The effect of EGR on HCCI combustion – impact of diluting, thermal and chemical aspects: experimental and numerical approaches

H. Machrafi*, P. Guibert, S. Cavadias
Laboratoire de Mécanique Physique, CNRS FRE 2867, Université Pierre et Marie Curie (Paris 6), 2, Place de la Gare de Ceinture, 78210 Saint Cyr l'Ecole, France

Abstract

Three effects of EGR that influence the auto-ignition are investigated in this paper: the diluting effect (N_2 and CO_2), the thermal effect (T_{EGR}) and the chemical effect (CO, CH_2O, CH_3CHO and NO). The diluting effect delayed the auto-ignition delay. So did the addition of the chemical species CH_2O and CH_3CHO. The EGR temperature showed a slightly promoting effect, while CO did not show any effect at the range investigated. Both a promoting and inhibiting effect were observed by the addition of NO. To allow for further interpretation and enlargement of the investigation domain, a previously validated and reduced PRF mechanism is presented.

Introduction

The environmental restrictions and automobile strategies call for an alternative combustion mode, reducing the pollution, while keeping at least the engine efficiency of present conventional engines. The Homogeneous Charged Compression Ignition (HCCI) mode seems to be very promising. The major problem that arises is a way to control the auto-ignition process, since no spark plug or fuel injection is used as is the case in respectively a Spark Ignition engine and a Diesel engine. One of the most interesting ways to control the auto-ignition, is EGR as turns out from various work **[1-7]**. The effect of EGR on auto-ignition is then the main investigation subject of this paper. The effect of EGR can be divided into three parts. The diluting part of EGR, representing inert gasses that constitute largely the essence of EGR. In this work nitrogen and CO_2, highly present in EGR are taken as representatives of these inert gasses. The thermal effect is the second parameter with which the auto-ignition could be influenced. This effect is represented by the EGR temperature. Finally, the chemical effect is a complex factor of EGR on which will be focused more than the other two EGR effects. This effect translates itself into the interaction of some reactive chemical species, contained in EGR, with the auto-ignition reaction path. The chemical species that are discussed in this paper are carbon oxide (CO), formaldehyde (CH_2O), acetaldehyde (CH_3CHO) and nitrogen oxide (NO). A contradicting observation was made by Subramanian et al. **[8]**, concerning the influence of CO on the auto-ignition. In their work they compared three different kinetic mechanisms in order to find out the influence of CO addition on the auto-ignition delay at constant pressure. They observed opposite views, regarding the effect of CO on the auto-ignition, suggesting that, depending on the initial conditions (with a varying initial temperature and equivalence ratio of respectively 600 to 1000 K and 0,7 to 1,0), CO can either promote, inhibit the auto-ignition delay or even show no significant influence. Yamaya et al. **[9]** examined the effect of formaldehyde addition using a single cylinder diesel engine and different fuel/air mixtures (the fuel being methane, ethane, propane and/or n-butane). Depending on the fuel type in the mixture and temperature to which mixtures are compressed, the effect of formaldehyde adulteration is found to be either suppressing or promoting for the ignition. The effect is suppressing for fuels that naturally show an early cool flame ignition tendency (a two stage combustion) and promoting for fuels that naturally show no cool flame tendencies (a one stage combustion). Salooja **[10]** states that all aldehydes except formaldehyde generally promote combustion, acetaldehyde being the most effective promotor. The same was observed by Moore and Tipper **[11]** in a flow system. Faravelli et al. **[5]** 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. Faravelli et al. **[5]** 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. These results where also obtained by others **[6,7,12-14]**. The research performed on the influence of chemical species, present in EGR, show that these species can have a considerable effect on the auto-ignition process. Moreover, the effects are different from one another, which makes the effect of EGR on the combustion rather complicated. Nonetheless, the observations that are found in the literature encourage to investigate further the influence of EGR on the auto-ignition.

Experimental set-up

Table 1 shows the characteristics of the CFR engine and figure 1 shows the experimental set-up.

---

* Corresponding author : machrafi@ccr.jussieu.fr

Compression ratio[a]	4 ~16
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 1: CFR engine specifications

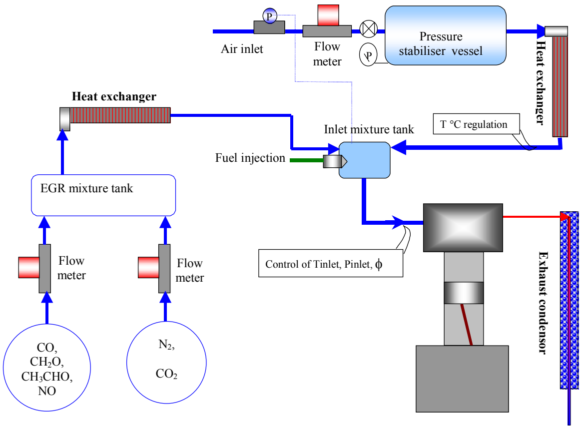

Figure 1 : Schematic of the experimental set-up of the CFR engine

The auto-ignition delays were determined by calculating the heat release from the pressure data, obtained from a pressure sensor during the experiments. The next equation is used for this calculation.

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

A 0D model is developed that uses the First Law of Thermodynamics and a calibrated heat loss correlation to determine the heat release. All the heat releases showed two maximums, corresponding to a so-defined cool flame delay and final ignition delay, reflecting a two-stage HCCI auto-ignition combustion. These delays are defined with respect to the Bottom Dead Center (BDC) at the beginning of the compression stroke.

Specific objectives

As mentioned before, the investigations performed with regard to the effect of EGR on the HCCI auto-ignition process show some disagreements. However, they also show the significant impact they can have on the auto-ignition. Therefore it is of great interest to investigate the effect of EGR. This paper treats the three effects of EGR, discussed before. The real effect of EGR is a sum of all these effects. Therefore, the main goal is to provide an image of how these different aspects of EGR, each, influence the auto-ignition. The experimental investigation is performed on a CFR engine with an EGR installation attached to it, to simulate an EGR mixture. The inlet temperature is always kept at 70 °C, the equivalence ratio at either 0,32 or 0,41 and the compression ratio at 10,2. The fuels investigated are n-heptane and the mixture “60 vol% n-heptane / 40 vol% iso-octane”. The effect of EGR is a function of the fuel composition. Therefore, these two fuels are chosen to show the influence the octane number could have on the effect of EGR. The EGR ratio of N_2 and CO_2 ranged between 0 and 46 vol%. The EGR temperature was altered from 30 to 120 °C. The CO addition was varied between 0 and 170 ppmv and both the CH_2O and CH_3CHO addition varied between 0 and 1400 ppmv. The addition of NO was changed from 0 to 170 ppmv. Since, with experimental equipment one can not investigate all ranges of the parameters, an in previous work **[15,16]** successfully validated reduced PRF mechanism is used. With this mechanism the auto-ignition delays are calculated that are effected by the EGR parameters in a wider range. This results into a data base that provides a detailed mapping of the ignition delays as a function of the EGR parameters.

Results and Discussion

The dilution effect, is presented next. The diluting effect is represented by nitrogen and carbon dioxide. Figures 2 and 3 show respectively the effect of N_2 and CO_2 on the cool flame delay and the final ignition delay for an equivalence ratio of 0,32, a compression ratio of 10,2, an inlet temperature of 70 °C with both the fuels n-heptane and PRF40 used. The compression ratio and the inlet temperature will be the same in the rest of the paper and are therefore no longer mentioned in the text.

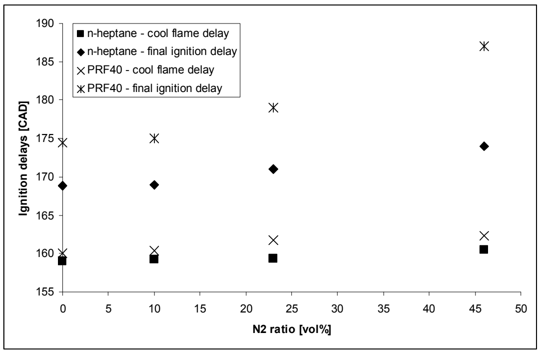

Figure 2: Influence of N_2 on the auto-ignition delays at an equivalence ratio of 0,32 with n-heptane and PRF40 as the fuels

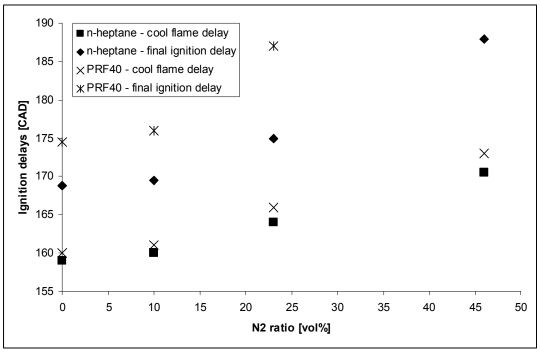

Figure 3: Influence of CO_2 on the auto-ignition delays at an equivalence ratio of 0,32 with n-heptane and PRF40 as the fuels

Figure 2 shows that the N_2 has a retarding effect on the final ignition delay. The same effect is observed for the cool flame delay, but much weaker. The dilution causes an overall decrease of the concentrations of the species during the combustion process. The overall reactivity decreases. At the cool flame the concerned fuel is much less than at the final ignition and therefore the effect is much less. The effect seems to be more important for the fuel PRF40 than for n-heptane. N-heptane has a higher burn rate than PRF40 and therefore more dilution is needed to decrease the overall reactivity. Figure 3 shows that the same tendencies as figure 2. However, CO_2 seems to effect the delay of the ignition delays more strongly. CO_2 has a significantly larger heat capacity than N_2 has. Therefore, CO_2 not only dilutes, but also makes the system "loose its energetic content" due to compressional heating. These figures show that the fuel that is used, influences in itself the effect dilution can have. Having discussed this aspect, the other experiments will be shown with the fuel PRF 40. Another aspect of the EGR is the EGR temperature. Figure 4 shows the effect of the EGR temperature on the auto-ignition delays at an equivalence ratio of 0,41 and PRF40 as the fuel. The EGR temperature was simulated by heating the N_2 flow at a certain ratio.

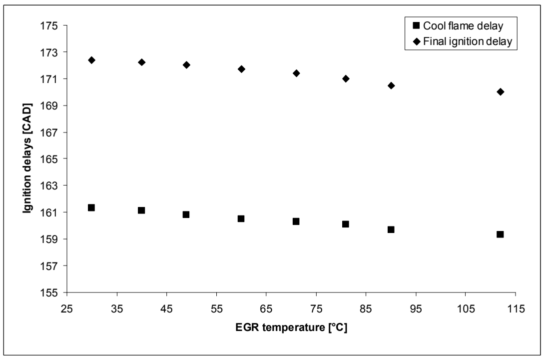

Figure 4: Influence of the EGR temperature on the auto-ignition delays at an equivalence ratio of 0,41 with PRF40 as the fuel and an EGR ratio of 23 vol%

Figure 4 shows that the EGR temperature decreases slightly the auto-ignition delays. Both the cool flame delay and the final ignition delay are affected at about the same degree. A higher EGR temperature causes the overall kinetics to increase and thus the overall reactivity via the reaction rates. The third effect that was mentioned is the chemical effect. Since this effect seems to be the most important one, more attention will be given to it. The first species considered is CO. The addition of the chemical species is performed in an EGR ratio of 23 vol% and an EGR temperature of 70 °C. The same conditions hold for the rest of the paper. Figure 5 shows the influence of the addition of CO on the auto-ignition delays at an equivalence ratio of 0,32 and the fuel PRF40.

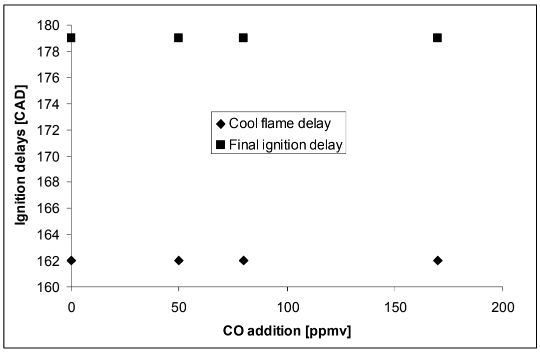

Figure 5: Influence of CO on the auto-ignition delays at an equivalence ratio of 0,32 with PRF40 as the fuel

This figure shows clearly that CO has no significant influence on both the ignition delays. The literature does not agree entirely with this observation. The CO interaction is considered by the following reactions in the case of an engine **[17]**, forming CO_2:

CO + OH• = CO2 + H•

H• + O2 + M = HO2• + M

An addition of CO results into a higher consummation of OH radicals, replacing them by the less reactive HO2 radicals, leaving less for the consummation of the fuel, thus retarding the final ignition. The retarding effect was explained by the preceding reaction **[17]**. Subramanian et al. **[8]**, observed next to a inhibiting effect also a promoting effect, depending on the initial conditions, explaining this by the following reaction:

$CO + O_2 = CO_2 + O$

Here two stable species, CO and O_2 lead to the formation of an active radical, atomic oxygen.

The effect of formaldehyde and acetaldehyde is shown in figure 6.

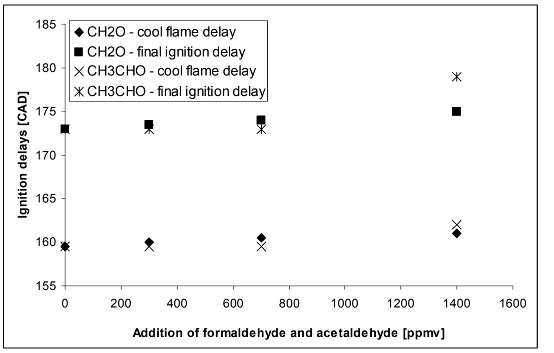

Figure 6: Influence of CH_2O and CH_3CHO on the auto-ignition delays at an equivalence ratio of 0,32 with PRF40 as the fuel

The effect of CH_2O seems to be quite clear, delaying the final ignition delay approximately linearly. Yamada et al. **[18]** performed kinetic measurements in HCCI combustion using dimethyl ether (DME), for the investigation of the role of the intermediate species formaldehyde, which controls chain branching in the low temperature oxidation mechanism. They write further that a significant intermediate of DME is formal CH_2O. When CH_2O is formed, it shares OH consumption with the fuel through the reaction:

CH_2O + OH = HCO + H2O

HCO readily reacts with O_2 to form CO and HO_2 (HCO + O_2 = CO + HO_2). These are not sources (on the contrary, they are consumers) of OH at this temperature range. Hence, this reaction acts as a chain termination step. This retards the final ignition. The cool flame delay is also delayed, but much less, since at the cool flame much less OH is present to be influenced by CH_2O. On the other hand the influence of acetaldehyde is not quite clear. CH_3CHO seems not to influence the auto-ignition delays until an addition of 1400 ppmv, where the effect of CH_3CHO seem even to be stronger than CH_2O. A possible explanation for this could be found in the reduced PRF mechanism that shows the same behaviour as the experiments did. The following reaction seems then to be the cause:

$CH_3CHO + OH + M = CH_3 + CO + M + H_2O$

Here acetaldehyde acts as an inhibitor, unlike Salooja **[10]** found in their work. The last chemical species investigated is NO. Figure 7 shows the effect of NO on the auto-ignition delays at an equivalence ratio of 0,32, comparing the fuels n-heptane and PRF 40.

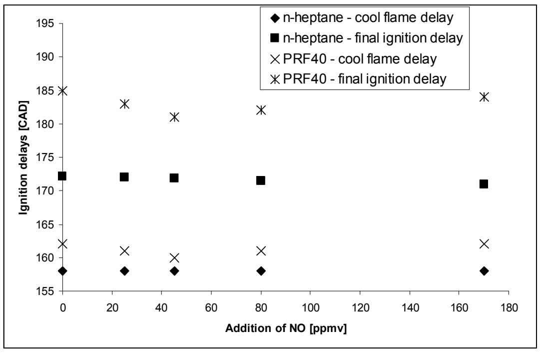

Figure 7: Influence of NO on the auto-ignition delays at an equivalence ratio of 0,32 with n-heptane and PRF40 as the fuels

Figure 7 shows that for n-heptane, the addition of NO has nearly no effect on the final ignition delay, except a slight promoting effect at an addition of 170 ppmv. The cool flame delay does not seem to be affected at all. The promoting effect can be explained as follows. Faravelli et al. **[5]** explain the effect of the addition of NO to hydrocarbons on the ignition delay. NO has the ability to activate peroxy radicals in:

$RO_2 + NO = RO + NO_2$

where R can be either H or an alkyl group. The transformation, however, of HO2 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 :

NO2 + 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 **[5,20]**. This effect is also observed for the fuel PRF40, but much more clearly. An addition of only 45 ppmv causes the final ignition delay to decrease by 4 CAD. It seems **[5]** that due to the lesser importance of peroxy radicals at higher temperatures, because they decompose, the enhancing effect of NO becomes of less importance and even disappears at very high temperatures, ~1400 K. In another study performed by Frassoldati et al. **[20]**, it appears that at higher temperatures, NO is losing its promoting role. N-heptane's cool flame occurs earlier than that of "60vol% n-heptane / 40vol% iso-octane", resulting into a higher temperature, having a higher burn rate. This higher burn rate leaves less time for NO to react with the peroxides. Therefore n-heptane

seems to be less influenced by NO than PRF40. Furthermore, the fuel PRF40 shows beyond the value of 45 ppmv of NO addition an inhibiting effect of NO. This seems to be cuased by the scavenging of OH radicals by the following reactions **[6,7,12-14]**:
$NO + OH + [M] = HONO + [M]$
$HONO + OH = NO_2 + H_2O$
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. Apparently, this concentration seems to be 45 ppmv in this investigation.

Reduced, validated PRF mechanism

In previous work **[20]** a reduced PRF mechanism was developed and validated for mixtures of n-heptane and iso-octane, containing 48 reactions and 39 species. Therein, the reduction and composition methodology of this mechanism and its numerical validation are presented. Also the experimental validation was carried out by using the same CFR engine as the one in this study. Thereby the model was validated by altering many physical and mechanical parameters such as the inlet temperature, the equivalence ratio, the compression ratio, the fuel composition. In the same previous work **[20]** the validation was carried out with respect to the addition of NO. This mechanism also produces good results with respect to the EGR parameters. Figures 8 and 9 show a comparison of experimental results and the mechanism, with respect to respectively the dilution by N_2 and the addition of CH_2O. The equivalence ratios are respectively 0,32 and 0,41 and the fuel used is PRF40.

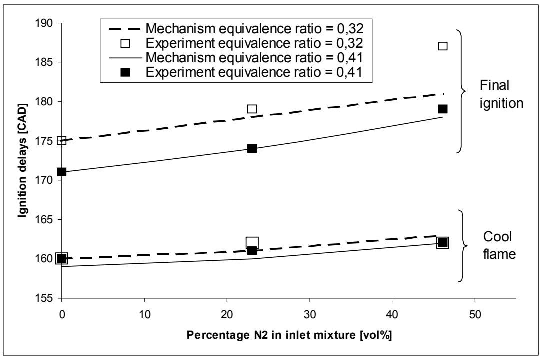

Figure 8: Comparison of the PRF mechanism and the experiments, regarding the influence of N_2 on the ignition delays at an equivalence ratio of 0,32 and 0,41 and PRF40 as the fuel

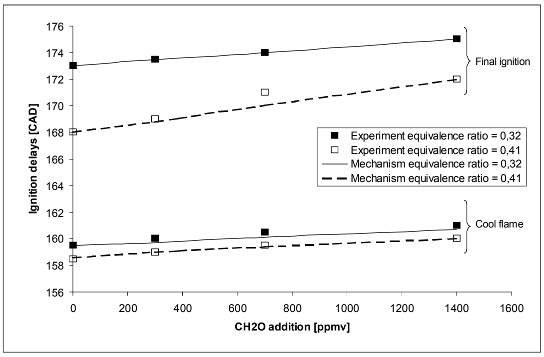

Figure 9: Comparison of the PRF mechanism and the experiments, regarding the influence of CH_2O in 23 vol% EGR on the ignition delays at an equivalence ratio of 0,32 and 0,41 and PRF40 as the fuel

Figures 8 and 9 clearly show that the reduced PRF mechanism is also validated experimentally with respect to the dilution (N_2) and formaldehyde. Along with previous work **[15,16,20]** it can be said the reduced PRF mechanism is validated for physical, mechanical and EGR parameters at HCCI engine inlet conditions. This allows for a much higher amount of data than can be collected by experimental work, to provide for a mapping of the ignition delays as a function of certain parameters. Since the extremities of the parameter range is validated, one may say that what the mechanism calculates within those extremities is rather correct, allowing for a complete image of the ignition delays. Figure 10 shows an example of this application of the reduced PRF mechanism, where the final ignition delay is presented as a function of the equivalence ratio and the addition of formaldehyde in 23 vol% EGR. The inlet temperature is 70 °C, the EGR temperature is also 70 °C, the compression ratio is 10,2 and the fuel used is PRF40. The experimental data are indicated with points.

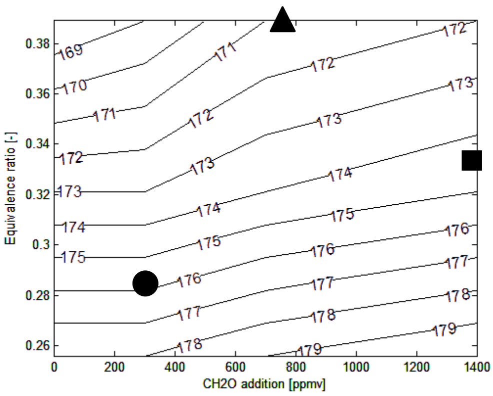

Figure 10: Iso-final ignition delays as a function of the equivalence ratio and the addition of

formaldehyde in 23 vol% EGR (70 °C) with an inlet temperature of 70 °C, a compression ratio of 10,2 and PRF40 as the fuel

The symbol ■ indicates a delay of 174,6 CAD, the symbol ▲ indicates 171,2 CAD and the symbol ● indicates 175,7.

The application can be performed for the other chemical species or EGR parameters. As such, the kinietic mechanism can be used for a multi-dimensional modelling research on the behaviour of the auto-ignition process, influenced by several parameters.

Conclusions

The influence of the different effects of EGR (diluting, thermal and chemical) on the cool flame and final ignition delays have been studied experimentally, using the fuels n-heptane and iso-octane. The diluting effect, represented by N_2 and CO_2 showed results that are in the line of expectance. The dilution reduced the overall reactivity, with CO_2 having the strongest effect. The importance of the fuel when studying the effect of EGR has been pointed out in this paper. In fact, the burn rate of the fuel could influence considerably the effect dilution can have on the auto-ignition. The type of fuel used is also of importance when considering the addition of chemical species as is pointed out by the addition of NO, where it had a slight promoting effect on the ignition delay of n-heptane combustion and a strong promoting and inhibiting effect on the ignition delay of a PRF40 fuel combustion, depending on the amount of NO added. The effect of the EGR temperature is kinetically quite clear. However, the effect of CO on auto-ignition using engine conditions was found to be rather insignificant, both in this study as in some of the literature. This effect should be studied in wider ranges, though not too wide, since a too great addition of CO would not be feasible in real engine situations. The effect of formaldehyde seemed to be quite clear, inhibiting the ignition delays by consuming the OH radicals. The effect of acetaldehyde stays ambiguous, finding also contradictory results with the literature. The largest effects were observed by the diluting species, while the EGR temperature and CO were of less interest. As for the chemical species NO and formaldehyde show quite responsive results for the ignition delays. In all, one would say that the chemical species NO and CH_2O with combination of a diluting species as N_2 or CO_2 are very interesting candidates for the control of the HCCI auto-ignition process. Finally, the reduced kinetic PRF mechanism has been validated satisfactorily for HCCI engine inlet conditions and it can be used for a more detailed study of the influence of minor species, present in EGR, on the auto-ignition process.

References

[1] M.S. Kumar, A. Ramesh, B. Nagalingam, Internat. J. of Hydrogen Energy 28 (2002) 1143-1154.
[2] C.J. Sung, Y. Huang, J.A. Eng, Combust. Flame 126 (2001) 1699-1713.
[3] P.F. Pinard, A.J. Higgins, J.H.S. Lee, Combust. Flame 136 (2003) 146-154.
[4] R.G. Papagiannakis, D.T. Hountalas, Applied Therm. Eng. 23 (2003) 353-365.
[5] T. Faravelli, A. Frassoldati, E. Ranzi, Combust. Flame 132 (2003) 188-207.
[6] D.L. Mitchell, J.A. Pinson, T.A. Litzinger, SAE International, Fuels & Lubricants Meeting & Exhibition SAE-932798, 1993.
[7] J. Li, J.O. Chae, S.B. Park, H.J. Paik, J.K. Park, Y.S. Jeong, S.M. Lee, Y.J. Choi, SAE International, International Congress & Exposition SAE-970322, 1997.
[8] G. Subramanian, A. Pires Da Cruz, L. Vervisch, R. Bonaceur, Proceedings of the European Combustion Meeting, 2005.
[9] Y. Yamaya, M. Furutani, Y. Ohta, The 6th International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines, 2004.
[10] K.C. Salooja, Combust. Flame 9 (1965) 373-382.
[11] F. Moore, C.F.H. Tipper, Combust. Flame 19 (1972) 81-87.
[12] N. Ladommatos, S.M. Abdelhalim, H. Zhao, Z. Hu, SAE International, International Spring Fuels and Lubricants Meeting SAE-961165, 1996.
[13] N. Ladommatos, S.M. Abdelhalim, H. Zhao, Z. Hu, SAE International, International Spring Fuels and Lubricants Meeting SAE-961167, 1996.
[14] N. Ladommatos, S.M. Abdelhalim, H. Zhao, Z. Hu, SAE International, International Spring Fuels and Lubricants Meeting SAE-971660, 1997.
[15] H. Machrafi, K. Lombaert, S. Cavadias, P. Guibert, J. Amouroux, Fuel 84:18 (2004) 2330-2340.
[16] H. Machrafi, K. Lombaert, S. Cavadias, P. Guibert, SAE - Internal Combustion Engines, 2005-24-035, 2005.
[17] J.B. Heywood, Fundamentals of Internal combustion, McGrawHill, 1988, p.573.
[18] P.G. Lignola, E. Reverchon, Prog. Energy Combust. Sci. 13 (1987) 75.
[19] A. Frassoldati, T. Faravelli, E. Ranzi, Combust. Flame 135 (2003) 97-112.
[20] H. Machrafi, Development and experimental validation of kinetic schemes for hydrocarbon mixtures for HCCI applications. Investigation of the auto-ignition process and the application to internal combustion engines, *PhD thesis*, 2006, Université Paris 6, Paris, France.