HCCI engine modeling and experimental investigations – Part 2: The composition of a NO-PRF interaction mechanism and the influence of NO in EGR on auto-ignition

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Abstract

This paper presents an investigation of the effect of NO in EGR on HCCI auto-ignition, by means of experiments and a NO-PRF interaction mechanism. The influence is investigated both numerically and experimentally. The numerical part is effected by a composition of a NO submechanism and the subsequent addition of this sub mechanism to a reduced validated n-heptane/iso-octane PRF mechanism, the latter of which is presented in a previous paper, named paper 1 (Machrafi et al., submitted 2006). The experimental part is effected on a CFR engine, operating at HCCI conditions, with an inlet temperature of 70 °C and a compression ratio of 10,2. Hereby n-heptane and PRF40 are used as the fuels, using different equivalence ratios in order to extend the interpretation domain. The NO adding concentration is experimentally varied between 0 and 160 ppm. The results showed that adding NO at low concentrations advances the ignition delays, the promoting reactions being more reactive than the inhibitory ones. The promoting effect seems to be at its maximum at an addition of 45 ppm concerning the fuel PRF40. At higher adding concentrations of NO the promoting effect becomes less and the inhibitory reactions become more reactive. The effect of NO on the auto-ignition of n-heptane seemed, however, to be unsignificant. The effect of NO was

qualitatively well represented by the mechanism, whilst quantitatively the mechanism predicted a lower effect of NO at an addition of 45 ppm.

Keywords: HCCI engine application, auto ignition control, reduced mechanism kinetics, influence of NO in EGR

Short version of the title: A reduced NO-PRF interaction mechanism for HCCI engine applications

1 Introduction

To meet environmental requirements and new technology demands a need is arisen to develop new engines that function on low equivalence ratios, lower fuel consumptions and lower CO_2 and hydrocarbon emissions. A few years ago, the interest is increased in a promising alternative to SI and Diesel combustion: the Homogeneous Charge Compression Ignition (HCCI). This combustion process lends itself for an engine running generally on a lean, diluted mixture of fuel, air and combustion products, ignition by compression auto-ignition. The most important challenge that persists is the control of the HCCI auto-ignition. Many ways are proposed for this purpose. Controlling the auto-ignition by Exhaust Gas Recirculation (EGR) seems to have gained much interest. Interesting work has been done in this field (Mitchell et al., 1993, Li et al., 1997, Ladommatos et al. 1996a, Ladommatos et al. 1996b, Ladommatos et al., 1997). One can imagine controlling the auto-ignition by the aspects present in EGR, dividing this in three interacting effects: the dilution effect by inert gasses, the thermal effect by the EGR temperature and the chemical effect by the way of chemical additives. The last effect is of interest in this paper, particularly the chemical species nitrogenoxides. Much research is performed in the field of the interaction of nitrogenoxides

with hydrocarbons as for instance the work of Eng et al. (1997). Other examples in the field of interaction of nitrogen oxides with hydrocarbons are kinetics of nitrogen chemistry in combustion (Miller and Bowman, 1989), kinetics of nitrous oxide decomposition (Glarborg et al., 1994a) and the modelling of thermal deNO_x (Glarborg et al., 1994b) and reburning (Kilpinen et al., 1992) to mention a few. However, not much research is performed concerning the influence NO can particularly have on the auto-ignition control in HCCI engines. Examples of such work are Dubreuil et al. (2006), Sheppard et al. (2006), Moreac et al. (2002) and Stenlaas et al. (2002). Faravelli et al. (2003) show that the addition of NO to hydrocarbons at low temperatures enhances ignition. This enhancement, however becomes an inhibition at higher amounts of NO addition, as explained in the section HCCI chemistry. Faravelli et al. (2003) found also that at high temperatures the addition of NO loses its enhancing capabilities (above ~1000 K it becomes less effective and above ~1400 K is disappears) because the alkyl radicals decompose and become of less importance. The performed research shows that the effect of NO on the auto-ignition has a particularly interesting feature, being able to both promote and inhibit auto-ignition. In the case of an engine one may speak of an advancing and retarding effect on the auto-ignition delays. The main purpose of this paper is to investigate the effect of NO in EGR on the auto-ignition delay both numerically and experimentally. A reduced PRF-NO mechanism combination is proposed that deals with the interaction of NO with n-heptane and iso-octane. Table 1 presents the PRF mechanism presented in a previous paper named part 1 and table 2 presents the composed NO sub mechanism. The calculations are performed, using the internal combustion model of Chemkin. A cooperative Fuel Research (CFR) engine is used for the experiments, varying the NO addition using the fuels n-heptane and a PRF40 (60 vol% n-heptane and 40 vol% iso-octane) with a fixed inlet temperature of 70 °C, a fixed equivalence ratio of 0,41 and a fixed compression ratio of 10,2.

2 NO-hydrocarbon chemistry overview

The HCCI chemistry of n-heptane and iso-octane has been discussed in the paper part 1. This paper part 2 will discuss the interaction between NO and the hydrocarbons n-heptane and iso-octane. N-heptane will be taken as an example. Hydrocarbon ignition can occur in one or two, significantly different, stages (Tanaka et al., 2003a, Tanaka et al. 2003b, Griffiths et al., 2002), which depends mainly on the initial temperature and the fuel structure. The chemical species NO seems to interact primarily on the first stage, that is the cool flame. NO has the ability to activate peroxy radicals as follows:

$RO_2 + NO = RO + NO_2$

where R can be either H or an alkyl group. The transformation, however, of HO_2 to OH is responsible for over 80 % of the conversion of NO to NO_2, with the peroxy radicals ROO playing only a minor role:

$HO_2 + NO = OH + NO_2$

NO is thereafter furthermore formed, at least partially by :

$NO_2 + H = NO + OH$

which is a much faster reaction than the one before, so that NO_2 is depleted in the system. Adding up these two reactions gives:

$HO_2 + H = 2\ OH$

which is more reactive than the recombination reaction:

$HO_2 + H = H_2O_2$

that would otherwise take place with no addition of NO. So the addition of NO enhances the ignition delay by producing eventually more OH radicals that consume the fuel (Faravelli et al., 2003, Frassoldati et al., 2003, Moreac et al., 2002). However, excessive amounts of NO inhibit the oxidation at low and intermediate temperatures, because of the scavenging of OH

radicals by the reactions (Mitchell et al., 1993, Li et al., 1997, Ladommatos et al. 1996a, Ladommatos et al. 1996b, Ladommatos et al., 1997):

$NO + OH + [M] = HONO + [M]$

$HONO + OH = NO_2 + H_2O$

that add up to:

$NO + 2\ OH = NO_2 + H_2O$

The scavenging of reactive OH radicals is increased by the following reaction

$NO_2 + HO_2 = HONO + O_2$

The competition of this reaction with $HO_2 + NO = OH + NO_2$ provides the first inhibiting effect, while the subsequent reaction of HONO with an OH radical to form NO_2 and H_2O is the second. When the [NO] is such that the ratio of the rates of NO + OH and fuel + OH becomes slightly greater than one, the system's reactivity drops sharply and the NO addition becomes an inhibition. The following reactions:

$NO+H+[M]=HNO+[M]$

$NO_2+O=NO+O_2$

$NO+O+[M]=NO_2+[M]$

are other chain termination processes which limit the growth of the radical pool. The first reaction of this set is extremely important when the fuel concerned is hydrogen or whenever a large amount of hydrogen is present in the system. In fuel-lean conditions, on the other hand, the oxidation of HNO is an important source of radicals and this reaction loses ability for termination. The other two always inhibit and become more important as $[O_2]$ increases. Furthermore it seems (Faravelli et al., 2003) that due to the lesser importance of peroxy radicals at higher temperatures, because they decompose, the enhancing effect of NO becomes of less importance (even though RO_2 plays the minor role in NO chemistry, this role is sufficient to reduce the NO enhancing capabilities of NO at higher temperatures) and even

disappears at very high temperatures, ~1400 K, according to experiments with propane in an isothermal flow reactor performed by Faravelli et al. (2003). In another study performed by Frassoldati et al. (2003), it appears that at higher temperatures, NO is losing its promoting role, but in another way than stated by Faravelli et al. (2003). The main role is now played by CH_i for methane and HCCO radicals for other hydrocarbons. The most important reactions are the reactions of the ketenyl radical (HCCO):

HCCO + NO = HCNO + CO

HCCO + NO = HCN + CO_2

Dagaut et al. studied this reburning process using a jet stirred reactor and different small hydrocarbons as reburning fuels: acetylene (Dagaut et al. 1999a), ethylene (Dagaut et al. 1999b), propane (Dagaut et al. 2001) and propene (Dagaut et al. 2000). Also, in another study, Glarborg et al. (1998) analyzed the effect of several hydrocarbons in a flow reactor at temperatures between 1100 and 1500 K. All these studies confirm the critical role of the ketenyl radical in the reduction of NO. The above two reactions between NO and HCCO mostly proceed through two different channels (Dagaut et al. 1999a). These literature studies show that generally the first reaction of the two above to form fulminic acid and CO prevails largely on the second reaction that forms HCN and CO_2.

3 Composition of the NO-PRF mechanism

This section describes the composition of the NO submechanism with the PRF mechanism discussed and validated in part 1. As said before, EGR is an important aspect for the control of the auto-ignition process. EGR has several aspects as the dilution effect, the thermal effect and the chemical effect. The first two effects can be modeled with the PRF mechanism. The chemical species that will be tested in this work is NO. This species is not present in the PRF mechanism. For this purpose a reduced sub mechanism of NO will be added to the PRF

mechanism. According to Faravelli et al. (2003) a little addition of NO advances ignition whereas too much addition of NO rather inhibits the ignition. So, to study the NO-hydrocarbon interaction chemistry numerically it is necessary to add a NO sub-mechanism to the reduced PRF mechanism. Faravelli et al. (2003) proposed a NO sub-mechanism that was composed using their investigation and the work of several authors. Other authors (Miller and Bowman, 1989, Glarborg et al. 1998), especially Faravelli et al. (2003), have proposed reactions that characterize the influence of NO on the ignition of hydrocarbons.

At high temperatures, NO loses its promoting effect, due to the decreasing concentration of peroxide radicals. This is presented in the work done by Faravelli et al. (2003), Heywood (1988), Frassoldati et al. (2003) and Dagaut et al. (1999a). Dubreuil et al. (2006) suggest a detailed NO sub mechanism that interacts with n-heptane/iso-octane mixtures. This mechanism is reduced using the same methods used for the PRF mechanism and using the investigation work mentioned before. As far as concerns the formation of NO at high temperatures, the following reactions have been proposed, often denoted as the extended Zeldovich mechanism (Bowman et al., 1975, Lavoie et al., 1970):

$N + NO = N_2 + O$

$N + O_2 = NO + O$

$N + OH = NO + H$

All these contributions led to the reduced NO sub mechanism, presented in table 2, having 19 reactions and 12 additional species (with respect to the PRF mechanism).

4 Numerical validation results

The numerical validation of the reduced mechanism is performed using Chemkin. The parameter that is investigated, is the addition of NO. For the numerical validation of the NO sub-mechanism, both this reduced sub-mechanism and the detailed NO mechanism delivered

by Dubreuil et al. (2006) are added to the PRF mechanism. This mechanism was validated by Dubreuil et al. (2006) in a jet-stirred reactor under dilute conditions at 10 atm, at an equivalence ratio of 0,3, an intake temperature of 350 K, varying the EGR rates from 0 to 50 % and the NO addition from 0 to 500 ppmv. Then, the addition concentration of NO is changed under adiabatic conditions. The calculation of the ignition delay from modelling experiments is based on the same thermodynamic engine model, shown and explained in paper 1 (Machrafi et al., submitted 2006), resulting into a heat release profile, with two maximums, indicating a two-stage combustion. The heat release is calculated by the following expression:

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

Here V represents the volume as a function of the crank angle degree (θ), using the engine geometry and P is the calculated pressure, obtained from the engine model. 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. Figure 1 shows this numerical validation for the auto-ignition delays. This same comparison was done for several equivalence ratios. Figure 1 shows that the reduced NO sub mechanism agrees satisfactorily with respect to the cool flame and final ignition delays, with no significant differences. It seems that the two mechanisms agree satisfactorily with each others. Figure 2 shows the difference of the final ignition of the reduced NO sub mechanism and the detailed one in crank angle degrees as a function of the equivalence ratio and the NO addition for the final ignition. The agreement between the detailed mechanism and the reduced mechanism is obtained for a wide range of the addition of NO and the equivalence ratio. The translucent area depicts the region of parameters where the difference is more than 1 CAD. Figure 2

shows indeed that for almost all the values of the investigated NO addition and equivalence ratio, the reduced NO model shows agreement with the detailed one. So the NO submechanism can be considered validated numerically.

5 Experimental validation of the NO-PRF mechanism with respect to addition of NO

Experimental set-up

The goal in this section is the experimental comparison of the combination of the PRF mechanism and the numerically validated NO sub mechanism. The same CFR engine is used as in paper 1 (Machrafi et al., submitted 2006), of which the characteristics are shown in table 3. Additionally a EGR system is added to this CFR engine. For the purposes of this paper, lets consider only the EGR components that are discussed in this paper. The chemical active species is NO and the diluting species, representing the EGR is N_2. The nitrogen volumetric flow permits to determine, along with the volumetric air flow (that is mixed with the fuel), the volumetric EGR ratio. The nitrogen flow as well as the NO flow are controlled with in a confidence interval of respectly +/- 2 vol% and +/- 10 vol%. By regulating their volumetric flows, the required NO content within the EGR ratio is determined. Thereafter, in a mixing tank, the fuel is injected and mixed with the incoming air and the EGR flows. The fuel composition is prepared in advance and connected to an injection system attached to a nebulizer. The total inlet air mixture flow is regulated such that the mass at IVC remains constant and that the inlet pressure remains atmospheric, neglecting the influence of the fuel mass. Between the intake valve and the mixing tank, a twisted tube is placed to ensure a as highly possible homogeneity as possible. The effect that is obtained is, in this case, twofold: the dilution effect of EGR, represented by nitrogen and the chemical effect of EGR, represented by NO. The thermal effect could have been investigated by altering the EGR temperature. In the auto-ignition controlling point of view, a parameter should response

relatively quickly to a certain demand. Since the inlet temperature or the temperature generally are parameters that take relatively long to respond, the thermal aspect of EGR is not considered here. Therefore the EGR temperature is held constant at 70 °C to equal the inlet temperature, having a confidence interval of +/- 1 °C. Nitrogen can react at high temperatures with an oxygen radical to form NO and a nitrogen radical. This, however, takes place at very high temperatures, that are often out of the range of the HCCI operating ranges and in any way do not interfere at temperatures around the cool flame and final ignition delays. The ignition delays were obtained by calculating maximums of the heat release rate. The ignition delays showed a confidence interval of +/- 0,5 CAD, the equivalence ratios +/- 0,005 and the fuel composition +/- 0,1 vol%. The pressure is measured by a calibrated pressure sensor attached to the cylinder head. The pressure curves are a mean of 50 cycles with a dispersion of 1 bar at the maximum pressure. Then, the heat release is calculated, adding the heat loss term:

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

The heat loss term is expressed as follows:

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

Here, A represents the surface of the cylinder wall, the piston and the cylinder head, T the gas temperature obtained from the ideal gas law and T_{wall}, the temperature of the cylinder wall estimated by measuring the temperature difference of the cooling water, while holding the cooling water temperature at the entrance constant. The heat transfer coefficient, h, is calculated by using the Woschni heat transfer correlation, being calibrated for HCCI purposes by Chang et al. (2004).

Results of the experimental validation

Figure 3 shows the comparison of the cool flame and final ignition delays between the reduced NO-PRF combined mechanism and the experimental results, using the fuels PRF40 and n-heptane. It is quit visible that, concerning the fuel PRF40, the combination of the PRF model and the NO submechanism give reasonably good comparison at low NO additions and at high NO additions, but a non-negligible difference is present there where the impact of NO is at its highest. The experiments show a minimum cool flame and final ignition delays at an NO addition of 45 ppm as the mechanism does. However, the impact of NO on the ignition delays, especially the final ignition delay, is higher for the experiments than it is predicted by the mechanism. As far as it goes for n-heptane, the comparison is good. This is not surprising, since not much change is observed for the influence of NO on the auto-ignition of n-heptane in the studied range. Figure 4 shows the comparison of the pressure and the heat release between the mechanism and the experimental results. More experimental heat release curves will be shown in the last section. The results in figures 3 and 4 imply that the combined NO-PRF mechanism underestimates the effect of NO. The NO sub mechanism has been validated in a jet-stirred reactor, while the experiments are performed in an engine. The pressure conditions in a jet-stirred reactor and in an engine are quite different. Some reactions that are present in the PRF mechanism (such as reaction 40, where the OH radicals are formed form the dissociation of H_2O_2) are pressure dependent. Since in an engine the pressure changes differently, this has a different impact on the kinetics. Nonetheless, qualitatively the trend is well predicted by the model. Therefore for analysis of NO influences, these combined mechanisms can be used for predictions of the behaviour of NO influencing n-heptane and/or iso-octane at other conditions. However, for precise quantitative analysis of NO influences at higher NO additions, the combination of the reduced NO submechanism and the PRF mechanism does not seem suitable, though the trends seem to be correct.

6 The effect of N_2 on the auto-ignition

Since the effect of NO on the auto-ignition is studied under EGR conditions, using nitrogen as the representative gas for EGR, the effect of nitrogen on the auto-ignition should be studied first. The two fuels studied are n-heptane and PRF 40. Figure 5 shows the effect of nitrogen and the equivalence ratio on the ignition delays for n-heptane and PRF40. Figure 5 shows that and addition of nitrogen to the inlet mixture, thereby diluting it, lowers the overall concentration of the reacting species. The effect is quite obvious. However, it is not the effect itself that is of interest here. It is rather the difference in the strength of the effect, when comparing n-heptane with PRF40. It seems that the effect on n-heptane is less at the same conditions than on the fuel PRF40. This could be explained by the burning rate. N-heptane is known to have a higher burning rate and reactiviy than any n-heptane/iso-octane mixture fuel (Tanaka et al., 2003a, Tanaka et al., 2003b). This means that when one investigates the effect of NO on the auto-ignition, one must take into account the higher burning rate of n-heptane, which is less affected by the diluting of nitrogen, in which NO is present. This discussion continues in the next section.

7 The effect of NO on the auto-ignition

To investigate the role of NO, experiments have been performed, using the same CFR engine with an inlet temperature of 70 °C, a compression ratio of 10,2 and a fuel consisting of "60 vol% n-heptane and 40 vol% iso-octane" and the reference n-heptane. The equivalence fuel air ratio was chosen to be 0,32 and 0,41, while the addition of NO was varied from 0 to 160 ppm (with respect to the volume at IVC). The EGR ratio was maintained at 23 vol%, a minimum valued that is needed for the experimental set-up to assure the range of NO addition. Figure 6 shows, that for n-heptane, the effect of NO at the investigated range is

rather negligible. Only at an addition of 160 ppm, the heat release seems to advance slightly for an equivalence ratio of 0,32. Figure 7 shows the effect of NO on auto-ignition on the fuel PRF40 at the conditions mentioned previously. The values of the ignition delays represent a confidence interval of +/- 0,5 CAD and that for the NO concentration 10 %. According to figure 7, the fuel PRF40, however, shows a quite different effect by NO. A minimum is visible at a NO addition of 45 ppm at IVC. This suggests that up to a NO concentration of 45 ppm at IVC, NO plays a promoting role, advancing the ignition delays. At this stage the promoting reactions of NO are more reactive. At higher NO additions, the ignition delays begin to retard, due to the increasing reactivity of the inhibiting reactions, thus retarding the ignition delays. At the studied conditions, the ignition delays at maximum NO addition do not become higher than the cases without NO addition, though the inhibiting role of NO at 160 ppm is clearly visible with respect to 45 ppm addition. The values of the final ignition are clearly more influenced by the addition of NO than the cool flame delay which remains nearly constant. Only 45 ppm NO advances the final ignition delay 4 CAD at an equivalence ratio of 0,32. For a lower equivalence ratio this effect is slightly less, as figure 5 shows. It has been said that the formation of more OH radicals by the intervention of NO, is primarily due to the reaction between NO and HO_2. As the PRF mechanism shows in table 1, HO_2 is initially formed by the reaction between the fuel and oxygen. In lean mixtures for HCCI conditions, enough oxygen is present, so that a lower equivalence ratio entails less fuel and less HO_2 formed. This is probably the reason, why the effect of NO is less at lower equivalens ratios.

The mechanism is used to offer a possible explanation of the lesser effect of NO on n-heptane than on the fuel PRF40. The OH concentration at the cool flame is calculated, using the combined PRF-NO mechanism, for both n-heptane and the PRF40 fuel at the same conditions. Figure 8 shows the results, where it can be seen that an addition of NO of 50 ppm to n-heptane does hardly influence the OH concentration at the cool flame, while for the

PRF40, the influence is clearly visible. This means that addition of NO to n-heptane does hardly influence its auto-ignition, the influence on the ignition delays being therefore non-significant. In the case of PRF40, addition of NO of 50 ppm seems to be enough in order to increase the reactivity. Therefore n-heptane seems to be less influenced by NO than "60vol% n-heptane / 40vol% iso-octane". These results are based on the studied conditions. It is possible that at other conditions the effect of NO on the n-heptane auto-ignition phasing becomes relevant. For instance, Dubreuil et al. (2006) found a decrease in the final ignition delay of about 1,5 CAD for a NO addition of 100 ppm at an equivalence ratio of 0,3 and an engine speed of 1500 rpm. The addition of NO is observed to alter the rate of oxidation of all fuels investigated. However, the magnitude of the effects vary according to the temperature regime and to the nature of the fuel. Figure 9 shows the evolution of the heat release as a function of the addition of NO for the fuel PRF40.

This experimental study enables to look at the evolution of the positioning of the cool flames and the final ignition. Figure 9 shows that the cool flame hardly moves (~ 1 CAD) with respect to the concentration of NO at IVC. The value the heat release (~10 J/CAD) at the cool flame delays stay the same. The final ignition, however, is clearly influenced by the NO addition, having both a promoting and inhibiting effect. The value of the heat release (~ 40 to ~ 60 J/CAD) vary considerably. So NO can be used to advance the final ignition delay or retard it, whilst keeping the cool flame delay nearly constant, controlling the emissions and the engine efficiency and thus an interesting tool for controlling HCCI combustion.

8 Conclusion

In this study, a combination of a reduced and validated PRF mechanism and the NO sub mechanism is proposed, obtaining a good numerical agreement and a rather satisfactory

experiment agreement in certain conditions. The NO submechanism presents reactions of NO formation and reactions of NO-hydrocarbon interaction. This combination between the NO submechanism and the PRF mechanism predicts satisfactorily the advancing and retarding effect of NO on the auto-ignition delays. Also the importance of the fuel, that is used, is presented. It has also been shown that a strongly reduced mechanism is still able to account for the complex energetic process of auto-ignition, since the auto-ignition delays are predicted well. The experiments with the addition of NO to the air/fuel mixture showed interesting results regarding the ignition delays. At concentrations up to 45 ppm, NO advanced the auto-ignition delay and beyond that value the delay was retarded. This could mean that the chemical species NO can also be used as a tool for the control of HCCI combustion, by controlling the amount of EGR. A reduced mechanism that is able to predict this auto-ignition process well is very suitable for a lot of kinds of auto-ignition research as 3D simulation or a multi-component mechanism accounting of gasoline, diesel and other chemical species in EGR to be applied for the control of the HCCI auto-ignition process.

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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
	Reverse reaction	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
	Reverse reaction	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
	Reverse reaction		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
	Reverse reaction		3,25E+11	0	153427

Table 2.

The reduced sub mechanism for NO interaction with 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	N + NO = N2 + O	3,500E+13	0,0	1379
2	N + O2 = NO + O	2,650E+12	0,0	26752
3	N + OH = NO + H	7,333E+13	0,0	4682
4	NO + HO2 = NO2 + OH	2,100E+12	0,00	-2006
5	NO + OH + M = HONO + M	5,100E+23	-2,31	-284
6	NO2 + H = NO + OH	1,000E+14	0,00	1513
7	NO2 + HO2 = HONO + O2	6,300E+08	1,25	20900
8	HONO + OH = NO2 + H2O	1,26E+10	1,00	2383
9	CH2O + NO2 = HCO + HONO	8,00E+02	2,77	57391
10	CH3 + NO2 = CH3O + NO	1,51E+13	0,0	0,0
11	CH3O + NO2 = CH2O + HONO	6,02E+12	0,0	9551
12	CH3O2 + NO = CH3O + NO2	5,50E+11	0,00	-4983
13	C2H5 + NO2 = C2H5O + NO	1,00E+13	0,0	0,0
14	C2H5O + NO2 = CH3CHO + HONO	4,00E+11	0,0	0,0
15	C2H5O2 + NO = C2H5O + NO2	3,00E+12	0,0	-1496
16	C7H15O2 + NO = C7H15O + NO2	1,630E+14	0,0	-2989
17	C7H15 + NO2 = C7H15O + NO	1,510E+13	0,0	0,0
18	C8H17O2 + NO = C8H17O + NO2	2,590E+12	0,0	0,0
19	C8H17 + NO2 = C8H17O + NO	1,5E+13	0,0	0,0

Table 3.

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

Figure captions

Figure 1: The comparison between the detailed NO mechanism and the deduced NO mechanism at an equivalence ratio of 0,5, a compression ratio 10,2, an inlet temperature of 340 K and n-heptane as the fuel and the NO addition as the function.

Figure 2: The comparison of the errors of the final ignition in CAD as a function of the equivalence ratio and the NO addition at a compression ratio 10,2, an inlet temperature of 340 K and n-heptane as the fuel.

Figure 3: The comparison between the mechanism ignition delays and the experimental ignition delays at an inlet temperature of 70 °C, an equivalence ratio of 0,32, a compression ratio of 10,2, "60 vol% n-heptane / 40 vol% iso-octane" as the fuel, varying the addition of NO.

Figure 4: The comparison between the mechanism and experimental pressure and heat release at an inlet temperature of 70 °C, an equivalence ratio of 0,321, a compression ratio of 10,2 and "60 vol% n-heptane and 40 vol% iso-octane" as the fuel with an NO addition of 45 ppm.

Figure 5: Iso-delays for the cool flame (left) and the final ignition (right) as a function of the added percentage N_2 in the inlet mixture and the equivalence ratio for n-heptane (top) and "60 vol% n-heptane and 40 vol% iso-octane" (bottom) at an inlet temperature of 70 °C and a compression ratio of 10,2.

Figure 6: Heat release as a function of the added percentage NO in the inlet mixture at an inlet temperature of 70 °C, an equivalence ratio of 0,32, a compression ratio of 10,2 and n-heptane as the fuel, the dilution by N_2 is 23 vol%.

Figure 7: Iso-delays for the cool flame and the final ignition as a function of the added NO concentration in the inlet mixture and the equivalence ratio for the fuel PRF40 at an inlet temperature of 70 °C and a compression ratio of 10,2.

Figure 8: Normalized OH concentrations at the cool flame for both n-heptane and PRF40 at a compression ratio of 10,2, an equivalence ratio of 0,32 and an inlet temperature of 70 °C, using the combined PRF-NO mechanism.

Figure 9: Heat release as a function of the added percentage NO in the inlet mixture at an inlet temperature of 70 °C, an equivalence ratio of 0,32, a compression ratio of 10,2 and a mixture of 60 vol% n-heptane and 40 vol% iso-octane as the fuel, the dilution by N_2 is 23 vol%.

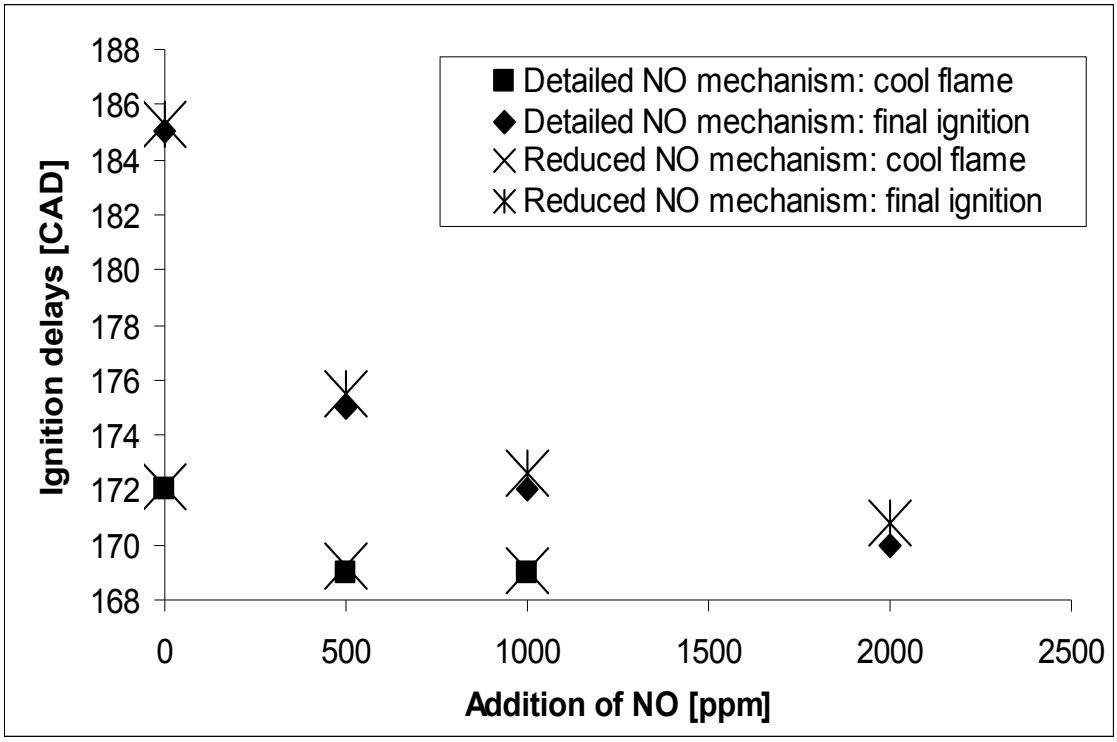

Fig. 1. The comparison between the detailed NO mechanism and the deduced NO mechanism at an equivalence ratio of 0,5, a compression ratio 10,2, an inlet temperature of 340 K and n-heptane as the fuel and the NO addition as the function

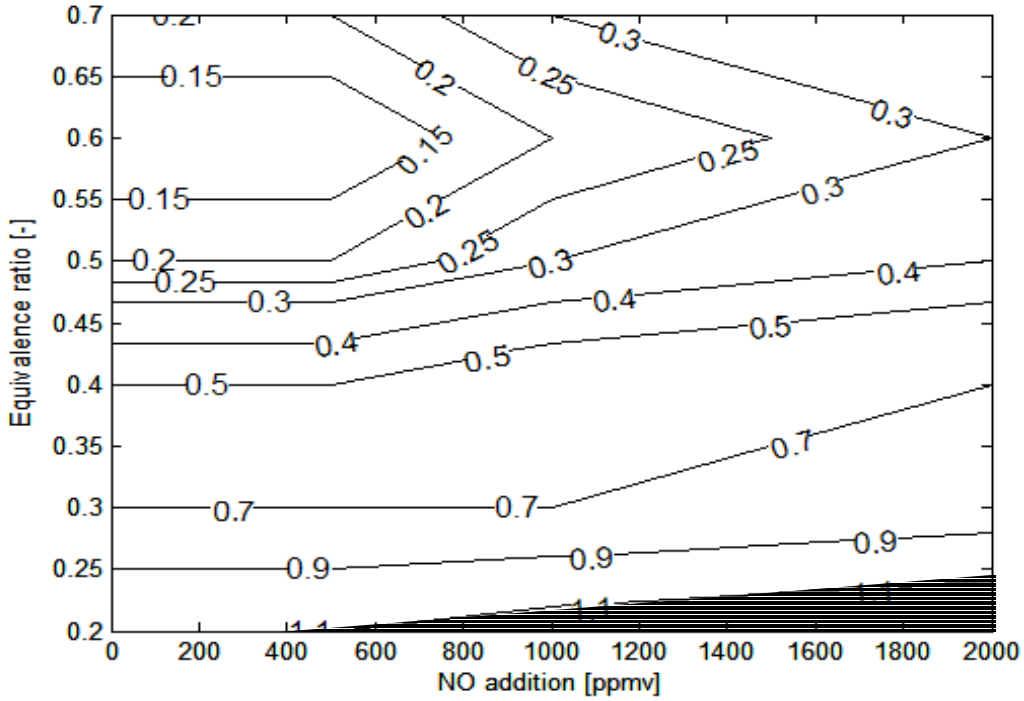

Fig. 2. The comparison of the errors of the final ignition in CAD as a function of the equivalence ratio and the NO addition at a compression ratio 10,2, an inlet temperature of 340 K and n-heptane as the fuel

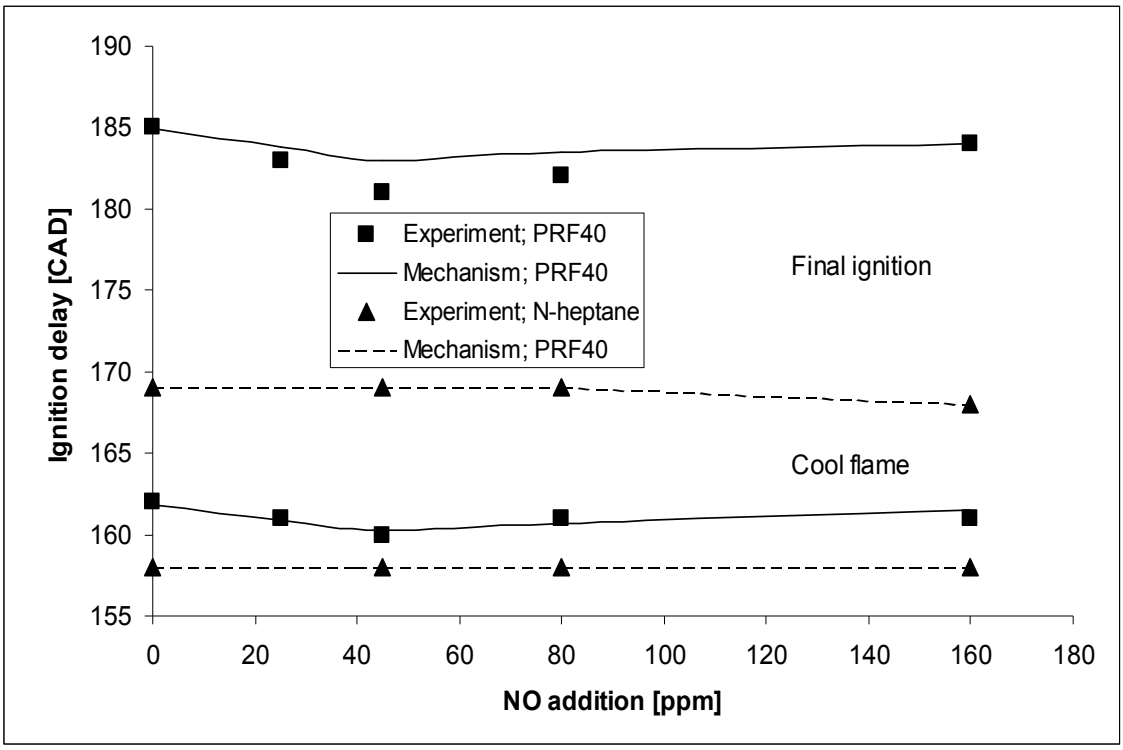

Fig. 3. The comparison between the mechanism ignition delays and the experimental ignition delays at an inlet temperature of 70 °C, an equivalence ratio of 0,32, a compression ratio of 10,2, “60 vol% n-heptane / 40 vol% iso-octane” and n-heptane as the fuels, varying the addition of NO

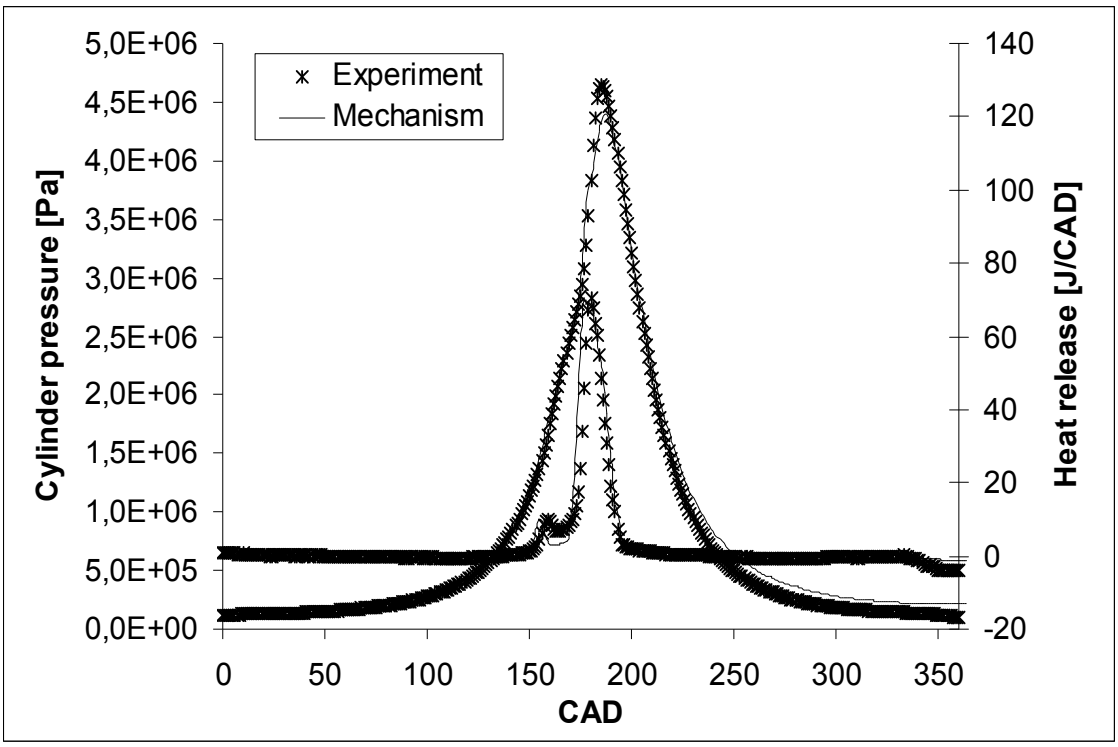

Fig. 4. The comparison between the mechanism and experimental pressure and heat release at an inlet temperature of 70 °C, an equivalence ratio of 0,321, a compression ratio of 10,2 and “60 vol% n-heptane and 40 vol% iso-octane” as the fuel with an NO addition of 45 ppm

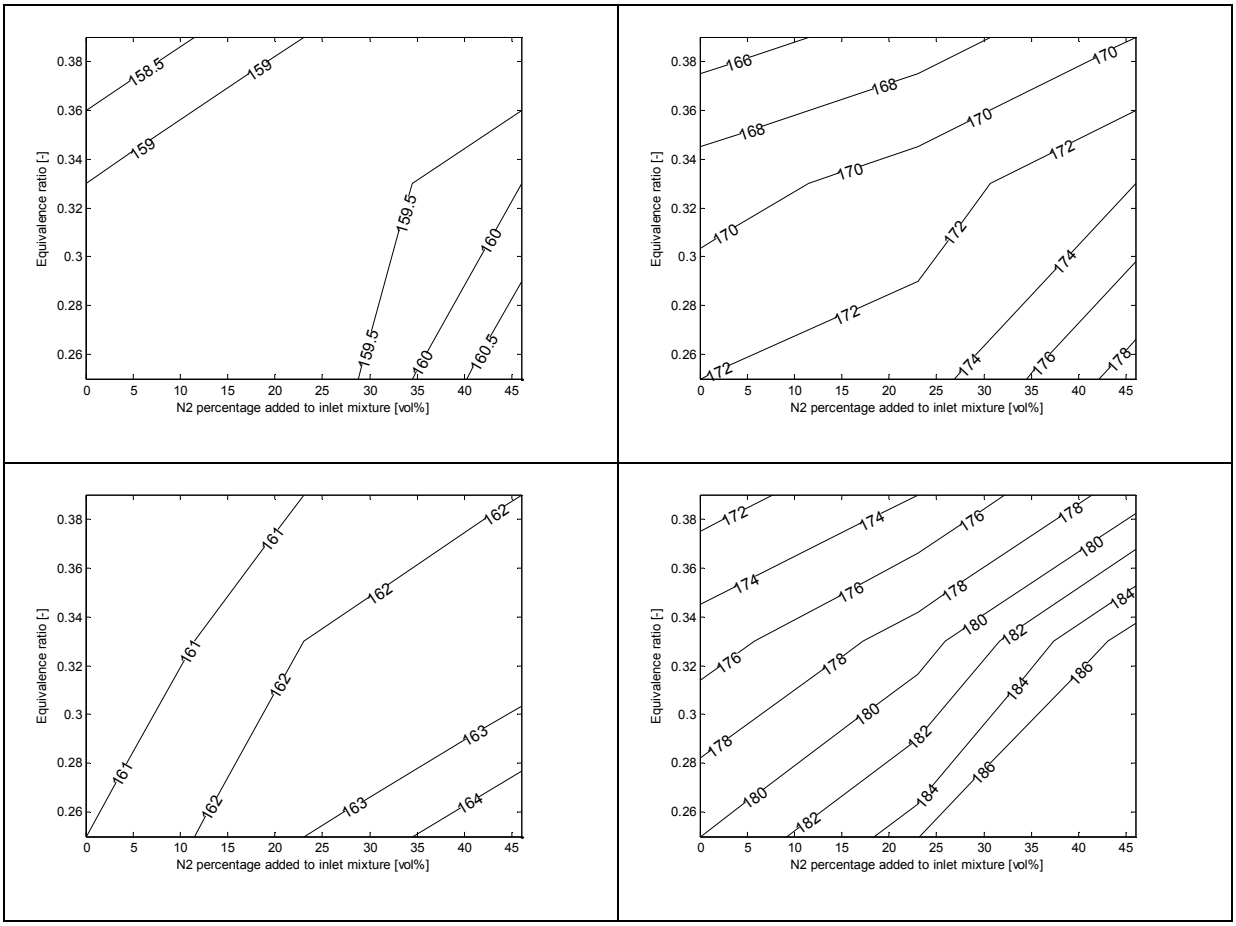

Fig. 5.: Iso-delays for the cool flame (left) and the final ignition (right) as a function of the added percentage N_2 in the inlet mixture and the equivalence ratio for n-heptane (top) and "60 vol% n-heptane and 40 vol% iso-octane" (bottom) at an inlet temperature of 70 °C and a compression ratio of 10,2

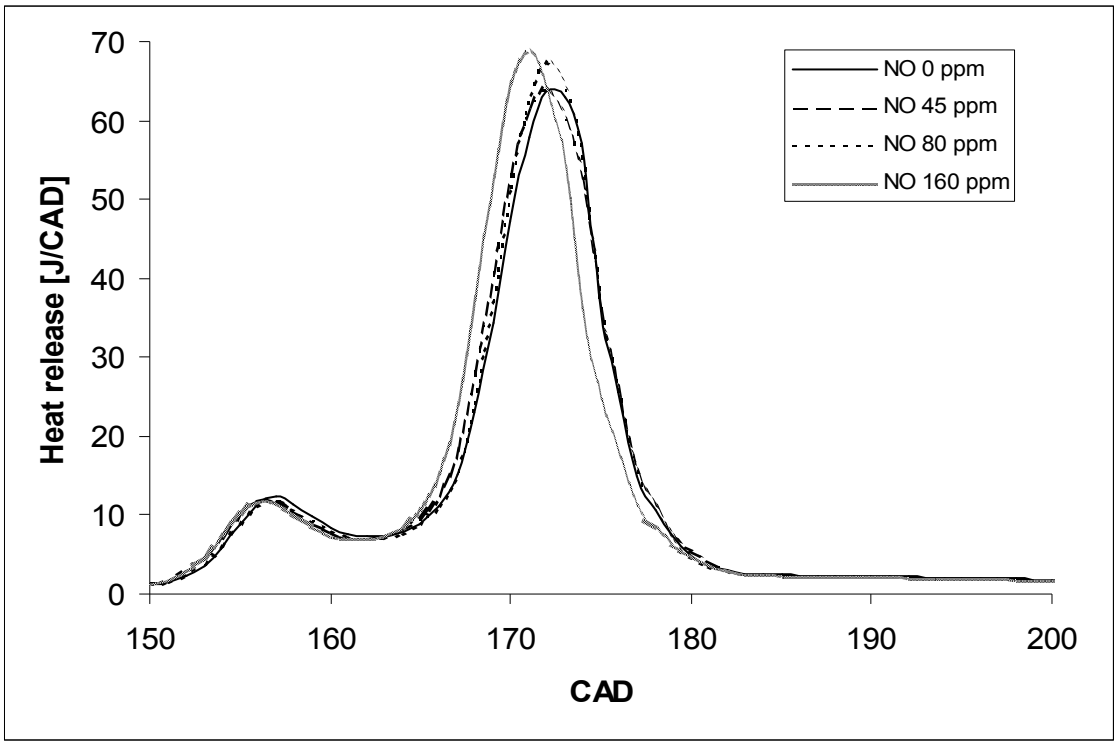

Fig. 6. Heat release as a function of the added percentage NO in the inlet mixture at an inlet temperature of 70 °C, an equivalence ratio of 0,32, a compression ratio of 10,2 and n-heptane as the fuel, the dilution by N_2 is 23 vol%

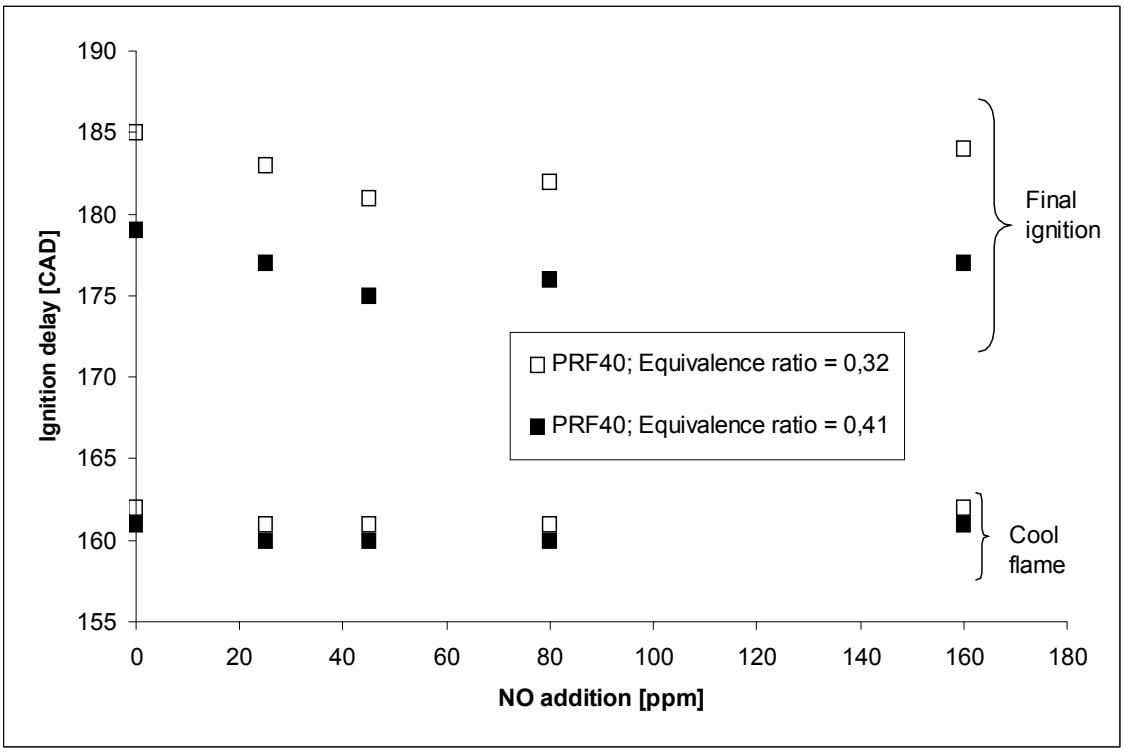

Fig. 7. Iso-delays for the cool flame and the final ignition as a function of the added NO concentration in the inlet mixture and the equivalence ratio for the fuel PRF40 at an inlet temperature of 70 °C and a compression ratio of 10,2

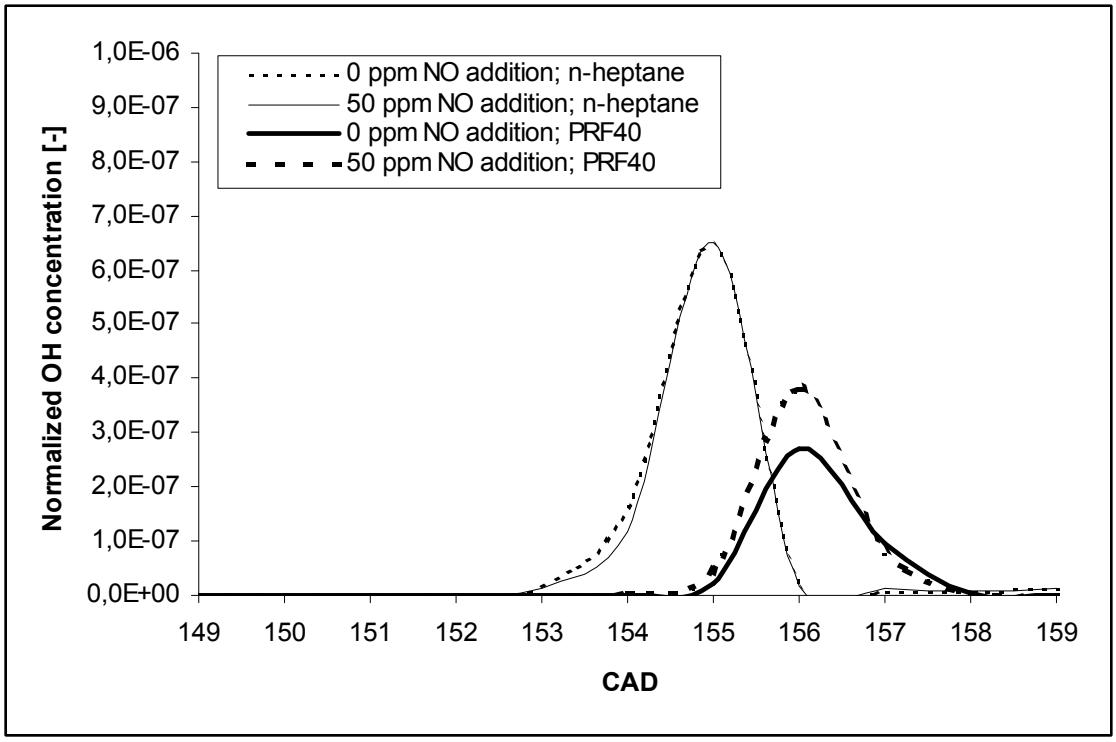

Fig. 8: Normalized OH concentrations at the cool flame for both n-heptane and PRF40 at a compression ratio of 10,2, an equivalence ratio of 0,32 and an inlet temperature of 70 °C, using the combined PRF-NO mechanism

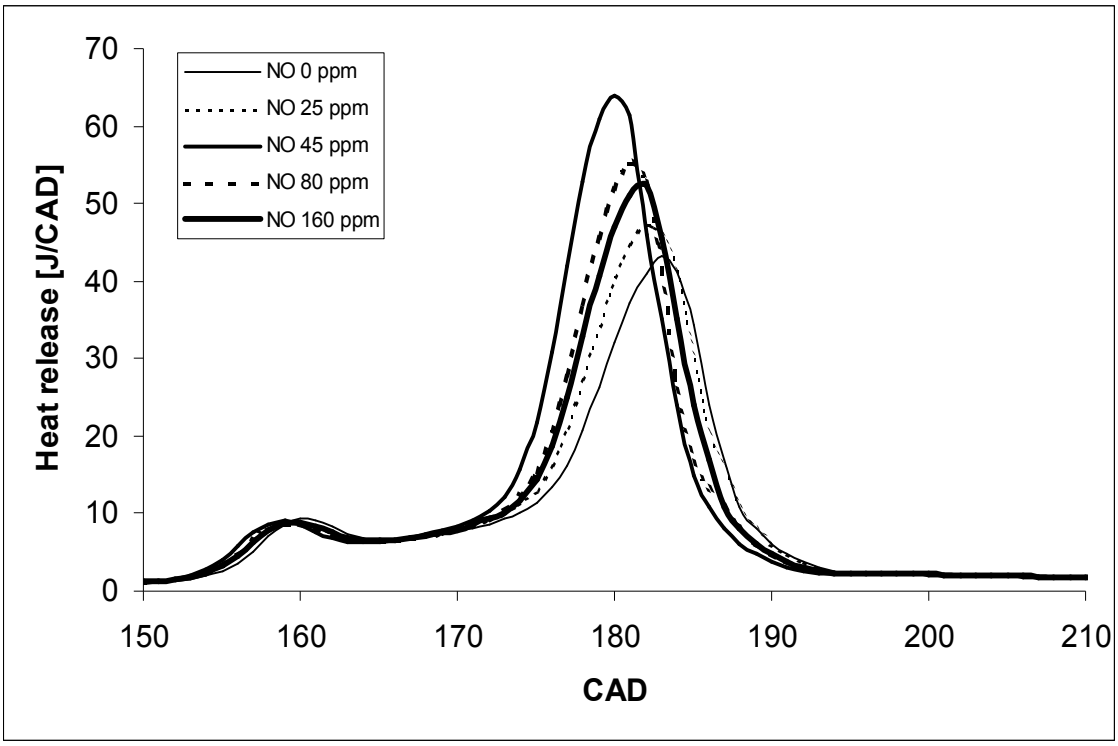

Fig. 9. Heat release as a function of the added percentage NO in the inlet mixture at an inlet temperature of 70 °C, an equivalence ratio of 0,32, a compression ratio of 10,2 and a mixture of 60 vol% n-heptane and 40 vol% iso-octane as the fuel, the dilution by N_2 is 23 vol%