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HIGH PRESSURE HYDROGEN OXYGEN COMBUSTION KINETIC ASSESSMENT FOR AIR-BREATHING PROPULSION SUPERSONIC GREEN AVIATION

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Abstract

In the framework of the MDO and Regulations for Low-boom and Environmentally Sustainable Supersonic aviation (MORE&LESS) project, pursued by a consortium of European government and academic institutions, coordinated by Politecnico di Torino under the EC Horizon 2020 financial support, the Italian Aerospace Research Centre (CIRA) is computationally investigating the high-pressure hydrogen/air kinetic combustion in the operative conditions typically encountered in supersonic aeronautic ramjet engines. This task is being carried out starting from the zero-dimensional chemical kinetic assessment of the complex and strongly pressure-sensitive ignition behavior of hydrogen combustion through the validation against experimental shock tube measurements.

Keywords: high-pressure supersonic combustion, hydrogen oxidation, air-breathing propulsion, green aviation.

1. Introduction

MORE&LESS is a research project pursued by a consortium of European government and academic institutions including CIRA and is coordinated by Politecnico di Torino under the EC Horizon 2020 financial support.

This project aims to address the challenges regarding the environmental impact of supersonic, air-breathing aviation implementing a holistic approach based on a synergic coupling between low and high-fidelity modelling of several processes e.g., aerodynamics, jet-noise, sonic-boom, propulsion, and above all pollutant and climate-changing chemical emissions.

Advanced propulsion systems are essential enablers of supersonic aviation and the proper understanding of their working principles is required to operate them efficiently and with low pollutant emissions, so extending the design space and flight envelope. Modelling of propulsion systems of these aircrafts, the optimization of their components, and the proper estimation of their performance is one of the main goals of the MORE&LESS project, together with the estimation of bio-fuel and hydrogen combustion with associated emissions. Consequently, solid strategies are developed to reduce pollutant emissions for future supersonic aircraft.

CIRA has in charge of the assessment of available hydrogen/air reaction mechanisms, in particular with: i) a thorough investigation of detailed and reduced kinetic mechanisms performed through literature survey, ii) theoretical investigations and identification of the most performing kinetic schemes for hydrogen/air combustion at selected operative flight conditions, iii) 0D simulations of hydrogen/air combustion and comparison of ignition delay times and adiabatic flame temperatures against literature available experimental data. The work described in the present paper emanates directly from what was recently accomplished in the previous H2020 STRATOFLY project [3, 4] and the present task represents a continuation and extension of it to a wider range of operative conditions.

2. Why Hydrogen?

Hydrogen is a promising candidate as fuel for supersonic, air-breathing, trans-atmospheric, long-term passenger transportation aircraft because it can be burned efficiently and reliably in supersonic combustion engines [1]. Moreover, among the various available fuels, it possesses the highest heat release with the shortest kinetic time, wide flammability limits (4% – 75% by volume in air), and excellent cooling properties [2]. Table 1 summarizes some physical and chemical parameters of hydrogen related to its combustion behavior.

Molecular weight [a. m. u.]	2.01588
Boiling point [K]	20.268
Melting point [K]	14.01
Density of gas @ STP [kg/m^3]	0.08990
Specific heat @ STP [kJ/(kg K)]	14.304
Thermal conductivity @ STP [W/(m K)]	0.187
Flammability limits in the air [vol %]	4.0 – 75.0
Detonability limits in the air [vol %]	13.0 – 70.0
Auto-ignition temperature in the air [K]	793 – 1023
Gross heat of combustion or HHV [kJ/mol] @ 298 K	286.1
Net heat of combustion or LHV [kJ/mol] @ 298 K	241.7
Stoichiometric adiabatic flame temperature in the air [K]	2318
Laminar burning velocity in the air [m/s]	2.65 – 3.25
Visible laminar flame speed [m/s]	18.6
Detonation velocity [m/s]	1480 – 2150
Deflagration pressure ratio	8.15
Quenching distance @ STP [m]	0.00064

Table 1 – Physical and chemical combustion parameters of hydrogen.

Additionally, H_2 is a clean fuel since the overall product of its complete oxy-combustion is only water, even if, when reacts with air, it produces also NO_x, due to the very elevated flame temperatures reached during combustion. In any case, the advantage of burning hydrogen from an environmental point of view is that it does not produce the greenhouse gas CO_2, nor any of the several other pollutant species i.e., CO, unburned hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAH) and soot. For the above-mentioned reasons, hydrogen is esteemed as a fundamental energy vector for the decarbonized economy.

Supersonic hydrogen/air combustion is a very challenging process, consisting of several critical phenomena e.g., injection, compressible mixing, chemical kinetics, ignition, flame holding, vortices generation, flashbacks, combustion instability, turbulence combustion, interactions among shock waves, boundary layer and heat release, etc. Moreover, ramjet engine operations are further complicated by the very short residence time ($\sim 10^{-3}$ s) of the flow inside the thrust chamber, which is of the same order of magnitude as the chemical kinetic ignition time of hydrogen/air mixtures at the typical conditions of ramjet operation. Since experimental investigations are often unfeasible due to several difficulties in measuring multispecies, reacting, high-speed, unsteady flow fields [1], the most convenient way to design and develop ramjet engine propelled vehicles relies on Computational Fluid Dynamics (CFD) modelling and simulations.

Hydrogen/air kinetic mechanisms assessment is an important, preliminary task for the development of physical-chemical combustion models to be implemented into CFD codes. The optimal scheme arises as a suitable trade-off between the accuracy, required for a precise description of ignition and combustion phenomena, and the computational costs, associated with the available calculation speed and memory storage capacity. On this topic, hydrogen/air kinetic mechanisms assessment is an important, preliminary task for the development of physical-chemical combustion models to be implemented in CFD codes. The optimal scheme arises as a suitable trade-off between the accuracy, required for a truthful description of ignition and combustion phenomena and the computational costs, associated with the available calculation speed and memory storage capacity.

Furthermore, since in aeronautic engines the working pressure is often much more than the

atmospheric level reaching values up to 30 bars, to design hydrogen/air combustion chambers able to guarantee a minimum NO_x release, the deepened understanding of the complex and nonlinear hydrogen/oxygen ignition kinetics at so elevated pressure is of paramount importance.

3. Kinetic Assessment

3.1 Selection of the kinetic mechanisms

Hydrogen/air oxidation chemistry was studied for decades and Table 2 reports a list of the main literature available on kinetic mechanisms together with the number of the active chemical species (without the inert noble gases) and reactions.

Kinetic scheme	Species	Reactions
NUIG-NGM-2010	9	21
Hong-2011	9	31
Burke-2012	9	27
SaxenaWilliams-2006	9	21
Konnov-2008	9	33
Li-2007	9	25
Davis-2005	9	25
USC-II-2007	9	28
CREK-2012	9	21
San Diego-2011	9	21
Sun-2007	9	32
Rasmussen-2008	9	30
O'Coinaire-2004	9	21
Ahmed-2007	9	20
Zsély-2005	9	32
Dagaut-2003	9	21
Vajda-1990	9	19
Jachimowski	9	33
Kéromnès – 2013	10	33
CRECK - 2012	9	23
Z22 – 2018	9	22

Table 2 – Main hydrogen/air combustion literature available kinetic mechanisms [2].

Based on the author's experience [3, 4] and the review of Hu and co-workers [5], only the following six literature available schemes are considered as the most promising kinetic mechanisms since they were specifically designed and developed to describe not only the hydrogen/oxygen combustion at atmospheric conditions, but also at intermediate to high pressures:

1) Ó Conaire – 2004 [6-9].
2) CRECK – 2012 [10-15].
3) Z22 – 2018 [16-18].
4) GRI-Mech 3.0 [19].
5) USC-II [20].
6) Aramco-II [2, 21-26].

The last three schemes are large kinetic mechanisms dedicated not only to hydrogen oxidation, but suitably formulated for the description of natural gas i.e., GRI-Mech 3.0 [19] and USC-II [20] and high molecular weight hydrocarbons combustion in petrochemical applications i.e., Aramco-II [2, 21-26]. In any case, they include accurate H/O sub-mechanism, which is of paramount importance also in the combustion of every hydrocarbon, and they were used in the present work as fully, detailed mechanisms for reference purposes.

Table 3 summarizes the main features of the considered kinetic mechanisms ordered with an increasing number of chemical species.

Kinetic scheme	Species	Reactions
Ó Conaire	9	19
Z22 – 2018	9	22
CRECK –2012	9	23
GRI-Mech 3.0	53	325
USC-II	111	784
Aramco-II	493	2174

Table 3 – The six hydrogen/oxygen combustion kinetic mechanisms investigated in the present work.

Generally, the kinetic assessment of hydrogen/air combustion is carried out by uncoupling this very complex chemical process in two main consecutive phases:

i. Oxi-combustion of hydrogen i.e., the reaction of H_2 with only O_2 consisting of several initiation, propagation, chain branching, and termination radical steps leading to the formation of the water vapor and release of heat by means of exothermic reactions. For this purpose, reacting mixtures composed of only the fuel i.e., hydrogen, and the pure oxidant i.e., oxygen, but in presence of diluent inert bath gases e.g., argon, helium, neon, etc., generally used in shock tube and Rapid Compression Machine (RCM) experimental tests are investigated.

ii. Generation of NO_x in presence of air (0.21% O_2 and 0.79 N_2), mainly produced due to the very elevated flame temperature (~2000 K) achieved during the oxidation of hydrogen, which are sufficient to thermally break the very strong triple covalent bond of the nitrogen molecule forming radical N· and promoting the combinations between N·and O·with a consequent yield of nitrogen oxides following essentially the Zel'dovich route [27].

In the first phase, the inherent oxidation behavior of the fuel is analyzed aimed to identify the most accurate and reliable H/O mechanism for the selected operative box and considering only the chemical species i.e., molecules, atoms, and radicals involved in the pristine reactants i.e., fuel and oxidant. The objective of this phase is the understanding of the intrinsic ignition behavior, without the chemical interference of other components e.g., N_2, which can combine with the radicals arising from the pure reactants leading to different and even more complex reaction paths.

Completed the assessment of the hydrogen combustion using as oxidant only the pure O_2, the second phase is of paramount importance for the hydrogen/air combustion kinetic analysis. It consists of the integration, according to a building block approach, of the previously developed H/O kinetic mechanism with the most suitable H/O/N sub-mechanism, selected based on the operative envelope under investigation, to arrange a reliable chemical kinetic sub-model to be used for pollutant i.e., NO_x
and climate-changing i.e., water vapor emissions evaluation.

The present study focuses on the first part of the chemical kinetic assessment of hydrogen combustion, while the second phase will be a matter of future work.

3.2 Ó Conaire – 2004

Ó Conaire scheme is a detailed kinetic mechanism developed to simulate the combustion of H_2/O_2 mixtures, over a wide range of temperatures from 298 and 2700 K, pressures in the 0.05 – 87 atm range, and equivalence ratios from 0.2 to 6 [6]. This model is an updated version of the previous Mueller et al. scheme [7] in turn derived from the $CO/H_2/O_2$ reaction mechanism of Yetter et al. [8], later revised by Kim et al. [9]. In the final model, some of the original Arrhenius parameters were modified to achieve an improved agreement with experimental data concerning not only flow reactors, but also shock-tube and burner stabilized flame speeds in the broader possible operative envelope.

The revision process concentrated especially on the fundamental pressure-sensitive reaction:

$$[OR8] \; H + OH \; (+M) \leftrightarrow H_2O \; (+M)$$

This reversible step consists of the termolecular collision of the key radicals: H· i.e., the primary product of the thermal decomposition of the stable hydrogen molecule, and the OH·radical i.e., the flame marker and the main radical involved in the chain branching process with a third body i.e., (M), whose

presence promotes the [OR8] reaction.

3.3 CRECK – 2012

It is a hierarchical mechanism developed by the CRECK Modelling Group of Politecnico di Milano as a fundamental sub-mechanism to be incorporated into heavier fuels i.e., from hydrocarbons up to jet biodiesels. This kinetic mechanism was assessed using 0D ignition delay times and 1D laminar flame speed calculations, and comparison against the available experimental data using a specifically formulated and developed in-house kinetic and thermodynamic tool i.e., OpenSMOKE.

It was upgraded and updated starting from a detailed kinetic H_2/O_2 combustion scheme using new kinetic and thermodynamic measurements and it was validated over a wide range of temperatures, pressures and equivalence ratios [10-15]. Moreover, the mechanism's performance at high pressures was greatly improved in particular by adapting higher rate parameters for the following termolecular reaction:

$$[CR10] \quad H + OH \,(+M) \leftrightarrow H_2O \,(+M)$$

The frequency factor of this step was doubled in comparison to the original mechanism [10, 11] since further investigations demonstrated that the [CR10] reaction is of noticeable importance for the laminar flame speed propagation at high pressure, while it is less sensitive under flow reactor and shock tube conditions. Furthermore, the Chaperon efficiency of the bath gases were slightly modified to improve the agreement with the whole considered set of experimental measurements.

Additionally, the high-pressure limit was added to the mechanism according to Troe's parameters models aimed to suitably describe the fall-off behavior of the reaction [CR10], which plays a paramount role, especially for the very elevated pressure applications.

Finally, all the thermodynamic and transport properties of the CRECK – 2012 mechanism were taken from the CHEMKIN database with the significant exception of the enthalpy of the radicals OH and HO_2 formation, which were revised according to the theoretical and experimental recommendations of Ruscic et al. [12].

More recently, the CRECK - 2012 model was further improved and it coupled the H_2/O_2 with C1-C2 sub-mechanisms from [13], as revised in [14], and heavier fuels sub-mechanisms from Ranzi et al. [15] to be efficiently used as syngas combustion chemical kinetic mechanism.

3.4 Z22 – 2018

This is a detailed, hydrogen/oxygen kinetic mechanism consisting of 9 species and 22 irreversible elementary reactions [16]. It arises the H_2-O_2 chemical structure from [17] with three additional fuel breakdown reactions from [6, 19].

Zettervall and Fureby [16] highlight the importance of the competition between the chain-branching reaction [ZR4]: $H + O_2 \rightarrow OH + O$ and the chain-propagating reaction [ZR12]: $H + O_2 \,(+M) \rightarrow HO_2 \,(+M)$. The first creates a pool of radical species effectively decreasing the ignition time, while the second produces the hydroperoxyl radical, which inhibits the chain-branching combustion process and therefore increases the induction time.

The competition between these reactions, and the consequent distribution of fast O, H, and OH radicals and the slow radical HO_2, is strongly temperature dependent. Furthermore, in the P-T diagram shown in Figure 1 a region of rapid ignition corresponding to chain-branching explosion at high temperatures and a region of slow ignition, associated with the thermal explosion at low temperatures are separated by a crossover region, corresponding to intermediate temperatures and dominated by extremely complex chemical processes.

However, for instance, several ramjets, scramjets, and dual-mode engines operate exactly in this connecting, critical zone.
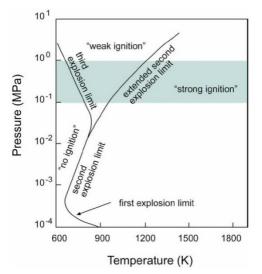
Figure1 – Explosion diagram of hydrogen/air system.

Z22 includes reactions important for the complete temperature spectrum, below and above the crossover region. In the mechanism development, authors spent particular efforts on improving its capability to match the ignition experimental behaviour also in the intermediate connecting region, because it is extremely useful for ensuring flame anchoring and stabilization within the supersonic combustion engines [1].

At low temperatures, reaction [ZR12] predominates over reaction [ZR4], the HO_2 concentration enhances and new reaction paths become more important i.e., [ZR16]: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ and [ZR20]: $H_2O + HO_2 \rightarrow H_2O_2 + OH$.

These reactions increase the concentration of H_2O_2, which main consumption route is carried out by means of reaction [ZR17]: $H_2O_2 (+M) \rightarrow OH + OH (+M)$, which produces two OH radicals, which in turn generate H radical through [ZR8]: $H_2 + OH \rightarrow H_2O + H$.

3.5 Considered Detailed Kinetic Mechanisms

Detailed mechanisms were analyzed to strengthen the kinetic assessment and to achieve a more complete chemical description of the ignition and combustion processes. The considered full mechanisms are GRI-Mech 3.0 [19], USC-II [20], and Aramco-II [2, 21-26].

GRI-Mech 3.0 is a widely known and well consolidated detailed scheme formulated and thoroughly optimized with robust sensitivity studies to model the ignition and combustion of natural gas, essentially methane, including NO formation and the reburn chemistry. It was developed through computational and experimental research sponsored by the Gas Research Institute (GRI) and carried out at The University of California Berkeley, Stanford University, The University of Texas at Austin and SRI International [19].

USC-II is a detailed kinetic scheme generated by the University of Southern California with the main objective to describe many combustion processes from C0 to C4 with 111 species in 784 reversible reactions. Significant attention was placed on obtaining a comprehensive and kinetically accurate model able to predict a wide variety of H_2–CO combustion data. The mechanism was subjected to systematic optimization and validation tests against reliable H_2–CO combustion data, from global combustion properties e.g., shock-tube ignition delays, laminar flame speeds, and extinction strain rates up to detailed species profiles during H_2 and CO oxidation in flow reactors and in laminar premixed flames [20].

Aramco-II was developed by the National University of Ireland Galway in a hierarchical way using a bottom-up approach and starting with an H_2/O_2 sub-mechanism, followed by a C1 sub-mechanism, and has grown to include larger carbon species such as ethane, ethylene, acetylene, allene, propyne, propene, n-butane, isobutane, isobutene, 1-butene and 2-butene, and oxygenated species including formaldehyde, acetaldehyde, methanol, ethanol, and dimethyl ether [2, 21-26]. This mechanism was validated against a large array of experimental measurements including data from shock tubes, rapid compression machines, flames, jet-stirred and plug-flow reactors [2, 21-26].

3.6 0D Mathematical Chemical Modeling

Zero-dimensional kinetic analysis of hydrogen/air combustion at the most representative operative conditions for the investigated applications was performed using the kinetic and thermodynamic Cantera open-source software [28] through calculation of induction times in homogeneous, adiabatic, isochoric, batch reactors using the six mechanisms listed in Table 3.

The mathematical-chemical model consists of the following mass and energy balance equations:

$$m_{tot} = \sum_{k=1}^{K} m_k = const. \Leftrightarrow \frac{dm_{tot}}{dt} = 0 \qquad (1)$$

$$\frac{dm_k}{dt} = V r_k M_{w,k} \qquad (2)$$

$$c_{p,mix} \frac{dT}{dt} + v \cdot \sum_{k=1}^{K} h_k \cdot r_k \cdot M_{w,k} = 0 \qquad (3)$$

The initial temperature, pressure, and equivalence ratios for every run were selected according to the considered shock tube experiments.

The pressure of the reacting mixture was evaluated using the ideal gas law.
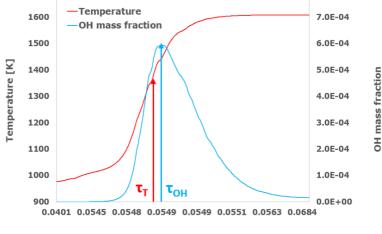
3.7 Comparison against Shock Tube Measurements

The accuracy and reliability of detailed and reduced chemical mechanisms of fuel/oxidant combustion are generally assessed as the first fundamental step through the calculation of the ignition delay times using 0D kinetic time-dependent simulations.

Indeed, the computation of the induction times in perfectly stirred, adiabatic, isochoric batch reactors are exclusively determined by the followed reaction pathways and the kinetic reversible interactions among the various chemical species involved in the combustion scheme. Moreover, the ignition delay times are combustion characteristics completely uncoupled from the turbulence and fluid dynamics variables, i.e. mixing, and totally associated with the chemical kinetic behavior.
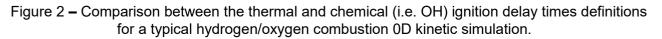
In literature, several diagnostic techniques were designed and used to effectively measure the ignition of the combustion process. The most widely accepted and frequently implemented are:

a) Thermal definition as the time elapsed between the generation of a combustible mixture at a given temperature, pressure, and composition (e.g., the equivalence ratio) and the exponential temperature and pressure enhancement associated with chain branching reactions and the radical pool formation.

b) Chemical definition as the time spacing between the arrival of the reflected shock waves at the end-wall of the shock tube combustion rigs and the time corresponding to the maximum concentration (e.g., the mass fraction) of a characteristic radical species (i.e., OH or its excited version OH*) in the case of hydrogen oxidation. The OH radical is also the flame marker associated with chemiluminescence phenomena.

Generally, both the thermal and chemical definitions provide times very similar between them as schematically illustrated in Figure 2.

Figure 2 – Comparison between the thermal and chemical (i.e. OH) ignition delay times definitions for a typical hydrogen/oxygen combustion 0D kinetic simulation.

However, the kinetic chemical definition is considered more reliable, since it can be directly compared with the chemiluminescence measurements and it is not based on the temperature profile. Indeed, the heat transport is more sensitive to the specific construction and settings characteristics of the combustion facility used for the acquisition of the experimental data.

Two different test rigs are commonly used:

    1)   Shock Tubes.
    2)   RCM.

Nevertheless, in order to carry out a reliable comparison between the experimental measurements of the ignition delay times acquired in RCM, the non-ideal gas dynamic effects cannot be safely neglected. Therefore, the 0D kinetic simulations of experiments carried out in RCM require the setup of a more sophisticated reactor network model, including not only the adiabatic, isochoric, and perfectly stirred reactor reproducing the combustion chamber, but also a communicating reservoir for the heat exchange, which cannot be ignored in RCM tests.

Instead, the adopted assumptions of ignition phenomena at constant internal energy and volume can be reliably used to simulate experimental data measured in reflected shock tubes, if the induction times are lower than ~4 ms [5, 29].

For this reason, the 0D kinetic assessment of hydrogen/oxygen combustion was preliminarily accomplished using only experimental data arising from shock tube measurements, and the following three datasets were selected to investigate a wider pressure range spanning from 4 up to about 33 bar:

    a)   Herzler – 2009 [30].
    b)   Petersen – 2011 [31].
    c)   Hu – 2016 [5].

In the experimental study and the related kinetic rebuilding carried out by Hu and coworkers [5], the ignition delay times were defined as time spacing between the arrival of the reflected shock waves at the end-wall of the used test rigs and the linear extrapolation of the steepest rise of OH* emission signal to zero level, which is slightly lower than the time corresponding to the maximum mass fraction of the radical OH or its excited version OH*.

3.8 Operative Conditions

Hydrogen/air kinetic mechanisms assessment is an important, preliminary task for the development of physical-chemical combustion models to be implemented in CFD codes.

The optimal scheme arises as a suitable trade-off between the accuracy, required for a straightforward description of ignition and combustion phenomena and the computational costs, associated with the available calculation speed and memory storage capacity.

Furthermore, since in aeronautic turbine gas combustors the working pressure is often much more than the atmospheric level, reaching values up to 30 bars, to design hydrogen/air combustion chambers

able to guarantee a minimum NO$_x$ release, the deepened understanding of the complex and nonlinear hydrogen/oxygen ignition kinetics at so elevated pressures is of paramount importance.

The initial temperatures were selected as the lowest possible corresponding to the available experimental data, while as composition only the fuel-lean region was assessed, since the preliminary propulsive system flow path corresponding to the configuration of the MR5 vehicle designed in the framework of MORE&LESS project operates in this combustion regime to minimize the NO$_x$ emissions. Therefore, the initial thermodynamic conditions for the 0D time-dependent kinetic simulations were selected exactly equal to the experimental starting values, and they belong to the overall operative box reported in Table 4.

Temperature [K]	Pressure [bar]	Equivalence ratio
975 - 1150	4 - 33	0.5

Table 4 – Operative conditions selected for 0D kinetic simulations.

4. Results and Discussions

In the following plots from Figure 3 to Figure 9 the comparison between the ignition delay times calculated by means of 0D kinetic simulations carried out under the same operative conditions as the shock tube experiments is provided.
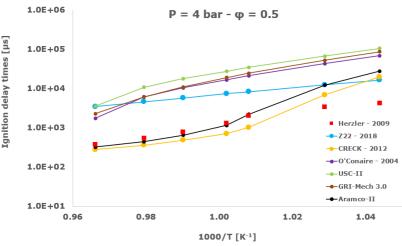

Figure 3 – Ignition delay times comparison between 0D predictions and the experimental data of Herzler – 2009 [30] at 4 bar.
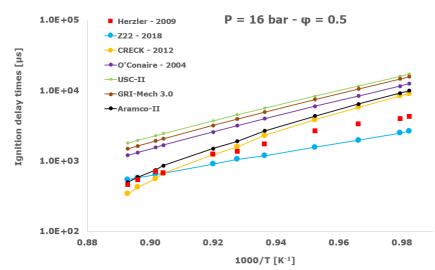

Figure 4 – Ignition delay times comparison between 0D predictions and the experimental data of Herzler – 2009 [30] at 16 bar.
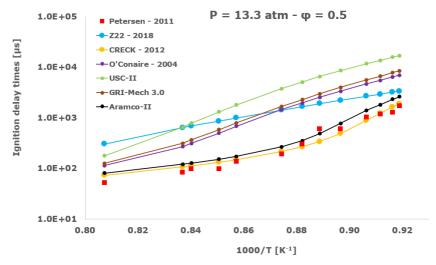
Figure 5 – Ignition delay times comparison between 0D predictions and the experimental data of Petersen – 2011 [31] at 13.3 atm.
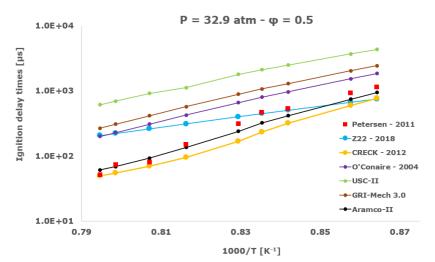

Figure 6 – Ignition delay times comparison between 0D predictions and the experimental data of Petersen – 2011 [31] at 32.9 atm.
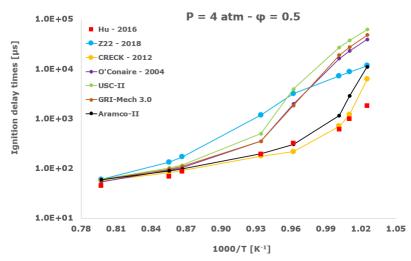

Figure 7 – Ignition delay times comparison between 0D predictions and the experimental data of Hu – 2016 [5] at 4 atm.
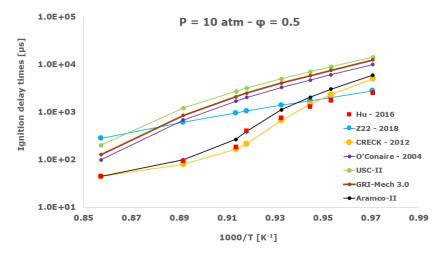
Figure 8 – Ignition delay times comparison between 0D predictions and the experimental data of Hu – 2016 [5] at 10 atm.
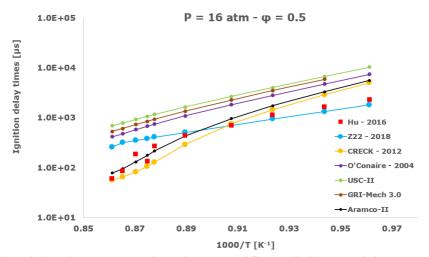

Figure 9 – Ignition delay times comparison between 0D predictions and the experimental data of Hu – 2016 [5] at 16 atm.

In order to calculate a sort of degree of mismatching between the experimental measurements reported in the three considered experimental datasets and the corresponding numerical predictions computed at the same initial operative conditions and using the six investigated kinetic mechanisms, the following disagreement indicator I was defined.

$$I = \frac{\left| \tau_{ign-numerical} - \tau_{ign-experimental} \right|}{\tau_{ign-experimental}} \cdot 100 \qquad (4)$$

where τ_{ign} is the ignition delay times and the subscripts *numerical* and *experimental* refer to the results of the 0D kinetic simulations and the experimental measurements respectively. Moreover, the average values for every analyzed scheme were evaluated at each investigated combustion pressure, as reported in the following Table 5, Table 6, and Table 7.

P [bar]	T [K]	$I_{Keromnes}$	I_{Z22}	I_{CRECK}	$I_{Ó\ Conaire}$	I_{USC-II}	$I_{GRI-Mech\ 3.0}$	$I_{Aramco-II}$
4	958	528.21	282.98	358.51	1510.02	2363.87	1919.81	544.99
	972	239.88	264.52	103.40	1160.70	1871.26	1452.20	259.53
	992	8.40	302.72	50.68	929.61	1576.70	1096.12	6.70
	998	20.00	459.47	46.23	1158.33	1990.15	1350.00	12.58
	1010	19.96	640.95	38.18	1246.60	2199.10	1312.07	16.48
	1021	19.31	758.63	32.84	1039.70	1924.12	1033.40	17.38
	1035	15.01	826.27	25.04	368.10	850.13	511.80	13.73
		121.54	**505.08**	**93.55**	**1059.01**	**1825.05**	**1239.34**	**124.48**
16	1018	140.71	37.22	113.01	195.76	306.59	270.12	134.09
	1021	136.06	37.93	108.98	189.78	297.76	265.59	129.48
	1035	97.25	40.78	73.71	151.80	247.31	217.07	92.78
	1050	65.11	41.31	43.88	123.77	211.49	179.74	62.46
	1068	55.84	31.04	33.12	130.92	225.55	187.11	54.57
	1078	40.37	22.21	16.03	133.75	234.93	190.59	40.22
	1087	20.32	27.64	1.60	107.36	198.24	157.12	20.48
	1106	26.36	1.64	1.49	148.23	263.13	205.60	27.33
	1109	4.75	8.84	20.76	120.65	225.32	172.84	5.88
	1116	8.51	7.43	20.93	146.47	266.73	204.46	10.07
	1120	6.87	18.67	25.09	161.30	291.74	223.70	8.83
		54.74	**16.78**	**17.00**	**135.53**	**243.66**	**191.63**	**23.91**

Table 5 – Degree of mismatching for every investigated kinetic mechanism and their average values at each considered pressure of the Herzler– 2009 [30] dataset.

P [atm]	T [K]	I_{Z22}	I_{CRECK}	$I_{\text{Ó Conaire}}$	I_{USC-II}	$I_{GRI-Mech\ 3.0}$	$I_{Aramco-II}$
13.3	1239	477.89	39.47	118.51	238.93	140.28	53.58
	1195	658.45	28.05	221.44	675.32	273.82	44.44
	1190	597.08	14.42	215.35	691.96	269.44	29.53
	1176	784.02	35.89	412.31	1249.74	499.46	56.53
	1167	627.08	8.96	402.95	1224.48	482.23	27.20
	1144	637.08	11.60	657.24	1866.24	768.89	39.51
	1134	451.32	11.34	553.70	1590.07	657.07	17.69
	1125	215.90	43.58	322.14	985.84	394.51	18.66
	1115	268.28	18.78	458.45	1322.89	562.38	29.58
	1103	158.65	13.71	352.77	1034.57	443.65	35.94
	1097	145.73	2.89	360.88	1043.42	456.41	53.29
	1091	152.70	30.00	406.90	1144.32	514.79	83.28
	1088	97.25	11.30	308.98	897.34	397.03	53.22
		405.50	**20.77**	**368.58**	**1074.24**	**450.77**	**41.73**
32.9	1266	301.25	3.71	287.90	1086.53	420.04	19.02
	1260	202.08	25.72	211.40	844.75	317.91	6.63
	1247	228.00	12.07	287.57	1049.73	421.35	16.05
	1233	106.21	36.65	180.48	639.47	278.11	9.89
	1213	27.52	46.14	109.56	469.35	182.17	23.55
	1204	3.72	49.97	71.51	353.90	130.16	30.78
	1195	5.16	39.99	82.56	370.17	144.20	21.76
	1173	28.18	35.26	65.24	297.09	118.63	19.70
	1164	34.46	32.74	61.43	277.57	112.04	17.65
		130.85	**28.57**	**185.02**	**669.10**	**270.22**	**23.63**

Table 6 – Degree of mismatching for every investigated kinetic mechanism and their average values at each considered pressure of the Petersen – 2011 [31] dataset.

P [atm]	T [K]	I_{Z22}	I_{CRECK}	$I_{Ó\ Conaire}$	I_{USC-II}	$I_{GRI\text{-}Mech\ 3.0}$	$I_{Aramco\text{-}II}$
	1254	32.49	23.02	19.25	33.55	30.82	31.67
	1169	91.57	19.34	32.64	46.59	39.10	27.86
	1154	94.80	4.03	19.89	33.24	25.19	11.64
	1070	509.19	8.91	80.85	156.62	81.11	1.10
4	1039	897.23	32.01	518.63	1135.69	479.67	4.49
	999	1082.91	15.70	2558.06	4324.62	2999.70	89.63
	990	761.40	19.60	2188.00	3613.00	2630.00	185.40
	975	533.01	237.99	2043.94	3261.86	2526.08	505.14
		500.32	**45.07**	**932.66**	**1575.65**	**1101.46**	**107.11**
	1167	521.48	1.70	121.99	353.05	185.30	0.21
	1122	553.75	13.38	629.21	1219.50	815.29	6.65
	1095	417.59	9.88	820.16	1386.12	1033.54	44.39
	1089	160.14	46.84	401.79	696.70	517.69	3.07
8	1072	84.15	11.59	336.03	566.25	437.01	48.11
	1059	32.42	12.50	259.64	437.89	344.25	56.56
	1049	16.89	34.28	250.22	416.92	334.00	74.45
	1030	10.56	96.75	294.13	470.63	392.17	137.56
		224.62	**28.36**	**389.15**	**693.38**	**507.40**	**46.38**
	1161	72.02	7.13	585.95	1043.09	777.75	28.84
	1156	56.18	24.07	460.95	818.37	613.10	11.08
	1149	0.78	55.74	212.15	399.83	293.81	29.50
	1143	37.85	20.83	407.54	706.63	537.03	33.22
	1139	40.81	52.37	177.89	333.25	247.81	19.13
16	1124	116.83	34.21	146.07	271.58	205.68	1.86
	1102	194.25	6.75	158.55	277.49	220.13	36.19
	1083	332.76	26.63	146.66	252.62	205.89	51.64
	1060	409.51	75.83	187.95	303.92	258.43	101.78
	1040	512.58	117.39	221.64	345.50	303.36	142.45
		205.67	**48.72**	**207.30**	**361.35**	**284.02**	**51.97**

Table 7 – Degree of mismatching for every investigated kinetic mechanism and their average values at each considered pressure of the Hu – 2016 [5] dataset.

Preliminary results indicate that the CRECK - 2012 [10-15] scheme exhibits the best agreement with the experimental shock tube measurements in all the investigated operative envelopes up to an engine pressure of about 33 bar. Indeed, its degree of mismatching *I* is always less than 50 except in the case of the Herzler [30] dataset for 4 bars.

Moreover, the reported results show that the Z22 – 2018 [16-18] mechanism can satisfactorily capture the non-linear ignition behavior of hydrogen oxidation very good with *I* in some cases less than 30 also at high pressures, but only at low-to-intermediate temperatures below 1100 K corresponding to the right sides of the induction time plots. Therefore, Z22 – 2018 [16-18] confirms to capture more accurately than the other schemes the complex ignition kinetics characterizing the critical crossover region.

Instead, the other mechanisms, reported for the sake of completeness to provide a wide kinetic assessment, except from the Aramco-II [2, 21-26], fail to predict the induction times with a disagreement among the computational calculations and the experimental data greater than 100 and in some cases higher than 1000 with an increasing trend as the initial temperature decreases and the operative pressure growths.

5. Conclusions

In this work, a preliminary kinetic assessment of the most suitable combustion mechanisms to accurately describe the ignition characteristics of hydrogen oxidation at intermediates/high pressures, and temperatures and compositions representative of the typical operative conditions of the air-breathing, high-speed aeronautic green propulsive systems investigated in the MORE&LESS project was carried out. This was accomplished through comparison with the available shock tube experimental data.

Based on the published results, the CRECK – 2012 [10-15] shows a good agreement at almost all the investigated conditions equating only to the Aramco-II mechanism, which is too numerically heavy to be implemented and successfully used in CFD (both RANS and LES) fully 3D simulations of the engine's combustion chamber.

These results uphold the non-linear and strongly pressure-dependent behavior of hydrogen combustion, which is a peculiar feature of this non-carbon, low molecular weight, highly diffusive, and powerfully exothermic fuel.

Finally, the presented 0D kinetic assessment reveals that the CRECK – 2012 [10-15] is the most promising kinetic mechanism of hydrogen oxy-combustion at the investigated more elevated pressures. Therefore, this kinetic model is worthy to be further updated and improved with the suitable inclusion of the most relevant NO_x generation reactions for an accurate and reliable chemical evaluation of hydrogen/air pollutant and greenhouse gases emissions released by high-pressure, supersonic, airbreathing hydrogen fueled ramjet/scramjet engines.

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8. Copyright Statement

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