

INFLUENCE OF EXHAUST GAS ON DETONATION PROPENSITY OF A MIXTURE OF CARBON MONOXIDE, HYDROGEN AND AIR

Agnieszka Jach, Andrzej Teodorczyk

Warsaw University of Technology, Institute of Heat Engineering
Nowowiejska Street 21/25, 00-665 Warsaw, Poland
tel. +48 22 234 52 66, +48 22 234 52 26
e-mail: agnieszka.jach@itc.pw.edu.pl, andrzej.teodorczyk@itc.pw.edu.pl

Abstract

A detonation is the strongest form of all gas explosions. The ease with which a flammable mixture can be detonated (detonability) commonly and traditionally is classified by a detonation cell width λ and an ignition delay time behind the detonation leading shock τ . Additionally, two more parameters were proposed 3 years ago – χ and RSB, which inform about regularity of a detonation structure. The problem of a detonation is significant in industry, in particular in power engineering, where restricted emission standard impose to introduce hydrogen-rich fuels, such as syngas. The most possible initiation of a detonation in industrial conditions is deflagration to detonation transition (DDT), where a deflagration under some conditions (obstacles, confinement, etc.) accelerates and a transition to a detonation takes places. In industry, this acceleration of a flame may progress in initially smoke-filled space. The goal of this paper is to analyse influence of exhaust gas on detonation propensity of a mixture of carbon monoxide and hydrogen. The analysis concerns the detonation cell width λ , ignition delay time τ , RSB and χ parameters. The composition of exhaust gas is calculated by setting it to a state of chemical equilibrium. Combustion temperature influence on exhaust gas composition is assessed. Species, which have the strongest influence on detonability, are assessed. Computations are performed with the use of Cantera tool.

Keywords: detonation propensity, syngas, χ , RSB, detonation cell width, exhaust gas, combustion products

1. Introduction

A detonation is the strongest form of all gas explosions. It does not require confinement or obstructions in order to propagate at high velocity. A detonation is a supersonic combustion wave which velocity is typically 1500 – 2000 m/s and the peak pressure generated by the detonation wave is 15 – 20 bar [2]. The problem is significant in industry, in particular in power engineering, where restricted emission standard impose to introduce hydrogen-rich fuels, such as syngas. Variable composition of syngas and a requirement to flexible operation of a power plant expose a plant to a risk of an explosion or a detonation. A detonation may be initiated in a direct way when sufficiently high energy is provided to a small volume of a flammable mixture, but the most possible initiation in industrial condition is a deflagration to a detonation transition (DDT). This mode may happen in initially smoke-filled confinement. The aim of this paper is to assess influence of combustion products from syngas – air combustion on detonation propensity of syngas – air mixture.

The ease with which a flammable mixture can be detonated (detonability, detonation propensity) commonly and traditionally is classified by a detonation cell width λ and an ignition delay time behind the detonation leading shock τ [2]. When these parameters get smaller, a flammable mixture gets more prone to develop a detonation.

Gavrikov et al. [3] proposed a semi-empirical correlation of a detonation cell width λ . Gavrikov's formula depends on a mixture composition and initial conditions. The correlation is a function of parameters influencing the wave stability and regularity of the cellular structure – the dimensionless effective activation energy E_a/RT_{vn} and parameter T_{vn}/T_0 (E_a – activation energy,

R – specific gas constant, T_{vN} – temperature in von Neumann condition, T_0 – initial temperature). It gives the best results for computational velocities: 1.3 V_{CJ} , 1.6 V_{CJ} , 1.0 V_{CJ} (V_{CJ} – Chapman–Jouguet velocity), in the range of E_a/RT_{vN} from 3 to 16, and T_{vN}/T_0 from 1.5 to 8. Authors inform about 50% mean deviation of calculated values from the experimental data.

Nevertheless, λ and τ do not differentiate between mixtures, which are known empirically to behave differently – they do not inform about regularity of a detonation structure which condition detonability. For that reason, 3 years ago new parameters were introduced by three researchers [7] – χ and RSB, which are being validated against small-scale laboratory experiments [8].

Low values of χ parameter are expected to provide a coherent phenomenon in time and space as a result of overlapping power pulses from neighbouring particles. For higher values of χ , these power pulses will not be coherent and can lead to instabilities in the 3D reaction zone structure. Ranges of χ and respective cellular regularity [7] are presented in Tab. 1. Dimensional form of χ is called RSB, and it indicates the propensity of different reactive mixtures to develop instabilities, strong internal pressure waves and turbulence in the reaction zone [6, 7].

Tab. 1. The variation of the parameter χ computed for a wide range of mixtures and comparison with the regularity of the detonation cellular structure [7]

Mixture	χ	Cellular regularity
H ₂ /O ₂ + 70% Ar, $\phi = 1.0$	2	Very regular
C ₂ H ₂ /O ₂ + 75% Ar, $\phi = 1.0$	20	Regular
H ₂ /Air, $\phi = 1.0$	60	Irregular
C ₂ H ₂ /Air, $\phi = 1.0$	110	Irregular
C ₂ H ₂ /O ₂ , $\phi = 1.0$	310	Irregular
C ₃ H ₈ /Air, $\phi = 1.0$	370	Irregular with substructure
CH ₄ /Air, $\phi = 1.0$	2800	Very irregular with substructure
H ₂ /Air, $\phi = 0.5$	3300	Very irregular with substructure

2. Calculations

Calculations are performed in Cantera 2.1.2 tools [4] in Matlab R2010a environment. The Konnov 0.5 detailed chemical kinetics mechanism [5] is used for chemical kinetics calculations, as its performance of combustion of syngas fuels is very good. Fig. 1. presents a workflow of calculations. The first part of calculations is determination of products composition from hydrogen – carbon monoxide – air mixture combustion as a function of combustion temperature. In the next step, these combustion products are added to the fresh mixture of hydrogen – carbon monoxide – air mixture and detonation propensity assessment is performed.

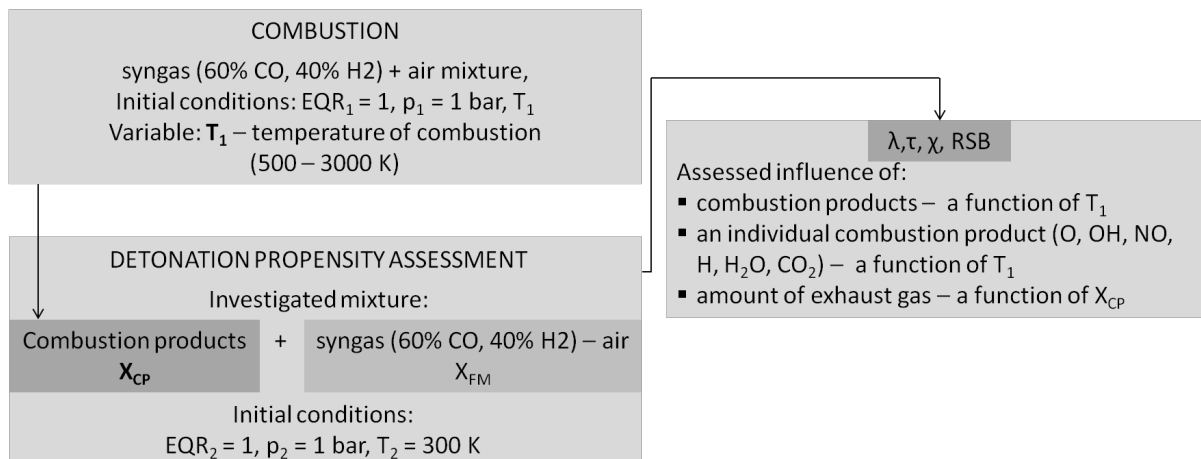


Fig. 1. The workflow of calculations

2.1. Composition of combustion products

Composition of combustion products is determined by setting a gas mixture to a state of chemical equilibrium holding temperature and pressure fixed using *equilibrate()* method from Cantera. The mixture of interest is 60% of CO and 40% of H₂ fuel added to air to reach EQR = 1 ('H₂:0.4 CO:0.6 O₂:0.5 N₂:1.88'). The pressure is 1 bar. Temperature T₁ is a variable changing from 500 to 3000 K. The calculated compositions are presented in Fig. 2.

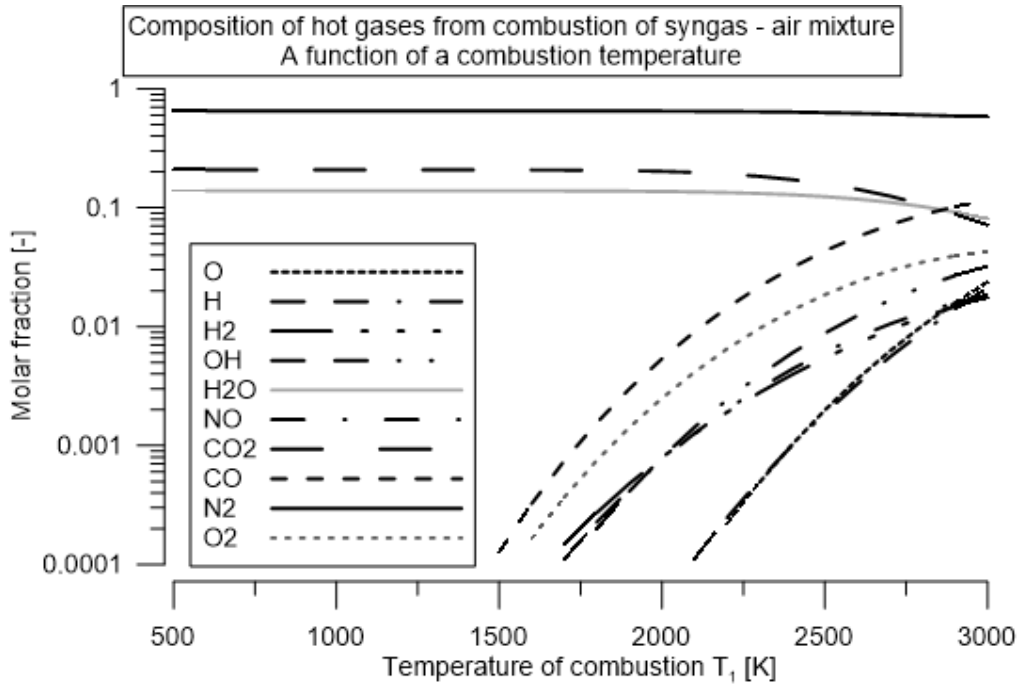


Fig. 2. The composition of combustion products as a function of combustion temperature (combusted mixture: 60% CO/40% H₂ + air, EQR = 1, p₁ = 1 bar)

Species with molar fraction higher than 0.0001 are presented on Fig. 2. In a temperature range of 500 – 1500 K the composition of products is almost constant. The main 3 species are N₂, OH, H₂O. Above 1500 K next species start to appear – firstly CO, then O₂, OH, NO, H₂, O, H, of which molar fractions increase with temperature.

2.2. Detonability assessment

In the next step a mixture consisting of X_{CP} = 20% of combustion products and X_{FM} = 80% of syngas (60% CO, 40% H₂) – air mixture (EQR=1) is investigated. Four detonability parameters (λ , τ , RSB, χ) are calculated as a function of combustion temperature T₁. Initial conditions for detonation calculations are T₂ = 300 K and p₂ = 1 bar.

2.2.1. Calculation of λ , τ , RSB and χ

Formulas used in the paper for λ , τ , RSB, χ calculations are as follows:

– Gavrikov's detonation cell width λ :

$$\log\left(\frac{\lambda}{\delta}\right) = Y \cdot (a \cdot Y - b) + X \cdot [(c \cdot X - d + (e - f \cdot Y) \cdot Y)] + \quad (1)$$

$$+ g \cdot \ln(Y) + (X) + Y \cdot (i/X - k \cdot Y/X^m) - j,$$

where: X = E_a/RT_{vN}, Y = T_{vN}/T₀, δ – reaction zone width. Constants a – m are presented in Tab. 2.

Tab. 2. Parameters used in Equation 1. [2]

Parameters	Values	Parameters	Values
a	-0.007843787493	g	-1.446582357
b	0.1777662961	h	8.730494354
c	0.02371845901	i	4.599907939
d	1.477047968	j	7.443410379
e	0.1545112957	k	0.4058325462
f	0.01547021569	m	1.453392165

– χ and RSB parameters:

$$\chi = \frac{E_a}{RT} \cdot \frac{\tau}{\tau_r} \cdot \frac{Q}{RT}, \quad (2)$$

$$RSB = \chi \cdot \frac{c}{\tau}, \quad (3)$$

where:

τ_r – time of reaction,

c – speed of sound,

Q/RT – dimensionless heat release.

– ignition delay time behind the detonation shock wave τ is ignition delay time behind a shock wave travelling with Chapman – Jouguet velocity.

Dimensionless χ parameter and its dimensional form RSB [6, 7] are calculated assuming that initial state is the von Neumann state and a detonation wave propagates with Chapman-Jouguet velocity.

The von Neumann state is calculated using $znd()$ function from S&D Toolbox [9], CJ velocity $CJ_speed()$. Mixture composition is unchanged across detonation wave (frozen Hugoniot), $PostShock_fr()$.

Dependence (2) can be written as:

$$\chi = \frac{\tau_i}{\tau_r} \frac{E_a}{RT_{vn}} \frac{Q}{RT_0} \left(\frac{T_{vn}}{T_0} \right)^{-1}. \quad (4)$$

Dimensionless activation energy E_a/RT_{vN} needed to λ , RSB, and χ calculations is assessed based on reaction times behind shocks τ and τ_+ with two different speed D and D_+ . The difference in these times is an effect of different corresponding temperatures T_{vn} and T_{vn+} .

$$\frac{E_a}{RT_{vn}} = \frac{1}{T_{vn}} \frac{\ln(\tau_+) - \ln(\tau)}{\frac{1}{T_{vn+}} - \frac{1}{T_{vn}}} \quad (5)$$

Next equations origin from CJ theory. The adiabatic exponent γ and molar masses remain the same across the shock (frozen Hugoniot) and $M_{CJ} \gg 1$.

$$\frac{Q}{RT_0} = \frac{\gamma}{2(\gamma^2 - 1)} \left(M_{CJ} - \frac{1}{M_{CJ}} \right)^2, \quad (6)$$

$$\frac{T_{vn}}{T_0} = 1 + \frac{2(\gamma - 1)}{(\gamma + 1)^2} \frac{\gamma M_{CJ}^2 + 1}{M_{CJ}^2} (M_{CJ}^2 - 1). \quad (7)$$

2.2.2. Influence of combustion products on the investigated mixture

Figure 3. presents the influence of combustion products from Fig. 2. on detonability parameters of the investigated mixture. By the black arrows baseline level of detonability indicators is marked. Baseline level means no combustion products in the mixture ($X_{CP} = 0\%$) – $X_{FM} = 100\%$ of syngas – air mixture.

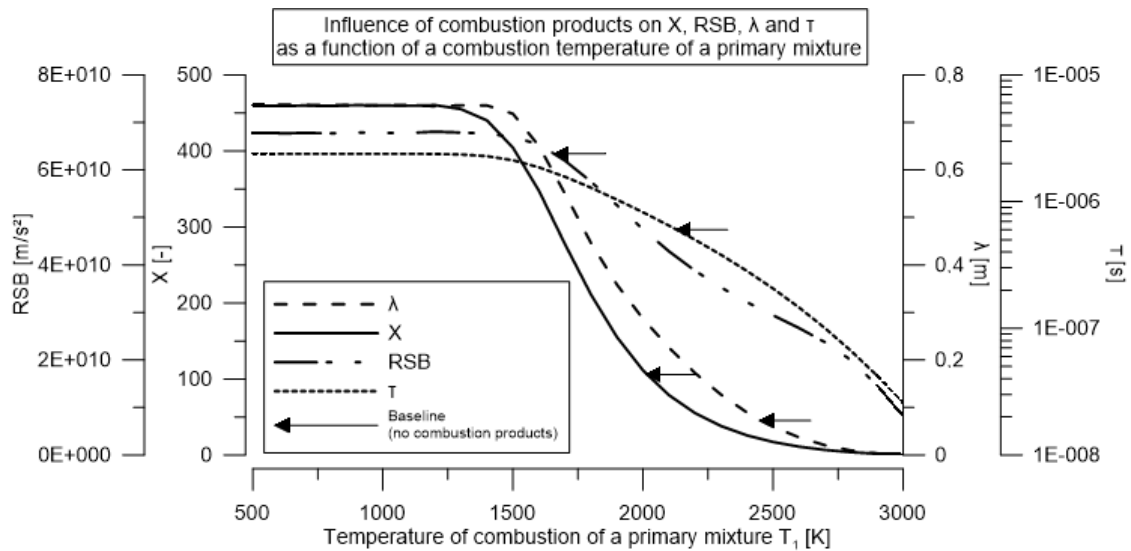


Fig. 3. The influence of combustion products on detonation propensity parameters

In the temperature range of 500 – 1500 K λ , τ , RSB and χ are constant. The behaviour is consistent with observation based on Fig. 2. – in this range, the composition of combustion products is almost constant. With increase of combustion temperature T_1 all detonation propensity parameters decreases, which means that the mixture is more prone to development of a detonation. Addition of combustion products when temperature of combustion is relatively small works as an inhibitor of detonation propensity largely due to dilution with N_2 . The moment when combustion products stop to work as an inhibitor and start to advance detonability is different for all four parameters. The detonation cell width starts to be smaller than compared to the mixture without combustion products when temperature of combustion increases above 2447 K, τ for temperature higher than 2128 K, χ for 2011 K and RSB for 1658 K. The adiabatic flame temperature of this particular syngas – air mixture is 2447 K, which means that only the detonation cell is bigger than the baseline in the whole temperature range, which theoretically can be reached. The rest indicators predict that the fraction of combustion products into the flammable mixture advance detonation propensity above temperatures mentioned above.

2.2.3. Influence of an individual combustion product on detonability parameters

In this section influence of an individual combustion product on a detonation cell width λ , an ignition delay time τ , RSB and χ parameters is presented. To the previous amount of syngas – air mixture calculated amount (Fig. 2.) of a combustion product is added (the amounts of a mixture and a product are the same – only molar fractions change). Influence of species, which are not present in syngas – air mixture (N_2 , O_2 , H_2 , CO), are investigated (O , H_2O , CO_2 , H , NO , OH). This influence is a cumulate effect of reactivity and a molar fraction of a species present in combustion products (Fig. 2.).

Figure 4. presents influence of an individual combustion product on a detonation cell width λ . The baseline level (no combustion products) is marked by a thick line. Carbon dioxide is an inhibitor of detonability. Decrease of λ with temperature is an effect of decrease of CO_2 molar fraction (Fig. 2.). Water has a similar effect on λ to CO_2 . Water and carbon dioxide dilute a flammable mixture. Presence of the next species advances detonation propensity. OH , O and H have the strongest influence, as they are highly chemically reactive towards other substances. The influence of NO is relatively weak.

The detonation cell width for a baseline case might be overestimated by calculations. Syngas detonation cellular structure is not well tested. Austin and Shepherd [1] investigated experimentally detonation cell widths of stoichiometric hydrogen – carbon monoxide – air

mixtures, but the exact composition from this paper was not tested. The paper of Austin and Shepherd may indicate that λ for the investigated mixture is very similar to a detonation cell width of stoichiometric hydrogen – air mixture, which is equal to 8 mm. However, one must keep in mind that for irregular structures it is hard for experimentally assess with high precision a detonation cell width. Behaviour of τ , RSB and χ vs. a temperature of combustion of a primary mixture is analogical to the detonation cell width.

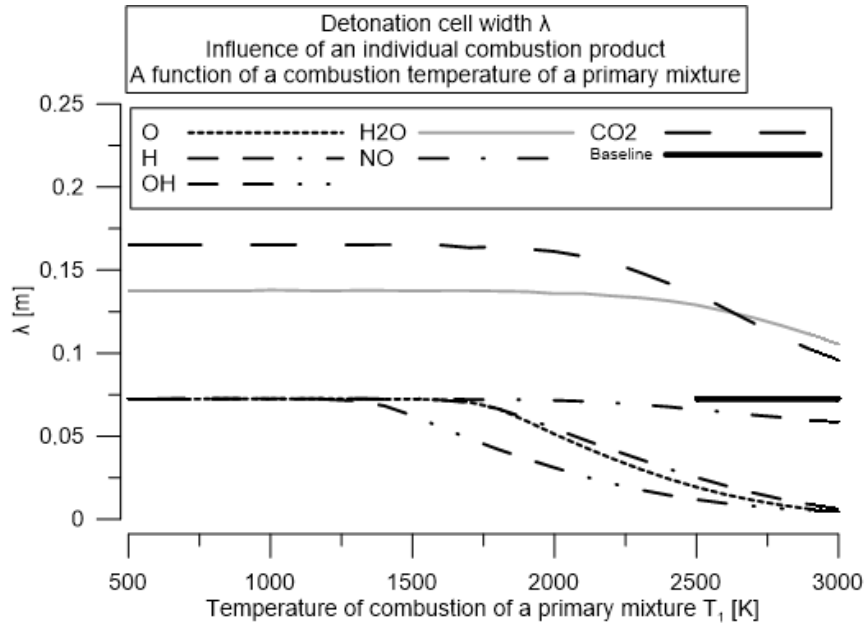


Fig. 4. The influence of an individual combustion product on a detonation cell width λ

2.2.4. Influence of X_{CP} on λ , τ , RSB and χ

Figure 5. presents the influence of combustion products molar fraction X_{CP} in the investigated mixture on detonability parameters. Calculation of the parameters is not possible for combustion products molar fraction higher than 45%. It may be an indicator that a detonation is not possible for this particular mixture when contains more than $X_{CP} = 45\%$ of exhaust gases. The most important information is that the minimum of λ , τ and χ is not for the mixture which contains only syngas and air, $X_{FM} = 100\%$. The minimum of the detonation cell width is for $X_{CP} = 2\%$ and equals 4.8 mm, when for the mixture without combustion products it is 7.2 mm. It is a decrease of 33%. The minimum of τ it for $X_{CP} = 6\%$ and it is equal to 0.376 μs , when for $X_{CP} = 0\%$ it is 0.598 μs . It is a decrease of 37%. The minimum of χ is for $X_{CP} = 9\%$ and it is 48, when for the mixture without exhaust gases it is 106. It is a decrease of 55%. Small amount of exhaust gases may significantly advance a detonability of a mixture.

3. Conclusion

The method presented in the paper can be used for initial assessment of exhaust gases influence on detonation propensity when added to fuel – air mixtures. This assessment may be crucial in industrial installations, when during an accident uncontrolled flame produces combustion products, which may be under favourable conditions advance a detonation propensity of the rest mixture.

The next step of developing the method is to investigate time dependence of combustion products composition. Practically a thermodynamic equilibrium state, which is used for combustion products composition calculations, is reached after a long time. Then, influence of pressure, equivalence ratio of a primary mixture and combustion products with molar fraction lower than 0.0001 need to be evaluated.

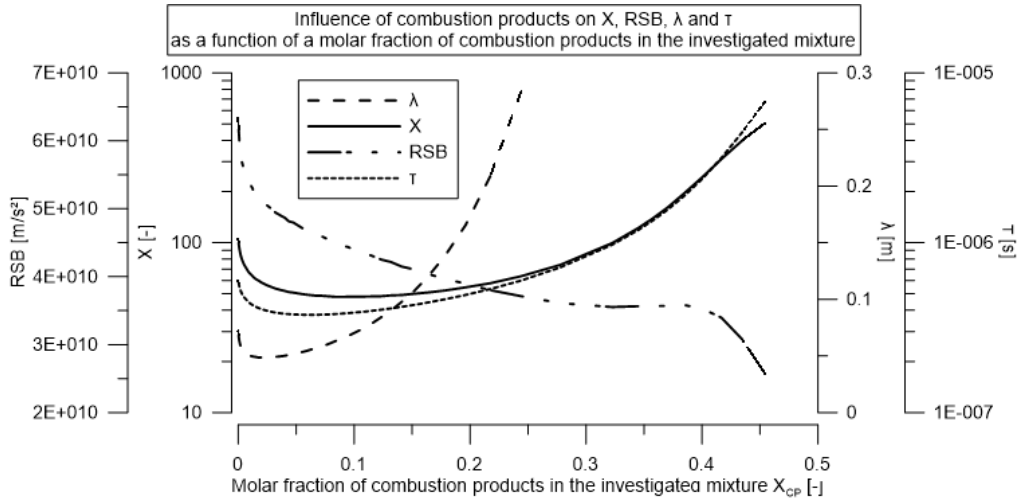


Fig. 5. The influence of combustion products molar fraction X_{CP} in the investigated mixture on λ , τ , RSB and χ parameters

References

- [1] Austin, J. M., Shepherd J. E., *Detonation in hydrocarbon fuel blends*, Combustion and Flame, No. 132, pp. 79-90, 2003.
- [2] Fickett, W., Davis W. C., *Detonation*, University of California Press, Berkeley – Los Angeles – London 1979.
- [3] Gavrikov, A. I., Efimenko, A. A., Dorofeev S. B., *A Model for Detonation Cell Size Prediction from Chemical Kinetics*, Combustion And Flame, No. 120, pp. 19-33, 2000.
- [4] Goodwin, D. G., Moffat H. K., Speth R. L., *Cantera: An object- oriented software toolkit for chemical kinetics, thermodynamics, and transport processes*, <http://www.cantera.org>, Version 2.1.2, 2015.
- [5] Konnov A. A., *Detailed reaction mechanism for small hydrocarbons combustion*, Release 0.5, available at <http://homepages.vub.ac.be/~akonnov/>, 2000.
- [6] Radulescu, M. I., Borzou, B., *Evaluation of hydrogen, propane and methane-air detonations instability and detonability*, International Conference of Hydrogen Safety, 2013.
- [7] Radulescu, M. I., Sharpe, G. J., Bradley D., *A universal parameter quantifying explosion hazards, detonability and hot spot formation: χ number*, ISFEH7 Proceedings of the Seventh International Seminar, 2013.
- [8] Saif, M., Wang, W., Pękalski, A., Levin, M., Radulescu, M. I., *Chapman-Jouguet deflagrations and their transition to detonation*, Proceedings of the Combustion Institute, Seoul 2016.
- [9] Shock & Detonation Toolbox, Graduate Aerospace Laboratories of the California Institute of Technology, Caltech, http://www2.galcit.caltech.edu/EDL/public/cantera/html/SD_Toolbox.

