Theoretical Physics-based Definition and Accurate Characterization of Lower Concentration Limit for Hydrogen-Air Mixtures

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ABSTRACT

Understanding of nature and knowledge of the specific numerical values of the concentration limits for explosions in hydrogen-containing mixtures is important for existing nuclear power plants, future thermonuclear installations, multiple industrial applications in petrochemical and chemical industry, coming generation of the hydrogen-fueled vehicles and hydrogen energy infrastructure. In this paper a theoretical physics-based definition for the concentration limits of hydrogen-air gas explosions. Gas explosions have been and are attributed to the self-spreading frontal deflagration flames, whose evolution through flammable gas cloud after ignition results in the substantial baric effects. Specifically in the hydrogen-air mixtures within flammability limits two generic flames can propagate – self-propagating frontal deflagration flames (described by Zeldovich-Frank-Kamenetskii model) and confined in space the buoyant flame-balls (aka Zeldovich model). Fundamental concentration limit difference between these two generic types of flames could be regarded as a critical value for severity of hydrogen-air explosions. Within a Deflagration-to-Flame Ball Transition (DFBT) concentration range (7-12 vol% H_2) three traceable candidates exist – two empirical and one theoretical concentration limits. Relations between these candidates and their specific physico-chemical features are described. Targets for three future studies are proposed – one for direct (empirical or computational) evidence in support of a fundamental character of concentration limits under consideration and two studies for accurate quantitative characterization of the ultimate lower concentration limit for hydrogen-air explosions.

KEYWORDS: Hydrogen safety, explosion, concentration limits, deflagration flames, flame balls, deflagration-to-detonation-transition, deflagration-to-flame ball-transition.

INTRODUCTION

Understanding of nature and knowledge of the specific numerical values of the concentration limits for explosions in hydrogen-containing gaseous mixtures is important for existing nuclear power plants, future thermonuclear installations, multiple industrial applications in petrochemical and chemical industry, coming generation of the hydrogen-fueled vehicles and hydrogen energy infrastructure. Today an ample knowledge exists on the different modes of hydrogen-air explosions, encountered in industrial practice. The associated phenomena (deflagrations, detonations, fast flames, DDT, etc.) are described and characterized in traceable and verifiable manner in multiple research and engineering publications [1].

However, unambiguous and generally agreed definition of the concept of gas explosion is still absent. In pre-normative study [2] it was attempted to provide a consistent and non-contradictory definition of term "explosion" from three perspectives – a societal, regulatory and scientific ones. Focus of work [2] was on the inconsistencies in the prior art definitions of term "explosion" from viewpoint of the experts involved in developing Regulations, Codes and Standards (RCS).

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Empirical-based approach [3-10] to hazardous hydrogen-air gas explosions definition and characterization is based on the “Slow-to-Fast Flame Transition” (SFFT) framework and/or “Deflagration-to-Detonation-Transition” (DDT) framework. In both cases the key physical process under consideration is a deflagration flame (laminar, turbulent or accelerated). Accelerated flames can result in the high baric loads, which are the inherent attributes of the explosions. Results of the experiments on the fast flame concentration limits are well documented and are used now in the multiple hydrogen safety applications. However, mentioned empirical approach has its own limits, restrictions and inconsistencies, which cannot be overcome without appropriate theoretical interpretation and refinement.

In order to reduce the uncertainties in the empirical-based estimations of the flame acceleration concentration limits, an alternative, model-based framework was proposed in [11]. The proposed theoretical approach to definition of the concentration limits for hydrogen-air explosions is based on “Deflagration-to-Flame-Ball-Transition” (DFBT) framework. It was hypothesized, that the fundamental concentration limits for deflagration flames are the ultimate edges (envelopes) for the empirical concentration limits for flame acceleration and for downward flame propagation. The quantitative estimations of the fundamental concentration limits for the plane hydrogen-air deflagration flames have been made using a non-empiric, kinetic-thermodynamic method, developed in [12]. It was revealed in [11] that the theoretical estimations for the fundamental concentration limits provide more conservative approximations of the lower concentration limits then the empirical ones.

From practical viewpoint (in the hydrogen-air gas explosion protection applications) it will be reasonable to clarify – what kind of the new studies (physical or computational ones) does it necessary to prepare and to perform for accurate characterization of the lower concentration limits for hydrogen-air explosions? This is the main goal of this paper.

The paper structure is as follows. For readers’ convenience the key concepts of the proposed theoretical approach are briefly described in Section 2 and 3 by citing previous works [11, 12]. The following questions are discussed accordingly - what are the fundamental concentration limits for plane deflagration flames? What are the relations between the empirical and fundamental concentration limits for deflagration flames propagation? In Section 4 three targets for the future physical (real) or computational (virtual) experiments are proposed. All proposed in Section 4 studies are focused on understanding of physico-chemical nature and further quantitative refining of the lower concentration limit for “Deflagration-to-Flame-Fall-Transition”.

FUNDAMENTAL CONCENTRATION LIMITS FOR PLANE DEFLAGRATION

In the non-empirical theoretical estimations [11, 13, 14] (see Table 1 below), term “fundamental concentration limit” means - an inherent physico-chemical property of a combustible mixture, independent of external influences, associated with or defined by specific experimental setup, particular measurement procedure or empirical observation criterion for a given combustion regime (flame ball, deflagration, detonation, etc.).

In [11] it was assumed that, fundamental lower concentration limit for deflagration flame propagation (see Fig. 1 below) is a natural border between two generic types of flames – the baric frontal deflagration flames, described by Zeldovich-Frank-Kamenetskii model, and the quasi-isobaric spherical flame balls, described by Zeldovich model.

Table 1. Fundamental concentration limits for the plane deflagration flames in premixed, quiescent, dry hydrogen-air mixtures under normal initial conditions (T_u = 298 K, P=1 atm), calculated "from-the-first-principles"

Lower limit, equivalence ratio (vol.% H_2)	Upper limit, equivalence ratio (vol.% H_2)	Criterion	Source
-	10.1 (80,9)	Kinetic: flammability exponent $\alpha = 1$	[13]
0.251 (9.5)	-	Kinetic-thermodynamic: $T_b = T_c$	[14]
0.247 (9.4)	8.697 (78.5)	Kinetic-thermodynamic: $T_b = T_c$	[11]

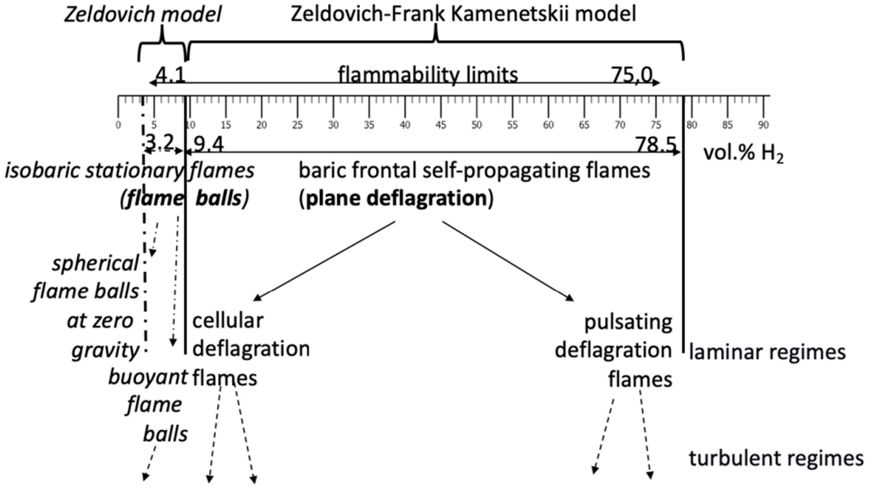


Fig. 1. Theoretical taxonomy of the concentration limits for the basic laminar combustion regimes in premixed, quiescent, dry hydrogen-air gas mixtures under normal conditions (1 atm, 298 K) [11].

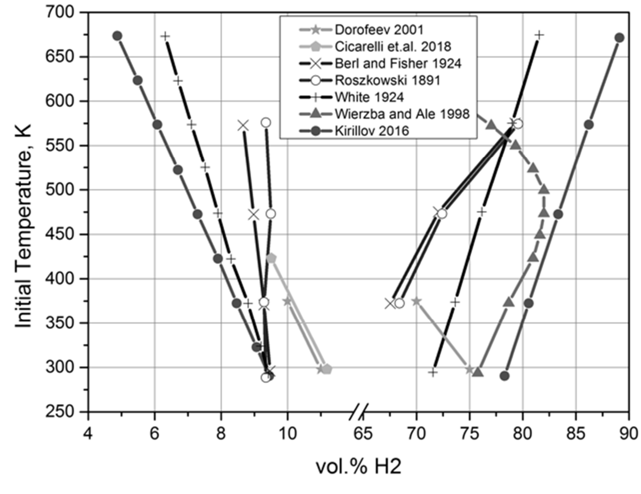


Fig. 2. Fundamental concentration limit for plane deflagration propagation model (black circles) as an ultimate limit for the different empirical data sets [11].

Comparison of the temperature dependencies of the empirical and theoretical concentration limits (shown in Fig. 2) for the different combustion regimes/models gives a rational basis for considering of the fundamental concentration limit for plane ZFK deflagration flame propagation as an ultimate (or edge) value for lower concentration limit of the hydrogen-air explosions. In Fig. 2, the theoretical envelope (shown by black circles) represents an envelope for the empirical concentration limits for

- the fast flames, shown by stars (Dorofeev 2001) and by white circles (Cicarelli 2018),
- downward flame propagation, shown by crests (+) (White 1924), by sign (x) (Berl 1924), by triangles (Wierzba 1998)).

RELATIONS BETWEEN EMPIRICAL AND FUNDAMENTAL CONCENTRATION LIMITS

Within a transient concentration range (namely 7-12 vol% H_2), which in fact is a “Deflagration-to-Flame-Ball-Transition” concentration range, the potential candidates on lower concentration limit for hydrogen-air explosions (i.e. the flames with baric effect) are listed in Table 2 below.

Table 2. Candidates for a lower concentration limit of the hydrogen-air flames with baric effect

Assessment method	Lower Concentration Limit, (vol.% H2)	Content of water vapor for normal initial conditions (1 atm, 298K) under the normal gravity	Combustion phenomenon / model	Ref.
empirical	7.7	dried	downward deflagration flame propagation	[15]
empirical	9.0	dried	downward deflagration flame propagation	[16]
empirical	9.45	partly dried	downward deflagration flame propagation	[17]
empirical	7.5 ∓ 0.5	dry	downward deflagration flame propagation	[18]
empirical	10.0	not explicitly reported	flame acceleration in horizontal tube	[4]
empirical	11.0	not explicitly reported	flame acceleration in horizontal tube	[8]
theoretical	9.4	dry	plane deflagration flame propagation	[11]
theoretical	9.5	dry	plane deflagration flame propagation	[14]

In Table 2, three families of the numerical values of concentration limits for combustion phenomena/models are listed:

- empirical limits for flame acceleration,
- empirical limits for downward flame propagation,
- theoretical limits for plane ZFK deflagration flame propagation.

All families of the concentration limit values have their own uncertainties (aleatoric and/or epistemic). For example, now

- experiments on downward flame propagation [15-18] have large variability in the boundary (closed or open at firing end, radius of test tube) and initial (dry or wet gas mixture) conditions;

- experiments on flame acceleration [4, 8] have been performed in horizontal tubes only. Information on influence of buoyancy on flame acceleration phenomenon in vertical tubes is absent now;
- non-empiric calculations [14, 11] of ZFK flame propagation have been made for plane fronts only. They do not take into account cellular structure of deflagration flames in ultra-lean (< 12 vol% H2) hydrogen-air gas mixtures and the associated effects of preferential diffusion and Soret on internal structure of the deflagration reaction front.

Due to mentioned uncertainties in the available now numerical values of concentration limits for combustion regimes/models, which can be regarded as lower concentration limit for hydrogen-air explosions, it is necessary to refine their accuracy in a new studies.

TARGETS FOR FUTURE ACCURATE CHARACTERIZATION OF LOWER CONCENTRATION LIMIT FOR HYDROGEN-AIR EXPLOSIONS

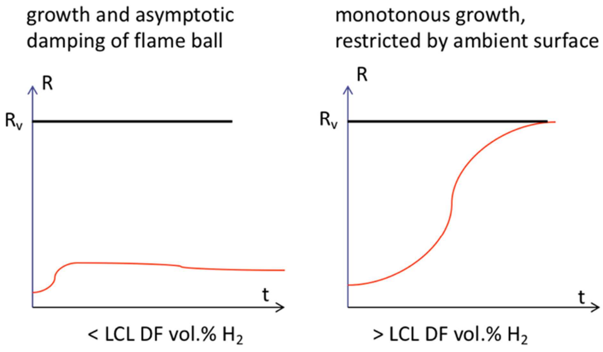
Determination of the ultimate lower concentration limit for hydrogen-air explosions with higher (then now) accuracy can be made either in future empirical experiments or in 3-dimensional high fidelity computations.

In both cases it will be necessary to perform a set of tests (real or virtual), which shall be in compliance with the following requirements

- increment 0.05 vol% H_2 in variation of hydrogen concentration at least,
- control of humidity level in hydrogen-air gas mixtures. A high sensitivity of fundamental concentration limits upon initial steam concentration in hydrogen-air mixture is a well-established fact [19].

Direct experimental evidence on existence of two generic combustion flames in premixed hydrogen-air gas mixtures under zero gravity conditions

For direct experimental evidence, that deflagration flames and flame ball-like flames have principally different macroscopic behavior the following experiment under zero gravity conditions is required.



(a) (b)

Fig. 3. Critical behavior of flame front during variation of chemical composition in Deflagration-to-Flame Ball-Transition concentration range (7 -12 vol% H_2) under zero gravity conditions.

In closed vessel with characteristic size R_v ignition of flammable (within concentration range 4.1-75 vol% H_2) hydrogen-air gas mixtures will results in one of the two possible types of combustion front behavior. In cases of the hydrogen-air mixtures, which are leaner (see Fig. 3a) then Lower

Concertation Limit for Deflagration propagation (LCL DF), an initial ignition kernel will grow up into spherical flame ball with limited (in comparison with vessel size) radius, defined by chemical composition, temperature and pressure of mixture. In case of the hydrogen-air mixtures, which are richer (see Fig. 3b) then Lower Concertation Limit for Deflagration propagation, an initial ignition kernel converts into self-expanding flame front, which will occupy all available space with combustible mixture and will be extinguished at border of test vessel.

Two targets for future experiments under zero gravity conditions are:

- determination of the numerical value of the Lower Concentration Limit for Deflagration propagation and its comparison with candidates from Table 2,
- determination of possible stochastic nature of Deflagration-to-Flame Ball-Transition.

Principally different dependence of maximal flame temperature upon hydrogen concentration in the deflagration flames and in the flame balls

On the base of theoretical analysis of the fundamental concentration limits in [11], it is possible to formulate a goal for the future physical or computational experiments, aimed at exploring a second direct evidence, that deflagration flames and flame ball-like flames have the different physical natures and, hence, exhibit different macroscopic behavior during gradual variation of the hydrogen concentration in initial gas mixture under the Earth gravity conditions.

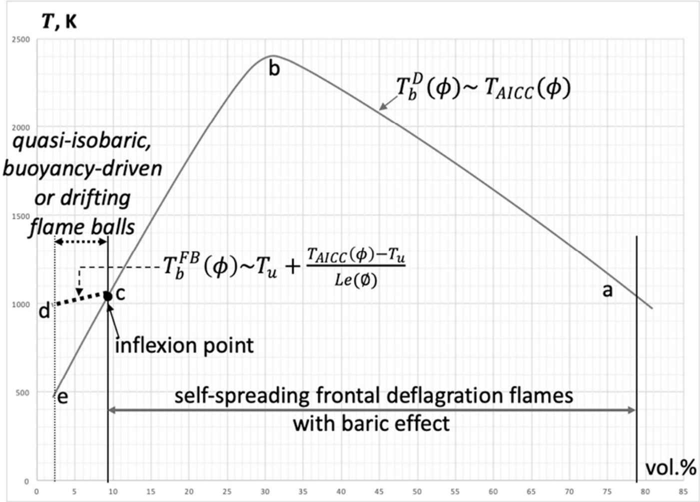


Fig. 2. Two different types of maximal flame temperature dependence upon hydrogen concentration in hydrogen-air mixtures.

During a gradual decrement of hydrogen concentration in the hydrogen-air mixtures (it can be named as a Deflagration-to-Flame Ball-Transition, DFBT) maximum flame temperature T_b will follow (will be symbatic to) two different asymptotic curves (see Fig. 4):

1) path “a-b-c” on Fig. 4, where $T_b^D(\phi)\sim T_{AICC}(\phi)$ in concentration range [9.4 – 78.5] vol.% H_2 and $T_{AICC}(\phi)$ is a dependence of the adiabatic isobaric complete combustion temperature upon hydrogen concentration for given initial conditions (temperature T_u and pressure p_u). Function $T_{AICC}(\phi)$ is shown by continuous line “a-b-c-e”;

2) path “c-d” on Fig. 4, where $T_b^{FB}(\phi)\sim T_u+\frac{T_{AICC}(\phi)-T_u}{Le(\emptyset)}$ in concentration range [3.35 – 9.4]

vol.%H_2. Here $Le(\phi)$ is a dependence of the effective Lewis number [20] for hydrogen-air mixture upon stoichiometric ratio for a given initial pressure p_u. Function $T_b^{FB}(\phi)$ is shown below by dotted line “c-d”. Due to impact of the Lewis number, it is dependence upon ϕ is less steep than for the deflagration case.

Dependence of the lower concentration limit for hydrogen-air flame acceleration upon propagation direction with respect to the Earth gravity

All currently available empirical data on the concentration limits for deflagration flame acceleration have been obtained in medium (10^0 m) [8] or in large (10^1-10^2 m) scale [3, 4] experimental tubes, allocated in horizontal direction (perpendicular to the Earth gravity direction).

However, in the near-limit deflagration flames (for 7–12 vol% H_2) role of buoyancy is substantial [21]. It will be reasonable to expect, that in the experimental tubes, allocated in vertical direction (collinear to the Earth gravity direction), the concentration limits for deflagration flame acceleration will be dependent upon propagation direction – one quantitative value for flame acceleration in upward direction, and the other ones for flame acceleration in downward direction.

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CONCLUSIONS

1. In spite of a long term tradition in experimental and theoretical studies of the hydrogen-air combustion a clear understanding – that frontal self-propagating deflagration flames and confined flame balls are the two principally different combustion regimes existing within known flammability limits – is still absent in hydrogen safety and industrial safety professional communities.
2. Empirical evidences and theoretical arguments are described in support of the author’s hypothesis, that fundamental lower concentration limit for deflagration flame propagation is a natural border between these two generic types of flames – baric frontal deflagration flames, described by ZFK-like models, and quasi-isobaric buoyant flame balls, simulated on the base of ZFB-like models.
3. In the first time, a theoretical taxonomy of the concentration limits for the basic laminar combustion regimes in premixed, quiescent hydrogen-air gas mixtures is proposed on the base of “Deflagration-to-Flame-Ball-Transition” (DFBT) framework.
4. Uncertainties for accurate definition of the three families of concentration limits for laminar combustion are described for the Deflagration-to-Flame Ball-Transition (DFBT) range (7-12 vol.% H_2) in hydrogen-air gas mixtures.
5. Targets for three future studies are proposed. These studies can test the predictive capability of the proposed theoretical instruments – “Deflagration-to-Flame-Ball-Transition” (DFBT) framework, concept of “fundamental concentration limits” and kinetic-thermodynamic model for their quantitative estimation. One study is aimed at the exploration of the direct evidence in support of a fundamental character of concentration limits under consideration. Two other studies are focused on accurate quantitative characterization of the ultimate lower concentration limit for the hydrogen-air explosions.

REFERENCES

[1] A. Koutchourko , et al., State-of-Art and Research Priorities in Hydrogen Safety, ICHS 2013, paper 229.

[2] J.O. Keller, et al., What is an explosion? Int. J. Hydrogen Energy 39 (2014) 20426-29343.

[3] O. Peraldi, R. Knystautas, J.H. Lee, Criteria for transition to detonation in tubes, Proc. Combust. Inst. 21 (1986) 1629-1637.

[4] Dorofeev. S.V., et al, Effect of Scale and Mixture Properties on Behaviour of Turbulent Flames in Obstructed Areas, IAE-6137/3 or FZKA-6268, 1999.

[5] M. Kuznetsov, et al., Effect of Obstacle Geometry on Behavior of Turbulent Flames, IAE-6137/3 or FZKA-6328, 1999.

[6] S. Dorofeev, et al., Evaluation of limits for Effective Flame Acceleration in Hydrogen Mixtures, IAE-6150/3 or FZKA-6349, 1999.

[7] S.B. Dorofeev, M.S. Kuznetsov, V.I. Alekseev, A.A. Efimenko, W. Breitung, Evaluation of limits for effective flame acceleration in hydrogen mixtures, J. Loss Prev. Process Ind. 14 (2001) 583-589.

[8] G. Ciccarelli, N. Chaumeix, A.Z. Mendiburu, K.N. Guessan, A. Comandini, Fast-flame limit for hydrogen/methane-air mixtures, Proc. Combust. Inst. 37 (2019) 3661-3668.

[9] G. Cicarelli, S.B. Dorofeev, Flame acceleration and transition to detonation in ducts, Progr. Energy Combust. Sci. 34 (2008) 499-5508.

[10] R. Scarpa, E. Studer, S. Kudriakov, B. Cariteau, N. Chaumeix, Influence of initial pressure on hydrogen/air flame acceleration during severe accident in NPP, Int. J. Hydrogen Energy (2018), in press, https://doi.org/10.1016/j.ijhydene.2018.06.160

[11] I.A. Kirillov, Physics-based Approach for Reduction Uncertainties in Concentration Limits of “Slow-to-Fast” Flame Transtion in Hydrogen-Air Gas Mixtures, Hydrogen Management in Severe Accidents, Technical Meeting EVT1701911, 25-28 September 2018, Vienna, TECDOC, IAEA, in press.

[12] I.A. Kirillov, On fundamental concentration limits for basic regimes of combustion in premixed hydrogen-air gas mixtures, In: Research Seminar “Physico-chemical kinetics in gas dynamics”, Institute of Mechanics, Moscow State University, 7th April, 2016, Moscow, Russia, http://www.imec.msu.ru/content/education/seminars/chemphys/2016-04-07.pdf (in Russian).

[13] C.K. Law, F.N. Egolfopoulos, A Unified Chain-Thermal Theory of Fundamental Flammability Limits, Proc. Combust. Inst. 24 (1992) 137-144.

[14] D. Fernandez-Galisteo, Numerical and Asymptotic Analyses of Lean Hydrogen-air Deflagrations, PhD thesis, Universidad Carlos III De Madrid, 2009.

[15] A. La Fleur, Ternary and Quaternary Explosion Regions and Le Chatelier’s Formula, Rec. Travaux. Chim. Pays. Bas. 56 (1937) 442-473.

[16] A.G. White, Limits for the Propagation of Flames in Inflammable Gas-Air Mixtures. I. Mixtures of Air and One Gas at the Ordinary Temperature and Pressure, J. Chem. Soc. 125 (1924) 2387-2396.

[17] H.W. Thompson, Ztschr. Physikal. Chem, v.B18 (1932) 219-240.

[18] H. Cheikhravat, N. Chaumeix, A. Bentaib, C.-E. Paillard, Flammability limits of hydrogen-air mixtures, Nuclear Technology 178 (2012) 5-16.

[19] H.F. Coward, G.W. Jones, Limits of Flammability of Gases and Vapors, Bulletin 503, Bureau of Mines, 1952.

[20] F.A. Williams, Combustion Theory, Benjamin/Cummings, 1985.

[21] V.N. Krivulin, L.A. Lovachev E.A. Kudryavtsev, A.N. Baratov, Combust. Explos. Shock Waves 11 (1975) 759-764.