

Modelling and reduction of LOx-Methane chemical kinetics for rocket engine application

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Abstract

Methane is now considered as a key solution for future reusable engines. Although methane-air flames are well known, the specific operating conditions of rocket engines (i.e., high pressure and temperature for a wide spectrum of mixture ratios) have been rarely addressed and there is a lack of knowledge of methane oxycombustion kinetics for these applications. It is however expected that kinetics become important in rocket engines when using methane, due to a lower reactivity compared to other fuels. Hence, a new kinetic mechanism based on an existing model was developed. It was optimized on an experimental database of CH_4/O_2 flame speeds built on purpose using the OPTIPRIME setup.

1. Introduction

When developing a new rocket engine, sizing computations involving CFD calculations are an essential step of the process. In order to be accurate enough concerning the prediction of the combustion chamber conditions, the simulations must use, among others, a valid kinetic model. As methane is now envisioned as the fuel to be used for most of reusable rocket engines projects around the world [1] and also in Europe [2,3], it is vital to understand the kinetics at stake for high pressure and temperature conditions. However, despite a wide knowledge of CH_4 /air mixtures thanks to many studies [4], methane oxycombustion is still not yet fully understood. Since CH_4/O_2 mixtures lead to high burnt gases temperatures (up to 3000 K at stoichiometry and 1 bar against 2100 K in air) the conditions are generally too extreme for traditionally used experimental setups to measure flame speeds. Hence the literature on the subject is quite scarce, mainly focusing on measurements at atmospheric pressure with a Bunsen type burner for the flame speed [5–7]. As for the ignition delay times, they are always studied for diluted mixtures for the same reasons. The conditions closer to rocket engines conditions (low dilution, high pressure) where the measurements performed by Petersen et al. for the development of the RAMEC mechanism [8,9]. Hence, there is a need to perform experimental measurements for CH_4/O_2 mixtures at high pressure in order to be able to correctly depict the chemistry in rocket engine conditions.

With this objective in mind, the OPTIPRIME combustion chamber developed at ICARE [10] was used to build an extensive laminar premixed flame speed database for CH_4/O_2 mixtures on a large range of equivalence ratio φ (from 0.5 to 2.5). The pressure and temperature levels reached during the experiments are unprecedented for flame speed S_u measurements in oxycombustion conditions (up to 20 bar at $\varphi=2.5$). These values are the backbone of the experimental database built for this study. To complete the database, ignition delay times τ_{ign} at high pressure from the literature (study by Petersen et al.) [8,9] were also added.

Recent mechanisms, some of which were specially developed for CH_4 combustion in rocket engine conditions, were compared to the experimental database. The POLIMI C1-C3 [11] model is the one having the best overall behaviour. However, it still presents discrepancies with the experimental values for several conditions. Hence this mechanism needs to be modified to ensure that its predicted values fall in the experimental S_u and τ_{ign} uncertainty envelope. This can be achieved with an optimization process, as done in the OPTISMOKE++ code [12] developed by ULB and CRECK group, where the optimization targets the Arrhenius law coefficients of selected sensitive reactions.

This paper presents the methodologies and results of both experimental and numerical works conducted to obtain an optimized mechanism able to describe CH_4/O_2 combustion at high pressure.

2. Acquiring high pressure flame speeds for CH_4/O_2 mixtures

The flames encountered in rocket engines combustion chambers are generally purely diffusion flames at high levels of strain and pressure [14]. It is very difficult to perform any measurements in these conditions which require expensive dedicated test benches. Hence, the experimental database created here mainly focuses on premixed flame speeds S_u . Computations conducted at CERFACS tend to prove that chemistries initially derived for premixed flames are usually still valid for diffusion flame configurations [14].

The S_u parameter can be measured with various methods. However, as mentioned in the introduction, CH_4/O_2 mixtures lead to extreme pressure and temperature conditions making the measurement of the flame speed quite challenging. Hence, all the studies made so far were focused at atmospheric pressure [5–7] using a Bunsen type burner. In order to access high pressure data closer to the one encountered in rocket engines, the method of spherical expanding flames at constant volume (SEF-CONV) can be used. The fresh gas mixture is placed in a spherical combustion chamber. Once the gases are ignited at the center of the setup with a spark plug system, the flame propagates outward till it reaches the wall. For isochoric combustion, the flame speed can be expressed as a function of both the pressure and flame radius evolution over time inside the chamber [15] following the equation below:

$$S_u = \frac{dR_f}{dt} - \frac{R_0^3 - R_f^3}{3\gamma_u R_f^2 P} \frac{dP}{dt} \quad (1)$$

R_f being the flame radius, R_0 the chamber radius and γ_u the heat capacity ratio of the fresh gases. However, several assumptions are necessary to establish equation (1):

- The pressure P is spatially uniform in the chamber
- Burnt and unburnt gases are considered as ideal gases
- There are no chemical reactions in the fresh gases
- The flame is perfectly spherical with an infinitely thin flame front
- The unburnt gas is compressed isentropically

The pressure monitoring inside the chamber can be made with high speed sensors. However, it is usually very challenging to access the flame radius evolution because of the extreme pressure and temperature reached at the end of flame propagation. In order to overcome this problem, a special setup called OPTIPRIME [10] was developed at ICARE (cf.

Figure 1).

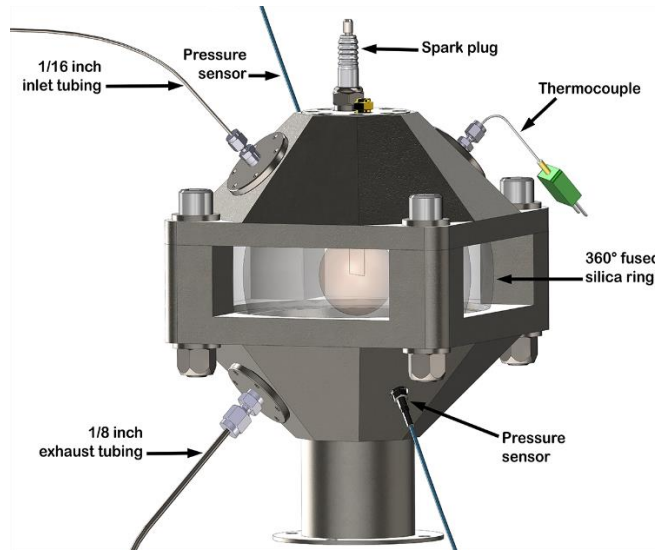


Figure 1: OPTIPRIME experimental setup

It consists in a perfectly spherical combustion chamber with a 360° silica ring allowing to track the flame radius over time thanks to a high-speed camera in the visible range. Pressure history is simultaneously recorded with high-speed transducers. Hence, for a mixture at given equivalence ratio ϕ , a single firing allows to compute a full trace of S_u corresponding to the flame front evolution over time as it consumes and compresses the fresh gases. However, as illustrated on Figure 2, the full trace can not be exploited. Indeed, the initial instants of flame propagation are affected by stretch effects while at the end the compression process of fresh gases cannot be considered as isentropic anymore. These limits are known and different criteria were developed to find them [10,16]. Hence the isochoric conditions where equation (1) is valid are identified in between these boundaries, allowing to obtain the flame speed evolution. It is important to notice that S_u evolves as both a function of the pressure and temperature over time.

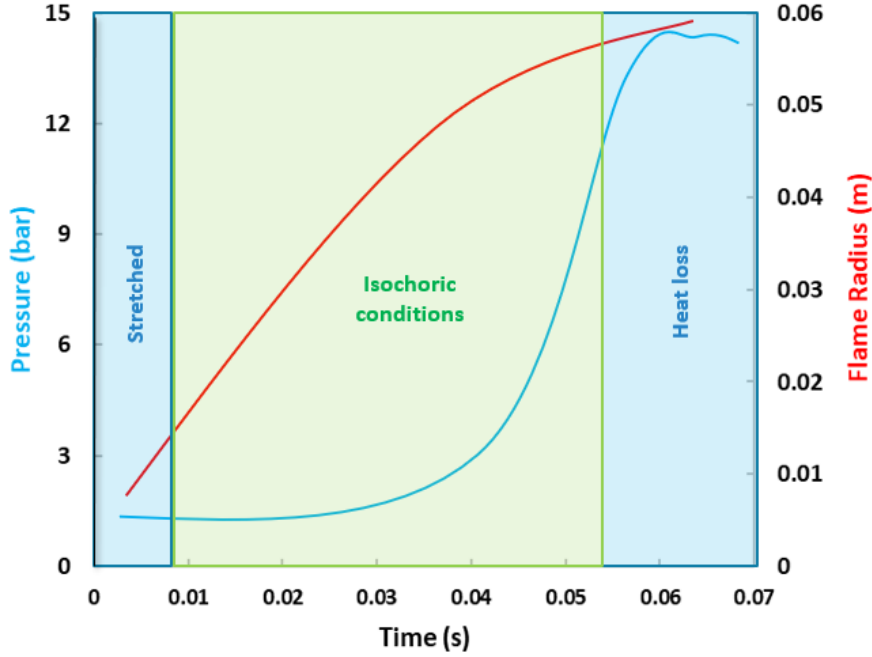


Figure 2: An example of pressure and flame radius evolution inside the OPTIPRIME setup

Flame speed data was acquired for a wide range of conditions, from lean to rich with ϕ varying from 0.5 to 2.5. The maximum temperature reached in the fresh gases was 603 K (3115 K in the burnt gases) for a pressure of 20 bar. The most extreme conditions are encountered at stoichiometry ($\phi=1$) with flame speed up to almost 6 m.s^{-1} . The high level of S_u and corresponding pressure and temperature reached at the end of the flame propagation prevented to go higher than 1.5 bar for this condition. Hence complementary firings with a diluted oxidizing mixture were performed at stoichiometry only to get additional data at high pressure. Diluent proportion was varied from 0 to 82.5% in molar fraction of the oxidizing mixture. It is composed of 70% He and 30% Ar.

3. Comparison with existing models

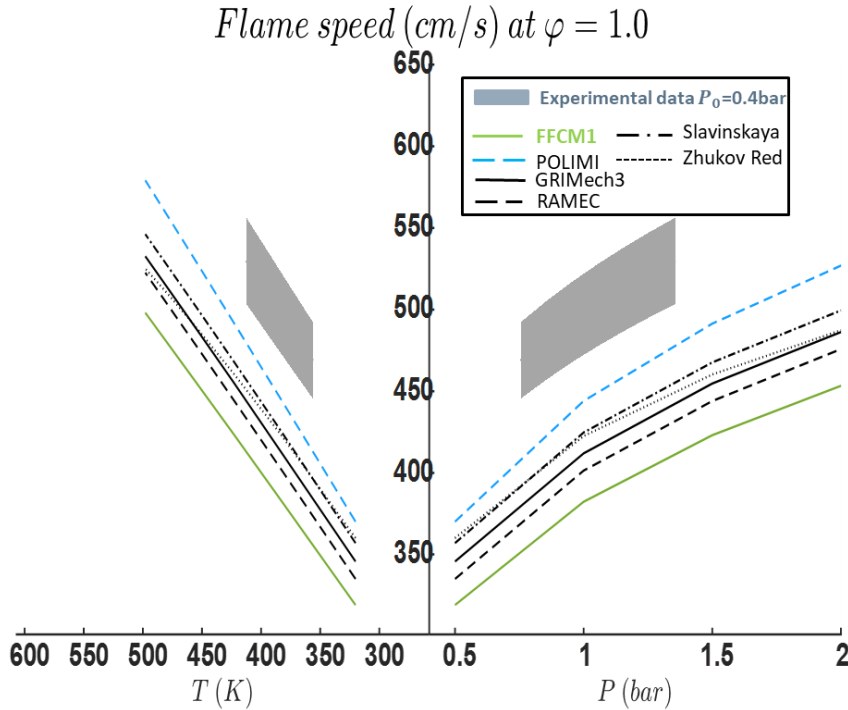
Different kinetic mechanisms from the literature were compared with the CH_4/O_2 flame speeds obtained with OPTIPRIME. In order to evaluate a model for the same conditions as the experiment, the initial (P, T) conditions as well as the whole pressure history of the firing is recovered. Supposing that the compression of the fresh gases is isentropic (cf. hypotheses in section 1) the corresponding temperature T_u is computed. Hence, knowing the mixture composition and all the (P, T) conditions of the trace, it is possible to perform a 1D premixed flame calculation, using laminar flame codes like CHEMKIN or CANTERA to recover the numerical S_u .

The mechanisms chosen for comparison are recent mechanisms (POLIMI C1-C3 [11], FFCM1 [17]) as well as models initially developed for CH_4/O_2 applications (RAMEC [18], Slavinskaya [19], Zhukov [20]). As shown in Table 1 they are of various sizes in terms of number of species and reactions.

Mechanism	#Species	#Reactions
Slavinskaya [19]	22	97
Zhukov [20]	23	51
RAMEC [18]	38	190
FFCM1 [17]	38	291
GRI-Mech 3.0 [21]	53	325
POLIMI C1-C3 [11]	114	1999

Table 1: Tested mechanisms

The models were evaluated for all the conditions tested experimentally, from lean to rich mixtures. Figure 3 below displays the obtained experimental and the numerical flame speeds at stoichiometry. As both the pressure and temperature evolve simultaneously during flame propagation in the OPTIPRIME closed volume, the dependance of S_u on both parameters is recovered. The flame speed acquired with OPTIPRIME is represented with its relative uncertainty of $\pm 5\%$. The mixture condition displayed here is CH_4/O_2 at stoichiometry as it is representative of the overall behavior of the mechanisms relative to the experimental data.

Figure 3: Experimental vs numerical flame speed for CH_4/O_2 mixture at stoichiometry

Although the tested mechanisms reproduce the trend of the experiment, there is some important discrepancies between the numerical and experimental flame speeds. In the stoichiometric case, the numerical prediction of S_u tends to underestimate the experimental value, while it is the opposite for rich conditions ($\varphi=2.5$). Among all the tested models, POLIMI C1-C3 is the one having the best behavior. Indeed, it exhibits the smallest relative difference between numerical and experimental values for the conditions of Figure 3 and all the tested conditions. On the other hand, mechanisms specially tailored for CH_4/O_2 like RAMEC, Slavinskaya or Zhukov tend to show high discrepancies with the experiment. For RAMEC and Zhukov it may come from the fact that only ignition delay times were used to validate the mechanism [18,20]. Concerning Slavinskaya, laminar flame speeds were studied but only for CH_4 /air mixtures at atmospheric pressure, i.e., far from the extreme conditions encountered with OPTIPRIME. The FFCM1 and GRIMech 3 mechanisms were validated against a wide range of ignition delay times and flame speeds [17], some of the latter at high pressure for highly diluted conditions. However, they do not reach the temperature levels of CH_4/O_2 conditions, which could explain part of the observed discrepancies. Moreover, many of the important (i.e., sensitive) Arrhenius laws are defined differently from one mechanism to another.

Despite having the best overall behavior, POLIMI C1-C3 still displays a level of error far from negligible. Hence, it is a good starting point for an optimization process using the experimental database acquired with OPTIPRIME in order to obtain a detailed mechanism tailored for CH_4/O_2 combustion at high pressure and temperature.

3. Mechanism optimization

3.1 Initial performance of the chemical scheme

In order to quantify the relative differences between the experimental and the numerical flame speed, the gap was measured at 3 points per tested conditions. Figure 4 represents S_u results at $\varphi=2.5$ for OPTIPRIME and POLIMI C1-C3 with the 3 measurement points at low, intermediate and high pressure. As mentioned above, for these conditions the model overestimates the experimental data.

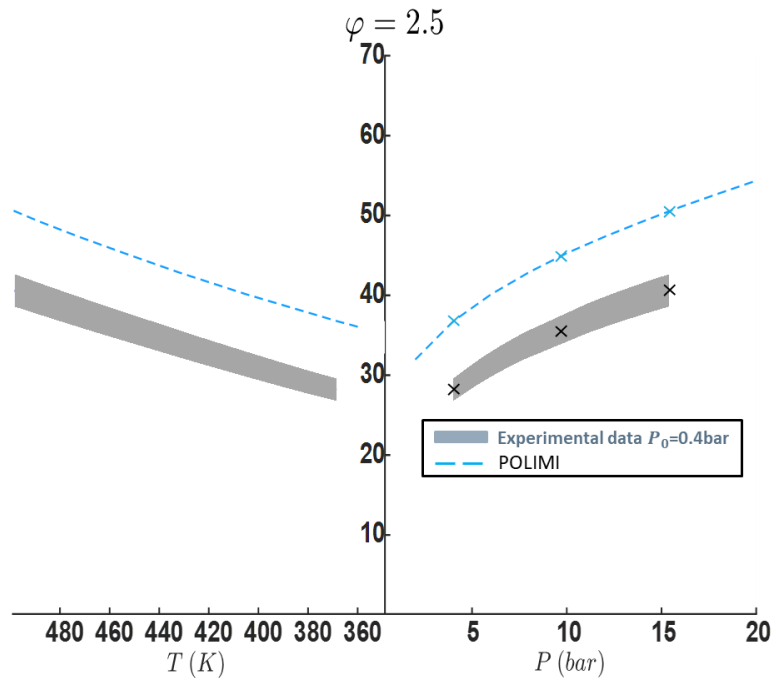
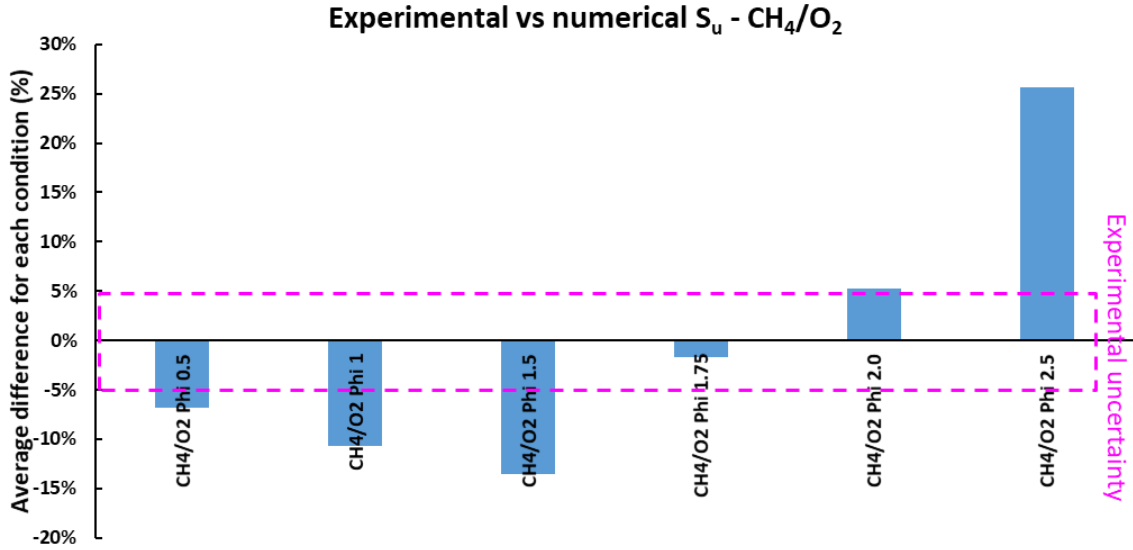


Figure 4: Experimental vs numerical flame speed with error measurement points for CH_4/O_2 mixture at $\varphi = 2.5$

For each tested condition (i.e., equivalence ratio), an average relative difference is computed from these 3 points. This leads to Figure 5 displaying the average gap between POLIMI C1-C3 and the experiment on CH_4/O_2 targets before optimization. The error target for optimization is set within the uncertainty envelope of $\pm 5\%$ for each condition.

Figure 5: Average error for CH₄/O₂ targets

3.2 Optimization strategy

As for every optimization problem, targets and free parameters must be defined. The experimental conditions corresponding to CH₄/O₂ mixtures at $\phi=0.5-1.0-2.0-2.5$ and diluted mixtures at stoichiometry (82.5 and 50% diluent in the oxidizing mixture) are selected. The other tested conditions are used as control targets, in order to assess the quality of the optimization process afterwards. As shown in the previous section, there are 3 S_u points per condition which means a total of 15 S_u target points. In order to give more consistency to the final mechanism, ignition delay times τ_{ign} taken from Petersen et al. [8] are added as targets. Indeed, their low dilution rate and high pressure compared to other studies make them interesting for CH₄/O₂ applications. The data used consists in 5 different mixture conditions (mainly rich mixtures at $\phi=3$) listed in Table 2. For each mixture, different pressures are tested for different temperatures. Minimum, intermediary and maximum temperatures are chosen for a given pressure, making a total of 36 τ_{ign} targets. On the overall, 51 experimental points are used as targets.

Table 2: Ignition delay times conditions from RAMEC

Mixture	ϕ	% diluent for the mixture
1	0.4	77.0% Ar
2	3.0	66.7% Ar
3	3.0	66.7% N2
4	3.0	54.3% Ar
5	3.0	54.3% N2

In order to modify the POLIMI C1-C3 mechanism to match the experimental S_u and τ_{ign} the 3 Arrhenius parameters (the pre-exponential factor A , temperature exponent b and the energy activation Ea) of different key reactions are modified. Indeed, the reaction constant k directly plays a role on the progress rate of each reaction, having an impact on the reaction rates, directly affecting the flame speeds and ignition delays. Key reactions must verify 2 conditions to be selected as free parameters:

- High sensitivity of the flame speed for tested conditions to maximize the impact on S_u and τ_{ign} (sensitivity analyses were performed for the tested conditions prior to the optimization process)

- High uncertainty on the pre-exponential factor to have a large margin for optimization. The uncertainty of selected reactions come from the study by Baulch [22,23]

Following these rules, 27 key reactions are selected, meaning 81 free parameters. Indeed, since the experimental database covers a wide range of conditions, an important number of reactions are necessary to complete the process.

3.3 Optimization process

Since POLIMI C1-C3 presents a lot of species and reactions, the computation of the 15 flame speeds is time consuming. Especially for any optimization process where this operation must be iterated a significant number of times. In order to decrease the computational cost, the mechanism is reduced using the ARCANE tool [13] developed by CERFACS. The optimization experimental S_u and τ_{ign} are chosen as targets for the reduction process. This means that the reduced mechanism has exactly the same behavior as the reference one on the targets chosen for optimization. ARCANE leads to a 30 species and 128 reactions mechanism against 114 species and 1999 reactions initially. This leads to much faster flame speed computations.

The tool used for the optimization process is the OptiSMOKE++ code [12] developed by ULB and Creck. The code couples the OpenSMOKE++ solver [24] developed by Creck and the Dakota optimization library [25] developed by Sandia. The structure of the code is described by the flowchart on Figure 6 extracted from [12]. The user provides the experimental target (S_u and τ_{ign}) which will be evaluated numerically by OpenSMOKE++. The reaction rates to be modified are also provided as inputs with the relative uncertainty on their reaction constant k . The code will then propagate the uncertainty on the 3 Arrhenius parameters. The relative difference between the experimental and numerical values are computed with an objective function, here an L2 norm. At each iteration a new set of free parameters is proposed and tested, obtained thanks to an optimization algorithm. Different algorithms are proposed by the Dakota library. For this study, the DIRECT method is used, as it is the one recommended by the author [12]. This is a gradient-free method dividing the parameter space in promising and non-promising zones, well suited to kinetic mechanisms optimization. Also, in case one of the modified kinetic parameters goes out of bounds during the process, a penalty function is employed to correct the problem.

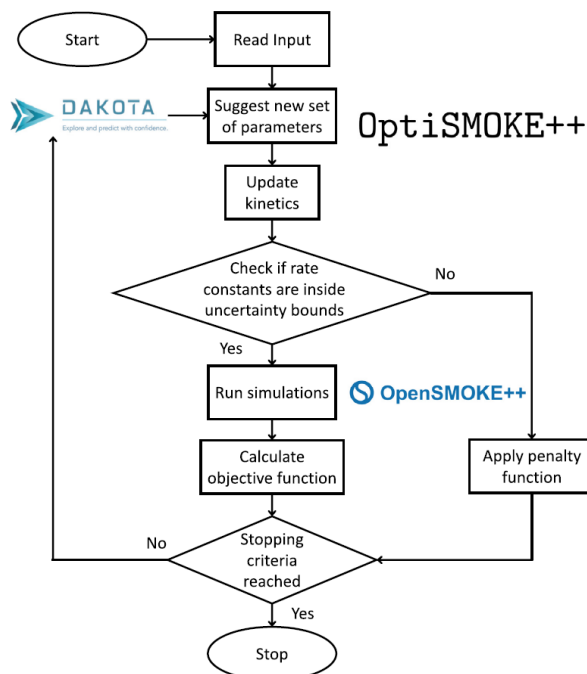


Figure 6: OptiSMOKE++ code flowchart

3.4 Optimization results

The optimization process using the current experimental targets and selected set of reactions give satisfying results as illustrated on Figure 7:

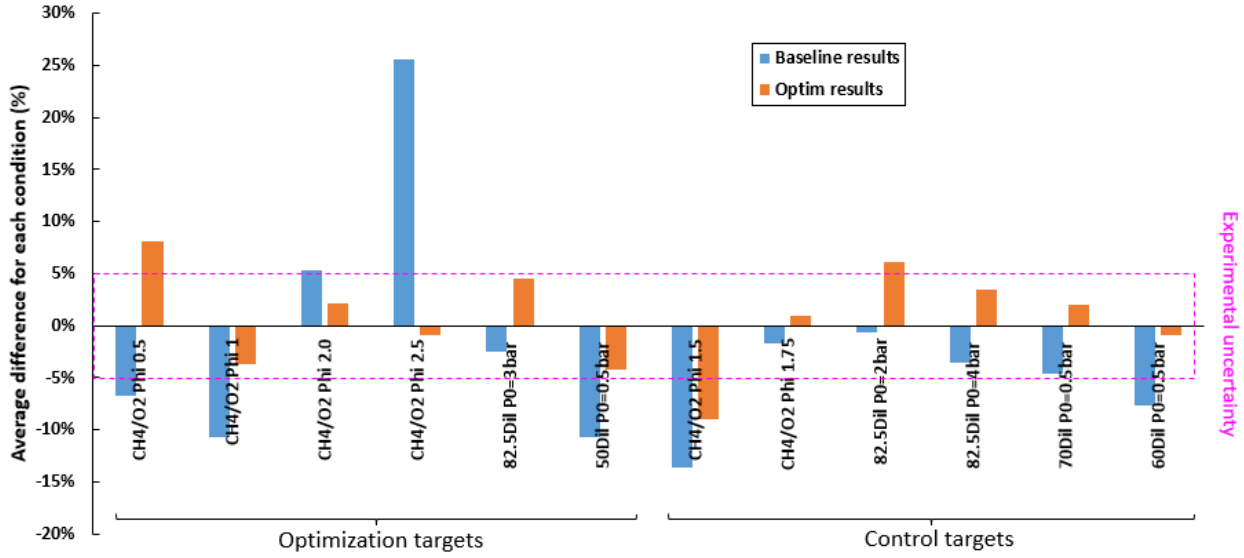


Figure 7: Optimization results on flame speed

As mentioned in the previous section, only the optimization targets were processed by OptiSMOKE++ while the control targets were used for quality assessment. The majority of the average errors were decreased down to the experimental uncertainty of $\pm 5\%$. Some conditions remain above, like CH_4/O_2 at $\phi=0.5$, but it remains in the acceptable range. Control targets behave very well with the exception of CH_4/O_2 at $\phi=1.5$. However, the average error is still acceptable. Figure 8 illustrates some of the targets in terms of flame speed as a function of pressure. It shows how the optimization respects the S_u trend.

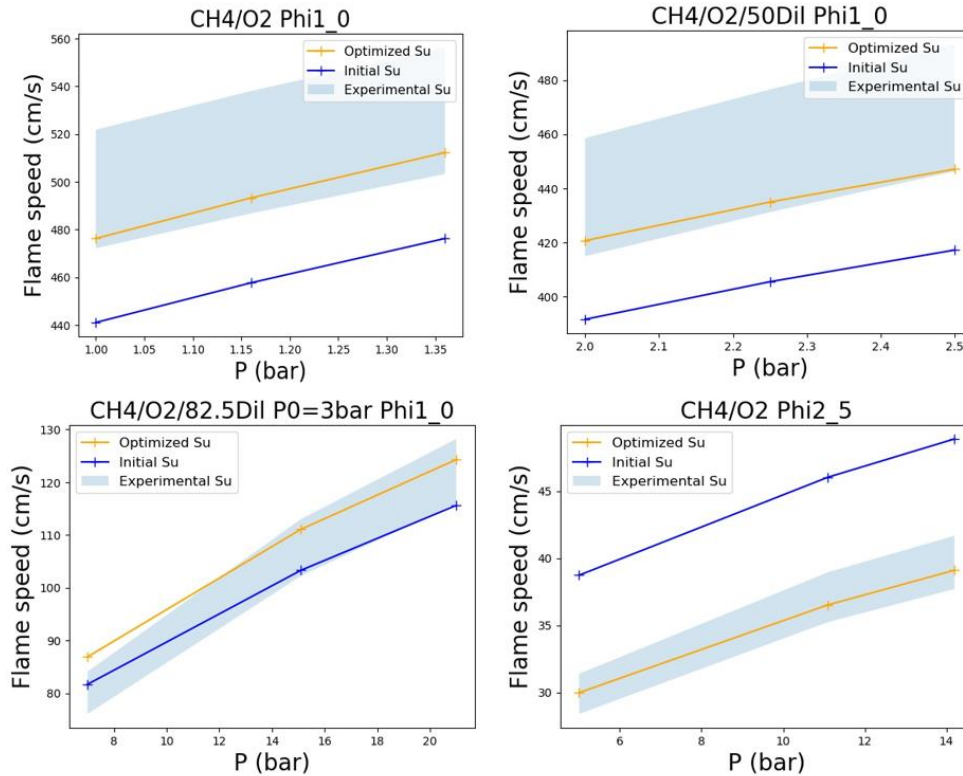


Figure 8 $S_u=f(P)$ optimization results at $\phi=1$ (pure CH_4/O_2 , 50% diluent, 82.5% diluent) and $\phi=2.5$

The optimization was also successful concerning the ignition delay times where all the average errors were decreased below the uncertainty, as shown on Figure 9:

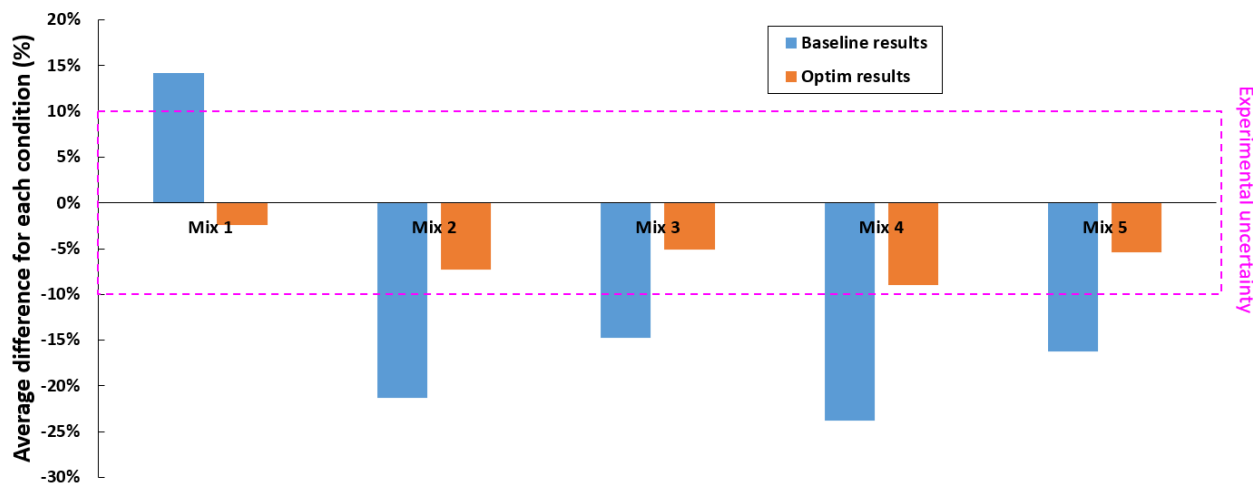


Figure 9: Ignition delay times optimization results

4. Conclusions and perspectives

An experimental database of premixed flame speeds for CH_4/O_2 mixtures was created using the OPTIPRIME experimental setup. The data was acquired for a large spectrum of equivalence ratios (from lean $\varphi=0.5$ to rich $\varphi=2.5$) and never reached before high pressure and temperature conditions. It allowed to challenge recent models from the literature, some of which were developed on purpose for methane-LOx rocket applications. Among all the POLIMI C1-C3 mechanism was selected as it was closest to the experiment. In order to correct the remaining error, POLIMI was optimized on the experimental S_u but also on low dilution high pressure ignition delay times taken from the literature. In order to complete the process, sensitive reactions to be modified were identified. The OptiSMOKE++ code allowed to obtain a mechanism tailored for CH_4/O_2 combustion at high pressure and temperature. This mechanism can be used for 1D flame computations for sizing purposes or can be reduced to be used in CFD code. Current work is to implement the reduced version in the 3D LES code AVBP of CERFACS in order to perform the simulation of a CH_4/O_2 mono-injector configuration.

References

- [1] T. Neill, D. Judd, E. Veith, D. Rousar, Practical uses of liquid methane in rocket engine applications, *Acta Astronaut.* 65 (2009) 696–705.
- [2] P. Simontacchi, E. Edeline, R. Blasi, S. Sagnier, N. Ravier, A. Espinosa-Ramos, J. Breteau, Prometheus: Precursor of new low-cost rocket engine family, *Proc. Int. Astronaut. Congr. IAC.* 2018-Octob (2018) 1–12.
- [3] A. Patureau De Mirand, J.-M. Bahu, E. Louaas, Ariane Next, a vision for a reusable cost efficient European rocket, (2019) 1–9.
- [4] A. Movaghar, R. Lawson, F.N. Egolfopoulos, Confined spherically expanding flame method for measuring laminar flame speeds: Revisiting the assumptions and application to C1C4 hydrocarbon flames, *Combust. Flame.* 212 (2020) 79–92.
- [5] A.N. Mazas, D.A. Lacoste, T. Schuller, Experimental and numerical investigation on the laminar flame speed of CH_4/O_2 mixtures diluted with CO_2 and H_2O , *Proc. ASME Turbo Expo.* 2 (2010) 411–421.
- [6] A. Mazas, Etude des flammes prémélangées enrichies en oxygène : analyse des effets de dilution par la vapeur d'eau et le dioxyde de carbone., 33 (2010).
- [7] B. Lewis, G. Von Elbe, Bernard Lewis and Guenther von Elbe - Combustion, Flames and Explosions of Gases-Academic Press (1987), 1987.
- [8] E.L. Petersen, D.F. Davidson, R.K. Hanson, Ignition delay times of ram accelerator mixtures, 32nd Jt. Propuls. Conf. Exhib. 15 (1996).

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- [9] E.L. Petersen, D.F. Davidson, R.K. Hanson, Kinetics modeling of shock-induced ignition in low-dilution CH₄/O₂ mixtures at high pressures and intermediate temperatures, *Combust. Flame*. 117 (1999) 272–290.
 - [10] F. Halter, Z. Chen, G. Dayma, C. Bariki, Y. Wang, P. Dagaut, C. Chauveau, Development of an optically accessible apparatus to characterize the evolution of spherically expanding flames under constant volume conditions, *Combust. Flame*. 212 (2020) 165–176.
 - [11] G. Bagheri, E. Ranzi, M. Pelucchi, A. Parente, A. Frassoldati, T. Faravelli, Comprehensive kinetic study of combustion technologies for low environmental impact: MILD and OXY-fuel combustion of methane, *Combust. Flame*. 212 (2020) 142–155.
 - [12] M. Fürst, A. Bertolino, A. Cuoci, T. Faravelli, A. Frassoldati, A. Parente, OptiSMOKE++: A toolbox for optimization of chemical kinetic mechanisms, *Comput. Phys. Commun.* 264 (2021) 107940.
 - [13] ARCANE - Q. Cazes, P. Pepiot <https://chemistry.cerfacs.fr/en/arcane/>, (n.d.).
 - [14] S. Blanchard, Multi-physics Large-Eddy Simulation of methane oxy-combustion in Liquid Rocket Engines, Institut National Polytechnique de Toulouse, 2021.
 - [15] F. Fiock, F. Marvin, R. Caldwell, FLAME SPEEDS AND ENERGY CONSIDERATIONS FOR EXPLOSIONS IN A SPHERICAL BOMB, (n.d.).
 - [16] A. Mouze-Mornettas, H. Keck, Y. Wang, Z. Chen, G. Dayma, C. Chauveau, F. Halter, Effect of wall heat transfer on the dynamics of premixed spherical expanding flames, *Therm. Sci. Eng. Prog.* 29 (2022) 101227.
 - [17] G.P. Smith, Y. Tao, and H. Wang, Foundational Fuel Chemistry Model Version 1.0 (FFCM-1), <http://nanoenergy.stanford.edu/ffcm1>, 2016., (n.d.).
 - [18] E.L. Petersen, R.K. Hanson, Reduced kinetics mechanisms for ram accelerator combustion, *J. Propuls. Power*. 15 (1999) 591–600.
 - [19] N. Slavinskaya, M. Abbasi, J.-H. Starcke, A. Mirzayeva, O.J. Haidn, Skeletal Mechanism of the Methane Oxidation for Space Propulsion Applications, (2016) 1–11.
 - [20] V.P. Zhukov, A.F. Kong, A compact reaction mechanism of methane oxidation at high pressures, *Prog. React. Kinet. Mech.* 43 (2018) 62–78.
 - [21] and Z.Q. Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, William C. Gardiner, Jr., Vitali V. Lissianski, GRI-MECH 3.0, (n.d.).
 - [22] D.L. Baulch, M.J. Pilling, C.J. Cobos, R.A. Cox, P. Frank, G. Hayman, T. Just, J.A. Kerr, T. Murrells, J. Troe, R.W. Walker, J. Warnatz, Evaluated Kinetic Data for Combustion Modeling. Supplement I, *J. Phys. Chem. Ref. Data*. 23 (1994) 847–848.
 - [23] D.L. Baulch, C.T. Bowman, C.J. Cobos, R.A. Cox, T. Just, J.A. Kerr, M.J. Pilling, D. Stocker, J. Troe, W. Tsang, R.W. Walker, J. Warnatz, Evaluated kinetic data for combustion modeling: Supplement II, *J. Phys. Chem. Ref. Data*. 34 (2005) 757–1397.
 - [24] A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, OpenSMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms, *Comput. Phys. Commun.* 192 (2015) 237–264.
 - [25] B.M. Adams, W.J. Bohnhoff, K.R. Dalbey, M.S. Ebeida, J.P. Eddy, M.S. Eldred, R.W. Hooper, P.D. Hough, K.T. Hu, J.D. Jakeman, M. Khalil, K.A. Maupin, J.A. Monschke, E.M. Ridgway, A.A. Rushdi, D. Thomas, J.A. Stephens, L.P. Swiler, J.G. Winokur, Dakota, A Multilevel Parallel Object-Oriented Framework for Design Optimization, Parameter Estimation, Uncertainty Quantification, and Sensitivity Analysis: Version 6.15 User's Manual, (2021).