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Study on pressure dependences of ethanol oxidation by separated weak flames in a micro flow reactor with a controlled temperature profile

Hisashi Nakamura, Akira Yamamoto, Mikito Hori, Takuya Tezuka, Susumu Hasegawa and Kaoru Maruta

Institute of Fluid Science, Tohoku University

Background

Ethanol is one of the major products from biofuels

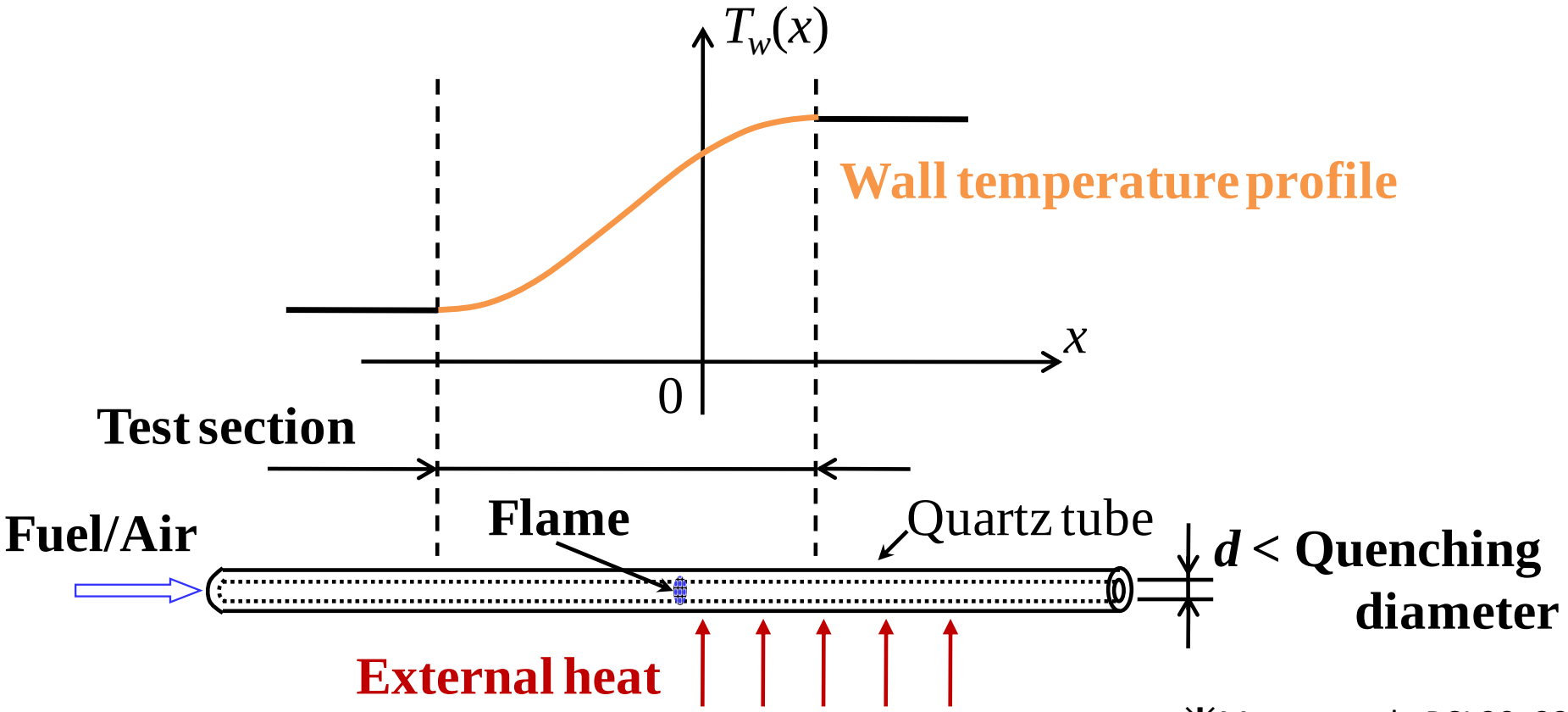
- Reliable chemical kinetic model is required
- Developed models were compared with various experimental results in the world

Methods
- Bunsen burner
- Flat-flame burner
- Counterflow flames
- Shock tube
- Rapid compression machine
- Flow reactor
- Jet-stirred reactor

Targets
- Laminar burning velocity
- Ignition delay time
- Species profiles

Attempt to provide additional combustion characteristics by a micro flow reactor with a controlled temperature profile

Micro flow reactor with controlled temperature profile

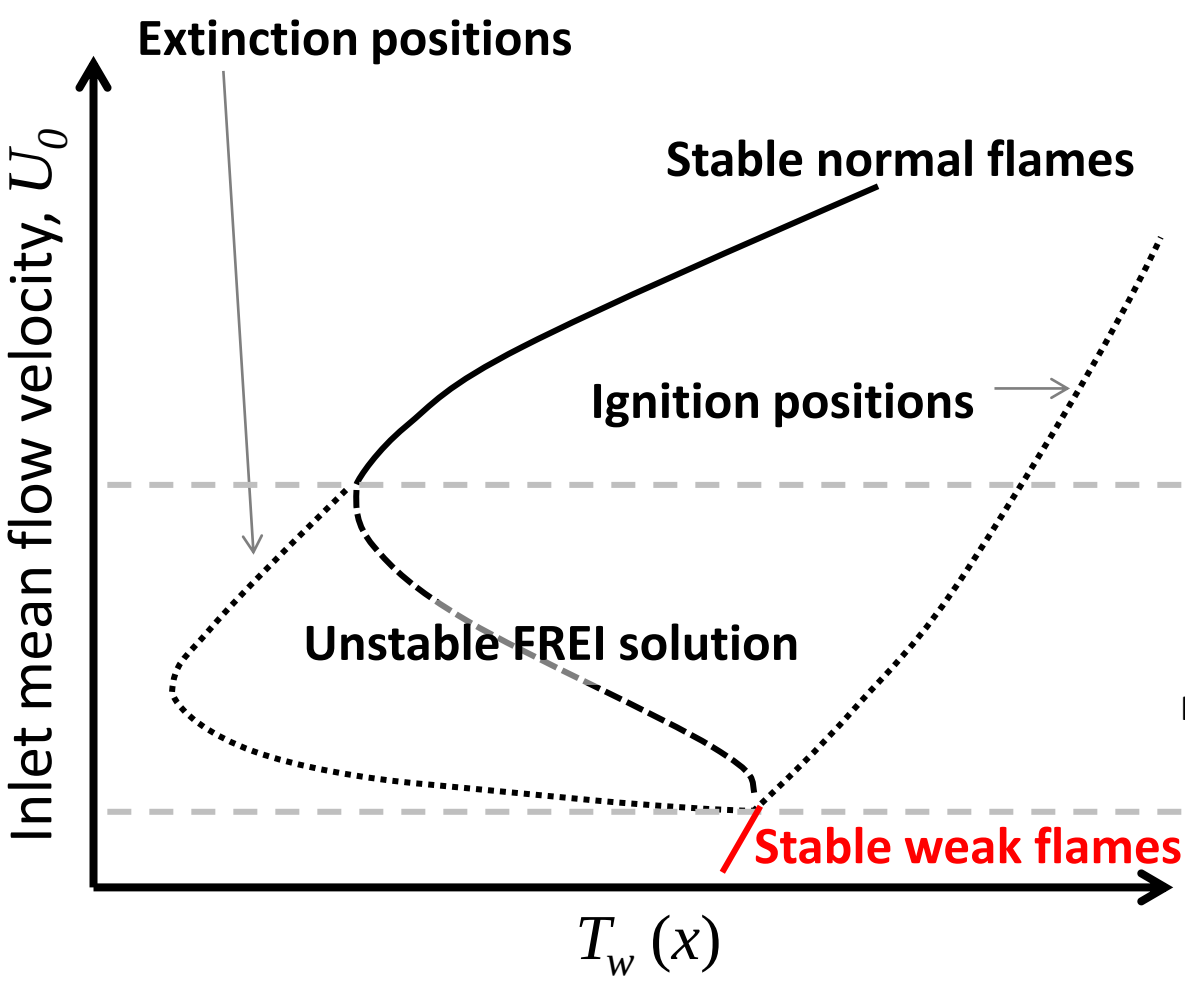


※Maruta et al., PCI 30, 32

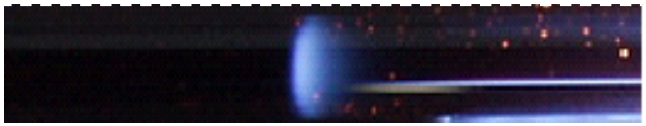
- Imposed wall-temperature profile along inner surface of reactor
- Inner diameter of the tube < Quenching diameter
- Laminar flow ($Re \approx 1$ - 100)
- Constant pressure

Interpretation of flame behavior in micro reactor

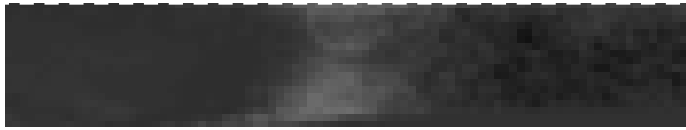
* Maruta et al., PCI 30, 32
* Minaev et al., CTM 11



ϕ = 1, CH_4/air



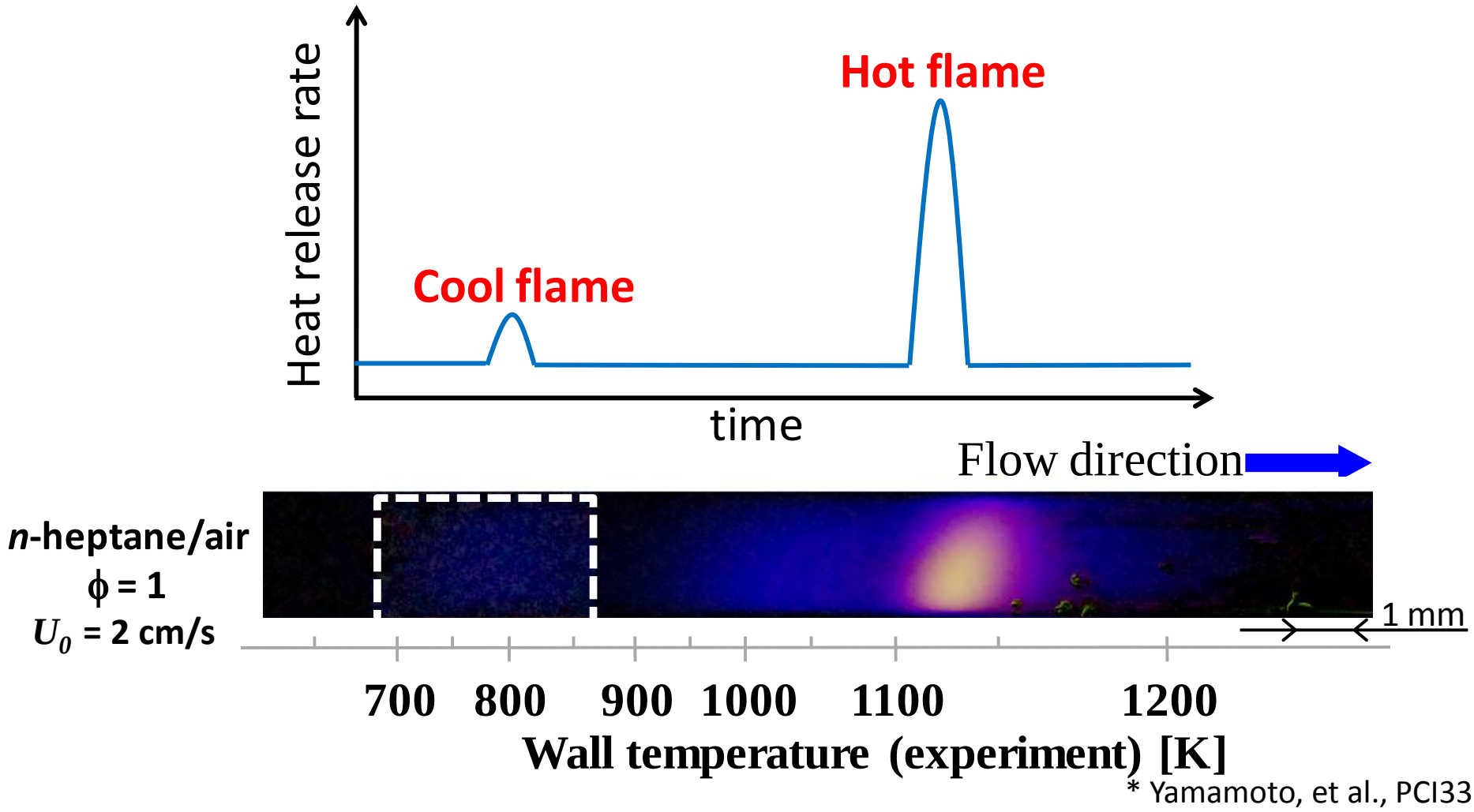
Flames with Repetitive Extinction and Ignition



- Three regimes were observed experimentally, numerically and theoretically
- Weak flame branch = ignition branch in Fendell curve
- Weak flame temperature ≈ wall temperature

Reactions in the temperature zone relevant for initiation of ignition

Separated weak flames and multi-stage ignition

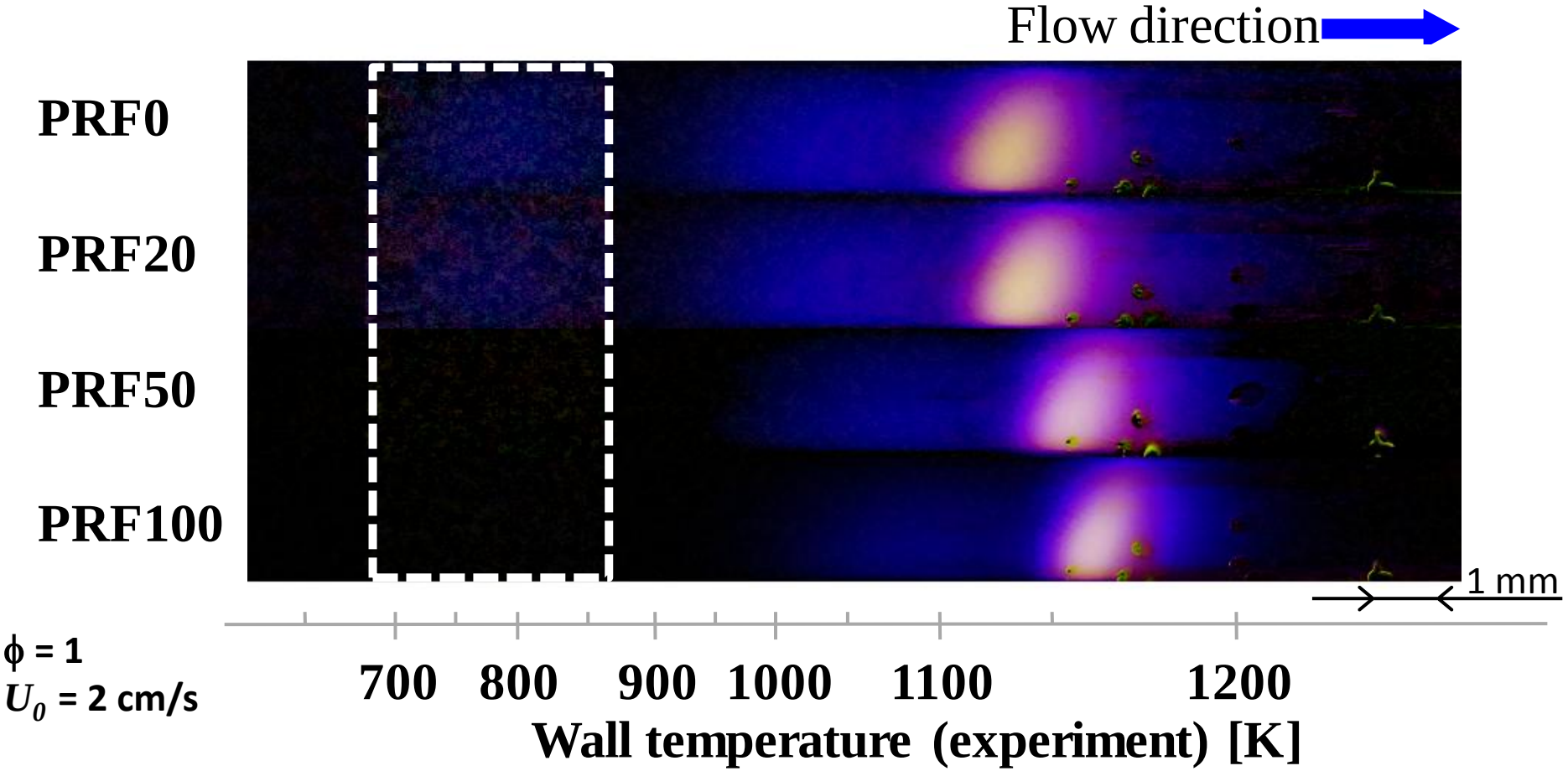


* Yamamoto, et al., PCI33

- Reactions in initiation of ignition can be investigated by steady, spatially-separated weak flames
- Spatial separation = identification of onset temperature of reactions

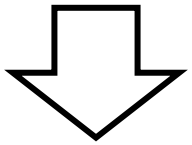
Fuel reactivity measurement

* Hori, et al., CNF (2012)



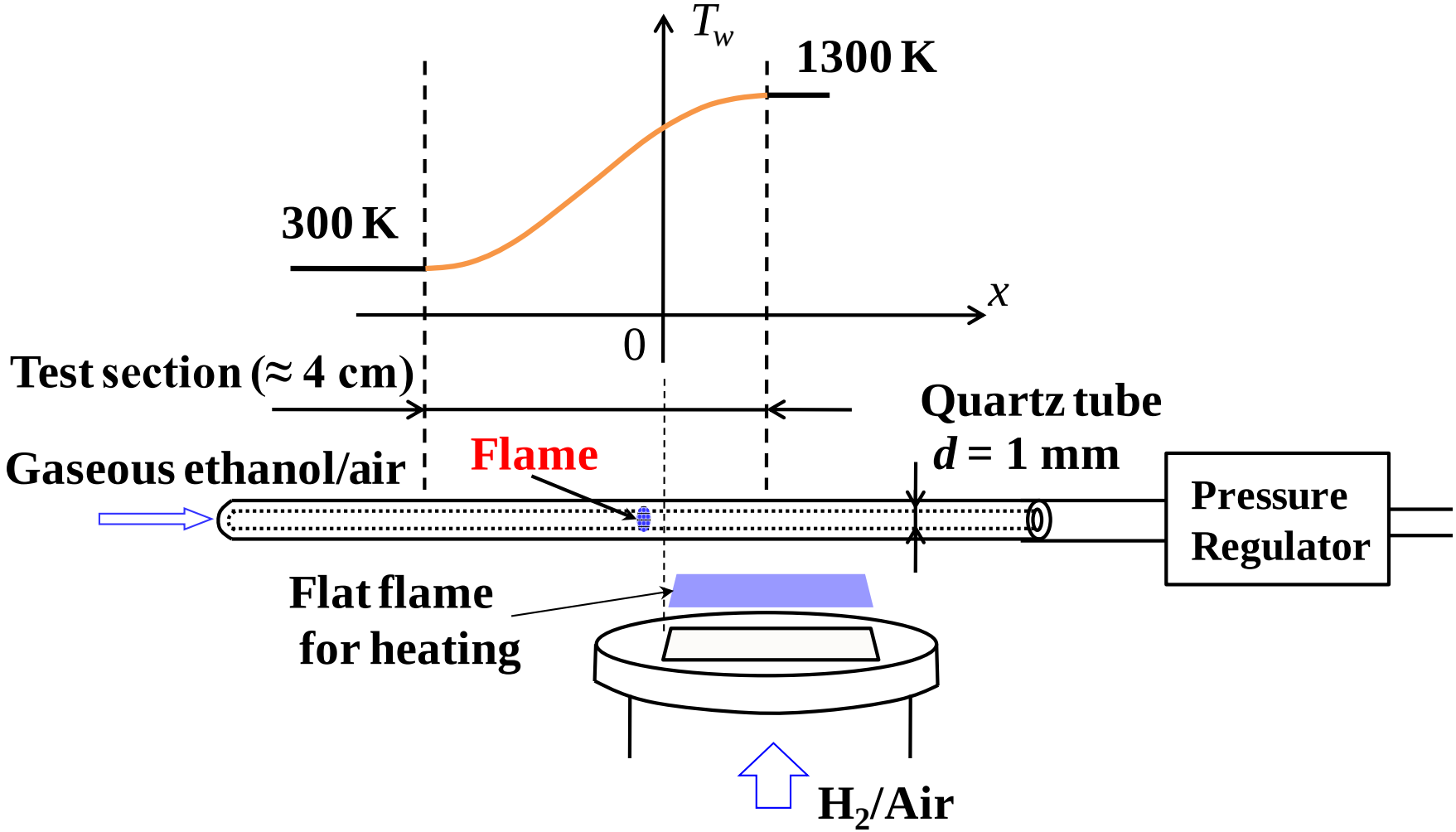
Objective

The methodology of a micro flow reactor with a controlled temperature profile is employed for an ethanol/air mixture



Investigate ethanol/air weak flames to examine detailed oxidation process and its pressure dependence

Experimental setup



- Stationary temperature profile along inner surface of reactor (300–1300 K for 4 cm) measured by a thermocouple
- ϕ = 1; U_0 = 2 cm/s; P = 1, 2, 3, 4 and 5 atm
- Flame images were taken by CH-filtered camera at 2 min. exposure

Computational method

Flame code: PREMIX-based 1-D steady code

Gas-phase energy equation:

Heat transfer with wall

$$\dot{M}\frac{dT}{dx}-\frac{1}{c_p}\frac{d}{dx}\left(\lambda A\frac{dT}{dx}\right)+\frac{A}{c_p}\sum_{k=1}^{K}\rho Y_k V_k c_{pk}\frac{dT}{dx}+\frac{A}{c_p}\sum_{k=1}^{K}\dot{\omega}_k h_k W_k-\frac{A}{c_p}\frac{4\lambda Nu}{d^2}(T_w-T)=0$$

Measured wall-temperature profile along inner surface of reactor was given to T_w

Kinetic models: UCSD mechanism Saxena & Williams, PCI 31 (2007)

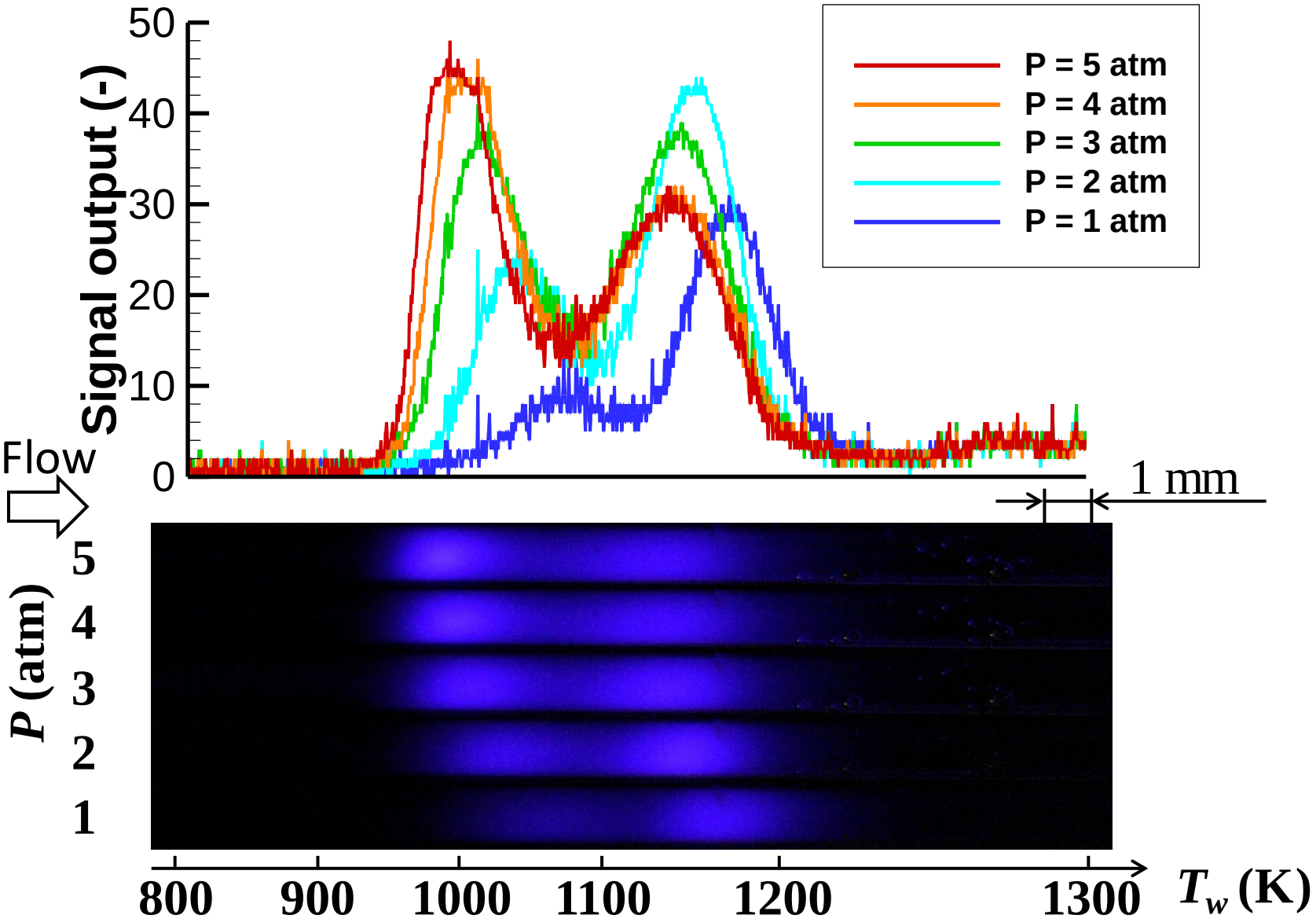
LLNL mechanism Marinov, Int. J. Chem. Kinet. 31 (1999)

Conditions:

- ϕ = 1 gaseous ethanol/air
- d = 1 mm
- U_0 = 2 cm/s
- P = 1, 2, 3, 4 and 5 atm

Pressure dependence of weak flames

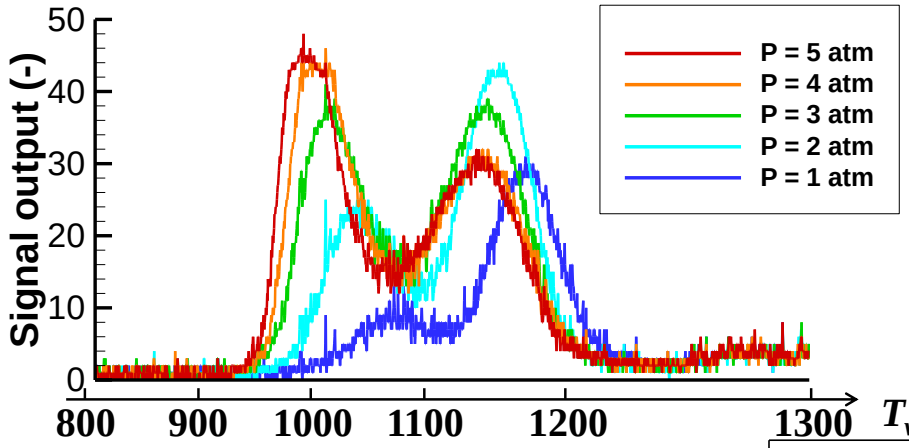
Pressure dependence of weak flames

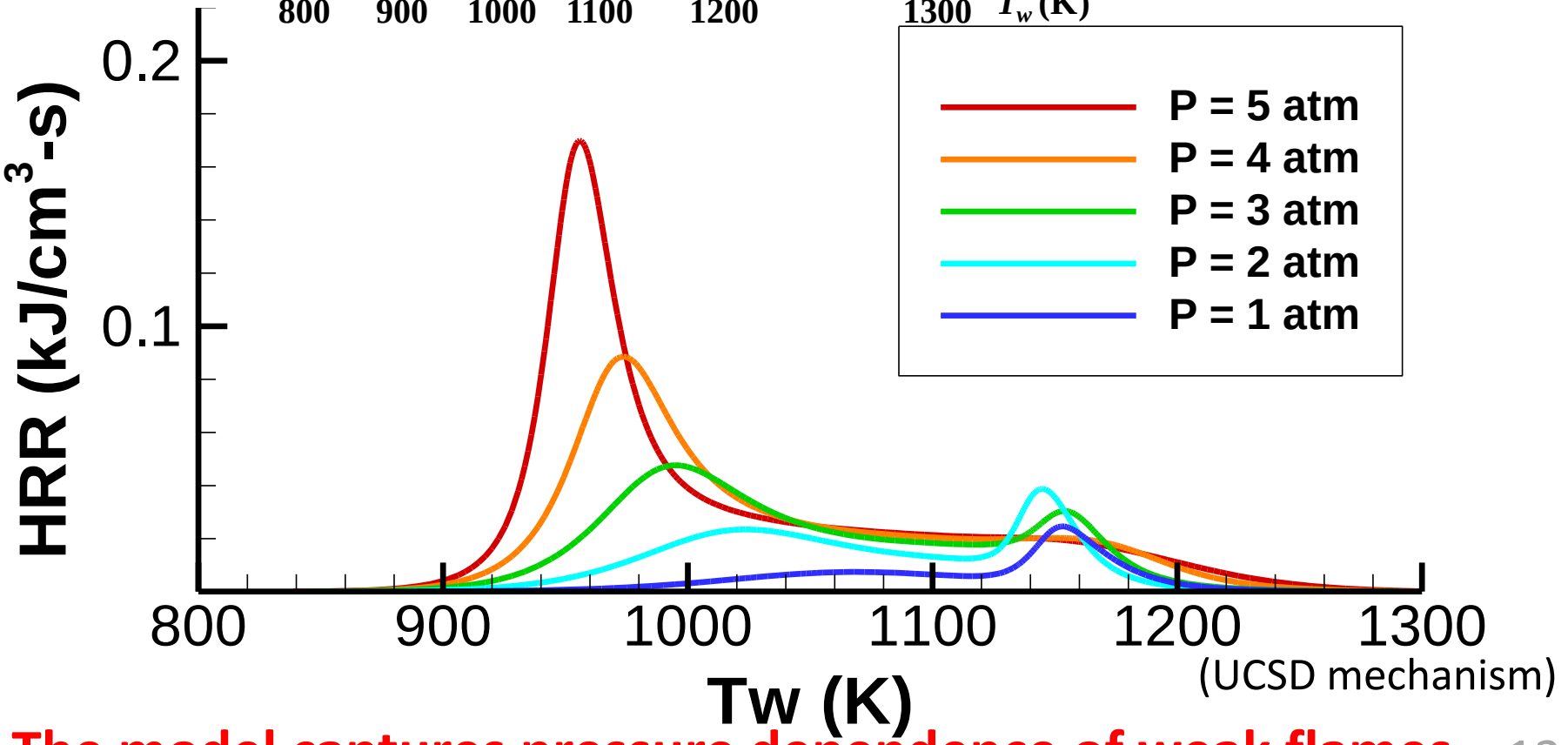


The first hot flame becomes more significant at higher pressure

Computational results and discussion (UCSD mechanism)

Pressure dependence of HRR



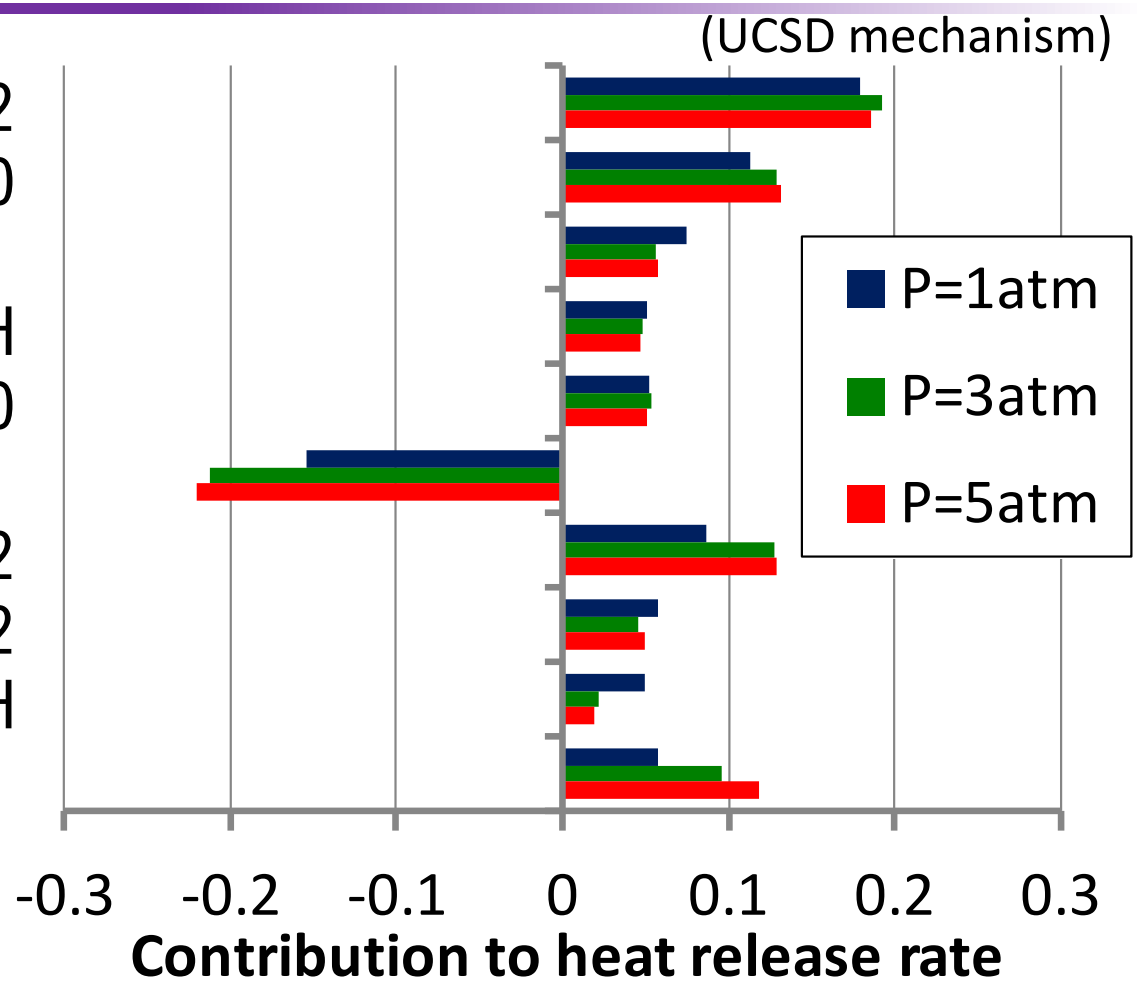


(UCSD mechanism)

The model captures pressure dependence of weak flames

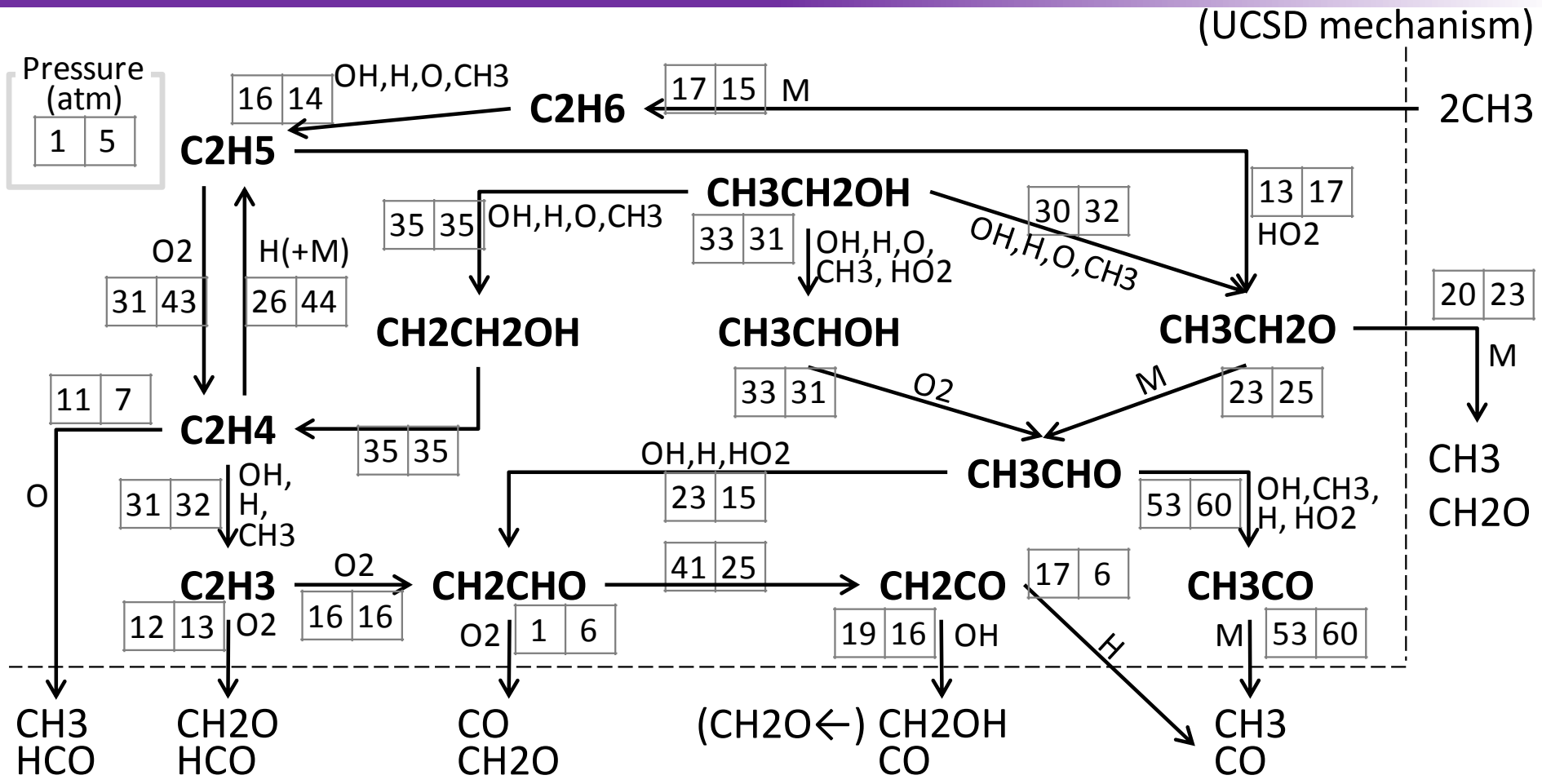
Contribution to HRR of first weak flame

R1 : HCO+O2<=>CO+HO2
R2 : CH2O+OH<=>HCO+H2O
R3 : 2CH3(+M)<=>C2H6(+M)
R4 : CH3+O2<=>CH2O+OH
R5 : C2H3+O2<=>CH2O+HCO
R6 : 2OH(+M)<=>H2O2(+M)
R7 : 2HO2<=>H2O2+O2
R8 : OH+HO2<=>H2O+O2
R9 : H+HO2<=>2OH
R10: H+O2(+M)<=>HO2(+M)



- C1 path (CH_3→CH_2O→HCO→CO: R4→R2→R1) contributes but CO→CO_2 does not contribute
- OH formation paths (HO_2→H_2O_2→OH: R10→R7→R6 and HO_2→OH: R10→R9) show pressure dependence

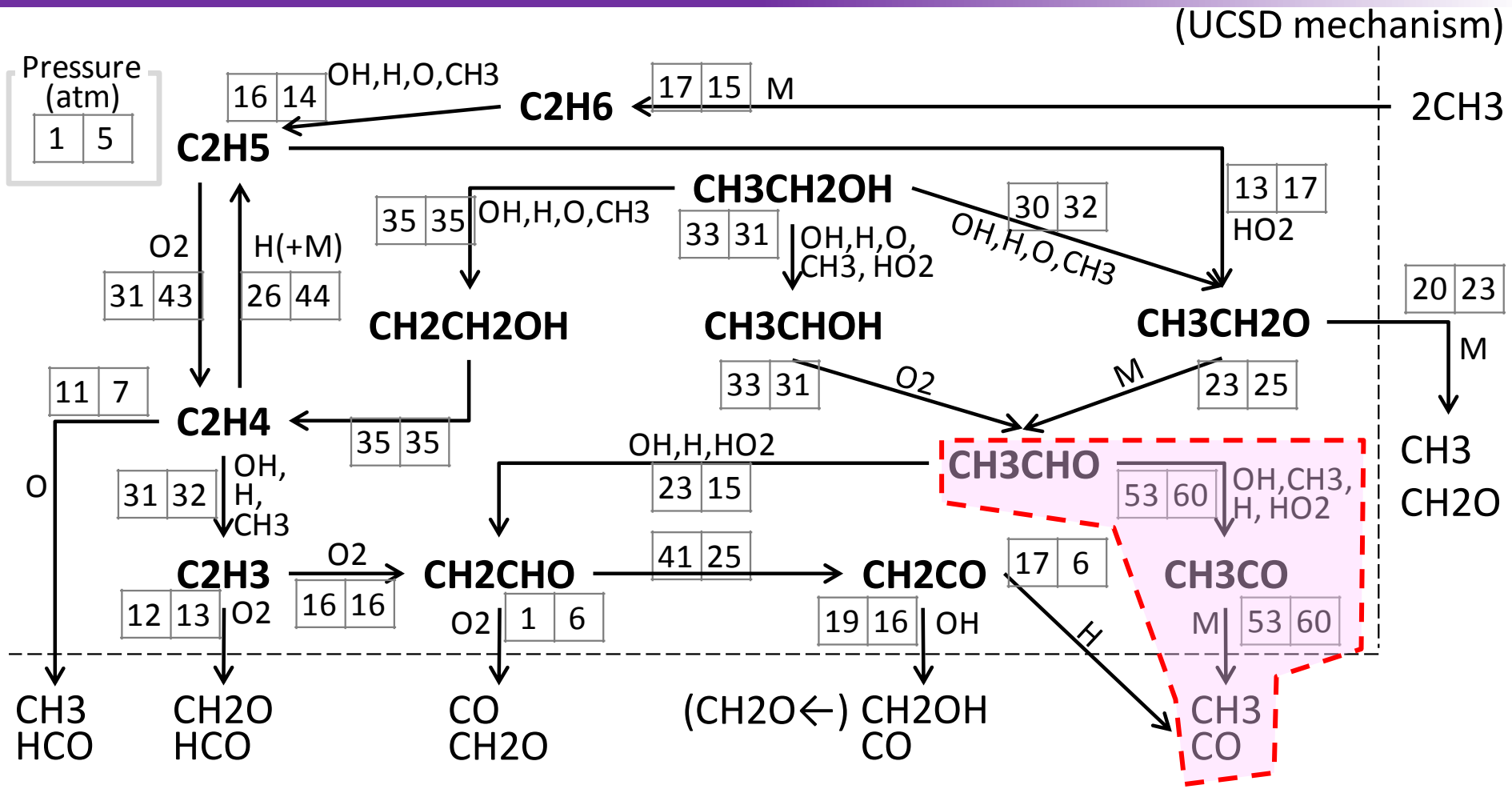
Reaction-path diagram of first weak flame



Normalized production rate by ethanol consumption rate is shown

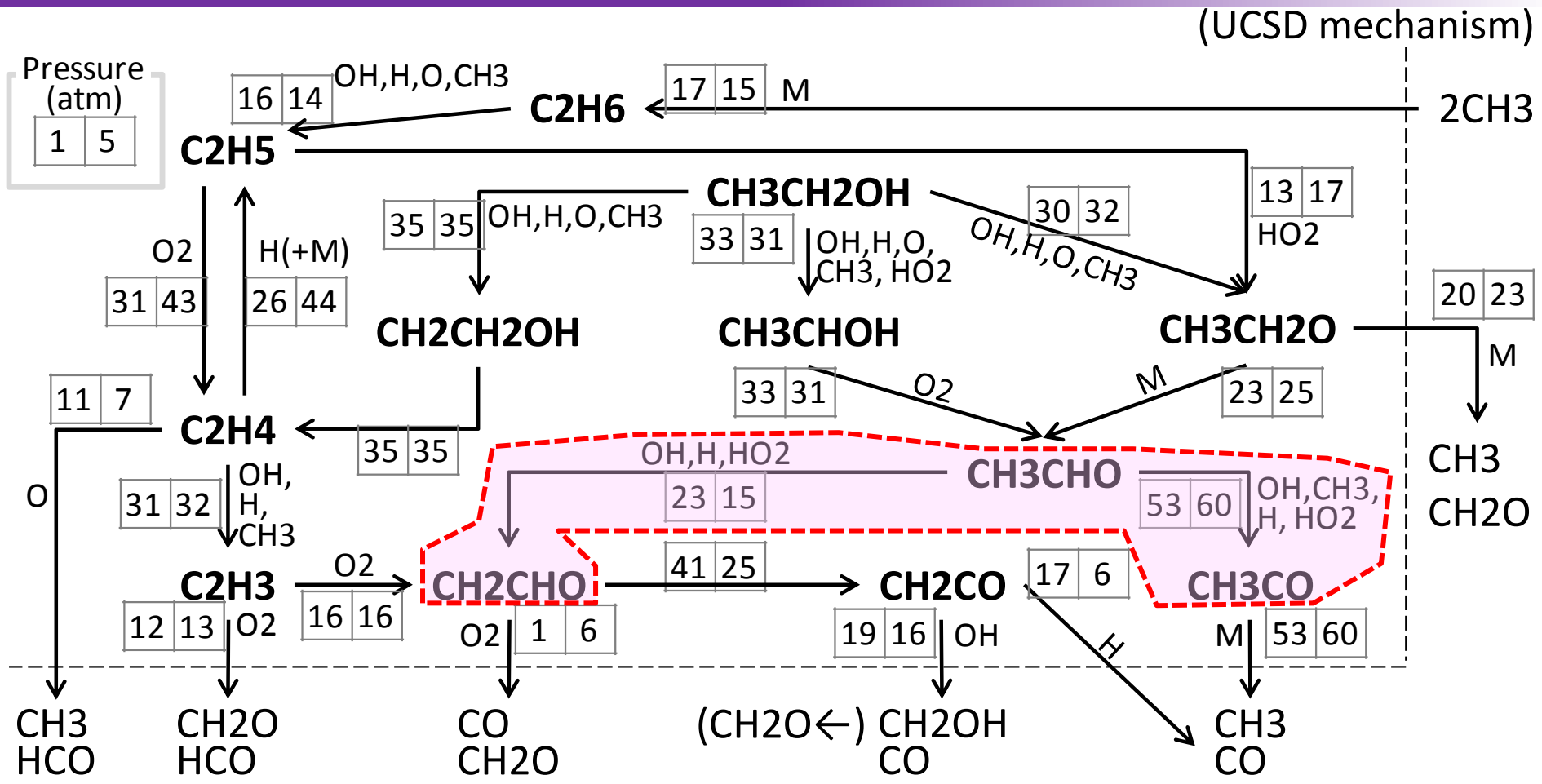
Larger value means more dominant reaction path for the whole oxidation process

Reaction-path diagram of first weak flame



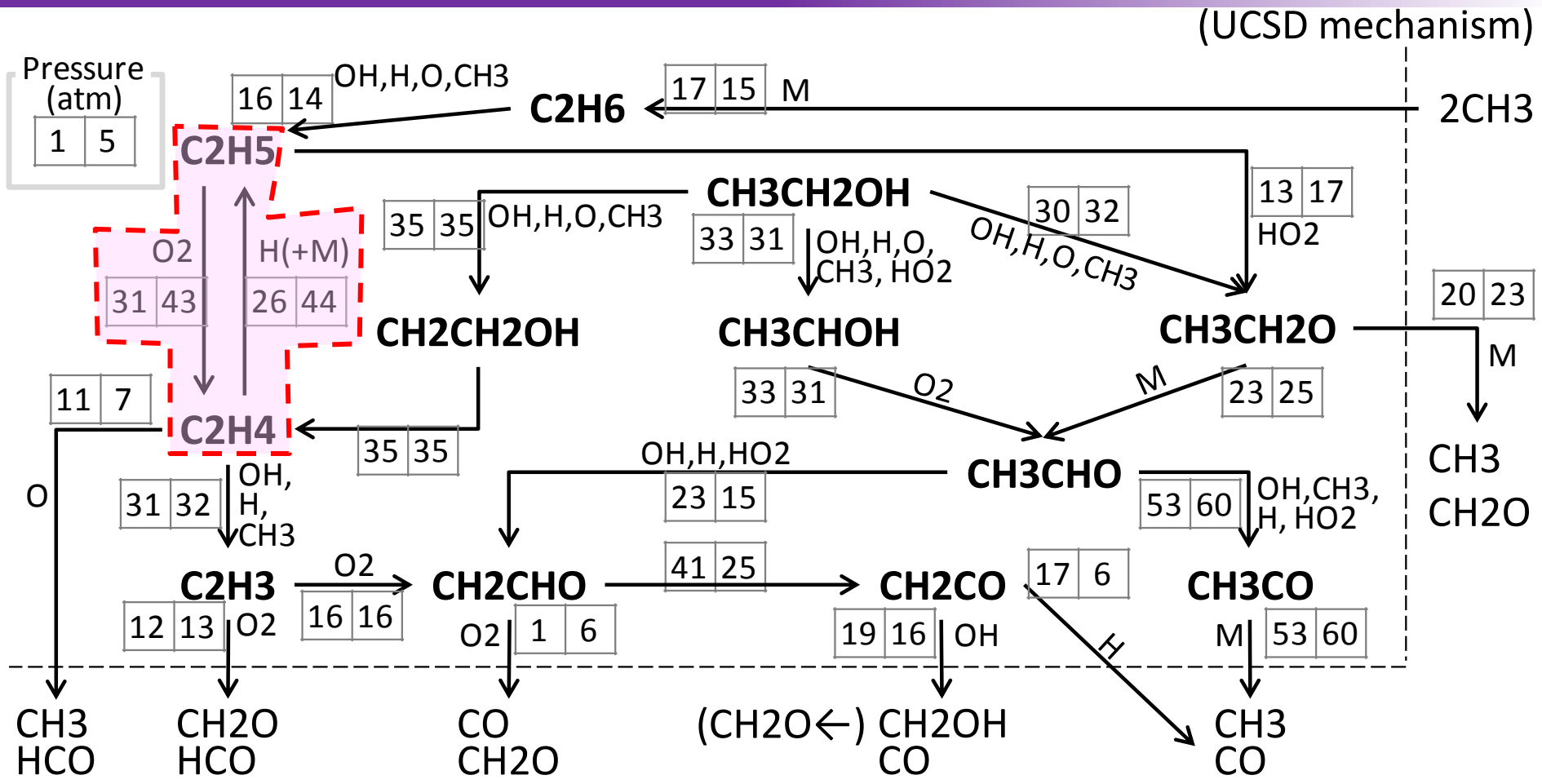
Production of C1 species through $CH_3CHO \rightarrow CH_3CO$ is dominant

Reaction-path diagram of first weak flame



Reaction path further shifts to $CH_3CHO \rightarrow CH_3CO$ at high pressure

Reaction-path diagram of first weak flame



$C_2H_4+H(+M)\rightarrow C_2H_5(+M)$

$C_2H_5+O2\rightarrow C_2H_4+HO_2$

$\Rightarrow$ $H+O_2\rightarrow HO_2$

HO_2 production through $C_2H_4 \Leftrightarrow C_2H_5$ is greater at higher pressure

Contribution to HRR of second weak flame

(UCSD mechanism)

R8 : HO2+OH<=>H2O+O2

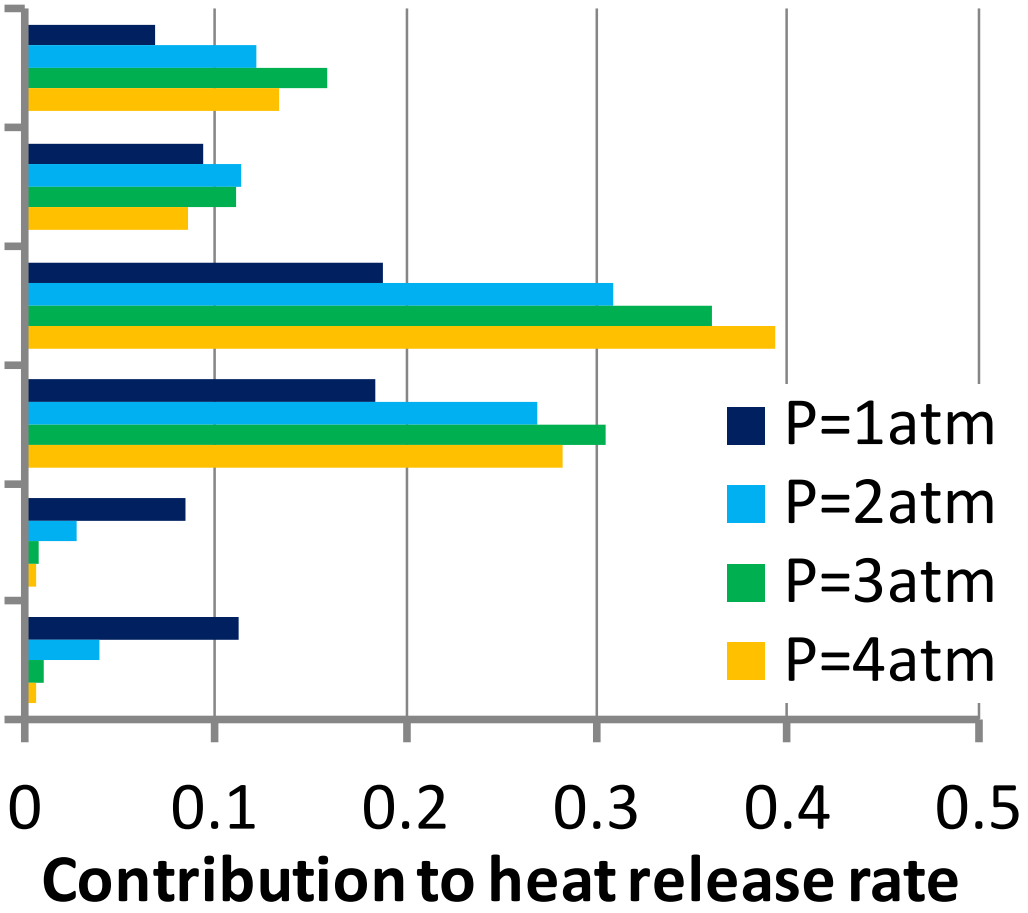
R9 : HO2+H<=>2OH

R10: H+O2(+M)<=>HO2(+M)

R11: CO+OH<=>CO2+H

R12: CH3+O<=>CH2O+H

R13: H+CH3(+M)<=>CH4(+M)



R8–10 (hydrogen-oxygen reactions) and R11 (CO oxidation) are dominant for contribution to HRR

Comparison with other fuels

First weak flame: Partial oxidation from fuel to CO
Second weak flame: CO oxidation and H_2-O_2 reactions

(P = 1 atm)

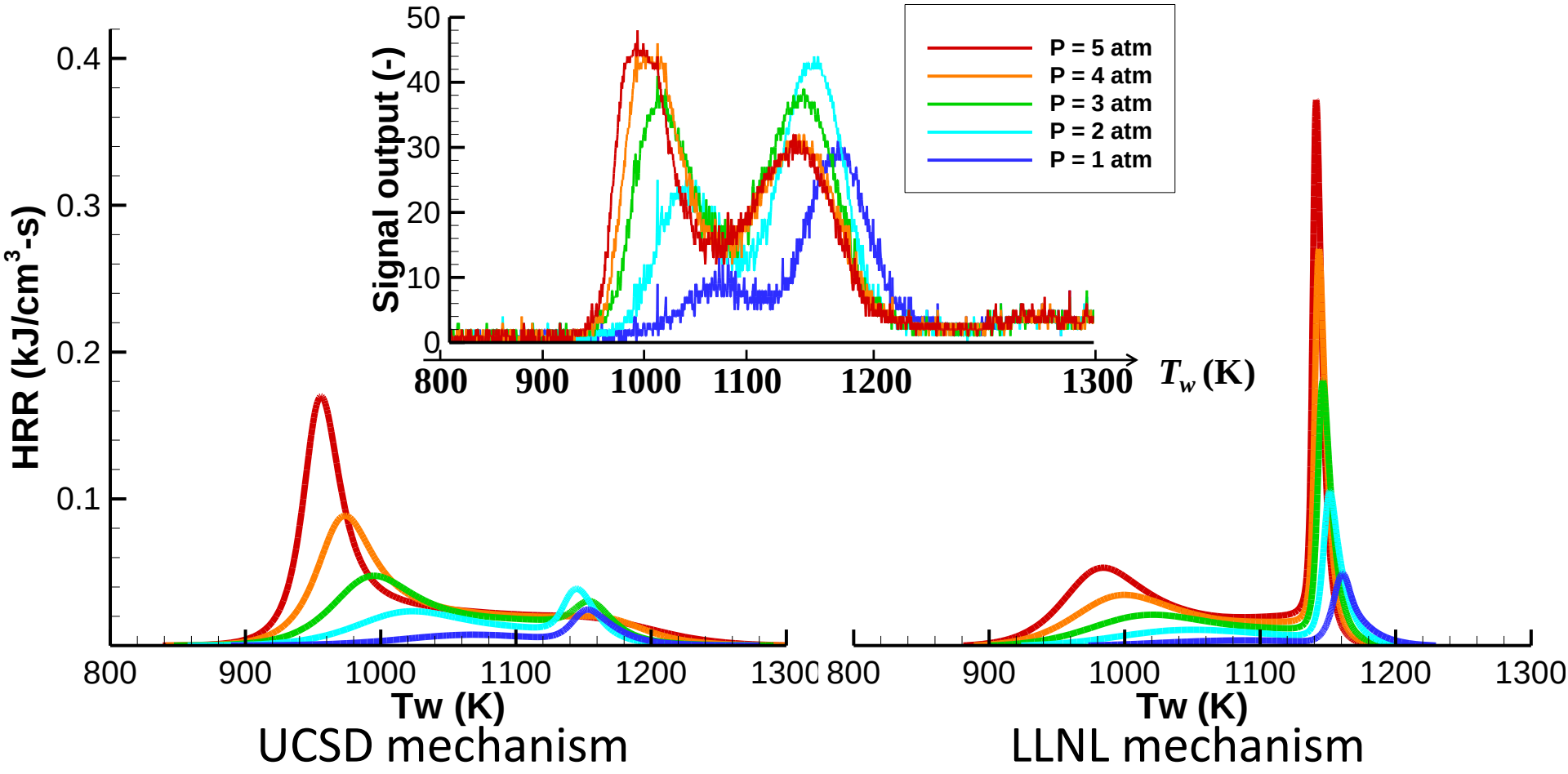
	Methane		*iso*-Octane		Ethanol
T_w at first weak flame (K)	1225[a]	>	1074[b]	≈	1073[c]
Bond-dissociation energy of H-abstraction (kcal/mol)	105[d]	>	96.5[d]	≈	96.1[d]

Good correlation between T_w at first weak flame and BDE

a: Tsuboi, et al., PCI 32 (2009);
One weak flame (no separated weak flames)
b: Hori, et al., CNF 159 (2012)
c: This study
d: Blanksby and Ellison, Acc. Chem. Res. 36 (2003)

Differences between UCSD and LLNL mechanisms

Pressure dependence of HRR



UCSD mechanism

LLNL mechanism

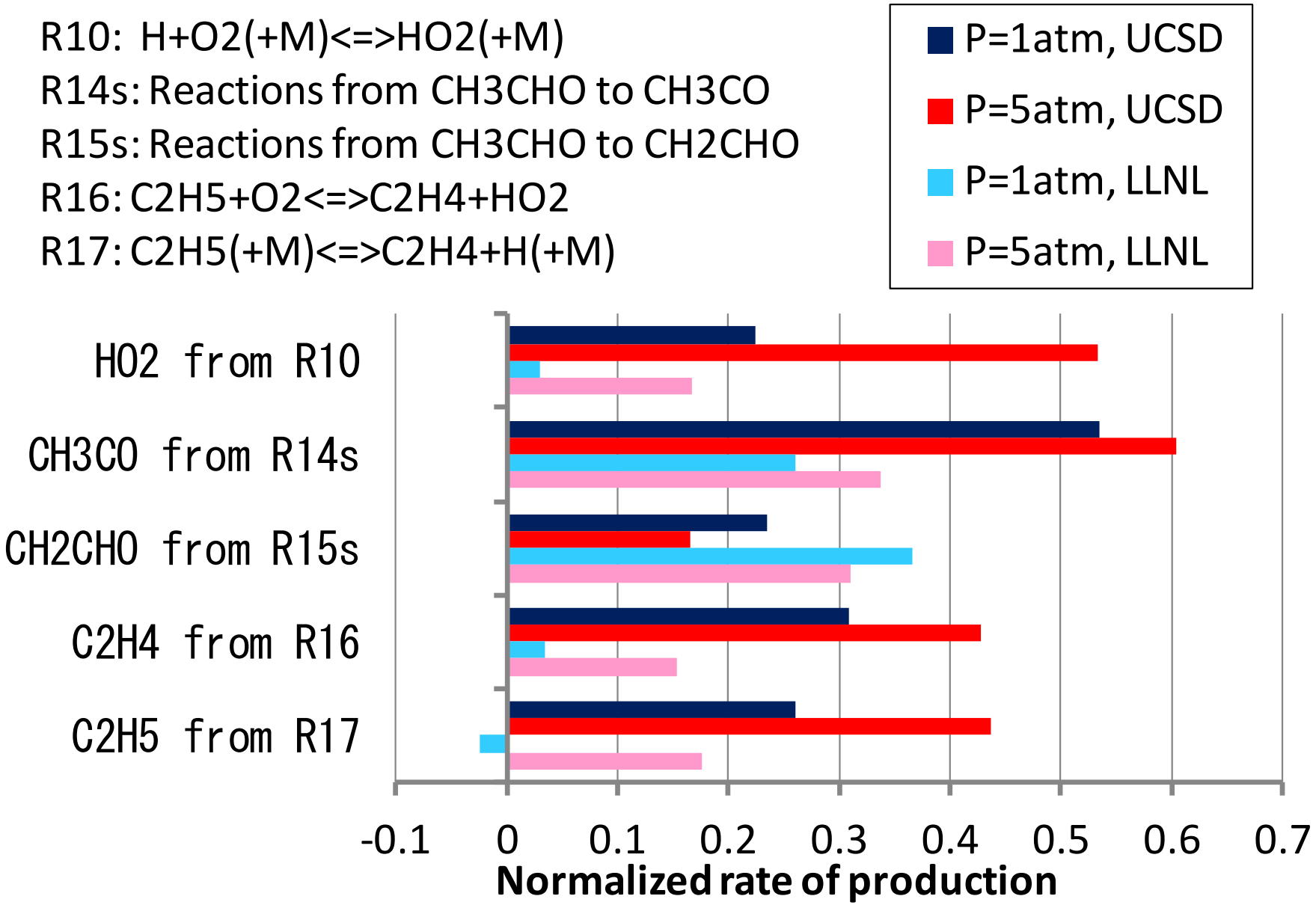
Two mechanisms show totally different pressure dependence of HRR

UCSD: first weak flame is too strong

LLNL: first weak flame is too weak

Rate of production analysis at first weak flame

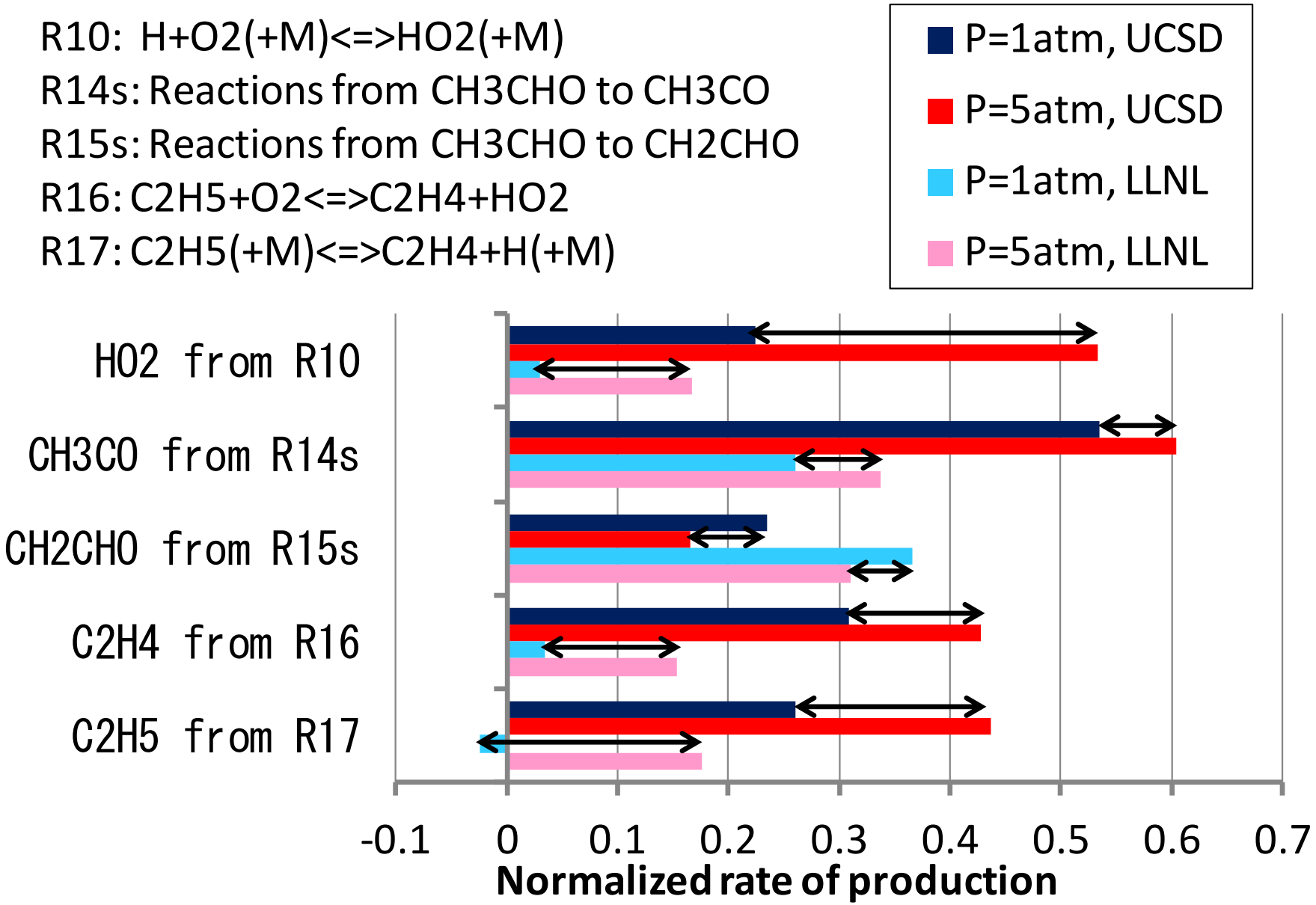
R10: H+O2(+M)<=>HO2(+M)
R14s: Reactions from CH3CHO to CH3CO
R15s: Reactions from CH3CHO to CH2CHO
R16: C2H5+O2<=>C2H4+HO2
R17: C2H5(+M)<=>C2H4+H(+M)



UCSD shows higher production rates than LLNL except CH_2CHO

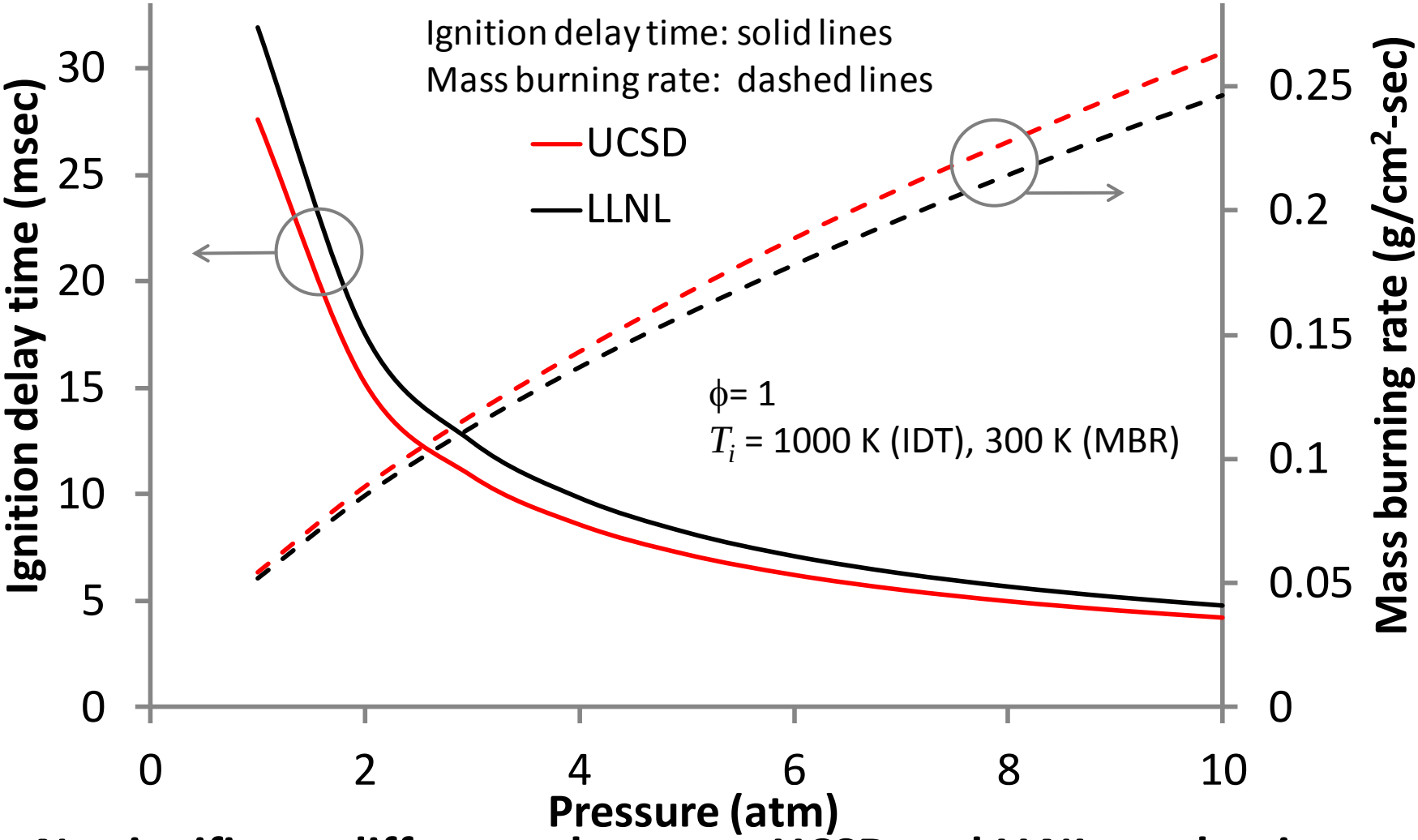
Rate of production analysis at first weak flame

R10: H+O2(+M)<=>HO2(+M)
R14s: Reactions from CH3CHO to CH3CO
R15s: Reactions from CH3CHO to CH2CHO
R16: C2H5+O2<=>C2H4+HO2
R17: C2H5(+M)<=>C2H4+H(+M)



UCSD R10 shows higher pressure dependence than LLNL R10

Ignition delay time and mass burning rate



No significant difference between UCSD and LLNL mechanisms

The micro flow reactor methodology would provide additional information of ethanol combustion characteristics which are not clearly shown by other methods.

Conclusions (1)

The methodology of a micro flow reactor with a controlled temperature profile has been employed for an ethanol/air mixture.

1. The separated weak flames were observed.

2. Pressure dependences of weak flames were identified. The first weak flame becomes more significant at higher pressure.

3. The first weak flame is characterized as partial oxidation from ethanol to CO. The second weak flame is characterized as CO oxidation and H_2-O_2 reactions.

Conclusions (2)

4. Good correlation between T_w at the first weak flame and BDE were identified.

5. UCSD and LLNL mechanisms shows no significant difference of pressure dependences of ignition delay time and mass burning rate. However, two mechanisms shows different pressure dependences of weak flames.

6. $H+O_2(+M) \Leftrightarrow HO_2(+M)$, CH_3CHO oxidation, $C_2H_5+O_2 \Leftrightarrow C_2H_4+HO_2$ and $C_2H_4+H(+M) \Leftrightarrow C_2H_5(+M)$ are dominant reactions at the first weak flame, and shows significant difference between UCSD and LLNL mechanisms.