Towards Consolidation of Hydrogen-Air Ignition Data from Shock Tube and Flow Reactor Experiments

Sergey P. Medvedev, Sergey V. Khomik
Heterogeneous Combustion Laboratory, N.N.Semenov Institute of Chemical Physics, RAS
Moscow, Russia

Aleksander K. Heufer, Herbert Olivier
Shock Wave Laboratory, RWTH Aachen University
Aachen, Germany

1 Introduction

Experimental data on self-ignition delays τ play key role in validation and development of the kinetics schemes that serve to describe properly the combustion dynamics in practical devices. Hydrogen is considered as a perspective fuel for power applications. The measurements of τ in hydrogen-air mixtures in the temperature range of 600 < T < 950 K and pressure range of 4 < P < 30 bar represent especial interest for simulating gas-turbine conditions [1]. Recent flow reactor experiments [1] at T = 750-810 K revealed that the measured values of τ are one-two order less than that calculated by means of a detailed kinetics scheme. The similar behavior was found for syngas-air mixtures where fuel is comprised of H_2 and CO [2,3]. It should be noted, that the shock-tube data on low-temperature hydrogen ignition demonstrate the same tendency [3-7]. In spite of the intensive discussion in the literature [1-9], the reason of “abnormally short” ignition delays in the hydrogenous mixtures is still an open question. Another problem is the inconsistency of shock tube data and flow reactor observations because a typical residence time in flow reactors is longer than 30-50 ms [1-3], while in the shock tubes special efforts are necessary to extend an observation time up to 10-15 ms (behind a reflected shock wave).

Three objectives of the present investigation are:

(1) to modify traditional shock-tube scheme of ignition delay measurements by application of over-tailored conditions for extension of observation time behind a reflected shock wave;
(2) to collect additional data on ignition delay of lean hydrogen-air mixtures for the temperature and pressure range relevant to gas-turbine conditions;
(3) to compare new shock-tube data with flow reactor experimental results on autoignition of hydrogen-air mixtures.

2 Experimental Details

The experiments were performed in a shock tube with the total length of 11.4 m. The high-pressure section features the length of 5.1 m and circular cross-section of 100 mm in diameter. The 6.3 m long low pressure section has rectangular cross-section of 54 x 54 mm^2. In the end part of the low-pressure

Correspondence to: podwal_ac@yahoo.com

section the sidewalls are equipped with two quartz windows. The ignition dynamics behind a reflected shock wave was monitored by schlieren visualization along with pressure recording. Besides, the onset of ignition was detected by a germanium photodiode (with amplifier) mounted in the end wall. The parameters of the shock wave were measured by means of standard transducers (Kistler 603B, Kulite XCQ-080-35). Schlieren images were recorded by a high-speed Shimadzu HPV-1 camera. The mixture under investigation (15% hydrogen in air) was prepared in a separate mixer by the partial pressure technique.

The study of low-temperature ignition requires long observation time. For a given tube the application of standard tailored conditions extends observation time up to 10-12 ms. It seems, however, that the pressure (temperature) behind a reflected shock is inevitably disturbed due to non-ideality of shock tube flow [5-10]. Nearly constant volume (constant internal energy) conditions can be achieved by use of a proper insert into the high pressure section of the shock tube [10]. The method of [10] is effective but not universal and does not extend the observation time.

In the present ignition delay study we employ **over-tailored** conditions instead of standard reflected shock procedure (tailored or under-tailored cases). Hence argon is used as a driver gas.

3 Results and Discussion

To estimate flow parameters the calculations were performed using the one-dimensional shock tube simulation program KASIMIR [11]. The wave diagram in Fig. 1 demonstrates an example of shock wave reflection under over-tailored conditions. As it is seen, the reflected shock – contact surface interaction leads to the formation of compression wave that propagates towards the end of the tube. During about 15 ms the mixture under investigation experiences multiple shock reflections before reaching the end state (*3*). The conditions under pressure P_3 and temperature T_3 are sustained nearly 20 ms until arrival of a rarefaction wave. Thus, an observation time under the over-tailored mode can be twice as long as that in the case of the tailored conditions. Apparently, a fairly long time of pressure/temperature rise at the over-tailored operation should be taken into account in the ignition studies. Meanwhile, a similar problem of transient pressure/temperature is typical for the low-temperature measurements of long ignition delay when using standard shock tubes (under tailored mode) and rapid compression machines [3-10].

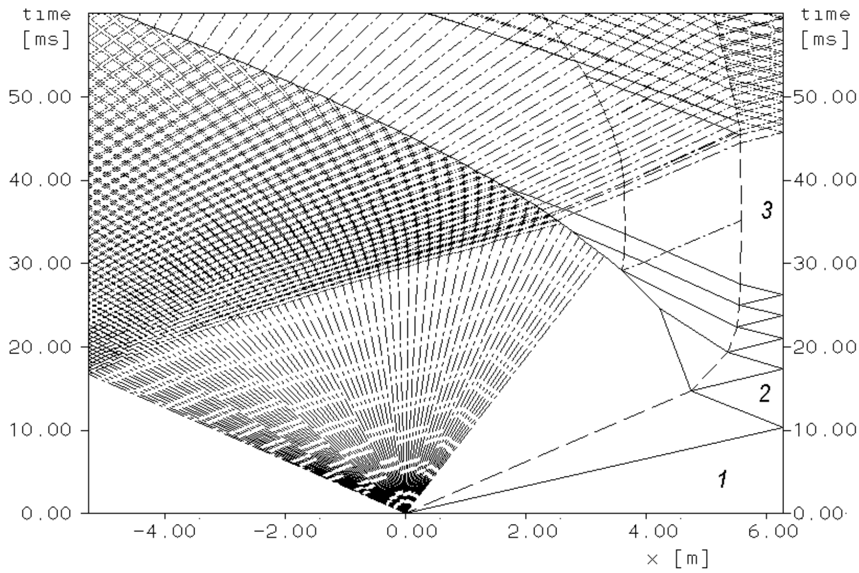

Figure 1. Wave diagram in the over-tailored case. Driver gas – argon, driven gas – 15%H_2+Air (inert equivalent). Incident shock velocity 608 m/s. *1* – initial conditions P_1 = 0.45 bar, T_1 = 293 K; *2* – first reflection P_2 = 3.43 bar, T_2 = 545 K; *3* – end state P_3 = 9.85 bar, T_3 = 720 K.

Figure 2*a* represents pressure history at the distance of 8 mm from the end-flange of the shock tube in the experiment with reactive 15%H_2+Air mixture under initial conditions, described in the caption of Fig. 1. Two peculiarities can be important for the ignition study under over-tailored conditions. First, note that pressure trace increases gradually without clearly defined system of shocks. The second feature is a continuous slight pressure increase after 15 ms, while in the simulation the pressure (temperature) is steady (Fig. 1). Both phenomena reflect the non-ideality of flow in a real shock tube. As known, incident and reflected shock waves are disturbed due to the boundary layer effects. Besides, the shape of the contact surface can be complicated. Finally, the difference between cross-sections of a driver and driven sections can influence flow-pattern. The ignition event is indicated in Fig. 2*a* by sharp increase of the photodiode output at $t \approx 32$ ms. Simultaneously, the pressure rise is observed. Further, a rarefaction wave arrives at $t \approx 36$ ms.

Temperature – time history is the most relevant parameter that can be obtained using pressure recording. We accept the commonly used model of adiabatic isentropic compression. The temperature dependence on time is calculated by the following formula:

$$T(t) = T_2 \left(\frac{P(t)}{P_2} \right)^{\frac{\gamma-1}{\gamma}}, \qquad (1)$$

where P_2,T_2 are respectively pressure and temperature behind a reflected shock wave that is defined by the velocity (Mach number) of the incident shock wave; γ - specific heat ratio (mean value estimated by KASIMIR between states *2* and *3* (see Fig. 1). The temperature – time dependence obtained in the experiment under consideration is represented in Fig. 2 *b* (γ=1.35). Ignition starts at about 750 K, and it is important that during 15 ms before ignition the rate of temperature increase does not exceed 0.2% per ms. This value is smaller than the temperature gradients of 0.5-5% found in conventional experiments with reflected shock waves [12].

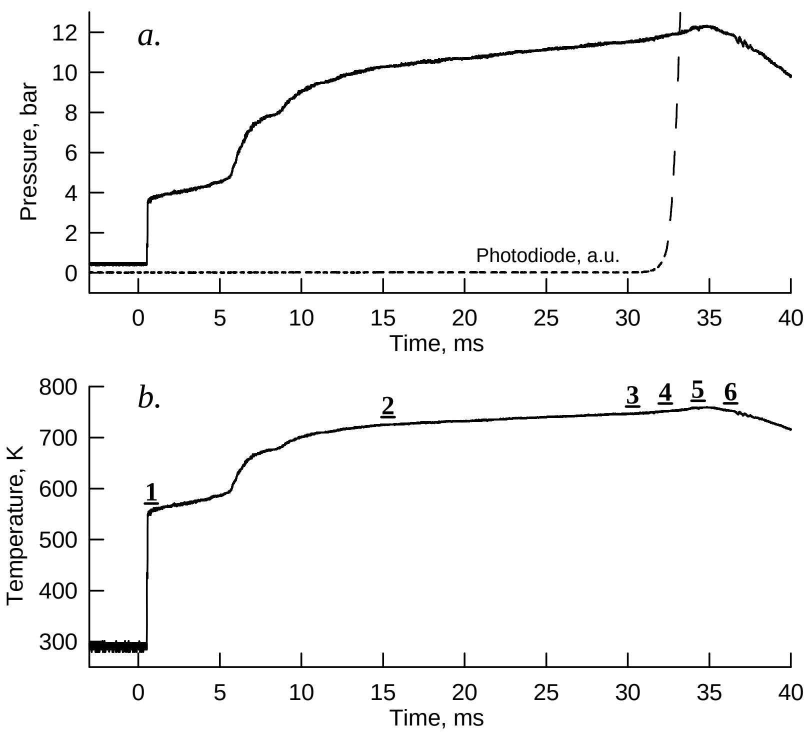

Figure 2. Pressure (*a*) and temperature (*b*) time history in the experiment with 15%H_2+Air. Driver gas – argon. Incident shock velocity 608 m/s, P_1 = 0.45 bar. Dashed curve – photodiode output (arbitrary units). Numbers 1-6 (*b*) corresponds to instants of high-speed video frames described below.

Valuable information on details of ignition process can be obtained from high-speed schlieren visualization. Figure 3 represents a series of images taken in the above described experiment. The instants of the pictures are given in Fig. 2*b* by placing the corresponding numbers along the temperature curve. The exposure time of each frame is 0.064 ms, so the reflected shock wave appears as a blurred line on the left of the photo 1. The second photo was taken at about 15 ms after the reflection when the compression phase is completed. The comparison between photos 1 and 2 reveals clear difference in the flow pattern. There are no significant density gradients immediately after shock wave reflection (photo 1), while secondary compression waves create distinct turbulence (photo 2). Local ignition starts at approx. 30 ms after shock reflection (photo 3, in the vicinity of right top corner). Then the reaction front propagates rapidly and combustion products fill the overall field of view.

The analysis of experimental results was performed by applying the Livengood-Wu integral technique [13]. In accordance with [13] the ignition delay time τ_i under transient conditions will elapse when the condition given by the following equation (Livengood-Wu integral) is matched:

$$\int_0^{\tau_i} \frac{dt}{\tau(p(t),T(t))} = 1 \tag{2}$$

Where $\tau(p,T)$ - the dependence of self-ignition delay on pressure and temperature, t - time. Historically the Eq.(2) (also known as “knock integral” or “Arrhenius integral”) was successfully applied to analysis of the auto-ignition phenomena in internal combustion engines (ICE) and rapid compression machines (RCM). Due to fairly long compression phase the operation of a shock tube under over-tailored mode has much in common with ICE and RCM.

The application of Eq.(2) to the interpretation of experimental results opens up a possibility for evaluation of an adequacy of specified kinetics model or correlation of $\tau(p,T)$. For the sake of comparison with flow reactors data we use the correlation of [2] with a correction factor:

$$\tau = A \cdot 1.02 \cdot 10^{-4} [O_2]^{-0.5} [H_2]^{-0.25} \exp\left(\frac{3985}{T}\right), \tag{3}$$

where τ is the ignition delay in milliseconds, A is the correction factor (introduced by us), $[O_2]$ and $[H_2]$ are the molar concentrations of oxygen and hydrogen in the mixture, and T is temperature in K.

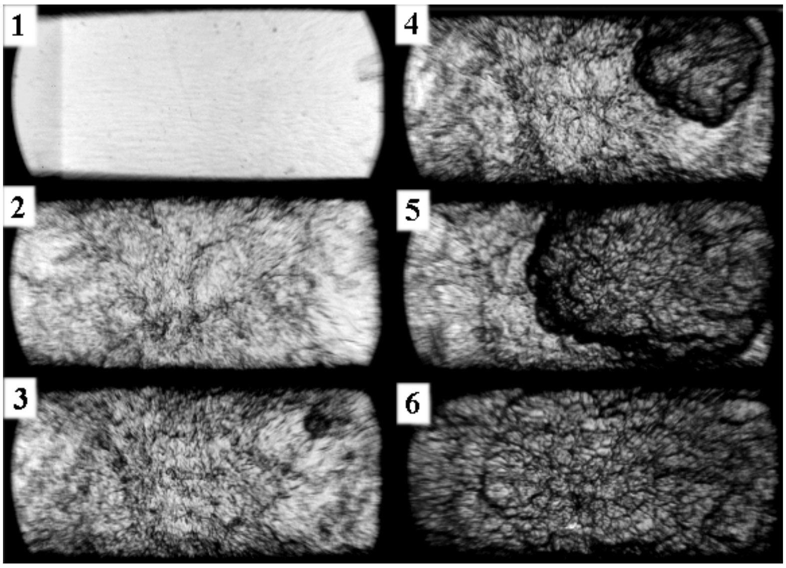

Figure 3. Schlieren images in the experiment with 15%H_2+Air. The end-flange of the tube is on the right of the photos.

The procedure of data processing was as follows. The experimentally measured pressure-time history together with the calculated temperature-time history and initial conditions were substituted into Eq.(3) for obtaining an expression of $\tau(p(t),T(t))$. Then the value of A was determined by numerical integration of Eq. (2). In all the experiments the correction factor A is less than 1. Using Eq. (3) with proper correction factor, one can evaluate an ignition delay under experimentally determined pressure P_i and temperature T_i. In the example described in Figs. 2,3 the ignition starts at P_i = 11.5 bar and T_i = 750 K (A = 0.4). Figure 4 represents the comparison of current results with the correlation from [2] and recent data from flow reactor experiments [1] for lean hydrogen-air mixtures. It should be noted that in the low-temperature range (T < 900 K) the present normalized ignition delay parameters are nearly two times less than that predicted by Eq. (3). And vise versa, the ignition delay times obtained in the flow reactor experiments insignificantly exceed the values given by the correlation from [2]. Both shock tube and flow reactor data exhibit a clearly marked discrepancy from the ignition delay times calculated by the detail kinetics model. Similar phenomena were found in many studies of ignition in hydrogenous mixtures [3-10].

We emphasize that present shock tube and previous flow reactor experimental data on ignition of lean hydrogen-air mixtures are reasonably grouped around the correlation of Peschke and Spadaccini [2]. Such agreement shows that the proposed technique of over-tailored shock tube operation is suitable for simulating ignition processes under gas-turbine conditions.

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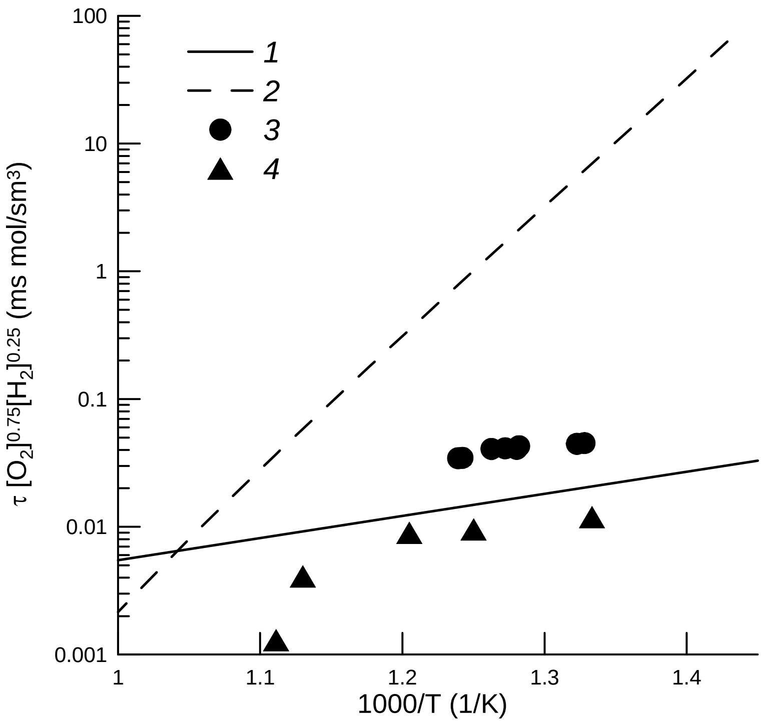

Figure 4. Comparison of present results with previous correlations and flow reactor measurements. *1* – correlation from [2], *2* – ignition delay times calculations for 15%H_2+Air mixture [9], *3* – flow reactor data [1], *4* – present results.

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