Theoretical Estimation of Concentration Limits for Water Steam Capability to Suppress Flame Acceleration in Hydrogen-Air Mixtures

Igor A. Kirillov[1], Natalia L. Kharitonova[2], Alexander V. Lebedev[3], Sergey V. Nikiforov[4], Vadim Yu. Plaksin[3]
[1]National Research Centre "Kurchatov Institute", Kurchatov sq. 1, 123098, Moscow, Russia
[2]S&E Centre for Nuclear and Radiation Safety, M. Krasnoselskaya 2/8, 107140, Moscow, Russia
[3]Kintech Lab, 3-ya Khoroshevskaya 12, 123298, Moscow, Russia
[4]Moscow Institute of Physics and Technology, Dolgoprudny, Institutskiy 9, 141701, Russia

1 Introduction

Flame acceleration (FA) in the hydrogen-air-steam mixtures is essential contributor to explosion risk in the containment of Pressurized Water Reactors and in the hydrogen-related industrial/transport/storage facilities [1]. Water steam is widely used in the fire- and explosion protection engineering applications as an effective combustion suppressant with the forceful inhibiting and inerting properties [2]. Empirical framework for evaluation for potential of FA and fitting correlation have been proposed [3] for quantitative estimation of the concentration limits for flame acceleration in hydrogen-air-steam mixtures in obstructed areas. Different engineering correlations for the FA concentration limits approximating have been developed [4, 5] during the last decade. They are using the physico-chemical characteristics of the gas mixtures (expansion ratio, Zeldovich number, Lewis number) and geometrical characteristics for a fitting of the available empirical data sets. Empirical approach has intrinsic limitations and up to now does not provide a traceable quantitative data on the minimal values of steam concentration, which can to prevent an occurrence of the flame acceleration under severe accident conditions. In order to improve an understanding of nature of and to reduce quantitative range of the uncertainties in the concentration limits for hydrogen-air-steam mixtures, where effective acceleration of flames is possible, a theoretical framework has been developed [6] as an alternative to empirical ones. It is based on concept of the fundamental concentration limits and on predictive kinetic-thermodynamic (K-T) model for quantitative estimation of the plane deflagration flames concentration limits. This paper is focused on – 1) non-empiric, computationally inexpensive method for conservative estimation an ultimate value of steam concentration, which can totally suppress the flame acceleration for the given initial conditions (gas mixture temperature and pressure). Method uses only the fundamental kinetic and thermodynamic parameters of the hydrogen-air-steam mixtures; 2) dependence of

Correspondence to: kirillov_ia@nrcki.ru

the ultimate steam concentration upon temperature (373 – 813 K) at normal pressure (100 kPa), computed according to the proposed K-T model.

2 Theoretical framework and numerical calculations

2-1 Fundamental concentration limits for plane deflagration propagation as conservative envelope for the empirical flame acceleration concentration limits

2-1-1 *Deflagration flame can be accelerated only in the hydrogen-air-steam mixtures, which support its self-spreading, i.e. within their concentration limits*. The self-spreading, frontal deflagration flames, which demonstrate baric effects, cannot be accelerated outside the concentration limits of their existence.

In experimental work [7] Coward described two basic forms ("weak" and "strong") of the flame existence in hydrogen-air mixtures. Criterion of delimitation for the "weak" and "strong" flames was not discussed.

2-1-2 E*mpirical concentration limits are depended upon experimental setup's design/material/geometry and/or criterion/procedure for observation* on the *critical combustion behavior (*[8]*)*. For example, the numerical values of the flammability limits of gas-air mixtures, derived according to the actual technical standards, are different (up to 16%) in the different explosion vessels and in the tubes [9].

2-1-3 *"Fundamental concentration limits" can be derived from the unambiguous predictive theoretical models of the combustion phenomenon under consideration.* The term "fundamental limit" means an inherent physico-chemical property of a combustible mixture, independent of external influences, associated with or defined by experimental setup, measurement procedure or observation criterion. Fundamental concentration limits for detonation propagation have been theoretically estimated in [10]. Theoretical estimations of the fundamental concentration limits for existence of the plane adiabatic deflagration flames in the dry hydrogen-air gas mixtures under normal conditions (298K, 100kPa) have been made for rich limit [11] and lean limit [12] by using different theoretical criteria.

2-1-4 F*undamental concentration limits for plane deflagration propagation can be regarded as conservative estimation for the flame acceleration concentration limits.* In [5] it was shown, that the non-empirical estimations of the temperature dependency of the fundamental concentration limits for plane deflagration flames at normal pressure could be regarded as conservative "envelope" or "ultimate edge" for empirical data on the flame acceleration concentration limits and on the downward propagation concentration limits. This paper is aimed to provide a first (to the best of the author's knowledge) systematic theoretical quantitative estimations of the ultimate values of steam concentration, which can totally suppress the flame acceleration in hydrogen-air mixtures for the given initial conditions – elevated temperatures (373 – 813 K) and normal pressure (100 kPa).

2-2 Kinetic-thermodynamic model for the fundamental concentration limits of the plane deflagration flames

Model assumptions and details are described in [5]. Computational workflow includes the following steps:

1. calculation of dependence of adiabatic isobaric complete combustion temperature $T_{AICC}(\phi)$ upon equivalence ratio ϕ (or hydrogen concentration) for the given initial conditions (temperature T_0 and pressure p_0) of the hydrogen-air-steam mixture ($2\emptyset H_2 \ + O_2 \ + 3{,}76N_2 \ + \alpha H_2 \ O$). Dependence of the temperature of adiabatic isopycnic complete combustion $T_{AICC}(\phi)$ upon hydrogen concentration ϕ has

been calculated either by the Chemical Workbench software suite (for the initial guess estimations) or by Cantera library (for the large parametric estimations) [10].

2. calculation of crossover temperature $T_{cross}(\phi)$ dependence upon equivalence ratio ϕ for the given initial pressure p_u by equating the rates of the leading elementary reactions for chain branching $H + O_2 = OH + O$ and termination $H + O_2 + M = HO_2 + M$ -

$$k_b(T) = k_t(T) \cdot c_M(\phi, \alpha, p_u, T \ \ , \varepsilon_{H_2O}) \quad (1)$$

3. definition of fundamental concentration limits at the intersection points, where kinetic-thermodynamic criterion for plane deflagration flames is satisfied

$$T_{AICC}\ (\emptyset_{lim}) = T_{cross}\ (\emptyset_{lim}). \quad (2)$$

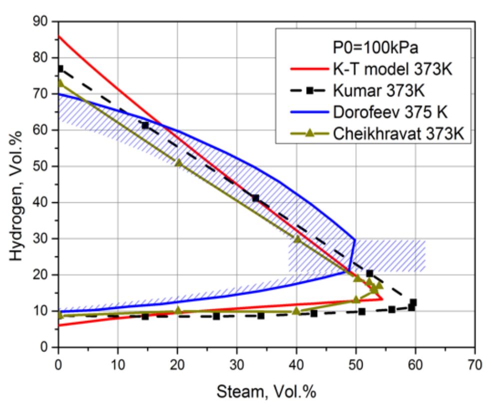
Intersection of the adiabatic and crossover temperature have been estimated by using the "Nelder-mead" minimization algorithm.

Kinetic parameters for the elementary reaction rates $k_b(T) = A \cdot T^n exp\ (-\frac{T_a}{T})$ and $k_t(T) = f(k_0, k_\infty, F)$ have been selected according to the recommendations from [15]: $A = 3.52 \cdot 10^{16}$, n= - 0.7, $T_a = 8590K$, Chaperon efficiencies are ε_{H_2} =2.5 for H_2, ε_{H_2O} =16.0 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 $F_c = 0.5$.

3 Results

3-1 Concentrations limits for hydrogen-air-steam mixtures at elevated temperatures (373K, 473K) and normal pressure (100 kPa)

Computed fundamental concentration limits for the plane deflagration flames can be compared with two empirical datasets for the different deflagration flames propagation limits at Figure 1. Here red line is for visualization of the theoretical limits for plane deflagration flames, black squares – data from [12], yellow triangles - data from [13], blue line – data from [3]. Blue hatched area represents the uncertainties of the empirical correlation [3].



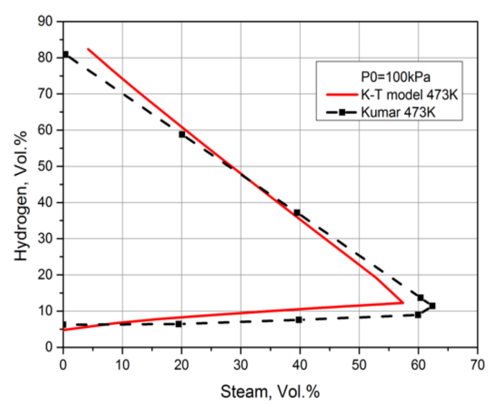


Figure 1. Theoretical and empirical concentration limits for the hydrogen-air-steam mixtures at 100 kPa and elevated temperatures. Left: T_0=373K, right: T_0 = 473K.

3-2 Temperature dependence of the ultimate steam concentration (suppression limit)

Concentration limits, which can suppress any possible FA in the hydrogen-air-steam mixtures (FA suppressing steam concentration limits), computed according to the proposed K-T model for temperature interval 300K-1073K, are shown at Figure 2.

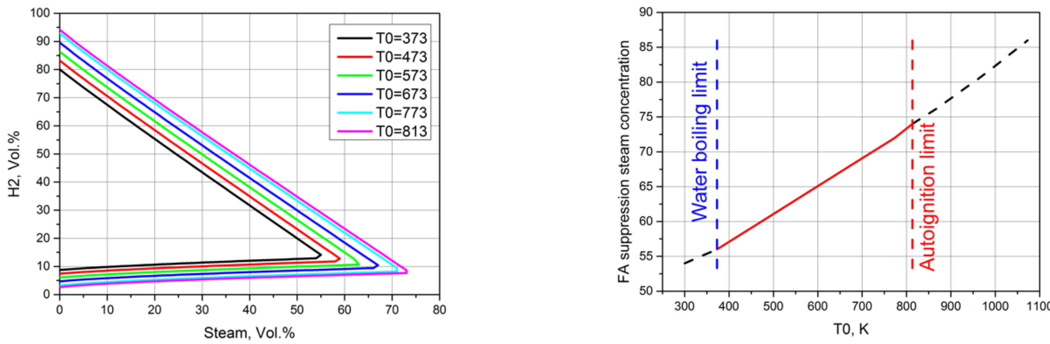


Figure 2. Temperature dependence of the steam concentration limits, which can suppress any flame acceleration in the hydrogen-air-steam mixtures at 100 kPa and elevated temperatures.

4 Discussion

4-1 Sensitivity of the theoretical estimations to the K-T model parameters variation

All computations in this paper have been performed without any fitting of the selected fundamental thermodynamic and kinetic parameters – 1) the Gibbs energies for the H_2, O_2, N_2, H_2O, O, H, OH, HO_2 species, 2) the parameters of the elementary reaction rates k_b and k_t. Sensitivity analysis revealed, that the Chaperon coefficient value ε_{H_2O} has a greatest impact (see Figure 3) on the simulation results.

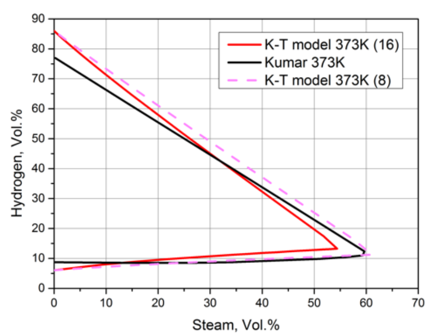


Figure 3. Sensitivity of the K-T model simulations to variation of the Chaperon coefficient ε_{H_2O} (16 and 8).

4-2 Behavior of two fundamental thermodynamic T_{AICC} and kinetic T_{cross} parameters

Dependencies of the fundamental concentration limits for plane deflagration propagation upon initial temperature and steam concentration in the hydrogen-sir-steam mixtures can be interpreted (see Figure 4) by the different behavior of the T_{AICC} and T_{cross}. It is reasonable to assume, that the numerical values of the ultimate steam concentration (suppressing limit) are not related with the transition between stable and unstable flames for mixtures with equivalence ration between 0.7 and 1.0, described in [3]. The theoretical estimations from Figure 2 can be used as the reference points for planning of the accurate experiments, aimed at reduction of the uncertainties in the FA concentration limits dependence upon steam concentration.

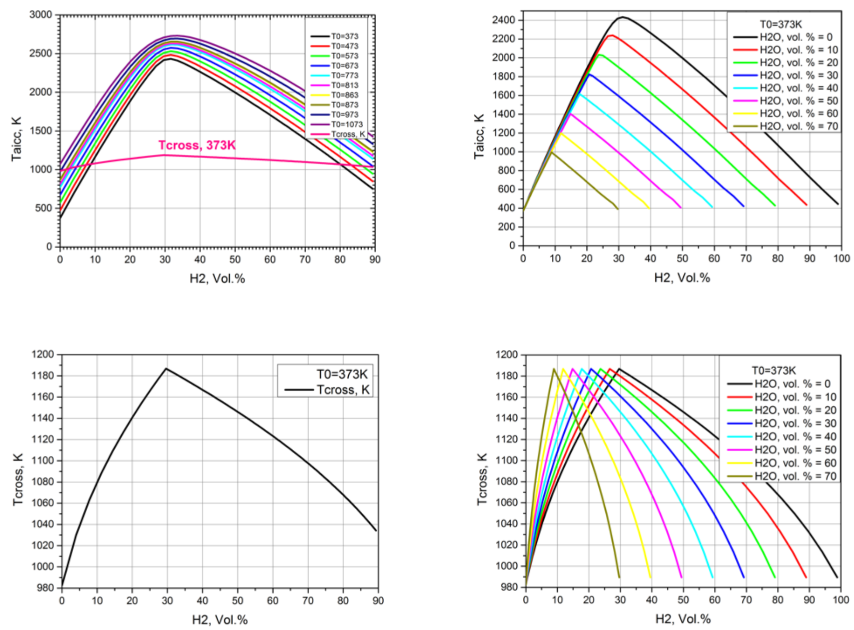


Figure 4. Dependencies of the T_{AICC} and T_{cross} upon variation of the initial temperature T_0, K and steam concentration $X_0^{H_2O}, vol.\%$ in the hydrogen-air-steam mixtures at 100 kPa

4-3 Inconsistencies between available empirical datasets and empirical FA limits estimations

From viewpoint of the practical safety, the empirical estimations for the FA concentration limits, based on the expansion ratio [3], have at least two weaknesses. First, for the rich mixtures ($\phi > 1$) (see left side of Figure 1), the expansion-ratio-based empirical estimations [3] contradict to the available experimental datasets for the downward deflagration propagation limits [12, 13]. Flame acceleration "is possible" outside of the downward flame propagation limits. Second, from viewpoint of [3] the most hazardous mixtures are expected in the range 20-30 H_2 vol.%., while the experiments [12, 13] and the K-T model admit, that range 10-20 H_2 vol.%. will be most difficult for FA suppressing by steam.

5 Conclusion

Ultimate steam concentrations, which can suppress totally the flame acceleration in the hydrogen-air-steam mixtures at high (373-813K) temperatures and normal (100 kPa) pressure, have been studied using non-empiric kinetic-thermodynamic model. The effect of initial mixture temperature on the ultimate steam concentrations (suppressing limits) has been also studied. The simulation results are in a good agreement with the experimental datasets for the downward deflagration propagation limits in the hydrogen-air-steam mixtures at elevated temperatures (373, 473K) and at normal pressure.

Suppression limit is defined by interplay of the temperature dependencies of the adiabatic complete combustion temperature T_{AICC} and crossover temperature T_{cross}. Its numerical value has largest sensitivity to Chaperon coefficient for the water molecules. Experimental or computational (from the first-principles) refinement of this coefficient is required.

Some inconsistencies in the available empirical datasets on the FA concentration limits are shortly described. Quantitative data, computed according to the proposed non-empiric kinetic-thermodynamic model, can be used as the reference points for planning of the accurate experiments, aimed at uncertainty reduction in the concentration limits for water steam capability to suppress flame acceleration in the hydrogen-air-steam mixtures.

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