Kinetic Modeling for the Insight into Combustion

燃焼をわかるための化学反応モデリング

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Selecting Kinetic Models

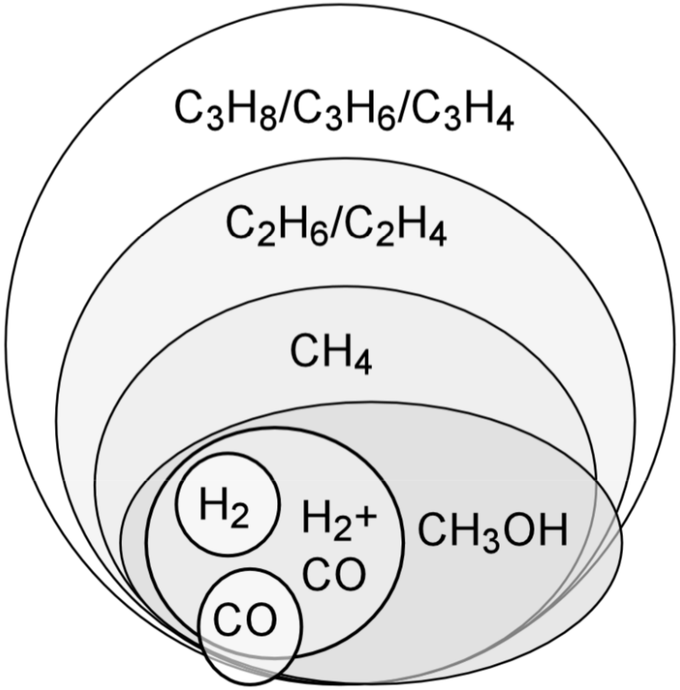
- Fuel ....
- High-T & Low-T oxidation

  Flame propagation
    - need High-T mech only (usually!)
    - small fuel dependency

  Autoignition
    - require both High-T & Low-T
    - strong fuel dependency

- Sub-mechs (NO*x*, PM/PAH, etc. ...)
- Reduction

  Nearly automatic down to 1/5~1/10
    - ANSYS Reaction Workbench
      (license for which is now included in academic labo license)



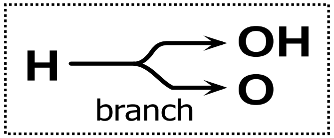
hierarchy of combustion
kinetic mechanisms

Kinetics of Autoignition

Branched Chain Reactions

H_2-O_2 — Typical branched chain reactions (Chain Explosion)

$$\mathbf{H} + \mathbf{O_2} \rightarrow \mathbf{OH} + \mathbf{O}$$
$$\mathbf{O} + \mathbf{H_2} \rightarrow \mathbf{OH} + \mathbf{H}$$
$$\mathbf{OH} + \mathbf{H_2} \rightarrow \mathbf{H_2O} + \mathbf{H}$$



net: **$2\ H_2 + O_2 \rightarrow OH + H + H_2O$**

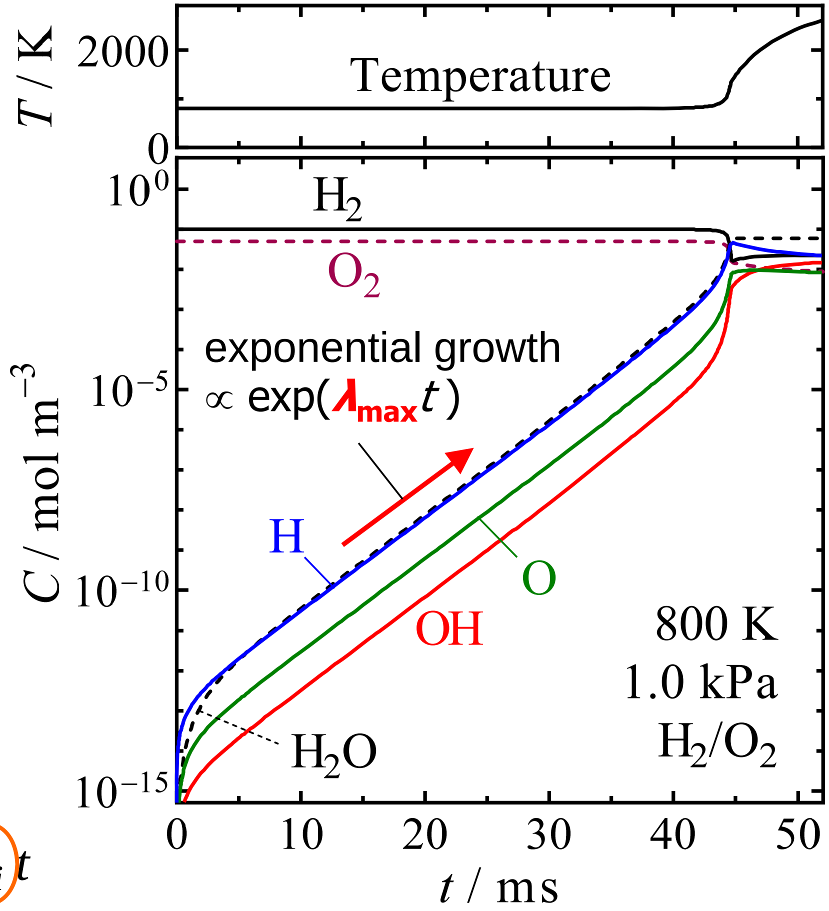
└ **Chain carriers cannot be cancelled out**

- Selfmultiplication of chain carriers
  ➔ Autoacceleration ➔ Explosion

$x = [\mathrm{H}]$, $y = [\mathrm{O}]$, $z = [\mathrm{OH}]$,
$R_1 = k_1[\mathrm{O_2}]$, $R_2 = k_2[\mathrm{H_2}]$, $R_3 = k_3[\mathrm{H_2}]$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -R_1 & R_2 & R_3 \\ R_1 & -R_2 & 0 \\ R_1 & R_2 & -R_3 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\mathbf{x} = \sum_i a_i \mathbf{s}_i\, e^{\boxed{\lambda_i} t}$$



$\lambda_{max} > 0$ ... diverging term

Jacobian Matrix

remains unchanged during the induction period where *p*, *T* and *x* are nearly constants

Autoignition Limit : $\lambda_{max} = 0$

$H + O_2 \rightarrow OH + O$

$H + O_2 \rightarrow HO_2$

$O + H_2 \rightarrow OH + H$

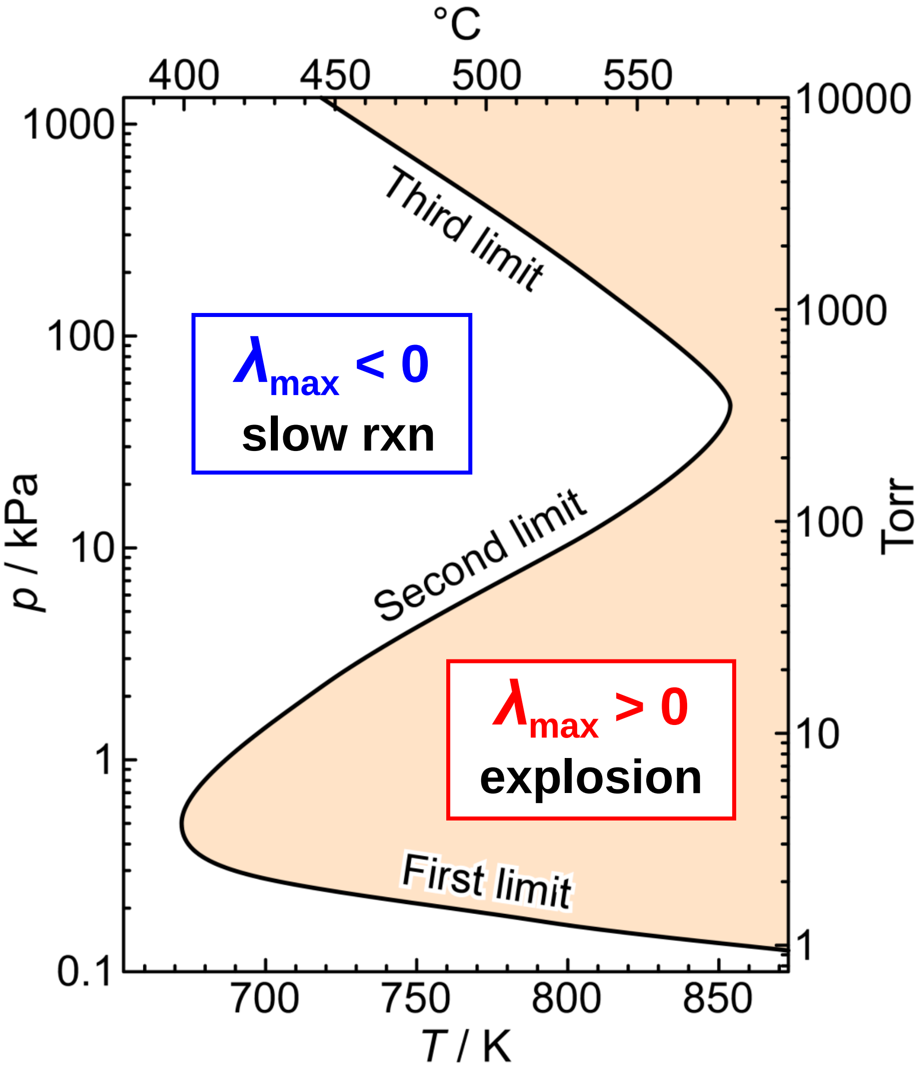
$OH + H_2 \rightarrow H_2O + H$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -R_1 - R_4 & R_2 & R_3 \\ R_1 & -R_2 & 0 \\ R_1 & R_2 & -R_3 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Jacobian Matrix

$$\mathbf{x} = \sum_i a_i \mathbf{s}_i \, e^{\boxed{\lambda_i} t}$$

Autoignition Limit of $H_2:O_2 = 2:1$ mixture

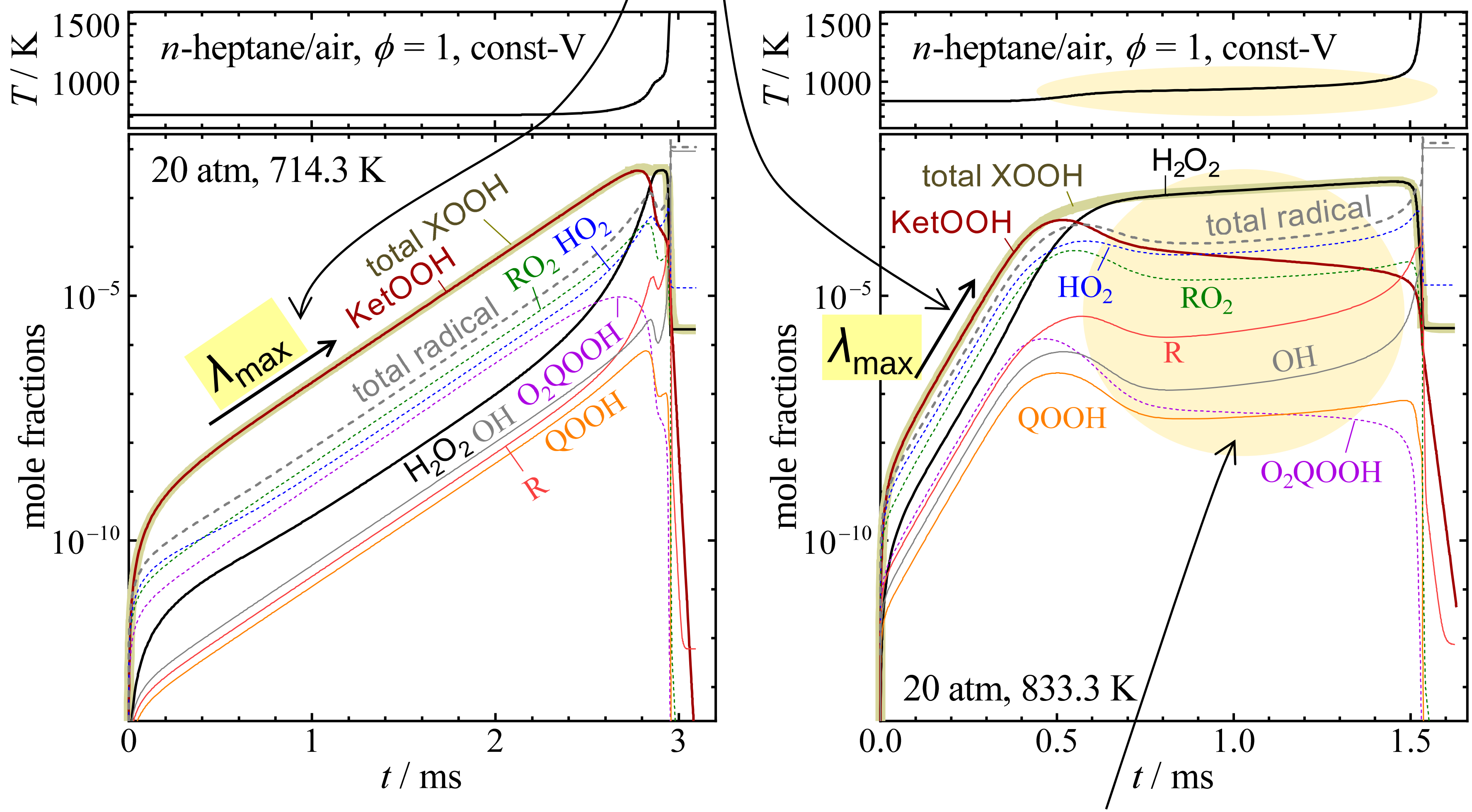


The 1st and 2nd explosion limits can be explained by nearly constant Jacobian matrix

Autoignition of Alkanes

Ignition mechanism depends on the condition !

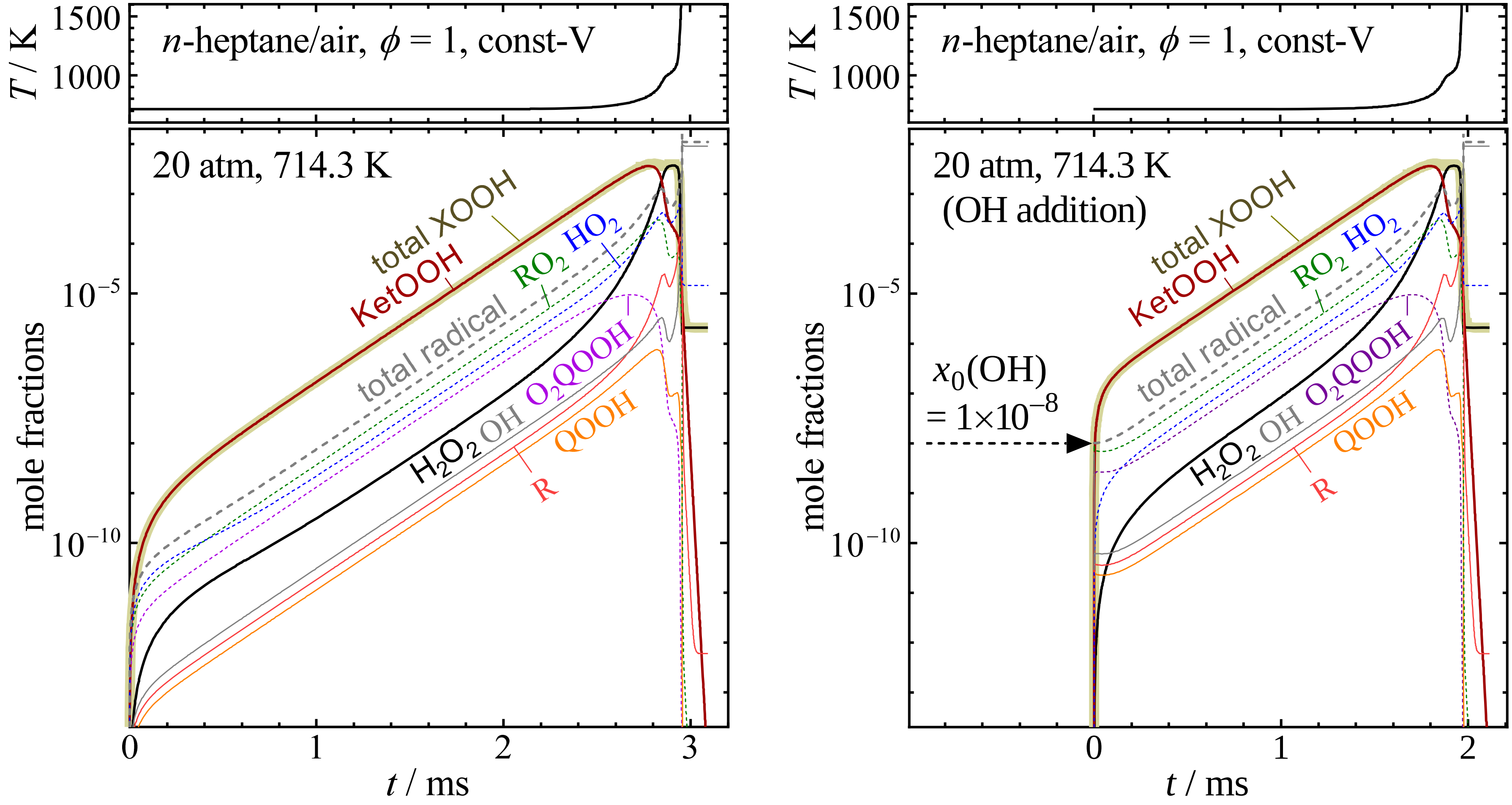
Before Cool Flame: Chain-Reaction Controlled (*chain explosion*)



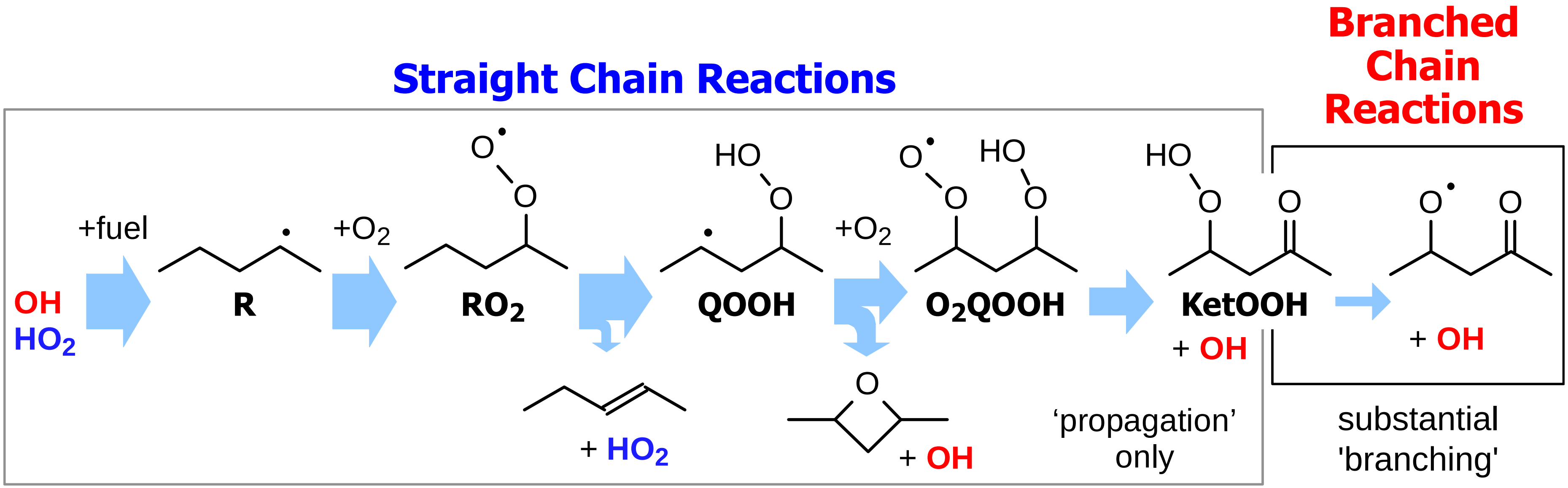
After Cool Flame: Thermally Controlled (*thermal explosion*)

Active Species Addition

- **x(OH) ≈ x(total radical)** → **independent** of species added
- x(OH) promptly decays to steady state → robust steady state
- Additive effect diminishes exponentially with time



Low-Temperature Oxidation Steady State



- Reactions up to KetOOH formation are **Straight Chain Reactions** (No increase in active species)
- Only the decomposition of KetOOH is **Chain Branching Reaction**

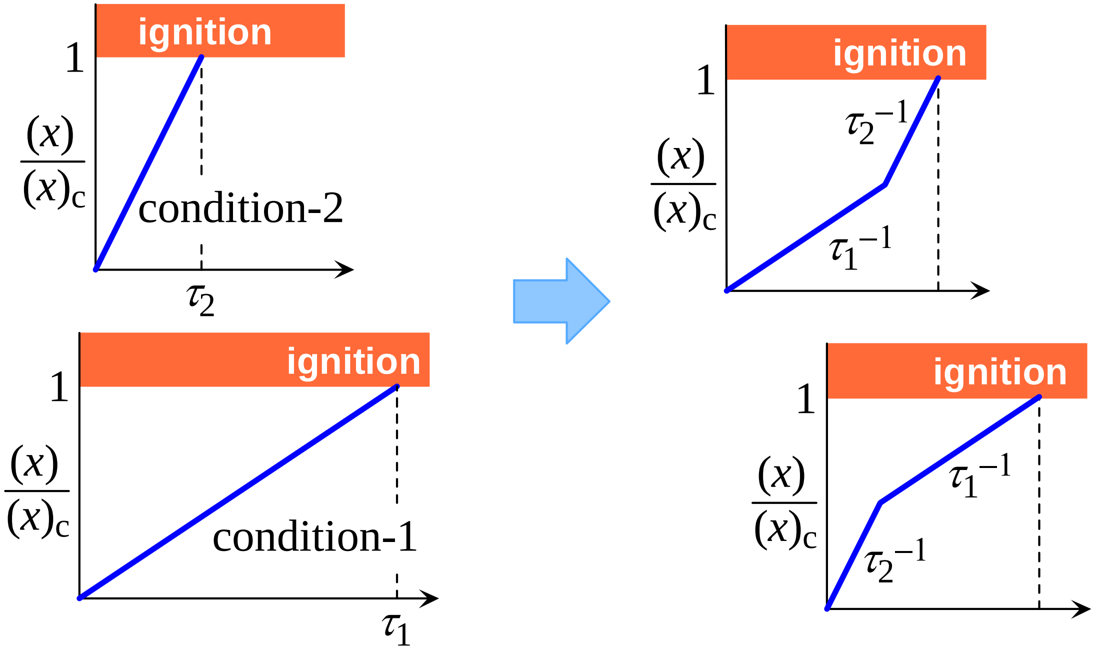
Livengood-Wu (L-W) Integral

J. C. Livengood and P. C. Wu, *Proc. Combust. Inst.*, 5, 347–356 (1955).

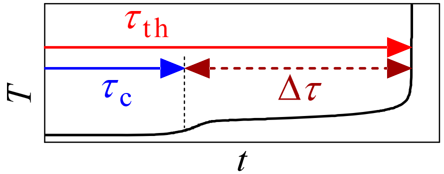
Assumptions:

- Autoignition occurs when the concentration of "pertinent reaction product x" reaches the critical value $(x)_c$.
- The rate of increase of $(x)/(x)_c$ is a function of T and p and equal to $\tau^{-1}(T, p)$, reciprocal of the ignition delay time, $\tau(T, p)$, at this condition.
- This relation holds for all T and p during the piston compression and expansion

$$1 = \int_0^{t_{ign}} \frac{dt}{\tau(T,p)}$$



Integrand of Livengood-Wu

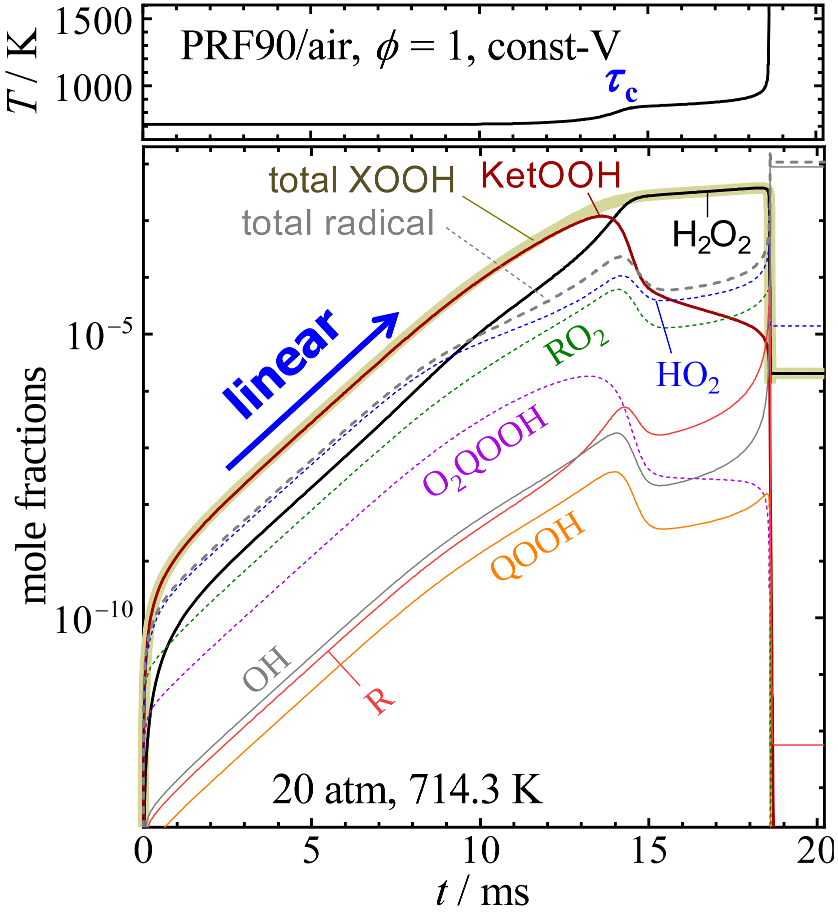


- Integrand is log(**XOOH**) or log(**radical**) for $t < \tau_c$.

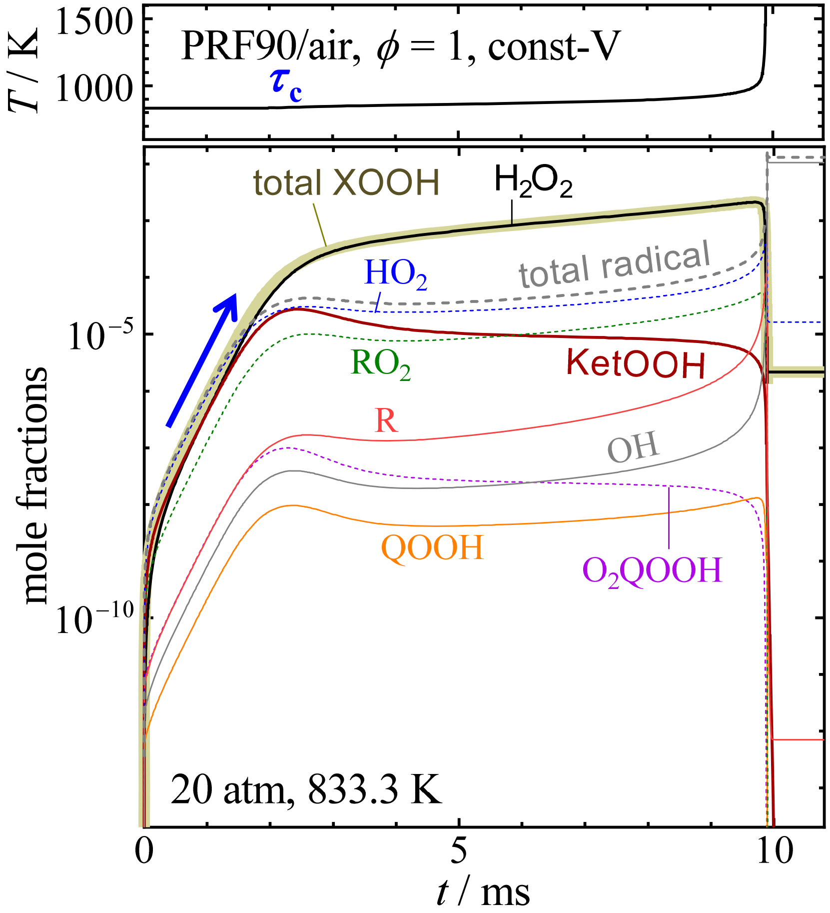
- Integrand is heat for $t > \tau_c$.

H. Ando, Y. Ohta, K. Kuwahara, and Y. Sakai, Rev. Automotive Eng., 30, 363–370 (2009).

(*a*) $\boldsymbol{\tau}_{\mathbf{c}}$ dominant $\boldsymbol{\tau}_{\mathbf{c}} > \Delta\tau$

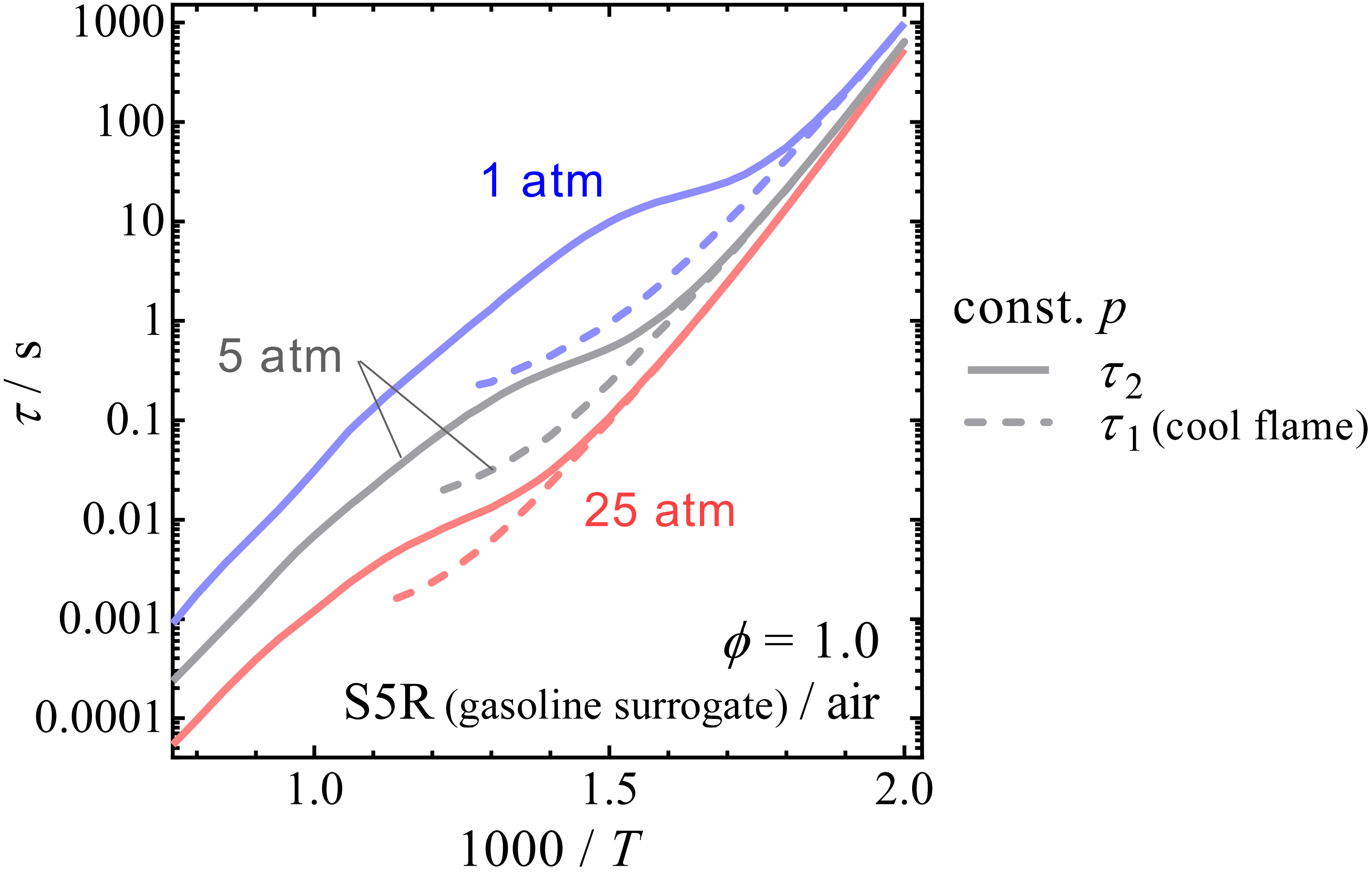


(*b*) $\boldsymbol{\Delta\tau}$ dominant $\tau_c < \boldsymbol{\Delta\tau}$



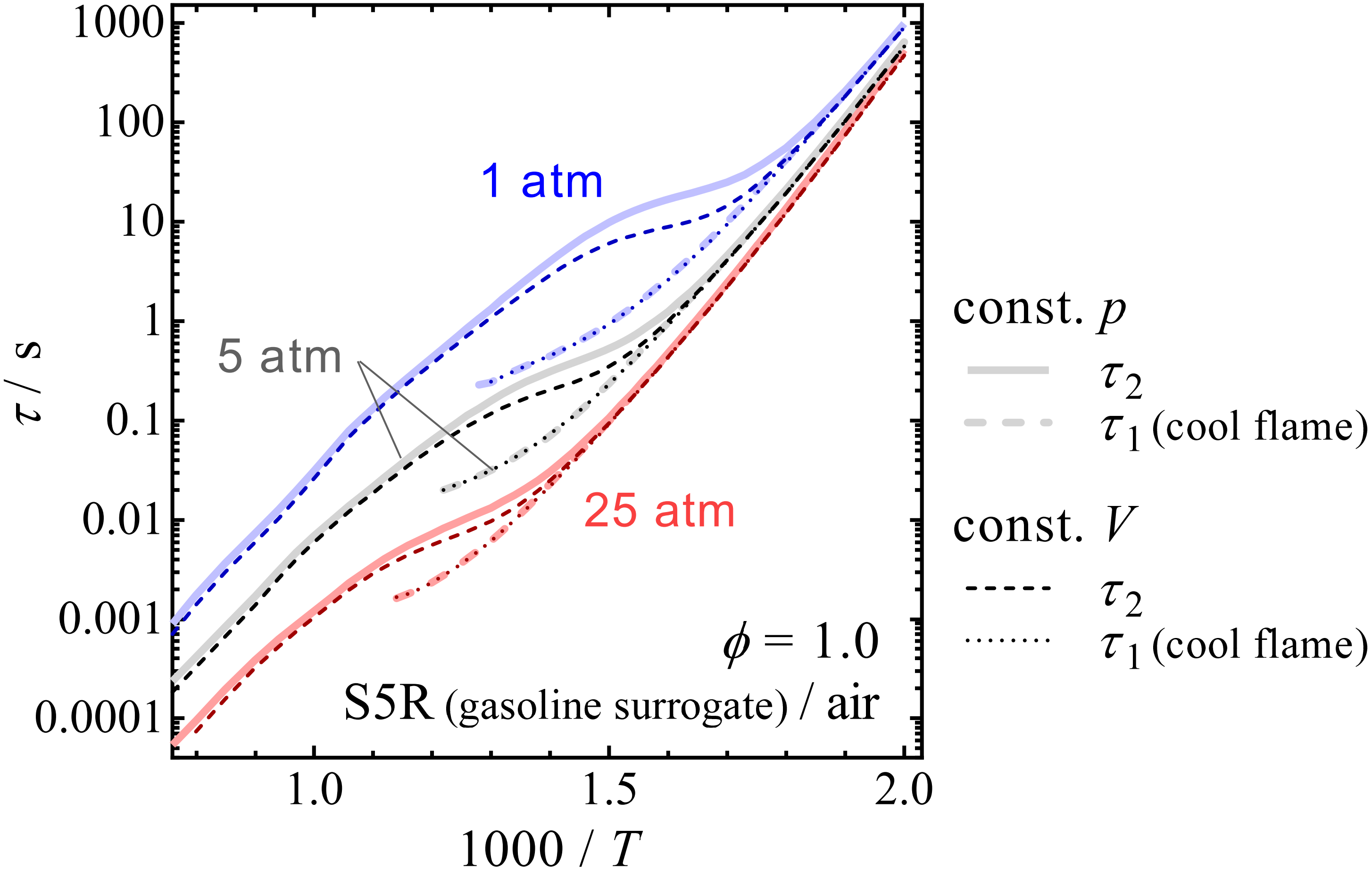
Autoignition of Gasoline/air (*p*-dependence)

- Shifts upper-right with decrease of *p*
- Larger $\tau_2 - \tau_1$ separation at lower *p*



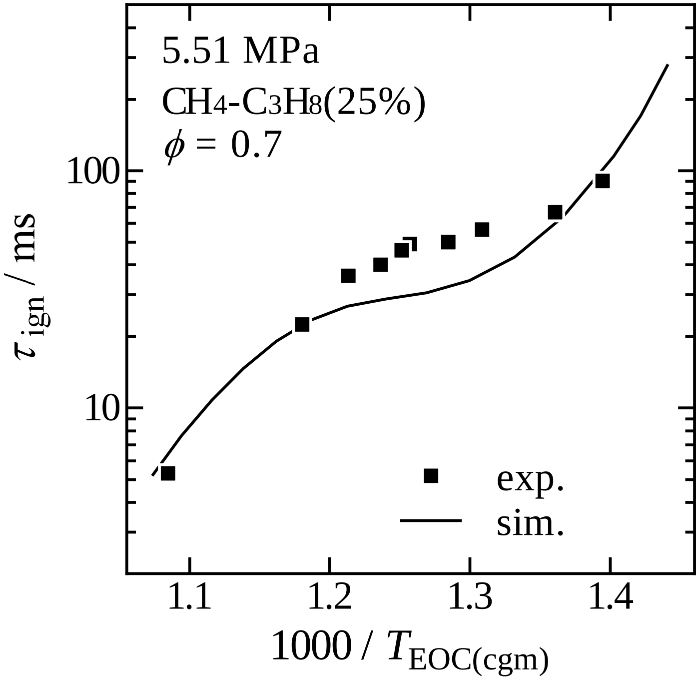
Difference between const-*p* & const-*V*

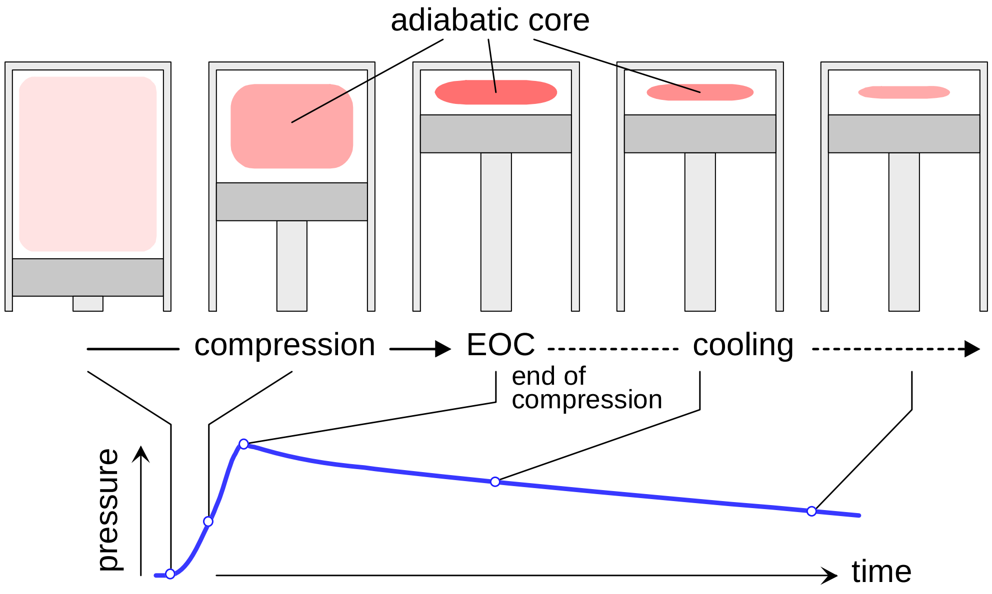
- Essentially NO difference for τ_1
- τ_2 is slightly shorter for const-*V* than const-*p*



Problem in Given-*V* Simulation for RCM

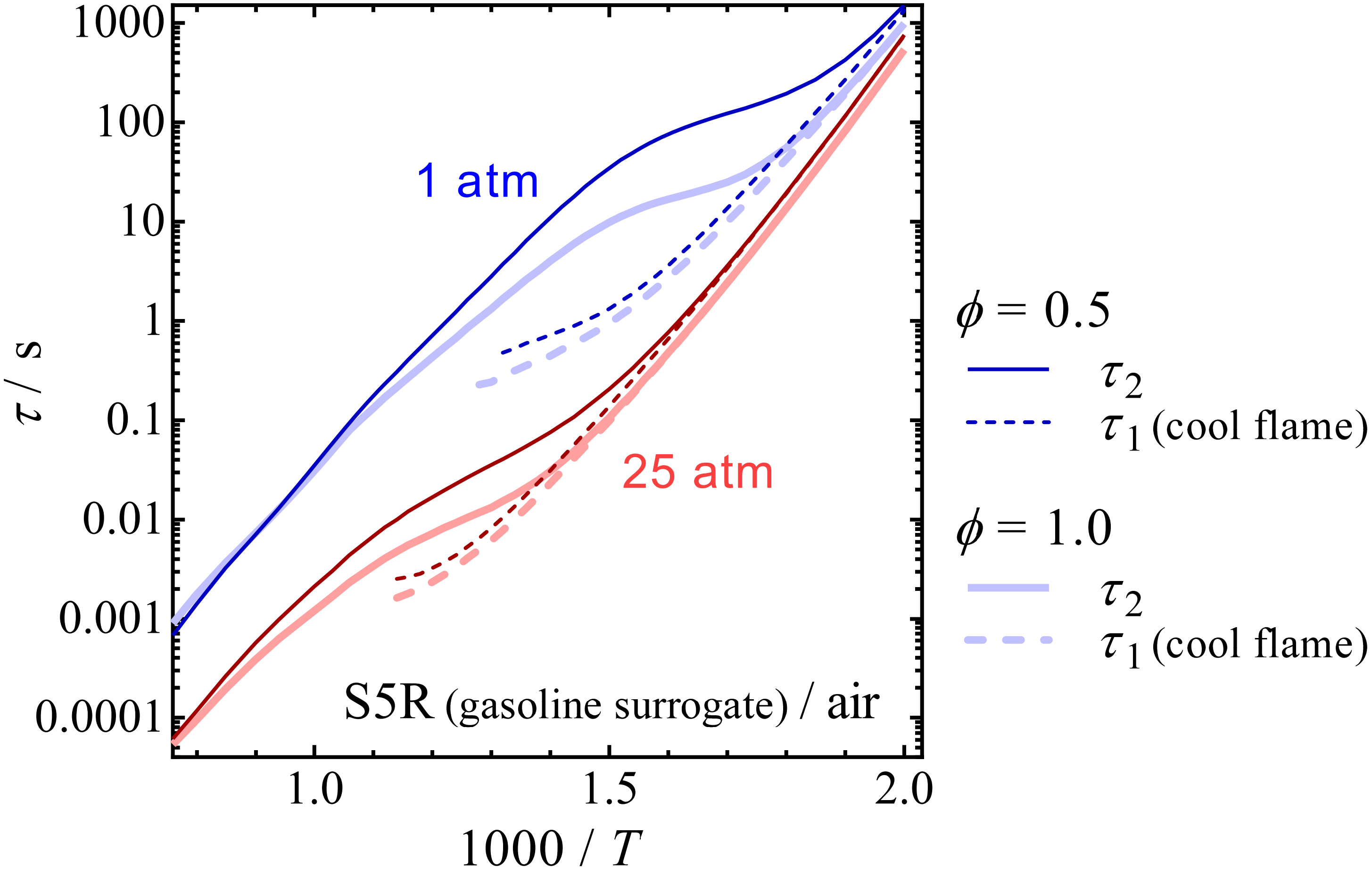
- Cool flame expansion cannot be reproduced in core-gas model
- Deviation of from experiments where $\tau_2 - \tau_1$ separation is visible





Effect of the Change of Equivalence Ratio

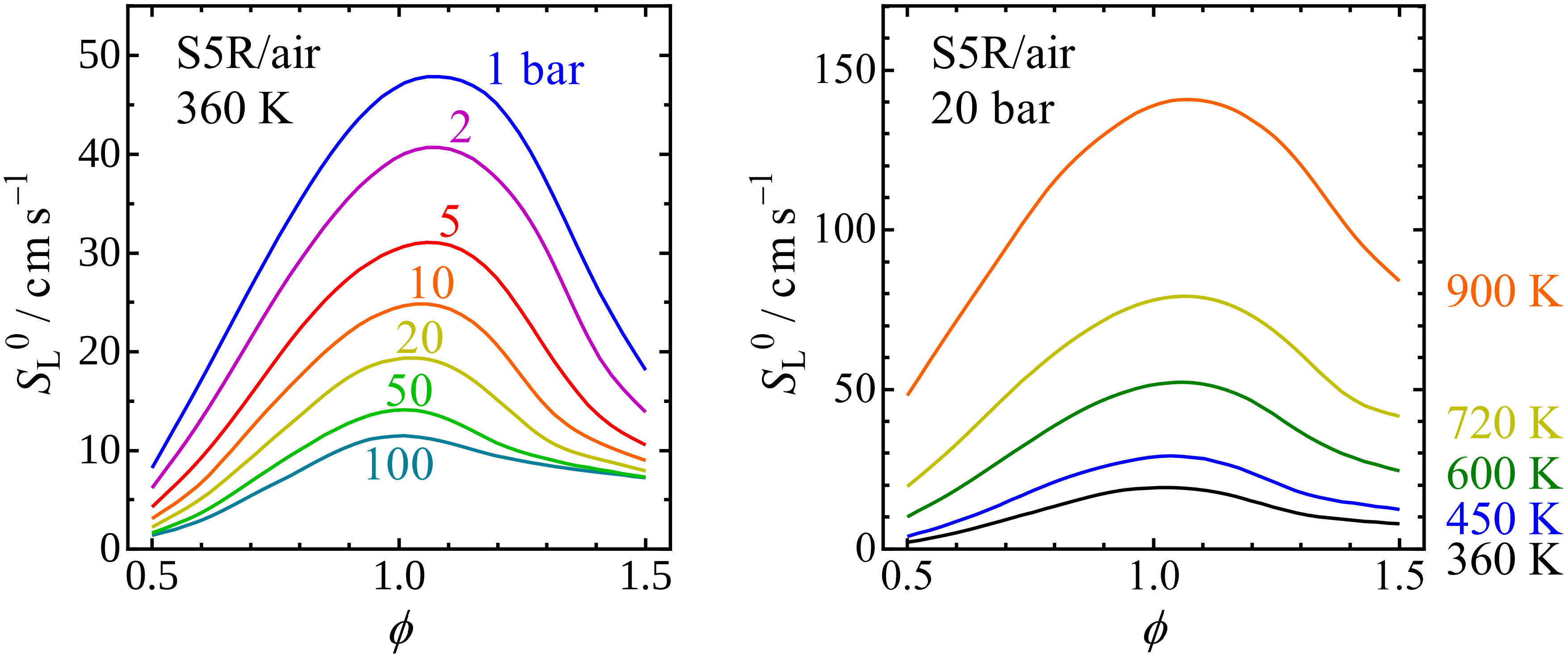
- Shifts upper-right with decrease of ϕ
- Changes mostly τ_2 but not so much of τ_1



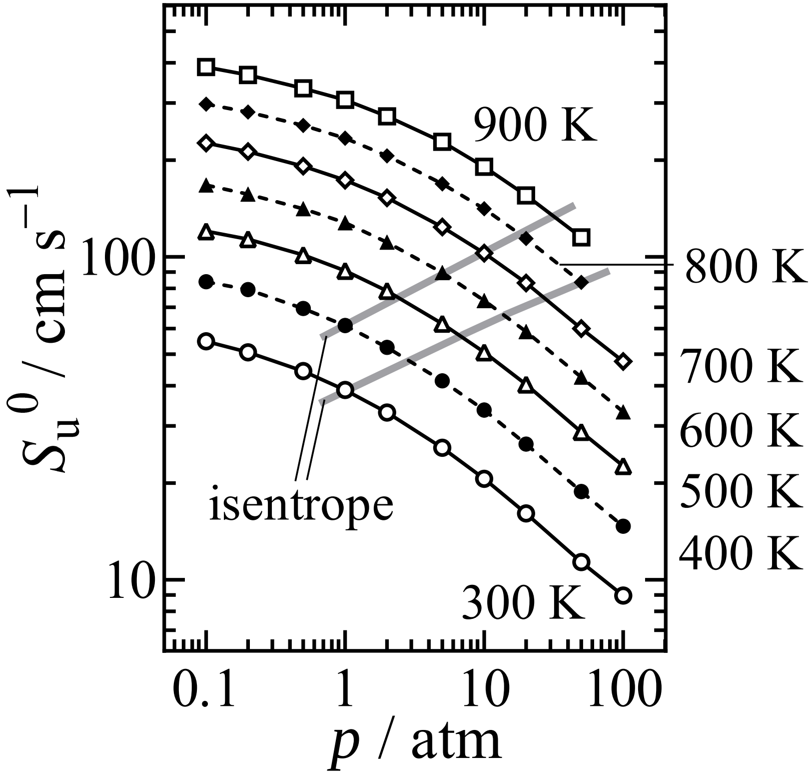
Flame Propagation

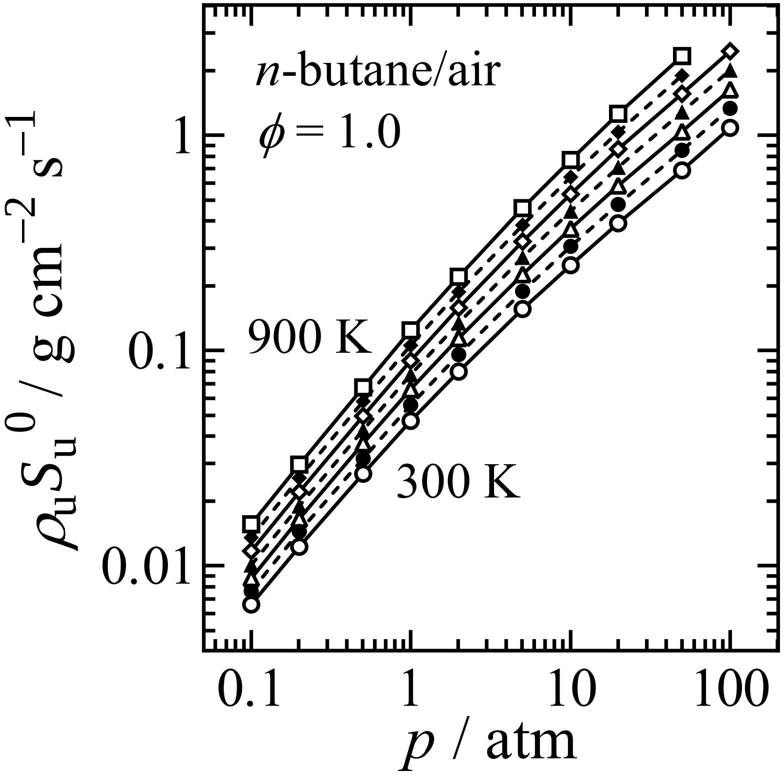
Laminar Flame Propagation

- Laminar flame speed ($S_L{}^0$) decreases with pressure and increases with temperature



Flame Propagation at High *p* and *T*

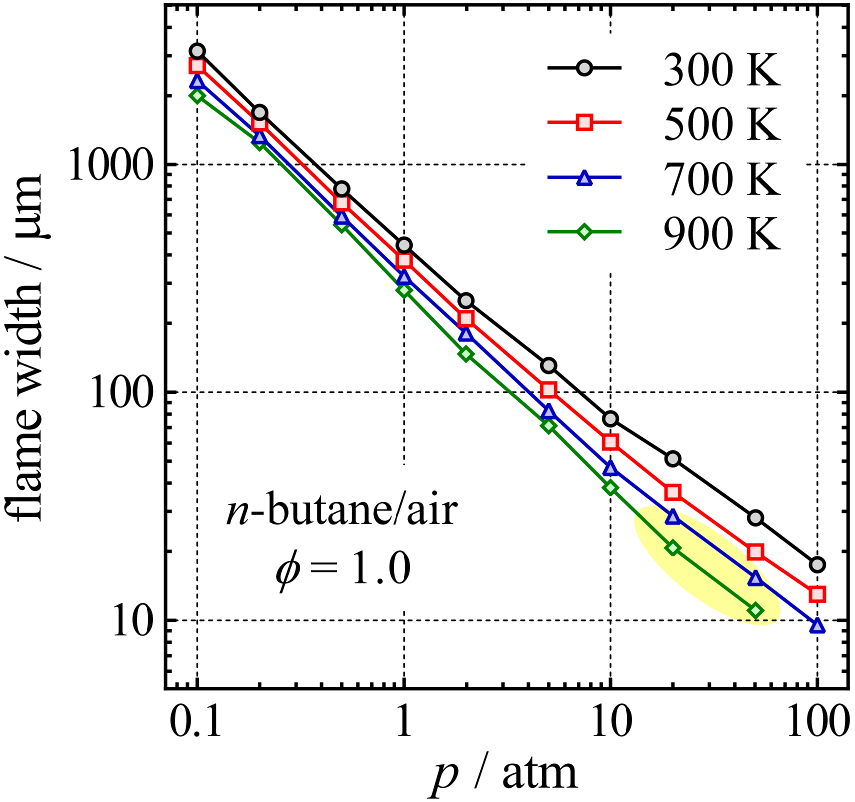


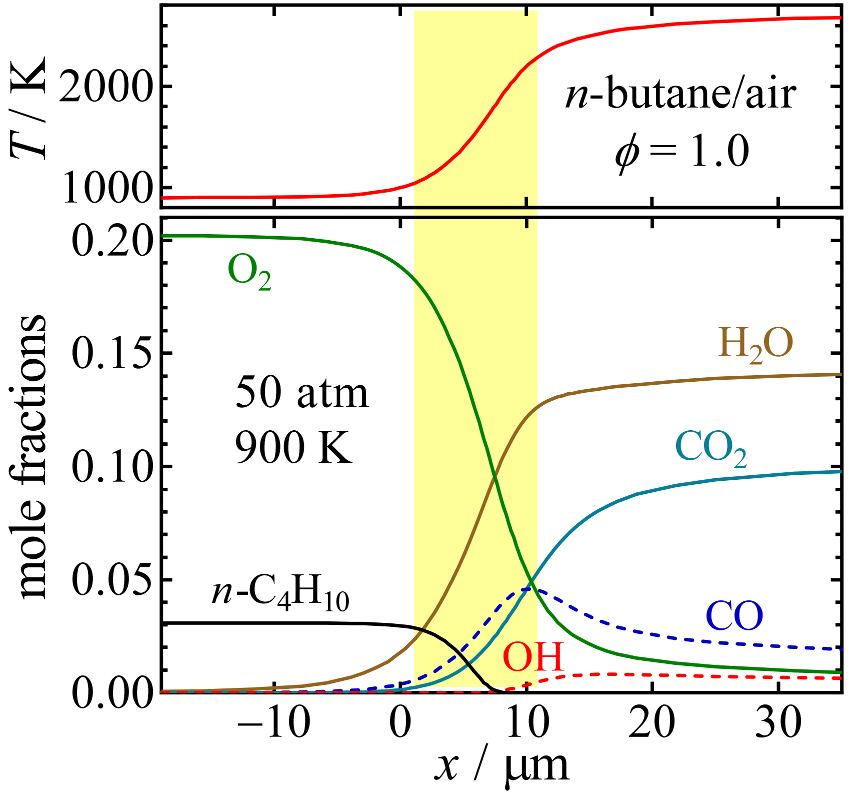


100 cm s^{-1} under in-cylinder condition

Laminar Flame Structure

— Structure & flame thickness

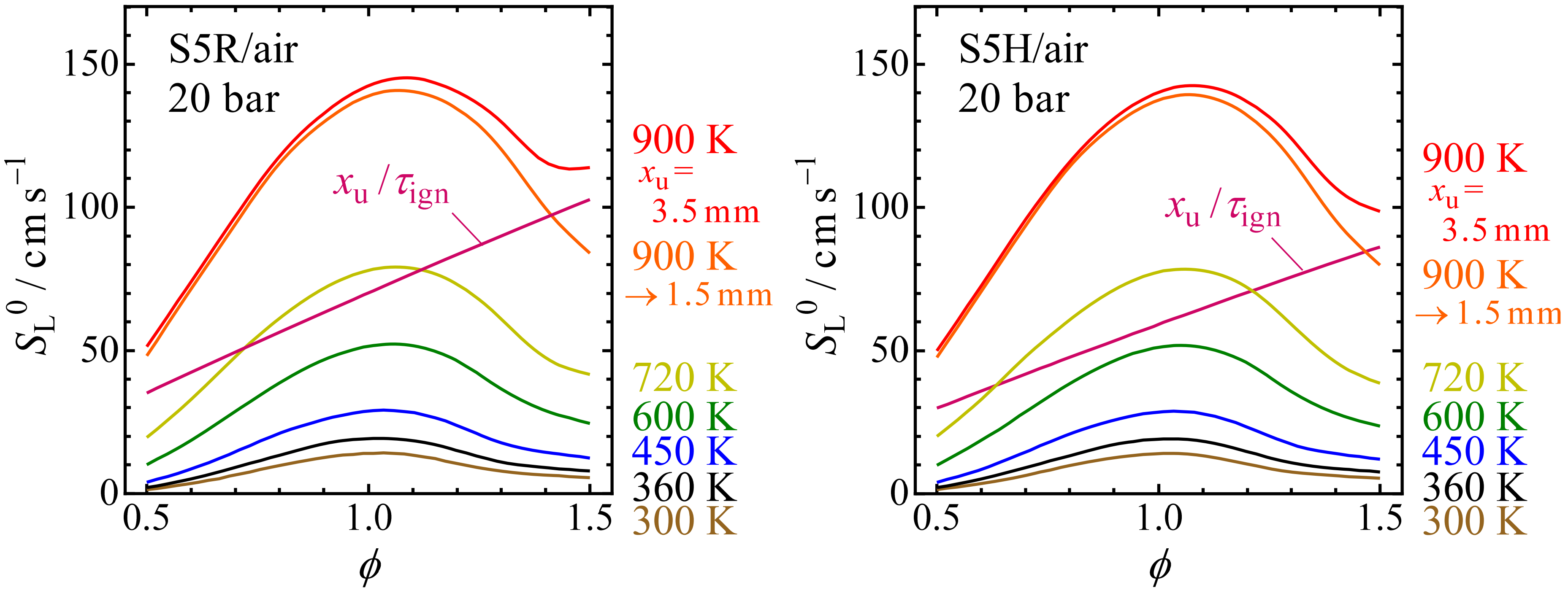




- In-cylinder flame thickness: **10~20 µm** (require **submicron** resolution)

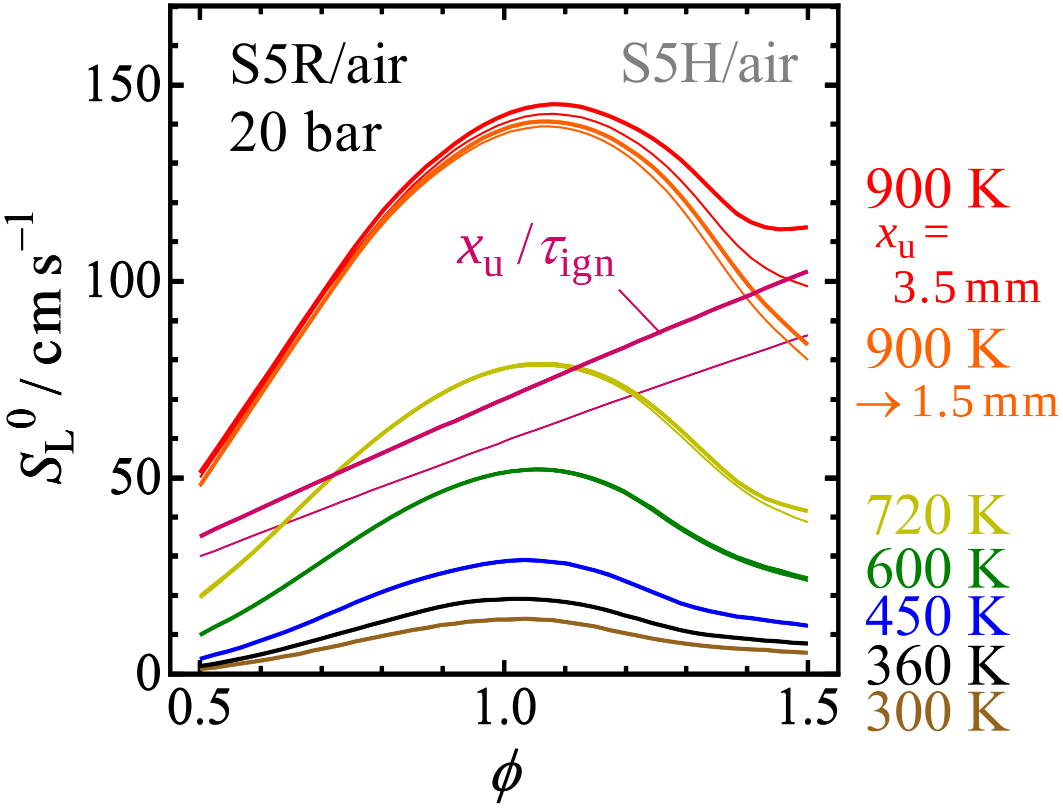
Flame Propagation vs. Autoignition

- Autoignition kinetics affects the calculation of laminar flame speed at high temperatures (artefact - NOT true laminar burning velocity)



Flame Propagation vs. Autoignition

- Small difference between RON~100 S5H (high-octane) & RON~90 S5R (regular)



Summary

— Kinetics of Autoignition

[before cool flame]

- Chain carrier conc. increases exponentially with time, or log x(radical) increases LINEARLY with time

[after cool flame]

- Thermal ignition dominates

— Flame Propagation

- Autoignition competes under in-cylinder condition