An improved passive scalar model for hazardous H_2-Air ignition prediction

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Motivations

- Increasing use of hydrogen (industry, transport, ...)
- Extended flammability limits
- Low minimum ignition energy
- High-pressure storage (up to 700 bars)

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Motivations

- Increasing use of hydrogen (industry, transport, ...)
- Extended flammability limits
- Low minimum ignition energy
- High-pressure storage (up to 700 bars)

Objectives

- Accurate and low-cost model to predict H_2 ignition
- Extend validity for higher pressure

Previous model: minimal kinetic description

For H_2-Air, detailed mechanisms use around 20 reactions[1].

Ignition alone can be described with only 8 reactions[2]:

1	$H+O_2 \rightarrow OH+O$	5	$H_2+O_2 \rightarrow HO_2+H$
2	$H_2+O \rightarrow OH+H$	6	$2HO_2 \rightarrow H_2O_2+O_2$
3	$H_2+OH \rightarrow H_2O+H$	7	$HO_2+H_2 \rightarrow H_2O_2+H$
4	$H+O_2+M \rightarrow HO_2+M$	8	$H_2O_2+M \rightarrow 2OH+M$

[1] F.A. Williams et al. *Chemical-kinetic mechanisms for combustion applications, University of California, San Diego.* version 2016-12-14, last accessed on 2023-02-22. URL: http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html.

[2] P. Boivin. "Reduced-kinetic mechanisms for hydrogen and syngas combustion including autoignition". PhD. Universidad Carlos III de Madrid, Dec. 2011.

Previous model: ignition as a linear system

Ignition can be solved as a linear system[3]:

$$\frac{d\bar{C}}{dt} = \mathbf{A}\bar{C} + \bar{\epsilon}$$

with the radicals vector $\bar{C} = [C_{\mathrm{H}}, C_{\mathrm{O}}, C_{\mathrm{OH}}, C_{\mathrm{HO_2}}, C_{\mathrm{H_2O_2}}]^T$,

the Jacobian $\mathbf{A} = \begin{bmatrix} -l_1 - l_4 & l_2 & l_3 & l_7 & 0 \\ l_1 & -l_2 & 0 & 0 & 0 \\ l_1 & l_2 & -l_3 & 0 & 2l_8 \\ l_4 & 0 & 0 & -l_7 & 0 \\ 0 & 0 & 0 & l_7 & -l_8 \end{bmatrix}$ and $\bar{\epsilon} = \begin{bmatrix} \omega_5 \\ 0 \\ 0 \\ \omega_5 \\ 0 \end{bmatrix}$

$l_1 = k_1 C_{\mathrm{O_2}}$, $l_2 = k_2 C_{\mathrm{H_2}}$, $l_3 = k_3 C_{\mathrm{H_2}}$, ...

[3] P. Boivin, A.L. Sánchez, and F.A. Williams. "Analytical prediction of syngas induction times". In: *Combust. Flame* 176 (2017), pp. 489–499.

Previous model: simplification of the linear system

Using the largest eigenvalue λ that rapidly dominates, the system can be reduced to a scalar equation[4]:

$$\frac{dC_\eta}{dt} = \lambda C_\eta + \epsilon_\eta$$

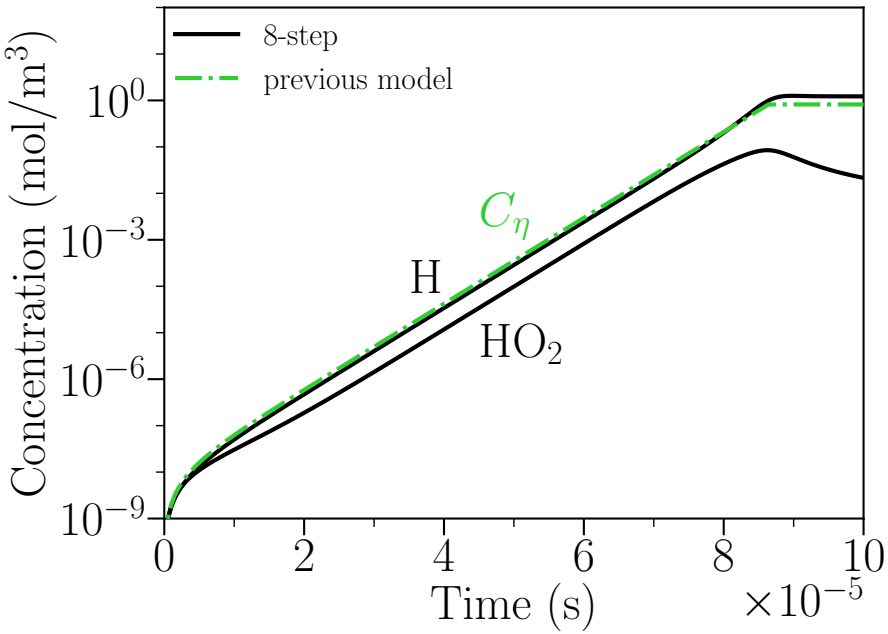


Figure: Concentrations evolution during isobaric homogeneous ignition process (φ=1.0, p=1 atm, T_0=1100 K)

[4] S. Taileb et al. "Lattice-Boltzmann modeling of lifted hydrogen jet flames: A new model for hazardous ignition prediction". In: *Combust. Flame* 245 (2022), p. 112317.

Previous model: limitations

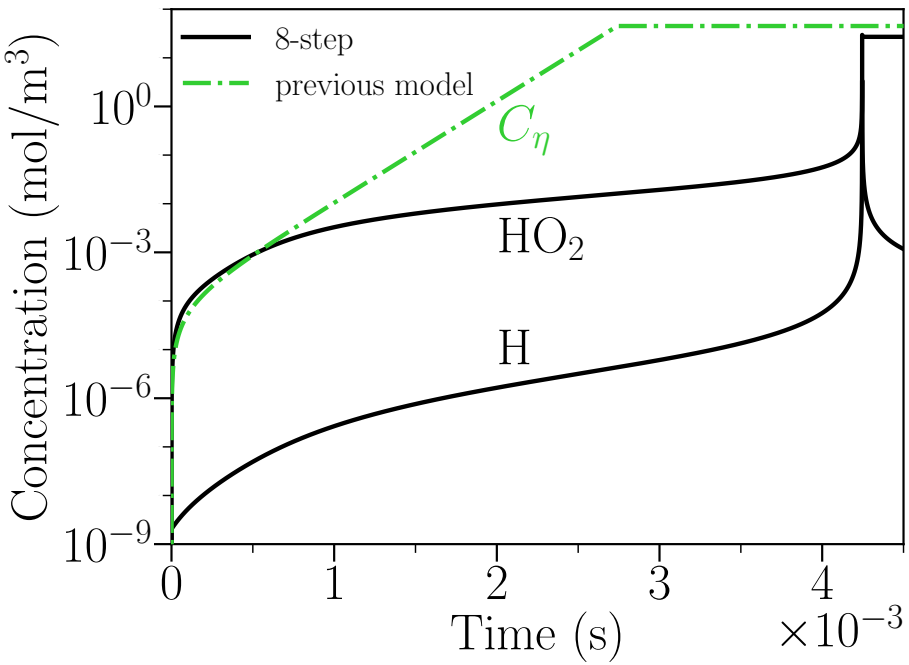
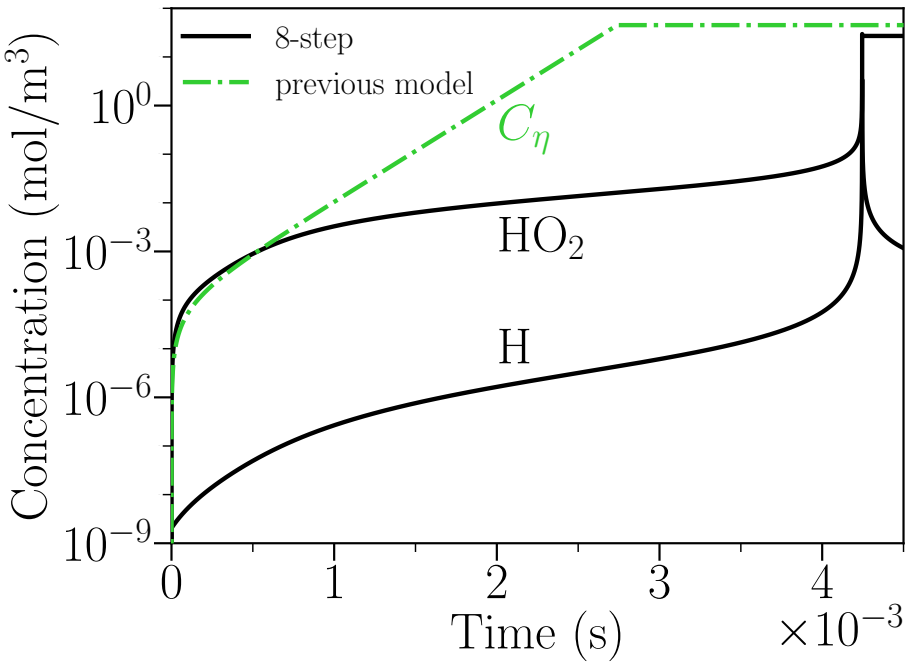


Figure: Concentrations evolution during a homogeneous isobaric ignition process (φ=1.0, p=50 atm, T_0=1000 K)

Previous model: limitations



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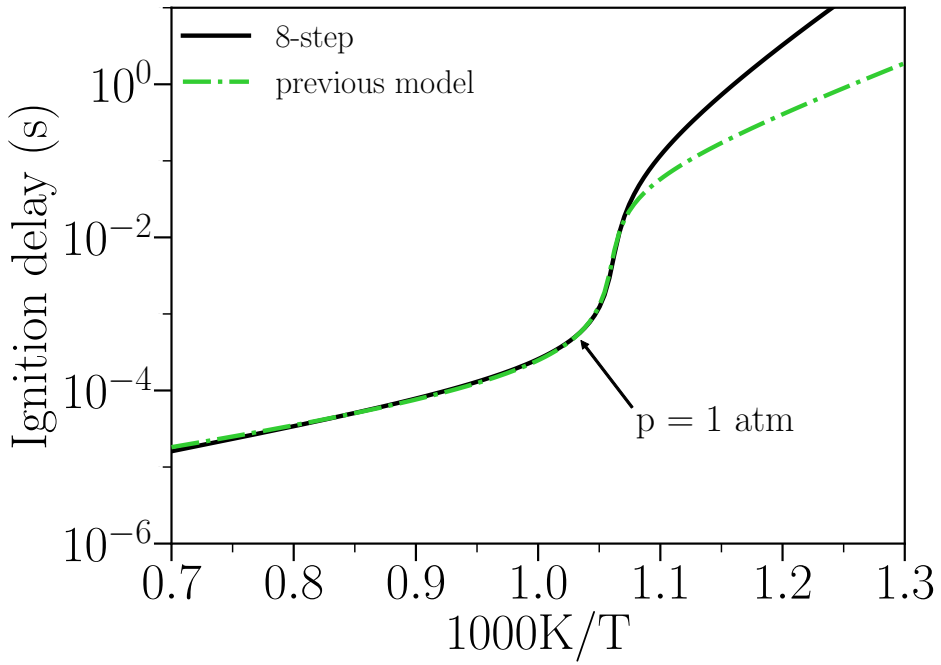
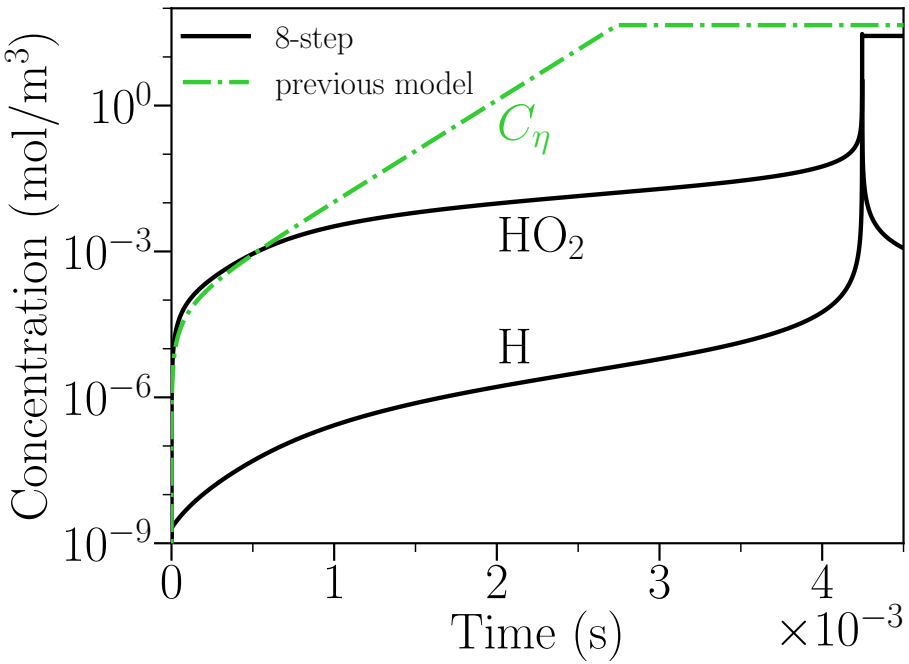


Figure: Autoignition delay as a function of temperature during a homogeneous isobaric process (φ=1.0)

Previous model: limitations



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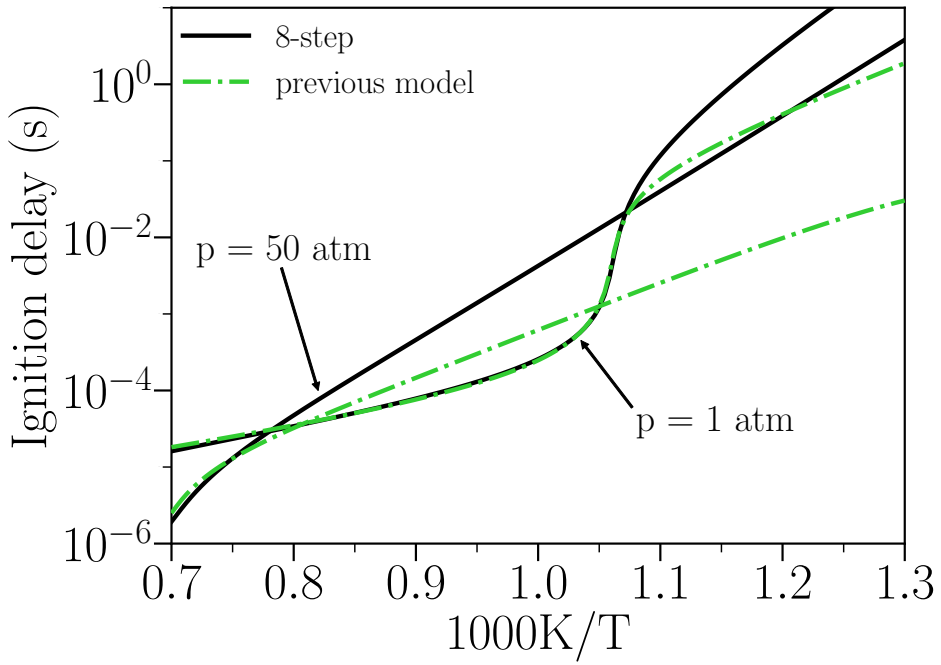


Figure: Autoignition delay as a function of temperature during a homogeneous isobaric process (φ=1.0)

Improved model: nonlinear branching

Linearisation of the reaction 6 term[5] ($HO_2 + HO_2 \rightarrow H_2O_2 + O_2$) into the new Jacobian:

$$\begin{bmatrix} -l_1 - l_4 & l_2 & l_3 & l_7 & 0 \\ l_1 & -l_2 & 0 & 0 & 0 \\ l_1 & l_2 & -l_3 & 0 & 2l_8 \\ l_4 & 0 & 0 & -l_7 - 4l_6 & 0 \\ 0 & 0 & 0 & l_7 + 2l_6 & -l_8 \end{bmatrix}$$

$$l_6 = k_6 C^*_{HO_2}(C_\eta)$$

$$\frac{dC_\eta}{dt} = \lambda(C^*_{HO_2})C_\eta + \epsilon_\eta$$

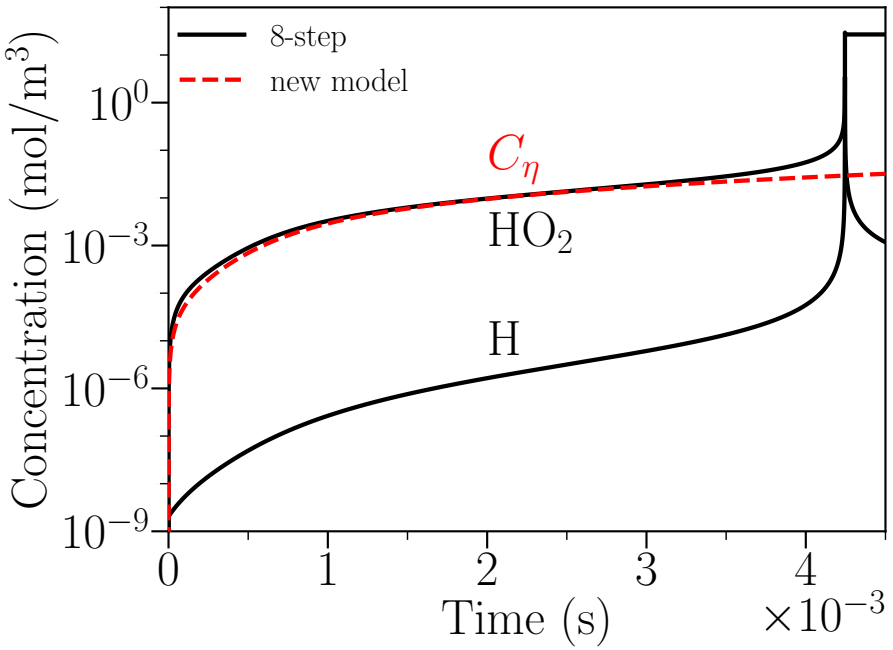


Figure: Concentrations evolution during a homogeneous isobaric ignition process (φ=1.0, p=50 atm, T_0=1000 K)

[5] Wenkai Liang and Chung K Law. "An analysis of the explosion limits of hydrogen/oxygen mixtures with nonlinear chain reactions". In: *Phys. Chem. Chem. Phys.* 20 (2018), pp. 742–751.

Improved model: thermal runaway

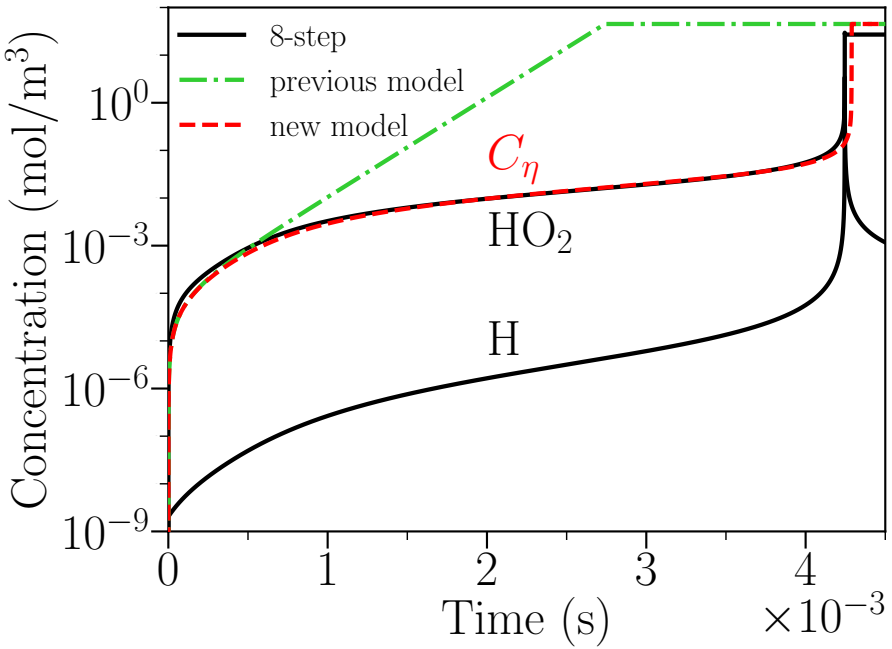
High activation energy development of λ:
$\lambda(\theta) = \lambda e^{\theta}$ with $\theta = \beta \frac{T - T_0}{T_0}$

The thermal runaway problem leads to: $\theta(C_\eta) = \ln\left(1 + \frac{qC_\eta^2}{2\lambda}\right)$.

The final scalar reaction rate now includes a correction term:

$$\frac{dC_\eta}{dt} = \lambda(C^*_{\mathrm{HO_2}})C_\eta + \frac{q}{2}C^{*3}_{\mathrm{HO_2}} + \epsilon_\eta = \dot{\omega}_\eta$$

Improved model: final reaction rate



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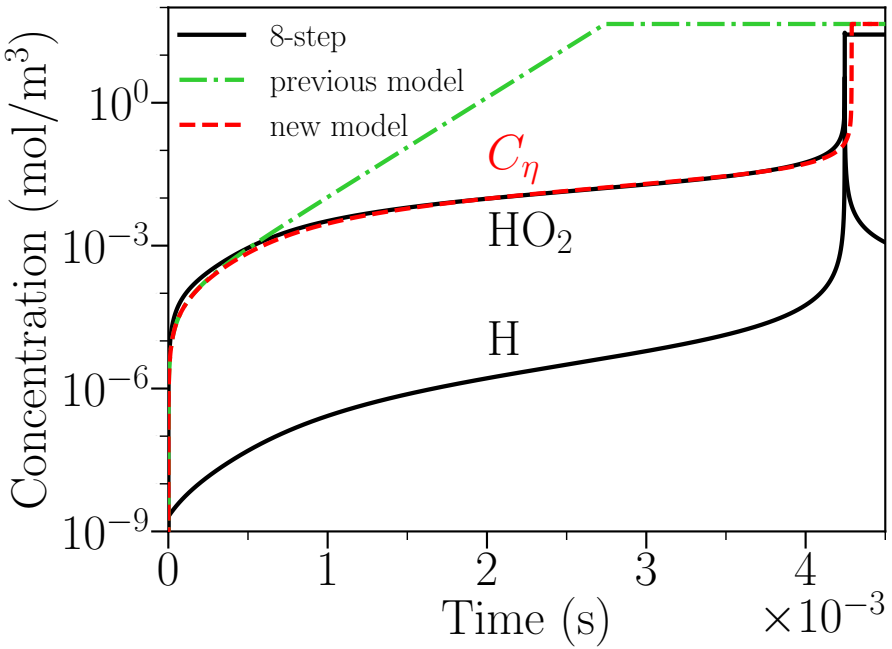

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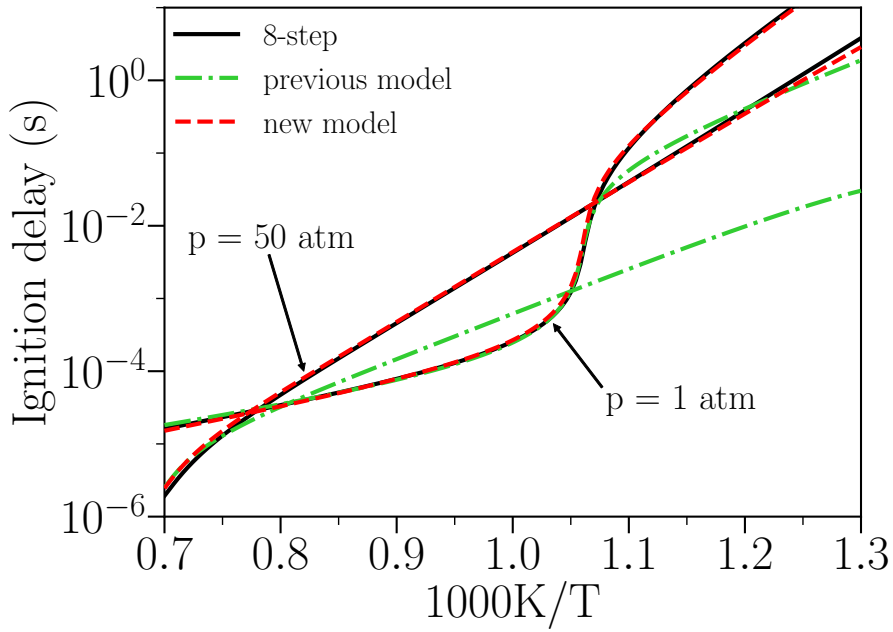

Figure: Autoignition delay as a function of temperature during a homogeneous isobaric process (φ=1.0)

Improved model: transport equation

Classic conservation equations of thermal flow:

- Only considering the main species (H_2, O_2, diluent)
- No reaction nor heat release
- Adding the self-reacting scalar C_η, not used to solve the flow and following a classic advection-diffusion-reaction equation:

$$\frac{\partial C_\eta}{\partial t} + u_\alpha \frac{\partial C_\eta}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha}\left(D_\eta \frac{\partial C_\eta}{\partial x_\alpha} \right) + \dot{\omega}_\eta$$

Improved model: diffusion properties

The previous model used $D_\eta = D_{\mathrm{H}}$

The improved model uses the eigenvector $\bar{V}$ of λ:

$$D_\eta = \frac{\sum_k D_k V_k}{\sum_k V_k}$$

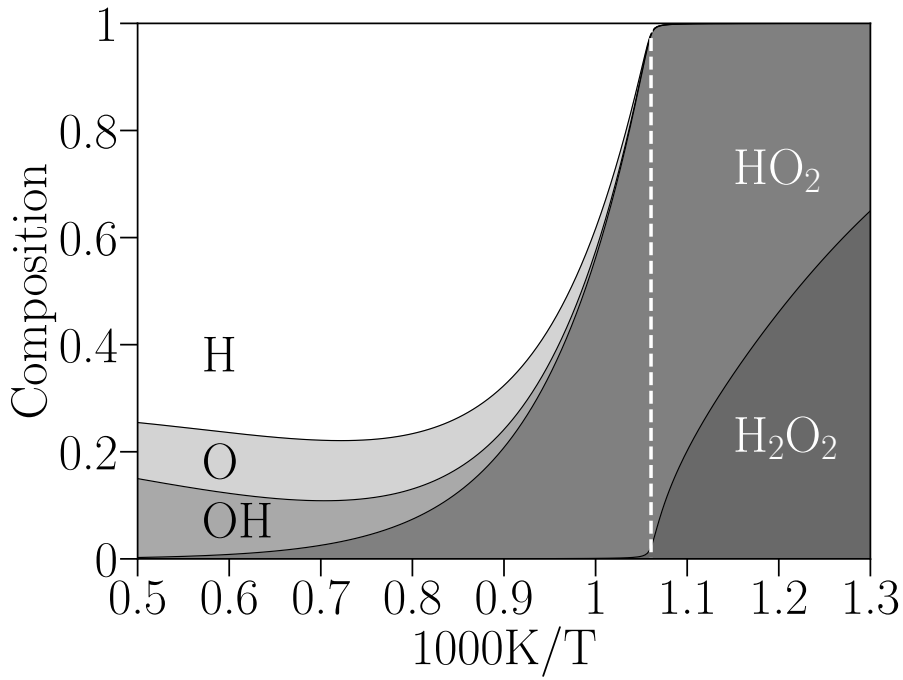

Figure: Composition of the radical pool given by the eigenvector $\bar{V}$ ($\varphi = 1.0$, $p = 1$ atm)

Mixing layer validation: configuration

2D double mixing layer:

- Hot air (1200 K)
- Cold diluted H_2 (50% in volume)
- High pressure (50 atm)
- Weak turbulence ($\tau_t > \tau_i$)
- 4.5mm×4.5mm (500×500 points)

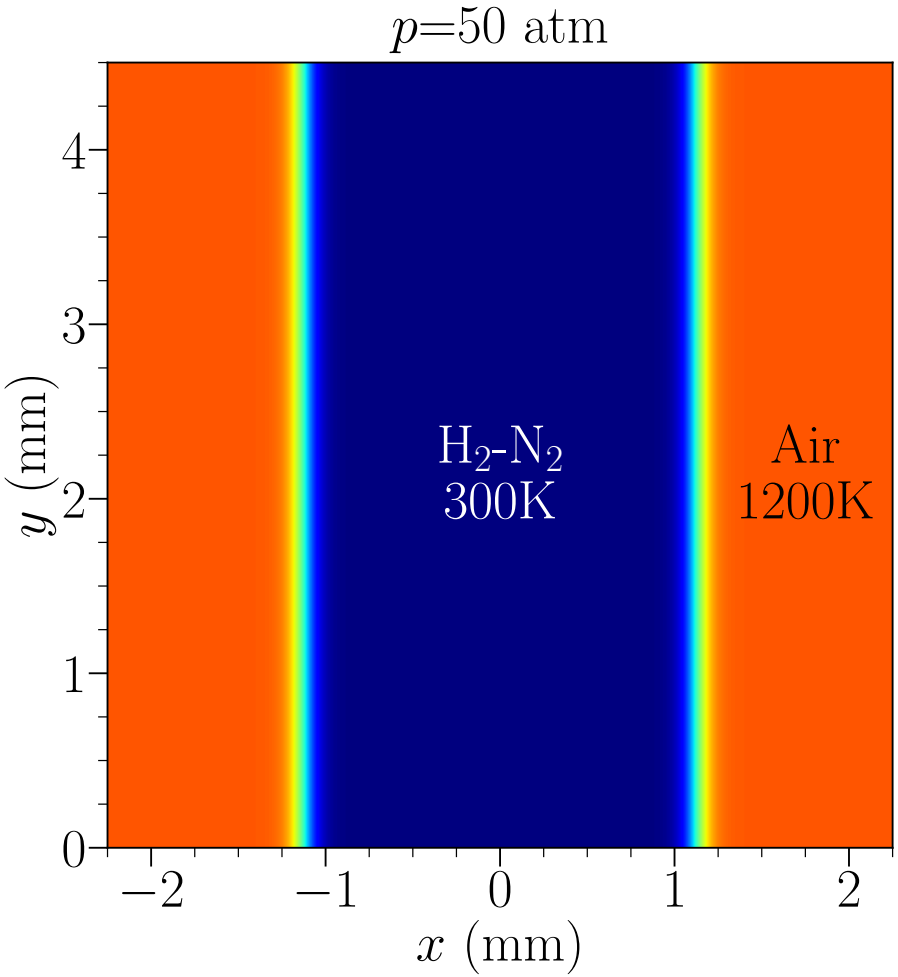

Figure: Initialization of the mixing layer

Mixing layer validation: results (1/2)

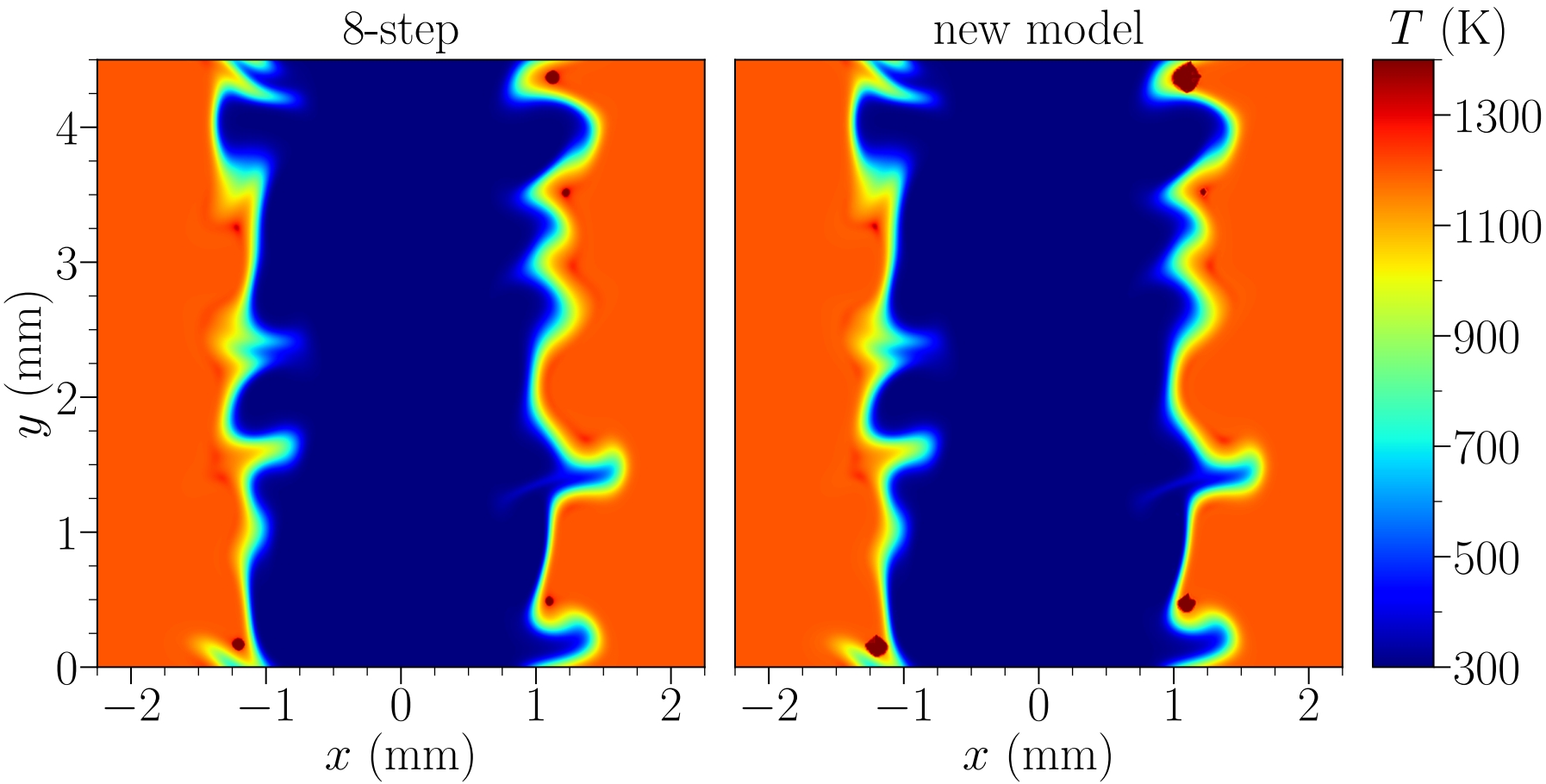

Figure: Temperature field (reconstructed for the scalar model) after ignition

Mixing layer validation: results (2/2)

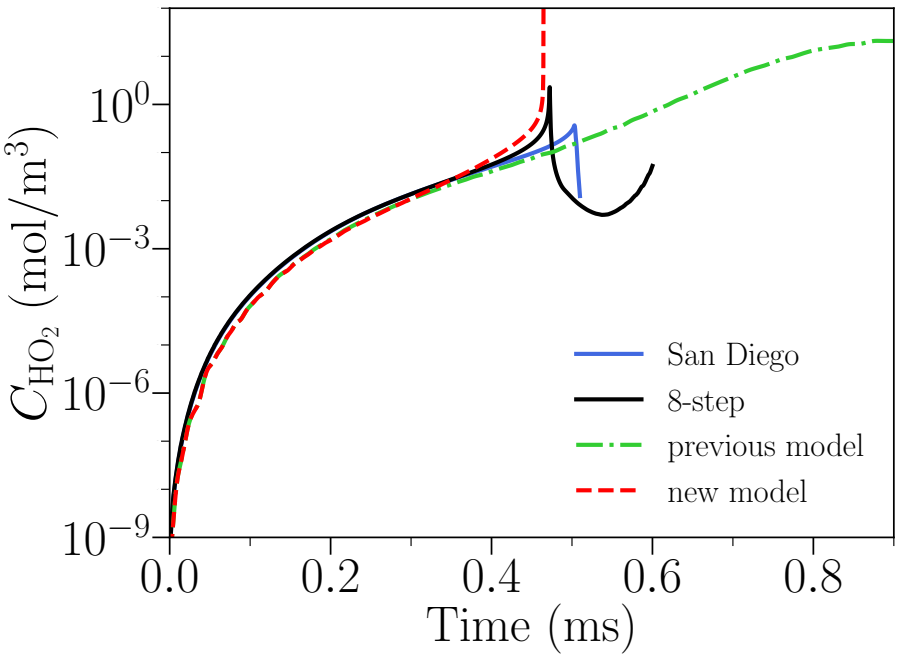

Figure: Evolution of C_{HO_2} and C_η at the first kernel to ignite.

case	τ_i (ms)	cost
San Diego	0.497	43.7
8-step	0.472	9.1
Previous model	0.826	1.0
New model	0.464	1.0

Conclusion & Perspectives

Conclusion:

- Considering the nonlinear reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
- Adding a correction term for thermal runaway
- Evaluating the scalar diffusion with the eigenvector
- Accurate for extended temperature and pressure ranges at a low-cost

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- Adding a correction term for thermal runaway
- Evaluating the scalar diffusion with the eigenvector
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Perspectives:

- Assessment of self-ignition risks for high-pressure tank leakage.
- Investigation of the potential of the model for the study of igniters.

Thank you

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