The effects of the exhaust gas recirculation on the autoignition of ternary n-decane/n-butylbenzene/n-propylcyclohexane mixtures

Andrea Comandini*, Thomas Dubois, Nabiha Chaumeix
ICARE-CNRS, 1C avenue de la recherché scientifique, 45071 Orléans, France

1   Introduction

The well-known adverse effects of pollutants both on human health and on the environment have triggered over the years a series of international regulatory actions characterized by more and more stringent standards for the emissions from ground and aero transportation engines. In order to comply with such requirements, engine manufacturers have implemented a series of mitigation techniques aimed at reducing the formation of pollutants, including carbon dioxide (CO_2), nitrogen oxides (NOx), and particulate matter (PM), in modern high-pressure combustion devices. In particular, among the various strategies developed for the reduction of NOx and PM emissions from diesel engines, the use of homogeneous charge compression ignition (HCCI) and exhaust gas recirculation (EGR) provides substantial benefits to engine performance. In fact, by diluting the fresh gases with a considerable percentage of gas exhausts, a lower overall equivalence ratio is attained which results in a decrease in soot production as well as fuel consumption. In addition, lower temperatures are reached during the combustion process with positive effects on NOx emissions.

The development of optimized HCCI engines necessitates accurate chemical kinetic models for both the fuel decomposition and the consequent pollutants formation, validated against experimental results such as ignition delay times and species measurements. On the other hand, real fuels are composed of hundreds of components and such complexity poses serious limitations to the development of detailed kinetic models. Thus, surrogate mixtures containing few species representative of the main classes of hydrocarbons in the real fuels are commonly used in practical applications. In particular, diesel fuels for HCCI engines are composed of three major classes of compounds, i.e. the paraffins, the aromatics, and the naphthenes. The purpose of the present investigation is to study the effects of EGR on the ignition delay times of highly diluted 4:3:3 mixtures of n-decane:n-butylbenzene:n-propylcyclohexane chosen as representative of the above mentioned diesel hydrocarbon classes.

2   Experimental and modeling techniques

Experimental apparatus. Ignition delay time measurements were obtained using a heated stainless steel shock tube. The shock tube is composed of a low pressure 5.15 m long driven section with 52.5 mm internal diameter and a high pressure 2 m long driver section (114.3 mm i.d.). The whole experimental apparatus is heated to 130 °C to avoid any condensation. The double diaphragm technique was used to generate the shock waves by rupture of two Terphane polyester diaphragms

located in series between the driven and the driver sections. The driven section is equipped with four piezoelectric sensors CHIMIE METAL A25L05B placed along the internal wall of the tube. The pressure profiles from the four sensors provide the measurement of the incident shock wave velocities. Such velocities are subsequently used together with the initial conditions to calculate the pressure and temperature conditions behind the reflected shock waves by solving the conservation equations. The method used for the calculations assumes thermal equilibrium and no reaction before ignition as well as variable γ (ratio between heat capacity at constant pressure and heat capacity at constant volume, Cp/Cv) to completely account for the effects of the fuel and oxygen concentrations on the reflected shock temperatures. The estimated errors in the temperature and pressure calculations are respectively 1% and 1.5%. A fifth pressure sensor is mounted at the end-wall perpendicularly to the flow to monitor the pressure in the tube during the observation time. Part of the experiments was conducted using a PCB 102A06 pressure transducer as end-wall sensor. In addition, spectrophotometric measurements were performed using a HAMAMATSU R928 photomultiplier with a narrow band filter at 431 nm for the CH* radicals and a HAMAMATSU 1P28 photomultiplier with filter at 307 nm for the OH* radicals. In the present work, the ignition delay time is defined as the time between the arrival of the incident shock wave at the end-wall and the time when the OH* profile reaches 50% of its maximum value. Uncertainty in the ignition delay time measurement is around 25%. Reagent mixtures composed of n-decane (Sigma-Aldrich, 99+%), n-butylbenzene (Aldrich, 99+%), n-propylcyclohexane (Aldrich, 99+%), and EGR gases, if any, diluted in 99% argon (Air Liquide, 99.999%) were prepared manometrically in a 30 L stainless steel stirred tank. For the experiments conducted with EGR gases, a 40% dilution of the reagent mixture typical of HCCI engines was assumed. The EGR composition is defined as follows: 78% N_2 + 11% O_2 + 7% CO_2 + 4% H_2O. The gas mixtures studied herein are summarized in Table 1.

Table 1: Mixture compositions in mole fraction

	Φ	n-$C_{10}H_{22}$	n-C_9H_{18}	n-$C_{10}H_{14}$	O_2	H_2O	CO_2	N_2	Ar
ternary	1.5	3.80E-4	2.85E-4	2.85E-4	9.06E-3	-	-	-	9.90E-1
	1.0	2.70E-4	1.95E-4	1.96E-4	9.34E-3	-	-	-	9.90E-1
	0.5	1.35E-4	1.02E-4	1.02E-4	9.68E-3	-	-	-	9.90E-1
	0.4	1.07E-4	8.00E-5	8.00E-5	9.75E-3	-	-	-	9.90E-1
	0.3	8.40E-5	6.30E-5	6.30E-5	9.80E-3	-	-	-	9.90E-1
	0.2	5.50E-5	4.10E-5	4.00E-5	9.87E-3	-	-	-	9.90E-1
ternary +EGR	1.5	2.47E-4	1.83E-4	1.84E-4	5.84E-3	1.53E-4	2.74E-4	3.12E-3	9.90E-1
	1.0	1.68E-4	1.26E-4	1.26E-4	6.00E-3	1.53E-4	2.75E-4	3.14E-3	9.90E-1
	0.5	8.70E-5	6.50E-5	6.50E-5	6.25E-3	1.53E-4	2.74E-4	3.12E-3	9.90E-1
	0.4	7.10E-5	5.30E-5	5.30E-5	6.29E-3	1.54E-4	2.77E-4	3.15E-3	9.90E-1
	0.3	5.40E-5	4.00E-5	4.00E-5	6.31E-3	1.55E-4	2.78E-4	3.17E-3	9.90E-1
	0.2	3.50E-5	2.70E-5	2.70E-5	6.38E-3	1.52E-4	2.79E-4	3.11E-3	9.90E-1

Chemical kinetic model. To the best of our knowledge, this work represents the first study on mixtures containing the three proposed components. Thus, a preliminary chemical kinetic model has been developed based on the single-component kinetic models available in literature. In particular, both the n-decane chemistry, which includes the base C0-C4 submechanism, and the n-propylcyclohexane chemistry were taken from JetSurF version 2.0 (Wang et al. [1]). The JetSurF model was coupled to the aromatic chemistry for n-butylbenzene from the work by Mzé-Ahmed [2] and Diévart [3]. The interactions between the chemistry of the various components are accounted for by the reactions of the components with the small radicals in the C0-C4 submechanism as in the original models. The blended model was tested against the n-butylbenzene data available in literature. The analysis showed that the model is able to simulate reasonably well the high-pressure jet stirred reactor [4] and shock tube data

[5], although at atmospheric pressure conditions the reactivity of n-butylbenzene is overestimated. The development of a comprehensive model for n-butylbenzene is beyond the scope of the present investigation, thus a detailed analysis and validation of the blended model will not be presented herein. All the simulations have been performed assuming constant volume conditions behind the reflected shock waves using Cosilab software, version 3.3.2 [6].

3   Results and discussion

Although several works have been performed in the past on the single components, including ignition delay measurements on n-decane [7–13], n-butylbenzene [5, 14–15], and n-propylcyclohexane [16], no data are available in the literature on the proposed mixture. First the ternary mixture has been studied as a base for the subsequent addition of EGR gases. Experiments have been conducted in the temperature range between 1243 K and 1745 K, at nominal pressure of 10 bar, and equivalence ratios between 1.5 and 0.2 (refer to Table 1 for mixture compositions). Selected experimental and modeling results for various equivalence ratio conditions are presented in Figure 1a. As expected, the reduction in the fuel concentrations from rich to lean mixtures leads to a decrease in the ignition delay times. This trend is well reproduced by the model which simulates quite accurately the experimental global activation energy of the ignition process. It is also noticeable how the experimental ignition delay times are well reproduced by the model at fuel lean conditions although slightly overpredicted at rich conditions. This suggests the necessity of additional modeling work on the pyrolytic mechanisms as well as the possible interactions between the chemistry of the various components.

Additional experiments have been performed in the presence of a 40% EGR component at similar conditions to the ones implemented in the ternary mixture study (T = 1263 K – 1829 K, p ~ 10 bar, and overall equivalence ratio between 1.5 and 0.2). The results, reported in Figure 1b, reproduce the same experimental and modeling trends observed in the first part of the study. Once again the model well simulates the global activation energy with slight overprediction of the ignition delay times at fuel rich and stoichiometric conditions.
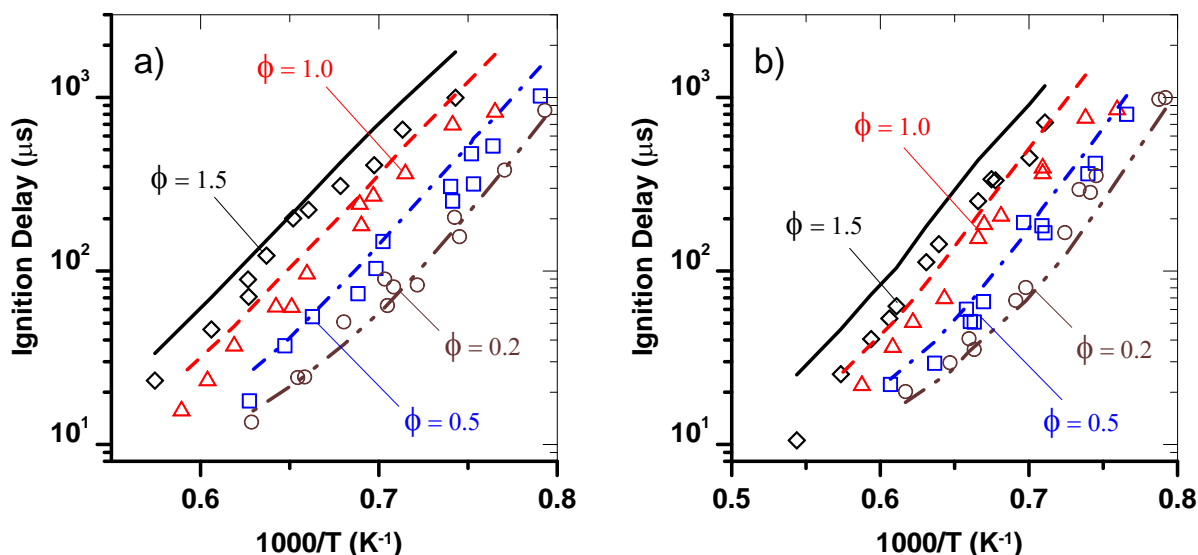

Figure 1. Ignition delay times of highly diluted mixtures in 99% argon; a) ternary; b) ternary + EGR. Experiments represented by symbols and simulations by lines.

In order to assess the influence of the EGR on the ignition delay times, a comparison between the different experimental results is necessary. In view of the practical relevance to HCCI engines, where the global equivalence ratio is controlled by adjusting the flows of fresh fuel, air, and EGR gases, ignition delay data for similar overall equivalence ratios have been compared. In figure 2, an exemplificative case for stoichiometric mixtures is reported. As expected, the presence of the EGR gases increases the ignition delay of the mixture for all the conditions studied, with an average measured increment which varies between 17.5% at $\Phi = 1.5$ and 50.7% at $\Phi = 0.2$. If all the experimental data sets are considered, the overall average ignition delay time increase due to EGR is close to 31%. Since this value was obtained by comparing the exponential fits of numerous experimental measurements obtained using the same experimental apparatus and procedure, the 31% increase due to the EGR can be considered significant even if the uncertainty on a single ignition delay time measurement corresponds to a maximum of 25%.
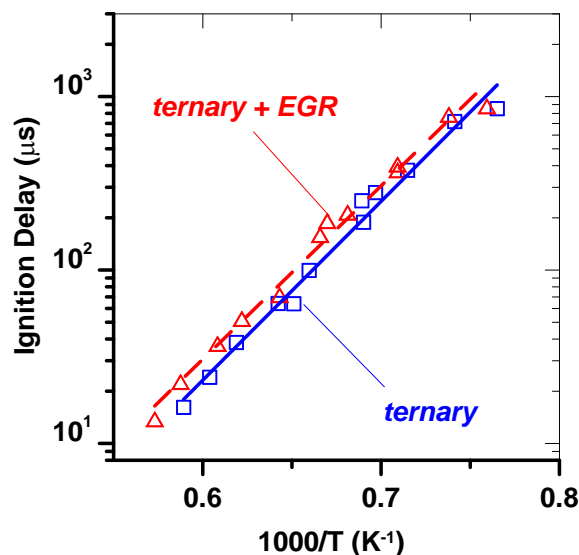
Figure 2. Ignition delay time measurements for ternary and ternary + EGR mixtures at stoichiometric conditions. The lines represent the exponential fit of the experimental data.

Although the experimental results clearly confirm that in real engine conditions the use of the exhaust gas recirculation technique will slow the fuel autoignition as depicted in Figure 2 for the ternary mixture studied herein, it is worth mentioning that the measured EGR effects could be due to two major factors, namely the chemistry of the fuel burning process and the decrease in the fuel concentration due to dilution. In order to determine the relative importance of these two factors, further analyses are required. First, the overall correlation for the ignition delay times of the ternary mixtures has been derived as

$$\tau(\mu s) = 5.28 \cdot 10^{-6} \times [fuel]^{0.92} \times [O_2]^{-1.20} \times \exp\left(+23216/T\right)$$

In this expression, the coefficient for the oxygen concentration has been imposed as similar to the coefficients derived from the studies performed on the single components n-decane, n-butylbenzene, and n-propylcyclohexane (data not presented here). A variation in the assumed coefficient does not cause a substantial change in the derived parameters since the oxygen concentrations do not vary considerably over the different experimental sets.

The correlation has been subsequently used to estimate the ignition delay times for hypothetical ternary mixtures having initial fuel and oxygen concentrations similar to the ones present in the corresponding ternary + EGR mixtures. The comparison between these estimates and the experimental measurements, presented in Figure 3a for stoichiometric conditions, clearly indicates that the chemistry of the fuel decomposition is not strongly affected by the presence of the EGR gases. Thus, the effects observed in Figure 2 are mainly due to the dilution of the fuel component. Similar results have been obtained for all the experimental sets with equivalence ratios between 1.5 and 0.3 where the ignition delay times from the correlation and from the experiments agree within the experimental uncertainties, while an average variation of 37.5% has been observed for $\Phi = 0.2$. It is not clear at the moment if such discrepancy is due to real chemical effects or to the summation of errors in the correlation for the specific conditions.

In order to further support the hypothesis that the experimental variation in the ignition delay times due to the presence of an EGR component is primarily a function of the dilution, additional modeling

tests have been performed. In this case the simulations of the ternary + EGR experimental results have been compared to simulations conducted at similar conditions with the main components of the EGR gas (CO_2, H_2O and N_2) replaced with argon. Selected modeling results for stoichiometric conditions are presented in Figure 3b. No appreciable difference between the two modeling sets has been observed for all the conditions considered in the present investigation, with a maximum discrepancy of around 5% obtained at stoichiometric conditions. This value is much lower than the average increase of 31% observed experimentally, thus the modeling results support the above mentioned hypothesis that the presence of the EGR has mainly a physical effect on the ignition delay.
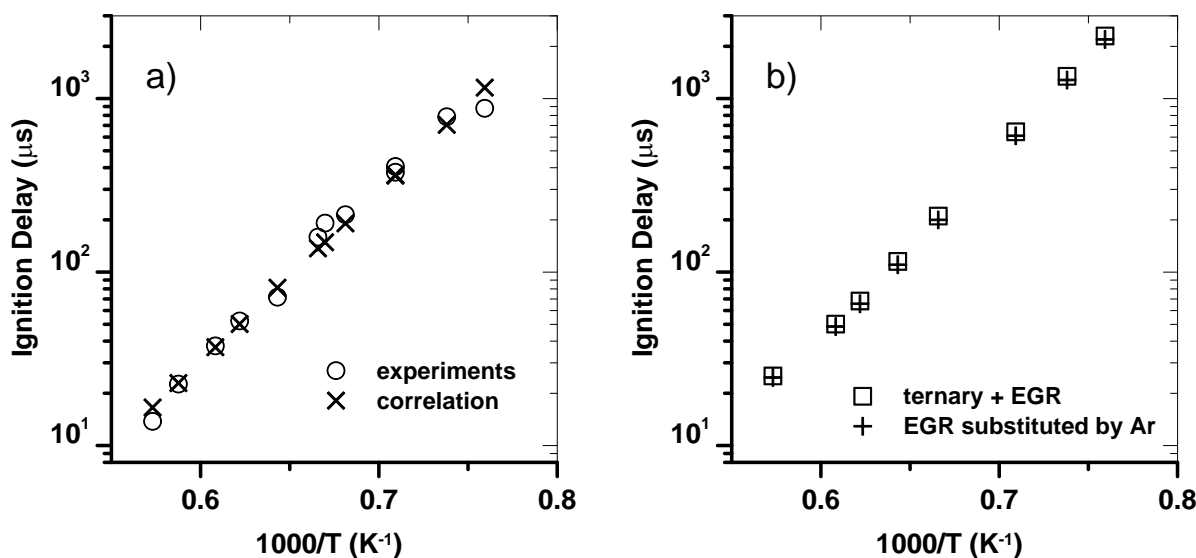

Figure 3. Ignition delay times at stoichiometric conditions; a) ○ experimental results on ternary mixture with EGR, × correlation predictions for ternary mixture; b) simulations on: □ ternary mixture with EGR, + EGR components substituted by Ar.

4 Conclusions

The effects of the presence of an EGR component on the autoignition of highly diluted n-decane:n-butylbenzene:n-propylcyclohexane mixtures have been studied both experimentally and numerically at conditions relevant to HCCI applications. Shock tube experiments have been performed on both ternary and ternary + EGR mixtures over a wide range of temperatures and stoichiometric conditions. In addition, a chemical kinetic model has been developed based on models available in literature; the simulations well reproduce both the experimental trends and the global activation energy, although the ignition delay times of fuel rich and stoichiometric mixtures are slightly overpredicted by the model.
The comparison between the experimental results shows that for similar stoichiometric conditions the average increase in the ignition delay times due to the EGR component is almost 31%. Further experimental analyses suggest that such an increment is mainly due to the different fuel dilution levels and not to the fuel decomposition chemistry. This hypothesis has been confirmed by additional simulation results performed using the chemical kinetic model.

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