

University of Groningen

Ignition properties of methane/hydrogen mixtures in a rapid compression machine

Gersen, S.; Anikin, N. B.; Mokhov, A. V.; Levinsky, H. B.

Published in:
International Journal of Hydrogen Energy

DOI:
[10.1016/j.ijhydene.2008.01.017](https://doi.org/10.1016/j.ijhydene.2008.01.017)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Gersen, S., Anikin, N. B., Mokhov, A. V., & Levinsky, H. B. (2008). Ignition properties of methane/hydrogen mixtures in a rapid compression machine. *International Journal of Hydrogen Energy*, 33(7), 1957-1964. <https://doi.org/10.1016/j.ijhydene.2008.01.017>

Copyright

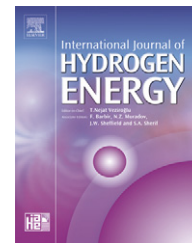
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/ijhe

Ignition properties of methane/hydrogen mixtures in a rapid compression machine

S. Gersen^a, N.B. Anikin^a, A.V. Mokhov^a, H.B. Levinsky^{a,b,*}

^aLaboratory for Fuel and Combustion Science, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

^bGasunie Engineering and Technology, P.O. Box 19, 9700 MA Groningen, The Netherlands

ARTICLE INFO

Article history:

Received 15 September 2007

Received in revised form

25 January 2008

Accepted 26 January 2008

Available online 10 March 2008

Keywords:

Autoignition

Methane

Hydrogen

ABSTRACT

We investigate changes in the combustion behavior of methane, the primary component of natural gas, upon hydrogen addition by characterizing the autoignition behavior of methane/hydrogen mixtures in a rapid compression machine (RCM). Ignition delay times were measured under stoichiometric conditions at pressures between 15 and 70 bar, and temperatures between 950 and 1060 K; the hydrogen fraction in the fuel varied between 0 and 1. The ignition delay times in methane/hydrogen mixtures are well correlated with the ignition delay times of the pure fuels by using a simple mixing relation reported in the literature. Simulations of the ignition delay times using various chemical mechanism are also reported. The mechanism given by Petersen et al. shows excellent agreement with the measurements for all mixtures studied. Initial results on fuel-lean mixtures show a modest effect of equivalence ratio on the delay times.

© 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Increasingly stringent regulations regarding CO₂ emissions, and the knowledge that fossil fuel reserves will be exhausted within this century, have called attention to the possible use of admixtures of hydrogen in natural gas as an alternative fuel in combustion devices. Experimental results [1] have shown that addition of small amounts of hydrogen to methane, the principal component of natural gas, enhance the performance of a gas-powered spark-ignited engine. In the same paper, numerical simulations were used to indicate that hydrogen addition to methane significantly increases the tendency to knock at hydrogen fractions larger than 20%. Knocking combustion in spark-ignited engines is closely related to autoignition of the unburned end gas, and should be avoided at all cost since it can physically damage the engine and increase pollutant emissions. The methane

number [2], used to characterize the knock tendency of natural gases, takes the difference in knock behavior between methane and hydrogen in a specific gas engine to define the extremes of the scale, with pure methane as most knock resistant and pure hydrogen as the least resistant. It would be of value to be able to use more fundamentally based ignition behavior rather than the semi-empirical approach used in the methane number. Understanding autoignition behavior is also important for designing gas turbines [3] and homogeneous charge compression ignition (HCCI) engines [4]. Moreover, autoignition delay times are used as targets for the development and benchmarking of chemical kinetic models for combustion.

While a large number of studies of the ignition of methane and hydrogen have been reported, most of them have been conducted in fuel-oxidizer mixtures diluted with inerts at relatively low pressures (<5 bar). Autoignition studies under

*Corresponding author at: Gasunie Engineering and Technology, P.O. Box 19, 9700 MA Groningen, The Netherlands. Tel.: +31 50 5212677; fax: +31 50 5211946.

E-mail address: h.levinsky@gasunie.nl (H.B. Levinsky).

0360-3199/\$ - see front matter © 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2008.01.017

conditions relevant to engines are scarce. Ignition properties of hydrogen have been studied using $H_2/O_2/Ar/N_2$ [5] and $H_2/O_2/Ar$ [6] mixtures in a rapid compression machine (RCM) at temperatures ranging from 950 to 1100 K, and pressures up to 50 bar. Shock tube measurements of the autoignition delay times in slightly diluted CH_4/O_2 mixtures (fuel + oxidizer ~30%) at high pressures (40–240 bar) and intermediate temperatures (1040–1500 K) have also been reported [7]. Ignition delay times in $CH_4/O_2/Ar$ mixtures using an RCM [8] have been measured at 16 bar between 980 and 1060 K. Ignition delay times obtained in non-diluted lean (equivalence ratio, $\phi = 0.5$) methane/air mixtures behind reflected shock waves between 3 and 450 bar and at temperatures from 1300 to 1700 K [9] were compared with those calculated using the GRI-Mech 3.0 chemical mechanism [10] and showed good agreement. To our knowledge, only three studies of autoignition in hydrogen/methane fuel mixtures have been reported [11–13]. In [11] the influence of small additions of hydrogen (2% and 15% of the fuel by volume) to highly diluted methane/air mixtures at high temperatures (1500–2150 K), moderate pressures (2–10 bar) and equivalence ratios ranging from 0.5 to 2.0 was studied using shock tubes. In this work, a thermal-based promotion theory was proposed to account for the effect of hydrogen addition. A very extensive shock tube study of hydrogen/methane mixtures (temperatures and pressures ranging from 800 to 2000 K and from 1 to 3 bar, respectively) has been reported in [12]. The ignition delay time, τ of dilute H_2/CH_4 mixtures was related to the ignition delay times of pure gases through the empirical relation

$$\tau = \tau_{CH_4}^{(1-\beta)} \tau_{H_2}^{\beta}, \quad (1)$$

where τ_{H_2} and τ_{CH_4} are the ignition delay times of hydrogen and methane, respectively, and β is the mole fraction of hydrogen in the fuel. Recently, the autoignition delay times of two stoichiometric CH_4/H_2 /air mixtures at pressures from 16 to 40 atm and temperatures between 1000 and 1300 K have been measured in a shock tube [13]. Because the well-controlled test conditions in a shock tube persist only for a few milliseconds, the combination of pressure and temperature in this study was chosen to give ignition delay times <3 ms. Interestingly, while a relatively large amount of hydrogen was added to the fuel (35%), only a relatively small reduction in ignition delay time was observed compared to that observed for pure methane. The experiments also show that the ignition-enhancing effect of hydrogen decreases upon reducing the mixture temperature, and decreases significantly upon increasing pressure from 16 to 40 atm. The experimental results were compared with calculations performed using a mechanism [13] that was a modified version of that taken from [7,14]; the comparison showed substantial disagreement, prompting the authors [13] to recommend additional experimental and kinetic studies aimed at the autoignition behavior of methane/hydrogen mixtures.

In this paper, we report the autoignition delay times of stoichiometric methane/hydrogen mixtures using oxygen/nitrogen/argon oxidizers at high pressures (10–70 bar), and temperatures from 950 to 1060 K. The pressures and temperatures of the unburned mixtures were chosen to give

ignition delay times ranging from 2 to 50 ms. The measurements were performed in an RCM and compared with numerical simulations using different chemical mechanisms, taking into account heat loss occurring in the period between compression and ignition.

2. Experimental approach

The measurements were performed in an RCM of the same design, dimensions and specifications reported in Refs. [15,16]. The total compression time in the experiments was 10–20 ms, with 80% of the compression occurring in less than 3 ms. The creviced piston head recommended for this design [16,17] was used to avoid the deleterious effects of roll-up vortices on heat and mass transfer during compression. The H_2/CH_4 mixtures containing 0%, 5%, 10%, 20%, 50% and 100% of hydrogen are used as fuel. The compositions of gas mixtures studied, expressed as mole proportions relative to the fuel, are given in Table 1. To consider the effects of heat loss between compression and ignition in the combustion chamber (see below), we also performed a number of experiments using inert mixtures.

All gas mixtures were prepared in advance in a 10-l gas bottle, used to charge the combustion chamber at the required pressure. The mixtures were allowed to mix ~24 h to ensure homogeneity. The fuel and oxygen concentrations in mixtures A–G are in stoichiometric proportions, while mixture H is at $\phi = 0.5$. The ratio of total inert gases to oxidizer is close to that of nitrogen to oxygen in air, while the N_2/Ar ratio is chosen to provide similar temperatures after compression for all fuels. For comparison with the results of a previous RCM study [6], the measurements are also performed for a $H_2/O_2/Ar$ mixture (mixture A in Table 1). As mentioned above, the pressures were varied between 10 and 70 bar, and temperatures in the range 950–1060 K. In addition, a substantial number of measurements were performed along an isotherm at a temperature after compression of 995 ± 4 K between ~25 and ~65 bar (see below), allowing an examination of the pressure dependence of ignition. For measurements under identical conditions (composition, initial/final pressure), the reproducibility of the measured ignition delay times is ~5% and the uncertainty in deriving the ignition delay time from the measurements is ~0.3 ms. For the data

Table 1 – Compositions of mixtures used in ignition experiments

Mixture	[H ₂]	CH ₄	[O ₂]	[N ₂]	[Ar]
A	1	0	0.5	0	2.5
B	1	0	0.5	1.05	0.95
C	0.5	0.5	1.25	2.18	2.83
D	0.2	0.8	1.7	2.85	3.95
E	0.1	0.9	1.85	3.07	4.34
F	0.05	0.95	1.93	3.18	4.53
G	0	1	2	3.3	4.7
H	0.5	0.5	2.49	3.36	6.6

taken along the isotherm, the variation in temperature at the end of compression ($\pm 4\text{K}$), caused primarily by the reproducibility in the setting of the compression ratio, yields a scatter in the results of 10–20%.

3. Numerical simulation and analysis of experimental data

3.1. Chemical mechanisms

For the calculation of the ignition delay times in this work, we compare a number of different chemical mechanisms, which will be referred to either by acronym (e.g., GRI-Mech) or by author. While one does not *a priori* anticipate good performance from the GRI-Mech 3.0 chemical mechanism [10] since it was optimized for natural gas combustion at lower pressures (0.013–10 atm) than those used here, the large popularity of this mechanism compels us to evaluate its predictive power under the experimental conditions studied here. Better predictions at high pressures can be expected from the RAMEC mechanism [7], which includes 190-reactions involving 38 species based on the GRI-Mech 1.2 mechanism [18], with additional reactions important in methane oxidation at lower temperatures or higher pressures. This mechanism emerged from the kinetic study based on the high-pressure shock tube measurements referred to above [7], and showed the increased importance of reactions involving HO_2 , CH_3O_2 and H_2O_2 at high pressures and low temperatures. The comprehensive chemical mechanism for methane oxidation, developed at the University of Leeds [19], is also used in the present study. This mechanism consists of 351 chemical reactions between 37 species, and is built on the same experimental base as GRI-Mech 3.0. Recently, two revised mechanisms for hydrogen oxidation have been reported. A mechanism for hydrogen oxidation consisting of 19 reversible elementary reactions has been developed by Ó Conaire et al. [20] and evaluated for temperatures ranging from 298 to 2700 K, pressures from 0.05 to 87 bar and equivalence ratios in the range from 0.2 to 6. The hydrogen mechanism developed by Li et al. [21] also consists of 19 chemical reactions, and is expected to perform close to that of Ó Conaire et al. The mechanism of Ó Conaire et al. is included in the comprehensive kinetic model of methane/propane oxidation of Petersen et al. [22], which consists of 663 chemical reactions among 118 species. In this mechanism, the methane oxidation chemistry incorporates recent theoretical and experimental data for the reaction rates. Clearly, the assumption is that a mechanism that performs well for both pure hydrogen and pure methane will adequately describe H_2/CH_4 mixtures as well.

3.2. Numerical simulations

For meaningful comparison between measurements and numerical simulations, it is necessary to account for the effects of heat loss and varying specific volume during the experiment in the simulations. Often, for this purpose the specific volume of the assumed adiabatic core is used as an input parameter [5,16,23], and is derived from the measured

pressure trace in an inert mixture with the thermochemical and transport properties close to those of the reactive mixture under investigation. This method accurately predicts the specific volume of the reactive mixture during the initial stage of the ignition process, when heat release is marginal. Just prior to ignition, the specific volume may be substantially different from that of the inert mixture as result of heat release in the adiabatic core due to chemical reactions. The possible error arising from the neglect of heat release in the estimate of the specific volume on the calculated ignition delay time is small if the duration of this phase is also small. We anticipate that this effect will be larger for complex alkanes showing multistage ignition [23] than for the simple fuels used here, for which only negligible heat release occurs prior to ignition.

In light of these considerations, in the present work we derive the specific volume from the measured pressure trace. In this procedure, we first synthesize the pressure trace that would be observed in the combustible mixture in the absence of chemical reactions. Then, we obtain the specific volume assuming adiabatic expansion of the resulting “non-reacting” mixture from the synthesized pressure trace. We note that incorporation of the compression period in the synthesis allows inclusion of chemical reaction during initial stages of ignition in the simulations. The procedure is as follows. Up to a point prior to significant heat release, t_{tr} , the synthesized pressure is set to the measured pressure. Subsequently, we approximate the pressure decay in the interval between the point of maximum pressure immediately after compression, t_c , and t_{tr} as

$$P(t) = (P_c - P_f) \exp\left(-\frac{t - t_c}{\tau_c}\right) + P_f, \quad (2)$$

where the characteristic time, τ_c , and final pressure, P_f , are obtained from a fit to the measured pressure trace. From simple physical considerations it is reasonable to assume that this functional dependence describes pressure decay of the “non-reacting” mixture for all times after compression. Based on this assumption, we calculate the synthesized pressure from Eq. (2) for $t > t_{\text{tr}}$. The method is illustrated in Fig. 1, which shows part of the synthesized pressure (Fig. 1a) and specific volume (Fig. 1b) derived from the measured pressure trace from one of the experiments for mixture B (Table 1). The point t_{tr} is fixed $\sim 1\text{ms}$ prior to the minimum in the pressure trace after compression. It should be pointed out that for longer ignition delay times, such as shown in Fig. 1, the trace for the pressure obtained using this choice for t_{tr} is indistinguishable from that obtained using inert mixtures having the same heat capacity under the same experimental conditions. For ignition delay times shorter than 2–3 ms, the experimental pressure traces generally showed no pressure decay, and the specific volume after compression was kept constant in the simulations of these conditions. Additional simulations including the largest heat losses observed in the experiments lead to differences of no more than 15% from the constant-volume results for these cases, which we take as a measure of the variations in the simulations as a result of using different models of heat loss at short delay times. The method described here bypasses time-consuming measurements in inert gas mixtures and yields fits to the pressure trace that

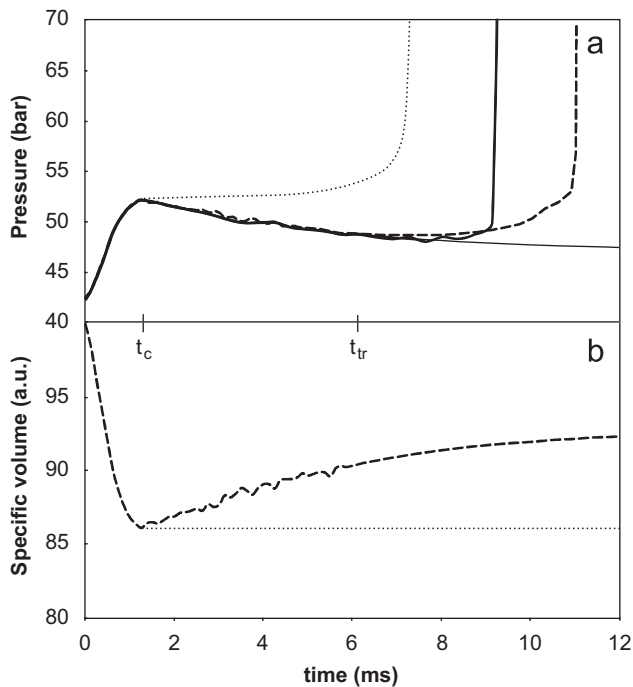


Fig. 1 – (a) Pressure traces for mixture B (Table 1) at 955 K: experimental pressure (thick solid line), synthesized pressure derived taking into account heat loss after compression without chemical reaction (thin solid line), simulated pressures in ignition experiment using specific volume accounting for heat loss (dashed line) and without heat loss (dotted line); (b) specific volume traces derived accounting for heat loss (dashed) and neglecting heat loss (dotted) after compression. For definitions of t_c and t_{tr} , see text.

are on par with those obtained by the other methods [5,23]. In Fig. 1a, we also compare the experimental pressure trace with simulations using the specific volumes shown in Fig. 1b, i.e., synthesized from Eq. (2) and assuming constant specific volume after compression. In both simulations the mechanism of Ó Conaire et al. [20] is used. As expected, the figure shows that neglecting expansion after compression results in significantly shorter ignition delay times. This implies that the measured ignition delay time is the property of a particular RCM, and suggests caution when comparing experimental ignition delay times obtained in different RCMs.

4. Results and discussion

4.1. Experimental results and general trends

To assess the quality of the experimental data, we compare the ignition delay times obtained here with the results of previous RCM studies of the autoignition of pure hydrogen [5,6]. The ignition delay times from different data sets are plotted as a product with the oxygen number density (mol/cm³) at the pre-ignition peak pressure after compression [6], and are presented in Fig. 2 as a function of the

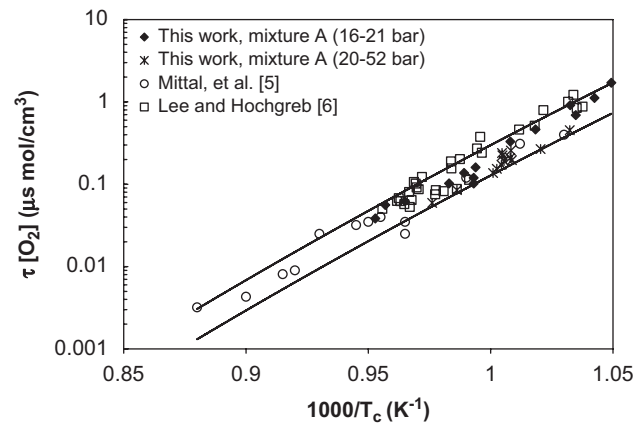


Fig. 2 – Scaled ignition delay times in pure hydrogen fuel as a function of reciprocal temperature after compression. Solid lines denote $\pm 35\%$ interval around the measurements in present work approximated by Eq. (2), see text.

reciprocal temperature after compression. As discussed above, the measured ignition delay time depends substantially upon the heat losses in the RCM combustion chamber. Simulations performed with and without heat loss, as in Fig. 1, indicate that heat loss in our RCM significantly increases the ignition delay time compared with an ideal adiabatic RCM. As can be seen from Fig. 2, all experimental results are within an interval of $\pm 35\%$ of our measurements. Taking into account the assumption of the validity of the scaling method, and that heat loss can vary significantly between the physically different machines, we consider the agreement of the results obtained here and the data in the literature to be excellent.

As can be seen from Fig. 2, the scaled ignition delay time in the pure hydrogen fuel is an exponential function of the reciprocal temperature. The same dependence is observed for pure methane (not shown). Incorporating the pressure dependence using a power function for number density, we obtain an Arrhenius-like empirical relation for the functional dependence of the ignition delay time upon maximum pressure and temperature after compression prior to heat release (P_c and T_c , respectively) for pure hydrogen and methane fuels:

$$\tau = A \left(\frac{P_c}{T_c} \right)^n \exp \left(\frac{E_a}{RT_c} \right). \quad (3)$$

The magnitudes of A , n and E_a (units: s, Pa, mol, kJ, K) derived for the stoichiometric mixtures of hydrogen and methane with oxygen are given Table 2. It should be pointed out that the negative value of the power n for both gases means decreasing ignition delay time with increasing pressure. We remark in passing that for the range of temperatures studied the apparent activation energy for hydrogen is in excellent agreement with that observed in Refs. [5,6], while for methane E_a is significantly lower than that obtained in recent studies [7,14].

To assess whether the recommended mixing expression (1) can also be used for methane/hydrogen mixtures studied in

Table 2 – Fit coefficients for pure fuels derived from Eq. (2)

	A	E_a	n
H ₂	2.82E – 13	336	–1.3
CH ₄	3.23E – 2	192	–2.1

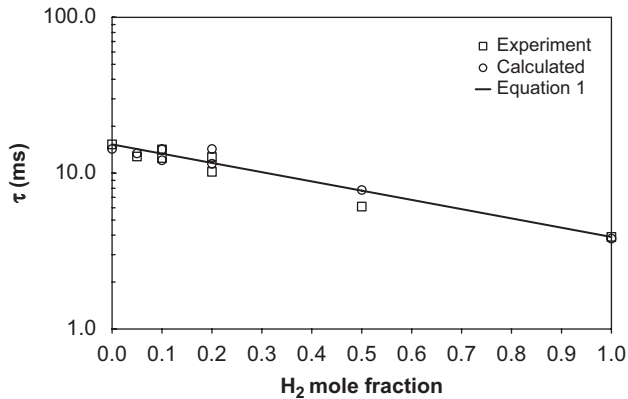


Fig. 3 – Measured and calculated ignition delay times vs. hydrogen mole fraction in fuel at $P_c = 33.5 \pm 1$ bar and $T_c = 995 \pm 4$ K. The simulations were performed accounting for heat loss using the mechanism of Petersen et al. [22]. The solid line is obtained from the mixing relation Eq. (1), see text.

the RCM, ignition delay times have been measured at constant peak pressure ($P_c = 33.5 \pm 1$ bar) and peak temperature ($T_c = 995 \pm 4$ K) as a function of hydrogen mole fractions in the fuel. As can be seen from the results, presented in Fig. 3, replacing methane by hydrogen decreases the ignition delay time, as reported in shock tube studies [11–13]. Moreover, within the limits of the experimental uncertainty, the logarithm of the ignition delay time appears to be a linear function of the hydrogen mole fraction, suggesting the utility of mixing expression (1). The results of applying relation (1) are also shown in the figure. Anticipating the discussion below, we note that the computed ignition delay times, using the mechanism from Ref. [22] and accounting for heat loss as described above, predict this trend within the limits of experimental error.

For further analysis, we rewrite the mixing expression (1) by using Eq. (3) for the ignition delay time in the pure fuels:

$$\tau = A_{H_2}^\beta \cdot A_{CH_4}^{(1-\beta)} \left(\frac{P_c}{T_c} \right)^{n_{H_2}\beta + n_{CH_4}(1-\beta)} \exp\left(\frac{E_{H_2}\beta + E_{CH_4}(1-\beta)}{RT} \right). \quad (4)$$

From this relation, at fixed hydrogen mole fraction we expect a linear dependence of the logarithm of ignition time divided by number density to the power $n = n_{H_2}\beta + n_{CH_4}(1-\beta)$ upon the reciprocal of the temperature. As can be seen from Fig. 4, which shows the results for different hydrogen mole fractions using the data from Table 2 in Eq. (4), mixing relation (4) approximates the experimental data very well. For the mixtures with H₂ content $\leq 20\%$ the effect of hydrogen

addition on the ignition delay time is relatively small, but becomes substantial when the hydrogen fraction is more than 50%. It is interesting to note that the slope of the lines in Fig. 4 increases with increasing hydrogen content in the mixture, reflecting the differences in the “overall” activation energy E_a between the two pure fuels; for hydrogen E_a is two times larger than for methane (Table 2). Thus, at high temperatures, effect of the added hydrogen on the ignition delay time is more pronounced than at low temperatures, as also observed [13] over a wider range of temperatures than those studied here. The mechanistic analysis [13] of those results indicated that the ignition-promoting effect of hydrogen at higher temperatures arose through the increased importance of the reaction $H + O_2 \rightarrow OH + O$ together with the reaction for hydrogen consumption $OH + H_2 \rightarrow O + H_2O$, while at lower temperatures the effect of hydrogen is expressed through the slower reaction $CH_3O_2 + H_2$, which is responsible for the reduced promotion of ignition.

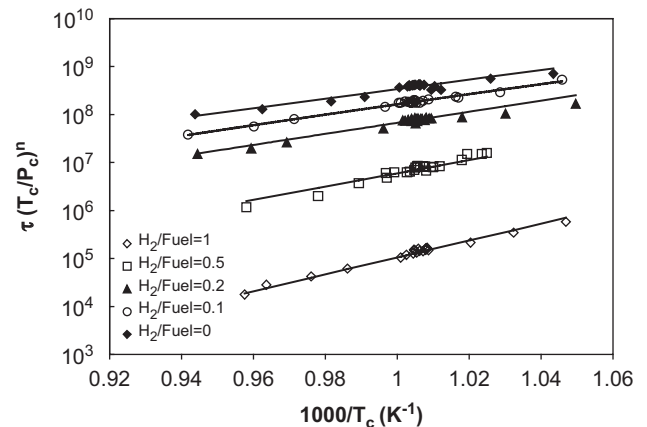


Fig. 4 – Measured ignition delay times scaled according to Eq. (2) as a function of reciprocal temperature (symbols), and the results calculated using mixing relation (4) (lines).

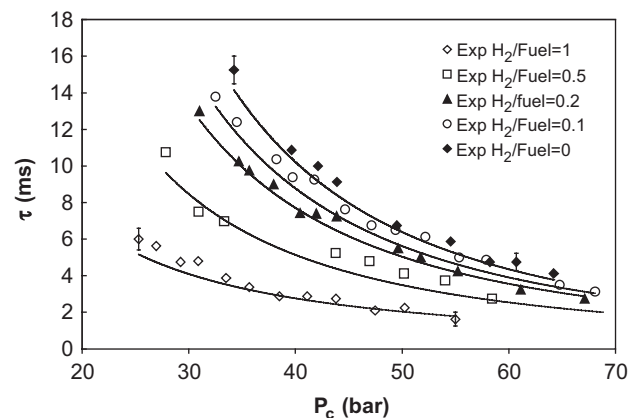


Fig. 5 – Measured (symbols) and calculated (lines) autoignition delay times, as a function of pressure at fixed peak compression temperature $T_c = 995 \pm 4$ K and different hydrogen mole fractions in fuel. The calculated curves were obtained using Eq. (4).

As can be seen in Fig. 4, all measurements obtained along the isotherm at a temperature after compression (T_c) of ~ 995 K and fixed hydrogen mole fraction collapse to a small cluster, which demonstrates that Eq. (4) correctly predicts the pressure dependence of the ignition delay time. Presenting the isotherm data on a linear scale in Fig. 5, as a function of pressure for different volume fractions of hydrogen, we observe some scatter around the lines from Eq. (4), which is caused by day-to-day variations in T_c (± 4 K) in the measurements, as mentioned in the Experimental section. As noted above, the ignition delay times decrease with increasing pressure for all hydrogen fractions measured, extending the observations of the recent shock tube study [13].

4.2. Comparison of experimental results with numerical simulations

Figs. 6–8 show the measured and calculated autoignition delay times using different chemical mechanisms. To avoid clutter in the figures, the simulated data are presented as

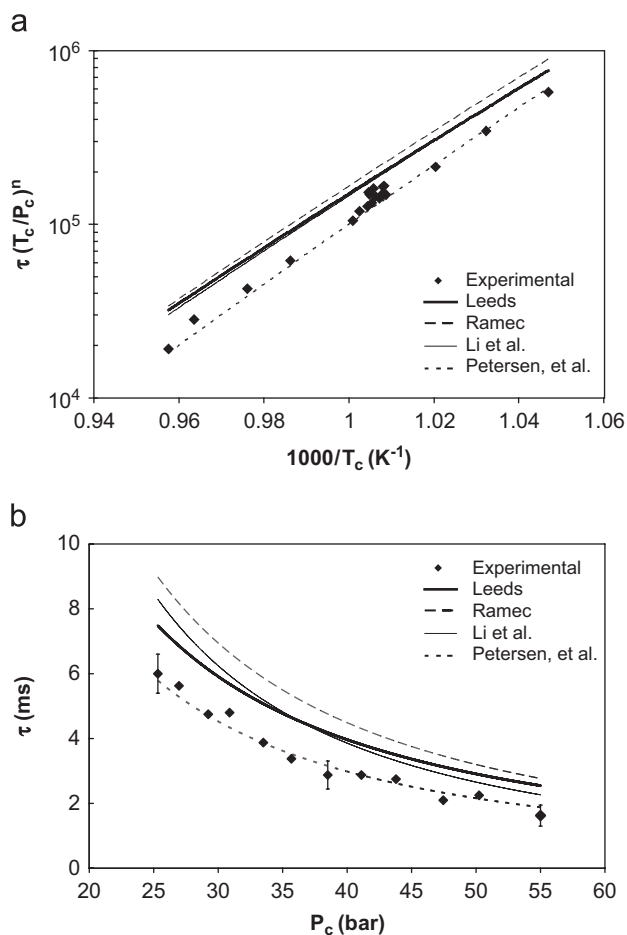


Fig. 6 – Measured (diamonds) and calculated (lines) autoignition delay times for pure hydrogen (mixture B in Table 1). (a) Scaled delay times vs. reciprocal temperature; (b) delay time vs. pressure at fixed temperature $T_c = 995 \pm 4$ K. The calculations were performed using the detailed mechanisms indicated.

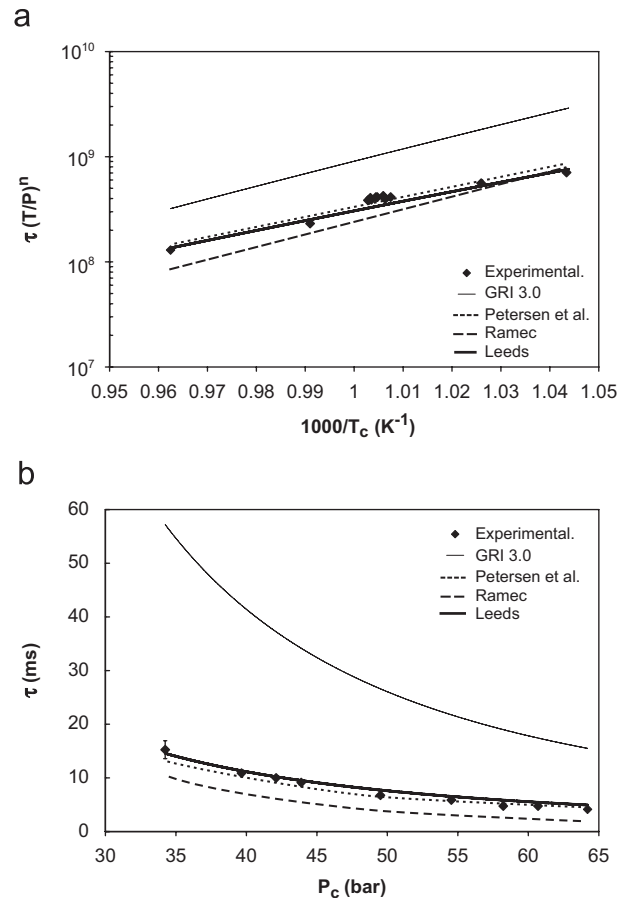


Fig. 7 – Measured (diamonds) and calculated (lines) ignition delay times for pure methane (mixture G in Table 1). (a) Scaled delay times vs. reciprocal temperature; (b) delay time vs. pressure at fixed temperature $T_c = 995 \pm 4$ K. The calculations were performed using the detailed mechanisms indicated.

polynomial trend lines through the calculated points. The measured and calculated ignition delay times are presented in two sets. The first set (Figs. 6a–8a) includes logarithms of the ignition delay times scaled by $(P/T)^n$ as a function of the reciprocal temperature to eliminate the density dependence, and highlight the expected Arrhenius behavior with temperature. The second set of figures (Figs. 6b–8b) presents the ignition delay times measured along the 995 ± 4 K compression isotherm.

The results for pure hydrogen (mixture B, Table 1) are presented in Fig. 6. As can be seen, the calculations using the mechanism from Petersen et al. show excellent agreement with the measurements over the range of pressure and temperature studied; Li et al. and Leeds are generally within 30% of the measurements, while RAMEC tends to overpredict the measured ignition delay times by more than 50%. Calculations using the Leeds mechanism and GRI-Mech 3.0 (not shown in Fig. 6) give identical results for all experimental conditions, which considering their similarity is perhaps not surprising. The decidedly better agreement obtained using Petersen et al. also suggests the use of this mechanism for ignition delay studies of hydrogen combustion under gas

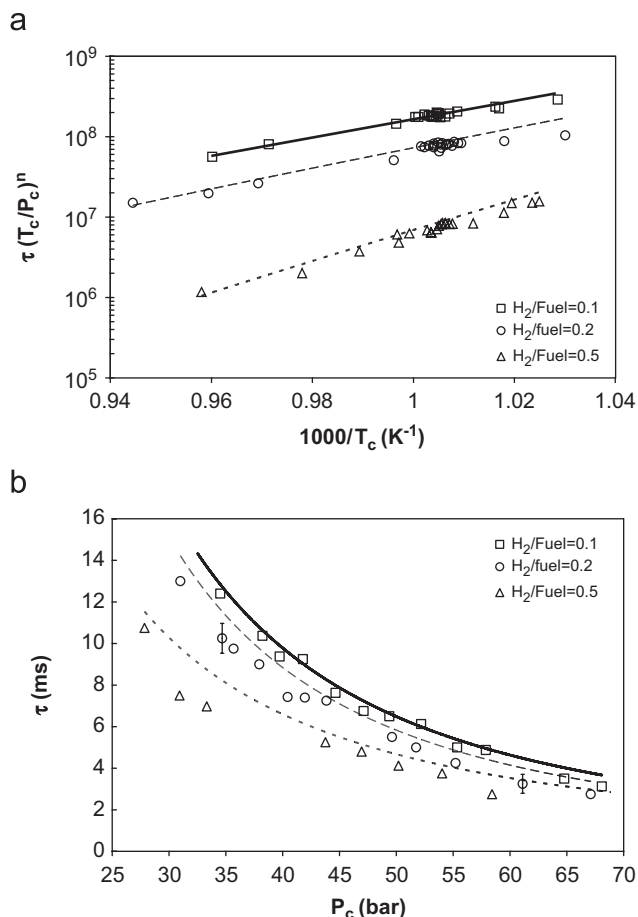


Fig. 8 – Measured (symbols) and calculated (lines) autoignition delay times for hydrogen/methane fuel (mixtures C, D and E in Table 1) as a function of reciprocal temperature (a) and pressure at fixed temperature $T_c = 995 \pm 4$ K (b). The calculations were performed using Petersen et al. [22].

turbine conditions, similar to the recommendation made in a recent study [24].

Fig. 7 presents the measured and calculated ignition delay times for pure methane (mixture G, Table 1). As can be seen from Fig. 7a, the calculations using the Leeds and Petersen et al. mechanisms are in excellent agreement with the experimental results for all conditions measured. The predictions of the RAMEC mechanism are within 10% of the experiments at the lowest temperatures but substantially underpredict (up to a factor of two) the ignition delay times at high temperatures. The results of the calculations with GRI-Mech 3.0 are more than a factor of two higher than the scaled measured ignition delay times for all data in Fig. 7a. The unscaled data for ignition delay times along the isotherm at $T_c = 995$ K presented in Fig. 7b also show excellent agreement between measurements and calculations with the Leeds and Petersen et al. mechanisms. At this temperature the RAMEC mechanism slightly underpredicts the measurements at pressures below 45 bar, but equals the other mechanisms at higher pressure. GRI-Mech 3.0, while following the experimental

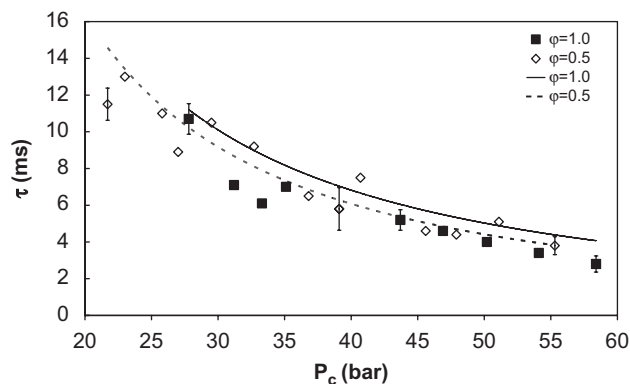


Fig. 9 – Measured (symbols) and calculated (lines) ignition delay times for 50% H₂ in the fuel at $\phi = 1.0$ and 0.5 (mixtures C and H, respectively, in Table 1) as a function of pressure at fixed temperature $T_c = 995 \pm 4$ K. The calculations were performed using Petersen et al. [22].

trend well, substantially overpredicts the ignition delay in this range.

The mechanism proposed by Petersen et al. thus predicts the ignition delay time in both pure hydrogen and methane very well, while the predictions of the other mechanisms considered here tend to show larger differences with the measurements, particularly regarding pure hydrogen. Furthermore, this mechanism also yields the best agreement with the experiments performed on the hydrogen/methane mixtures discussed below. Consequently, in the following comparisons we only show computational results using this mechanism. As can be seen from Fig. 8, the computed ignition delay times are in excellent agreement with the experiments in the hydrogen/methane mixtures. Over the range of pressure and temperature studied, the agreement between the calculations and measurements is better than 25%.

While the discussion above has focused entirely on stoichiometric mixtures, we have also obtained results under lean conditions ($\phi = 0.5$), for the 50/50 hydrogen/methane ratio (mixture H in Table 1). The ignition delay times measured along the 995 K isotherm are presented in Fig. 9, together with the stoichiometric results. Interestingly, we see no change in the measured delay times between the lean and stoichiometric mixtures within the experimental uncertainty (dominated by the ± 4 K temperature uncertainty discussed above). In addition, as seen in the previous figures, the computational results using Petersen et al. predict both trends and magnitude of the results excellently. Under the conditions of the experiments, the predicted differences for the two equivalence ratios are less than 1 ms. We are currently extending these measurements to other hydrogen/methane ratios.

5. Summary and conclusions

Autoignition delay times of methane/hydrogen mixtures at high pressure (10–70 bar) and moderate temperatures (960–1060 K) have been measured in a rapid compression

machine. The experimental results obtained under stoichiometric conditions show that replacing methane by hydrogen reduces the measured ignition delay time. Both measured and computed ignition delay times in the fuel mixtures are shown to be related quantitatively to the hydrogen mole fraction in fuel according to the mixing relation proposed in the literature [12]. At low mole fractions ($\leq 20\%$), hydrogen addition has a modest effect on the measured ignition time under the experimental conditions presented here. At 50% hydrogen mole fraction in the fuel a substantial reduction in ignition delay time is observed. The measurements show that the effect of hydrogen in promoting ignition increases with temperature and decreases with pressure. Interestingly, results for 50% hydrogen in the fuel at $\phi = 0.5$ are essentially identical to those at $\phi = 1.0$. Very good agreement between the measurements and calculations using the mechanism proposed by Petersen et al. [22] is observed for all fuel mixtures studied. Over the entire operational range of temperatures and pressures used in the present study, the differences between the measured and calculated values of the ignition delay time are less than 10% for pure fuels and better than 25% for the hydrogen/methane mixtures.

Acknowledgments

We are indebted to J. Keck, W. Cheng and T. DeWitt for providing us with the design of the MIT RCM, and for particularly helpful discussions on its use in ignition studies. We also thank F.L. Dryer and H.J. Curran for kindly providing us with chemical mechanisms. This work was financially supported by the Dutch fund for Economy, Ecology and Technology (EET).

REFERENCES

- [1] Karim GA. Hydrogen as a spark ignition engine fuel. *Int J Hydrogen Energy* 2003;28(5):569–77.
- [2] Leiker M, Cartelliere W, Christoph H, Pfeifer U, Rankl M. Evaluation of antiknocking property of gaseous fuels by means of methane number and its practical application to gas engines. *ASME* 1972;94(7):55.
- [3] Ren JY, Egolfopoulos FN, Tsotsis TT. NOX emission control of lean methane-air combustion with addition of methane reforming products. *Combust Sci Technol* 2002;174(3):181–205.
- [4] Tanaka S, Ayala F, Keck JC, Heywood JB. Two-stage ignition in HCCI combustion and HCCI control by fuels and additives. *Combust Flame* 2003;132(1–2):219–39.
- [5] Mittal G, Sung CJ, Yetter RA. Autoignition of H_2/CO at elevated pressures in a rapid compression machine. *Int J Chem Kinet* 2006;38(8):516–29.
- [6] Lee D, Hochgreb S. Hydrogen autoignition at pressures above the second explosion limit (0.6–4.0 MPa). *Int J Chem Kinet* 1998;30(6):385–406.
- [7] Petersen EL, Davidson DF, Hanson RK. Kinetics modeling of shock-induced ignition in low-dilution CH_4/O_2 mixtures at high pressures and intermediate temperatures. *Combust Flame* 1999;117(1–2):272–90.
- [8] Brett L, MacNamara J, Musch P, Simmie JM. Simulation of methane autoignition in a rapid compression machine with creviced pistons. *Combust Flame* 2001;124(1–2):326–9.
- [9] Zhukov VP, Sechenov VA, Starikovskii AY. Spontaneous ignition of methane-air mixtures in a wide range of pressures. *Combust Explos Shock Waves* 2003;39(5):487–95.
- [10] Smith GP, Golden DM, Frenklach M, Moriarty NW, Eiteneer B, Goldenberg M, et al. (http://www.me.berkeley.edu/gri_mech/).
- [11] Lifshitz A, Scheller K, Burcat A, Skinner GB. Shock-tube investigation of ignition in methane-oxygen-argon mixtures. *Combust Flame* 1971;16(3):311–21.
- [12] Cheng RK, Oppenheim AK. Autoignition in methane hydrogen mixtures. *Combust Flame* 1984;58(2):125–39.
- [13] Huang J, Bushe WK, Hill PG, Munshi SR. Experimental and kinetic study of shock initiated ignition in homogeneous methane-hydrogen-air mixtures at engine-relevant conditions. *Int J Chem Kinet* 2006;38(4):221–33.
- [14] Huang J, Hill PG, Bushe WK, Munshi SR. Shock-tube study of methane ignition under engine-relevant conditions: experiments and modeling. *Combust Flame* 2004;136(1–2):25–42.
- [15] Park P. Rapid Compression machine measurements of ignition delays for primary reference fuels. Ph.D. thesis, MIT; 1990.
- [16] Lee D, Hochgreb S. Rapid compression machines: heat transfer and suppression of corner vortex. *Combust Flame* 1998;114(3–4):531–45.
- [17] Lee D. Autoignition measurements and modelling in a rapid compression machine. Ph.D. thesis, MIT; 1997.
- [18] Bowman CT, Hanson RK, Davidson DF, Gardiner WC, Lissanski V, Smith GP, et al. (http://www.me.berkeley.edu/gri_mech/).
- [19] Hughes KJ, Turanyi T, Clague AR, Pilling MJ. Development and testing of a comprehensive chemical mechanism for the oxidation of methane. *Int J Chem Kinet* 2001;33(9):513–38.
- [20] Ó Conaire M, Curran HJ, Simmie JM, Pitz WJ, Westbrook CJ. A comprehensive modeling study of hydrogen oxidation. *Int J Chem Kinet* 2004;36(11):603–22.
- [21] Li J, Zhao ZW, Kazakov A, Dryer FL. An updated comprehensive kinetic model of hydrogen combustion. *Int J Chem Kinet* 2004;36(10):566–75.
- [22] Petersen EL, Kalitan DM, Simmons S, Bourque G, Curran HJ, Simmie JM. Methane/propane oxidation at high pressures: experimental and detailed chemical kinetic modeling. *Proc Combust Inst* 2007;31:447–54.
- [23] Tanaka S, Ayala F, Keck JC. A reduced chemical kinetic model for HCCI combustion of primary reference fuels in a rapid compression machine. *Combust Flame* 2003;133(3):467–81.
- [24] Strohle J, Myhrvold T. An evaluation of detailed reaction mechanisms for hydrogen combustion under gas turbine conditions. *Int J Hydrogen Energy* 2007;32(1):125–35.