Chemical inhibiting of hydrogen-air detonations

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Outline

- **Introduction**
- **Theoretical studies**
- Classical 1D approach (ZND-model)
- Detailed reaction mechanism
- Reaction mechanism for inhibitor
- Solution algorithm
- Results of calculations for H2 – air
- Results of calculations for H2 – air – inhibitor
- **Experimental studies**
- Experimental procedure
- Experimental results for H2 – air
- Experimental results for H2 – air – inhibitor
- **Conclusions**
- **Acknowledgments**

Introduction

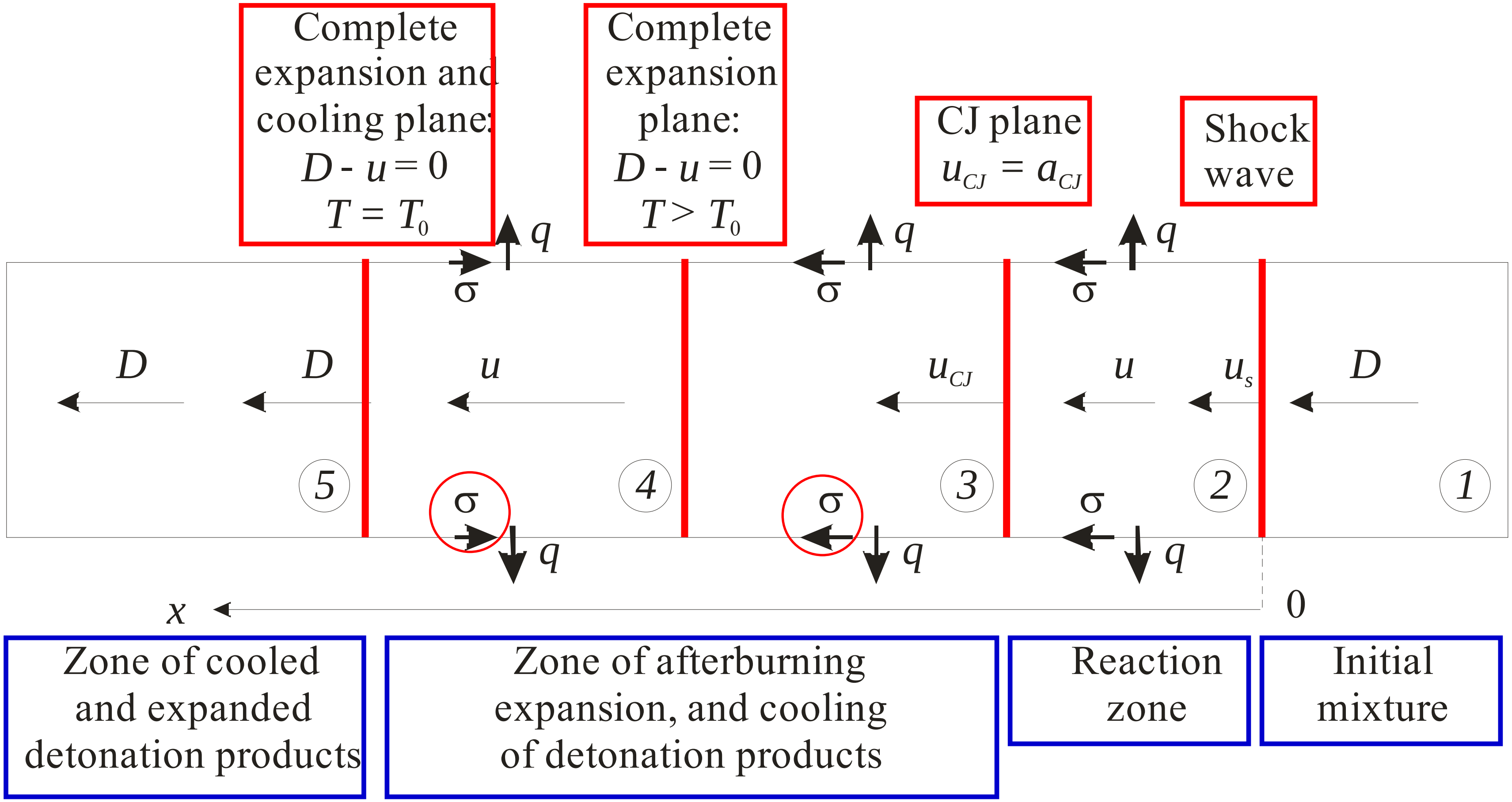
- Ideas on **chemical inhibiting of hydrogen – air detonations** were put forward long ago at testing piston engines operating on hydrogen.
- As **detonation suppression additives**, methane, iodine, iodine hydrogen, organic iodeeds, as well as various metalorganic and nitrogen-organic compounds were considered.
- The effect of detonation suppression additives on the detonation properties of hydrogen – air mixtures were explained mostly by **the low-temperature reactions of chain termination.**
- The search for effective detonation suppression additives has been revived recently in view of new developments in **hydrogen technologies**, in particular fuel cells.
- Recent studies demonstrate that small **additives of unsaturated hydrocarbons to hydrogen – air mixtures** can inhibit detonations due to termination of high-temperature chain-branching oxidation reactions.
- **1D Zel'dovich theory of detonability limits** was proved to provide satisfactory quantitative predictions for detonability limits depending on mixture composition, initial temperature and pressure, as well as the percentage of inert diluents in hydrogen – air mixture.

Objective

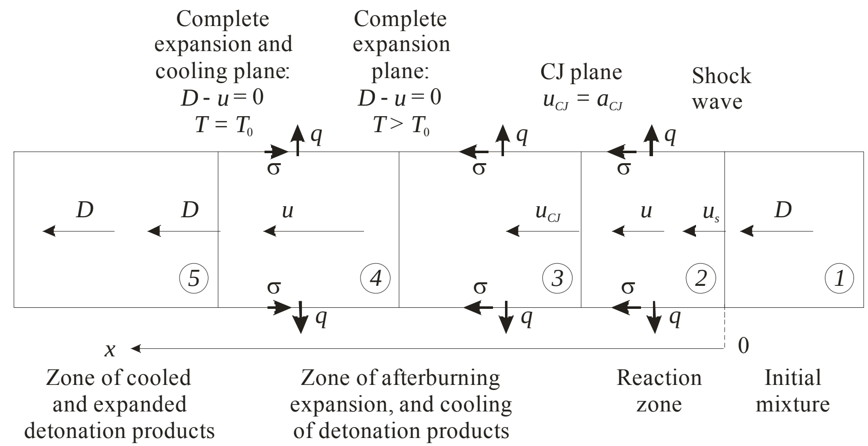
The objective of this work is to apply the **1D theory of detonability limits** to the problem of chemical inhibiting of hydrogen – air detonations by small additives of effective gaseous detonation-suppression agents.

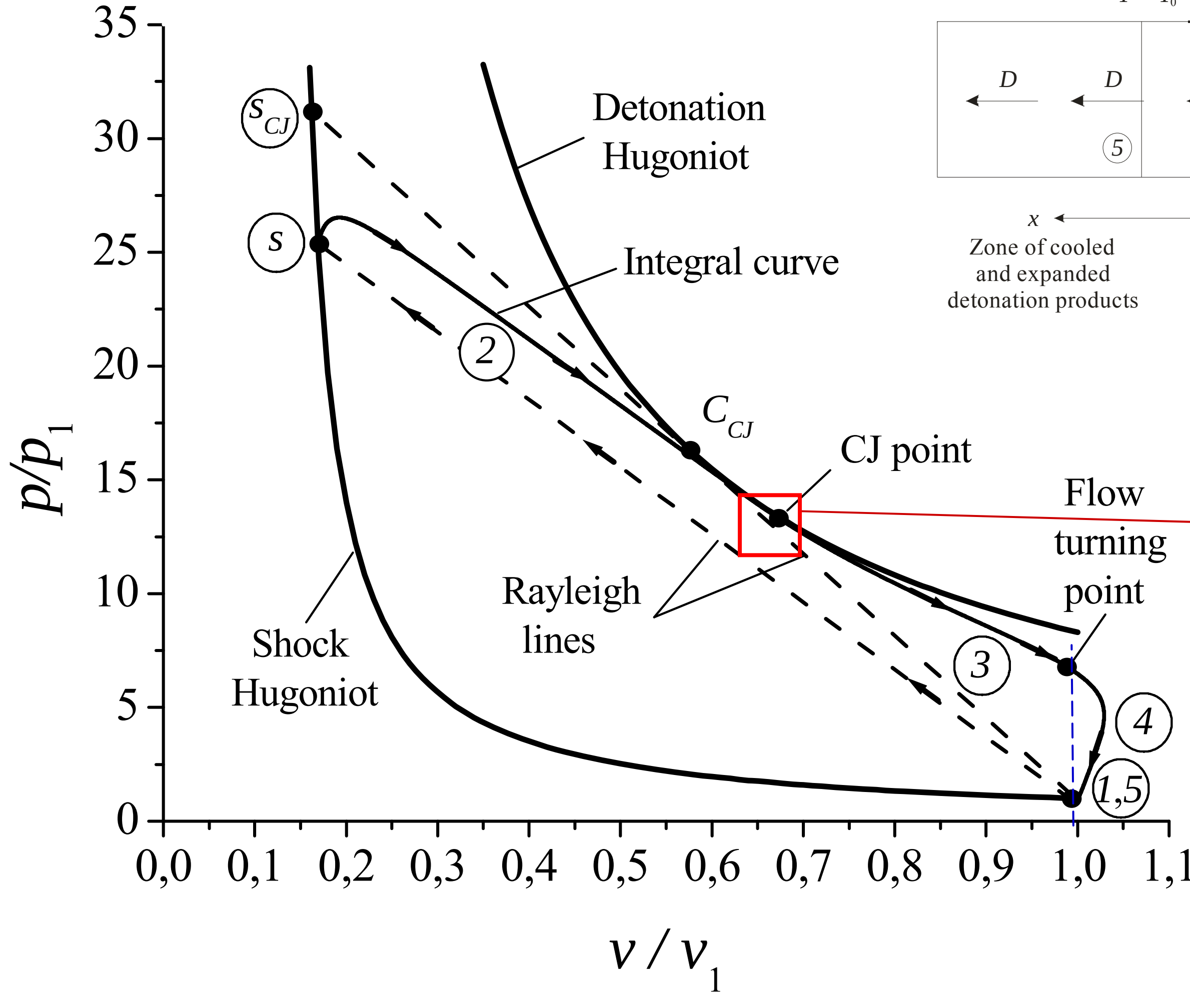
Theoretical studies

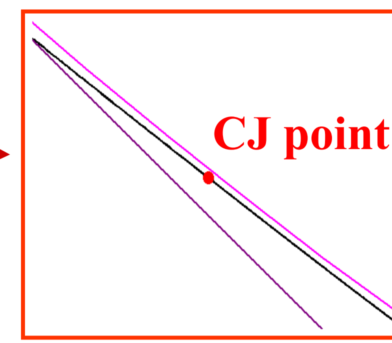
Structure of 1D steady-state detonation



Variation of mixture state







Governing equations

Zeldovich (1940), Rybanin (1966), Frolov (1986)

$$\frac{U}{v} = \frac{D}{v_o};$$

$$\frac{d(p + \frac{U^2}{v})}{dx} = \frac{\Pi}{\Phi} \cdot \sigma;$$

$$\frac{d\left[\frac{U}{v} \cdot (H + \frac{U^2}{2})\right]}{dx} = \frac{\Pi}{\Phi} \cdot (-q + \sigma \cdot D).$$

Skin friction (→ σ)

Heat flux (→ q)

Reynolds number

$$\mathrm{Re} = \frac{\rho \cdot d \cdot w}{\eta}$$

Drag coefficient $10^5 < \mathrm{Re} < 10^6$

$$C_f = \frac{0.3164}{\mathrm{Re}^{0.25}}$$

Heat transfer coefficient

$$\alpha = \lambda \cdot \frac{Nu}{d}$$

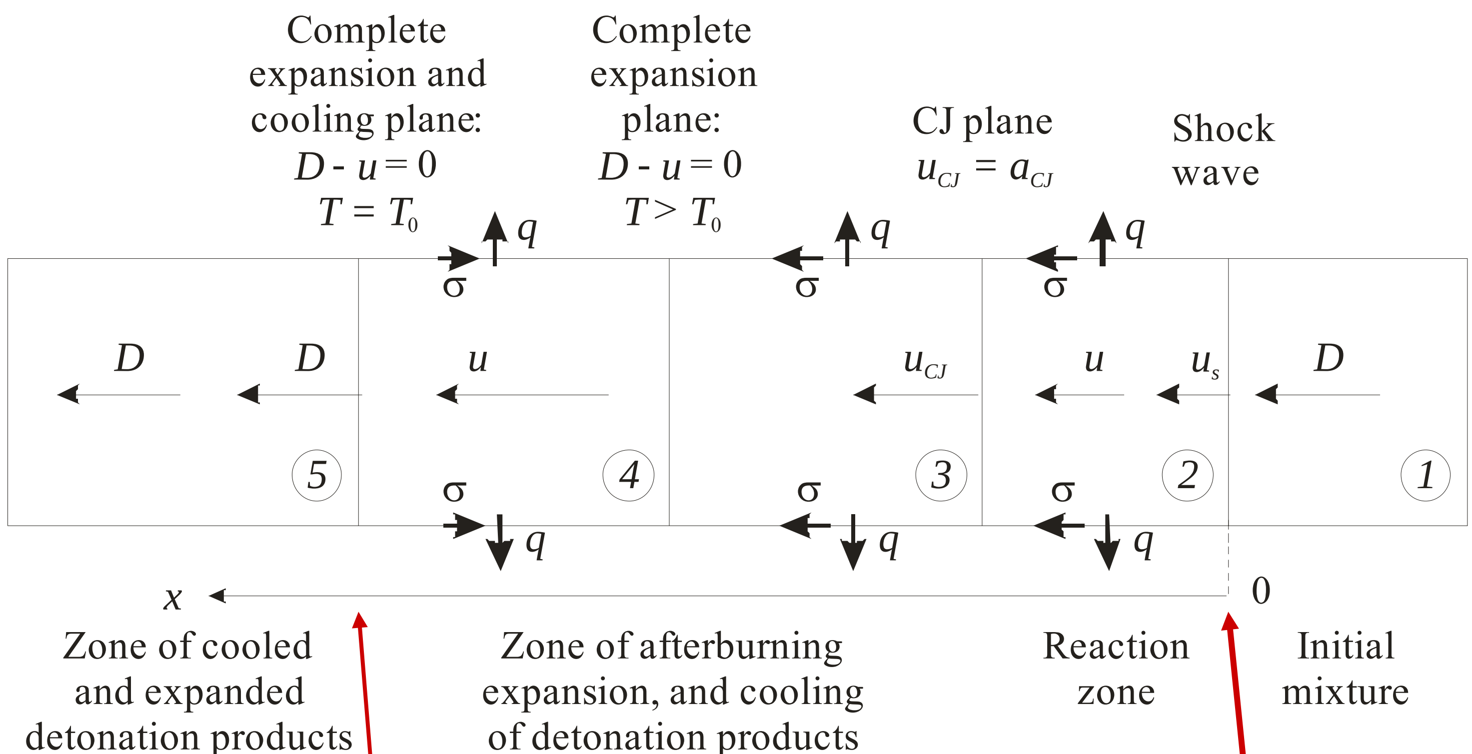
$$Nu \sim C_h \,\mathrm{Re}$$

Reynolds analogy

$$C_h = \tfrac{1}{2} \cdot C_f$$

+ Chemical kinetics

Boundary conditions



$$x \to \infty: \quad \rho \to \rho_1; T \to T_1$$

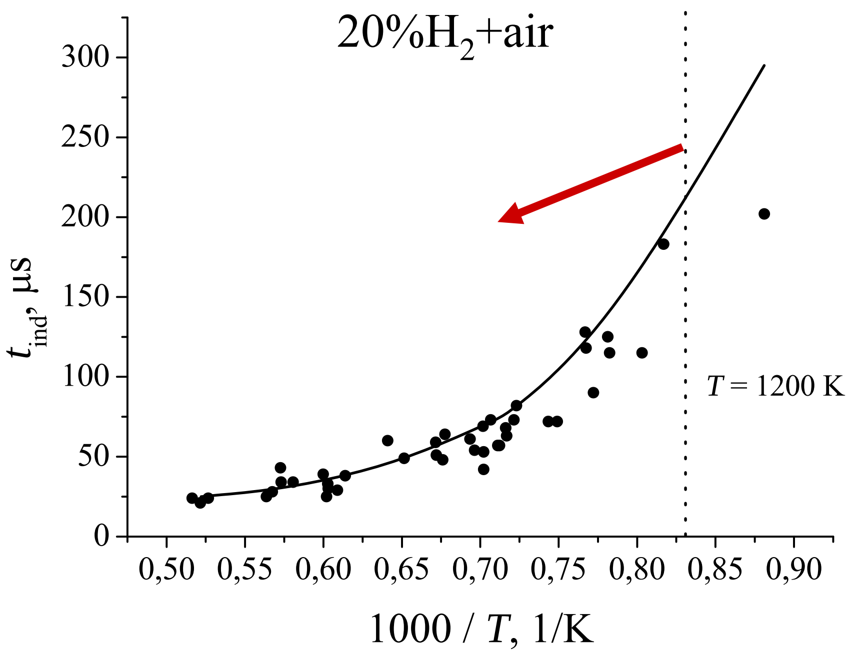
$$\rho_s u_s = \rho_1 D,$$

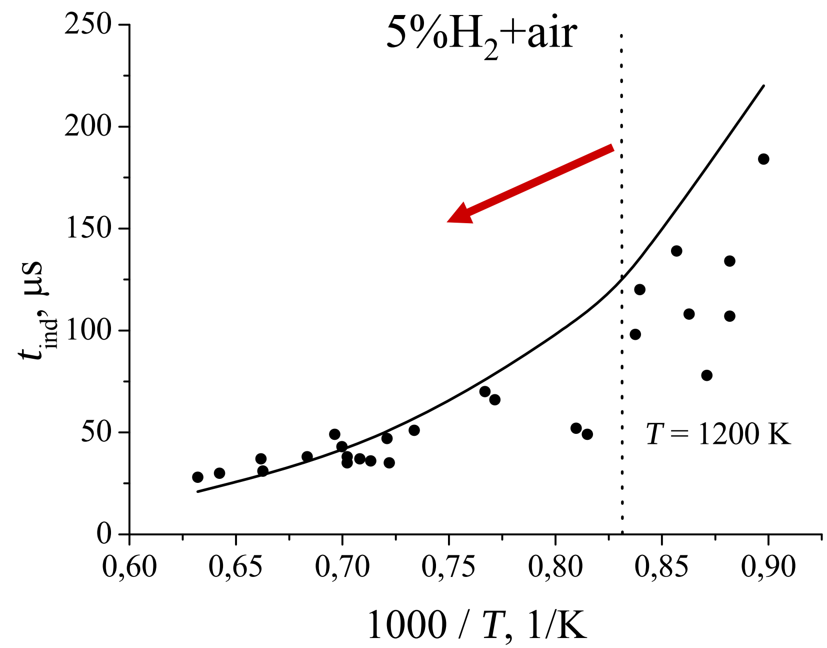
$$p_s + \rho_s u_s^2 = p_1 + \rho_1 D^2,$$

$$\frac{1}{\rho_s}\left(\sum_{i=1}^{N} H_i c_i\right)_s + u_s^2/2 = \frac{1}{\rho_1}\left(\sum_{i=1}^{N} H_i c_i\right)_1 + D^2/2,$$

$$(c_i)_s = (c_i)_1$$

Validation of hydrogen oxidation mechanism





Exp. Fukutani et al. (1999)

Temperature range of interest T > 1200 K

Reaction mechanism: inhibitor C3H6 (propylene)

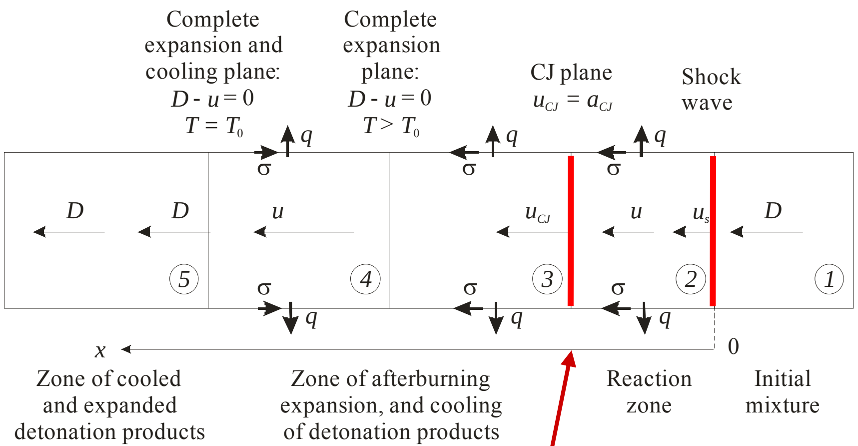
$$C_3H_6 + H\,(+M) \rightarrow C_3H_7\,(+M)$$

$$k = 1.3 \cdot 10^{10} \cdot \exp\left(-\frac{787.87}{T}\right)$$ (l, mole, s), **Tsang (1991)**

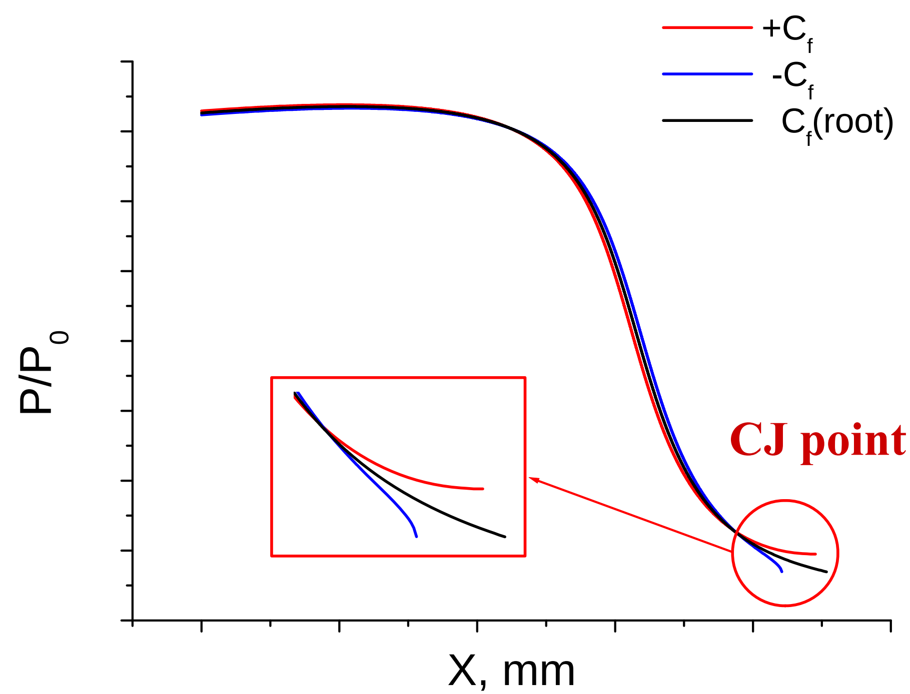
$$C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2$$

$$k = 1.26 \cdot 10^{8}$$ (l, mole, s), **Warnatz (1984)**

Solution algorithm: shooting technique

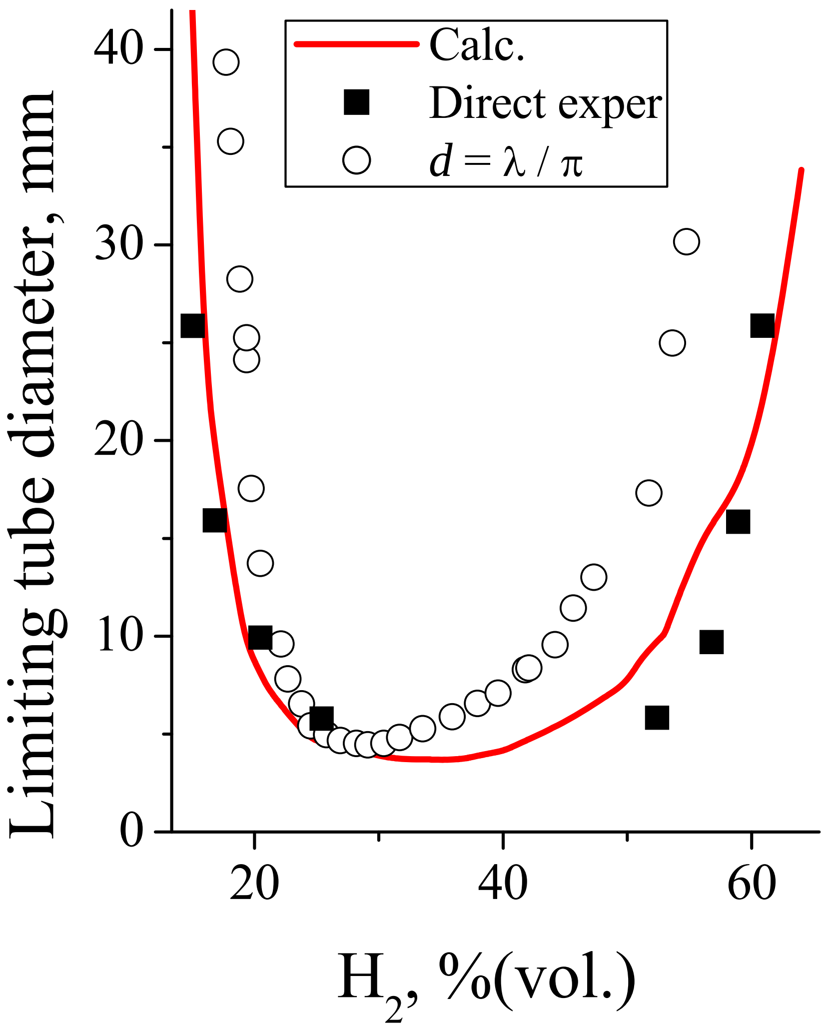


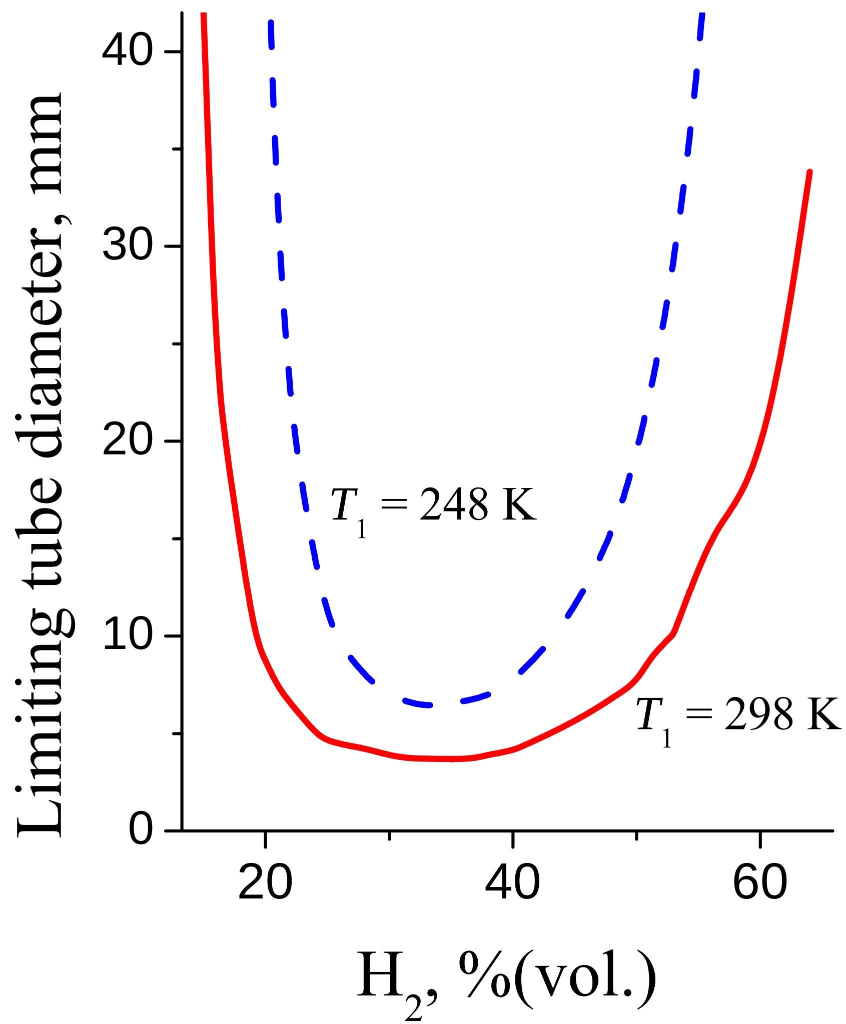
$$\frac{dV}{dx} = \frac{\varphi(P, M, ..)}{\phi(P, M, ..)} = \frac{0}{0}\bigg|_{CJ}$$



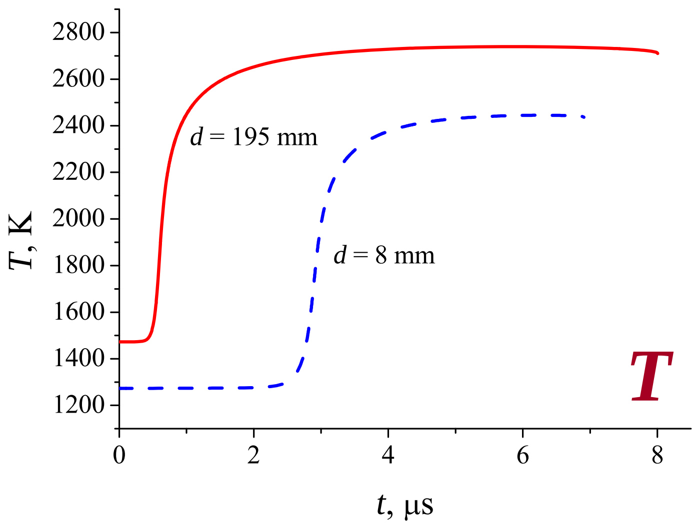
Detonation velocity *D* is the problem eigenvalue

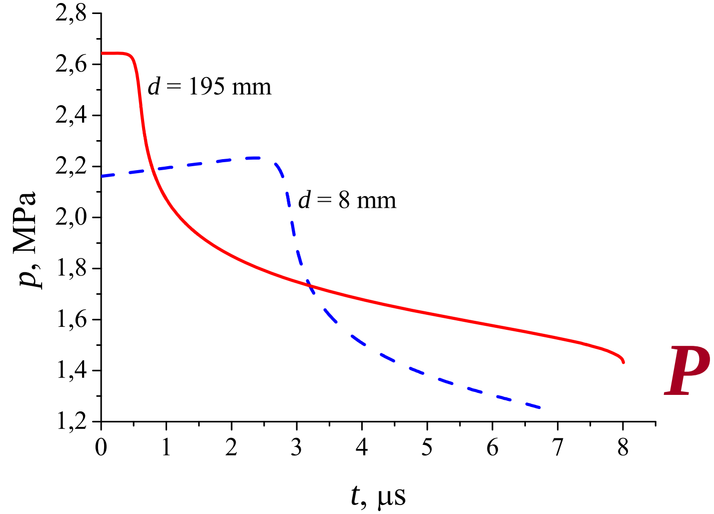
Detonability limits: hydrogen - air

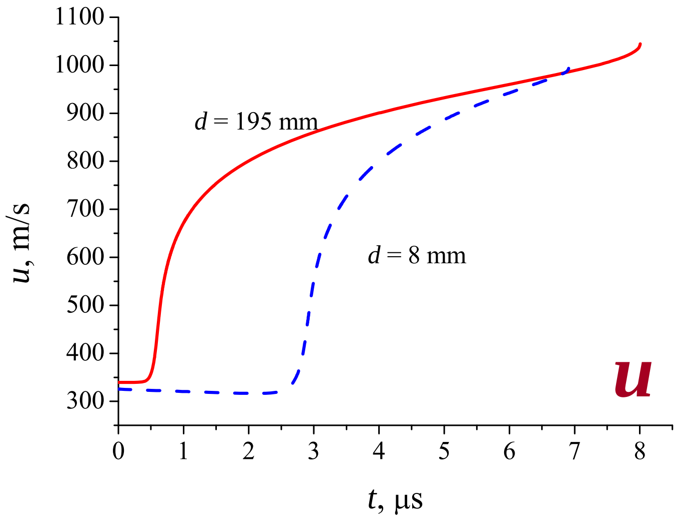


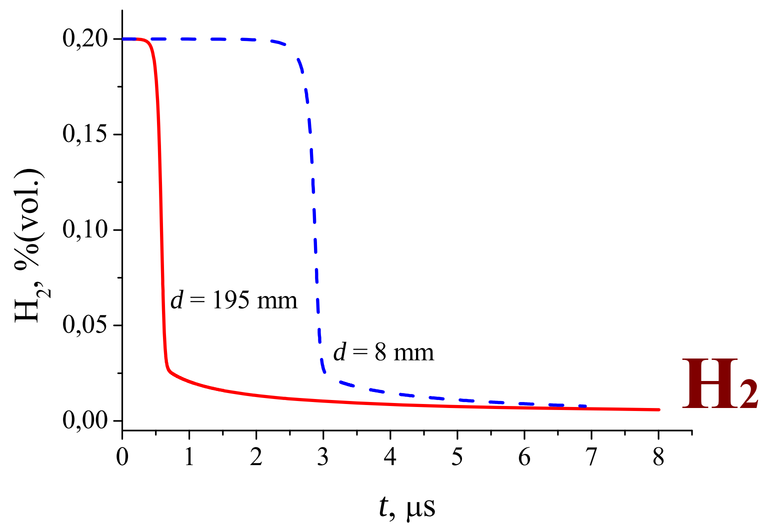


1D Detonation structure: 25%(vol.) H_2 - air

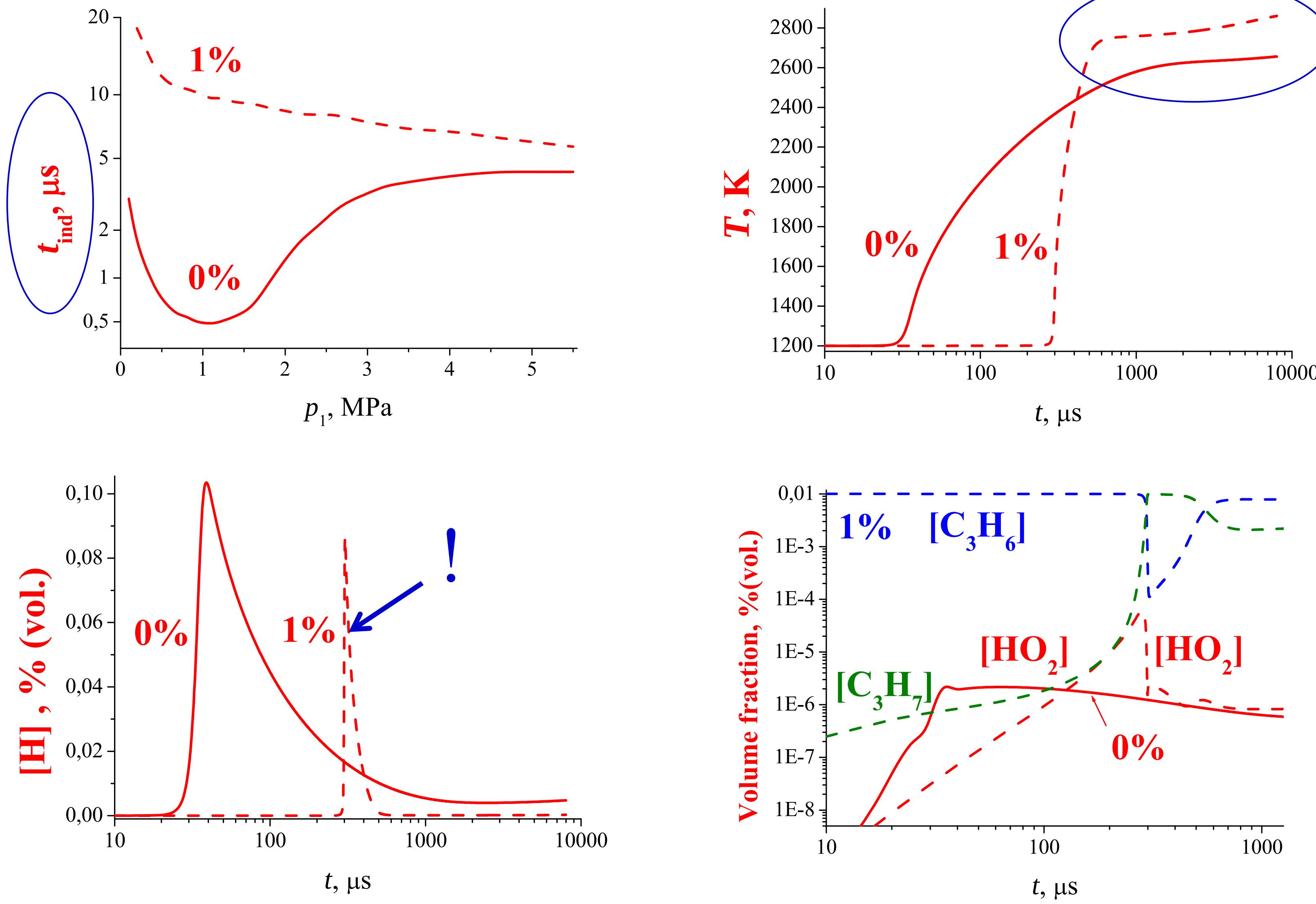




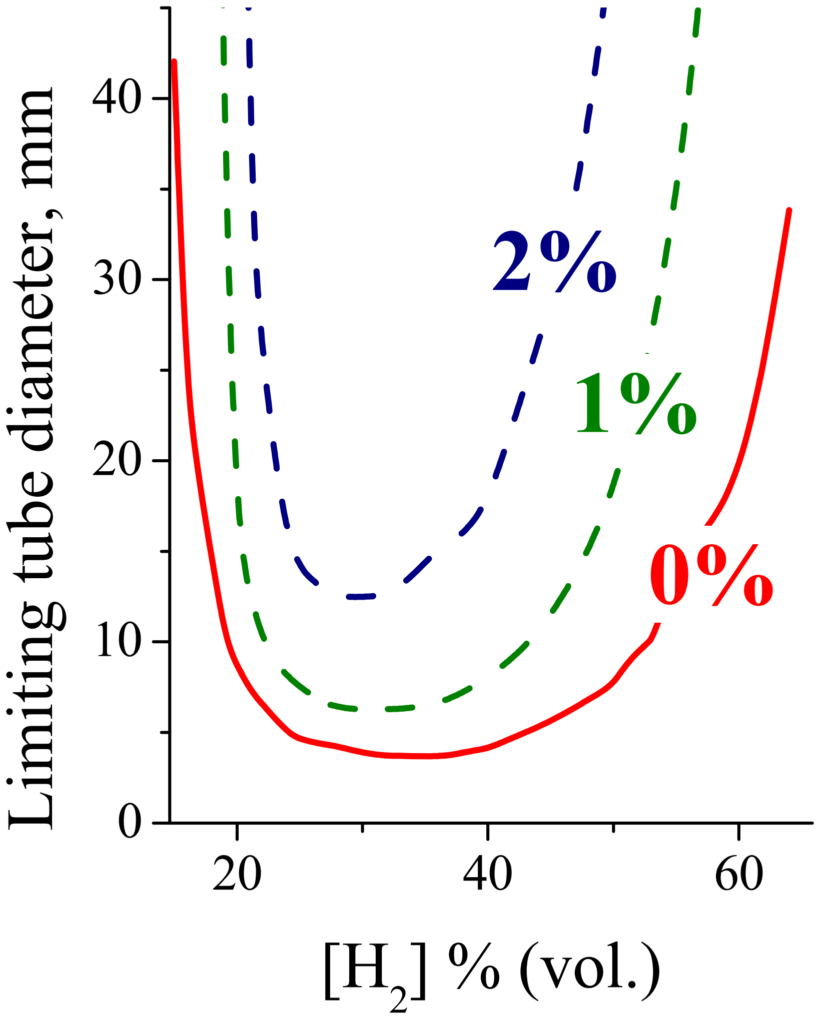




Effect of inhibitor on ignition delay of hydrogen – air mixture



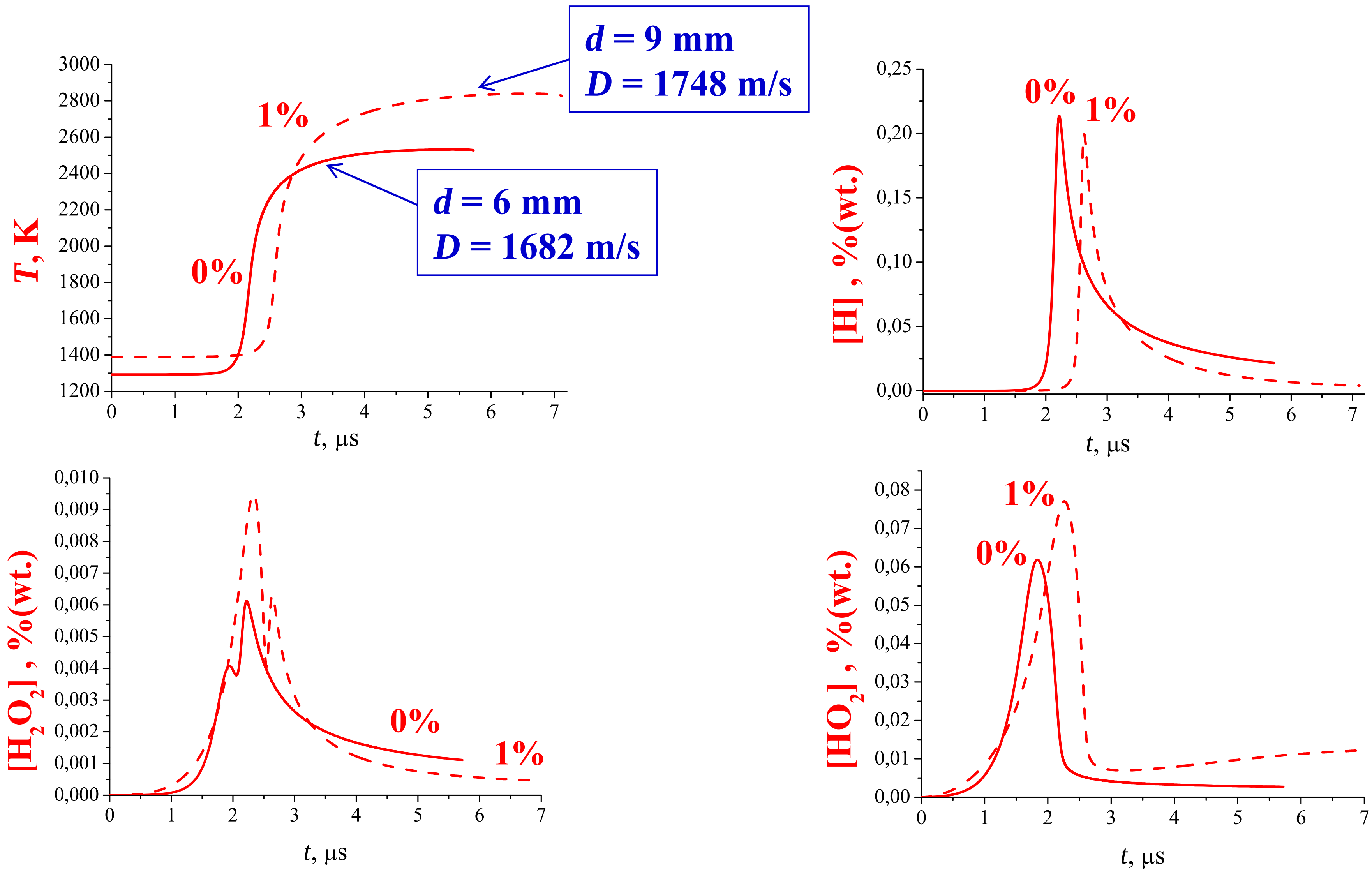
Detonability limits: hydrogen – air – inhibitor (C_3H_6)



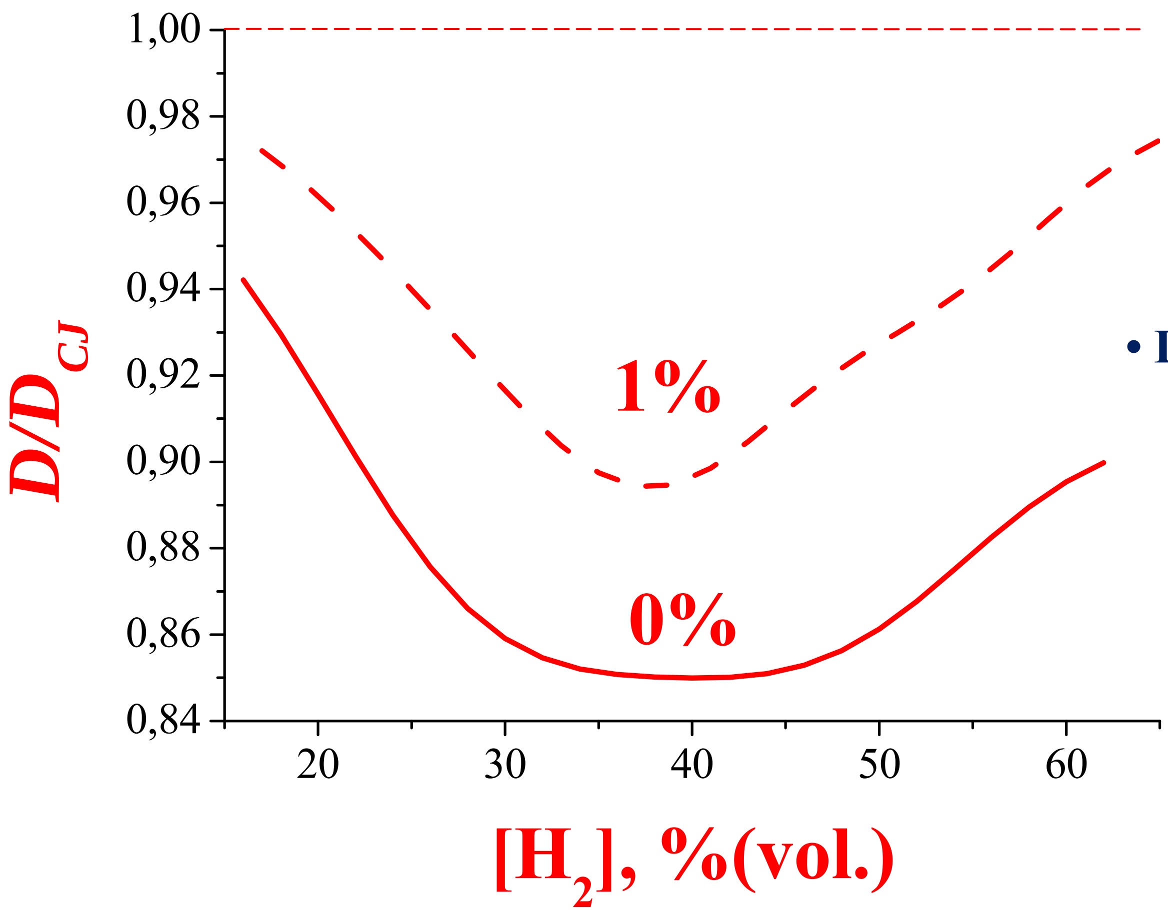
P_0 = 1 atm
T_0 = 298 K

- Narrowing of detonability limits (even in wide tubes!)
- Increasing the limiting tube diameter
- Shifting the minimum of U-curve

1D Near-limiting detonation structure: 22%(vol.) H_2 – air – inhibitor (C_3H_6)



Detonation velocity deficit without (0%) and with (1%) C_3H_6

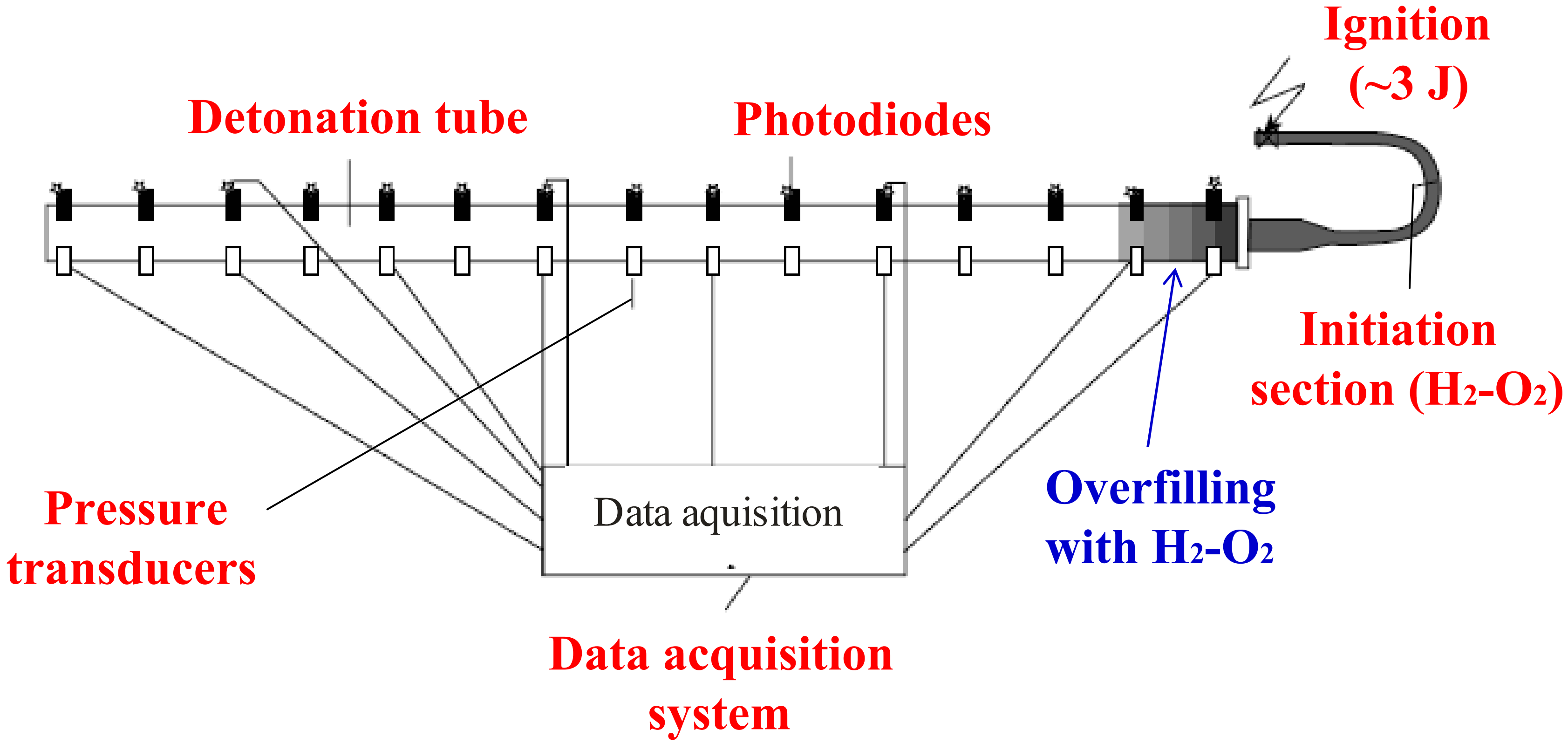


- Decreasing allowable deficit

Experimental studies

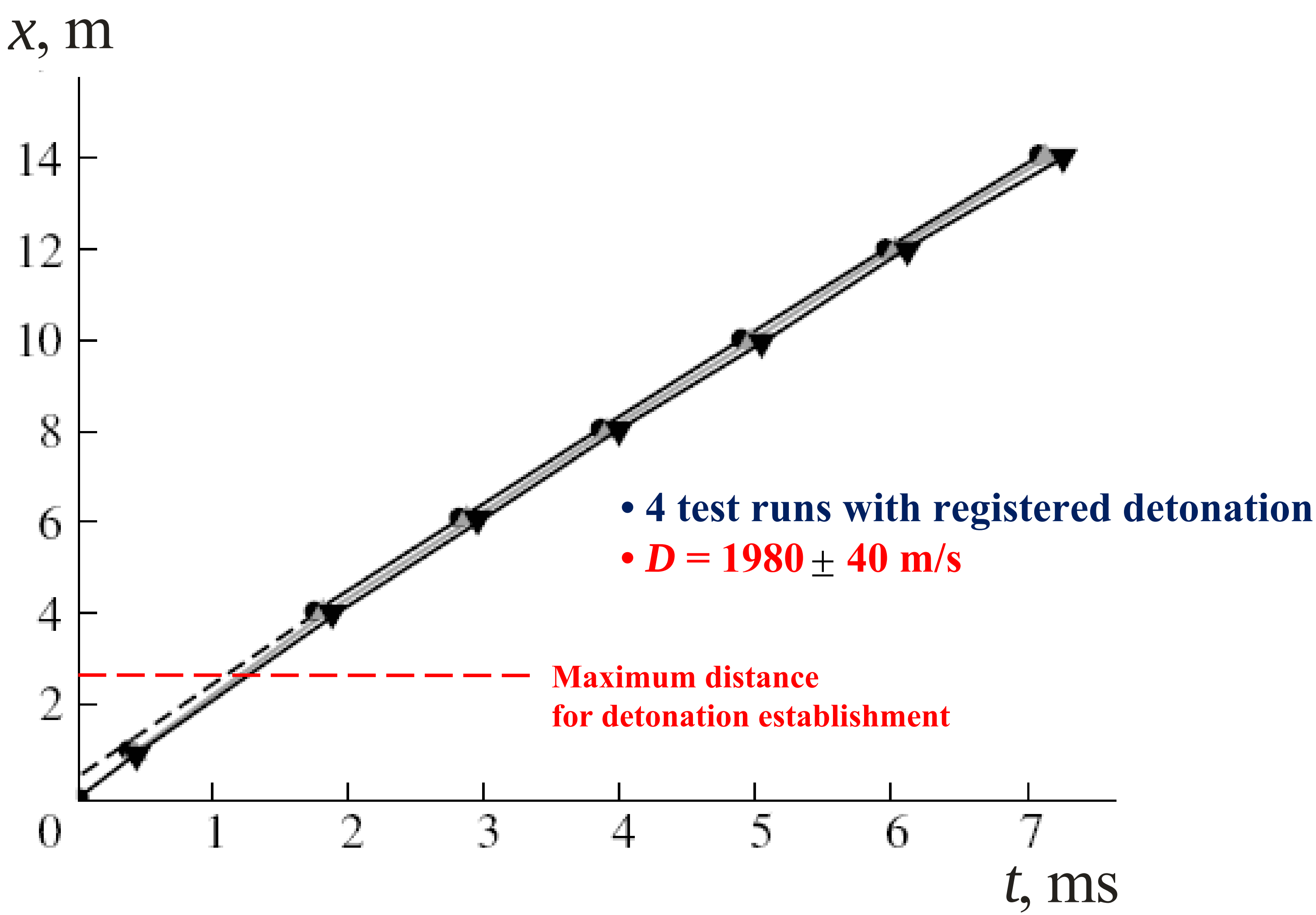
Detonation tube
at Institute of Structural Macrokinetics

Schematic of experimental setup



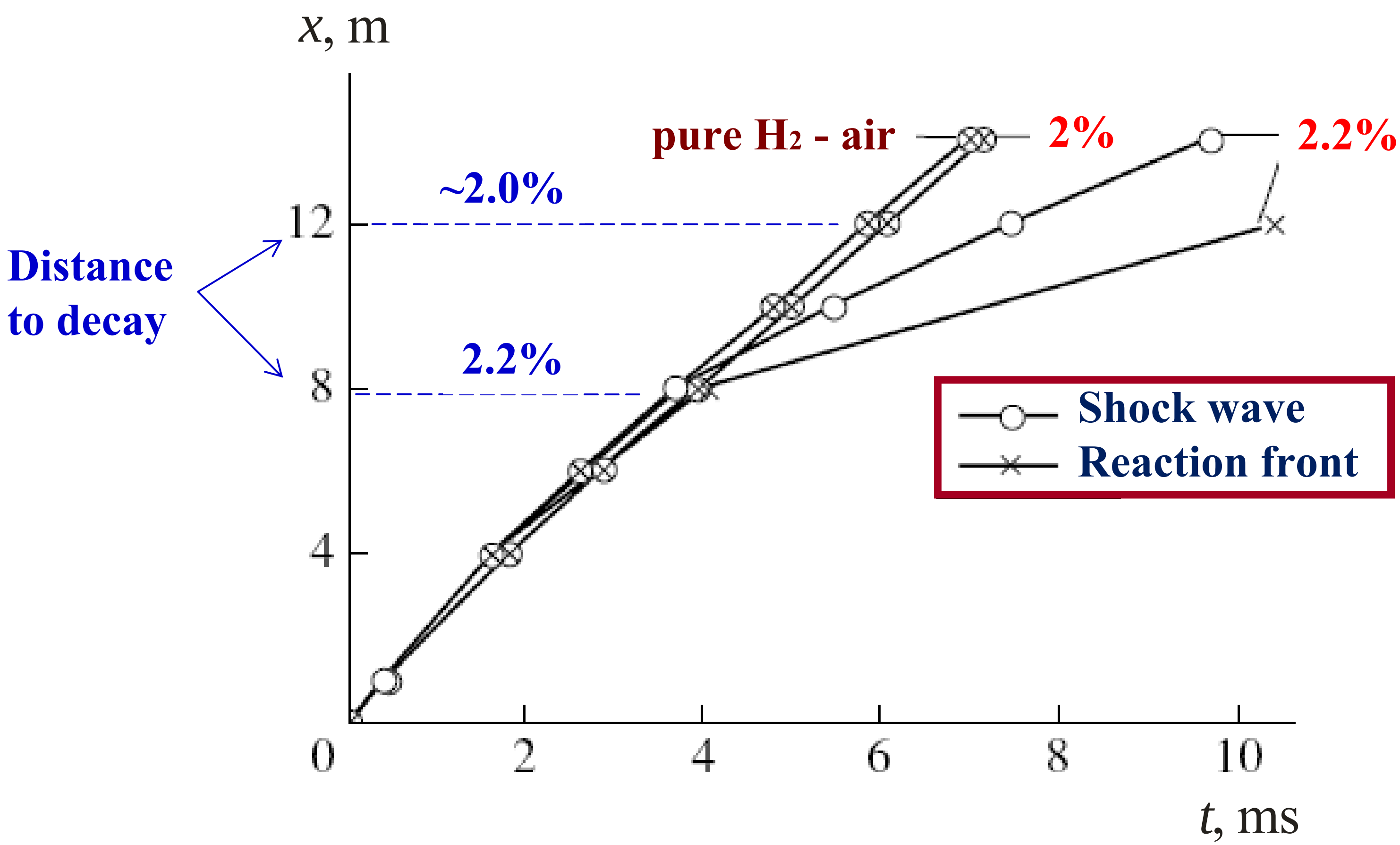
- Tube length: 15 m
- Tube diameter: 101 mm
- Mixtures: 33.8% H2 + air (+ C_4H_8)
  45.0% H2 + air (+ C_3H_6, C_4H_8)
- Initial conditions: P_0 = 1 atm, T_0 = 298 K

Time – distance diagram: 33.8% H_2 + air



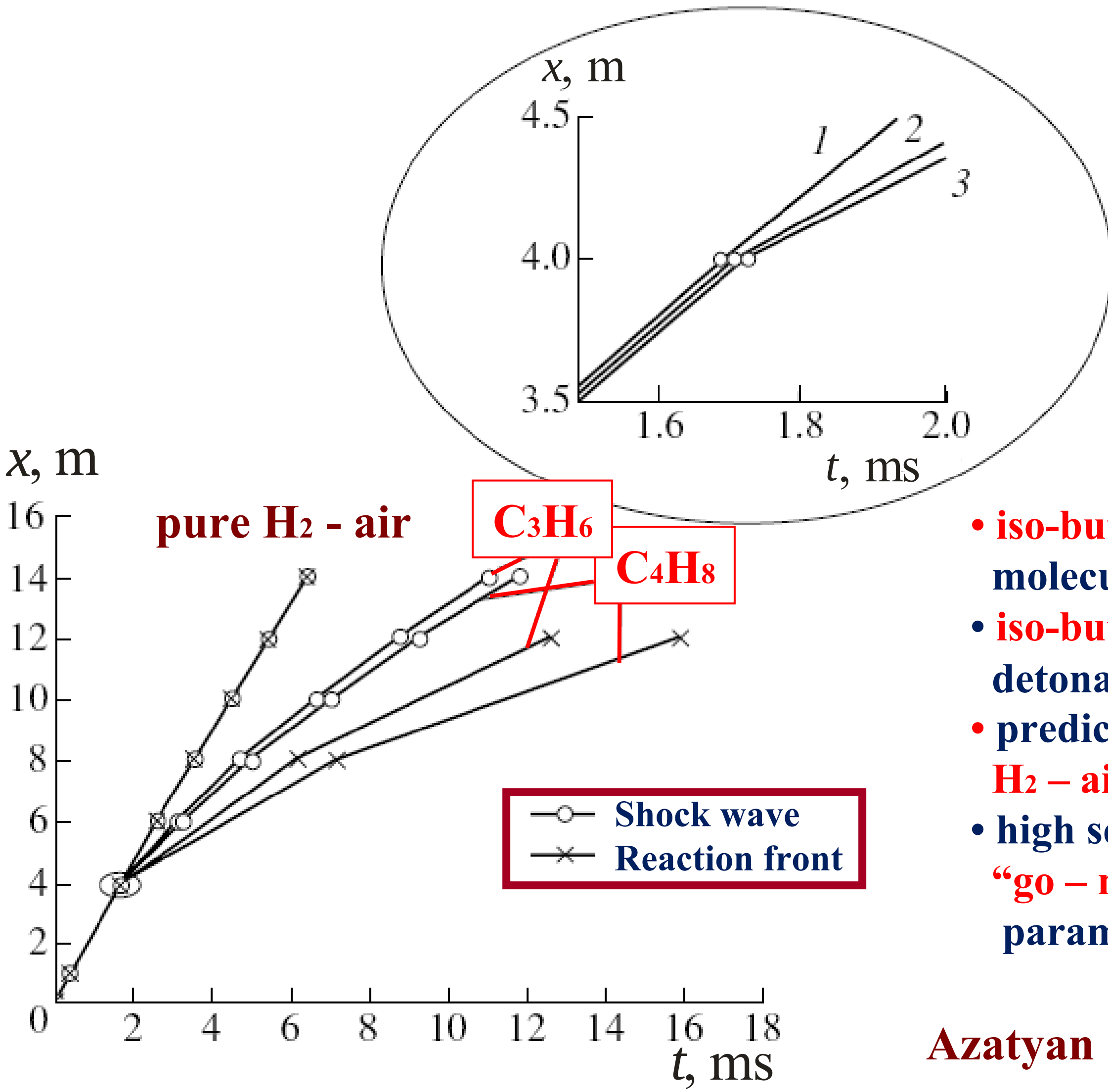
Azatyan et al. (2007)

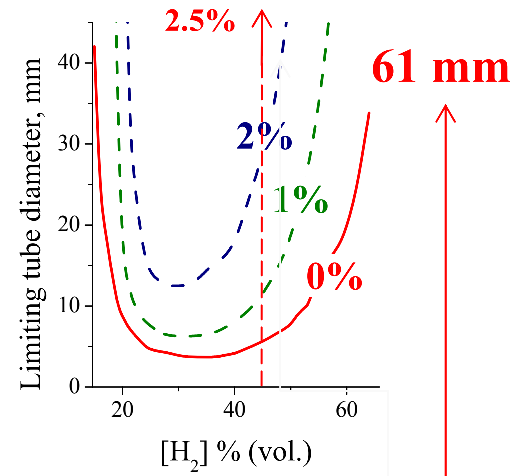
Time – distance diagram: 33.8% H_2 + air + iso-C_4H_8



Azatyan et al. (2007)

Time – distance diagram:
33.8% H_2 + air + 2.5% (iso-C_4H_8 or C_3H_6)





- iso-butylene vs. propylene: effect of molecular structure
- iso-butylene: easier and quicker detonation decay (π-bond)
- predicted limiting tube diameter for H_2 – air – 2.5% C_3H_6 is 61 mm
- high sensitivity of detonation "go – no go" conditions to governing parameters

Azatyan et al. (2007), Frolov et al. (2009)

Conclusions

- **Mathematical modeling** of chemical inhibiting of hydrogen – air detonations has been performed.
- 1D detonation model with detailed chain-branching reaction mechanism of hydrogen oxidation describes satisfactorily **all main effects of chemical inhibitors on the detonation**.
- Calculations indicate that chemical inhibitors **narrow the concentration limits of detonations and increase the limiting tube diameter**, in which the steady-state detonation propagation is still possible.
- Despite the inhibitors introduce additional exothermal reactions and additional hydrogen oxidation reactions, **their presence results in detonation suppression**.
- Inhibitors lead to the deceleration of the overall reaction process which manifests itself by **increasing ignition delay time and decreasing concentrations of atomic hydrogen** – main carrier of chain-branching reaction.
- The effect of inhibitors is mainly determined by the **specific dependence of the rate of chain-branching reaction on temperature** which differs considerably from the regular Arrhenius dependence.

Acknowledgments

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