Reduced Chemical Reaction Mechanisms: Experimental and HCCI Modelling Investigations of Autoignition Processes of n-Heptane in Internal Combustion Engines

H. Machrafi, K. Lombaert, S. Cavadias, P. Guibert

Laboratoire de Mécanique Physique, CNRS UMR 7068, Université Pierre et Marie Curie,

2, Place de la Gare de Ceinture, 78210 Saint Cyr l'Ecole, France.

Tél: +33 1 30 85 48 90 – Fax : +33 1 30 85 48 99

ABSTRACT

A skeletal (27 species and 21 reactions) chemical reaction mechanism for n-heptane is constructed from a semi-detailed n-heptane mechanism (57 species and 290 reactions) of the Chalmers University of Technology in Sweden. The construction of the reduced mechanisms is performed by using reduction methods such as the quasi-steady-state assumption and the partial equilibrium assumption. The inlet temperature and the equivalence ratio are varied and ignition delays are calculated from pressure curves, using the reduced n-heptane mechanism for several engine parameters adhering to HCCI conditions : inlet temperature (303 ~ 365 K) and equivalence ratio (0,2 ~ 0,4). Subsequently the reduced mechanism is successfully numerically validated against the Chalmers mechanism and another more detailed mechanism provided LLNL (Curran et al. with 561 species and 2539 reactions).

Furthermore the results obtained from the reduced n-heptane mechanism are experimentally validated by experiments performed on a CFR engine, using the same parameters.

INTRODUCTION

In view of the environmental effects, strategy of the automobile industry implies developing new engines functioning with a low equivalence ratio, lower fuel consumption and consequently reducing CO2, NOx and particle emissions. Respecting the Euro IV emission norms in 2005 (Table 1), possibilities as the catalytic oxidation, the NOx traps and the particulate traps can be used, in other words: post-treatment. Concerning the emission reduction during the combustion process, HCCI Homogeneous Charged Compression Ignition) appears to be a good solution to respect the future Euro norms (Table 1).

Table 1 : Evolution of Euro standards for automotive emissions

Norm	HC [g/km]	CO [g/km]		NOx [g/km]		Particules [g/km]
	Gasoline	Gasoline	Diesel	Gasoline	Diesel	Diesel
Euro II 1992	--	2,20	1,00	--	--	0,10
Euro III 2000	0,20	2,30	0,64	0,15	0,50	0,05
Euro IV 2005	0,10	1,00	0,50	0,08	0,25	0,025
Euro V 2008 or 2010	in Establishment					

Using a lean burn combustion process at lower temperatures and a premixed air-fuel mixture, the HCCI combustion allows for a higher thermal efficiency, less NOx emissions and less particulate-matter emissions [1]. 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 and its combustion progression is much more complicated. Much research [2,3,4,5,6,7] is performed in investigating this auto-ignition for many compounds. A great part of the HCCI investigations use the so-called Primary Reference Fuels such as iso-octane and n-heptane [8]. This due to the great interest in improving the engine efficiency and reducing their pollution. Hydrocarbon ignition can occur

in two significantly different stages [2,3,4,9,10], which depends on the initial temperature (for example during n-heptane and n-decane combustion at low temperatures [2,11]).

HCCI CHEMISTRY

The first stage is initiated by a serie of reactions at the lower temperature zone (T < 700 K), of which the most important reactions are considered to be the formation of the heptyl radicals. The first reaction is the initiation reaction, in which n-heptane reacts with oxygen. After the H-abstraction step, the heptyl radical can subsequently react with molecular oxygen to form an alkylperoxy radical.

More intermediate peroxy species are formed. During this first stage, temperature and pressure increase slightly, causing the cool flame to occur. Then, the temperature continues to increase until reaching an intermediate temperature zone (700 – 1000 K) where small radicals such as HO_2 are formed. The HO_2 radicals react further with the fuel to form H_2O_2. Then OH, formed by the decomposition of H_2O_2, leads to the second stage combustion [12]. In this step, the OH radicals (far more important than other radicals formed from chain branching) consume the fuel (the cool flame ends), resulting into a sudden temperature rise and pressure increase (the second stage begins). Depending on the type of fuel and the thermodynamics evolution (of an engine, a RCM or stirred reactors), in some cases at a given pressure and for some low initial temperature (lower than ~750 K), the oxidation process slows down whereas the temperature increases. This is the main characteristic of the Negative Temperature Coefficient (NTC) regime. In this zone, the formation of HO_2 radicals becomes more important than the isomerisation reactions and the peroxide formations. HO_2 radicals are more stable than OH. Moreover, the propagation reaction with HO_2 is less exothermic than that with the OH radical [13]. Then, when the temperature is high enough for the OH reaction to become more important, the reaction rate increases with the temperature. After this region, at higher inlet temperatures (T>900 K), the ignition takes place in a single stage. In this paper the cool flame delay defined as the number of crank angle degrees, from the start of the compression (BDC), to the moment where the net heat release reaches it's first maximum. The second delay, is defined as the number of crank angle degrees, from the start of the compression, to the moment where the net heat release reaches it's second maximum.

As is mentioned previously, the HCCI chemistry is mainly controlled by the chemical kinetics at lower temperatures that precede the auto-ignition. Indeed, the HCCI combustion process could be applied widely in engine applications if precise prediction of ignition timing for variable experimental conditions is involved. So it is of great importance to understand the underlying mechanisms that are responsible for the ignition delay. The first reactions that govern the combustion initiation, are the following:

$$C7H16 + O2 \rightarrow C7H15\bullet + HO2\bullet$$
$$C7H16 + X\bullet \rightarrow C7H15\bullet + XH$$
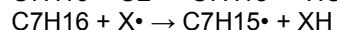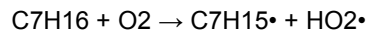
The X• in the second reaction is a radical. After the formation of heptyl radicals (C7H15*), these react further forming several peroxide radicals (C7H15OO*) starting with the reaction:

$$C7H15\bullet + O2 \rightarrow C7H15OO\bullet$$
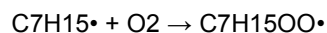
and eventually the hydroxyl radical OH* [14], via a sequence of reactions. These peroxide radicals and the hydroxyl radical play an important role in the oxidation process [12,14], since the reactions concerning the formation of the peroxide radicals and the hydroxyl radical release the energy that are the cause of the temperature and pressure rises (in addition of the compression stroke). Finally the hydroxyl radical consumes rapidly n-heptane, resulting into a rapid increase in the temperature and eventually the auto-ignition [2]:

$$H2O2 + M \rightarrow OH\bullet + OH\bullet + M$$
$$C7H16 + OH\bullet \rightarrow C7H15\bullet + H_2O$$
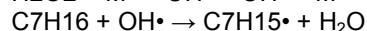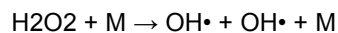
Here M denotes a third body, which could be any substance present in the cylinder. At higher temperatures (T > 1000 K), however, the reaction where n-heptane decomposes into two smaller radicals promotes the combustion process. This decomposition into smaller radicals and olefins govern the main combustion process which becomes a one-stage combustion [14,15].

EFFECTS OF THE PARAMETERS ON THE IGNITION DELAY

When implying HCCI combustion, the major problem that appears, is the control of the ignition delay. Several physical parameters affect the quality of the HCCI combustion and the ignition delay: mixture homogeneity, inlet temperature of air and fuel, fuel composition, kinetics of the fuel oxidation at lower temperatures and thermal effects (heat exchange, thermal loss to the wall, EGR ratio mixture quality) [2,11,14,16,17]. A better

understanding of the influence of these parameters on the ignition time is required, to have a more thorough knowledge of the HCCI combustion process and consequently of the application on an engine.

The main parameters, studied the most in the literature [2,11,14,16,17,18], are the inlet temperature and the equivalence ratio. In order to determine the influence on ignition delay, Ogink and Golovitchev [16] have performed modeling calculations on varying the inlet temperature (600 K to 1400 K) and pressure (10 atm to 40 atm). For iso-octane they have determined that a higher initial pressure and inlet temperature result into a lower ignition delay. Soyhan and Mauss [17] have determined the influence of the inlet temperature on the ignition delay, but only at inlet temperatures higher than 700 K. With respect to the influence of the inlet temperature on the ignition delay they have come to the same conclusion as Ogink and Golovitchev [16]. Gauthier et al. [18] performed stoichiometric n-heptane/air measurements a low-pressure shock tube near 2 and 11 atm at temperatures above 1200 K. To compare their data to the results of Fieweger et al. [19] they normalized their data to 13 bar, using a pressure scaling of $P^{-0.55}$ based on the correlation of Horning et al. [20]. Gauthier found also like Fieweger that the ignition delay decreased at increasing temperature, as well as a pronounced NTC region around 700 to 900 K. Depending on the experimental apparatus to measure the ignition delay (shock tube, RCM, reactors…), the application of these data to an engine is an extrapolation process which must be used with care. Most of the results are given in varying the temperature at a fixed pressure or varying the pressure at a fixed temperature, while in an engine both the temperature and pressure vary. The overall temperature evolution during the ignition process could be modified by a sort of a self combustion effect for instance if the dilution is not sufficient.

Specifically, to predict satisfactorily the auto-ignition delay in an engine, the pressure tendancy or the rate of heat release, it is necessary to use a realistic modelling of the chemical process with a lower inlet temperature. Since a large number of intermediate species participate in a great number of elementary reactions during fuel oxidation, it is very difficult to add this entire mechanism in a Computational Fluid Dynamics (CFD) code. Therefore, it is necessary to reduce a detailed mechanism and to determine the validity of the reduced mechanism, prior to its utilization for predicting the aerodynamic effects in an engine cylinder using CFD codes. This paper's main interest involves producing a reduced mechanism that predicts accurately the ignition delay and pressure curves for several equivalence ratios (0,2 ~ 0,4) and air inlet temperatures (303 ~ 365 K). Specific engine parameters (cylinder capacity 611 cm3, initial pressure 1 atm and engine speed 600 rpm) are used. In addition to previous experiments [16,17], very low temperatures are studied, since the goal of HCCI engines is to operate at lower temperatures.

In this paper, a description of the method used to reduce the n-heptane detailed chemical mechanism is presented and a validation of this mechanism on a CFR engine is also presented. The effects of the equivalence ratio and the inlet temperature on the ignition delay are presented as well.

REDUCTION OF THE N-HEPTANE MECHANISM

This section describes the reduction methodology of the n-heptane mechanism [21], developed and provided by the Chalmers University of Technology in Sweden, containing 290 reactions and 57 species. This mechanism has previously been validated successfully at the Chalmers University of Technology in a reactor between 10 and 40 bar [21]. Reduction is performed using Aurora, provided in Chemkin. 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 very accurate and only 5 % fluctuations on the ignition delays is allowed). The reduction is performed using a method developed by Peters in 1987 [21,23,24], which comprises several steps [13,24]. Firstly, using the analysis of the conversion rate of the reactant species, the redundant species were removed [22] from the Chalmers mechanisms. Secondly, by introducing the quasi-steady-state assumption [23] and, thirdly, the partial equilibrium assumption [22], obtaining 21 reactions and 27 species for the n-heptane mechanism (shown in the appendix). 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 [22,24] (on calculating the rate constants), with a short lifetime [25] and in small quantities (due to the high reactivity). For example, a certain species' concentration is very low [24] and constant due to the fact that it is produced very slowly and

consumed very rapidly. Here this species can be eliminated and the two concerning reactions can be merged into one, hereby eliminating one [22]. The partial equilibrium assumption is also a classical hypothesis whereby an equilibrium is assumed between the reaction rates in the direct and the inverse direction of certain reversible reactions that are very rapid [22,24]. This approach (or even just the quasi-steady-state assumption alone) proved to be successful for the construction of reduced chemical kinetic schemes [22,23,24,25] for the combustion of several hydrocarbons [14,26].

RESULTS AND DISCUSSION

NUMERICAL VALIDATION OF THE REDUCED N-HEPTANE MECHANISM

For the calculations a HCCI internal combustion engine model in Chemkin is used, having the same engine characteristics as presented in the section experimental set-up later on. To check the validity of the reduced mechanism, it was not only compared to the Chalmers n-heptane mechanism, but also to the more detailed mechanism provided by LLNL [27] by Curran et al. in USA (2539 reactions and 561 species). Figure 1 shows the cool flame and the final ignition delay values of n-heptane, calculated using the reduced n-heptane mechanism (n-hept21) and compared with the ones calculated by the detailed Chalmers and Curran n-heptane mechanisms.
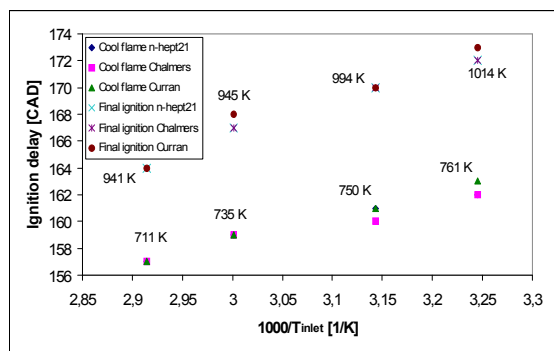

Figure 1 : Comparison different mechanisms with respect to the cool flame and final ignition delays of n-heptane combustion at a compression ratio of 10,2 and an equivalence ratio of 0,39, with at each delay the ignition temperature

Figure 1 shows that the cool flame and final ignition delay values of the reduced mechanism of n-heptane show good correspondance with the values of the detailed mechanisms of Chalmers and Curran.
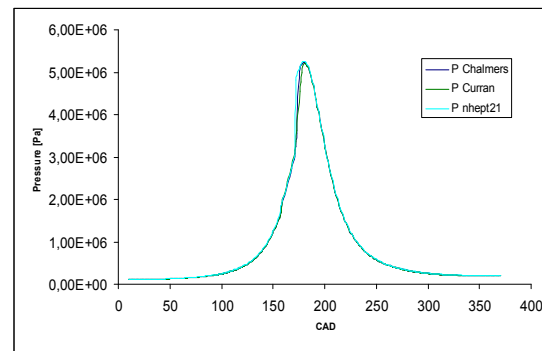

Figure 2 : Comparison different mechanisms with respect to the pressure curves, with a compression ratio of 12, an equivalence ratio of 0,2 and an inlet temperature of 365 K for n-heptane
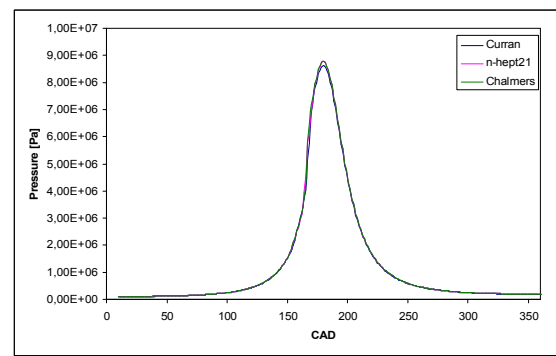

Figure 3 : Comparison different mechanisms with respect to the pressure curves, with a compression ratio of 18, an equivalence ratio of 0,3 and an inlet temperature of 350 K for n-heptane

Figures 2 and 3 show that the pressure curves of the reduced mechanism of n-heptane correspond well with those of the detailed mechanisms of Chalmers and Curran. The two numerical validations (ignition delay and pressure curves) are two classical criteria. One could complete this approach by introducing a comparison involving the heat release or the pollutants' emissions. The next paragraph expands the validation procedure by means of experiments performed on a CFR engine.

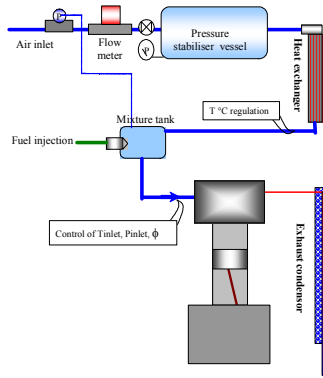EXPERIMENTAL VALIDATION BY A CFR ENGINE

Experimental set-up

Figure 4 : Schematic of the experimental set-up of the CFR engine

Figure 4 shows the experimental set-up of the CFR engine on which the experiments have been performed. In this paper, two parameters are mainly studied, the effects of the equivalence ratio and the inlet temperature. Table 2 shows characteristics of this CFR engine.

Table 2: CFR engine description

Compression ratio[a]	4 ~16
Bore	82,55 mm
Stroke	114,5 mm
Displacement volume	611 cm3
Engine connecting rod to crank radius ratio	3.26
Exhaust valve open	140 °ATDC
Exhaust valve close	15 °ATDC
Intake valve open	10 °ATDC
Intake valve close	146 °BTDC

[a] The compression ratio was always set at 10,2 for the experiments in this study.

<u>Comparison experimental results with modelling results</u>
This section shows the experimental validation of the reduced n-heptane mechanism by means of the experiments performed on the CFR engine. The effects of residual gasses in the CFR engine were compensated in the calculations by adding a mixture of N2, CO2 and O2 at a temperature of 1000 K consisting of a mass fraction of 6% of the initial fuel/air mixture.
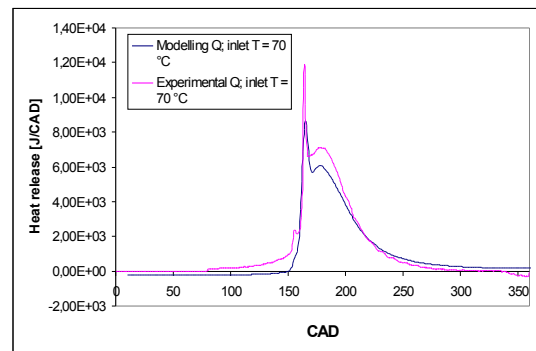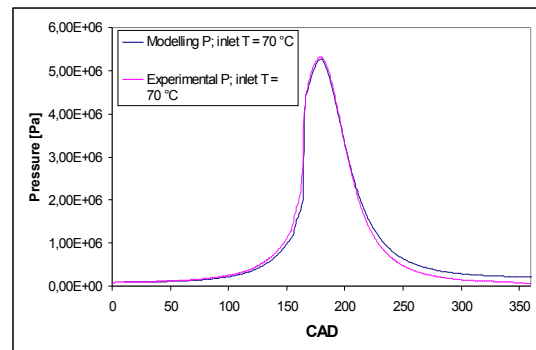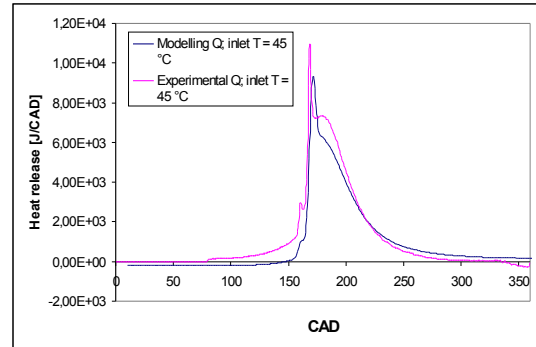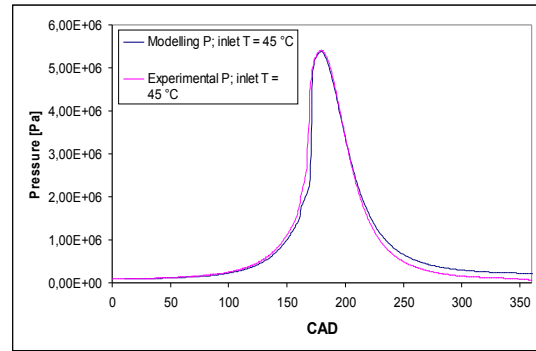

Figure 5 : In cylinder pressure and the comparison of experimental and modeling heat release. Experimental conditions : equivalence ratio 0.4 – inlet temperature 45 and 70 °C
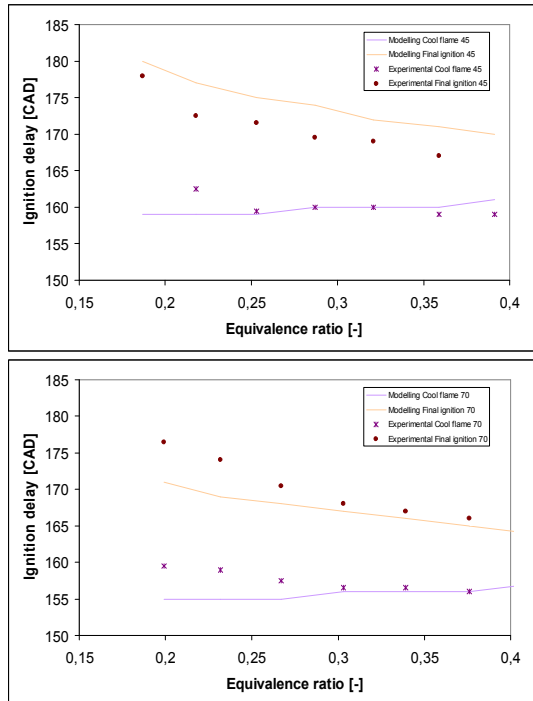
Figure 6 : Comparison of the calculations and the experimental results regarding the cool flame delays, the final ignition delays: Inlet temperature (a) 45 °C (b) 70°C

Figure 5 and 6 show the experimental validation of the n-heptane mechanism. The compression ratio is held at 10,2, while the inlet temperature for these results is chosen to be 45 or 70 °C, as is indicated in each of the figures. The fuel used is n-heptane. The pressure and the heat release curves presented are obtained with an equivalence ratio held at 0,4.

The pressure and the heat release curves show a good comparison between the n-heptane reduced model and the experiments on the CFR engine. The heat release shows a small discrepancy between the modeling and the experimental results, because of the following reasons: the reduction method was focused on the ignition delay and the cool flame phase, the wall heat transfer modelling is not yet well fitted in Chemkin and Chemkin simulates the cycle only in one homogeneous zone and does not take into account the real physical processes.
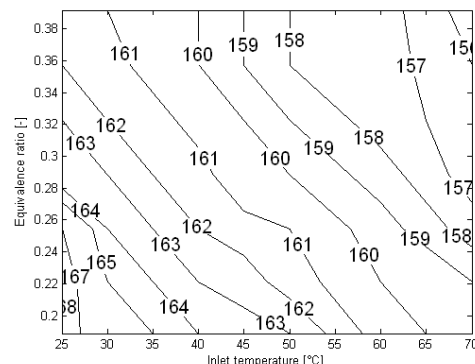
In Figure 6, the cool flame delays and the final ignition delays, calculated by the reduced n-heptane mechanism seem to correspond very well with the experimental results, especially at higher equivalence ratios. At lower equivalence ratios, the combustion is probably not optimal, a fact of which the mechanism does not take account. As a matter of fact, again the mechanism considers an ideal homogeneous mixture in the cylinder, which is not the case in the experiments.

In this section the reduced n-heptane mechanism is both numerically and experimentally validated and could be used for other purposes as the usage in a CFD code to examine the aerodynamics influence on the combustion process. The next section summarizes the trends that were observed from the experimental results obtained from the CFR engine.

EFFECTS OF THE PHYSICAL PARAMETERS ON THE IGNITION DELAYS

Figure 7 shows the cool flame delays and the final ignition delays obtained using n-heptane as the fuel. The compression ratio is held at 10,2, while the influence of the equivalence ratio and the inlet temperature on the ignition delays is examined. The equivalence ratio plays a role in the amount of fuel present for the formation of the peroxides, but as the formation of the peroxides does not need much fuel, the equivalence ratio does not influence much the cool flame delay. Nevertheless an increase in the equivalence ratio results into a decrease in the cool flame delay, because there is simply more fuel and thus more energy which cause the kinetics of the formation of the peroxides to accelerate, even slightly. As for the inlet temperature, it is clear that a higher inlet temperature accelerates the kinetics and thus decreases the cool flame delay, in the same way as it decreases the final ignition delay. The final ignition delay decreases when the equivalence ratio is increased, since this, as is the case for the cool flame delay – only much stronger –, provides more energy and enhances the chemical kinetics.
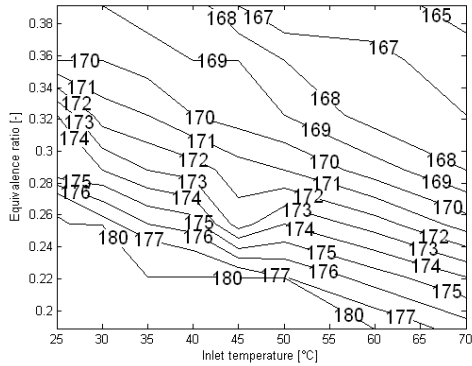
Figure 7 : The cool flame delays and the final ignition delays obtained from the experimental results from the CFR engine

Figure 8 : Pressure curves and heat release curves as a function of the inlet temperature at an equivalence ratio of 0,36, a compression ratio of 10,2 and n-heptane as the fuel
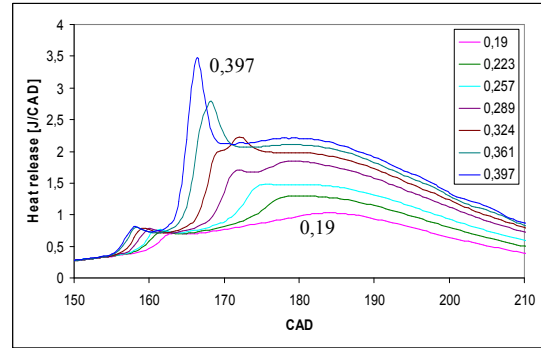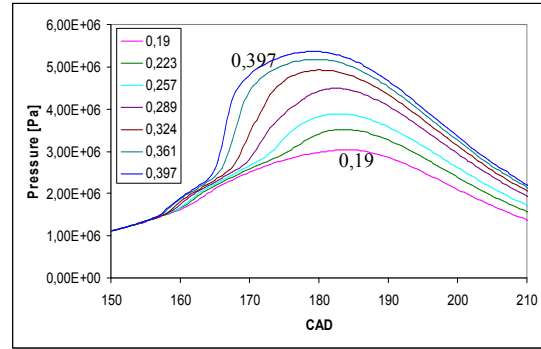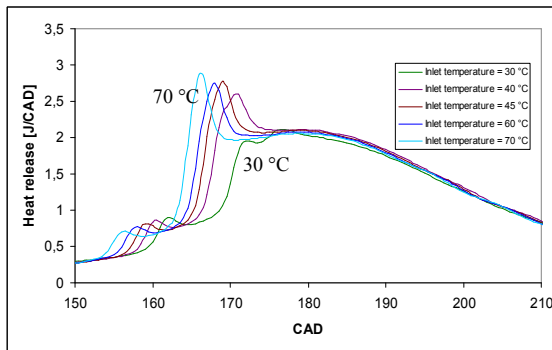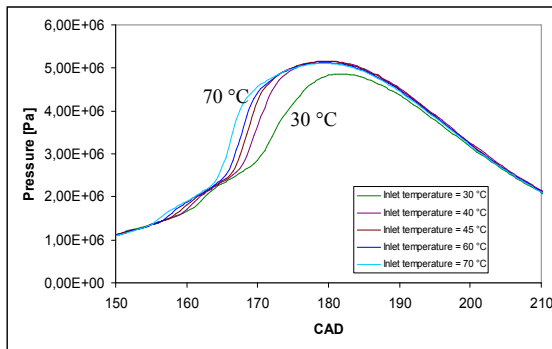

Figure 9 : Pressure curves and heat release curves as a function of the equivalence ratio at an inlet temperature of 50 °C, a compression ratio of 10,2 and n-heptane as the fuel

As figure 8 shows the maximum pressure and heat release are hardly influenced by the inlet temperature but rather by the equivalence ratio as figure 9 shows. This implies that the energy and power or work delivered to the piston is mainly delivered by the fuel, while the inlet temperature does not seem to play a major role for that matter. It appears from figure 8 that with the inlet temperature the auto-ignition timing could be predicted. The difference between the cool flame and the final ignition stays practically the same. So the inlet temperature can be used as a tool for choosing the start of the ignition, from the cool flame on. Figures 8 and 9 show also that there is a slow combustion right after the two ignitions, depicted by the long curve after the final ignition. The equivalence ratio seems to alter the final ignition delay much more than the cool flame delay. So the energy content and duration between the cool flame and the final ignition is largely influenced by the equivalence ratio and the equivalence ratio could be used as a tool for choosing the timing between the start of the ignition, the cool flame, and the final ignition.

CONCLUSION

The skeletal (27 species, 29 reactions) reduced chemical reaction mechanisms for n-heptane is constructed successfully from a detailed n-heptane mechanism (57 species and 290 reactions).

For HCCI conditions (equivalence ratio of 0,2 ~ 0,4 and inlet temperatures of 303 ~ 365 K) the calculated cool flame delays and final ignition delays by the reduced n-heptane mechanism as well as the pressure curves and the heat release curves are in good agreement with those obtained with the detailed Chalmers n-heptane mechanism and the detailed Curran n-heptane mechanism. Concerning the comparison of the reduced n-heptane mechanism with the CFR experimental results, the mechanism is successfully validated, though at equivalence ratios lower than ~ 0,25 a small difference is observed between the calculations and the experiments. This is probably due to a bad combustion, of which the mechanism does not take account. Nevertheless, generally, in the afore mentioned conditions, the mechanism's calculations correspond very well with the experimental results with regard to the ignition delays, the pressure curves and the heat release curves. The reduced n-heptane mechanism is considered both numerically and experimentally validated for HCCI purposes and can be perfectly used for future aerodynamics applications in CFD codes.

Concerning the ignition delay it is shown that it decreased with

- an increasing temperature,
- an increasing equivalence ratio.

However, fuel composition can also play an important role in the ignition and its effects will be studied for several mixtures of n-heptane and iso-octane. In a previous work a reduced mechanism of iso-octane has been validated numerically and experimentally. The possibility of a composition of these two reduced mechanisms will be investigated for a construction of a n-heptane/iso-octane mixture mechanism. A brief study of emissions emitted by the engine will be investigated as well.

REFERENCES

1   Huang Y., Sung C. J., and Eng J. A., Dilution limits of n-butane/air mixtures under conditions relevant to HCCI combustion. Combust. Flame 2004 ; 136 : 457-466.

2   Curran H.J., Gaffuri P., Pitz, W.J. and Westbrook C.K. A comprehensive modeling study of iso-octane oxidation. Combust. Flame 2002 ; 129 : 253-280.

3   Tanaka S., Ayala F. and Keck J.C. A Reduced Chemical Kinetic Model For HCCI Combustion Of Primary Reference Fuels In A Rapid Compression Machine. Combust. Flame 2003 ; 133 : 467-481.

4   Tanaka S., Ayala, F., Keck J. C. and Heywood J. B. Two-stage ignition in HCCI combustion and HCCI control by fuels and additives. Combust. Flame 2003 ; 132 : 219-239.

5   Griffiths J. F., MacNamara J. P., Sheppard C. G. W., Turton D. A. and Whitaker B. J. The relationship of knock during controlled autoignition to temperature inhomogeneities and fuel reactivity. Fuel 2002 ; 81 : 2219-2225.

6   C. Stan, P. Guibert, Thermodynamic aspects of auto-ignition generated combustion AIGC (Part I), MTZ, Part I, 2004

7   P. Guibert, S. Mokhtari, C. Morin, Experimental analysis of auto-ignition generated combustion AIGC, MTZ, Part II, 2004

8   ikas G. and Peters N., Kinetic Modelling of n-Decane Combustion and Autoignition. Combust. Flame 2001 ; 126 : 1456-1475.

9   H. Li, D.L. Miller, N.P. Cernansky 1996 Society of Automotive Engineers SAE-960498

10   Zheng, W. Yang, D.L. Miller, N.P. Cernansky 2002 Society of Automotive Engineers 2002-01-0423

11   Glassman I., Combustion, third edition, Academic Press ; 1996.

12   Blin-Simiand N., Rigny R., Viossat V., Circan S. and Sahetchian K. Auto-ignition of hydrocarbon/air mixtures in a CFR engine: experimental and modeling study, Combust Sci Technol 1993 ; 88 : 329-348.

13   Ogink R. and Golovitchev V., Generalized skeletal reaction mechanism for Aliphatic hydrocarbons (from methane to iso-octane) for CFD Engine Modeling. First Biennial Meeting of The Scandinavian-Nordic Section of the Combustion Institute, Göteborg, Sweden, 2001 : 151-156.

14   H.S. Soyhan, F. Mauss and C. Sorusbay Chemical Kinetic Modeling of Combustion in Internal Combustion Engines Using Reduced Chemistry 2002 Combustion Science and Technology 174 (11&12) 73-91

15   Lewis B. and Von Elbe G., Combustion, Flames and Explosions of Gases, 3rd edition, Academic Press ; 1987.

16   Aneja R., Bolton B., Hakim N. and Pavlova-Mackinnon Z., Attaining Tier 2 Emissions Through Diesel Engine and Aftertreatment Integration – strategy and experimental results. Eighth Diesel Engine Emissions Reduction Conference - Detroit ; 2002.

17   M. Senthil Kumar, A. Ramesh, B. Nagalingam Use of hydrogen to enhance the performance of a vegetable oil fuelled compression ignition engine 2002 International Journal of Hydrogen Energy 28 1143-1154

18   B.M. Gauthier, D.F. Davidson, R.K. Hanson Shock tube determination of ignition delay times in full-blend and surrogate fuel mixtures 2004 Combustion and Flame 139 300-311

19   K. Fieweger, R. Blumenthal and G. Adomeit Self-ignition of S.I. Engine Model Fuels: A Shock Tube Investigation at High Pressure 1997 Combustion and Flame 109, 599-619

20   D.C. Horning, D.F. Davidson, R.K. Hanson, Study of the High-Temperature Autoignition of n-Alkane/O/Ar Mixtures 2002 Journal Propulsion Power 18, 363-371

21   Golovitchev V semi-detailed mechanism of n-heptane, www.tfd.chalmers.se/~valeri/MECH.html janv-04

22   Warnatz J., Maas U. and Dibble R.W. Combustion Physical and chemical fundamentals, modelling and simulation, experiments, pollutant formation, 2000, 3rd. edition. Springer

23   Banerjee I. and Ierapetritou M. G. Development of an adaptive chemistry model considering micromixing effects 2003 Chem. Eng. Sci 58 4537-4555

24   Dixon-Lewis G Computer modeling of combustion reactions in flowing systems with transport : combustion chemistry 1984 Springer-Verlag

25   Lovas T., Nilsson D. and Mauss F. Automatic reduction procedure for chemical mechanisms applied to premixed methane/air flames 2000 Twenty-Eighth Symposium (International) on Combustion 1809-1815

26   Simon Y., Scacchi G. and Baronnet F. Etude des réactions d'oxydation du n-heptane et de l'isooctane 1996 Can. J. Chem. 74 1391-1402

27   Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. V. Callahan, and F. L. Dryer Complete mechanism for the oxidation of n-heptane, http://www-cms.llnl.gov/combustion/combustion2.html#n-C7H16_detailed_mechanism December 2004

APPENDIX – REACTION SCHEME OF THE REDUCED N-HEPTANE MECHANISM

$k = A\,T^b\exp(-E_a/RT)$				
Reaction number	Reaction	A [mole-cm-s-K]	b [-]	E_a [J/mole]
1	C7H16+O2=>C7H15-2+HO2	2.80E+14	0.00	197533
2	C7H16+OH=>C7H15-2+H2O	4.80E+09	1.30	2891
3	C7H16+HO2=>C7H15-2+H2O2	1.00E+13	0.00	70966
4	C7H15-2+O2=C7H15O2	2.00E+12	0.00	0
5	C7H15O2=C7H14O2H	6.00E+11	0.00	85327
6	C7H14O2H+O2=C7H14O2HO2	2.34E+11	0.00	0
7	C7H14O2HO2=>C7KET21+OH	2.97E+13	0.00	111788
8	C7KET21=>C5H11+CO+CH2O+OH	1.00E+16	0.00	177520
9	C5H11=>C2H5+C3H6	3.20E+13	0.00	118486
10	C3H6+OH=>CH3CHO+CH3	3.50E+11	0.00	0
11	CH3CHO+OH+M=>CH3+CO+M+H2O	1.80E+17	0.00	60290
12	CH3O(+M)=CH2O+H(+M)	2.00E+13	0.00	114802
	Low pressure limit	2.34E+25	-2.70	128116
13	CH3+HO2=>CH3O+OH	4.30E+13	0.00	0
14	CO+OH=>CO2+H	3.51E+07	1.30	-3174
15	O+OH=>O2+H	4.00E+14	-0.50	0
16	H+O2+N2=>HO2+N2	2.60E+19	-1.24	0
17	HO2+HO2=>H2O2+O2	2.00E+12	0.00	0
18	OH+OH(+M)=H2O2(+M)	7.60E+13	-0.37	0
	Low pressure limit	4.30E+18	-0.90	-7118
	Troe coefficients 0.7346; 94; 1756; 5182	--	--	--
	Enhancement factors	--	--	--
	H2 2.00	--	--	--
	H2O 6.00	--	--	--
	CH4 2.00	--	--	--
	CO 1.50	--	--	--
	CO2 2.00	--	--	--
	N2 0.70	--	--	--
19	CH2O+OH+O2=>H2O+HO2+CO	6.69E+14	1.18	-1871
20	C2H4+OH=>CH2O+CH3	6.00E+13	0.00	4019
21	C2H5+O2=>C2H4+HO2	2.00E+10	0.00	-9211