AUTOIGNITION OF A GASOLINE SURROGATE CONTAINING VARIOUS BLEND RATIOS OF ETHANOL: SHOCK TUBE EXPERIMENTS AND DETAILED KINETIC MODELING

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Abstract

Autoignition delay times were measured behind reflected shock waves for a gasoline surrogate (50% *iso*-octane / 35% toluene / 15% 1-hexene by mole %) containing various blend ratios of ethanol (10, 20, 50 and 85% by mole %). Experiments were performed under stoichiometric conditions around 200 kPa and for temperatures ranging from 1220 to 2315 K. Results show that the addition of ethanol decreases the ignition delay. This decrease in the delay is however not proportional to the blended amount of ethanol as most of the reduction was achieved with an addition of 20% ethanol. A detailed kinetic model developed in a former study was used to successfully predict the results.

Introduction

Ethanol is nowadays the most widely used biofuel for road transportation [1]. Although ethanol has been considered as an alternative fuel for compression ignition [2] and homogeneous charge compression ignition (HCCI) [3] engines, its physical and combustion properties make it a very suitable fuel component for spark ignition (SI) engines [1]. Ethanol can be blended with gasoline at various ratios or even employed pure with minor engine modifications [4]. Beside the renewable nature of ethanol, one of its most attractive properties is to be a good octane enhancer for SI engines.

Research and motored octane numbers (RON and MON, respectively) use *iso*-octane and *n*-heptane mixtures to estimate the autoignition propensity of fuels. The autoignition is a crutial combustion property for SI engine fuels, since autoignition leads to knock which can rapidly damage the engine. In the other hand, preventing knock by restricting the advance of the spark timing limits the engine efficiency. This indicates that fuels which are not prone to autoignition are wanted for SI engines.

Recent literature shows that octane numbers are however not always fully adequate to characterize the autoignition propensity of modern engines [5] and, consequently, Andrae et al. [6] and Fikri et al. [7] stated that autoignition would be ideally defined by modeling the autoignition chemistry as function of temperature and pressure. In order to help for the development and for the validation of models capable of predicting autoignition, these authors performed shock tube experiments to measure the autoignition delay times (τ_{ind}) of model gasoline, so-called gasoline surrogates, constituted of a little number of components. These model gasolines are necessary for this kind of study because of the complexity of transportation fuels derived from crude oil (hundreds of hydrocarbons in which a few

individual hydrocarbons exceed 1% in volume) that makes impossible to follow in detail the physical and chemical processes involved in combustion [8].

Over the past few years, only a small number of studies dealing with τ_{ind} measurements of gasoline surrogates in shock tubes can be found into literature [7, 9, 10, 11, 12]. Amongst these studies, a few mixtures containing ethanol were investigated (in mole %): ethanol (41%) / *iso*-octane (14.5%) / *n*-heptane (44.5%) [7], ethanol (62.5%) / *iso*-octane (20.8%) / *n*-heptane (6.4%) / toluene (10.3%) [11]; and ethanol (48.7%) / *iso*-octane (51.3%) and ethanol (20.8%) / *iso*-octane (22%) / *n*-heptane (18.2%) / toluene (28.9%) / diisobutylene (10.1%) [12]. Within these studies, the amount of ethanol was however fixed at a given percentage for each surrogate, thus preventing a study of the effect of the ethanol concentration on the ignition delay time. Moreover, there is no available comparison between results obtained without and with ethanol.

The aim of this work is to investigate the effect of the ethanol amount when blended with a gasoline surrogate by focusing on the autoignition properties using a shock tube. This gasoline surrogate was studied in a former study [9] and is constituted of *iso*-octane (50%) / toluene (35%) / 1-hexene (15%) (mole %). The effect of ethanol on the autoignition properties of this surrogate was investigated by adding 10, 20, 50 and 85% of ethanol (% mole). Corresponding mixtures are labeled E10, E20, E50 and E85, respectively. The mixture labeled E0 in this study corresponds to the gasoline surrogate without ethanol, as studied in [9]. The detailed kinetic mechanism developed previously by Yahyaoui *et al.* [9] was used to model the experiments with ethanol.

Experimental Setup

Experiments were carried out behind reflected shock waves. A shock tube, with a 2 m long metallic high pressure driver section and a 9 m long pyrex low pressure driven section with a 50 mm internal diameter, was used. Both sections of the shock tube were evacuated using two primary vacuum pumps. The shock velocity was measured via four pressure transducers equally spaced by 150 mm, mounted flush with the inner surface of the tube, the last one being 10 mm before the shock tube end wall. At the same plane as the last pressure transducer, a fused silica window (9 mm optical diameter and 6 mm thickness) is mounted across a Jobin-Yvon monochromator, M25, equipped with a UV-sensitive photomultiplier, R928. The monochromator was set to 306 nm which is characteristic of OH emission. Both pressure and emission signals were transferred and registered using digital oscilloscope

The shock wave velocity was deduced from the pressure jump monitored by the pressure transducers. Reflected shock conditions (P_5, T_5) were calculated from standard procedure [13]. The high pressure gas used is He (purity > 99.995%) distributed by Air Liquide. The reactive gas mixtures were prepared using the partial pressure method with iso-octane (C_8H_{18}) from Acros Organics (99.5%), toluene (C_7H_8) (Aldrich > 99.5%), 1-hexene (C_6H_{12}) (Aldrich 99%), O_2 (Air liquide 99.999%), ethanol (C_2H_5OH) (Aldrich > 99.8%), Ar (Air liquide 99.999%), in a 10 l Pyrex glass bulb. The liquid hydrocarbons were degassed several times before to prepare the mixtures. Pure hydrocarbons are liquid at ambient temperature so that they had to be vaporized under vacuum conditions. The vapor pressure of the liquid hydrocarbons was maintained below the saturated vapor pressure. To ensure homogeneous composition, mixtures were mixed for 1 to 2 hours. The experimental conditions investigated during this study are summarized in Table 1.

Table 1: Experimental condition investigated during this study

	C_8H_{18} (mole %)	C_7H_8 (mole %)	C_6H_{12} (mole %)	C_2H_5OH (mole %)	O_2 (mole %)	Argon (mole %)	T_5 (K)	P_5 (kPa)
E10	0.45	0.315	0.135	0.1	9.975	89.025	1345-1790	183±20
E20	0.4	0.28	0.12	0.2	9.2	89.8	1325-1670	194±5
E50	0.25	0.175	0.075	0.5	6.875	92.125	1220-2170	170±50
E85	0.075	0.0525	0.0225	0.85	4.16	94.84	1310-2315	150±30

Experimental results

The autoignition delay time is defined in this study as the time interval between the moment at which the gas mixture is heated up to the reflected temperature, T_5, and the moment corresponding to 50% of the maximum intensity of the OH emission signal at 306 nm (see [9] for more details). Experimental results for the different mixtures investigated are summarized in Table 2:

Table 2: Ignition delay times and conditions behind the reflective shock waves for the mixtures investigated in this study under stoichiometric conditions.

P_5 (kPa)	T_5 (K)	Ignition delay (µs)	P_5 (kPa)	T_5 (K)	Ignition delay (µs)
E10			**E50**		
204	1347	977	170	1220	2111
199	1382	905	180	1260	1540
186	1400	716	193	1362	805
184	1498	361	137	1511	240
175	1582	195	140	1619	78
165	1602	168	123	1620	81
178	1737	49	133	1756	25
176	1789	33	218	2167	5.2
E20			**E85**		
191	1325	993	178	1307	918
198	1404	383.6	179	1377	512
196	1432	323	171	1394	372
189	1508	118	123	1429	319.2
198	1603	48.3	162	1509	122
199	1670	28.2	148	1601	49.1
			158	1765	13.2
			147	1788	8

The data provided in table 2 are plotted in Figure 2. As can be seen from this figure, the presence of various amount of ethanol tends to decrease the ignition delay in the range of conditions investigated with E0. However, this decrease appears to be not directly proportional to the amount of ethanol introduced. Indeed, the comparison between E10 and E20 shows an important reduction in the ignition delay with the increase of ethanol, whereas E20 and E85 exhibit similar ignition delay times at a given temperature. The E50 exhibits even longer ignition delays than the E20 above 1300K. Another noticeable result is the fact that the energy of activation is reduced by at least 33kJ/mol when ethanol is added (a value of 226 kJ/mol was found for E0). It is also interesting to note that E20 and E85 present a similar

activation energy around 192±1 kJ/mol while another value can be found for E10 and E50 (150±5 kJ/mol).
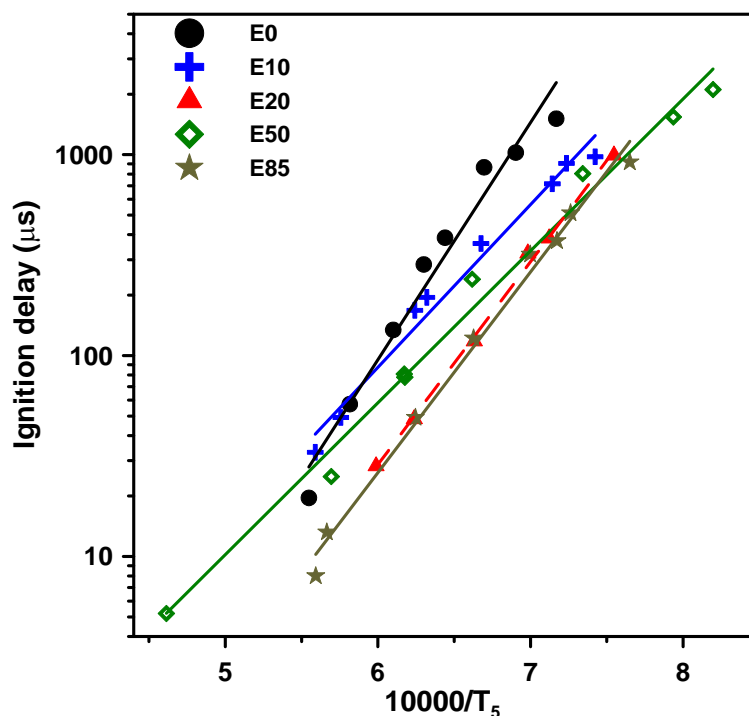

Figure 2: Evolution of the ignition delay with the temperature for the gasoline surrogate (E0), and various blend of this surrogate with ethanol: 10% ethanol (E10), 20% ethanol (E20), 50% ethanol (E50) and 85% ethanol (E85) (mole %) under stoichiometric conditions and around a pressure of 200 kPa. Lines: experimental fit.

Another way of representing the influence of the percentage of ethanol on the ignition delay is to plot the ignition delay for various selected temperatures against the percentage of ethanol blended into the gasoline surrogate, as presented in figure 3. As can be seen on this figure, an addition of 10% of ethanol leads to a decrease in the ignition delay. However, the amplitude of the decrease in the delay is reduced when the temperature increases. An addition of 20% of ethanol leads to a further decrease in the delay. The amplitude of this decrease, compared to E0, is however not influenced by the temperature. Above 20% of ethanol, the variation in the delay is generally less important (ignition delays for E20 and E85 are very similar as visible on Fig.2). It is however interesting to note that the delay increases above 1350K for E50 compared to E20. This increase in the delay is more prominent as the temperature rises.

Modeling results
The mechanism used involves 234 species and 1860 reversible reactions. Each component in the surrogate gasoline mixtures (iso-octane, toluene and 1-hexene) was represented in the detailed kinetic mechanism. The original mechanism includes a sub-mechanism for ETBE combustion chemistry. The ETBE sub-mechanism contains also an ethanol sub-mechanism since ethanol is one of the main combustion product of ETBE [14, 15, 16]. More particularly, the ethanol sub-mechanism used here is that of Marinov [17].
A former study showed [18] that interactions between hydrocarbons are not limited to small labile radicals and that other interactions involving large radicals produced during the course of the oxidation process are possible. The present kinetic mechanism contains interactions between the sub-schemes of each fuel molecule. These interactions mainly consist of

hydrogen abstraction reactions of one of the gasoline surrogate component or its radical by a large radical coming from another component of the surrogate. For example, propyl, allyl and hexenyl radicals which are the major radicals produced during 1-hexene oxidation at high temperature can abstract hydrogen from toluene and iso-octane. More details concerning the detailed mechanism can be found in [9].
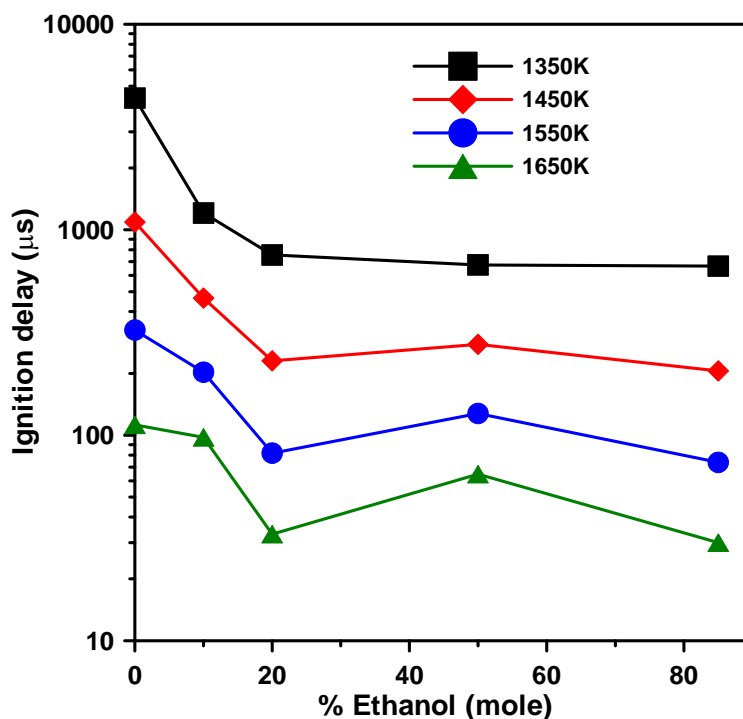

Figure 3: Evolution of the ignition delay with the % (mol.) of ethanol blended with a gasoline surrogate at various temperatures under stoichiometric conditions and around a pressure of 200 kPa. Lines are here to guide the eyes.

To validate the ethanol sub-mechanism, we computed the ignition delay measurements for pure ethanol in a shock tube from Natarajan and Bhaskaran [19] under conditions similar to the present study (2 atmospheres and at stoichiometric conditions) (Figure 4). The results obtained with the recent ethanol model obtained by Leplat et al. [20] are also displayed on Fig.4. As can be seen on this figure, the model used in this work is in agreement with the literature data. Results obtained with the model of Leplat et al. [20] present a better determination of the activation energy but the predictions of the ignition delay are less accurate in average. However, it is worth mentioning that the ignition delays in [20] were determined using the first visible light emissions, a measurement that is difficult to reproduce with the model. In our opinion, due to the dilution level in Ar of these experiments (90% dilution in Ar), the temperature and pressure rise provided by the model are not steep enough to accurately determine the ignition delay (even though good results are reported in [20] with the temperature rise). This is why the beginning of OH emission was used to determine the delay in Fig. 4. This difference in the delay measurement can explain, at least partly, the small discrepancies between the model and the experiments.

As a conclusion, the results displayed in Fig.4 give us confidence in the model's predictions with ethanol as a component of the fuel surrogate in the conditions investigated. In our opinion, the model can therefore be used as a diagnostic tool to explain the results. This is further demonstrated with the figure 5 (a)-(d) where the model is used to predict the auto-ignition delay of the experiments presented in Fig.2. As can be seen on this figure, the results

obtained with E20, E50 and E85 are very well predicted by the model. Surprisingly enough, the model predicts ignition delays that are however much shorter than the experimental results for E10. The prediction of the activation energy seems nonetheless to be correct in this last case.
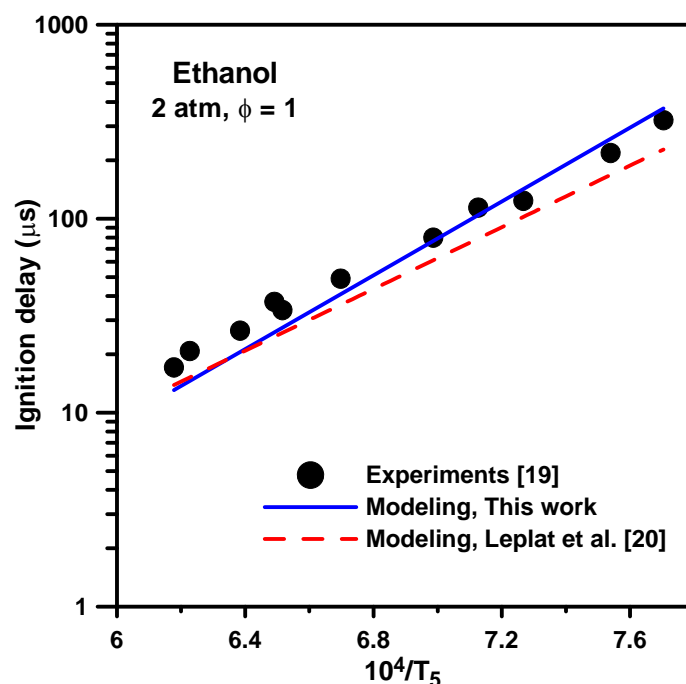

Figure 4: Evolution of the ignition delay with the temperature behind reflected shock waves as per [19] for pure ethanol at 2 atm and at the stoichiometry. Full line: modeling, this study and dashed line: modeling, Leplat et al. [20].

Discussion

It is interesting to note that the octane boosting effect of ethanol observed in engines is not translated into longer ignition delay time in shock tube. It is not immediately clear as to why this is but it can be due to the time – pressure/temperature history that is found in an engine during the compression event but does not exist in a shock tube. For example, it was showed recently that ethanol reduces the low temperature heat release into a HCCI engine (in other words, ethanol inhibits the low temperature chemistry during the compression event) when blended with *n*-heptane [21]. This inhibition of the low temperature chemistry by ethanol was also observed numerically by several authors when comparing the autoignition delays of *n*-heptane with those of a mixture of *n*-heptane and ethanol [21] or with a mixture of *iso*-octane and *n*-heptane and a mixture of these two compounds with ethanol [22]. These studies showed that, at low temperatures, an addition of ethanol decreases the overall rate of production of OH and therefore decreases the chain branching, explaining the inhibition of the low temperature chemistry. In the study of Haas *et al.* [22], it is also interesting to note that results similar to this study were found as their detailed mechanism predicts shorter ignition times for the mixture that contains ethanol above 1000K and at 10 bar.

It is also worth mentioning that the octane boosting effect in engine can be due to some physical parameters since an increase of the charge cooling associated with the fuel vaporization is observed when ethanol is blended (due to the high latent heat of vaporization for ethanol compared to gasoline [23]). Unfortunately, the importance of all these factors cannot be investigated in this study because of the nature of the experiments conducted. The

model will be however used in the near future to interrogate the results, especially at high temperatures where E50 exhibits longer ignition delay than E20 and E85 (Fig.2).
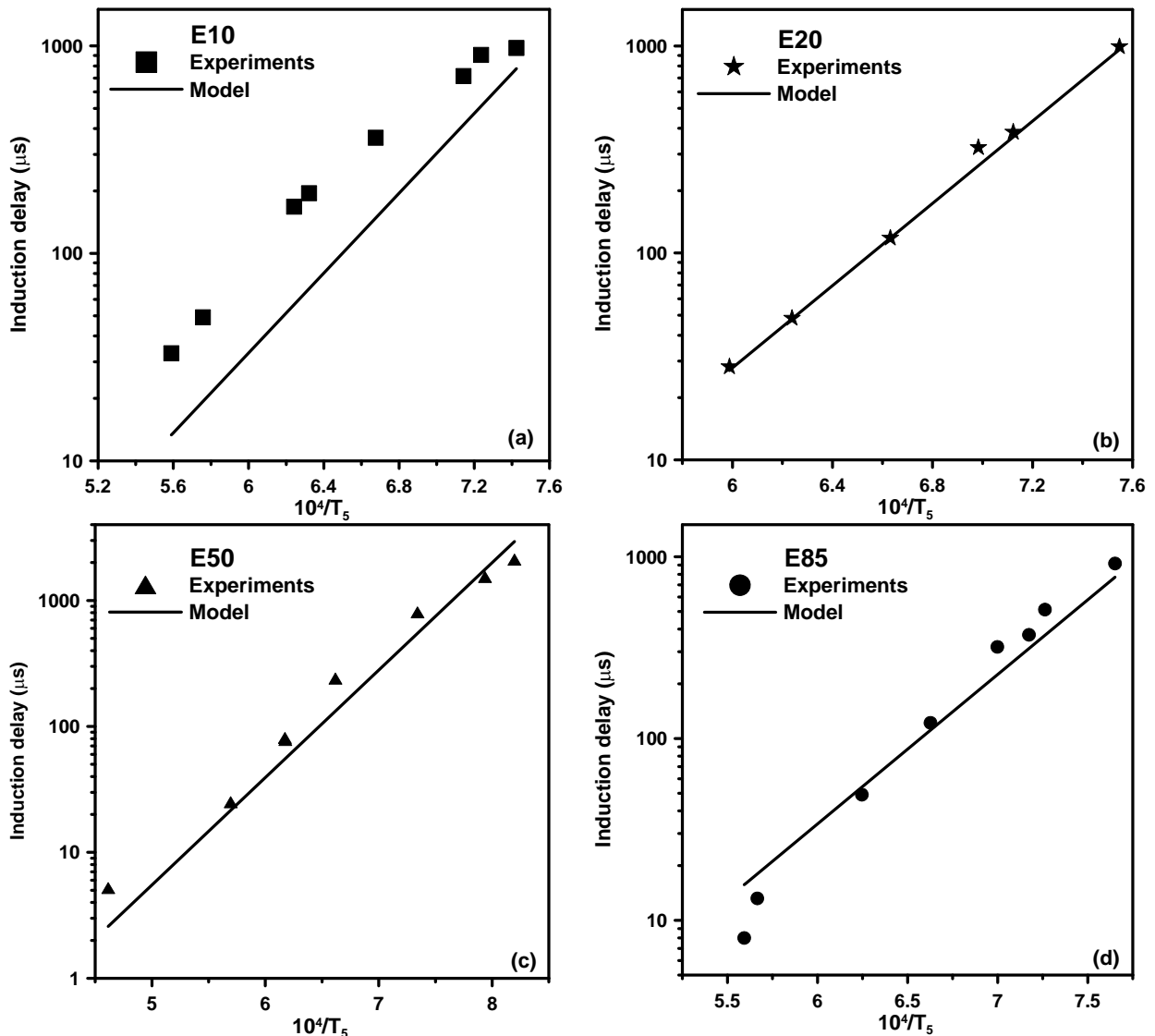

Figure 5: Comparison between the model and the experiments of the evolution of the ignition delay with the temperature behind reflected shock waves for E10 (a), E20 (b), E50 (c) and E85 (d) at the stoichiometry and at a pressure of around 200 kPa. Full line: modeling.

Conclusions

The effect on the ignition delay of various blend ratios of ethanol with a gasoline surrogate was studied experimentally in a shock tube at high temperature, under stoichiometric conditions and at a pressure of about 200 kPa. Results show that an addition of ethanol reduces the ignition delay time. This reduction in the delay is however not proportional to the ethanol percentage in the mixture as most of the reduction in the ignition delay was achieved with 20% mol. ethanol only. These results can appear to be somewhat contradictory to the results observed in engines where ethanol acts as an octane booster (i.e. ethanol reduces the auto-ignition tendency of the fuel when blended). This can be due to the fact that this study focuses on the high temperature combustion regime whereas the ethanol octane boosting effect proceeds at the low temperature chemistry level. A model developed Yahyaoui *et al.* [9] was used to successfully predict the data. Further modeling work is planned to interrogate

the experiments and to study the interactions between ethanol and the gasoline surrogate and to explain the results.

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