High-Temperature Non-Homogeneous Ignition of Small Alcohols Behind Reflected Shock Waves

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1 Introduction

Shock tubes have been used for decades to measure ignition delay times (τ_{ign}) to validate the overall reactivity of detailed kinetics mechanisms for a large variety of fuels. Historically, shock tubes operated at high temperature because of their test-time limitation, typically below 2 ms. Many studies also routinely utilized highly diluted conditions to suppress energy release. Under these conditions, shock tubes can be associated with nearly ideal chemical reactors [1]. However, over the past 15-20 years, several techniques have been applied to extend the test time of shock tubes, so intermediate- and low-temperature combustion chemistry can be investigated. Test times of over 100 ms have been achieved [2], and intermediate- and low-temperature combustion regimes have been routinely investigated [3-7]. As these temperature regimes were investigated, it appeared that non-idealities such as dP/dt or inhomogeneous ignition have to be taken into account for longer test times, whereas they can be neglected at higher temperatures [1,8].

These non-ideal effects and their impacts on τ_{ign} have been studied and described in detail in the literature. For instance, Javed et al. [7] studied the impact of shock-tube non-idealities on long τ_{ign} for fuels exhibiting negative temperature coefficient behavior. They observed significant discrepancies between the measurements and the simulation for the intermediate temperature range (700–1100 K). They concluded that localized ignition kernels could affect τ_{ign} at intermediate temperatures, which lead to compression (and heating) of the bulk gas and result in shorter, overall τ_{ign}. They distinguished three different ignition regimes, and explained why ignition kernels have a negligible effect on the high- and low-temperature regimes. These ignition kernels have been observed directly in squared-section shock tubes with large observation windows. Fieweger et al. [5] followed the ignition event from fuel/air mixtures using CH*, pressure signals, and a shadowgraph method. For low temperatures and long test times, they observed that the ignition started with a small kernel, which translated to a slow pressure increase and CH* emission as the kernel grew, before a strong ignition event. A similar study was performed by Uygun et al. [9], using a schlieren technique and a high-speed camera. Like for Fieweger et al., the presence of flame kernels was associated with a slow

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pressure increase before the main ignition. These flame kernels were located very close to the edge of the thermal boundary layer.

Recently, several groups installed a quartz endwall on their tubular shock-tubes, in conjunction with a high-speed camera to observe non-idealities associated with the ignition event [10-13]. Inhomogeneous ignition has been observed at the bottom part of the tube. The role of solid particles coming from diaphragm material was identified by Hanson et al. [10,11]. However, the role of solid particles was not identified by Figueroa-Labastida et al. [13], and no differences in the results were observed between a clean and "dirty" shock tube for Ninnemann et al. [12]; though the observation of their published images showed that the inhomogeneous ignition also started from the bottom part of the shock tubes. Similar to the previous studies, Figueroa-Labastida et al. concluded that the low-temperature ignition events are initiated from an individual, growing, hot spot, while the main ignition starts from many spots simultaneously at high temperatures. This difference translates to a slow pressure and temperature increase before the main ignition for the low-temperature case (leading to τ_{ign} shorter than anticipated). These pre-ignition events were more likely to happen as the fuel concentration increased.

The present study reports on the observation of inhomogeneous ignition events for small alcohols, methanol and ethanol, but at high-temperature conditions and for relatively short test times. The roles of shock-tube cleanliness, wall temperature, pressure, equivalence ratio (ϕ) and fuel concentration on the appearance of these inhomogeneous ignitions were investigated. The experimental setup is described first, followed by a presentation and discussion of the results.

2 Experimental setup

Experiments were conducted in a single-diaphragm, stainless-steel shock tube with a 7.62-cm i.d. driver section (2.46-m long) with a large-diameter driven section (15.24-cm i.d., 4.72-m long). A series of five PCB P113A piezoelectric pressure transducers were used along the driven section to measure the incident-wave velocities and to determine the wave speed at the endwall. Post reflected-shock conditions were obtained using this extrapolated wave speed in conjunction with the one-dimensional shock relations and the initial conditions in the test region. Test pressure was monitored by a PCB (endwall) and an additional transducer Kistler 603 B1 transducer was placed at the sidewall location (bottom of the tube), 16 mm from the endwall, in the same plane as the sapphire observation windows and facing the last PCB P113A.

Polycarbonate diaphragms were used for the 13-atm runs, and a cross-shaped cutter was employed to facilitate their breakage and prevent fragments from tearing off. For the 20- and 50-atm experiments, pre-scored aluminum diaphragms were used. The driven section was vacuumed down to 2×10^{-5} Torr or better prior to every run. Note that for the shock tube, its manifold and mixing tank were heated to allow for large-mixture preparation and high filling pressure of the driven section, necessary for the high-pressure experiments. A custom-made jacket was used for the driven section of the tube and for the mixing tank. A detailed description of the heating system and the shock tube can be found in Rebagay [14]. The mixing tank and manifold were heated to 373±2 K, while the driven section was heated to 348±2 K. To avoid fuel condensation during the mixture preparation, the partial pressure of the fuels was kept below 50% of their vapor pressure at the mixing tank condition. A thermocouple was mounted flush on the endwall, so that the temperature of the gas inside the driven section was accurately measured before the experiment. Mixtures were prepared in a stainless-steel mixing tank following the partial pressure method. Fuels were introduced via a septum using a syringe. Two temperature-regulated (348 K) MKS Baratons (0-100 torr and 0-1000 torr range) were used, in addition to a heated 0-25 bar transducer from ESI (model HI 2300). The conditions investigated herein are summarized in Table 1.

Table 1: conditions investigated during this study.

Mixture composition (% vol.)			Equiv. ratio	Pressure (atm)	Temperature (K)	Inhomogeneous ignition
Fuel	O_2	Diluent				
6.525% CH_3OH	19.644%	73.831% Ar	0.5	1.30±0.15	1220-1540	No
				13.5±1.0	1000-1165	**Yes**
12.281% CH_3OH	18.421%	69.298% Ar	1.0	1.35±0.25	1105-1445	No
				13.1±0.5	955-1090	**Yes**
21.875% CH_3OH	16.406%	61.719% Ar	2.0	1.55±0.15	1030-1310	No
				12.3±0.5	940-1135	No
3.38% C_2H_5OH	20.29%	0.763% Ar	0.5	1.30±0.10	1175-1410	No
				13.4±0.5	1015-1185	**Yes**
6.54% C_2H_5OH	19.63%	0.7382% Ar	1.0	1.50±0.40	1075-1590	No
				12.9±0.6	950-1150	**Yes**
12.281% C_2H_5OH	18.421%	69.298% Ar	2.0	1.70±0.15	1070-1290	No
				13.0±0.5	940-1135	No
6.54% C_2H_5OH	19.63%	73.82% N_2	1.0	27.0±3.5	950-1080	No
3.72% C_2H_5OH	11.17%	85.11% N_2	1.0	25.0±1.5	990-1125	No
				51.0±2.5	945-1085	No

For a homogeneous ignition event, Fig. 1(left), the time difference between the first detection of the ignition event (second sidewall pressure signal) and the last one (sidewall OH*) is only about 20 µs, for τ_{ign} of around 1940 µs, i.e. about 1% difference. Note that the second pressure transducer was not shielded with a very thin layer of RTV silicon and is therefore exposed to heat transfer from the hot gases. This heat transfer is responsible for the large, artificial, decrease in pressure. The dP/dt is also fairly low for these experiments, according to the endwall pressure transducer. Concerning inhomogeneous ignition, Fig. 1(right), the ignition happens at different times for the endwall and sidewall pressure transducers, as well as for the OH* emission profile. the time difference between the first detection of the ignition event and the last one (both on sidewall pressure transducers) is about 60 µs, for τ_{ign} of around 500 µs, i.e. about 12% difference. As seen below, the issue with these inhomogeneous ignition events is not so much the larger uncertainty on the ignition delay time, but rather how short these ignition delay times are when compared to homogeneous ignition.

It is worth mentioning that these inhomogeneous ignition events have been observed for specific conditions only, and that they did not appear in a systematic way. For instance, only experiments at ϕ = 0.5 and 1.0, around 13 atm, were concerned, for both methanol and ethanol. Note that neither of them was found to be more prone to inhomogeneous ignition than the other. The data at around 1.5 atm (ϕ = 0.5 and 1.0) and at ϕ = 2.0 (1.5 and 13 atm) did not present any inhomogeneous ignition behavior. Interestingly, we also investigated higher pressures with stoichiometric ethanol mixtures, undiluted (in "air", around 25 atm) and with a fuel concentration divided by two (around 25 and 50 atm) but with N_2 instead of Ar as diluent. Remarkably, increasing the pressure in conjunction with using N_2 instead of Ar as a diluent resulted in a lack of inhomogeneous ignition for both kind of mixtures.

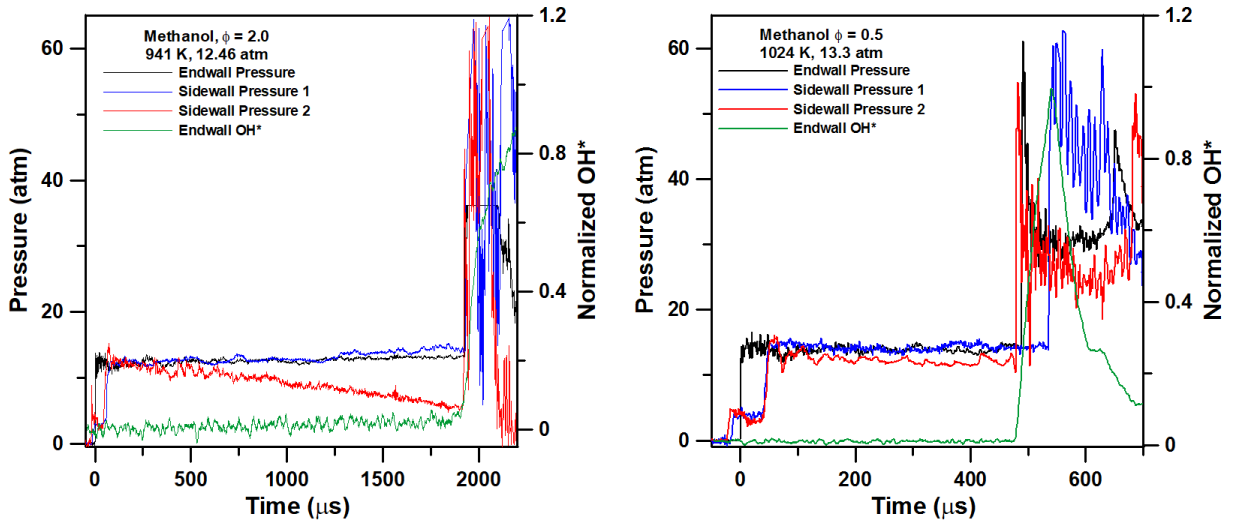

Figure 1. Left: typical signals for a homogeneous ignition; right: typical signals for an inhomogeneous ignition.

The effect of inhomogeneous ignition on the overall τ_{ign} is quite dramatic, as can be seen in Fig. 2. For both fuels, the resulting τ_{ign} are significantly shorter than expected, by a factor of 3 to 5. For methanol, Fig. 2(left), the inhomogeneous ignition happened on the lower-temperature side of the range investigated, whereas it is less the case for ethanol, especially for the fuel-lean mixture. Note that the 1.5-atm data have not been plotted for figure-readability purposes. The agreement of the homogeneous ignition data with the literature is excellent, at least on the extremes for ethanol [5,15].

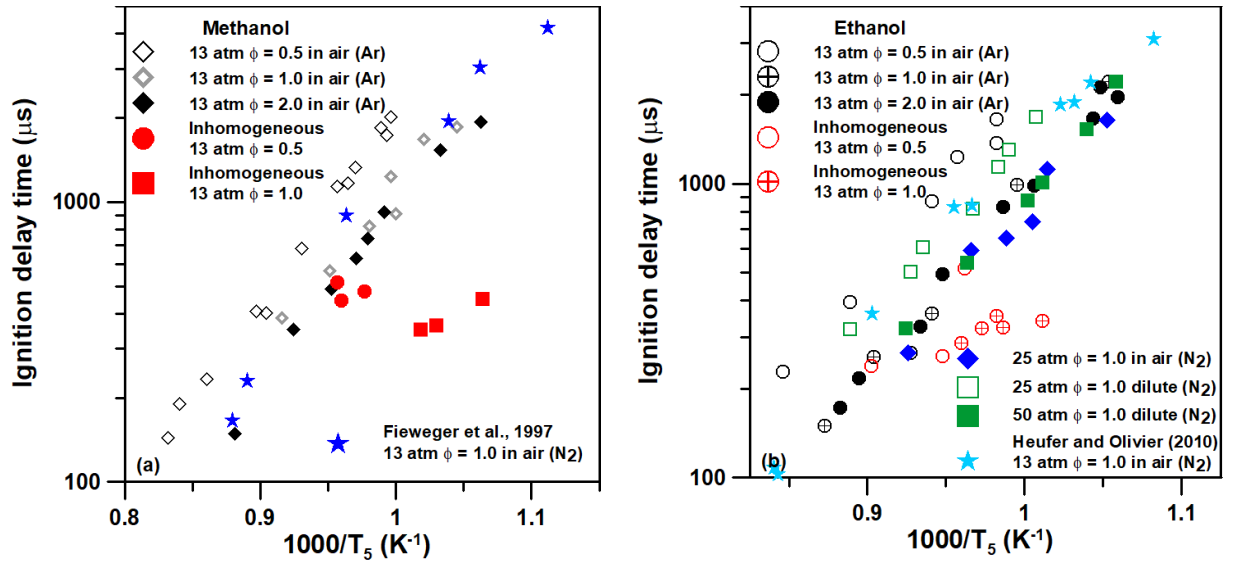

Figure 2. Left: ignition delay time for methanol; right: ignition delay time for ethanol.

To provide a tentative explanation to the high-temperature inhomogeneous ignition observed herein, it is worth mentioning again that no slow increase in the pressure signal before the main ignition event was observed in such cases. The absence of inhomogeneous ignition at lower pressures can be explained by the

higher thermal diffusivity of the mixture, compared to the higher-pressure cases. This result is in agreement with the notion of a minimum critical value of the thermal diffusivity to observed inhomogeneous ignition, as discussed in the literature [13,16].

A likely explanation to explain these inhomogeneous ignition events is that the pre-ignition occurs from a hot spot, as in other studies [9-13], but these pre-ignition events do not result in a slow flame/compression event that is strong and/or long enough to be observed by the sidewall sensors (Fig. 2) but is rather quickly transformed to an explosion-type wave that is faster moving. This behavior is also evident in Fig. 1(right) by the fact that the sharp pressure rise on the second sidewall pressure transducer, corresponding to a fast-moving ignition wave, occurs before the main ignition at the endwall location. The difference with the literature studies can be due to several factors such as the range of T_5 investigated, the type of fuel and its concentration, or the pressure range covered (the highest ethanol concentration and pressure investigated by Figueroa-Labastida et al. being 5% ethanol and 4 atm, respectively).

Following the idea that these inhomogeneous ignition events are due to diaphragm fragments [10,11], a thorough cleaning of the shock tube between runs was performed. Like for Ninnemann et al. [12], this cleaning did not prevent inhomogeneous ignition from occurring. The effect of the wall temperature was investigated as well, by reducing the temperature of the heating system on the driven section, but this also did not prevent inhomogeneous ignition from occurring either.

Finally, the fact that mixtures diluted in N_2 instead of Ar did not present any inhomogeneous ignition despite being more reactive, due to the larger pressure, can be explained by the notion of flame thickness developed in Figueroa-Labastida and coworkers [13] and based on the work of Kalghatgi and Bradley [17]. In these studies, it is suggested that the laminar flame thickness of a mixture would dictate its likelihood to pre-ignite. A critical flame thickness can be defined and if a hot spot is larger than this critical thickness, then it would be able to develop as a flame. As shown in Figueroa-Labastida et al., using N_2 as a bath gas induces a thicker flame than for Ar, which decreases the predisposition of the development of a kernel and can explain the results of this study. At 25 atm with Ar as bath gas, the thermal diffusivity of the mixture would have been lower than for the 13-atm case, and inhomogeneous ignition would have been very likely to occur. The fact that no inhomogeneous ignition was observed for Fieweger et al. [5] with methanol in similar conditions to our 13-atm results herein can also be explained by the difference in bath gas, as they used N_2 instead of Ar. It is also possible that the heat capacity differences between N_2 and Ar could also play a role here, with nitrogen of course having vibrational modes that can absorb energy.

4 Conclusions

The ignition of methanol and ethanol was studied for various equivalence ratios, pressures, dilution levels, and using different bath gases (for ethanol) for test times shorter than 2 ms. Results are in agreement with the literature, but inhomogeneous ignition was detected at around 13 atm for fuel-lean and stoichiometric mixtures with Ar as the bath gas. The inhomogeneous ignition translated into ignition delay times significantly shorter than expected. While inhomogeneous ignition behavior has been recorded with methanol and ethanol in the literature, under similar equivalence ratios, fuel concentrations, and pressure conditions, these were observed for longer test times/colder temperatures, and no inhomogeneous ignition was observed within the temperature range investigated herein. This difference with the literature seems to be due to the use of Ar as bath gas in the present study, instead of N_2 in the literature. The use of N_2 allows for a larger flame thickness than Ar, which could prevent hot spots from developing into flame kernels that lead to inhomogeneous ignition.

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