A chemical kinetic modelling study of the combustion of $CH_4 - CO - H_2 - CO_2$ fuel mixtures

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Abstract

In the present study, five detailed reaction mechanisms have been employed for simulating 530 ignition delay times involving mixtures containing methane, hydrogen, carbon monoxide and carbon dioxide. A novel concept, Reaction Significance Analysis (RSA), has been used for identifying those kinetic parameters which have the greatest influence on the disparities between a given set of experimental data and the model predictions. Overall, most mechanisms capture at best the combustion of biogas and display their poorest performance in relation to the combustion of bio-syngas. NUIG (a reaction mechanism developed at the National University of Ireland, Galway) proves to be the best choice for simulating the burning of bio-syngas, its imperfection notwithstanding. Generally, models tend to over-predict ignition delay times measured at the lowest temperatures. This effect is mostly related to the inhomogeneous behaviour of shock tubes under those conditions. Besides that, Reaction Significance Analyses revealed a correlation between poor modelling performance and reactions belonging to the subsystem $HO_2 - H_2O_2$. We identified situations where such chemical kinetic factors appear to play a role in inaccurate predictions. Overall, the present study strongly indicates that the kinetic modelling of the combustion of $CH_4 - CO - H_2 - CO_2$ should not be seen as a problem successfully solved in the past once and for all. There is a genuine need for more kinetic experiments targeting reaction parameters which remain widely uncertain owing to their weak influence on most available measurements.

1. Introduction

While the combustion of heavy hydrocarbons (such as aromatic hydrocarbons, cycloalcanes and high alcanes) plays a major role in the use of transportation engines and burners [1–3], the combustion of methane remains extremely important for power and

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Table 1: Typical composition of biogas and bio-syngas from biomass gasification

Constituent (Volume %)	Biogas	Bio-syngas
CH_4	50 - 75	8 - 11
CO_2	25 - 50	21 - 30
CO	-	28 - 36
H_2	0 - 1	22 - 32
N_2	0 - 10	-

heat generation. On the one hand, all detailed reaction mechanisms describing the oxidation and pyrolysis of aromatic compounds and high alcanes have to contain an accurate sub-model accounting for the combustion of CH_4 [4, 5]. The reactions it involves can determine to a large extent the concentrations of methyl and hydroxyl radicals and thus the major features of any flame [6]. On the other hand, methane itself is one of the main constituents of fuels which are frequently used at the dawn of the third millennium. Natural gas is a fossil resource mainly composed of methane which is still massively utilised for the production of heat and electricity [7]. It is currently also being increasingly used as a fuel for engines [8].

Since methane is an important compound of promising renewable fuels such as biogas and bio-syngas, an accurate understanding of its burning is crucial for its environment-friendly and sustainable use [9, 10]. Mostly composed of 40-75% of methane, 25-55% of carbon dioxide (and possibly 0-10% of hydrogen), biogas stems from the fermentation of biomass by anaerobic bacteria. It can be produced from organic wastes and energetic plants. Its manifold applications include the combined generation of heat and electricity and its conversion into liquid or gaseous fuels and hydrogen [11]. Bio-syngas is a synthetic gas obtained from the thermal gasification of biomass. It contains CO, CO_2, CH_4, and H_2 and is thought to be a cleaner fuel than biogas owing to its higher hydrogen content [12]. Table 1 sums up the typical composition of biogas and bio-syngas [13]. Both biogas and bio-syngas are promising renewable fuels. Their combustion can be critically dependent on reactions undergone by methane and the methyl radical [14, 15].

All of the above indicates that a very good understanding of CH_4 oxidation and its *interaction* with CO, CO_2, and H_2 is necessary if one is to meet the economical and environmental challenges of our century in an optimal way. CFD (Computational Fluid Dynamics) simulations are now being widely recognised as a necessary part of the efficient design of power generation systems [16]. Their reliable use requires a good underlying detailed reaction mechanism which must be reduced [17–19] in order to become suitable for their high computational requirements. Given the central importance of methane, most reaction mechanisms have been specifically validated with respect to its combustion. In our previous studies [14, 15], we considered five of them:

- GRI 3.0 (Gas Research Institute), which has been systematically optimised with respect to a great number of measurements pertaining to the combustion of natural gas.

- DRM (Detailed Reduced Model), a skeletal version of the GRI-mechanism.
- Frenklach's mechanism, a detailed reaction mechanism extending the GRI-mechanism to pyrolytic conditions.
- Heghes' mechanism, a reaction mechanism accounting for the oxidation of $C_1 - C_4$ hydrocarbons.
- A large-scale mechanism accounting for the combustion of $C_1 - C_5$ hydrocarbons designated as NUIG (National University of Ireland, Galway).

A priori, GRI 3.0 is expected to lead to the best results given the fact that its kinetic parameters have been specifically optimised with respect to a highly diverse set of experiments involving CH_4.

Despite this intensive modelling endeavour, the situation is not always satisfactory. For example, the predictions of the mechanisms are in strong conflict with shock-tube experiments that specifically target the chemistry of CH_3 recombination which can play an important role in the formation of NO during the combustion of biogas [20]. So far as bio-syngas is concerned, the ignition delay times for high pressures and high temperatures as well as low temperatures and low pressures are poorly matched by GRI 3.0 [14]. These problems indicate that it may be worthwhile to extend our comparative evaluation of the five models (which was limited to bio-syngas [14] and biogas [15]) to a much greater number of experimental data, many of which directly involve the combustion of methane. To that end, we considered **530** ignition delay times measured behind reflected shock waves so as to allow a uniform quantification of the discrepancies between experiments and model results.

This article is organised as follows. In Section 2, the methodology is presented. In Section 3, the simulations of sets of experiments using the five reaction mechanisms is described and analysed. In Section 4, the influence of various factors (such as temperature range, dilution or composition) on the accuracy of the model predictions is examined. Finally, in Section 5, the conclusion of the present study is given along the outlook.

2. Methodology

The simulations of the shock tube measurements have been carried out with the software Homrea [21–23] using homogeneous zero-dimensional assumptions involving a constant volume V and a constant internal energy U. Whilst these hypotheses prove insufficient for correctly accounting for a range of shock tube experiments (see [24–26] and our own discussion thereof in subsection 4.1), we adopted it uniformly here because we aimed at simulating a very wide variety of conditions relevant to the combustion of $CH_4 - CO - H_2 - CO_2$, comparing them to model predictions and computing statistical quantities **while keeping in mind that the discrepancies between model predictions and measurements often stem from a combination of faulty chemical and physical modelling**. While it might be desirable to *systematically* simulate experiments characterised by long ignition delays employing more realistic physical models such as CHEMSHOCK [27], doing so would require a long-term endeavour going beyond the resources available for the present work. We systematically defined the ignition delay as the time point at which the slope of the OH radical concentration (or that of H under pyrolytic conditions) takes on its greatest value. Our experience showed us that the difference with values obtained through the use of other variables are very small, as has been confirmed elsewhere [26].

Five detailed reaction mechanisms have been considered for the present study. The Gas Research Institute (GRI) mechanism 3.0 [28] has been developed for simulating the combustion of natural gas. This involved the systematic optimisation of its kinetic and thermo-chemical parameters with the Surface Mapping Method [29, 30]. It consists of 325 elementary reactions and encompasses 53 species which account for the combustion of H_2 ,CO, CH_4, N_2 (NOx formation) as well as reactions between nitrogenous species and the hydrocarbons. While this reaction mechanism is now relatively old, it represents the only systematic attempt to optimise its highly correlated kinetic parameters using a wide range of experimental measurements.

Frenklach et al. [30–32] and Wang and Sheen [33] have forcefully argued against the view that "proliferating" reaction mechanisms based on collections of individually evaluated rate constants is a strategy likely to produce trustworthy models. Given this unique feature of GRI 3.0., it seemed warranted to include it in our study despite its older age.

The Developed Reduced Mechanism (DRM) 22 [34] is a reduced skeletal mechanism based on an earlier version of GRI (1.2). It was developed through the use of a flux analysis and the constraints

$$\mathrm{R(i)} \ < \ \mathrm{e(r)|R(ref)|} \quad \text{and} \quad \mathrm{|R(i)\delta H(i)|} \ < \ \mathrm{e(q)Q}$$

whereby R(i) is the rate of reaction i, R(ref) is the rate of a reference reaction (such as, say, the maximum rate), δH(i) is the enthalpy change of reaction i, Q is the maximum value among all the terms $|\mathrm{R(i)}\delta\mathrm{H(i)}|$, and e(R) and e(q) are chosen parameters considerably smaller than unity. The reference rates were produced using the detailed GRI-mechanism version 1.2. Frenklach et al. [1, 5] constructed a reaction mechanism describing the formation of Polycyclic Aromatic Hydrocarbons (PAH) under rich and pyrolytic conditions. It relies on the GRI-mechanism (version 1.2) alongside steps accounting for the formation of growing aromatic compounds which are the precursors of soot. It led to good predictions for various profiles of aromatic species and their intermediates in laminar flames. We considered it for all our investigations in order to see if it can better describe combustion under rich conditions.

Heghes built up a reaction mechanism [4, 21, 35] for $C_1 - C_4$ hydrocarbons which was validated in relation to laminar flame speeds and ignition delay times measured in shock tubes. The mechanism consists of 412 elementary reactions and 61 species and is based on a rate-data compilation by Baulch et al. [36] grounded on kinetic experiments, quantum chemical computations and analogies with well-known reactions. It was tested with respect to the stoichiometric/ fuel-lean combustion of H_2 , H_2-CO, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, and C_4H_{10}. Overall, it yielded a good match to the measurements except for acetylene, which is probably of little relevance to the simulation of natural gas, biogas, bio-syngas and methane alone. Since we used it in our previous studies about biogas [15] and found it displayed interesting performances in relation to some CH_4-H_2 blends, we considered it worthwhile to also employ it for the present work.

The NUIG (National University of Ireland in Galway) mechanism is a C_0-C_5 reaction mechanism which stems from a long-term endeavour aiming at the construction of a model capable of describing the combustion of various hydrocarbons under a wide range of conditions. It has a hierarchical structure and includes H_2-O_2, $CO-CH_4$, C_2, C_3, C_4, and C_5 sub-mechanisms [3, 37–39]. Whilst the NUIG mechanism has not been specially fine-tuned to capture the chemistry of $H_2-CO-CH_4-O_2$ blends (such as in bio-syngas), it gave very satisfactory predictions of $CH_4/H_2/CO$ experiments performed by Gersen et al. [40] in a rapid compression machine. In the bio-syngas experiments conducted by Mathieu et al. [41] in shock tubes, the NUIG predictions are often much closer to the measurements than those of the GRI-mechanism. As a consequence, we have deemed it worthy of consideration for our studies. In contrast to the other four mechanisms mentioned above, its H_2-O_2 subpart has been separately developed [42] through a rigorous comparison with measurements under fairly diverse conditions (from 298 to 2700 K, 0.05 to 87 atm and an equivalence ratio varying between 0.2 and 6 for ignition delay times in shock tubes, flame speeds and concentration profiles in flames and laminar flow reactors). What is more, it employs the recommended rate expression for the elementary step $CO+HO_2=CO_2+OH$ [43] aiming at reconciling the effect of CO in H_2 mixtures on the measured ignition delay times at high pressure. The kinetics of the $CH_3-O_2-CH_3O_2$ system has also been adapted to high pressures and intermediate temperature ranges [44]. Taken all together, these factors might explain why NUIG performed better than GRI 3.0 with respect to the simulation of the experiments involving bio-syngas mentioned above.

In a recent publication [20], Fischer and Jiang argued that the evaluation and optimisation of chemical kinetics models call for some sort of probabilistic framework taking into account the unavoidable uncertainties of any measurements. Wang and Sheen [33], Frenklach et al. [31, 32], Olm et al. [45, 46], and Burke et al. [47] have offered complementary overviews of the evaluation and comparison of reaction mechanisms we refer the interested reader to.

An experimental data point e_i is usually assumed to follow a normal distribution with mean value μ_i and standard deviation σ_i so that its probability density is given by

$$P(e_i,\mu_i,\sigma_i)=\frac{1}{\sigma_i\sqrt{2\pi}}e^{-(e_i-\mu_i)^2/2\sigma_i^2}$$

Therefore, the probability density of all measurements given the validity of a reaction mechanism with parameter values p and the standard deviations σ_i is given by

$$L(e|p) = \prod_{i=1}^{n} P(e_i, m_i, \sigma_i) = \prod_{i=1}^{n} \frac{1}{\sigma_i\sqrt{2\pi}} e^{-(e_i - m_i(p))^2 / 2\sigma_i^2}$$

Maximising this term is tantamount to minimising the Chi-square norm

$$\chi^2(p) = \sum_{i=1}^{n} \frac{(e_i - m_i(p))^2}{\sigma_i^2}$$

which yields maximum likelihood estimates for the kinetic coefficients. In the present publication (where we limit ourselves to ignition delay times), we decided to use the distance between their logarithmic values defined as

$$d(p) = \sum_{i=1}^{n} |log_{10}(\tau_{m,i}) - log_{10}(\tau_{e,i})|$$

instead, whereby $\tau_{m,i}$ and $\tau_{e,i}$ are the model prediction and the experimental measurement, respectively. While this norm should be used with caution when estimating parameters, it allows a more intuitive visualisation of the strengths and weaknesses of the models under various conditions which all involve ignition delay times.

A new type of sensitivity analysis called **Reaction Significance Analysis** (RSA) has been developed by us [20]. Let us consider a parameter q included within the interval $[q_l; q_u]$. Its reaction significance is defined as

$$S = max\{d(q), q \in [q_l; q_u]\} - min\{d(q), q \in [q_l; q_u]\}$$

It is a natural measure of the influence of q on the overall distance d between model predictions and measurements. Unlike sensitivity coefficients which are mostly related to *a single species at a single time point*, an RSA provides us with a quantity informing us about the overall importance of a parameter with respect to an ensemble of experimental data. An RSA permits the *identification* of kinetic parameters whose optimisation can be expected to minimise the global discrepancies between model predictions and measurements. Traditional sensitivity analyses focus on a limited part of the experiment and a limited number of variables such as the concentration of OH measured at the time of the ignition. While dealing with a very large number of measurements , individual sensitivity analyses do not necessarily inform us about the reactions playing a major role in the global disparities between model predictions and measurements. Consequently, we think that RSA are worthy of consideration while attempting to evaluate the *relative merits* of a model with respects to pressure, temperature or composition regions involving many experiments. We recently applied RSA to identify a reaction set of GRI 3.0 accounting for the largest discrepancies with measured species profiles related to the combustion of CH_3 and C_2H_6 and could show that the mechanism is potentially optimisable in that respect

[20].

We believe that future studies systematically comparing RSA with advanced sensitivity analysis techniques (such as Global screening methods [48], Surface response methods [30], polynomial chaos methods [49] and techniques based on Bayesian analyses [33]) are worthwhile.

In order to allow comparisons between RSA performed for different experiments and diverse reaction mechanisms, we defined *relative* Reaction Significances. Let us suppose, for instance, that the reaction significances of n reactions have been computed. Let us call R_m the greatest value among them. The relative reaction significances are obtained by dividing all corresponding reaction significances by R_m. For the sake of simplicity, relative reaction significances will be simply called reaction significances from now on. The advantage of this redefinition is threefold:

- all values are comprised between 0 and 1
- the relative importance of the steps can be more easily visualised
- comparisons with RSA calculated under other conditions become possible.

Reaction Significance Analyses have been carried out for the different experimental sets of Section 3 using DRM by virtue of its smaller number of reactions which reduced the computational burden. While the numerical values of the RSA coefficients might depend on the reaction mechanism taken into consideration, our experience was that the important steps identified in this way can be also found using any other sufficiently reliable model instead [50].

RSA is a potential way to test *the self-consistency* of a set of experimental data. If the same reactions are significant for various experiments very well described by the model, we might cautiously draw the conclusion that their values are more or less trustworthy. If the same reactions are significant for various experiments poorly predicted by the model, we may either conclude that their parameters are erroneous or that the *physical assumptions* used to simulate the experiments are invalid. A considerable body of evidence [24, 51, 52] shows that shock tube experiments at low temperatures exceeding a certain duration (which might be as short as 500 μs [26]) can no longer be viewed as zero-dimensional systems whose variables only depend on the reaction time. Facility-dependent unstabilities may considerably quicken the ignition, thereby leading to much lower delays than those which would have been obtained if the system had been homogeneous. In order to make a distinction between this situation and cases where ignition delay times are mostly governed by homogeneous chemical kinetics, we separately computed the averaged discrepancies (and their standard deviations) for temperatures **below and above 1250 K** as the shape of the data employed seems to strongly indicate that the combustion can be considered homogeneous for values higher than this threshold.

Another potentially interesting aspect of RSA is its revealing the inconsistency of two experiments whose discrepancies with the model predictions are influenced by the same reactions. If one experiment presents a good match to the results of the mechanism

Table 2: Conditions of Kalitan [53]

Series	X_{H2}	X_{CO}	X_{CH4}	X_{CO2}	X_{AR}	X_{O2}	X_{N2}	p (bar)
1	1.15E-01	6.60E-03	5.67E-03	1.50E-02	1.40E-03	1.79E-01	6.78E-01	9.707
2	1.15E-01	6.60E-03	5.67E-03	1.50E-02	1.40E-03	1.79E-01	6.78E-01	30.195
3	1.80E-01	1.03E-02	8.87E-03	2.36E-02	2.19E-03	1.61E-01	6.14E-01	11.956
4	1.80E-01	1.03E-02	8.87E-03	2.36E-02	2.19E-03	1.61E-01	6.14E-01	36.578
5	4.03E-02	5.53E-02	7.50E-03	3.52E-02	2.50E-03	1.57E-01	7.02E-01	9.119
6	4.03E-02	5.53E-02	7.50E-03	3.52E-02	2.50E-03	1.57E-01	7.02E-01	25.838
7	5.93E-02	8.15E-02	1.11E-02	5.19E-02	3.70E-03	1.32E-01	6.60E-01	36.781

Table 3: Average logarithmic discrepancies for Kalitan [53]

Series	DRM	Frenklach	GRI	Heghes	NUIG
1	0.234	0.234	0.517	0.277	0.187
2	0.898	0.898	0.960	0.800	0.821
3	0.703	0.703	0.880	0.692	0.700
4	0.651	0.651	0.720	0.607	0.587
5	0.358	0.358	0.088	0.123	0.081
6	0.350	0.350	0.122	0.244	0.040
7	0.240	0.240	0.132	0.146	0.114
$T < 1250$ K	0.500	0.500	0.517	0.439	0.377
$T \geq 1250$ K	0.358	0.358	0.110	0.136	0.063

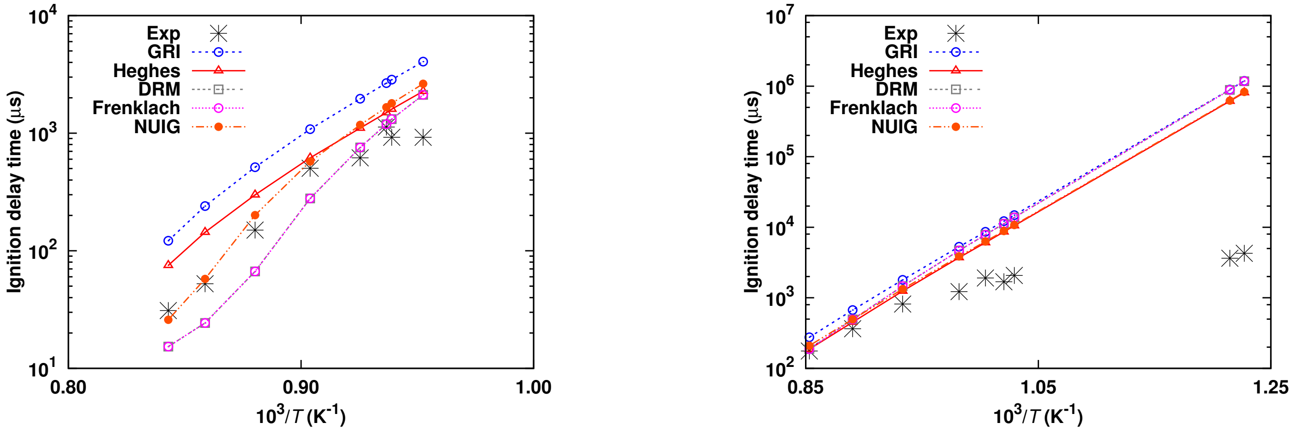
whereas the data of the other one are far off from them, we may safely conclude that at least one of them has not been correctly modelled physically or that some systematic error occurred. Such a conclusion might be harder to rigurously draw when using traditional sensitivity analyses which lack a direct connection to goodness of fit.

3. Simulation of sets of experiments

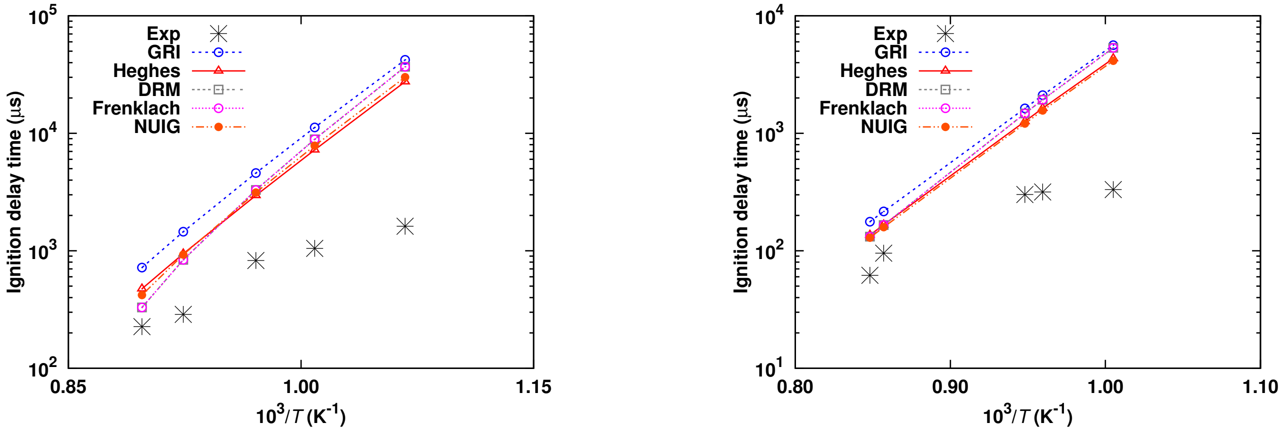
3.1. Experiments of Kalitan [53]

Kalitan [53] performed a series of shock tube experiments involving blends containing H_2, CO, CH_4, CO_2, and AR burning with air. The ignition delay times were measured behind reflected shock waves under a large range of conditions. They were experimentally determined from the chemiluminescence profiles of the hydroxyl radical coupled with the profile of the pressure behind the reflected shock wave. The experimental conditions relevant to methane are given in Table 2.

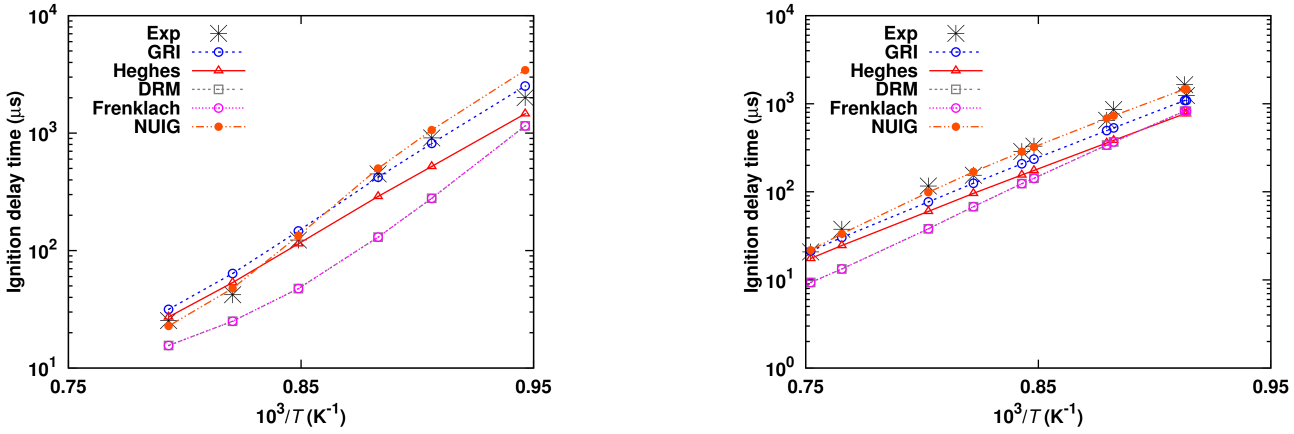
The simulated profiles themselves are represented in Figure 1 whereas the *average* logarithmic discrepancies for each series can be found in Table 3. It can be seen that for the experimental sets 2, 3, and 4 (as defined in Table 2), the ignition delay times are considerably overpredicted at smaller temperatures. No differences among the other input conditions could account for this. The Reaction Significance Analysis (RSA) (see Figure



(a) 1-st experimental series (b) 2-nd experimental series



(c) 3-rd experimental series (d) 4-th experimental series



(e) 5-th experimental series (f) 6-th experimental series

Figure 1: Simulation of the results of Kalitan [53]

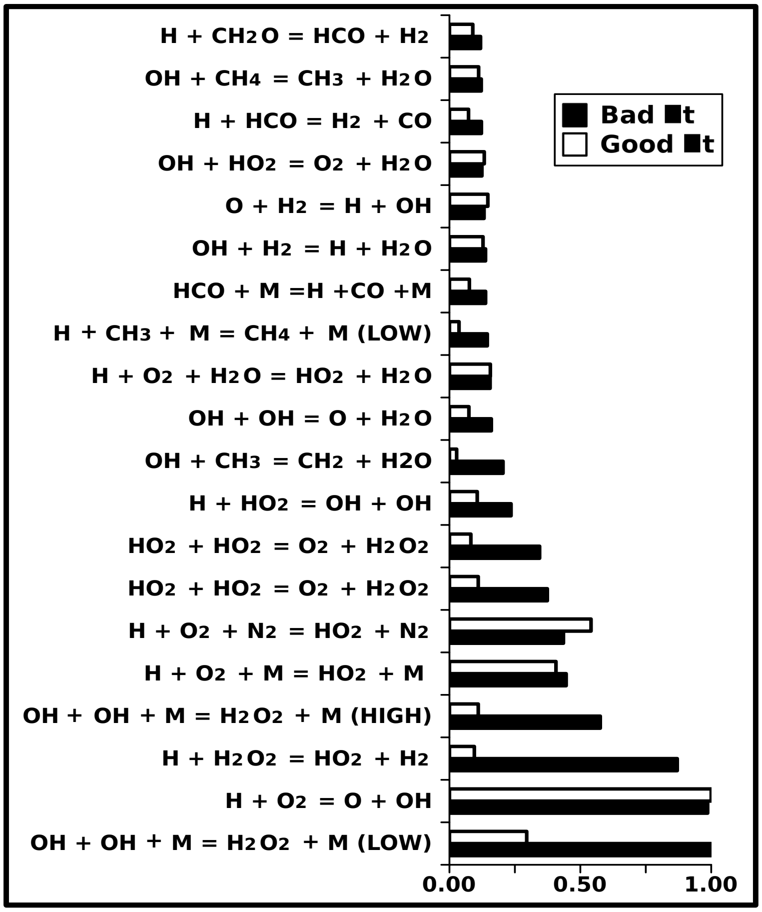


Figure 2: Reaction Significance Analysis for Kalitan et al. [53]

2) reveals, however, the existence of reactions which are at least twice more significant for the experiments leading to a poor fit.

- $OH + OH + M = H_2O_2 + M$ (LOW)
- $H + H_2O_2 = HO_2 + H_2$
- $OH + OH + M = H_2O_2 + M$ (HIGH)
- $HO_2 + HO_2 = O_2 + H_2O_2$
- $H + HO_2 = OH + OH$
- $OH + CH_3 = CH_2 + H_2O$
- $OH + OH = O + H_2O$
- $H + CH_3 + M = CH_4 + M$ (LOW)

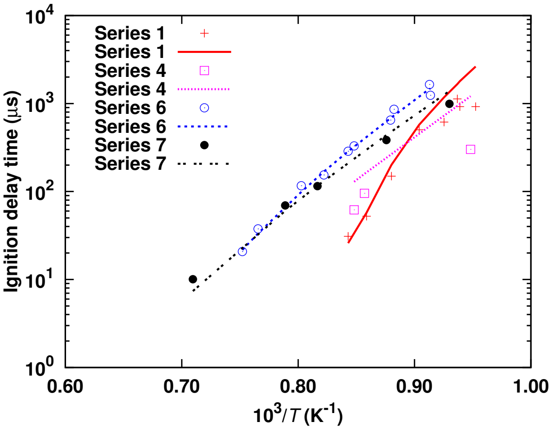
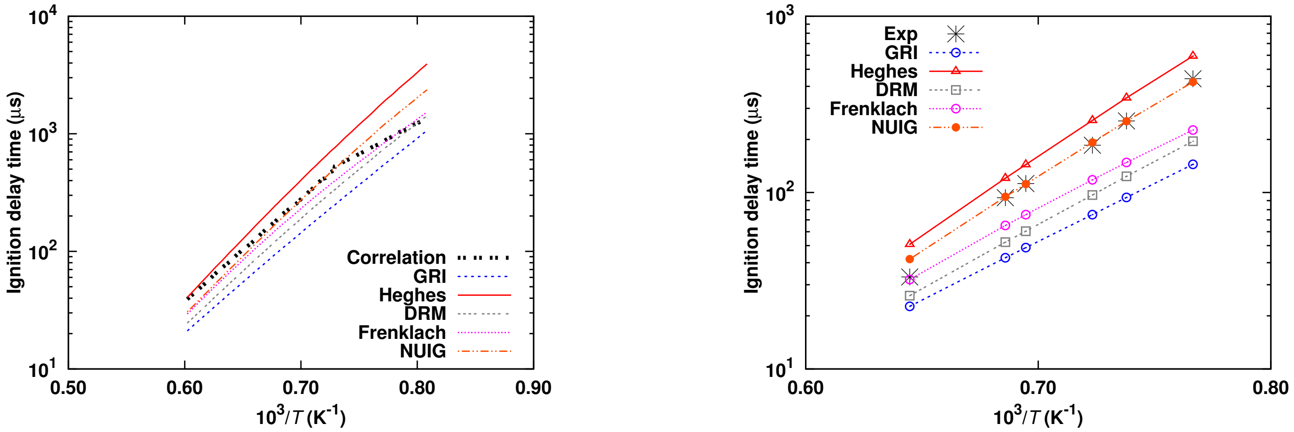


Figure 3: NUIG predictions for different series of Kalitan et al. [53]

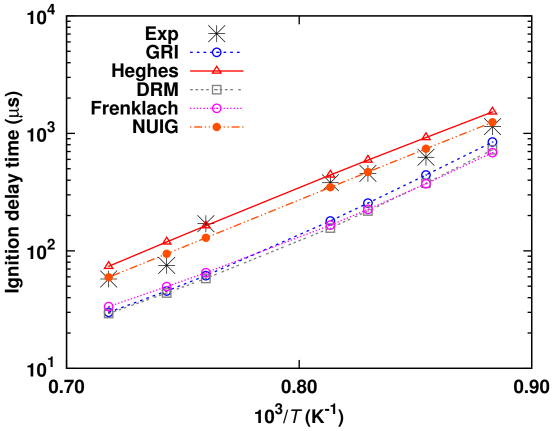
LOW and HIGH correspond to the parameters of a Troe reaction for low and high pressures, respectively. The discrepancies for the second, third and fourth experimental series (which offer a poor match to the results of the models) seem to occur under conditions where the chemistry of H_2O_2 and the radicals OH and HO_2 prevail. Since these are *also* the conditions where the physical system is inhomogeneous, no conclusion related to the invalidity of their kinetic description can be reached. As shown in Figure 3,a comparison between series 1, 4, 6, and 7 shows that those effects might not be entirely responsible for the whole mismatch, though. Series 6 and 7 present a reasonable agreement with the predictions of NUIG at all temperatures. Series 1 is characterised by a good match at the higher temperatures which becomes poorer as the temperature approaches 1050 K. However, series 4 is marked by a poor fit to the results of the model, even at high temperatures where the three other experimental series are in excellent agreement with the reaction mechanism. These disparities are unrelated to the high pressure of series 4 (36.578 bar) since series 6 (25.838 bar) and series 7 (36.781 bar) are also characterised by an elevated pressure. An examination of the initial concentrations of the reactants does not allow the identification of any *obvious* pattern which would cause different kinetic behaviours. Apart from a physical deviation from homogeneity, the discrepancies might also be due to the imprecision of some kinetic coefficients.

Table 4: Conditions of Petersen et al. [54]

Series	X_{H2}	X_{CH4}	X_{O2}	X_{N2}	p (bar)
1	0.0000	0.0502	0.2008	0.7490	20.3
2	0.0117	0.0466	0.1978	0.7439	20.3
3	0.0280	0.0420	0.1950	0.7350	23.5



(a) 1-st experimental series (b) 2-nd experimental series



(c) 3-rd experimental series

Figure 4: Comparison with the results of Petersen et al. [54] in Argon

3.2. Experiments of Petersen [54]

Petersen et al. [54] measured ignition delay times behind reflected shock waves. They were defined as the sudden increase in either CH* or OH*. The data we considered here deal with the effects of hydrogen addition to methane during an undiluted combustion using air as oxidant. Their conditions are reported in Table 4. The results are plotted in Figure 4.

Overall, NUIG provides a very good match to the measurements even though it leads

Table 5: Average logarithmic discrepancies for Petersen et al. [54]

Series	DRM	Frenklach	GRI	Heghes	NUIG
1	0.147	0.078	0.260	0.187	0.066
2	0.263	0.178	0.364	0.134	0.024
3	0.303	0.278	0.258	0.114	0.056
T < 1250 K	0.191	0.021	0.095	0.410	0.137
T $\geq$ 1250 K	0.177	0.076	0.180	0.446	0.158

to a poorer fit to ignition delay times characterising the combustion of pure methane without hydrogen at lower temperatures. The results of the three GRI-based mechanisms (namely GRI 3.0, DRM and Frenklach) are poor whereas those of Heghes lie between them and the results of NUIG in terms of agreement with the data. It is worth noting that for all mechanisms except DRM, the average discrepancies are higher for T $\geq$ 1250 K than for T $<$ 1250 K. This indicates that physical inhomogeneities at the lowest temperatures may play a much less important role than the kinetics for these series of experiments.

Two Reaction Significance Analyses have been conducted for mixtures containing CH_4 and the highest amount of H_2 and one containing only methane, respectively. Their results can be visualised in Figure 5. Not surprisingly, it can be seen that reactions involving the system $H_2 - O_2$ play a considerably more important role in the presence of hydrogen within the fuel as can be seen for the following steps

$$H + O_2 = O + OH$$

$$OH + H_2 = H + H_2O$$

$$H + HO_2 = O_2 + H_2$$

The next following steps are almost insignificant to the burning of pure methane whereas they become much more influential for the blend containing 40 % of hydrogen.

$$H + O_2 + N_2 = HO_2 + N_2$$

$$O + H_2 = H + OH$$

$$O + HO_2 = OH + O_2$$

$$H + O_2 + O_2 = HO_2 + O_2$$

$$H + O_2 + M = HO_2 + M$$

$$H + O_2 + H_2O = HO_2 + H_2O$$

$$OH + OH + M = H_2O_2 + M$$

Conversely, reactions usually important for the oxidation of methane such as

$$CH_3 + O_2 = O + CH_3O$$

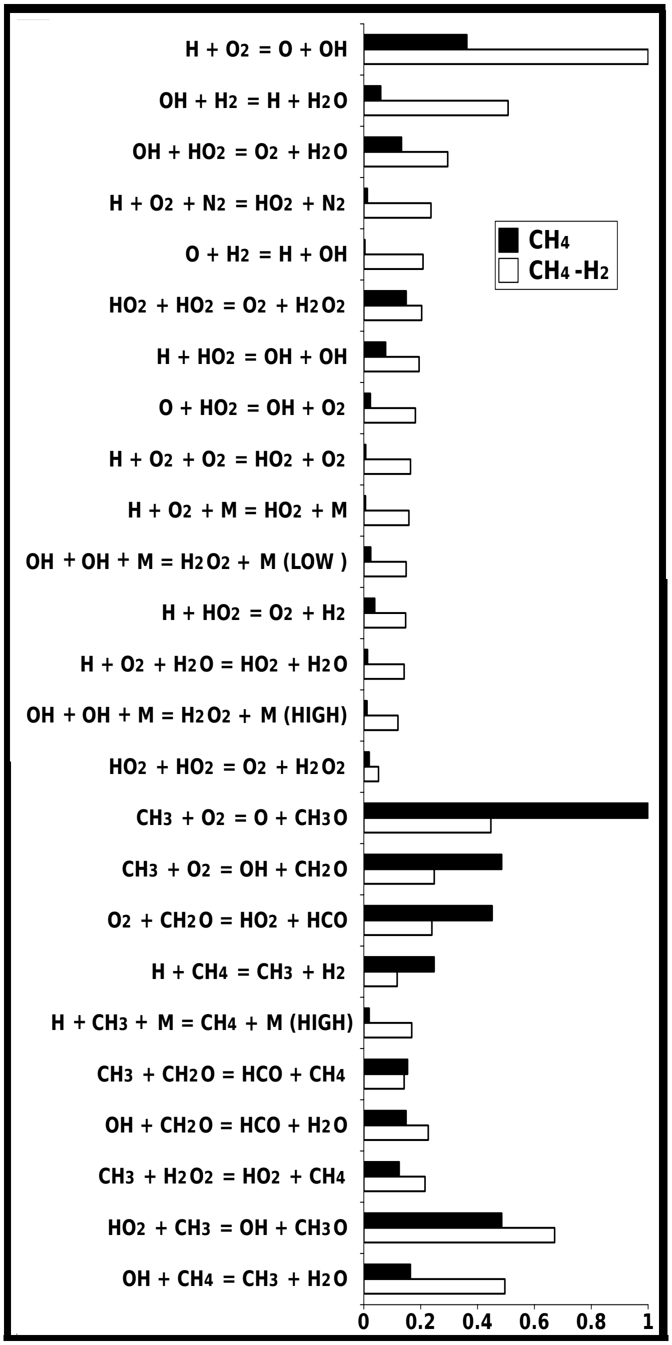


Figure 5: Reaction Significance Analysis for Petersen et al. [54]

Table 6: Conditions of Huang et al. [55]

Series	X_{CH4}	X_{O2}	X_{N2}	p (bar)
1	0.095	0.192	0.715	39.8
2	0.095	0.192	0.715	30.9
3	0.095	0.192	0.715	24.0
4	0.095	0.192	0.715	16.6
5	0.068	0.196	0.736	39.0
6	0.068	0.196	0.736	31.6
7	0.068	0.196	0.736	16.2
8	0.12	0.185	0.695	38.7

Table 7: Logarithmic discrepancies for Huang et al. [55]

Series	DRM	Frenklach	GRI	Heghes	NUIG
1	0.465	0.456	0.385	0.895	0.403
2	0.488	0.481	0.413	0.919	0.428
3	0.477	0.494	0.412	0.901	0.496
4	0.500	0.534	0.442	0.928	0.576
5	0.510	0.473	0.581	0.759	0.397
6	0.416	0.393	0.369	0.863	0.431
7	0.345	0.381	0.250	0.782	0.527
8	0.263	0.277	0.210	0.650	0.200
$T < 1250$ K	0.529	0.523	0.478	0.978	0.503
$T \geq 1250$ K	0.185	0.215	0.158	0.431	0.227

$$CH_3 + O_2 = OH + CH_2O$$

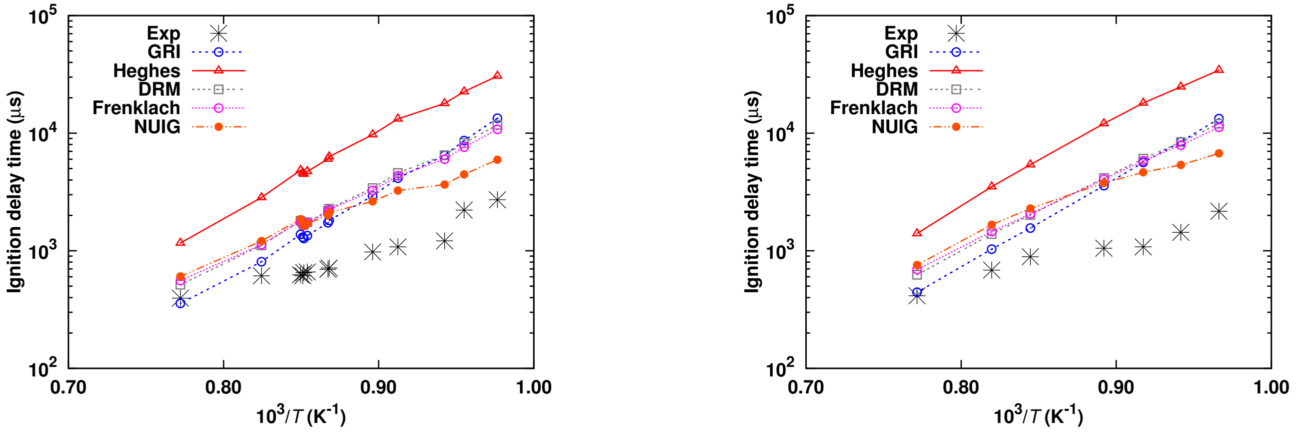
$$O_2 + CH_2O = HO_2 + HCO$$

$$H + CH_4 = CH_3 + H_2$$

are of less importance to the hydrogen-rich blend considered here.

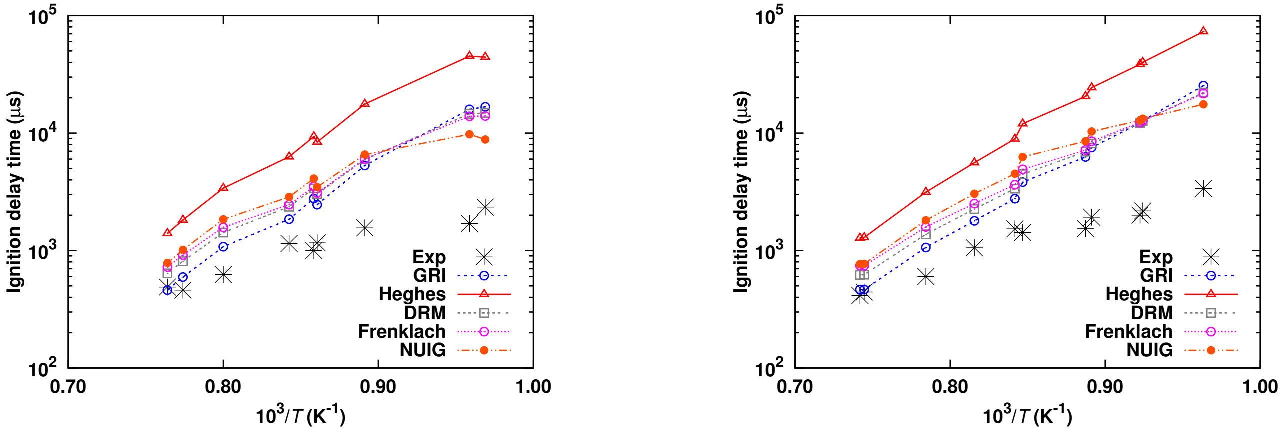
3.3. Experiments of Huang [55]

Huang et al. [55] carried out series of shock tube experiments involving undiluted methane reacting with air. The ignition delay times were measured behind reflected shock waves in relation to the maximum rate of pressure change. The experiments were performed under moderate temperatures (1000-1350 K), elevated pressures (16-40 atm) and a stoichiometric range of $\phi \in [0.7; 1.3]$. The conditions of the measurement series are reported in Table 6. Selected results of the simulations are given in Figure 6. Logarithmic discrepancies are reported in Table 7. As a rule, model predictions are satisfactory at the highest temperatures whereas they are too elevated at the lowest temperatures. Reaction Significance Analyses were carried out to identify the reactions having the highest influence on the discrepancies under these circumstances. The shape of the temperature-



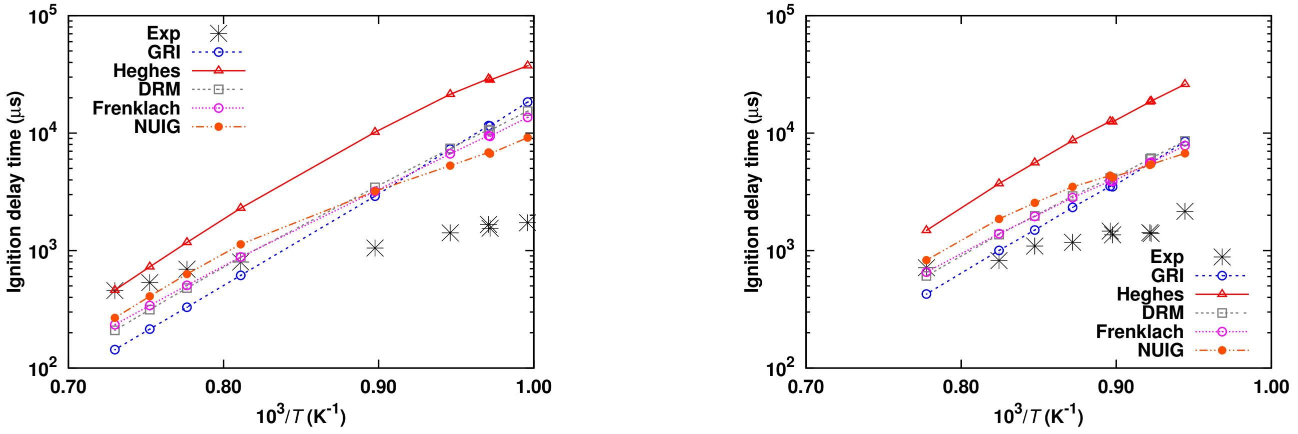
(a) 1-st experimental series

(b) 2-nd experimental series



(c) 3-rd experimental series

(d) 4-th experimental series



(e) 5-th experimental series

(f) 6-th experimental series

Figure 6: Comparison with the results of Huang et al. [55] in Argon

dependent profiles makes it very likely that physical inhomogeneities accelerating the ignition took place at temperatures inferior to a threshold as low as 1250 K. This is confirmed by the fact that the average discrepancies at temperatures higher than 1250 K are smaller than those at temperatures lower than 1250 K by at least a factor of 2. The first experimental series appears to be slightly anomalous in that the largest discrepancies are located around the middle of the temperature interval.

It can be seen that the chemistry of the $HO_2 - H_2O_2$ plays an important role in both lowest and highest temperatures. This feature is a well known effect of high pressures [6]. The chain termination step $OH + HO_2 = O_2 + H_2O$ proves to be the first and second most important elementary step for high and low temperatures, respectively. The importance of the HO_2 radical can also be seen through the existence of reactions it undergoes with hydrocarbon radicals such as $HO_2 + CH_3 = O_2 + CH_4$ and $HO_2 + CH_3 = CH_3O + OH$. Recombinations towards C_2H_6 and C_2H_5 also prove to play an important role. The reaction

$$OH + H_2O_2 = HO_2 + H_2O$$

is considerably more sensitive for low than for high temperatures.

The reactions

$$HO_2 + CH_2O = HCO + H_2O_2$$

$$HO_2 + CH_3 = O_2 + CH_4$$

$$OH + CH_4 = CH_3 + H_2O$$

$$OH + OH + M = H_2O_2 + M$$

also turn out to be more significant at low than at high temperatures, albeit to a lesser extent.

Since the effects of inadequate physical and chemical kinetic modelling are likely to be intertwined [52], it is not possible to draw any conclusions related to the validity of the reaction mechanisms apart from the fact that the ignition delays seem to be reasonably well captured at the highest temperatures of each series, where homogeneous chemical kinetics prevail. GRI 3.0 delivers the closest predictions in that regard.

3.4. Experiments of Zhang et al. [56]

Zhang et al. [56] performed series of shock tube experiments at a pressure of $p = 4$ bar and at temperatures varying between 1422 and 1877 K. The blends were made up of methane and hydrogen whereby the amount of H_2 varied between 0 % and 20 %. The equivalence ratio was $\phi = 2.0$ everywhere. The mixtures were highly diluted in N_2 which comprised 95 % of the overall volume. The ignition delay times were captured through the rapid increase of the pressure and OH radical profile. The experimental conditions are reported in Table 8 and the simulated results are shown in Figure 8. The logarithmic discrepancies are given in Table 9. The three GRI-based mechanisms (namely GRI 3.0, DRM, and Frenklach) provide the best match to the measurements. Overall, the predictions from GRI 3.0 are the best fit to this set of data. It can be seen, however, that for mixtures containing H_2, ignition delay times measured at the lowest temperatures are

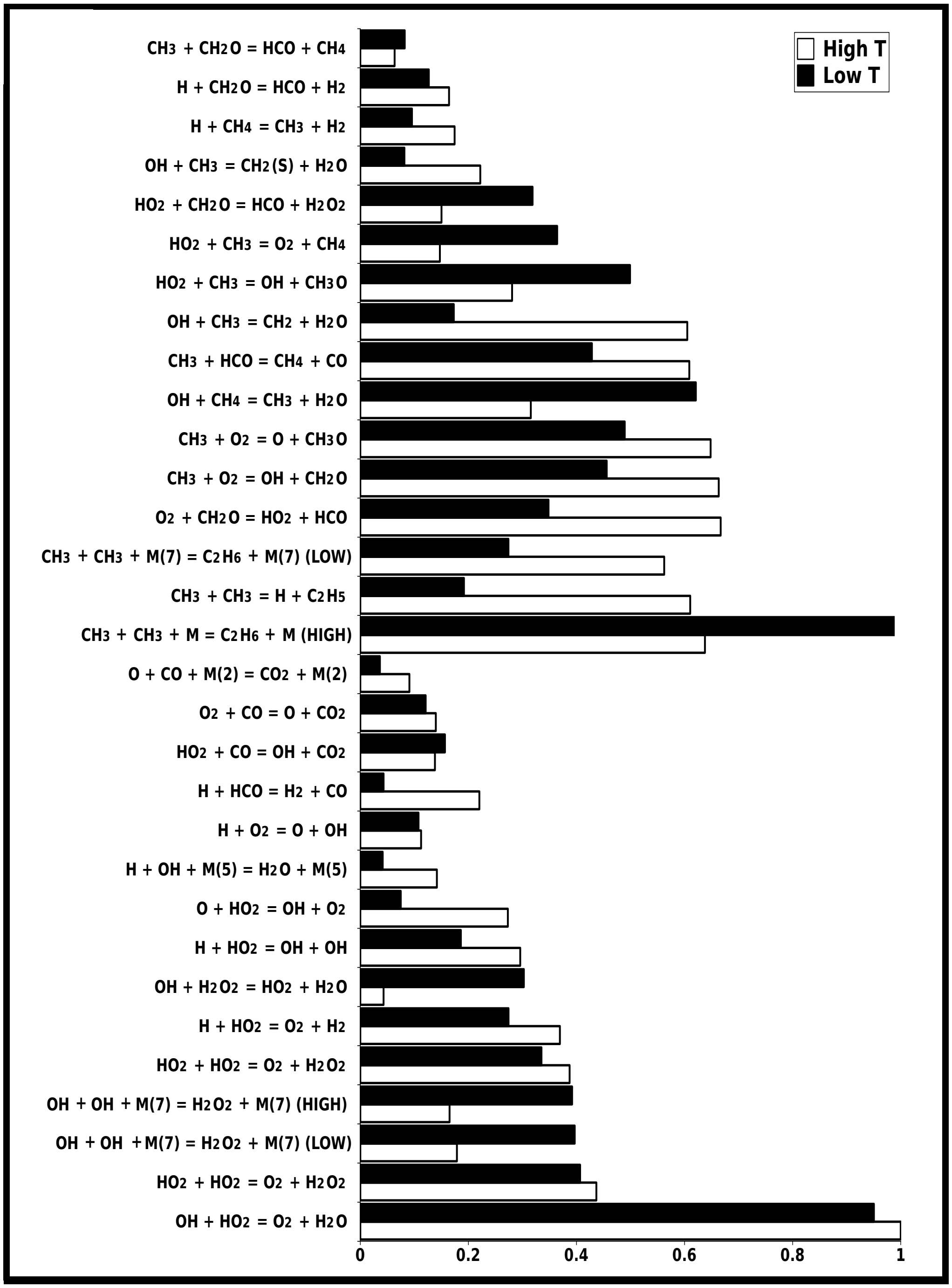
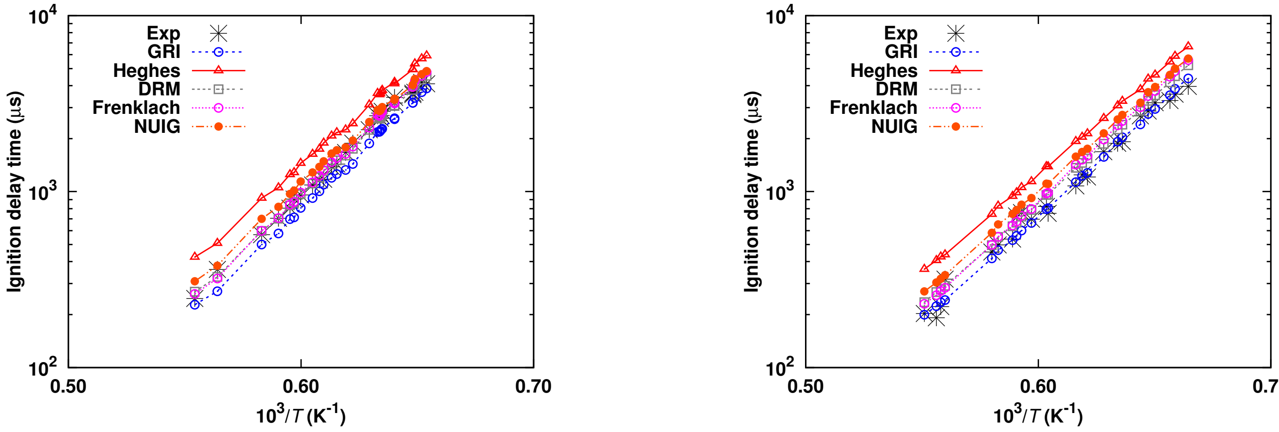


Figure 7: Reaction Significance Analysis for Huang et al. [55]

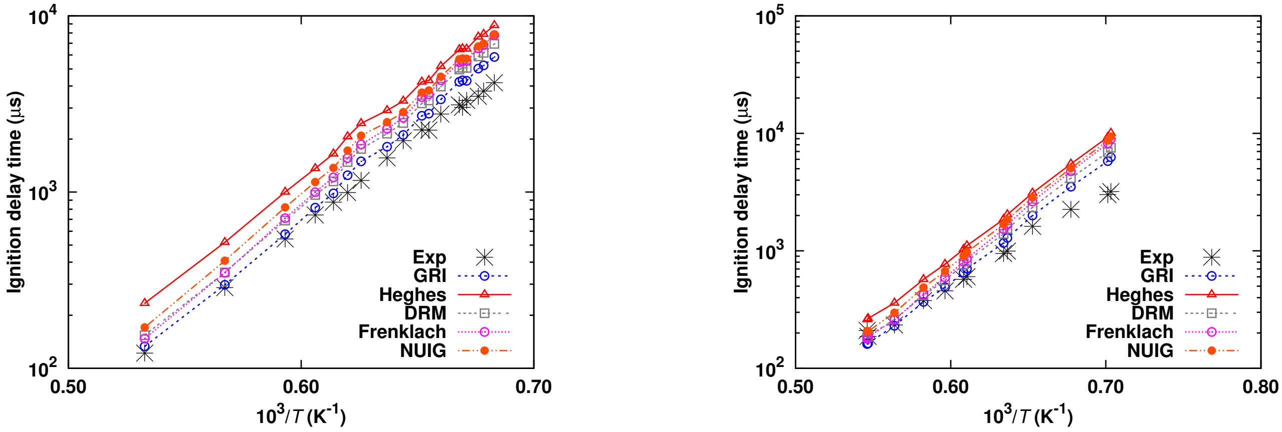
Table 8: Conditions of Zhang et al. [56]

Series	X_{H2}	X_{CH4}	X_{O2}	X_{N2}	p (bar)
1	0.000	0.025	0.025	0.95	4.0
2	0.001	0.024	0.002	0.95	4.0
3	0.003	0.023	0.024	0.95	4.0
4	0.005	0.022	0.023	0.95	4.0



(a) 1-st experimental series

(b) 2-nd experimental series



(c) 3-rd experimental series

(d) 4-th experimental series

Figure 8: Comparison with the results of Zhang et al. [56]

Table 9: Average logarithmic discrepancies for Zhang et al. [56]

Series	DRM	Frenklach	GRI	Heghes	NUIG
1	0.022	0.025	0.074	0.154	0.054
2	0.072	0.084	0.037	0.215	0.123
3	0.159	0.187	0.088	0.291	0.220
4	0.155	0.188	0.109	0.279	0.221
$T \geq 1250$ K	0.088	0.104	0.072	0.222	0.137

overpredicted. The relatively high ignition delay times measured experimentally (3.194 ms) might be seen as an indication that the homogeneity assumptions used for modelling shock tube experiments may no longer have been valid [26]. The problem with this explanation is that ignition delay times of the same order of magnitude were well captured by several models for mixtures 1 and 2 at the lowest temperatures. Coupled with the fact that the "gaps" are not as large as those typically originating from low-temperature facility-specific behaviour [24, 51], the effect seems rather related to higher amounts of hydrogen in the blends where the disparities are stronger. To identify the causes of this behaviour, RSA were carried out at the lowest and highest temperatures in the absence of H_2 (series 1) and in a blend containing the greatest abundance of hydrogen (series 4). The results are depicted in Figure 9. Several reactions play an important role in all four situations. This includes the recombination of CH_3 and H (whose reverse step is an important chain initiation),

$$\mathrm{H + CH_3 + M = CH_4 + M}$$

the recombination of CH_3 and HO_2 (whose reverse step can also be a chain initiation),

$$\mathrm{HO_2 + CH_3 = O_2 + CH_4}$$

steps leading to the formation of formaldehyde CH_2O and related radicals

$$\mathrm{CH_3 + O_2 = OH + CH_2O}$$

$$\mathrm{CH_3 + O_2 = O + CH_3O}$$

the formation of CO out of HCO,

$$\mathrm{CH_3 + HCO = CH_4 + CO}$$

$$\mathrm{H + HCO = H_2 + CO}$$

the recombination of CO and O towards CO_2,

$$\mathrm{O + CO + M = CO_2 + M}$$

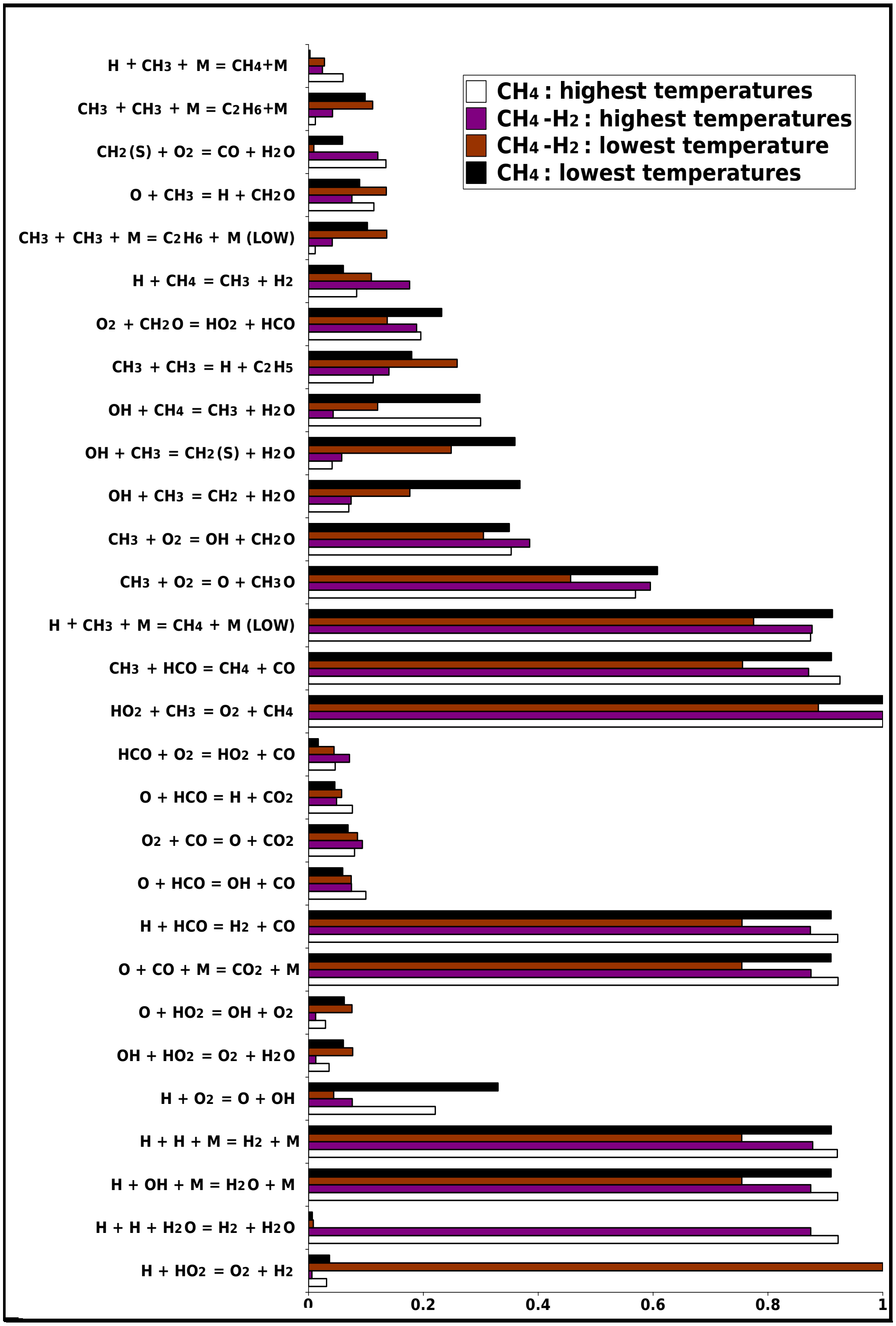


Figure 9: Reaction Significance Analysis for Zhang [56]

Table 10: Conditions of Zhukov et al. [57].

Series	p (bar)	T (K)
1	2.54 - 4.56	1409.00 - 1715.00
2	11.90 - 17.60	1347.00 - 1722.00
3	23.50 - 32.00	1351.00 - 1580.00
4	38.00 - 50.00	1369.00 - 1659.00
5	131.00 - 174.00	1209.00 - 1507.00
6	395.00 - 477.00	1196.00 - 1379.00

and two chain termination steps.

$$\mathrm{H + H + M = H_2 + M}$$

$$\mathrm{H + OH + M = H_2O + M}$$

It is worth noting that the reaction $\mathrm{O + CO + M = CO_2 + M}$ seems to be playing a more important role than $\mathrm{OH + CO = CO_2 + H}$ here even if the former is much slower kinetically [6].

As mentioned above, the poorest predictions concern series 4 (hydrogen-enhanced methane) at the lowest temperatures of the study. In Figure 9, it can be seen that the only reaction playing a significant role under these conditions is

$$\mathrm{H + HO_2 = O_2 + H_2}$$

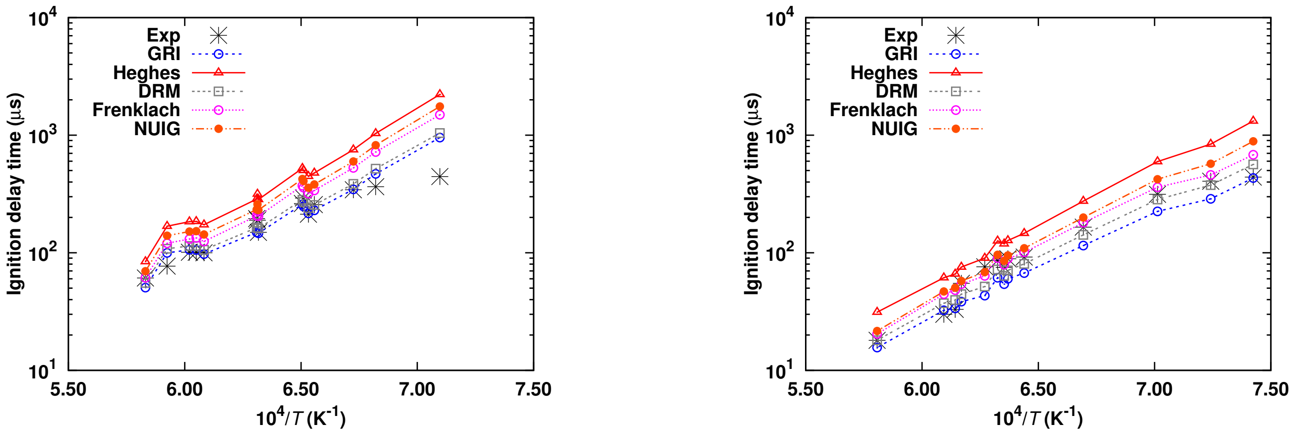
The discrepancies may stem from its kinetic coefficients not being accurate enough.

3.5. Experiments of Zhukov et al. [57]

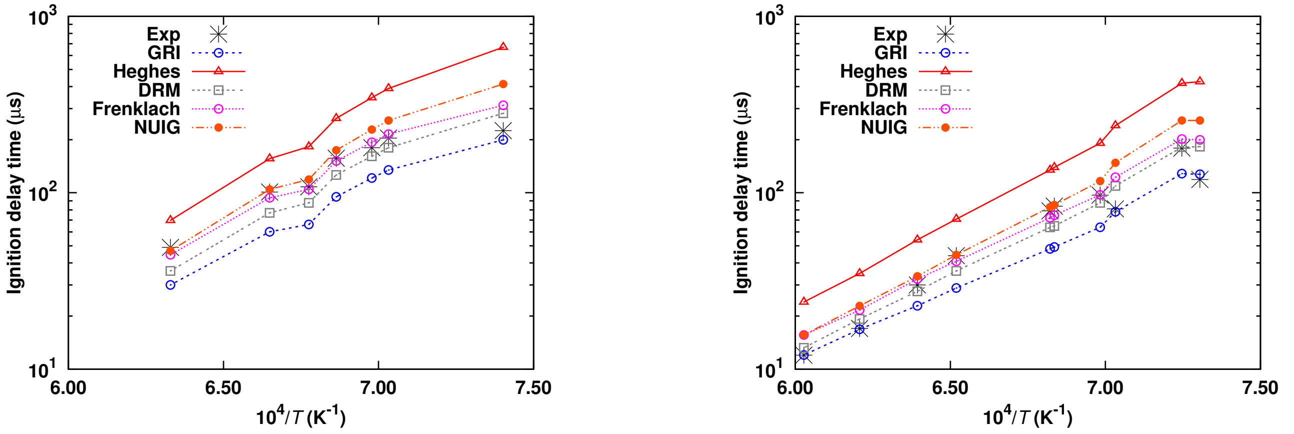
Zhukov et al. [57] studied the combustion of undiluted methane in shock tubes filled with methane and air satisfying the equivalence ratio $\phi = 0.5$. The ignition delay times were measured according to the emission of the OH radical. The experimental data they reported have been divided here in six profiles whose conditions are given in Table 10. The results of our simulations can be seen in Figure 10. The logarithmic discrepancies can be found in Table 11.

For all six series, Heghes' predictions are very far from the measurements. Whilst it is superior to Heghes' model, NUIG does not perform as well as the three GRI-based mechanisms (namely GRI 3.0, DRM, and Frenklach).

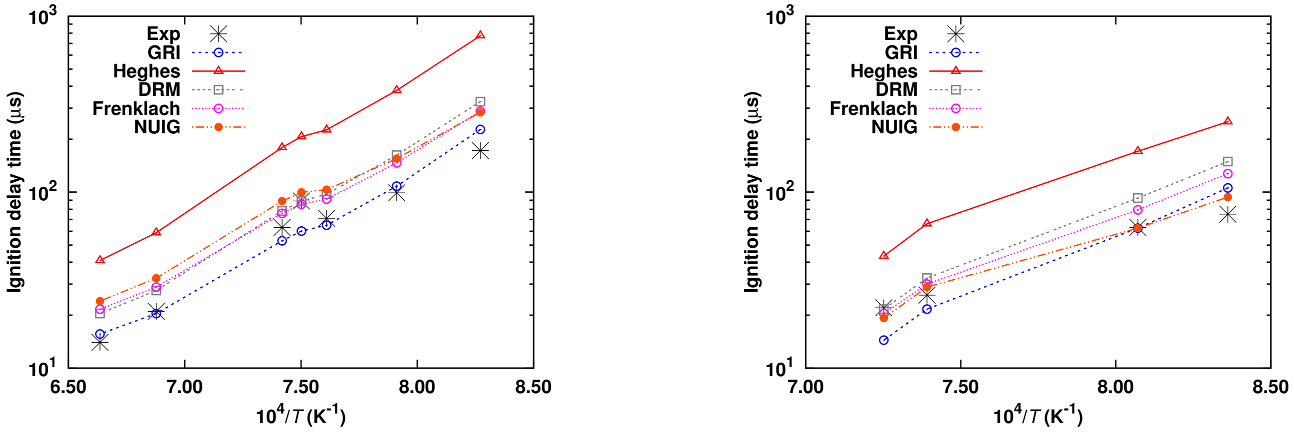
Whilst a good agreement has been achieved for series 2, the predictions of all models (except GRI 3.0) are far off from the measurements of series 5. This fact does not seem to result from the temperature or pressure range (and potential physical inhomogeneities brought about by them) since series 6 is characterised by even lower temperatures (1196.00 - 1379.00 K instead of 1209.00 - 1507.00 K) and higher pressures (395.00 - 477.00 bar instead of 131.00 - 174.00 bar) whereas it is very well predicted by NUIG. While other physical anomalies can never be ruled out, we considered it worthwhile to investigate



(a) 1-st experimental series (b) 2-nd experimental series



(c) 3-rd experimental series (d) 4-th experimental series



(e) 5-th experimental series (f) 6-th experimental series

Figure 10: Comparison with the results of Zhukov et al. [57].

Table 11: Average logarithmic discrepancies for Zhukov et al. [57]

Series	DRM	Frenklach	GRI	Heghes	NUIG
1	0.0765	0.1541	0.0671	0.3017	0.2113
2	0.0763	0.0692	0.1199	0.2370	0.1073
3	0.0912	0.0432	0.1821	0.2624	0.0840
4	0.0789	0.0835	0.1125	0.3217	0.1157
5	0.1439	0.1327	0.0721	0.4957	0.1710
6	0.1424	0.1061	0.1040	0.4140	0.0508
$T < 1250$ K	0.2480	0.1846	0.0911	0.5368	0.1058
$T \geq 1250$ K	0.0830	0.0971	0.1059	0.3052	0.1395
All	0.0918	0.1018	0.1051	0.3176	0.1377

chemical kinetic differences which could *partially* make sense of that state of affairs.

Reaction Significance Analyses have been performed for series 2 (where a good agreement has been achieved) and series 5 (where all predictions are very distant from the measurements). The diagrams are given in Figure 11. The following reactions proved considerably more significant for series 5 than for series 2.

$$\mathrm{OH + H_2O_2 = HO_2 + H_2O}$$

$$\mathrm{HO_2 + HO_2 = O_2 + H_2O_2}$$

$$\mathrm{HO_2 + CO = OH + CO_2}$$

$$\mathrm{OH + OH + M = H_2O_2 + M(LOW)}$$

$$\mathrm{OH + OH + M = H_2O_2 + M(HIGH)}$$

$$\mathrm{HO_2 + HO_2 = O_2 + H_2O_2}$$

They all involve $\mathrm{HO_2 - H_2O_2}$. It is worth noting that Fischer and Jiang also identified the same type of reactions as correlating with poor predictions of ignition delays of bio-syngas mixtures [14]. Hong et al. [27] pointed out that this class of reactions is not accurately known and needs more precise coefficients. This might be *one of* the causes of the large overpredictions concerning series 5.

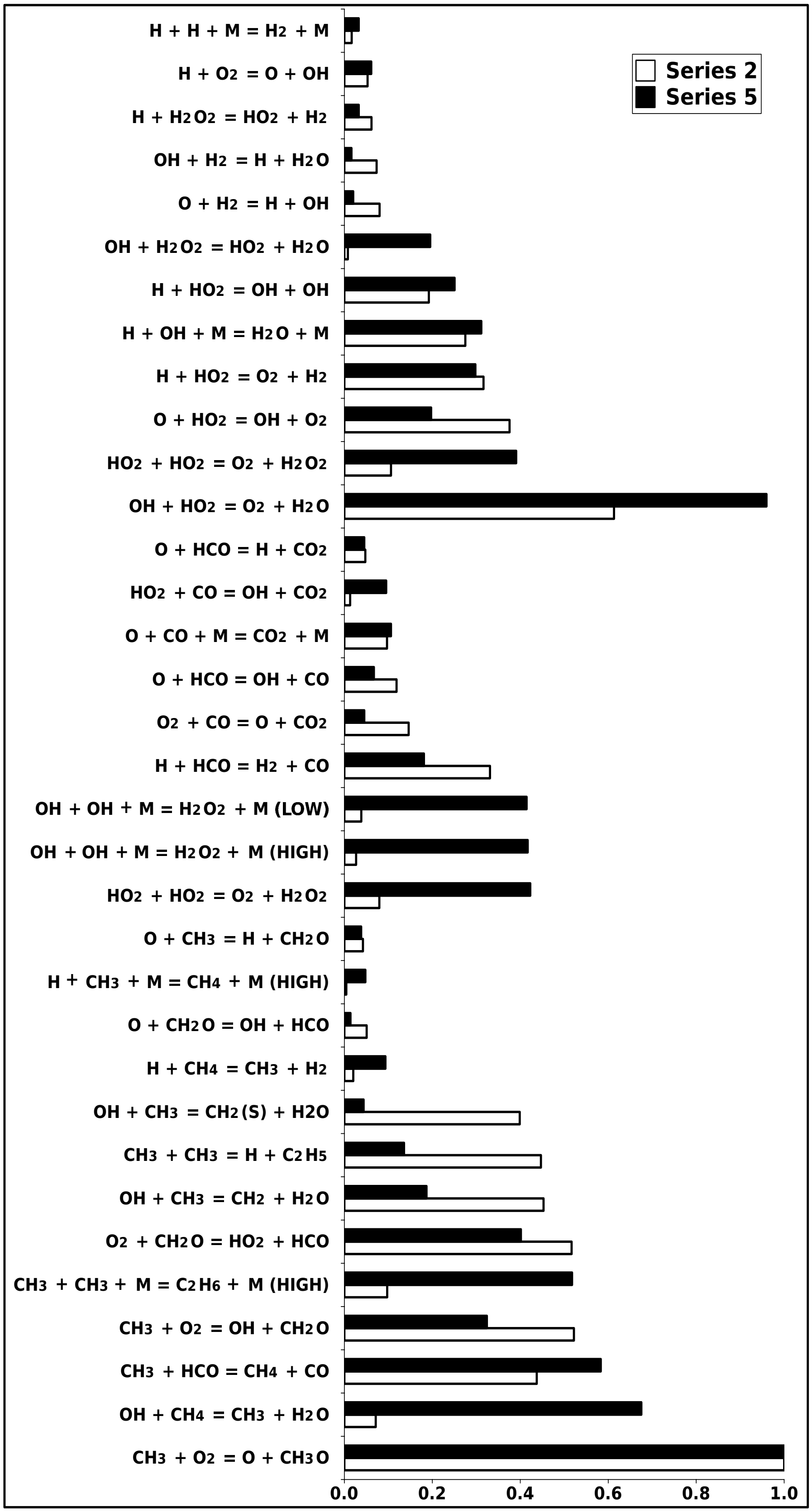


Figure 11: Reaction Significance Analysis for Zhukov's experiments [57]

Table 12: Conditions of Lifshitz et al. [58]

Series	X_{H2}	X_{CH4}	X_{AR}	X_{O2}
1	0.00E+00	0.035	0.8950	0.070
2	7.30E-04	0.035	0.8943	0.070
3	5.20E-03	0.035	0.8898	0.070

Table 13: Average logarithmic discrepancies for Lifshitz et al. [58]

Series	DRM	Frenklach	GRI	Heghes	NUIG
1	0.183	0.132	0.241	0.058	0.122
2	0.162	0.115	0.218	0.055	0.101
3	0.114	0.052	0.162	0.067	0.041
$T \geq 1250$ K	0.156	0.102	0.210	0.060	0.091

3.6. Results of previous studies on the modelling of biogas and bio-syngas combustion

To allow a more quantitative and informative study, we also considered results from two of our previous investigations [14, 15] which are going to be only briefly reported here. Lifshitz et al. [58] studied the ignition delay times of $CH_4 - O_2$ and $CH_4 - H_2 - O_2$. They used Argon AR as bath-gas. The density was *dens* = 7.5E-05 mol/cm3 whereas the initial mole fractions were $X_{CH4} = 0.035$ and $X_{O2} = 0.07$ The remaining conditions are summarised in Table 12. The experiments were simulated by Fischer and Jiang in [14]. The logarithmic discrepancies are reported in Table 13. The reader is referred to [14] for the interpretation of these results.

Several series of experiments concerning bio-syngas combustion were conducted by Mathieu et al. [41]. Ignition delay times were measured whereby AR played the role of a bath gas. The conditions of the trials involving CH_4 are given in table 14. The results of our simulations [14] are reported in Table 15. It is noteworthy that for the experiments performed by Mathieu et al. [41], low temperatures and pressures (such as in series 2) as well as high temperatures and pressures (such as in series 6) are characterised by a considerable overprediction of the ignition delay times. Figure 12 illustrates this state of affairs in relation to the combustion of bio-syngas at low and high pressures as modelled by NUIG. Surprisingly, at high pressures the ignition delays at *low temperatures* are much

Table 14: Conditions of Mathieu et al. [41] (Bath gas: AR)

Series	X_{H2}	X_{CO}	X_{CH4}	X_{CO2}	X_{O2}	p (bar)
1	4.06E-03	4.06E-03	7.50E-04	0.00E+00	1.11E-02	1.7
2	2.97E-03	2.97E-03	8.92E-04	1.58E-03	9.50E-03	1.7
3	4.06E-03	4.06E-03	7.50E-04	0.00E+00	1.11E-02	12.7
4	2.97E-03	2.97E-03	8.92E-04	1.58E-03	9.50E-03	12.7
5	4.06E-03	4.06E-03	7.50E-04	0.00E+00	1.11E-02	32.4
6	2.97E-03	2.97E-03	8.92E-04	1.58E-03	9.50E-03	32.4

Table 15: Average logarithmic discrepancies for Mathieu et al. [41]

Series	DRM	Frenklach	GRI	Heghes	NUIG
1	0.1600	0.1610	0.2256	0.1857	0.1570
2	0.1743	0.1754	0.2068	0.1778	0.1658
3	0.1674	0.1744	0.2192	0.1746	0.1964
4	0.2500	0.2557	0.2587	0.2458	0.3271
5	0.0438	0.0449	0.0390	0.0261	0.0786
6	0.1512	0.1506	0.1490	0.1706	0.1002
T $<$ 1250 K	0.200	0.202	0.236	0.218	0.229
T $\geq$ 1250 K	0.143	0.147	0.166	0.141	0.145

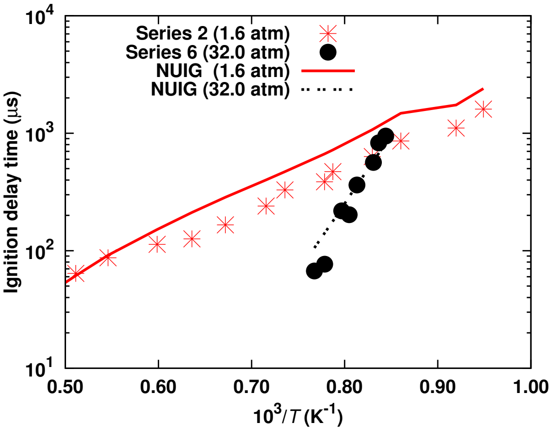


Figure 12: NUIG predictions for bio-syngas combustion [41]

better captured by the models than at high temperatures in spite of the *general* trend observed elsewhere [24, 51], and attributed to an inhomogeneous behaviour of the shock tube. Interestingly enough, for the conditions where the mismatch between model and experiments is the largest (low temperatures and pressures as well as high temperatures and pressures), five reactions **not** significant under conditions where a good fit is found play a non-negligible role [14]. These are

$$H + CH_3 + M \rightarrow CH_4 + M$$

$$H + HO_2 \rightarrow O2 + H_2$$

$$H + HO_2 \rightarrow 2OH$$

$$OH + HO_2 \rightarrow O_2 + H_2O$$

$$HO_2 + CH_3 \rightarrow OH + CH_3O$$

Four of the five reactions involve the radical HO_2 whose chemistry was also identified to *coincide* with poorer performances of the reaction mechanisms.

Table 16: Experimental conditions of Zeng et al. [59]

Run Series	Richness	p (bar)	X_{CH_4}	X_{O_2}	X_{N_2}	X_{CO_2}
1	0.5	1	0.0499	0.1995	0.7506	0
2	0.5	1	0.0399	0.1596	0.6005	0.2
3	0.5	1	0.0249	0.0998	0.3753	0.5
4	0.5	10	0.0499	0.1995	0.7506	0
5	0.5	10	0.0399	0.1596	0.6005	0.2
6	0.5	10	0.0249	0.0998	0.3753	0.5
7	1	1	0.095	0.19	0.715	0
8	1	1	0.076	0.152	0.572	0.2
9	1	1	0.0475	0.095	0.3575	0.5
10	1	10	0.095	0.19	0.715	0
11	1	10	0.076	0.152	0.572	0.2
12	1	10	0.0475	0.095	0.3575	0.5
13	2	1	0.1736	0.1736	0.6528	0
14	2	1	0.1389	0.1389	0.5222	0.2
15	2	1	0.08680	0.08680	0.3264	0.5

Nevertheless, we somewhat doubt that the inaccuracy of their kinetic parameters would be sufficient to explain the extent of the disagreement between the predictions of NUIG and the measurements of Mathieu et al. We therefore suspect that a deviation from ideal homogeneous conditions is also likely to *contribute* to the failure to reproduce these data.

Zeng et al. [59] performed shock tube experiments with various mixtures of CH_4, N_2 and CO_2 where they measured ignition delay times. The experimental conditions are given in Table 16. We simulated these measurements in a previous work [15] and reported the main results in Table 17. It is worth noting that the experiments of Zeng et al. [59] were carried out at temperatures between 1335 K and 2069 K and that physical inhomogeneities seem (at most) to be playing only a minor role in the ignition delays so that they appear to be particularly suitable for a chemical kinetic investigation of biogas combustion.

4. Influence of various factors on the discrepancies

In this section, we analysed the role of the temperature, composition, dilution, and pressure on the **mean** logarithmic distance between the model predictions and the measurements whereby the averaging was done over the values of every respective set such as all experiments performed in the temperature interval $[800; 1050]$ K.

Table 17: Average logarithmic discrepancies for Zeng et al. [59]

Series	DRM	Frenklach	GRI	Heghes	NUIG
1	0.028	0.065	0.023	0.246	0.146
2	0.032	0.044	0.020	0.225	0.110
3	0.040	0.023	0.043	0.150	0.031
4	0.087	0.034	0.164	0.211	0.079
5	0.050	0.071	0.109	0.255	0.129
6	0.044	0.073	0.078	0.229	0.120
7	0.060	0.119	0.041	0.291	0.158
8	0.036	0.052	0.049	0.222	0.094
9	0.036	0.043	0.034	0.197	0.069
10	0.063	0.057	0.140	0.203	0.038
11	0.051	0.122	0.075	0.254	0.100
12	0.054	0.065	0.103	0.157	0.061
13	0.187	0.254	0.132	0.429	0.255
14	0.026	0.033	0.087	0.192	0.031
15	0.077	0.105	0.024	0.266	0.116
$T \geq 1250$ K	0.058	0.081	0.070	0.241	0.109

Table 18: μ as a function of the temperature

T range	N	DRM	Frenklach	GRI	Heghes	NUIG
800-1050	22	0.9088	0.8965	0.9745	1.0241	0.7957
1050-1200	80	0.3761	0.3730	0.3587	0.5772	0.3269
1200-1400	109	0.1814	0.1786	0.1853	0.3017	0.1657
1400-1600	140	0.1115	0.1195	0.1373	0.2293	0.1277
1600-2100	179	0.0764	0.0737	0.0862	0.1843	0.0978
All	530	0.1874	0.1870	0.1984	0.3150	0.1835

4.1. Role of the temperature

The influence of the temperature on the average logarithmic discrepancies has been investigated. The mean values μ of the logarithmic discrepancies are given in Table 18. Table 19 contains the ratios between the standard deviations of the logarithmic discrepancies σ and their mean values μ. An important tendency can be observed in Table 18. The average discrepancies between model predictions and measurements increase with decreasing temperatures.

As we mentioned at the end of section 2, the modelling of shock tube experiments at low temperatures as a homogeneous system has been shown to be invalid. In a study about syngas combustion also involving results from a flow reactor [51], Petersen et al. noticed tremendous discrepancies between measured ignition delays and model predic-

Table 19: σ/μ as a function of the temperature

T range	N	DRM	Frenklach	GRI	Heghes	NUIG
800-1050	22	0.6052	0.6164	0.5389	0.5292	0.6597
1050-1200	80	0.5254	0.5173	0.5813	0.6949	0.6784
1200-1400	109	0.6667	0.6842	0.6328	0.6409	0.8459
1400-1600	140	0.7485	0.8296	0.6961	0.4796	0.8463
1600-2100	179	0.8462	0.8611	0.9177	0.5253	0.6742
All	530	1.2720	1.2701	1.2243	0.9470	1.2057

tions for all temperatures inferior to about 840 K. No reasonable adjustments of kinetic parameters could rectify the situation. Chaos and Dryer analysed the situation at length [24, 25, 60]. Long test times characteristic of low temperatures give rise to facility-bound physical effects (such as the growth of the boundary layer, the attenuation of the incident shock wave and residual gas velocities after the passage of the reflected shock wave) and deflagrative processes related to mild ignition. These, in turn, are responsible for an inhomogeneous ignition which might be considerably faster than what would have happened under idealised zero-dimensional conditions [26]. Different methods taking into account or approximating the pressure history of the shock tube have been developed and successfully applied to cases where the disparities between model and experiment seemed initially insurmountable [24, 27, 52, 61].

Since most experiments carried out under those conditions have, until now, been simulated under the wrong assumptions, there could be considerable uncertainties affecting the kinetic parameters of the $HO_2 - H_2O_2$ system which have not always been correctly calibrated [27, 52, 61]. While performing local adjustments might bring about small improvements, they are also likely to lead to disagreements with previously well captured experiments owing to the highly correlated nature of the *feasible set of parameters* [31]. Given the crucial importance of these reactions for the entire combustion community, we believe that a *large-scale optimisation* using all parameters and all available measurements should be carried out using a technique such as surface mapping [29, 30, 32]. Special care should then be taken to simulate every experimental device (be it a premixed flame, a rapid compression machine, a flow reactor, a shock tube etc.) using a physical model which does justice to the specific situation and might even differ from experiment to experiment.

NUIG is considerably superior to the four other reaction mechanisms for low and middle temperature ranges, although that better performance tend to level off with increasing temperatures where it is outperformed by DRM and Frenklach and then GRI 3.0. A similar effect has been noticed by Gersen et al. [40] and Mathieu et al. [41]. This seems to indicate that some combinations of kinetic parameters of NUIG influential at higher temperatures might need to be more accurately estimated.

Table 20: μ as a function of the composition

All temperatures	N	DRM	Frenklach	GRI	Heghes	NUIG
CH_4	261	0.1887	0.1844	0.2071	0.3971	0.1973
$CH_4 - H_2$	85	0.1481	0.1431	0.1296	0.1961	0.1347
$CH_4 - CO_2$	74	0.0432	0.0594	0.0607	0.2113	0.0823
$CH_4 - CO - H_2$	27	0.1369	0.1402	0.1818	0.1462	0.1542
$CH_4 - CO - H_2 - CO_2$	83	0.3669	0.3678	0.3675	0.3226	0.2885
All mixtures	530	0.1874	0.1870	0.1984	0.3150	0.1835
$T < 1250$ K	N	DRM	Frenklach	GRI	Heghes	NUIG
CH_4	58	0.4950	0.4873	0.4419	0.9352	0.4760
$CH_4 - H_2$	4	0.2810	0.2785	0.2153	0.1177	0.0399
$CH_4 - CO_2$	0	-	-	-	-	-
$CH_4 - CO - H_2$	14	0.1873	0.1902	0.2476	0.2152	0.2171
$CH_4 - CO - H_2 - CO_2$	58	0.4311	0.4313	0.4468	0.3862	0.3442
All mixtures	134	0.4288	0.4258	0.4170	0.5979	0.3789
$T \geq 1250$ K	N	DRM	Frenklach	GRI	Heghes	NUIG
CH_4	205	0.1020	0.0987	0.1407	0.2449	0.1184
$CH_4 - H_2$	85	0.1481	0.1431	0.1296	0.1961	0.1347
$CH_4 - CO_2$	73	0.0432	0.0594	0.0607	0.2113	0.0823
$CH_4 - CO - H_2$	27	0.1369	0.1402	0.1818	0.1462	0.1542
$CH_4 - CO - H_2 - CO_2$	83	0.3669	0.3678	0.3675	0.3226	0.2885
All mixtures	397	0.1059	0.1064	0.1246	0.2195	0.1175

4.2. Role of the composition

The average logarithmic discrepancies as a function of the mixture composition have been computed. The mean values μ of the logarithmic discrepancies are given in Table 20. Table 21 contains the ratios between the standard deviations of the logarithmic discrepancies and their mean values σ/μ.

The ratios between the standard deviations and the mean values of the logarithmic discrepancies are very large and often even exceed 1. In this situation, this means that for a given composition (such as pure methane or biogas $CH_4 - CO_2$), the causes of the discrepancies may be very inhomogeneous and dependent on factors other than composition. Nevertheless, some general features can be identified.

Overall, most mechanisms capture at best the combustion of biogas ($CH_4 - CO_2$) where all considered experiments involved temperatures superior to 1250 K where a homogeneous behaviour of the shock tube can be assumed. With the exception of Heghes, they display their poorest performance in relation to the combustion of bio-syngas ($CH_4 - CO - H_2 - CO_2$) even at temperatures higher than 1250 K. This supports the notion that the complex kinetic interactions ruling the combustion of such blends have not yet been optimally captured [14]. Overall, Heghes' mechanism leads to considerably worse predictions than

Table 21: σ/μ as a function of the composition

All temperatures	N	DRM	Frenklach	GRI	Heghes	NUIG
CH_4	263	1.0921	1.1119	0.9570	0.8407	0.9693
$CH_4 - H_2$	85	0.6474	0.6966	0.8814	0.5399	0.7328
$CH_4 - CO_2$	73	0.7400	0.8768	0.7213	0.3206	0.7484
$CH_4 - CO - H_2$	27	0.7957	0.7778	0.8591	0.9769	0.8653
$CH_4 - CO - H_2 - CO_2$	83	0.3669	0.3678	0.3675	0.3226	0.2885
All mixtures	531	1.2720	1.2701	1.2243	0.9470	1.2057
T < 1250 K	N	DRM	Frenklach	GRI	Heghes	NUIG
CH_4	58	0.4532	0.4383	0.5943	0.2690	0.3744
$CH_4 - H_2$	4	0.3105	0.2423	0.4218	0.3538	0.6176
$CH_4 - CO_2$	0	-	-	-	-	-
$CH_4 - CO - H_2$	14	0.6573	0.6446	0.7380	0.7708	0.7237
$CH_4 - CO - H_2 - CO_2$	58	1.0799	1.0791	1.0889	1.1182	1.3344
All mixtures	134	0.8239	0.8208	0.8953	0.7503	0.9039
T $\geq$ 1250 K	N	DRM	Frenklach	GRI	Heghes	NUIG
CH_4	205	0.7748	0.8932	0.7482	0.5756	0.8332
$CH_4 - H_2$	85	0.6474	0.6966	0.8814	0.5399	0.7328
$CH_4 - CO_2$	73	0.7400	0.8768	0.7213	0.3206	0.7484
$CH_4 - CO - H_2$	27	0.7957	0.7778	0.8591	0.9769	0.8653
$CH_4 - CO - H_2 - CO_2$	83	1.1038	1.1000	1.1603	1.1665	1.3734
All mixtures	397	0.8318	0.8758	0.8231	0.5627	0.7994

the other models. However, in the case of $CH_4 - CO - H_2$ it performs better than GRI (0.1462 against 0.1818) and in the case of bio-syngas ($CH_4 - CO - H_2 - CO_2$) it is closer to the measurements than DRM, Frenklach and GRI. Despite the systematic optimisation it was constructed through, GRI 3.0 is less performing than NUIG and DRM and Frenklach (both of which rely on a former version of GRI) with respect to methane combustion at high temperature.

So far as the burning of biogas is concerned, the three GRI-based mechanisms (namely DRM, Frenklach, and GRI 3.0) prove superior to the two other models. On average, NUIG is the best model and it clearly outperforms the four other candidates for what pertains to the simulation of bio-syngas, as was demonstrated in two other studies [40, 41]. However, for temperatures higher than 1250 K, its overall performance is inferior to that of DRM (a reduced version of the first GRI mechanism) and Frenklach. Given the fact that these experiments are the most reliable ones in terms of kinetic information unaffected by non-ideal physics, it shows that the much older DRM is not necessarily outdated in terms of accuracy.

Table 22: μ as a function of the inert gas

Bath gas	N	DRM	Frenklach	GRI	Heghes	NUIG
AR	92	0.1650	0.1488	0.2024	0.1370	0.1526
N_2	438	0.1921	0.1950	0.1975	0.3523	0.1900
T < 1250 K	N	DRM	Frenklach	GRI	Heghes	NUIG
AR	28	0.2005	0.2025	0.2363	0.2183	0.2293
N_2	105	0.4891	0.4848	0.4647	0.6982	0.4184
T ≥ 1250 K	N	DRM	Frenklach	GRI	Heghes	NUIG
AR	64	0.1494	0.1253	0.1875	0.1014	0.1191
N_2	333	0.0976	0.1028	0.1125	0.2422	0.1173

Table 23: σ/μ as a function of the inert gas

Bath gas	N	DRM	Frenklach	GRI	Heghes	NUIG
AR	92	0.5767	0.6884	0.5512	0.8607	0.8176
N_2	438	1.3449	1.3145	1.3278	0.8828	1.2429
T < 1250 K	N	DRM	Frenklach	GRI	Heghes	NUIG
AR	28	0.5874	0.5821	0.6410	0.6437	0.7134
N_2	105	0.7566	0.7560	0.8597	0.6426	0.8754
T ≥ 1250 K	N	DRM	Frenklach	GRI	Heghes	NUIG
AR	64	0.5322	0.6849	0.4589	0.8479	0.7158
N_2	333	0.8950	0.9169	0.8990	0.4813	0.8159

4.3. Role of the dilution

The influence of the dilution through the inert gas AR and the presence of N_2 has also been investigated. For all experiments considered in this study, the presence of AR and that of nitrogen as bath gas are mutually exclusive. The mean logarithmic discrepancies and the corresponding standard deviations have been computed and are reported in Tables 22 and 23, respectively.

On average, the presence of N_2 leads to greater discrepancies for all mechanisms except GRI 3.0. The deterioration of the overall performance even exceeds a factor of 2 in the case of Heghes. Given that the standard deviations are very high and that many unconsidered factors might play a role in these differences, no firm conclusions can be drawn. The fact that GRI 3.0 follows the reverse tendency and delivers better prediction in the presence of nitrogen might stem from it being the only mechanism including a set of elementary steps accounting for the formation of NO and other nitrogenous compounds [28]. Surprisingly, if only the higher temperatures are considered, all models (except Heghes) perform better in the presence of N_2 than in its absence, whereby the extent of the improvement is much greater in the case of GRI 3.0. For lower temperatures, all mechanisms (including GRI

Table 24: μ as a function of the pressure

p (bar)	N	DRM	Frenklach	GRI	Heghes	NUIG
1 - 5	210	0.0841	0.1081	0.0793	0.2353	0.1379
5 - 10	16	0.2716	0.2596	0.3195	0.1883	0.1361
10 - 20	125	0.1861	0.1824	0.2241	0.2870	0.2067
20 - 30	81	0.2277	0.1810	0.2609	0.2697	0.1085
30 - 40	72	0.4188	0.4115	0.4150	0.5947	0.3662
> 40	27	0.2099	0.1988	0.1685	0.5302	0.1971
$T < 1250$ K						
p (bar)	N	DRM	Frenklach	GRI	Heghes	NUIG
1 - 5	9	0.2383	0.2394	0.3472	0.2993	0.2260
5 - 10	13	0.2928	0.2928	0.3511	0.2252	0.1488
10 - 20	27	0.4709	0.4821	0.4824	0.6740	0.5560
20 - 30	20	0.3710	0.3737	0.2769	0.4936	0.2200
30 - 40	55	0.4968	0.4876	0.4855	0.6997	0.4391
> 40	10	0.4050	0.3785	0.2922	0.7951	0.3239
$T \geq 1250$ K						
p (bar)	N	DRM	Frenklach	GRI	Heghes	NUIG
1 - 5	201	0.0772	0.1022	0.0673	0.2324	0.1339
5 - 10	3	0.1793	0.1154	0.1826	0.0285	0.0810
10 - 20	98	0.1076	0.0999	0.1529	0.1804	0.1105
20 - 30	61	0.1807	0.1178	0.2556	0.1963	0.0719
30 - 40	17	0.1664	0.1651	0.1870	0.2549	0.1301
> 40	17	0.0951	0.0931	0.0958	0.3744	0.1225

3.0) display a much poorer performance (by a factor of 2 or so) with nitrogen than with argon being used as the bath gas. This result seems related to the finding of Davidson and Hanson [26] according to which the use of a mono-atomic inert gas such as AR avoids the physical inhomogeneities caused by N_2.

4.4. Role of the pressure

Likewise, the effect of the pressure on the average logarithmic discrepancies has been determined. The mean values μ of the logarithmic discrepancies are reported in Table 24. Table 25 contains the ratios between the standard deviations of the logarithmic discrepancies and their mean values σ/μ. There are few clear patterns emerging from these results. In general, GRI 3.0 delivers the best predictions in comparison to the four other models at relatively low pressures inferior to five bars. NUIG leads to the best results for pressures comprised between 20 bar and 30 bar. This might be related to the inclusion of high pressure experiments during its validation [2]. Separating the two principal temperature ranges did not bring up any significant additional information in

Table 25: σ/μ as a function of the pressure

p (bar)	N	DRM	Frenklach	GRI	Heghes	NUIG
1 - 5	210	0.9708	0.8979	1.1077	0.4203	0.6945
5 - 10	16	0.5284	0.6022	0.7063	0.7391	0.8815
10 - 20	125	1.1084	1.1709	0.9145	1.0195	1.1006
20 - 30	81	0.6937	0.9683	0.5515	0.9901	1.4622
30 - 40	72	1.0562	1.0622	1.0800	0.8459	1.0906
$>$ 40	27	0.8883	0.9156	1.0063	0.4963	0.8038
T $<$ 1250 K						
p (bar)	N	DRM	Frenklach	GRI	Heghes	NUIG
1 - 5	9	0.3909	0.3945	0.4444	0.4422	0.4580
5 - 10	13	0.5174	0.5174	0.6795	0.5677	0.8733
10 - 20	27	0.5838	0.5648	0.6182	0.5714	0.4135
20 - 30	20	0.6041	0.5710	0.8984	0.8315	1.1533
30 - 40	55	0.9550	0.9633	1.0010	0.7528	0.9793
$>$ 40	10	0.4034	0.4620	0.7202	0.2829	0.5127
T $\geq$ 1250 K						
p (bar)	N	DRM	Frenklach	GRI	Heghes	NUIG
1 - 5	201	0.9607	0.9114	0.9083	0.4155	0.6999
5 - 10	3	0.1724	0.7311	0.4171	0.2808	0.3942
10 - 20	98	0.6763	0.8119	0.5128	0.7124	0.8433
20 - 30	61	0.5030	0.8528	0.3474	0.7125	1.2156
30 - 40	17	0.8487	0.8256	0.7948	0.6315	0.5928
$>$ 40	17	0.6359	0.7266	0.8511	0.3209	0.7882

that regard.

5. Conclusion and outlook

Reliable models leading to realistic simulations of the combustion of methane-based fuels (such as natural gas, biogas and bio-syngas) are vital for both the industry and the academic world at the dawn of the third millennium. While much progress has been achieved since the 1960s, the current situation is far from being satisfactory as many experimental targets are still far off from the predictions of detailed reaction mechanisms [20, 40, 41]. In two of our previous articles, we endeavoured to accurately model the combustion of bio-syngas [14] and biogas [15]. It was found that while a reasonable agreement with experimental data could be attained under many circumstances, considerable disparities remained in other situations. This justifies the conclusion that the chemical kinetics of methane combustion (especially while combined with hydrogen, carbon monoxide or carbon dioxide) is not yet optimally understood. This prompted us to perform the present investigation where 530 experimental ignition delay times measured in shock tubes were considered for evaluating five detailed reaction mechanisms. We made use of a novel analysis tool we called RSA (Reaction Significance Analysis) described in section 2. It basically assesses the importance of a kinetic or thermochemical parameter for the overall distance d between a set of experimental values and the corresponding model predictions.

Kalitan conducted a series of shock tube experiments involving blends containing H_2, CO, CH_4, and CO_2. Ignition delay times are considerably overpredicted by the models at the lowest temperatures. RSA showed that under these conditions, reactions involving OH, HO_2 and H_2O_2 play a considerable role. While deviations from physical homogeneity at the lower temperatures may be the major cause of most disparities, the discrepancies characterising series 4 do not seem to be obviously related to the relatively low temperatures and high pressures being employed. Petersen et al. carried out experiments with mixtures of methane and hydrogen. NUIG delivered the best results. RSA revealed that the reactions of the $H_2 - O_2$ system play a much more important role in the mixture containing 40 % of hydrogen than in pure methane. Huang et al. investigated the combustion of CH_4 at relatively high pressures (16 - 40 bar). The predictions of the five mechanisms are generally good at higher temperatures but poor at lower ones. The main explanation appears to be the inhomogeneous behaviour of the shock tube at low temperatures. Zhang et al. performed a series of experiments at $p = 4$ bar between 1422 and 1877 K involving mixtures of CH_4 and H_2. Ignition delay times of hydrogen-rich mixtures measured at the lowest temperatures tend to be overpredicted by the models. A consideration of all profiles makes it implausible that physical inhomogeneities are the main cause of the discrepancies which seem to be rather correlated to the increased initial concentration of hydrogen. It is under the same conditions (and only them) that the reaction $H + HO_2 = O_2 + H_2$ plays an important role in the discrepancies between measurements and predictions. Zhukov et al. studied the lean combustion of methane over a large temperature range (1196.00 - 1722.00 K) and very large pressure range (2.54 - 477.00 bar). Whilst parts of the data are in good agreement with the model predictions, certain measurements are considerably overpredicted. Inhomogeneities caused by relatively high pressures and low temperatures are rather unlikely to be a significant factor here because of the existence of other measurements under these conditions well captured by the models.

While no overall cause could be discovered, RSA showed that reactions involving $HO_2 - H_2O_2$ (such as $OH + H_2O_2 = HO_2 + H_2O$) have a strong effect on the discrepancies. However, a relatively recent experimental study [62] and a theoretical work [47] investigated this reaction thoroughly and estimated values for the rate coefficient which are consistent to within 25-30%. As a consequence, the potential inaccuracy of its kinetic parameters could only account for a small part of the differences between measurements and model predictions.

Generally, when ignition delay times considered in this study are overpredicted, this tends to happen at the lowest temperatures and to be correlated with the chemistry of HO_2 and H_2O_2. While inhomogeneous physical conditions are *largely* responsible for these disparities, some of our results in subsections 3.1, 3.4, 3.5, and 3.6 do not seem to stem from this problem and may be due to kinetic inaccuracies. This indicates that some parameters of the $HO_2 - H_2O_2$ system probably need to be more precisely determined. Hong et al. [27] also emphasised that steps belonging to this family should be estimated more accurately. Other works also identified these reactions as important at low temperatures [6, 61, 63, 64]. Finally, the influence of the mixture composition, dilution, temperature and pressure on the discrepancies between measurements and model predictions has been statistically analysed. Overall, most mechanisms capture at best the combustion of biogas and display their poorest performance in relation to the combustion of bio-syngas. Despite its imperfection, NUIG proves to be the best choice for simulating the burning of bio-syngas. At high temperatures, the presence of N_2 in the reacting mixture increases the performance of all models and particularly that of GRI 3.0 accounting for the formation of NO. At low temperatures, however, the presence of N_2 reduces the predictive power of *all* models which is probably due to its causing a further departure from homogeneity [26].

On average, the models tend to lead to poorer predictions at lower temperatures, which is mostly due to physical inhomogeneities [60]. No clearly identifiable trend regarding the pressure could be identified.

To conclude, the present study revealed that the detailed kinetic modelling of methane (with or without H_2, CO or CO_2) cannot be yet considered satisfactorily completed. In [20], we argued that the *feasible set approach* championed by Frenklach et al. [30, 32, 65] is a promising and rigorous way of developing and systematically improving reaction mechanisms endowed with a solid predictive power. While this method has been followed for creating the successive versions of the GRI mechanisms, the quality of its predictions has been limited by the fact that many parameters of more isolated reactions such as $H + HO_2 = OH + OH$ are not sufficiently constrained by the available experimental data which are mostly governed by ignition chemistry. Therefore, we consider it a worthwhile goal for chemical kineticists to design new experiments yielding temporal and spatial species profiles strongly constraining the parameter spaces of reactions of the $CH_4 - CO - H_2$

system which are only vaguely known.

Special care needs to be taken to simulate them under the right physical assumptions. In the case of low temperatures and high pressures, more realistic physical models should be employed [25, 27].

Over the last years, there has been an increasing interest in so-called flameless (or mild) combustion relying on the use of pre-heated air because of its more optimal energy production and the more limited formation of CO_2, CO and NOx [66–69]. It has been estimated that the reduction of NOx production is more optimal at relatively low temperatures such as 950C [70, 71]. The failure to reliably predict crucial combustion features such as ignition delay times under these circumstances can certainly have an impact on the optimal design of burners minimising these pollutants. Thus, the growing accuracy of kinetic parameters influential under these conditions (e.g. reactions involving HO_2 and H_2O_2) coupled with the use of more realistic physical models goes hand in hand with the construction of more environment-friendly combustors.

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