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# A high pressure experimental and numerical study of methane ignition

Hilal El Merhubi *, Alan Kéromnès *, Gianni Catalano, Benoîte Lefort, Luis Le Moyne

DRIVE EA1859, Univ. Bourgogne Franche Comté, F58000 Nevers, France

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ABSTRACT

A high pressure shock tube "HPST" has been designed and validated for the purpose of chemical kinetics studies at elevated pressures and temperatures. Using this facility, auto-ignition investigations are conducted for methane at 10, 20 and 40 bar and temperatures from 1400 K up to 2000 K. Three equivalence ratios ($\phi$ = 0.5, 1 and 2) for a methane/oxygen/argon mixture were studied in this paper under diluted conditions (argon > 90%). Experimental data showed good agreement with previous literature measurements and predictions from three different chemical kinetic models (Aramco Mech 1.3, USC Mech II and GRI Mech 3.0) commonly used in the literature, which confirms the quality of the experimental data obtained with the new high pressure shock tube and allows the expansion of the validation range of the mechanisms for ignition delay times to higher pressures. The investigations performed to explain the differences observed for ignition delay times predictions highlighted an important sensitivity of the USC mechanism predictions to equivalence ratio and an important sensitivity to $CH_3 + O_2$ reactions. Finally, the impact of pressure and equivalence ratio on ignition delay time is evaluated over a broad range of pressure (1–50 bar) and equivalence ratio ($\phi$ = 0.2–3).



## 1. Introduction

Many investigators have focused on the study of alternative and clean fuels, due to fossil fuel depletion and strengthened emission regulation. Currently, the combustion of hydrocarbons remains the biggest producer of energy throughout the world [1]. The smallest hydrocarbon fuel, methane, one of the potential alternative fuels, can be derived from biomass through methanization. The availability, low cost and reduced emissions have made methane a primary fuel in many technological applications. Methane has been in use on many combustion devices such as industrial gas turbines and internal combustion engines operated at high pressure and temperature [2–8]. Therefore, methane is a key fuel candidate for research.

The auto-ignition of hydrocarbon–oxygen mixtures has been studied by many investigators [9–14]. However, attention has been focused mainly on methane because of the simplicity of its oxidation process compared with those of heavier hydrocarbons. For those reasons, the process of auto ignition of methane has long been studied. Despite the richness of experimental data obtained in previous studies ([7,8,15–26], see Table 1) in rapid compression machines and/or shock tubes and under various conditions (lean and rich mixtures; at high concentration and extremely dilute; diluted with air, nitrogen, argon or helium), there is a lack of data for high pressures, for relevant industrial applications. Therefore it is necessary to fill the data gaps in working conditions (pressure, temperature, dilution and equivalence ratio) completely different to former combustion experiments and closer to industrial application.

A shock tube is an ideal reactor for the study of chemical kinetics (auto-ignition characteristics of gas mixtures, flame velocity...) due to its gas-dynamic simplicity behind reflected shock waves [27]. Shock tubes create a high-temperature and high-pressure environment that ideally exhibits homogeneous, adiabatic, constant-volume, stagnant gas conditions for the reacting mixture. Therefore, since virtually all non-kinetic processes such as fluid flow, heat transfer, transport, and turbulence are negligible, a shock tube can be modeled as a simple homogeneous, constant volume, adiabatic reactor [28].

All of the experiments conducted in the shock-tube facility have been performed with two types of bath gas: argon or nitrogen. Argon is the preferred dilution gas for chemical kinetic studies because of its favorable gas dynamic properties for shockwave propagation and because it strongly limits the formation of bifurcations compared to $N_2$ [29]. The Arrhenius correlation used to define auto-ignition delay time in most shock tube studies indicates that the type of dilution gas has a negligible effect on ignition delay time. Petersen et al. [30] suggested that ignition is primarily

* Corresponding authors.
E-mail addresses: Hilal.El-Merhubi@u-bourgogne.fr (H. El Merhubi), alan.keromnes@u-bourgogne.fr (A. Kéromnès).

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**Table 1**
Experimental conditions for the ignition delay time measurement of methane reported in the literature performed in Shock Tube (ST) and Rapid Compression Machine (RCM).

| Ref. | $\phi$ | $P$ (bar) | $T$ (K) | Diluents (%) | Bath gas | Device |
|---|---|---|---|---|---|---|
| [7] | 0.5 | 20 | 800–1100 | 79 | Ar | ST |
| [8] | 0.5 | 0.54–30 | 1090–2000 | 79 | $N_2$ | ST |
| [15] | 0.5 | 5–20 | 1250–2000 | 95 | Ar | ST |
| [16] | 0.5–2 | 3–13 | 1485–1900 | 95–99 | Ar | ST |
| [17] | 0.4–6 | 10–260 | 1040–1500 | ⩽70 | Ar, $N_2$ and He | ST |
| [18] | 1 | 16–40 | 900–1400 | 79 | $N_2$ | ST |
| [19] | 0.5–1 | 0.65–1.42 | 1220–2250 | 75 or 98 | Ar | ST |
| [20] | 0.5–2 | 1–100 | 600–4000 | 75, 85 or 98 | Ar | ST |
| [21] | 1 | 1–10 | 1130–2100 | 95 | Ar | ST |
| [22] | 1 | 38–43 | 925–945 | 79 | $N_2$ | RCM |
| [23] | 1 | 25–50 | 900–1050 | 73–75 | $N_2$ and Ar | RCM |
| [24] | 0.5–2 | 8–30 | 630–1550 | 79 | $N_2$ or Ar | RCM + ST |
| [25] | 0.5–2 | 1–50 | 770–1580 | 68–79 | $N_2$ | RCM + ST |

based on $CH_4/O_2$ kinetics rather than on thermal effects. Although studies reporting the ignition delay time of methane/oxygen mixtures present two dilution proportions, experiments were mainly conducted under air proportion dilution and a few under high argon dilution conditions at high pressures (Table 1). In this study, the experimental conditions cover three equivalence ratios (0.5, 1 and 2) and high pressure (up to 40 bar) for methane/oxygen mixtures diluted in argon. Comparison of conditions explored during previous studies [15,20,21,31–33] with those of our work are shown in Fig. 1. None of previous studies for diluted methane/oxygen mixtures present a comprehensive study for each pressure condition and equivalence ratio. An extremely large set of conditions was studied by Petersen et al. [32] thanks to a reduced number of experiments. The other works shown in this figure present only one equivalence ratio studied between 1 and 20 bar. Each of the three pressure–temperature regions displayed in Fig. 1 corresponds to the three equivalence ratios explored in this study.

The first study of ignition delay times of methane–oxygen mixtures in a shock tube was carried out by Skinner and Ruehrwein [34]. They reported a set of activation energies ranging from 38 to 63 kcal/mole for various rich mixtures. Meanwhile, no attempt was been made in their study to evaluate the dependence of the auto-ignition delay time on equivalence ratio. Since then, a number of investigations have been reported in the literature ([13,15,35–38]). The team of Kogarko and Borisov [35] reported a very wide range of activation energies (26–85 kcal/mole) and pressure dependencies ($P^{-0.6}$–$P^{-1.2}$). Their studies consisted on a limited number of rather scattered data points. Spadaccini and Colket [13] have measured ignition delay times of methane/oxygen mixtures diluted in argon in a shock tube for pressures between 3 and 15 atm, temperatures varying from 1350 up to 2000 K and equivalence ratios between 0.45 and 1.25. The results are reproduced by the Eq. (1) here below, where τ is the ignition delay time in μs, $T$ is the temperature in K and $[O_2]$ and $[CH_4]$ are respectively the concentration of dioxygen and methane in units of mol cm$^{-3}$.

$$\tau = 2.21 \times 10^{-14} \exp\left(\frac{22,659}{T}\right)[O_2]^{-1.05}[CH_4]^{-0.33} \quad [13] \tag{1}$$

Hu et al. [38] studied laminar flame speeds and ignition delay times of methane–air mixtures at elevated temperatures (up to 2000 K) and pressures (up to 10 atm). A shock tube facility was used to measure the ignition delay times for mixtures at three different equivalence ratios (0.5, 1 and 2). GRI Mech 3.0 [39], USC Mech II [40] and Aramco Mech 1.3 [41] mechanism's performance were evaluated using the data obtained. A correlation of the ignition delay time data was given for methane–air mixtures where a good linear dependence of logarithmic ignition delay times was noted under the different test conditions. Hu et al. [38] suggested

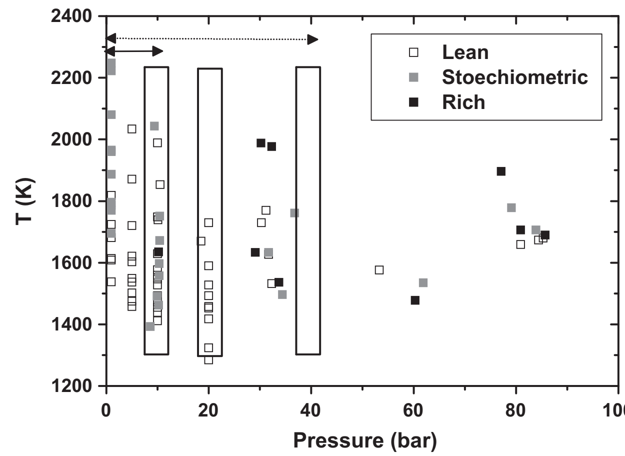


**Fig. 1.** Comparison of conditions studied for pure methane auto ignition delay time measurement between previous studies [12,20,21,24,25] (filled symbols) and this work (marked area). Solid arrow present GRI and USC II pressure domain validation and dashed one for Aramco mechanism.

a fitting correlation (Eq. (2)) of ignition delay times as a function of pressure, temperature and equivalence ratio for the mixtures through regression with a coefficient of determination $R^2 = 0.983$.

$$\tau = 1.09 \times 10^{-3} P^{-0.68} \phi^{-0.04} \times \exp\left(\frac{40.98 \pm 0.51\ \text{kcal mol}^{-1}}{RT}\right) \quad [38] \tag{2}$$

where τ is ignition delay time in μs, $P$ is pressure in atm, $\phi$ is equivalence ratio, $R = 1.986 \cdot 10^{-3}$ kcal/(mol K) and $T$ is temperature in K. For lean and stoichiometric equivalence ratios, both GRI Mech 3.0 [39] and USC Mech II [40] predict well ignition delay time at low pressures while AramcoMech 1.3 [41] was more precise at high pressures. The three kinetic models over-predicted ignition delay times for the fuel rich mixtures.

Some authors also investigated the auto-ignition of methane mixed with other fuels such as ethane/propane by Huang et al. [36] or Healy et al. [24,25] as part of natural gas studies, mixed with hydrogen by Zhang et al. [15], or more recently with dimethyl-ether (DME) by Burke et al. [37].

In our study, ignition delay times for methane are examined for high pressure and temperature conditions for diluted mixtures. First, the experimental data are compared with recently published experimental results from Zhang et al. [15] and Tang et al. [21] at two different pressures, 10 and 20 bar, in order to ascertain the validity of the new high pressure shock tube. Our data obtained presents a large range of experimental conditions for methane combustion. Most relevant mechanisms for methane (GRI Mech 3.0 [39], USC Mech II [40] and Aramco Mech 1.3 [41]) are tested and a sensitivity analysis is also performed to explain the trend of the experimental results, investigating the differences in the predictions and numerically studying the influence of pressure and equivalence ratio fluctuations on the occurrence of auto-ignition which can damage combustors.

## 2. Experimental setup and procedures

### 2.1. Apparatus

The present high-pressure shock tube (HPST) is designed as a versatile tool and includes the features of an adiabatic compression thanks to the shock wave, has optical accessibility, and capability to perform species measurements. Characterization experiments established the suitability of the tube for chemical kinetic studies