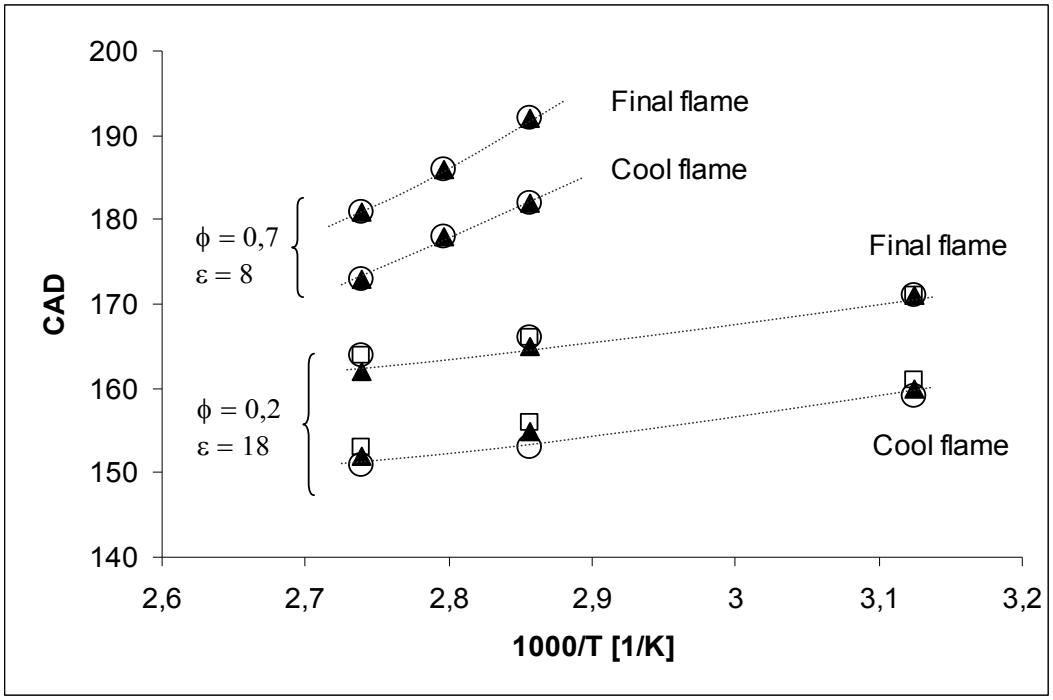
Figure 5: The comparison of the mixture mechanism and the CFR experimental results regarding the pressure and the heat release for an inlet temperature of 70 °C, an equivalence ratio of 0,41, a compression ratio of 10 and a mixture of 60vol% n-heptane and 40 vol% iso-octane as the fuel.

Figure 6: Ignition delays as function of the compression ratio at an inlet temperature of 70 °C, an equivalence ratio of 0,4, using "20 vol% n-heptane and 80 vol% iso-octane" as the fuel

Figure 7: The comparison of the mixture mechanism and the CFR experimental results regarding the equivalence ratio at an inlet temperature of 70 °C, a compression ratio of 13,5, using "20 vol% n-heptane and 80 vol% iso-octane" as the fuel

Figure 8: The comparison of the mixture mechanism and the CFR experimental results regarding the equivalence ratio at an inlet temperature of 70 °C, a compression ratio of 13,5, using iso-octane as the fuel

Figure 9: Chemkin modelling ignition delays as a function of equivalence ratio at a compression ratio of 15, an inlet temperature of 70 °C using iso-octane as the fuel



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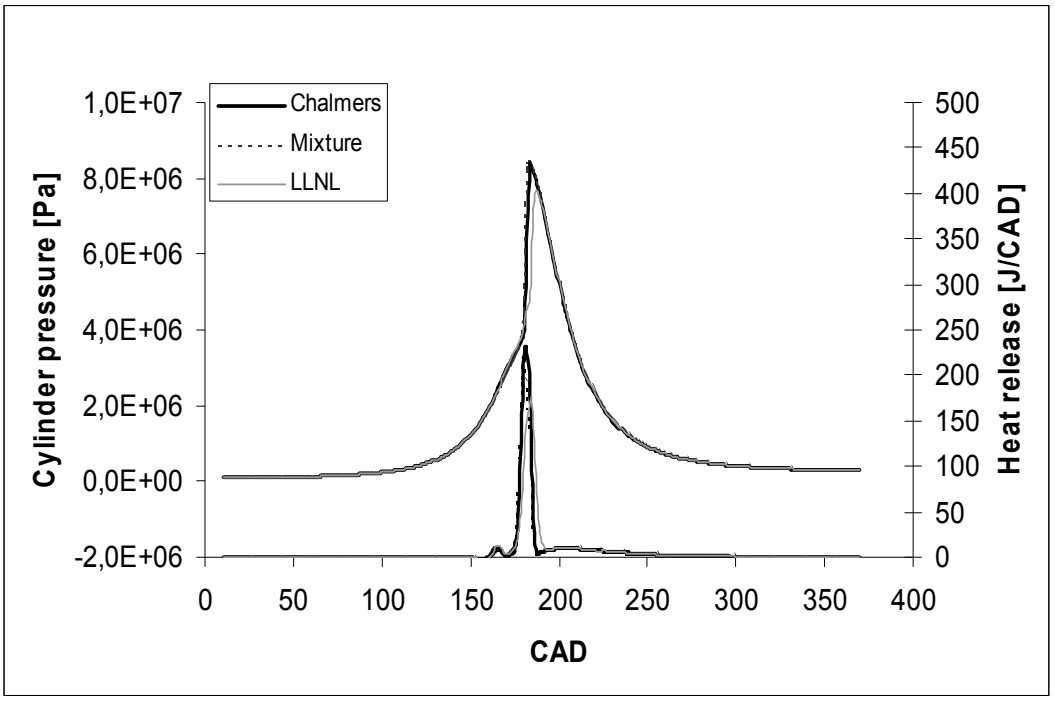

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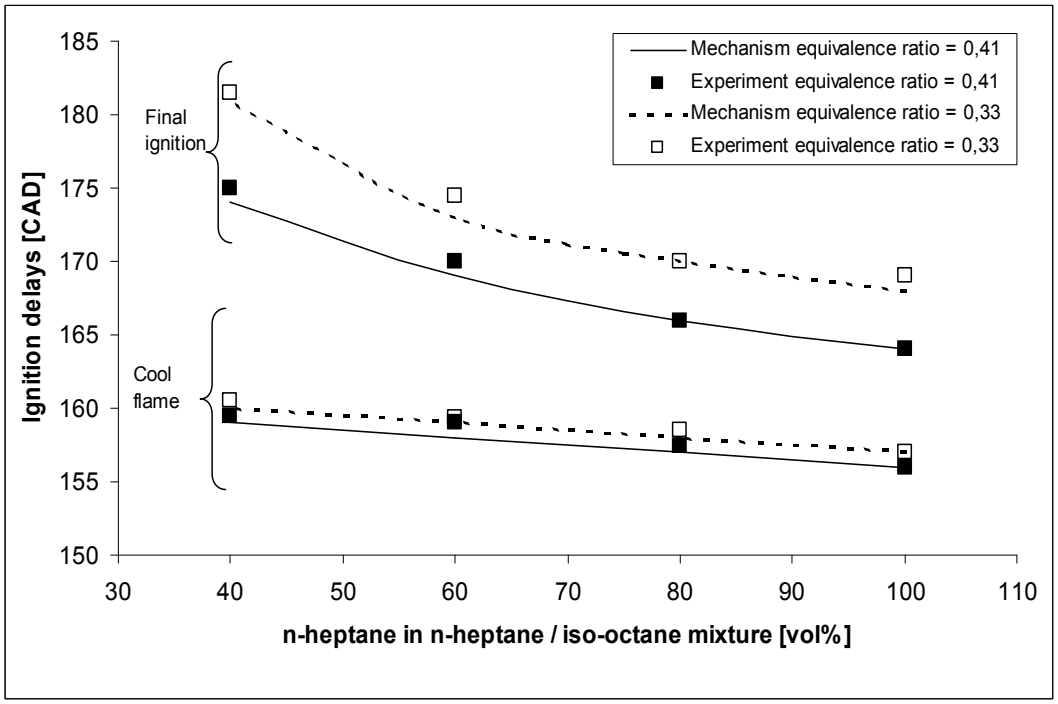

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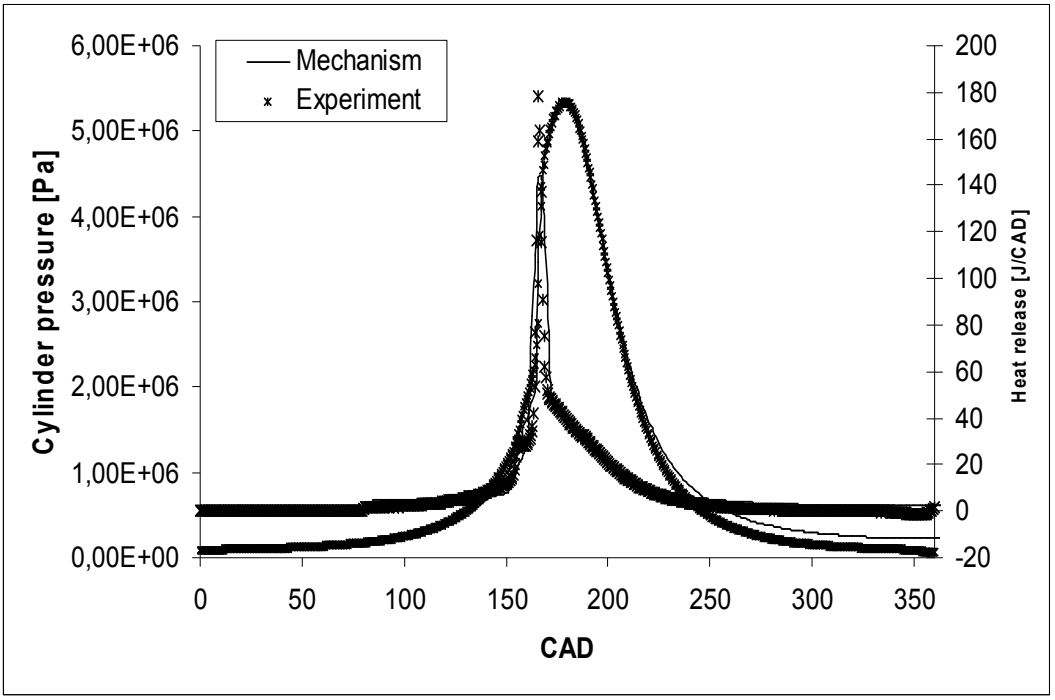
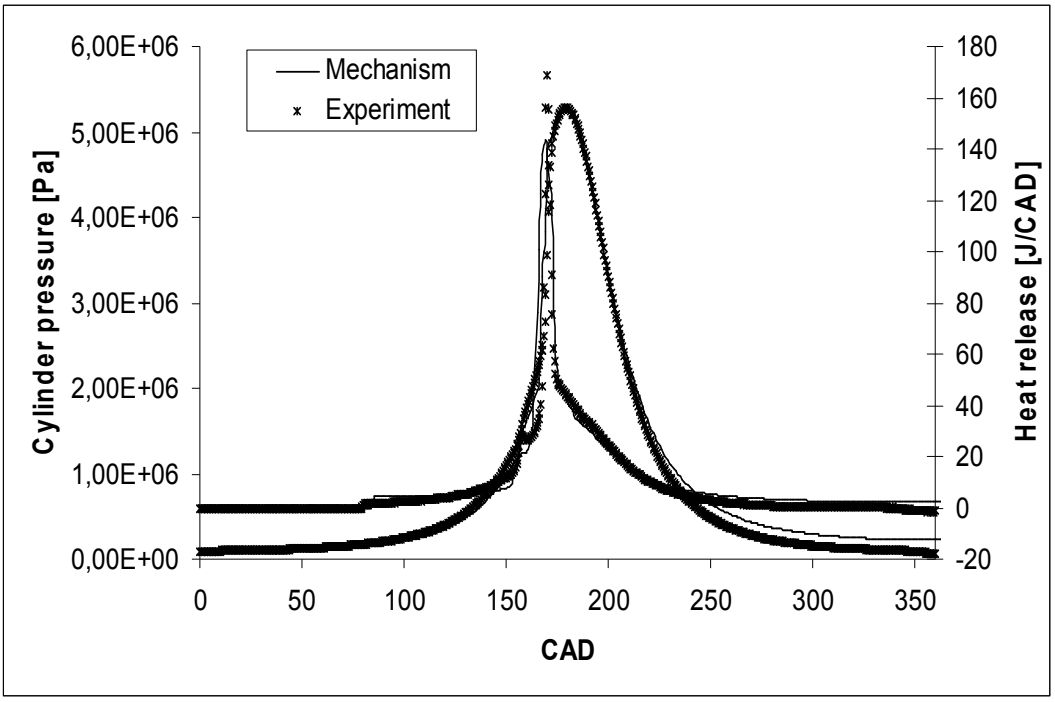


Fig. 4. The comparison of the mixture mechanism and the CFR experimental results regarding the pressure and the heat release for an inlet temperature of 70 °C, an equivalence ratio of 0,41, a compression ratio of 10 and a mixture of 80vol% n-heptane and 20 vol% iso-octane as the fuel.



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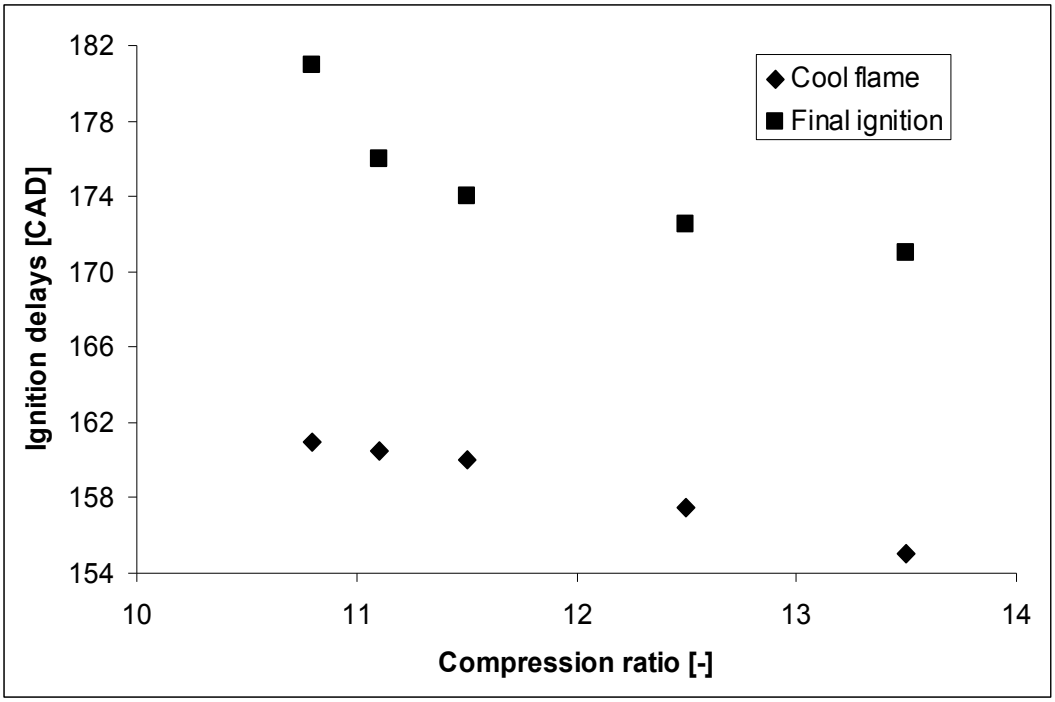

Fig. 6. Ignition delays as function of the compression ratio at an inlet temperature of 70 °C, an equivalence ratio of 0,4, using "20 vol% n-heptane and 80 vol% iso-octane" as the fuel

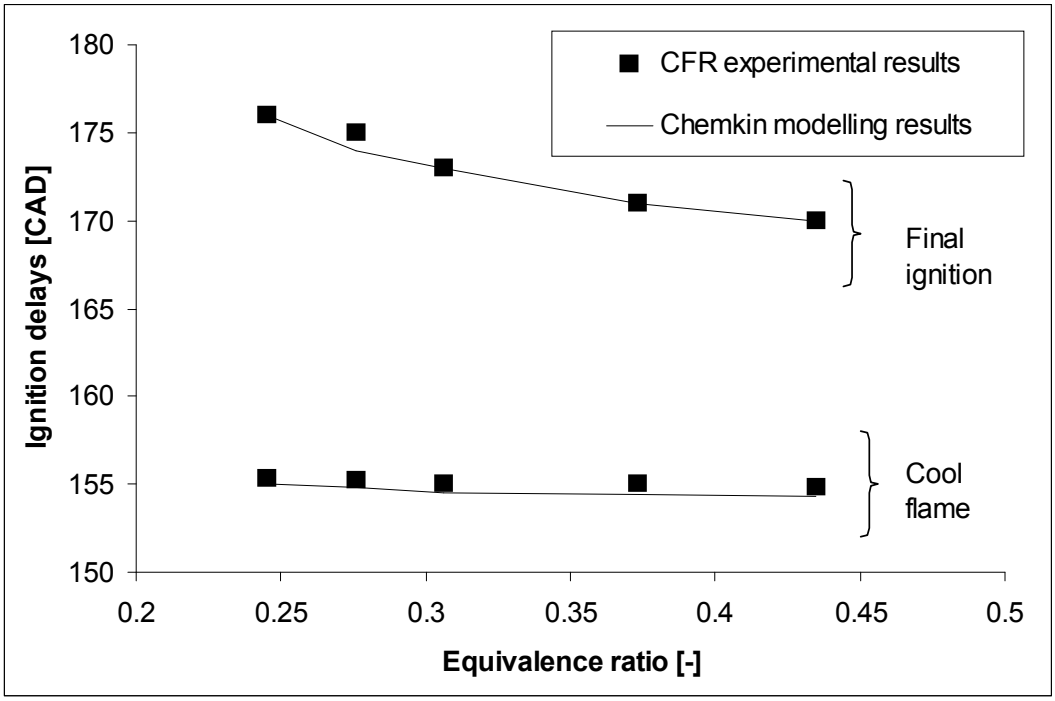

Fig. 7. The comparison of the mixture mechanism and the CFR experimental results regarding the equivalence ratio at an inlet temperature of 70 °C, a compression ratio of 13,5, using “20 vol% n-heptane and 80 vol% iso-octane” as the fuel

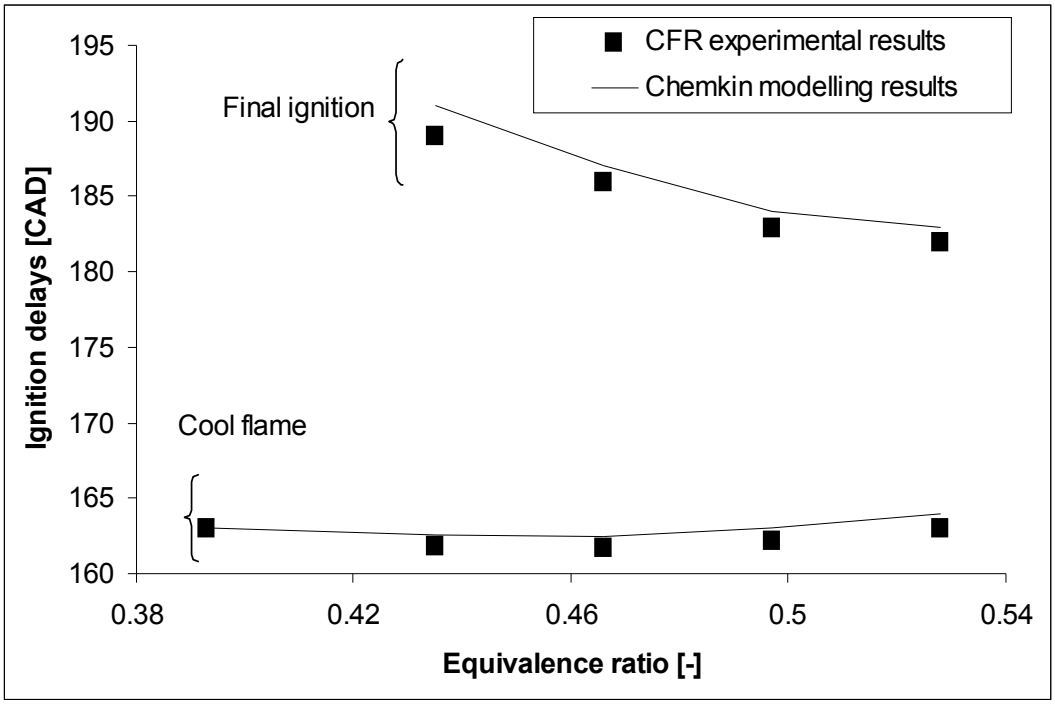

Fig. 8. The comparison of the mixture mechanism and the CFR experimental results regarding the equivalence ratio at an inlet temperature of 70 °C, a compression ratio of 13,5, using iso-octane as the fuel

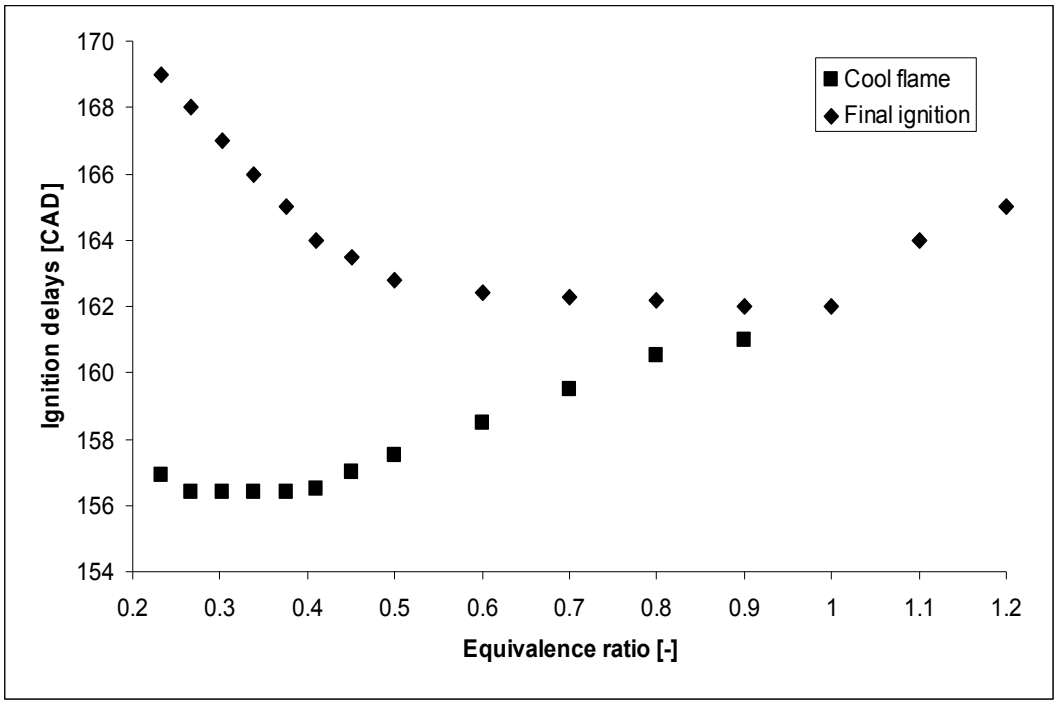

Fig. 9. Chemkin modelling ignition delays as a function of equivalence ratio at a compression ratio of 15, an inlet temperature of 70 °C using iso-octane as the fuel