A quasi-dimensional combustion model for performance and emissions of SI engines running on hydrogen-methane blends

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Abstract

The development of a predictive two-zone, quasi-dimensional model for the simulation of the combustion process in spark ignited engines fuelled with hydrogen, methane, or hydrogen-methane blends is presented. The code is based on a general-purpose thermodynamic framework for the simulation of the power cycle of internal combustion engines. Quasi-dimensional modelling describes the flame front development assuming a simplified spherical geometry, as well as infinitesimal thickness. The flame front subdivides the in-cylinder volume into a zone of unburned mixture, and a second zone of burned gases. As far as the combustion process is concerned, attention is paid to the description of the physical and chemical phenomena controlling the flame development and the formation of combustion products. First of all, an empirical correlation has been defined for estimating the laminar burning velocity. The equation, tailored for arbitrary fuel blendings and equivalence ratios, has been validated against detailed experimental data. Furthermore, the influence of turbulence on flame evolution has been implemented according to a fractal-based model. Then, a physical and chemical computing environment for evaluating both gaseous mixtures' thermodynamic properties, and equilibrium species concentrations of combustion products has been developed and coupled to the code.

The validation has been performed by comparing numerical pressure traces against literature experimental data, on a standard CFR single cylinder en-

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gine. A unique set-up of the model parameters has been obtained, suitable for both pure hydrogen and pure methane fuelings; finally, the predictive capabilities of the model have been applied to analyze different fuel blends and equivalence ratios: the comparison against experimental pollutant emissions (NO and CO) shows a reasonable accuracy.

Keywords: Hydrogen-Methane blends, quasi-dimensional model, spark ignition engine, pollutant emissions, laminar burning velocity, fractal model

1. Introduction

The enrichment of natural gas with hydrogen is a promising technique for decreasing engine pollutant emissions in terms of unburned hydrocarbons, CO and CO_2 , with only minor drawbacks on power output. Furthermore, NO_x emissions at partial load can be slightly reduced, as hydrogen extends the lean flammability limit of the mixture [1].

Since the end of the last century, many researchers have explored the performance and emissions of SI engines running on hydrogen-methane blends. In 1999, Bade Shrestha and Karim [2] adopted an analytical engine model for assessing the performance enhancement due to hydrogen addition in a methane-fueled SI engine, also studying the way of producing the necessary hydrogen by electrolysis on board. They concluded that this concept wouldn't be energetically viable. In 2001, Bauer and Forest [3, 4] presented a large spectrum experimental analysis on a CFR engine, set at an 8.5:1 compression ratio. They tested four different mixture compositions (0%, 20%, 20%)40% and 60% Hydrogen fraction) at two different engine speeds, at both full and partial loads. They then performed best-fit polynomial interpolation providing comprehensive correlation coefficients. Using a simple vehicle model, they applied the experimental data for simulating standard driving cycles, and thus estimating engine road performance and emissions. The paper by Akansu et al. [5] reviews the most important effects of hydrogen addition to SI engines running on natural gas, in terms of both performance and emissions characteristics, also considering the cost issue.

As far as numerical simulation of engines running on methane-hydrogen mixtures is concerned, a limited number of papers is available in literature. The paper by Verhelst and Sheppard [6] reviews the development of quasi-dimensional predictive models for spark ignited engines, analysing the thermodynamic framework of two-zone engine modelling, and proposing a comprehensive comparison of the submodels used to represent the most important processes, such as ignition, flame geometry, flame development and interaction with in-cylinder turbulence, heat transfer to the walls, etc. Verhelst also proposed a quasi-dimensional model for the closed-valve part of the cycle for a spark ignited engine running on hydrogen [7], supported by extensive experimental work carried on during his PhD [8] for characterizing both laminar and turbulent burning velocities of hydrogen-air flames, as well as their application in a CFR engine. A further contribution to the quasi-dimensional modelling of hydrogen-fuelled ICEs is presented by D'Errico et al. [9], who described an extended numerical and experimental research carried out on a single-cylinder engine with cryogenic port injection. Ma et al. [10] have proposed a two-zone, quasidimensional code for predicting engine performance, when running on blends of hydrogen and methane: the correlation for laminar burning velocity over a range of hydrogen fractions has been analysed in detail, and a comprehensive validation is carried out at the dynamometer bench for nine different engine operating conditions. Rakopoulos and Michos [11] performed an analysis of thermodynamic availability, using a quasi-dimensional model featuring a predictive, flamelet-based turbulent burning speed model, with multiple subdivisions of the burned zone, showing a slight increase in engine efficiency due to hydrogen enrichment. The same authors analysed in depth the performance of a similar quasi-dimensional combustion model in [12], for an engine running on synthetic gas, especially focusing on nitric oxide emissions, while instead imposing a Wiebe-law shaped combustion rate.

A number of numerical studies aimed to find approximate correlations for laminar burning velocities of hydrogen-methane-air premixed flames [13, 14, 15]. This is the base for providing accurate correlations to quasi-dimensional models, in order to reduce the influence of calibration constants.

The aim of the present work has been to develop a predictive quasidimensional combustion model for simulating performance and emissions of SI engines running on blends of hydrogen and methane at different hydrogen fractions. The predictive capability of the tool has been assessed for a single set-up of the calibration constants, exploring a wide range of hydrogen fractions and mixture equivalence ratios. The code demonstrated to be suitable for a fast, first-stage engine optimization.



Figure 1: Schematic of the two-zone modeling of the combustion chamber.

2. Combustion Simulation Model

The main difference between simple, zero-dimensional thermodynamic, and predictive quasi-dimensional models relies in the extension of the basic mass and energy balances with some simplified description of threedimensional phenomena occurring within the cylinder [6]. In the present paper, the well known, two-zone approach has been adopted: a schematic of the combustion chamber is illustrated in Figure 1. More in detail, the flame is represented as a spherical surface of infinitesimal thickness, truncated by the cylinder walls, propagating into the combustion chamber. This surface subdivides the in-cylinder charge into two zones: a first one, containing burned gases, behind; and a second one, made up of fresh charge mixture, fills the volume beyond the flame. For the sake of simplicity, it is assumed that no exchange occurs between the two zones. As far as the in-cylinder charge is concerned, it is assumed that both unburned and burned zones are mixtures of ideal gases, with different composition: unburned mixture consisting only of fuel and air (modeled as 21% oxygen and 79% nitrogen), and burned gases composition computed according to a chemical equilibrium algorithm, described in depth in Appendix A; a total of twelve components is considered. The subdivision into two zones implies the definition of two different temperatures, each one assumed constant within its zone; conversely, pressure is the same throughout the cylinder. Finally, blow-by flow to crevices is neglected.

From the first principle of thermodynamics - or energy conservation, the following differential equations can be obtained [6, 10]:

$$\frac{dp}{dt} = \left(\frac{c_{v,u}}{c_{p,u}}V_u - \frac{c_{v,b}}{c_{p,u}}\frac{R_{m,u}}{R_{m,b}}V_u + \frac{c_{v,b}}{R_{m,b}}V\right)^{-1} \\
\cdot \left\{ \left(1 + \frac{c_{v,b}}{R_{m,b}}\right)p\frac{dV}{dt} + \left[\left(u_b - u_u\right) - c_{v,b}\left(T_b - \frac{R_{m,u}}{R_{m,b}}T_u\right)\right]\frac{dm_b}{dt} \quad (1) \\
+ \left(\frac{c_{v,u}}{c_{p,u}} - \frac{c_{v,b}}{c_{p,u}}\frac{R_{m,u}}{R_{m,b}}\right) - \frac{dQ_u}{dt} - \frac{dQ}{dt} \right\} \\
\frac{dT_u}{dt} = \frac{1}{m_u c_{p,u}}\left(V_u\frac{dp}{dt} - \frac{dQ_u}{dt}\right) \quad (2)$$

$$\frac{dT_b}{dt} = \frac{1}{m_b c_{p,b}} \left[p \frac{dV}{dt} - (R_{m,b} T_b - R_{m,u} T_u) \frac{dm_b}{dt} - \frac{R_{m,u}}{c_{p,u}} \left(V_u \frac{dp}{dt} + \frac{dQ_u}{dt} \right) + V \frac{dp}{dt} \right]$$
(3)

where $Q = Q_u + Q_b$ represents the overall heat exchanged through the whole combustion chamber surface. During the compression and expansion strokes, the multizone approach is reduced to a single zone, and only two equations are solved for global pressure and temperature changes:

$$\frac{dp}{dt} = \frac{1}{V} \left(mR_m \frac{dT}{dt} - p \frac{dV}{dt} \right) \tag{4}$$

$$\frac{dT}{dt} = \frac{1}{mc_v} \left(-\frac{dQ}{dt} - p\frac{dV}{dt} \right) \tag{5}$$

3. Submodels

Most of the predictive capability of a quasi-dimensional model relies on the accuracy of the implemented submodels. Submodels are needed for closing the equations for pressure, temperatures and masses of the two zones: in particular, a combustion submodel for computing the mass burning rate, and a model of heat transfer through the walls. Furthermore, specific submodels have been developed for quantitative prediction of pollutant emissions; a detailed description of them is given in the following.

3.1. Laminar burning velocity

An appropriate correlation for the unstretched laminar flame speed in a SI engine is of crucial importance, as demonstrated by the number of papers in the last decade presenting correlations for laminar burning rates of hydrogen-air and methane-air premixed flames [16, 17, 18, 8, 19, 20], and - more recently - experimental and numerical data for methane-hydrogenair mixtures [13, 21, 15, 22, 23]. According to the analysis of Ma et al. [10], the laminar burning velocity of a hydrogen/methane/air mixture can be derived from the values of burning velocity of a hydrogen/air mixture and a methane/air mixture, respectively, through a relationship which considers methane as the base fuel, and calculates the increment in burning velocity due to addition of hydrogen:

$$S_L = S_{L,CH_4} + (S_{L,H_2} - S_{L,CH_4}) \left[C_1 exp(C_2 f_{H_2}) + C_3 \right], \tag{6}$$

where $C_1 = 7.37e - 03$, $C_2 = 4.91e - 02$, and $C_3 = 3.34e - 03$, respectively. This expression has shown to provide reasonable accuracy at low values of hydrogen content, this accuracy rapidly decreasing at medium and high hydrogen fractions. For this reason, Di Sarli and Di Benedetto proposed a different formulation based on Le Chatelier's rule [13], which has proven to give satisfactory results in both the transition combustion regime $(0.3 < f_{H_2} \le 0.9)$ and methane-inhibited hydrogen combustion zone $(f_{H_2} > 0.9)$:

$$S_L = \left[\frac{f_{H_2}}{S_{L,H_2}} + \frac{1 - f_{H_2}}{S_{L,CH_4}}\right]^{-1}.$$
(7)

In the present work, equation 6 has been applied for hydrogen fractions lower than 30%, and equation 7 otherwise.

As far as premixed hydrogen-air flames are concerned, it is acknowledged that they are unstable at high pressure values, thus experiencing both thermodiffusive and hydrodynamic instabilities which increase the burning rate [58]. For these reasons, equations correlating the unstretched, stable burning velocity of pure hydrogen-air flames can only achieved by either reconstruction based on stretched, stable flames at very low, non-engine-relevant, pressure and temperature values; or numerically through detailed kinetic mechanisms. However, the impossibility of experiencing stable, laminar hydrogenair flames reduces, in the opinion of the authors, the physical soundness of assuming laminar burning velocity values descending from kinetic calculations. For this reason, a correlation of laminar burning velocity including the effects of instabilities has been considered [58], even if the interactions instabilities have with turbulence haven't been modelled, and thus should be better investigated in the future.

In particular, the extensive experimental work done by Verhelst et al. [8, 17] has been chosen as a reference for the stable flame range at pressures lower than 10 bar: a correlation for the laminar velocity has been determined, including also the dependence on the air-fuel ratio, as well as on temperature, pressure and residual burned gas content:

$$S_{L,H_2}(\phi, p, T, f_{res}) = S_{L0} \left(\frac{T}{T_0}\right)^{\alpha} \left(\frac{p}{p_0}\right)^{\beta} \left(1 - \gamma f_{res}\right).$$
(8)

As far as the engine-relevant conditions at p > 10bar are concerned, the formulation by Gerke [58] has been chosen: the coefficients α, β in eq. (8), as well as the laminar burning velocity S_{L0} at the reference p = 20bar, T = 500Kconditions have been obtained as polynomials of degree sixth of the equivalence ratio. The combination of these two relationships provides thus values for the laminar burning velocities of pure hydrogen-air mixtures at the wide range of conditions which can be experienced during engine operation.

In figure 2, the unstretched laminar burning velocity values of equation 8 have been plotted at reference pressure and temperature values, showing very good agreement for equivalence ratios spanning the range [0.2, 1.2], and for each of the experimental datasets considered and referred to.

Concerning methane-air flames, the correlation expressing the laminar burning velocity of Müller et al. [16] has been adopted, since it is reliable for a wide range of pressures and preheat temperatures:

$$S_{L,CH_4}(\phi, p, T) = A(T^0) y_{F,u}^m \frac{T_u}{T^0} \left(\frac{T_b - T^0}{T_b - T_u}\right)^n$$
(9)

$$A(T^{0}) = F \exp\left(-\frac{G}{T^{0}}\right)$$
(10)



Figure 2: Comparison among the proposed correlation for the unstretched laminar burning velocity of hydrogen in air and experiments. Solid lines represent the analytical correlation from eq. (8); marks represent experiments: solid marks about unstable flames, open marks about stable flames.

In equation 9, $y_{F,u} = (1 + \alpha_s/\phi)$ represents the mass fuel fraction in the unburned mixture; $T^0 = -E/\ln(p/B)$ is a representative temperature of the inner layer, defined by Peters and Williams [24] as the thin layer within which the first oxidation of methane into CO, hydrogen and water occurs; p is pressure, and B, E, F, G, m, n are fuel-dependent constants. As it appears from figure 3, where it is compared to experimental data from different sources, this correlation is able to capture the laminar burning velocity of methane-air premixed flames with a high degree of accuracy, over a wide range of mixture equivalence ratios. Lastly, for the sake of reference, the results of the correlation for laminar burning velocity of blends of methane and hydrogen in air have been plotted against experimental references for two different blends in figure 4; from the plot, it may be observed that very accurate results are achieved for both hydrogen fractions.

3.2. Turbulence-flame interaction

As well known, premixed turbulent combustion occurring in spark ignition engines is strongly dependent on the structure of the turbulent spectrum



Figure 3: Comparison among the proposed correlation for the unstretched laminar burning velocity of methane in air and experiments. Solid lines represent the analytical correlation from eq. (9); marks represent experiments.



Figure 4: Comparison among the proposed correlation for the unstretched laminar burning velocity of hydrogen-methane blends in air (at two different hydrogen fractions, of 20% and 40%) and experiments. Solid lines represent the analytical correlation from eqs. (6,7); marks represent experiments.

[25, 26], and especially on the smallest scales, of the magnitude of Taylor's turbulence micro-scale L_T [27]. For this reason, quasi-dimensional modelling needs proper representation of the interaction between in-cylinder turbulence and flame development. As far as this approach is concerned, the first proposal by Blizzard and Keck [28], further extended in [29, 30], has been considered, in which the entrainment of unburned gas into the mean flame front due to turbulent eddies is modeled similarly to the expression which defines laminar burning velocity:

$$\frac{dm_e}{dt} = \rho_u A_f u_{te},\tag{11}$$

where a 'turbulent entrainment' velocity u_{te} is introduced, and A_f represents the mean flame front area. Then, the mass burning rate is assumed to be proportional to the mass of unburned mixture within the entrainment front:

$$\frac{dm_b}{dt} = \frac{m_e - m_b}{\tau_b}.$$
(12)

This process is controlled by a characteristic time constant, τ_b , calculated as the ratio of the Taylor micro-scale length to the laminar burning velocity: $\tau_b = C_{\tau_b} L_T / S_L$. This approach is directly related to the hypotheses introduced for the combustion modelling, where laminar combustion is assumed to occur within the scales of small eddies. Taylor's micro-scale is proportional to the ratio between the integral scale of turbulence and the square root of turbulent Reynolds number $L_T \propto L_I R e_t^{-1/2}$, and according to the analysis by Tabaczynski [29], the proportionality coefficient can be set to $\sqrt{15}$. C_{τ_b} is a calibration constant. The mean flame front is usually modeled as a spherical surface truncated at the cylinder walls; an analytical description is possible only assuming very simple, usually flat, combustion chambers [32]. In this study an arbitrary complex geometry can be analysed, adopting the approach by Poulos and Heywood [33]. A huge number of random points is projected on the sphere containing the flame front surface; then, the ratio between the area of the flame front and the surface of the whole sphere is well approximated by the ratio between the number of points on the flame front to the total number of points. For increasing the speed of computations, the pieces of information in terms of flame radii, burned volumes, flame front surfaces are stored into lookup tables, representing the combustion chamber geometry as a function of crank angle.

The assessment of the adopted procedure is given in Figure 5, where the data



Figure 5: Assessment of the approximated model adopted for flame area and radius estimation: plot of the estimated flame area versus flame radius for a non-physical, disc-shaped combustion chamber of height equal to unity and radius twice the height; comparison is made to the detailed data provided in Poulos and Heywood, [33].

estimated through the present algorithm are plotted in comparison with the detailed data available in [33], for a geometrical, disc-shaped combustion chamber of height equal to unity, and radius twice the height. Furthermore, Figure 6 shows the mapped surface of the flame area A_f of eq. 11 versus engine crank angle and normalized burned zone volume, for a reference CFR engine, set at a $\beta = 7.0$ compression ratio.

In conclusion, the two equations (11,12) for turbulent entrainment and burning rates account for the whole turbulent flame development process, including the combustion completion phase occurring after that the whole in-cylinder mass has entrained the mean flame front surface.

Among many models available in literature for the closure of this set of equations, the fractal-based approach [34] has been extensively applied with good results [35, 36, 37]. This approach relies on the assumption that the main effect of turbulence is the flame wrinkling, i.e., the increase of the flame front surface: thus, the turbulent burning velocity is expressed as the increment



Figure 6: Mapped lookup table of flame area versus crank angle and normalized burned gas volume, for a CFR-engine combustion chamber, at $\beta = 7.0$ engine compression ratio.

of burning velocity due to flame wrinkling:

$$u_t = u_L \left(\frac{L_{max}}{L_{min}}\right)^{D_3 - 2},\tag{13}$$

where u_L is the laminar burning velocity of the stretched flamefront, L_{min} , L_{max} represent the minimum and maximum turbulence wrinkling scales, respectively, and D_3 is the fractal dimension of a three-dimensional rough surface, characterizing the degree of wrinkling of the turbulent flame. To this respect, no assumptions have been made in order to consider the interaction of flame instabilities to wrinkling: the authors have chosen to include the effects of instabilities in the determination of the laminar burning velocity, in order to try to separate them from the effects of turbulence. This assumption leads to the observation that any interaction between wrinkling effects due to turbulence and instability have been neglected, and the model behaves as if this two separate effects would concur in series to determine a unique turbulent burning velocity value. Anyway, further investigation of this phenomenon should be carried on in the future.

A simple stretch model, proposed by Matthews and Chin [34] accounts for

the relationship between S_L and u_L ,:

$$u_L = S_L \left(1 - \frac{\eta_u}{\rho_u S_L^2} K_{st} \right), \tag{14}$$

in which η_u is the molecular viscosity of the unburned mixture, and K_{st} the flame stretch factor. This latest one, according to the analysis of Chung and Law [31], can be expressed as the sum of two parts:

$$K_{st} = K_E + K_S; \tag{15}$$

the first, K_E , associated with curvature due to flame expansion, and a second, K_S , associated with tangential strain in the turbulent eddies in the small scale, which characterizes the smallest flame wrinkles. In particular:

$$K_E = \frac{2}{r_f} \frac{dr_f}{dt};$$
 $K_S = 3.55^{-2/3} \sqrt{\frac{\rho_u \varepsilon}{\eta_u}};$ (16)

where the average turbulent dissipation is estimated as $\varepsilon = u'^3/L_I$, and the constant 3.55 relates the dimension of the smallest flame wrinkles to the Kolmogorov scale. Thus, this stretch model, dominated by flame strain, decreases as the combustion advances.

The most reliable expression for the prediction of D_3 seems the heuristic one by Santavicca and coworkers [38]:

$$D_3 = C_{D_3} 2.35 \frac{u'}{u' + S_L} + 2.0 \frac{S_L}{u' + S_L},\tag{17}$$

where the calibration constant C_{D_3} will be discussed in the following. Matthews and Chin [34] also suggested that the best assumption for the relationship between the inner and outer cut-off of the wrinkling scales were the ratio of maximum to minimum turbulence length scales, $L_{max}/L_{min} = L_I/L_K \simeq Re_t^{0.75}$. In this work, the estimation of the integral length scale L_I is assumed equal to the instantaneous flame radius [34], eventually bounded by the cylinder walls:

$$L_I = \min\left\{r_f; \frac{b}{2}; z_c\right\}.$$
(18)

Obviously, proper in-cylinder turbulence modelling needs to be implemented for estimating equation 17, as well as the turbulent Reynolds number. For this purpose, a simple turbulence model, firstly proposed by Hall and Bracco [39] has been considered:

$$u'_{TDC} = 0.75 \bar{u}_p = 0.75 (2sn) ,$$

$$u' = C_{u'} u'_{TDC} (1 - \theta/90) ,$$
(19)

where a linear decay of the rms turbulent velocity u' from top dead center is imposed.

Although many more detailed turbulence models are available in literature, the one adopted has been proved to well suit the geometry of standard CFR engines, such as the reference one on which the present model has been calibrated. This choice has been motivated by the need to limit the model uncertainties and calibration parameters to the combustion modelling only, and thus it will need to be updated in the future, to match a wider type of combustion chambers.

Finally, the correct prediction of turbulent burning velocity needs the phenomenon of transient flame development to be taken into account. This occurs when a flame kernel, growing fast after ignition, encounters a turbulent spectrum wider than that characterizing a stabilized turbulent flame [40]. Thus, an exponential time-dependent parameter is added for correcting the fully developed turbulent velocity u_t . In particular, Lipatnikov and Chomiak [40] suggested the following ratio:

$$\frac{u_{t,t}}{u_t} = \left\{ 1 + \frac{\tau'}{t} \left[\exp\left(-\frac{t}{\tau'} - 1\right) \right] \right\}^{1/2},\tag{20}$$

derived from the turbulent diffusion theory, where the timescale for turbulent development is defined as a function of the turbulent diffusivity, $\tau' = D_t/u'^2$, then related by the same authors to the integral scale of turbulence $\tau' = 0.55C_{\tau'}L_I/u'$ [41]; t represents instead the elapsed time from ignition. Eq. 20 allows thus the transient turbulent velocity value, $u_{t,t}$ to be estimated. A correcting calibration parameter $C_{\tau'}$, discussed in the following, has been also applied to the estimation of τ' , in order to calibrate the total turbulent development time.

The turbulent burning velocity obtained from eq. 13, and corrected with the exponential term for its transient development 20 provides the value for the turbulent entrainment velocity $u_{t,e}$ in eq. 11, and thus closes the differential model of turbulent flame development and combustion.

3.3. Combustion initialisation

The integration of the differential equations defining pressure history, as well as burned, unburned zone temperatures and entrained, burned, unburned masses needs proper initialisation at spark ignition. In this model, the early flame kernel growth following the spark discharge isn't model, but instead an initial flame kernel is assumed. Some authors impose flame kernel dimensions as a radius of a sphere [7, 34, 42]; an alternative assumption is instead that of considering the initial kernel having mass equal to 1% the total in-cylinder mass m_{tot} [6]. However, this latest assumption seems less appropriate when dealing with a variable composition fuel, since different hydrogen content can slightly affect the kernel internal energy, if the kernel mass is constant. For this reason, in our model a constant-volume kernel has been imposed, $V_{b,k} = 2.8e - 6m^3$. In order to better clarify the constantvolume kernel assumption, figure 7, shows the internal energy owned by the flame kernel, when considering either the mass-based or the volume-based assumption for its initialisation. From the figure, it's clear that imposing the flame kernel volume assures a more homogeneous energy content across the whole range of fuel hydrogen fractions. According to Verhelst and Sierens [7], the initial entrained mass is imposed twice the initial burned kernel mass. As far as temperatures are concerned, the initial kernel temperature is assumed to be the adiabatic combustion temperature of the mixture [10, 7], computed through an iterative procedure, equalling the mixture enthalpy of the reactants and of the products, as proposed by Warnatz et al. [26]. Finally, the temperature of the unburned mixture is computed applying the ideal gas state equation, on the basis of the initial unburned mass and volume. For both unburned and burned mixtures, thermodynamic gas properties are computed following the kinetic theory of gases, and chemical compositions are estimated through the application of a chemical equilibrium algorithm

3.4. Wall heat transfer

can be found in Appendix A.

A common approach exploiting a combined convective and radiative heat transfer coefficient has been implemented [43], as heat transfer through the cylinder walls is represented by the terms dQ/dt and dQ_u/dt in Eqs. (1,2,3). The formulation couples a conventional Woschni convective-equivalent heat transfer coefficient [44] to a radiative term, for taking into account the effects

which considers twelve species. A detailed explanation of these procedures



Figure 7: Internal energy content of modeled flame kernel, at various unburned mixture equivalence ratios. Left: flame kernel initialised according to the mass-based $m_{b,k} = 0.01 \cdot m_{tot}$ assumption; right: flame kernel initialised according to the volume-based $V_{b,k} = 2.8e - 6m^3$ assumption.

due to high temperature burned gases:

$$\frac{dQ}{dt} = C_Q \left(\frac{dQ_{Wo}}{dt} + \frac{dQ_r}{dt} \right), \tag{21}$$

where a calibration constant C_Q has been considered. The bulk radiative heat flux is hence computed as:

$$\frac{dQ_r}{dt} = \varepsilon_a \sigma_0 A_w \left(T_r^4 - T_w^4 \right), \qquad (22)$$

where $\sigma_0 = 5.67E - 08Jm^{-2}K^{-4}s^{-1}$ is the universal Stefan-Boltzmann's constant, A_w the global cylinder wall surface, T_r and T_w the estimated average bulk radiative temperature and wall temperature, respectively, and ε_a the apparent grey-body emissivity. As experimental campaigns show that the apparent grey body emissivity peaks at about 0.8 - 0.9 right after the start of combustion, and then drops following an almost linear decrease [43], it has been assumed to vary linearly between a maximum value $\varepsilon_{a,max} = 0.9$ at the start of combustion, and zero over the whole expansion stroke. As far as the bulk radiative temperature adopted for the calculation is concerned, it is acknowledged [43] that a good estimate over the whole combustion and expansion duration is the average between the adiabatic flame temperature and the average, bulk gas temperature in the whole cylinder:

$$T_r = 0.5 \ (T_g + T_{ad}) \,, \tag{23}$$

accounting for the non-uniform composition of the total in-cylinder charge. As this is a bulk approach, which considers an average temperature within the cylinder, the expression for the global heat transfer (21) has been applied to the whole instantaneous cylinder wall surface, and the term dQ_u/dt in eqs. (1),(2),(3) referring to the unburned zone has been obtained by applying the same wall heat flux of eq. (21) to the cylinder surface covered by the unburned zone only: $dQ_u/dt = A_u/A_w dQ/dt$.

3.5. Pollutant emissions

The minimisation of pollutant emissions from spark ignited engines is a fundamental design target, so that quasi-dimensional combustion simulation framework must include predictive submodels for emissions prediction. Even if the simplification of the chamber geometry implies the need of some reaction calibration constants, which are necessarily 'engine-dependent', quasi-D simulation is generally able of capturing the design trends as a function of the main engine operating conditions (equivalence ratio, ignition timing, intake charge conditions) with a high degree of reliability [45].

In the present combustion simulation framework, two submodels of pollutant emissions have been implemented, featuring simplified reaction schemes for nitric oxide (NO) and carbon monoxide (CO). As combustion takes place, two additional differential equations are solved for each zone, accounting for pollutant chemistry. As far as formation of nitric oxide in internal combustion engines is concerned, usually three main source mechanisms are considered [26]: a first one (thermal-NO), which is limited by a high activation energy, and thus is fast enough only at high temperature values; a second mechanism, ('prompt' or Fenimore NO), which describes the formation of NO at the flame fronts, deriving from the recombination of the transient CH species. The last identified source takes into account the recombination of nitrous oxide (N_2O) into NO, this contribution being significant especially in very lean mixture conditions and at low temperatures. Due to the low carbon content in the fuel, it has been assumed that Fenimore NO could be neglected, and thermal-NO has been considered the only source for NO formation, as assumed in most quasi-dimensional combustion models [45]. The authors acknowledge that the wide flammability limits of hydrogen may

extend combustion conditions to slightly lean equivalence ratios [3], and this may lead to less accurate results in the lower part of the ϕ range.

The well known extended Zel'dovich thermal NO mechanism has been considered and implemented:

$$N_{2} + O \rightleftharpoons NO + N$$

$$N + O_{2} \rightleftharpoons NO + O$$

$$N + OH \rightleftharpoons NO + H.$$

$$(24)$$

The reaction rate is computed according to the following ODE, where a unique calibration coefficient c_{NO} multiplies the forward reaction rate of reaction 1 in (24):

$$\frac{d[NO]}{dt} = c_{NO} k_{f,1}[N_2][O] - k_{b,1}[NO][N] + \\
+ k_{f,2}[N][O_2] - k_{b,2}[NO][O] + \\
+ k_{f,3}[N][OH] - k_{b,3}[NO][H]$$
(25)

The Arrhenius-type forward reaction coefficients are summarised in Table 1. As far as carbon monoxide emissions are concerned, it is acknowledged that

Reaction	А	b	Е
1. $N_2 + O \rightarrow NO + N$	$3.30e{+}12$	0.20	0.0
2. $N + O_2 \rightarrow NO + O$	6.40e + 09	1.00	3160.0
3. $N + OH \rightarrow NO + H$	3.80e + 13	0.00	0.0

Table 1: Arrhenius-type coefficients for forward reaction rates adopted in the extended Zel'dovich mechanism (24), in the form $k = AT^b \exp(-E/T)$. Units are cm, mol, s, K. [26]

CO formation is kinetically controlled, and predictions based on equilibrium assumptions only would yield poor results [25, 45]. For this reason, a specific model has been developed, considering the three reactions governing CO formation in the post-flame area:

$$CO + OH \rightleftharpoons CO_2 + H$$

$$CO_2 + O \rightleftharpoons CO + O_2$$

$$CO + O + M \rightleftharpoons CO_2 + M.$$
(26)

Due to its strong nonlinearity, according to Warnatz [26], the first reaction in (26) has been split into three concurrent reactions, with slightly different Arrhenius coefficients (cfr. Table 2). Furthermore, molecularity [M] has been defined as:

$$[M] = [H_2] + 6.5[H_2O] + 0.4[O_2] + 0.4[N_2] + 0.75[CO] + 1.5[CO_2].$$
(27)

The main advantage of considering the first reaction as three split concurring reactions – involving the same reactants and products – relies in the accuracy it allows to get at both low and high temperatures. As a matter of fact, the three concurrent reactions are characterized by slightly different activation energy values, which make each one of them rule over a specific temperature range. In Figure 8, the overall forward reaction rate of the first reaction, given by the sum of the three concurring reactions (namely, 1a, 1b and 1c), is plotted against some alternative correlations available in literature [46]. From the plot, it's clear that the adopted correlation suits both the lowest temperature values, as achieved by most of the explored correlations, and the range of temperatures higher than 1000K – which is of crucial importance when dealing with in-cylinder combustion of gaseous fuels –, where similar results can otherwise be achieved adopting correlations tailored for the high temperature range only.

Finally, the CO concentration is evaluated according to the following ODE:

$$\frac{d[CO]}{dt} = (c_{CO}R1 + R2 + R3) \left(1 - \frac{[CO]}{[CO]_{eq}}\right),$$
(28)

$$R1 = (k_{f,1a} + k_{f,1b} + k_{f,1c}) [CO]_{eq} [OH]_{eq};$$

$$R2 = k_{b,2} [CO]_{eq} [O_2]_{eq}$$

$$R3 = k_{f,3} [CO]_{eq} [O]_{eq} [M]_{eq};$$

where the species' concentrations defining the reactions progress are evaluated at the reference equilibrium conditions, and c_{CO} is a tuning constant affecting the rate of the first reaction in the mechanism.

4. Results and discussion

The calibration process has been focused on a set of five coefficients concerning flame development, turbulence-flame interaction and heat transfer submodels. Despite the differences between methane and hydrogen combustion, a unique set of values has been identified; two different in-cylinder



Figure 8: Comparison among the overall forward reaction rate for reaction no. 1 according to the CO formation model adopted, and some alternative correlations available in literature [46].

	Reaction	А	b	Е
1a.	$CO + OH \rightarrow CO_2 + H$	1.00e+13	0.00	8.05e + 3
1b.	$CO + OH \rightarrow CO_2 + H$	$1.01e{+}11$	0.00	30.0698
1c.	$CO + OH \rightarrow CO_2 + H$	$9.03e{+}11$	0.00	2.30e + 3
2.	$CO_2 + O \rightarrow CO + O_2$	$2.50e{+}12$	0.00	$2.41e{+4}$
3.	$CO + O + M \rightarrow CO_2 + M$	$1.54e{+}15$	0.00	1.50e + 3

Table 2: Arrhenius-type coefficients for forward reaction rates adopted in the CO formation mechanism (26), in the form $k = AT^b \exp(-E/T)$. Units are cm, mol, s, K. [26]

pressure traces, referred to the same engine while running either on pure methane, or on pure hydrogen, have been considered. These two fuel mixture compositions represent the extreme bounds of the desired validity range over which the model is expected to behave consistently. Due to the lack of experimental apparatus, model testing has been carried on over detailed experimental data available in literature and, in particular, the standard CFR, single cylinder, 0.6l-displacement engine has been chosen for the simulations. As far as hydrogen fueling is concerned, the extensive measurements by Verhelst [7] have been chosen as a reference, while the in-cylinder pressure traces by Bade Shrestha [2] have been considered when dealing with methane.

The first constant to be calibrated is the tuning coefficient C_Q , modelling heat transfer: the total heat flux through the cylinder walls is amplified/reduced according to the value of this constant. In order to broaden the applicability of this approach, this value applies, unchanged, to the whole engine cycle, as no differences have been imposed among compression, combustion and expansion. A second constant C_{D_3} has been used for tuning the fractal dimension of the developed flame front surface, which depends on wrinkling due to turbulent convective transport, as suggested by Matthews and Chin [34]. The parameter doesn't affect the fractal dimension of the smooth flame surface case, which only relies on laminar burning velocity. As suggested by Verhelst for CFR-engine-like conditions [7], C_{D_3} has been set to 1.013. The parameter $C_{u'}$ is a multiplier of the in-cylinder rms turbulence, calculated following Hall and Bracco's model, through equation (19). This multiplier is necessary, since eq. (19) doesn't take into account many geometrical factors which affect in-cylinder turbulence after IVC, such as intake system design, value-port geometry, and so forth. A fixed value $C_{u'} = 1.50$ has been imposed. The fourth calibration parameter, $C_{\tau'}$, is included in the submodel of transient turbulent flame development [40]: $C_{\tau'}$ multiplies the characteristic

time scale of turbulent development, τ' . As τ' reduces, the flame develops faster, thus the time needed for reaching fully turbulent combustion shortens. In this case, the most suitable value for $C_{\tau'}$ is 0.95. The last calibration constant is used for estimating the overall burning rate time scale, τ_b , thus correcting the approximation of the Taylor turbulence micro-scale, L_T . In this case, a fixed $C_{\tau_b} = 1.25$ has been adopted. For the sake of reference, the amount of constants and initialisation parameters for the two validation simulations has been summarised in Table 3. The simulation results, compared to the respective references [7, 2], have then been presented in Figures 9 and 10. As clearly visible from these figures, a very good agreement is found, despite no changes made to the calibration constants.

Parameter	Unit	Ref. [7]	Ref. [51]
Fuel comp.	_	$100\% H_2$	$100\% \ CH_4$
f_{H_2}	_	1.00	0.00
n	rpm	600	900
β	_	9.0	8.5
ϕ	_	0.588	0.990
$ heta_0$	CA ATDC	-136.0	-160.0
T_0	Κ	298	294
m_{tot}	kg	7.35e-04	7.94e-04
residuals	%	0.0	0.0
$ heta_{SOI}$	CA ATDC	-20	-20
C_{τ_b}	—	1.25	1.25
$C_{\tau'}$		0.95	0.95
$C_{u'}$	_	1.5	1.5
C_{D_3}	_	1.013	1.013
C_Q	_	1.50	1.50

Table 3: CFR engine simulations initialisation parameters, operating conditions and calibration constants for pure hydrogen and pure methane fuels, respectively.

Furthermore, the calibrated model has been tuned in order to predict pollutant emissions. For this purpose, a comprehensive set of measurements in terms of power output, as well as of pollutant emissions (NO, CO₂, CO, HC), carried out on a CFR engine running on different hydrogen/methane blends, at two different engine speeds [3] has been considered. In particular, two sets of measurements, corresponding to fuel hydrogen fractions $f_{H_2} = 0.2$ and $f_{H_2} = 0.4$, have been analysed, engine speed $n = 700 \, rpm$, and compres-



Figure 9: In-cylinder pressure validation for CFR engine fueled by $100\% H_2 - 0\% CH_4$.



Figure 10: In-cylinder pressure validation for CFR engine fueled by $0\% H_2$ - $100\% CH_4$.

sion ratio $\beta = 9.0$. These experiments, provided by Bauer and Forest, swept a wide range of mixture equivalence ratios, the only change among the cases being the spark advance timing. As already done in the engine performance calibration process, two different tuning constants have been imposed: C_{NO} and C_{CO} . Both parameters correct the forward reaction rate in the first reaction of the NO and CO mechanisms. The calibration constants are unique for all the simulations. In the same way, the calibration constants previously discussed, and presented in Table 3, remained unchanged. Figure 11 shows the results of the simulations performed considering 20% hydrogen fraction: a total of 40 simulations sweeping the $\phi \in [0.6, 1.1]$ range of equivalence ratios has been run. The first plot shows the imposed spark ignition advances: in order to match the experimental values of Bauer and Forest, a spline interpolation has been imposed. The second plot shows the comparison of predicted engine performance, in terms of brake specific fuel consumption. This plot shows very good agreement between the experimental and calculated BSFC values, for the whole range of equivalence ratios, proving the reliability of the quasi-dimensional model at the same values of the calibration constants as discussed above; the only slight differences arise at very lean equivalence ratios ($\phi < 0.6$), where predicted fuel consumption is higher than the experimental value. The third and fourth plots compare the results of global pollutant emissions, as computed by the quasi-dimensional combustion model, to the experimental values. As far as nitric oxide is concerned, the model is able to accurately predict the peak value, occurring at slightly lean mixtures; also the NO trend versus ϕ is quite correct, even if the pollutant concentration reduction at very lean mixtures is over-estimated. Conversely, the trend of carbon monoxide correctly fits the experimental measurements, for the whole range of equivalence ratios.

A second set of 40 simulations has been run for the 40%-Hydrogen-fraction fueling, and it is compared to the experiments in Figure 12. Again, no change in calibration parameters was applied, and a similar behaviour is observed. This is a further evidence of the model consistency.

5. Concluding Remarks

A quasi-dimensional model for the prediction of the combustion process in SI engines running on blends of methane and hydrogen has been developed and calibrated. The model relies on an engine thermodynamic framework,



Figure 11: Performance and emissions validation for CFR engine fueled by $20\% H_2$ - $80\% CH_4$ running at 700 rpm, compared to experimental data from Ref. [3].



Figure 12: Performance and emissions validation for CFR engine fueled by $40\% H_2$ - $60\% CH_4$ running at 700 rpm, compared to experimental data from Ref. [3]

including a series of submodels for in-cylinder turbulence, flame propagation, turbulence-flame interaction, wall heat exchange, as well as reacting flow treatment and pollutant formation. The comparison between the predicted and the experimental results available in literature shows a very good agreement in terms of indicated quantities, for engines running on blends at different hydrogen content, with a single setting of the calibration parameters. As far as pollutant formation is concerned, despite the lack of experimental data on which the models for NO and CO could be calibrated, the models yield very reasonable trends, properly capturing the dependence on different hydrogen fractions. Only the NO predictions at very lean mixtures are not satisfactory. In order to overcome this problem, the next development step will be a further subdivision of the burned zone into multiple zones, so that the temperature gradient within the burned volume can be accounted for. Finally, these following conclusions can be drawn:

- despite the limitation imposed by the quasi-dimensional model, very accurate predictions in terms of engine performance have been obtained, at various hydrogen fractions thanks to the adoption of well established and reliable models of turbulent combustion;
- the laminar flame speed correlation adopted in the calculation has proven to be accurate enough over a wide range of fuel blends, even if its reliability at extreme equivalence ratios should be further improved. A future work may include the development of a fast code for the simulation of 1D premixed laminar flames, and the implementation into the combustion model of detailed lookup tables of laminar flame speeds;
- the pollutants prediction is quite promising, since the models developed are able to capture both the absolute values and trends, except the NO concentration at very lean mixtures ($\phi < 0.8$); for this reason, the development of a multiple burned zone formulation may result in more accurate predictions [12];
- the predictive capability and accuracy of the code could be improved by introducing further submodels, accounting for the ignition kernel formation and development, knocking intensity, as well as detailed turbulence description.
- the reliability and the smooth behaviour showed by the present model

make it suitable for efficient optimization and further investigation on engines operating with gaseous mixtures of hydrogen and methane.

Appendix A. Computation of mixture thermodynamic properties and composition

Appendix A.1. Mixture properties.

The accurate calculation of the thermodynamic properties of the mixture of the hydrogen-methane blend fuel in air is of crucial importance for the correct prediction of the flame front behaviour and of the engine cycle. Therefore, a general environment for the computation of thermodynamic properties of gaseous mixtures has been implemented and coupled with the present simulation code. A set of the twelve most important species in hydrogen-methane blends combustion in air has been considered:

$$N_s = \{O_2, N_2, CO_2, H_2O, H, H_2, N, NO, O, OH, CO, CH_4\},$$
(A.1)

however, this procedure is general and can be virtually extended to any mixture of perfect gases. The composition of the unburned mixture is initialised on the basis of the hydrogen content of the fuel blend, defined in terms of molar fraction, $f_{H_2} = n_{H_2}/(n_{H_2} + n_{CH_4})$, and of the equivalence ratio ϕ of the air-fuel mixture.

For each *i*-th component in the mixture, the molar specific heat at constant pressure, and the molar specific enthalpy are computed as polynomial interpolations of the absolute temperature T:

$$c_{p,i} = a_{i,1} + a_{i,2}T + a_{i,3}T^2 + a_{i,4}T^3 + \frac{a_{i,5}}{T^2},$$
(A.2)

$$h_i = a_{i,1}T + a_{i,2}\frac{T^2}{2} + a_{i,3}\frac{T^3}{3} + a_{i,4}\frac{T^4}{4} - \frac{a_{i,5}}{T} + a_{i,6},$$
 (A.3)

where the polynomial coefficients *a* have been found on the NIST Chemistry Webbook [46]. The molar specific heat at constant volume is then computed as $c_{v,i} = c_{p,i} - R_u$ [26]. The specific gas constant of the mixture $R = R_u/W$ is then obtained, from its molecular weight:

$$W = \left(\sum_{i \in N_s} \frac{y_i}{W_i}\right)^{-1}.$$
 (A.4)

Finally, the averaged mixture thermodynamic properties ϑ ($\vartheta = \{c_p, c_v, h\}$) are computed as mass-averaged quantities [26]: $\vartheta = \sum_{i \in N_s} y_i \vartheta_i / W_i$.

As far as transport is concerned, a procedure based on the kinetic theory of gases has been developed for the computation of the average mixture viscosity, η . The viscosity value of each pure component is expressed as [47]:

$$\eta_i = \frac{5}{16} \frac{\sqrt{\pi m_i k_B T}}{\pi \sigma_i^2 \Omega^{(2,2)*}},\tag{A.5}$$

where m_i is the molecular mass, k_B Boltzmann's universal constant, T the absolute gas temperature, σ the Lennard-Jones collision diameter. The collision integral value $\Omega^{(2,2)*}$ is computed as a function of the reduced temperature $T_i^* = k_B T / \varepsilon_i$ and of the reduced molecule dipole moment $\delta_i = \mu_i^2 / (2\varepsilon_i \sigma_i^3)$ [48]:

$$\Omega^{(2,2)*} = \frac{4}{5} \left(1 + \frac{1}{T_i^*} + \frac{\delta_i^2}{4T_i^*} \right).$$
(A.6)

The Lennard-Jones collision diameters σ , potential well depths ε_i , dipole moments μ_i , polarizabilities and rotational relaxation collision numbers have been gathered from [49]. The final mixture viscosity is then obtained from [48]:

$$\eta = \sum_{i \in N_s} \frac{x_i \sqrt{\eta_i}}{\frac{x_i}{\sqrt{\eta}} + \sum_{j \in N_s, j \neq i} \left(\frac{x_j s_{ij} A_{ij}}{\sqrt{\eta_j}}\right)},\tag{A.7}$$

where A_{ij} is a function of molecular weights, and s_{ij} represents a corrective factor for collisions between unlike molecules [48]. The results have been compared to both experimental and numerical data in [48].

Appendix A.2. Stoichiometric combustion and mixture composition.

Chemical composition of the unburned mixture is simplified as containing only air (21% oxygen, 79% nitrogen) and the fuel blend, which is characterised by a molar hydrogen fraction f_{H_2} . Under this hypothesis, the composition of the mixture involved in the one-step combustion reaction has been estimated as [15]:

$$(1 - f_{H_2})CH_4 + f_{H_2}H_2 + \left[\frac{2}{\phi}(1 - f_{H_2}) + \frac{f_{H_2}}{2\phi}\right](O_2 + 3.762N_2); \quad (A.8)$$

and thus the combustion products have been evaluated as summarized in table A.4, where $\phi = \alpha_s/\alpha$ represents the mixture equivalence ratio, and the

Species	$\phi < 1$	$\phi = 1$	$\phi > 1$
CO_2	$1 - f_{H_2}$	$1 - f_{H_2}$	$\frac{1-f_{H_2}}{\phi}$
H_2O	$2 - f_{H_2}$	$2 - f_{H_2}$	$\frac{2-f_{H_2}}{\phi}$
N_2	$3.76 \frac{2-1.5f_{H_2}}{\phi}$	$3.76(2-1.5f_{H_2})$	$3.76 \frac{2-1.5f_{H_2}}{\phi}$
O_2	$(2-1.5f_{H_2})\frac{1-\phi}{\phi}$	0	0
H_2	0	0	$f_{H_2} \frac{\phi - 1}{\phi}$
CH_4	0	0	$(1 - f_{H_2}) \frac{\phi - 1}{\phi}$

Table A.4: Burned gas composition due to stoichiometric combustion: number of moles of products for each mole of fuel.

stoichiometric air-fuel mass ratio has been accordingly computed as [3]:

$$\alpha_s = \frac{4.76 \left(2.0 - 1.5 f_{H_2}\right) W_{air}}{\left(1 - f_{H_2}\right) W_{CH_4} + f_{H_2} W_{H_2}}.$$
(A.9)

The composition of the burned mixture after the stoichiometric combustion of the hydrogen-methane blend is needed to initialise the computation of the dissociation chemical equilibrium. In the following, the computation environment, developed on the basis of [50], is presented.

A one-step dissociation equation, from six to 11 species is considered for the equilibrium:

$$CH_{4} + O_{2} + N_{2} + CO_{2} + H_{2}O + H_{2} \rightarrow$$

$$O_{2} + N_{2} + CO_{2} + H_{2}O +$$

$$+H + H_{2} + N + NO + O + OH + CO.$$
(A.10)

This reaction yields four equations which describe the atomic balances of C, O, H, N atoms in the system:

$$\begin{aligned}
x_{CH_4}^o + x_{CO_2}^o &= \Psi \left[x_{CO_2} + x_{CO} \right] & (A.11) \\
4x_{CH_4}^o + 2x_{H_2O}^o + 2x_{H_2}^o &= \Psi \left[2x_{H_2O} + x_H + 2x_{H_2} + x_{OH} \right] \\
2x_{O_2}^o &= \Psi \left[2x_{N_2} + x_N + x_{NO} \right] \\
2x_{O_2}^o + 2x_{CO_2}^o + x_{H_2O}^o &= \Psi \left[2x_{O_2} + 2x_{CO_2} + 2x_{H_2O} + x_{NO} + x_{O} + x_{OH} + x_{CO} \right]
\end{aligned}$$

where the superscript o denotes initial contitions prior to the dissociation, and Ψ the ratio between the total number of moles of the products for each mole of reactants. Seven more equation descend from the seven following chemical dissociation equilibria:

$$H_{2} \rightleftharpoons 2H; \qquad O_{2} \rightleftharpoons 2O; \qquad H_{2}O \rightleftharpoons OH + \frac{1}{2}O_{2};$$

$$2H_{2}O \rightleftharpoons 2H_{2} + O_{2}; \qquad N_{2} \rightleftharpoons 2N; \qquad H_{2} + CO_{2} \rightleftharpoons H_{2}O + CO;$$

$$H_{2}O + \frac{1}{2}N_{2} \rightleftharpoons H_{2} + NO; \qquad (A.12)$$

where the equilibrium constants $K_{p,j}$ are known as a function of the absolute temperature, and computed from the Gibbs free-energy change [26]:

$$\ln K_p = \frac{1}{R_u T} \left[\sum_{j \in N_s} \left(\nu_j'' - \nu_j' \right) \Delta g^o \right].$$
 (A.13)

According to the definition, they are then expressed as a function of the molar fractions of products and reactants, as follows [26]:

$$K_p = \prod_{j \in N_s} \left[x_{M_j, eq} \, p \right]^{\left(\nu_j^{\prime\prime} - \nu_j^{\prime} \right)},\tag{A.14}$$

where M_j denotes the j-th species in the chemical set. The non-linear system of eleven equations from eqs. A.11, A.14 is finally solved adopting the iterative Newton-Raphson method. In figure A.13, the results of the computation of equilibrium concentrations of the species in the burned gas mixture are plotted for pure hydrogen, 50% hydrogen - 50% methane, and pure methane fueling, at different equivalence ratios, versus temperatures ranging from 1000K to 4000K.



Figure A.13: Computed burned gas composition under the chemical equilibrium assumption. a) first row: $\phi = 0.5$, lean mixture; b) second row: $\phi = 1.0$, stoichiometric mixture; c) $\phi = 2.3$, rich mixture. Reference pressure: 30 bar.

Nomenclature

- [] concentration $[mol/cm^3]$
- A, B, E, F, G laminar speed constants [16]
- A Area $[m^2]$
- C constant [-]
- D_3 fractal dimension of a 3D rough surface
- D_t turbulent diffusivity
- K_p chemical equilibrium constant
- K_{st} flame stretch factor
- L length [m]
- L_I Integral scale of turbulence [m]
- L_K Kolmogrov scale of turbulence [m]
- L_T Taylor's micro-scale of turbulence [m]
- N_s set of species
- Q heat [J]
- Re_t turbulent Reynolds number
- R_m specific gas constant of a mixture $[J kg^{-1} K^{-1}]$
- R_u universal gas constant $[JK^{-1}mol^{-1}]$
- S_L laminar burning velocity [m/s]
- T temperature [K]
- U internal energy [J]
- V volume $[m^3]$
- W species molecular weight [kg/kmol]

W	work [J]
~	n alum annial intan

- *a* polynomial interpolation coefficient
- b cylinder bore [m]
- c_p specific heat capacity at constant pressure $[J kg^{-1} K^{-1}]$
- c_v specific heat capacity at constant volume $[J k g^{-1} K^{-1}]$
- f fraction $(f \in [0, 1])$
- h specific enthalpy [J/kg]

 k_f, k_b forward, backward rate coefficients

- k_B Boltzmann's universal constant [J/K]
- $m \quad \text{mass [kg]}$
- n engine rotating speed [rpm], number of moles [mol]
- p pressure [Pa]
- r radius [m]
- s engine stroke [m]
- t time [s]
- u specific internal energy $[J kg^{-1}]$
- u velocity [m/s]
- u_L stretched laminar burning velocity [m/s]
- x molar fraction
- y mass fraction
- z_c instantaneous combustion chamber height [m]

Greek letters

 α air-fuel mass ratio

- β engine compression ratio [-]
- Δg^o Gibbs free-energy change
- ε average turbulent dissipation $[m^2 s^{-3}]$
- ε_a apparent grey-body emissivity [-]
- η molecular viscosity $[\mu P]$
- γ laminar speed residuals correlation coefficient [17]
- ν stoichiometric reaction coefficient

 $\Omega^{(2,2)}$ collision integral

- ϕ mixture equivalence ratio
- Ψ molar ratio between products and reactants
- $\rho \qquad {\rm density} \; [kg/m^3]$
- σ_0 Stefan-Boltzmann's constant $[J m^{-2} K^{-4} s^{-1}]$
- σ Lennard-Jones collision diameter [Å]
- τ time constant [s]
- θ engine crank angle [CA]
- ϑ generic variable

Superscripts

- ' RMS turbulent fluctuation
- time average
- α laminar speed temperature correlation exponent [17]
- β laminar speed pressure correlation exponent [17]
- m, n laminar speed fuel mass correlation exponents [16]
- *o* initial conditions

Subscripts

0	reference condition
a	apparent
ad	adiabatic flame
air	standard air
b	burning, burned zone
CH_4	methane
e	entrainment
eq	chemical equilibrium conditions
F	fuel
f	flame, flame front
g	bulk in-cylinder gas
H_2	hydrogen
K	Kolmogrov
k	flame kernel
max	maximum
min	minimum
p	engine piston
r	radiative heat transfer
res	residual gases
s	stoichiometric
t	turbulent

- tot total in-cylinder
- t, t in development (transient) turbulent
- u unburned zone
- w wall
- Wo Woschni convective term

Abbreviations

- ATDC after top dead center
- BTDC before top dead center
- CA crank angle degrees
- CFR Cooperative Fuel Research
- EVO Exhaust Valve Opening
- ICE Internal Combustion Engine
- IVC Intake Valve Closure
- NO_x Nitrogen oxides (NO, NO_2)
- SI spark ignition
- SOI start of ignition
- TDC top dead center
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