"Lean" Unified Non-Empiric Model for Fundamental Concentration Limits of Spherical Flame Balls and Plane Deflagration Flames in the Hydrogen-Containing Mixtures

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1   Introduction

Concentration limits for the different combustion modes in the hydrogen-containing (hydrogen-air and hydrogen-oxygen) gas mixtures is of vital importance for progress in academic combustion studies and for the multiple practical applications.

Traditionally the concentration limits, namely, - the flammability limits [1], the limits for upward and downward flame propagation [1], detonability limits [2, 3] and flame acceleration limits [4] - have been accessed from the experimental data, obtained in the different experimental setups (vertical/horizontal tubes, explosion vessels with spherical or else shape). The empirical concentration limits substantially depend [5] upon experimental setup structure, geometry, size, material etc. From experimental viewpoint, the empirical concentration limits do not have theoretical justification. They can be used in practice as the notional values, i.e. based on convention. Absence of theoretical foundation results in 1) inability to define range of the epistemic uncertainties of the empirical limits, and 2) insurmountable difficulties in reconciling [6] the direct and obvious contradictions between the different numerical values for the same notional limit, for example – lower flammability limit - assessed by using different experimental methods ([7] - EN 1839T vs EN 1839B) or with different criteria (ASTM [8] vs EN [7] or vs DIN [10]).

On the opposite (theoretical) side, Belles in [11] proposed a pure non-empiric framework for quantitative estimation of the detonability concentration limit, using the following two ideas – 1) at concentration limit detonation "occurs when the pre-flame shock becomes strong enough to cause the mixture to explode"; 2) "explosion (chain-branched) occurs when the rate of the chain-branching reaction is equal to half of rate of the chain-breaking reaction". This tradition was supported and extended in the subsequent studies of the fundamental concentration limits of the plane deflagration flames.

In [12] a unified (both the thermal losses and chain-branching approaches) concept of the fundamental concertation limits for the laminar premixed flames was proposed, using kinetic criterion – so called "flammability exponent". Value for the rich flammability limit in the hydrogen-air mixtures was

estimated. In [13] the lean and rich limits for the plane deflagration flames in hydrogen-oxygen mixtures were estimated using notion of crossover temperature, at which chemical chain propagation rate is equal to chain termination rate. In [14] lean concentration limit for the plane deflagration flames was estimated using two criteria. First criterion (which can be named as kinetic criterion) was a revision of the Belles' criterion – plane deflagration flames can sustain, if the rate of the chain-branching reaction is equal to rate of the chain-breaking reaction (cut-off factor $\alpha = 1$). Second criterion (which can be named as thermodynamic (or energy) criterion) – cross-over temperature T_{cross}, calculated from kinetic criterion, will be equal or higher than adiabatic flame temperature T_b at flame front. For plane deflagration $T_b = T_{AICC}$ - flame temperature is equal to adiabatic isobaric complete combustion temperature. Value for the lean concentration limit of the plane deflagration flames in hydrogen air mixtures was estimated. The similar kinetic and thermodynamic criteria, firstly described in [14], were applied to estimate the fundamental concentration limits for plane deflagration flames in the following cases. In [15] the rich concentration limit of the plane deflagration flames in dry hydrogen air mixtures at normal temperature and pressure was estimated. In [16] a dependence of the lean and the rich fundamental concentration limits upon elevated initial temperature at normal pressure was estimated. In [17] a triangular diagram (hydrogen-air-water steam concentration) for the concentration limits of the plane deflagration flames has been estimated both for the lean and the rich hydrogen-air mixtures.

It should be stressed that in the abovementioned [12-17] non-empiric models (which can be named as a Mallard-Le Chatelier ([18]) -Michelson ([19]) – Belles [11] (MCMB) inspired theoretical models) calculation of the concentration limits are based on two fundamental characteristics of the hydrogen-air mixtures – 1) kinetic characteristic - crossover temperature $T_{cross}(\phi)$, which is defined by a balance between two "bottlenecks": namely, the reactions pathways for chemical chain propagation and chain termination, and 2) thermodynamic characteristic - adiabatic flame temperature T_b, - and do not use detailed kinetic mechanism.

Goals of this report – 1) to extend the minimalistic (in other words "lean" - in term of computational resources in comparison with the one-dimensional [18, 19] or 2dim/3dim Reactive CFD simulations of deflagration flame concentration limits) non-empirical model, previously applied to plane deflagration flames, for one more practically important case - the fundamental concentration limits for the stationary flame balls; 2) estimate the dependence of the fundamental concentration limits for the stationary flame balls upon initial water steam content in hydrogen-air-steam mixtures; 3) compare the simulated non-empiric results with the empirical concentration limits and describe the relations between them.

2   "Lean" Non-empiric Model for the Fundamental Concentration Limits for the Stationary Flame Balls

For quantitative estimation of the fundamental concentration limits of the different basic combustion regimes (deflagrations, flame balls, detonation, etc.) in the hydrogen-containing gas mixtures the following unified computational procedure was proposed:

Step 1: kinetic index estimation:

Calculate dependencies of the crossover temperature $T_{cross}(\phi)$ upon equivalence ratio ϕ (or hydrogen concentration) for the lean and rich mixtures under given initial conditions (temperature T_u and pressure p_u) by equating the rates of the leading elementary reactions for chain branching $H + O_2 = OH + O$ and termination $H + O_2 + M = HO_2 + M$ -

$$k_b(T_{cross}) = k_t(T_{cross}) \cdot c_M(\phi, \alpha, p_u, T_u, \varepsilon_{H_2O}) \tag{1}$$

Kinetic parameters for the elementary reaction rates $k_b(T) = A \cdot T^n \exp\left(-T_a/T\right)$ and $k_t(T) = f(k_0, k_\infty, F)$ have been selected as: $A = 3.52 \cdot 10^{16}$, n= - 0.7, $T_a = 8590K$, Chaperon efficiencies are

ε_{H_2} =2.5 for H$_2$, ε_{H_2O} =12.7 for H_2O, and 1.0 for all other species; $k_0 = [5.75 \cdot 10^{19}, -1.4]$, $k_\infty = [4.65 \cdot 10^{12}, 0.44]$, Troe falloff with $F_c = 0.5$.

Step 2: thermodynamic index estimation:

Calculate dependencies of adiabatic flame temperature T_b upon equivalence ratio ϕ (or hydrogen concentration) for the lean and rich mixtures under given initial conditions (temperature T_u, pressure p_u, initial water steam fraction α);

Step 3: fundamental concentration limits estimation:

Define fundamental concentration limits at the intersection points, where kinetic-thermodynamic criterion is satisfied

$$T_b\ (\emptyset_{lim}) = T_{cross}\ (\emptyset_{lim}). \tag{2}$$

During estimation of the fundamental limits for the plane deflagrations in [13-17] the following assumptions was used:

- flame temperature $T_b(\phi, T_u, p_u, \alpha\ ) = T_{AICC}(\phi, T_u, p_u, \alpha)$ (3)

where T_{AICC} – adiabatic isobaric complete combustion temperature;

- stoichiometric mixture - border between lean and rich gas mixtures – is characterized by value $\phi_{DF} = 1\ (29{,}6\ vol.\%H2)$. (4)

For estimation of the fundamental limits for the stationary flame balls, where spherical geometry of mass diffusion and heat transfer is essential, set of the assumptions is different from planar case of the deflagration flames:

1) flame ball $T_b^{FB}(\phi, T_u, p_u, \alpha) = T_Z\ (\phi, T_u, p_u, \alpha) = T_u + \frac{T_{AICC}(\phi, T_u, p_u, \alpha) - T_u}{Le(\emptyset, \alpha)}$ (5)

where $Le\ (\phi, \alpha)$ – effective Lewis number of hydrogen-containing mixture;

2) stoichiometric mixture - border between lean and rich gas mixtures – is characterized by value

$\phi_{FB} = \frac{D_{O_2}}{D} = 0{,}2342.$ (6)

where D_{O_2} - binary diffusion coefficient of oxygen, $D\ = 1{,}154 \cdot D_{H_2}$ – binary diffusion coefficient of hydrogen with explicit considering thermo-diffusion (Soret effect). Physical meaning of equation (6) is - at spherical surface of stationary flame ball stoichiometry is attained [22] because of balance between two diffusion fluxes – oxygen and hydrogen. This is the case for 8,95 vol.% H2 in hydrogen-air mixtures and 18.98 vol.% H2 in hydrogen-oxygen mixtures.

3 Dependence of the Fundamental Concentration Limits for the Flame Balls upon Initial Water Steam Concentration in H2-Air-H2O and in H2-O2-H2O Mixtures

Results of the computations according to proposed procedure are shown at Figures 1 and 2.
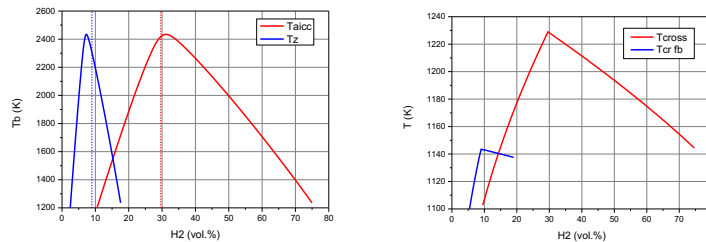
a)   b)

Figure 1: Flame temperatures (a) and crossover temperatures (b) vs initial hydrogen concentration in hydrogen-air-steam mixtures: (in red) T_{AICC} and T_{cross} for plane deflagrations, (in blue) T_Z and $T_{cr\ FB}$ for stationary spherical flame balls.

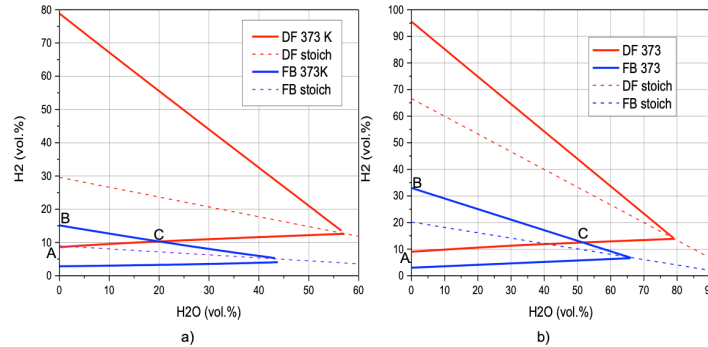a)   b)

Figure 2: Fundamental concentration limits for plane deflagrations (red line) and spherical stationary flame balls (blue line) vs initial hydrogen concentration in hydrogen-air-steam mixtures (a) and in hydrogen-oxygen-steam mixtures (b) at $T_u = 373$ K and $p_u = 1$ atm. Dotted lines: equivalence ratio $\phi_{DF} = 1$ for planar deflagrations (red) and $\phi_{FB} = 0{,}2342$ for spherical flame balls (blue).

Two important points can be inferred from Figure 2. First, in addition to a generally accepted empirical observation: within flammability limits of hydrogen-mixtures two regions exists, where the ascending and the descending flames can propagate, a non-empiric differentiation of the flames can be proposed: two principal flame families exists – the locally plane, continuous deflagration flames and the locally spherical, discrete flame balls (the appropriate concentration limits are shown at Fig.2 by the red and blue curves). Second, both in the hydrogen-air and hydrogen-oxygen mixtures there are exit an overlapping of two principal flame families (shown at **Error! Reference source not found.** by triangles ABC). In can be interpreted from two viewpoints: 1) in mentioned concentration range the cellular deflagration flames exist due to diffusional-thermal instability of initially plane deflagration flames or 2) cellular deflagration flames are results of a strong interaction of system of the flame balls (see experimental evidence in [23]).

4 Comparison of the Non-Empiric and Empiric Concentration Limits

The non-empirical concentration limits, calculated according to proposed procedure, and the empirical ones are compared at Figure 3. Despite a very "lean" modelling a reasonable agreement with empiric data was attained. Different behaviour of the empiric and non-empiric limits around the "tips" of the ternary diagrams is a result of oversimplification, accepted in current version of "lean" model. Fundamental concentration limits were computed for the lean and rich mixtures without considering of the dissociation of the reagents at the reaction front. This restriction will be dismantled later.

A new interpretation of the widely used Shapiro-Moffette diagram [24] can be proposed: between the lower fundamental concentration limit for deflagration flames with continuous front and the lower fundamental limit of the flame balls the descending coherent (integral) flames cannot propagate. In other words - here only discrete (intact) flame balls can exist.

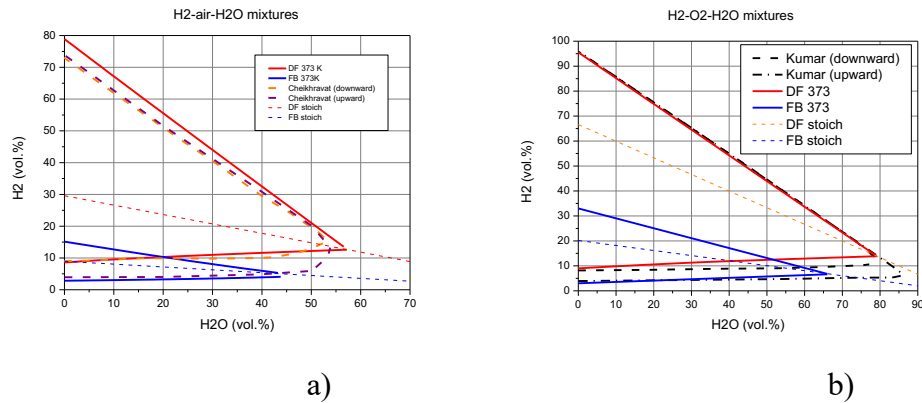<center>a)   b)</center>

Figure 3: Comparison of the fundamental (continuous lines) and the empirical (dashed lines) concentration limits: (a) for the upward (orange [24]) and downward (purple [24])) propagating flames in H_2-air-H_2O and (b) for the upward (black [25]) and downward (black dashed-dot [25] flames in H_2-O_2-H_2O mixtures at $T_u = 373$ K and $p_u = 1$ atm.

5 Conclusions

1. "Lean" non-empiric (aka Mallard-Le Chatelier-Michelson–Belles (MCMB)) model for the fundamental concentration limits is extended for the case of the stationary spherical flame balls. General unified procedure and the specific features for spherical geometry and associated kinetic features are described and compared with the previous works for the plane deflagration limits.
2. Lean fundamental concentration limits for deflagration flames can be regarded as "conservative" or "absolute" envelope for the rich empirical limits of the downward propagating flames.
3. Lean fundamental concentration limits for stationary flame balls can be regarded as "conservative" or "absolute" envelope for the lean empirical limits of the upward propagating flames.
4. Numerical values of the fundamental concentration limits are sensitive to variation of Shaperon coefficient for water steam.
5. Additional experiments are necessary for 1) determination of the absolute value of water steam Shaperon coefficient for trimolecular chain termination reaction, 2) exemplary determination of the minimal water steam concentration for total flame inertization at 373 K and 1 atm.

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