# Possibility of Thermal Ignition Enhancement by Spark Discharge

## - Explanation by $RO_2$ and $H_2O_2$ Chemistry -

**IEA TLM**

**Nara Royal Hotel**

**2010.07.29**

**Hiromitsu ANDO** *University of Fukui*
**Yasuyuki SAKAI**

**Kazunari KUWAHARA** *Osaka Inst. of Technology*

# Key Word

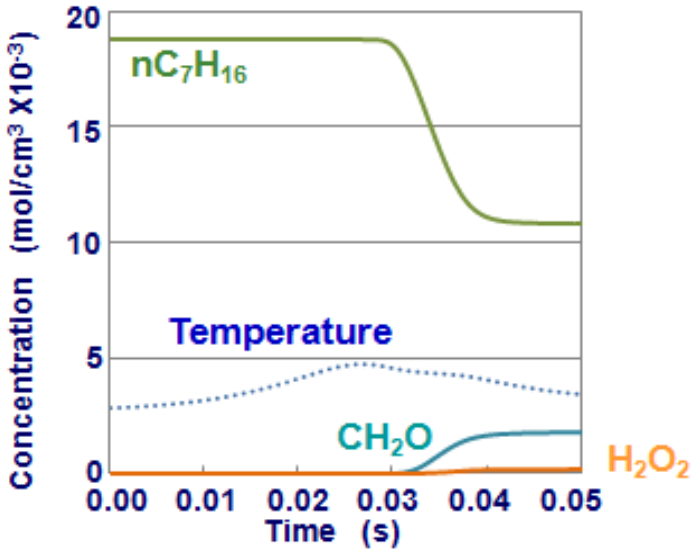
## Back Ground

# Why Ignition-delay should be Shortened ?

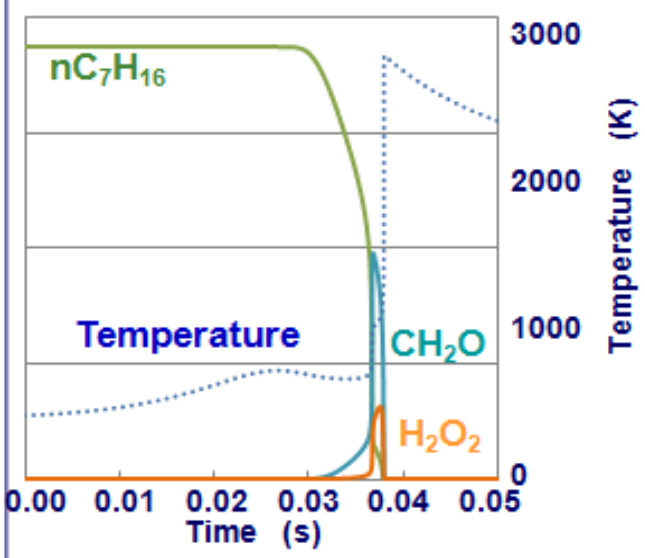
nc7h16
ϕ=0.5

Comp. Ratio : 6.15

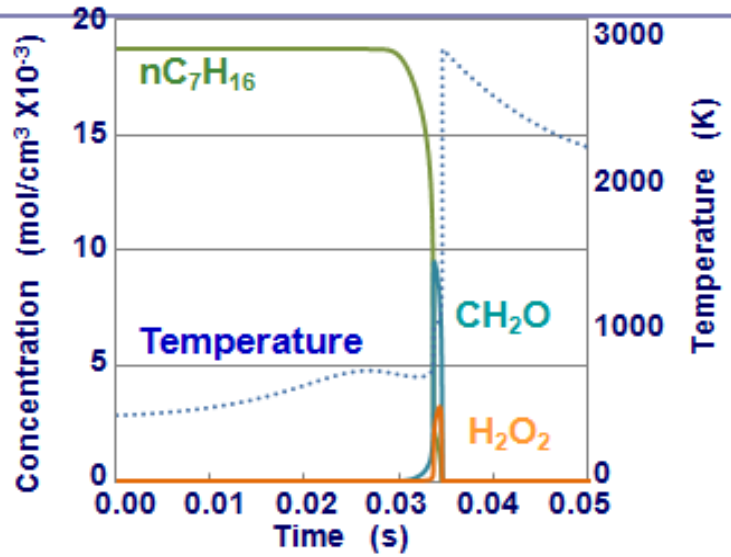
Engine Speed : 900 (rpm)

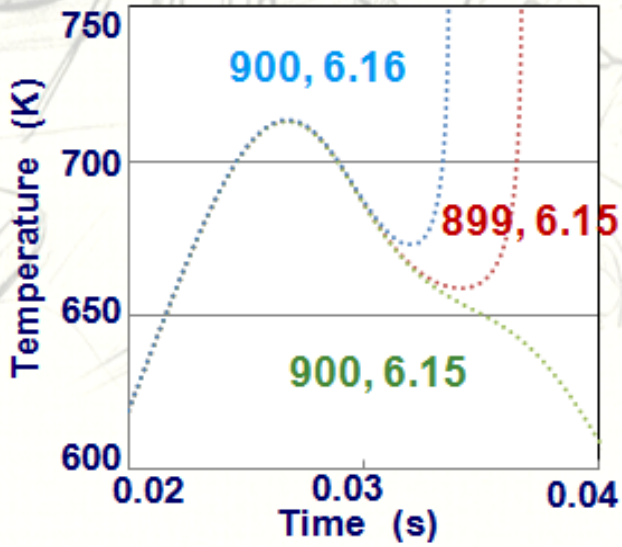



Engine Speed : 899 (rpm)

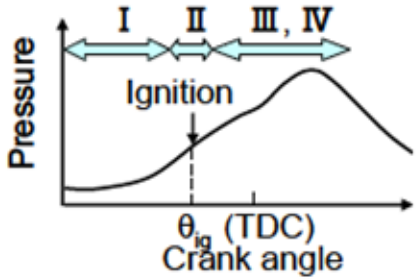



Comp. Ratio : 6.16

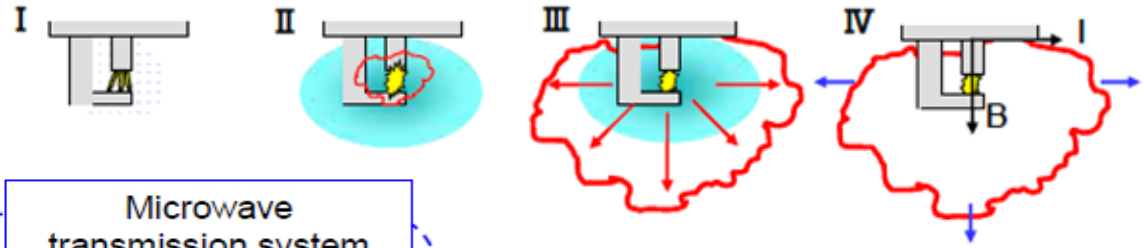


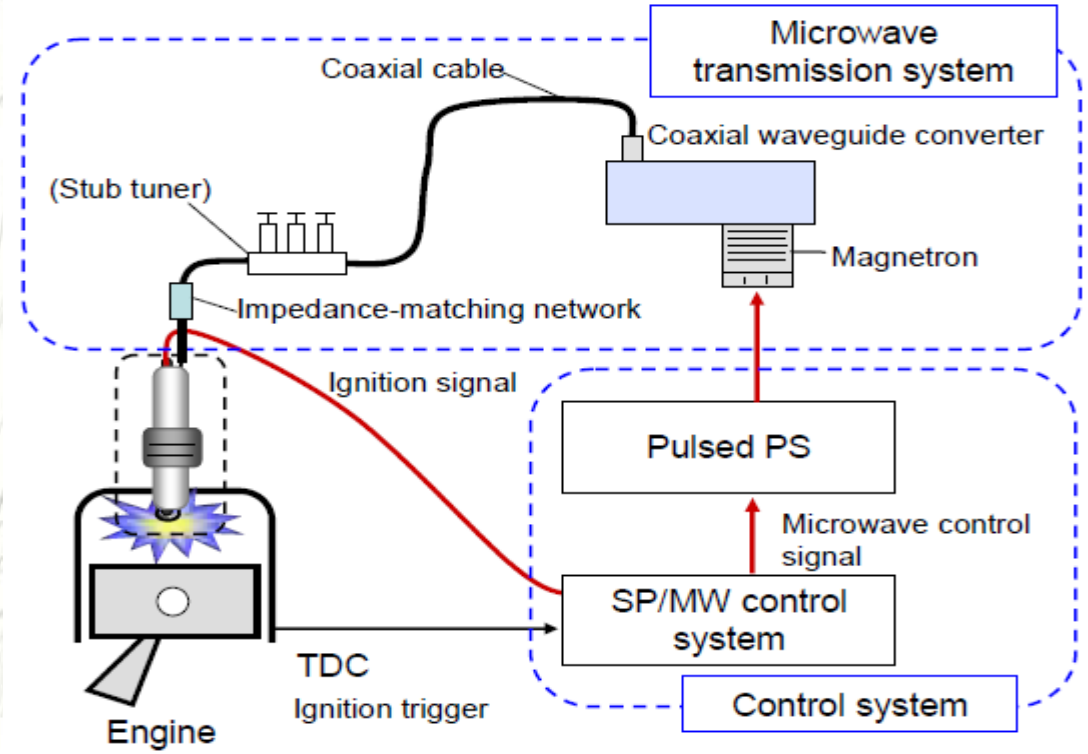



# A Tool for OH Formation ?



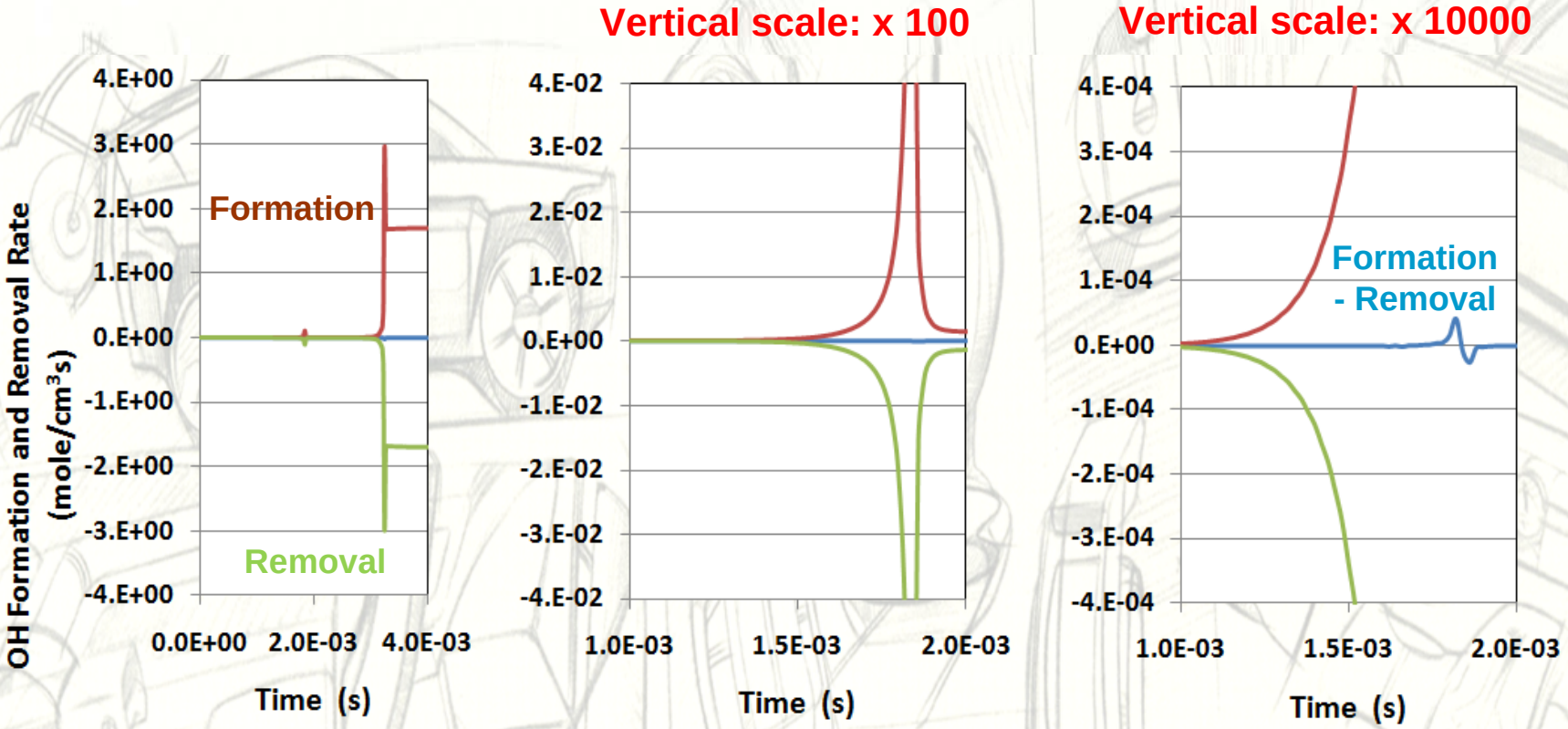

Ⅰ. Intensive microwave filed formation(< MIE)
Ⅱ. Plasma formation by spark plug trigger
Ⅲ. Spontaneous/volume ignition, radical generation, combustion
Ⅳ. Flame propagation enhancement by magnetic field




**Ikeda, Y. , Nishiyama, A., Wachi, Y., Kaneko. M., SAE Paper No.2009-01-1049 (2009)**

# Can OH Initiate Avalanche




nc7h16
$T_0$=759 K
$p_0$=2.0 MPa
$\phi$=0.5

# Common Understandings and Misunderstandings

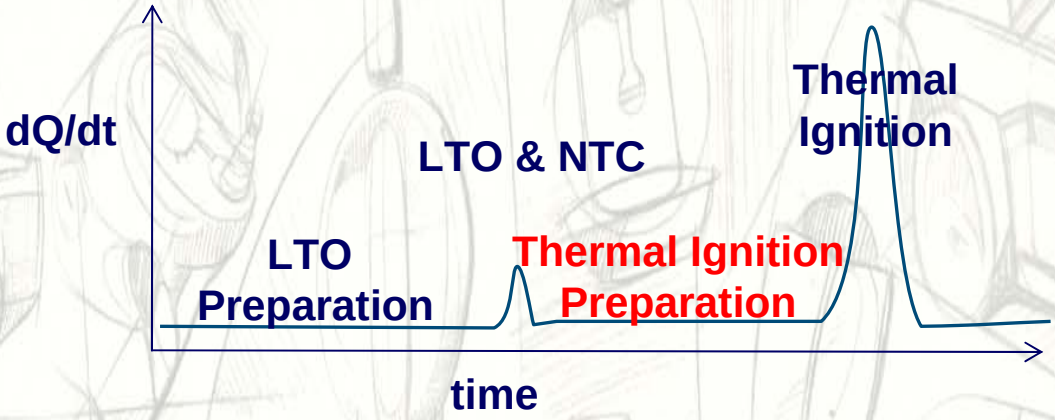
1. OH plays a significant role in LTO → True
2. Thermal ignition takes place by radical chain branching → True
3. In the radical chain branching phase, → True
   OH increases exponentially
4. Thermal ignition can be triggered by trace amount of OH → False
5. Ignition is triggered;

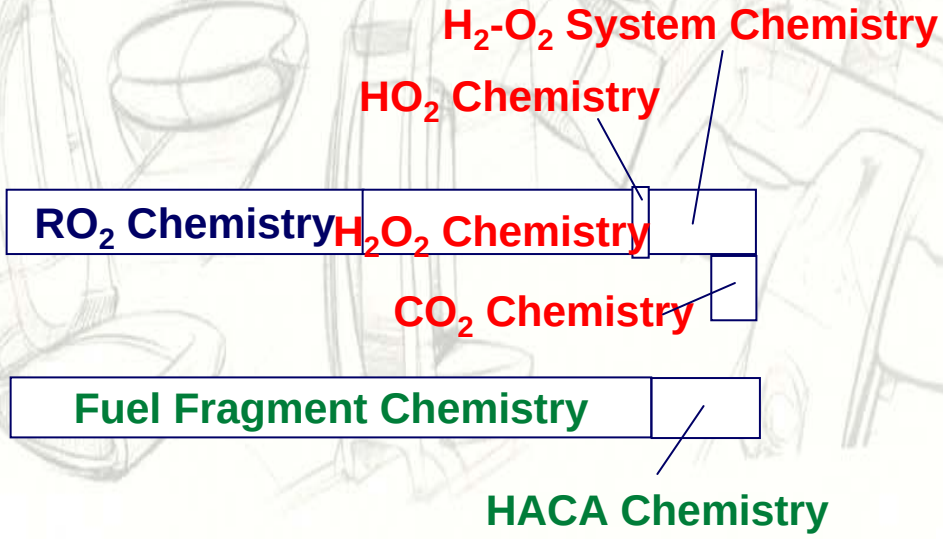
   not by radical → True
   but by radical increasing condition

# Global Understanding of Combustion Chemistry

# Regimes of Combustion Chemistry

1. $RO_2$ Chemistry
2. $H_2O_2$ Chemistry
3. $HO_2$ Chemistry
4. $H_2$-$O_2$ System Chemistry
5. $CO_2$ Chemistry
6. Fuel Fragment Chemistry
7. HACA Chemistry



# $RO_2$ Chemistry and Fragment Chemistry

# $RO_2$ Chemistry

$nC_7H_{16}$, $T_0$=759 K,
$p_0$=2.0 Mpa, $\phi$=0.5

nc7h16

oh/h2o

| R | RO2 | QOOH | QOOHO2 | ketcarcoxyl |
|---|---|---|---|---|
| c7h15-3 | c7h15o2-3 | c7h14ooh3-5 | c7h14ooh3-5o2 | nc7ket35 |
| c7h15-2 | c7h15o2-2 | c7h14ooh2-4 | c7h14ooh2-4o2 | nc7ket24 |
| c7h15-1 | c7h15o2-1 | c7h14ooh1-3 | c7h14ooh1-3o2 | nc7ket13 |
| c7h15-4 | c7h15o2-4 | c7h14ooh4-2 | c7h14ooh4-2o2 | nc7ket42 |
| c7h15-3 | c7h15o2-3 | c7h14ooh3-6 | c7h14ooh3-6o2 | nc7ket36 |
| c7h15-3 | c7h15o2-3 | c7h14ooh3-4 | c7h14ooh3-4o2 | nc7ket34 |
| c7h15-3 | c7h15o2-3 | c7h14ooh3-2 | c7h14ooh3-2o2 | nc7ket32 |
| c7h15-3 | c7h15o2-3 | c7h14ooh3-1 | c7h14ooh3-1o2 | nc7ket31 |
| c7h15-2 | c7h15o2-2 | c7h14ooh2-5 | c7h14ooh2-5o2 | nc7ket25 |
| c7h15-2 | c7h15o2-2 | c7h14ooh2-3 | c7h14ooh2-3o2 | nc7ket23 |
| c7h15-1 | c7h15o2-1 | c7h14ooh1-4 | c7h14ooh1-4o2 | nc7ket14 |
| c7h15-1 | c7h15o2-1 | c7h14ooh1-2 | c7h14ooh1-2o2 | nc7ket12 |
| c7h15-4 | c7h15o2-4 | c7h14ooh4-3 | c7h14ooh4-3o2 | nc7ket43 |

o2/ iso /oh /oh

oh/h2o

| R | RO2 | QOOH | alkene |
|---|---|---|---|
| c7h15-3 | c7h15o2-3 | c7h14ooh3-4 | c7h14-3 |
| c7h15-3 | c7h15o2-3 | c7h14ooh3-2 | c7h14-2 |
| c7h15-2 | c7h15o2-2 | c7h14ooh2-3 | c7h14-2 |
| c7h15-1 | c7h15o2-1 | c7h14ooh1-2 | c7h14-1 |

o2/ iso /ho2

oh/h2o

| R | RO2 | QOOH | cyclo-ether |
|---|---|---|---|
| c7h15-3 | c7h15o2-3 | c7h14ooh3-6 | c7h14o2-5 |
| c7h15-3 | c7h15o2-3 | c7h14ooh3-1 | c7h14o1-3 |
| c7h15-2 | c7h15o2-2 | c7h14ooh2-5 | c7h14o2-5 |
| c7h15-1 | c7h15o2-1 | c7h14ooh1-3 | c7h14o1-3 |
| c7h15-1 | c7h15o2-1 | c7h14ooh1-4 | c7h14o1-4 |
| c7h15-3 | c7h15o2-3 | c7h14ooh3-1 | |

o2/ iso /oh

**Expression of Reaction**

X aa/bb Y

X+aa=Y+bb

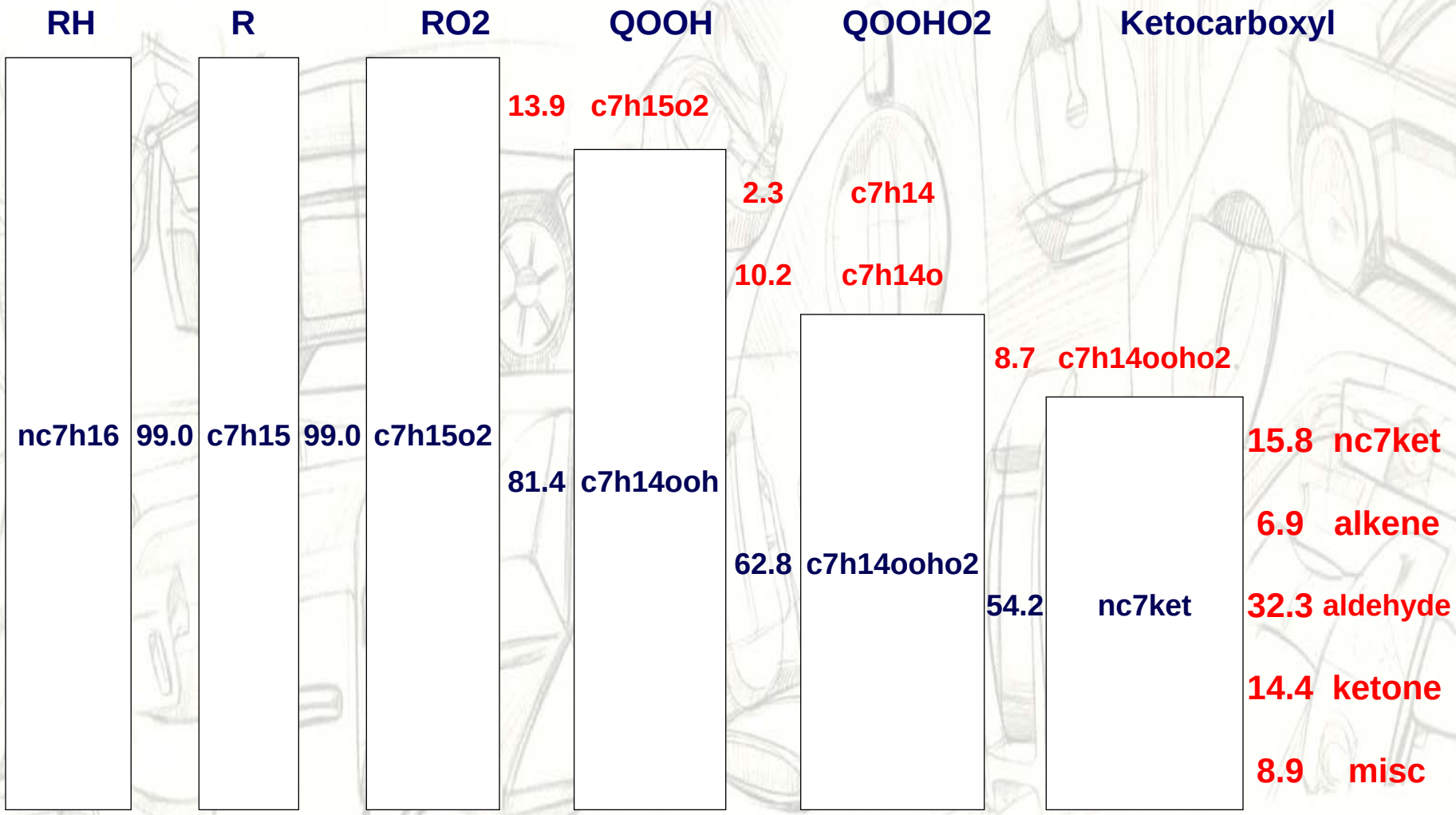
iso: isomerization
β: β scission

# Fragment Chemistry

## β Scission

| ketcarcoxyl | alkene | aldehyde | | | | ketone | miscelleneous | |
|---|---|---|---|---|---|---|---|---|
| nc7ket35 | c2h4 | /oh | c2h5cho | | | c2h5coch2 | ch2co | c2h5o2 |
| nc7ket24 | | /oh | nc3h7cho | /oh | ch2o | ch3coch2o2 | ch3co3 | ch3coch2o2h |
| nc7ket13 | | /oh | nc4h9cho | /oh | ch2o | | | |
| nc7ket42 | | /oh | ch3cho | | | nc3h7coch2 | | |
| nc7ket36 | c2h4 | /oh | ch3cho | | | c2h5coc2h4p | c2h5co | c2h5o2 |
| nc7ket34 | c2h4 | /oh | nc3h7cho | | | | c2h5o2 | |
| nc7ket32 | c2h4 | /oh | ch3cho | /oh | ch2o | | c4h8ooh1-3o2 | nc4ket13 |
| nc7ket31 | | /oh | ch2o | | | nc4h9coch2 | | |
| nc7ket25 | c2h4 | /oh | c2h5cho | | | | ch3o2h | ch3co3 |
| nc7ket23 | | /oh | nc4h9cho | /oh | ch2o | | ch3o2 | |
| nc7ket14 | c2h4 | /oh | nc3h7cho | | | | | |
| nc7ket12 | | /oh | nc5h11cho | | | | | |
| nc7ket43 | c3h6 | /oh | c2h5cho | | | | nc3h7o2 | |

# $RO_2$ Chemistry

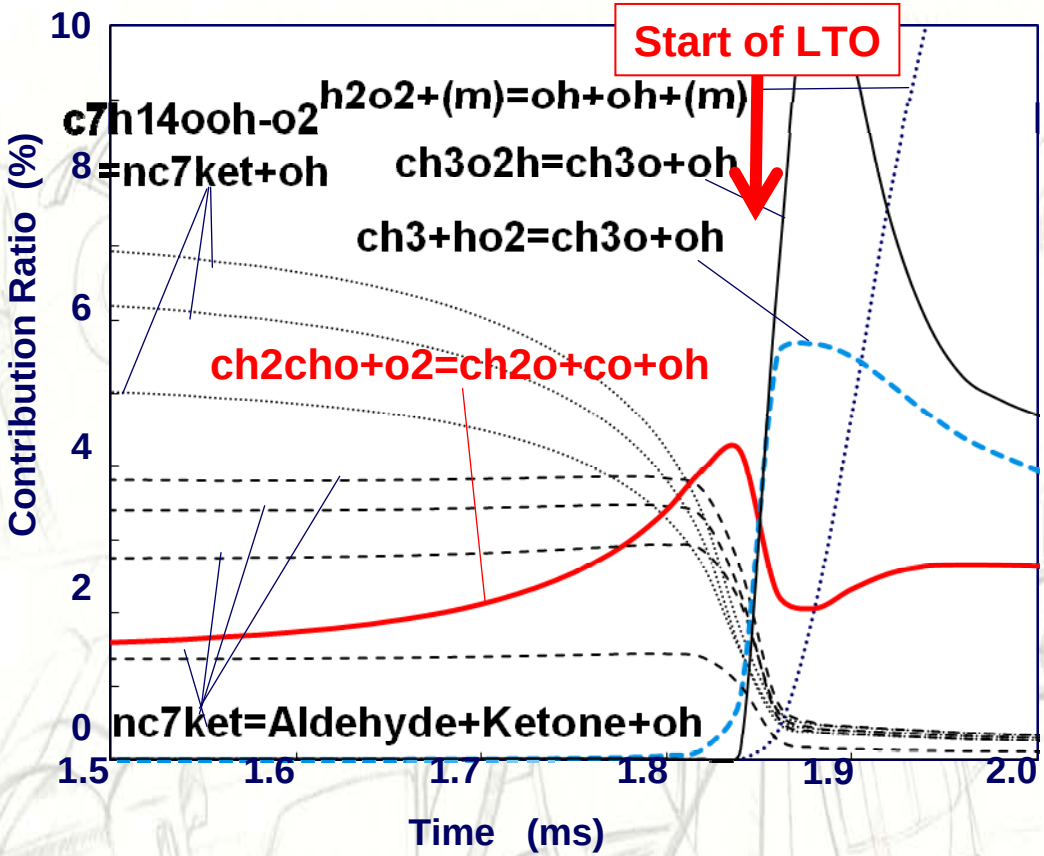


# Fragment Chemistry

## β Scission

| ketcarcoxyl | alkene | aldehyde | | | | ketone | miscelleneous | |
|---|---|---|---|---|---|---|---|---|
| nc7ket35 | c2h4 | /oh | c2h5cho | | | c2h5coch2 | ch2co | c2h5o2 |
| nc7ket24 | | /oh | nc3h7cho | /oh | ch2o | ch3coch2o2 | ch3co3 | ch3coch2o2h |
| nc7ket13 | | /oh | nc4h9cho | /oh | ch2o | | | |
| nc7ket42 | | /oh | ch3cho | | | nc3h7coch2 | | |
| nc7ket36 | c2h4 | /oh | ch3cho | | | c2h5coc2h4p | c2h5co | c2h5o2 |
| nc7ket34 | c2h4 | /oh | nc3h7cho | | | | c2h5o2 | |
| nc7ket32 | c2h4 | /oh | ch3cho | /oh | ch2o | | c4h8ooh1-3o2 | nc4ket13 |
| nc7ket31 | | /oh | ch2o | | | nc4h9coch2 | | |
| nc7ket25 | c2h4 | /oh | c2h5cho | | | | ch3o2h | ch3co3 |
| nc7ket23 | | /oh | nc4h9cho | /oh | ch2o | | ch3o2 | |
| nc7ket14 | c2h4 | /oh | nc3h7cho | | | | | |
| nc7ket12 | | /oh | nc5h11cho | | | | | |
| nc7ket43 | c3h6 | /oh | c2h5cho | | | | nc3h7o2 | |

# Elementary Reactions Triggering LTO

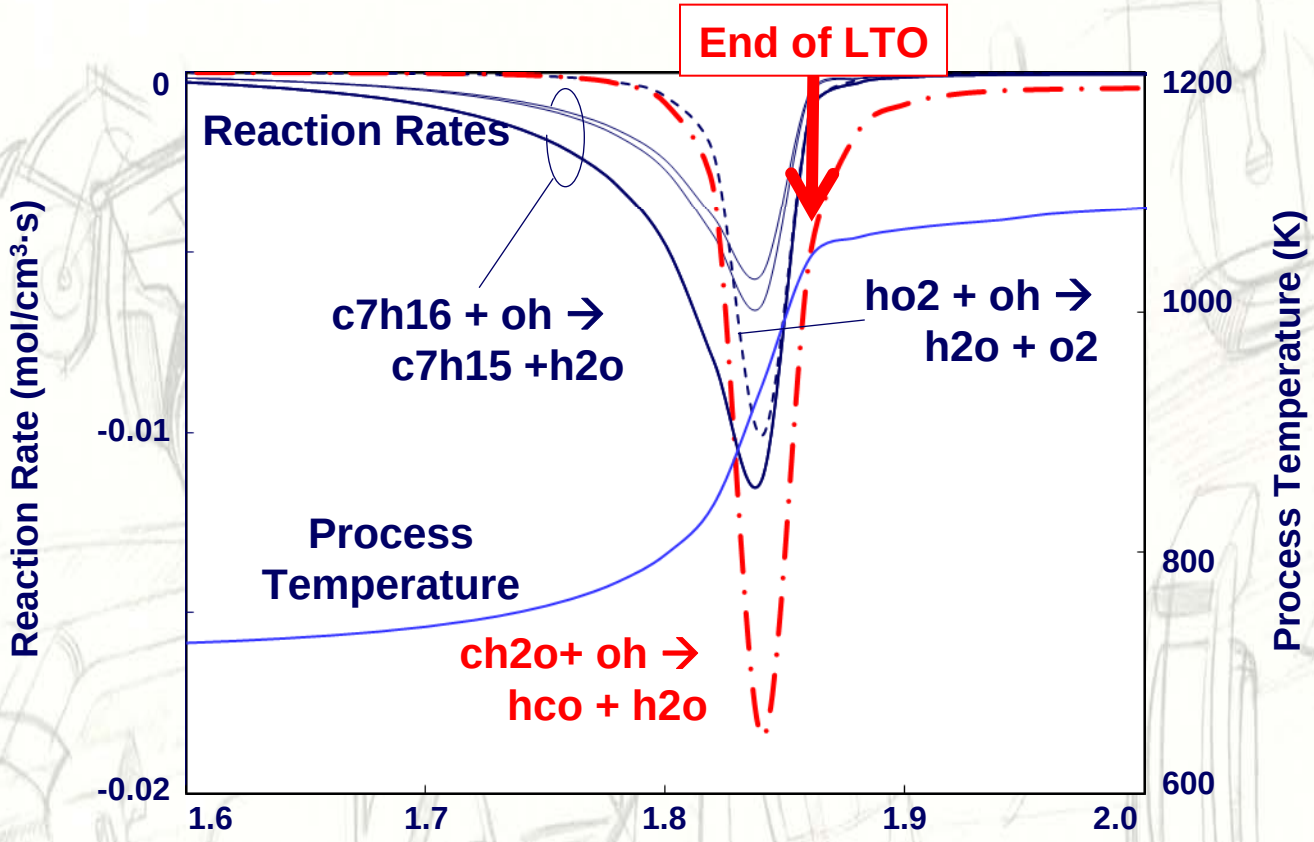



$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
f=0.5

$nC_7H_{16}$ + OH → OH + $nC_7Ket32$

$nC_7Ket32$ → OH + $CH_4H_9CO$ → $pC_4H_9$ → $PC_4H_9O_2$ →
$C_4H_8OOH1\text{-}3$ → $C_4H_8OOH1\text{-}3O_2$ → OH + nc4Ket13 →
$CH_3CHO$ + $CH_2CHO$ + OH
$CH_2CHO$ + $O_2$ → $CH_2O$ + OH + CO

# Elementary Reactions Terminating LTO




$nC_7Hh_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
f=0.5

***Scheme 1***

| | |
|---|---|
| RH + OH | → R + $H_2O$ |
| R + $O_2$ | → $RO_2$ |
| $RO_2$ | → QOOH |
| QOOH + $O_2$ | → $QOOHO_2$ |
| $QOOHO_2$ | → Ketocarboxyl +OH |
| Ketocarboxyl | → Aldehyde + Ketone + OH |

***Over-all Expression***

*RH +2$O_2$ → Aldehyde + Ketone + OH*

***Scheme 2***

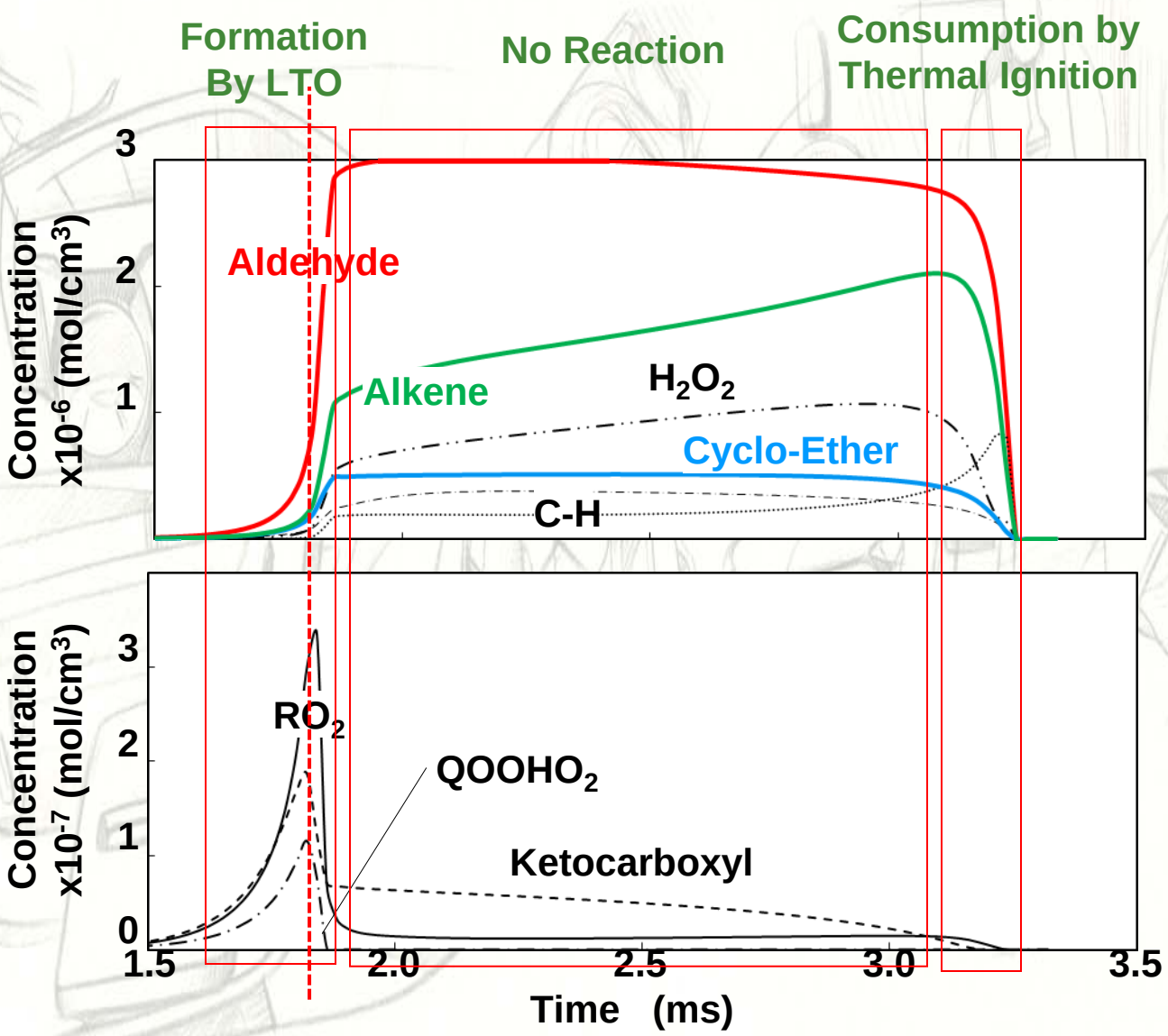
***Scheme 1 +***

| | |
|---|---|
| Aldehyde | → $CH_2O$ |
| Ketone | → $CH_2O$ + Alkene |
| $CH_2O$ +OH | → HCO + $H_2O$ |
| HCO + OH | → CO + $H_2O$ |

***Over-all Expression***

*RH + 2$O_2$ + OH → Alkene + 2CO + 2$H_2O$*

# $RO_2$ Chemistry




$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
$\phi$=0.5

# Definition and Heat Balance of $H_2O_2$ Loop Reactions

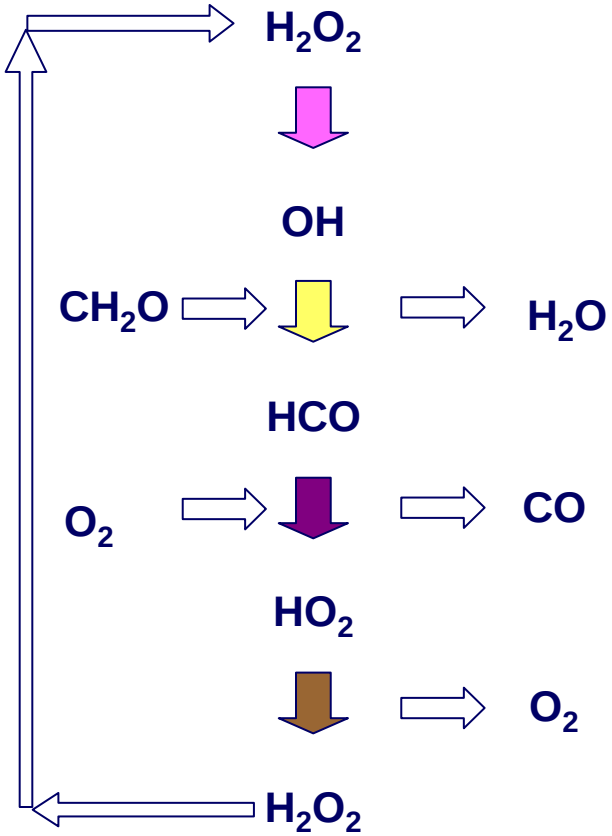
$H_2O_2$+(m) + 216kJ → 2OH+(m)

$2CH_2O$+2OH → 2HCO+$2H_2O$ + 244kJ

2HCO+$2O_2$ → 2CO+$2HO_2$ + 278kJ

$2HO_2$ → $H_2O_2$+$O_2$ + 164kJ

$2CH_2O + O_2$ →
$2H_2O + 2CO + 470$ kJ

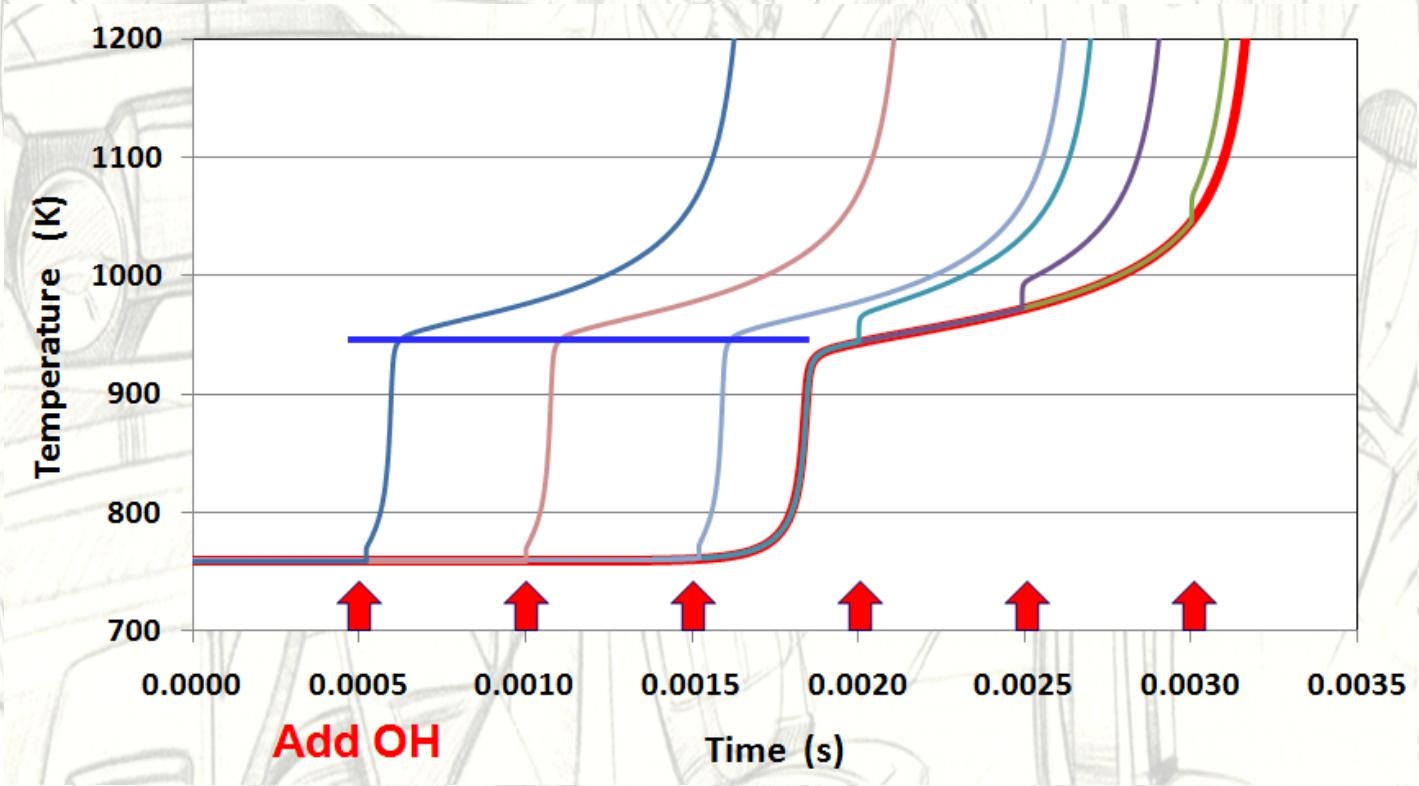


# Influence of OH Addition

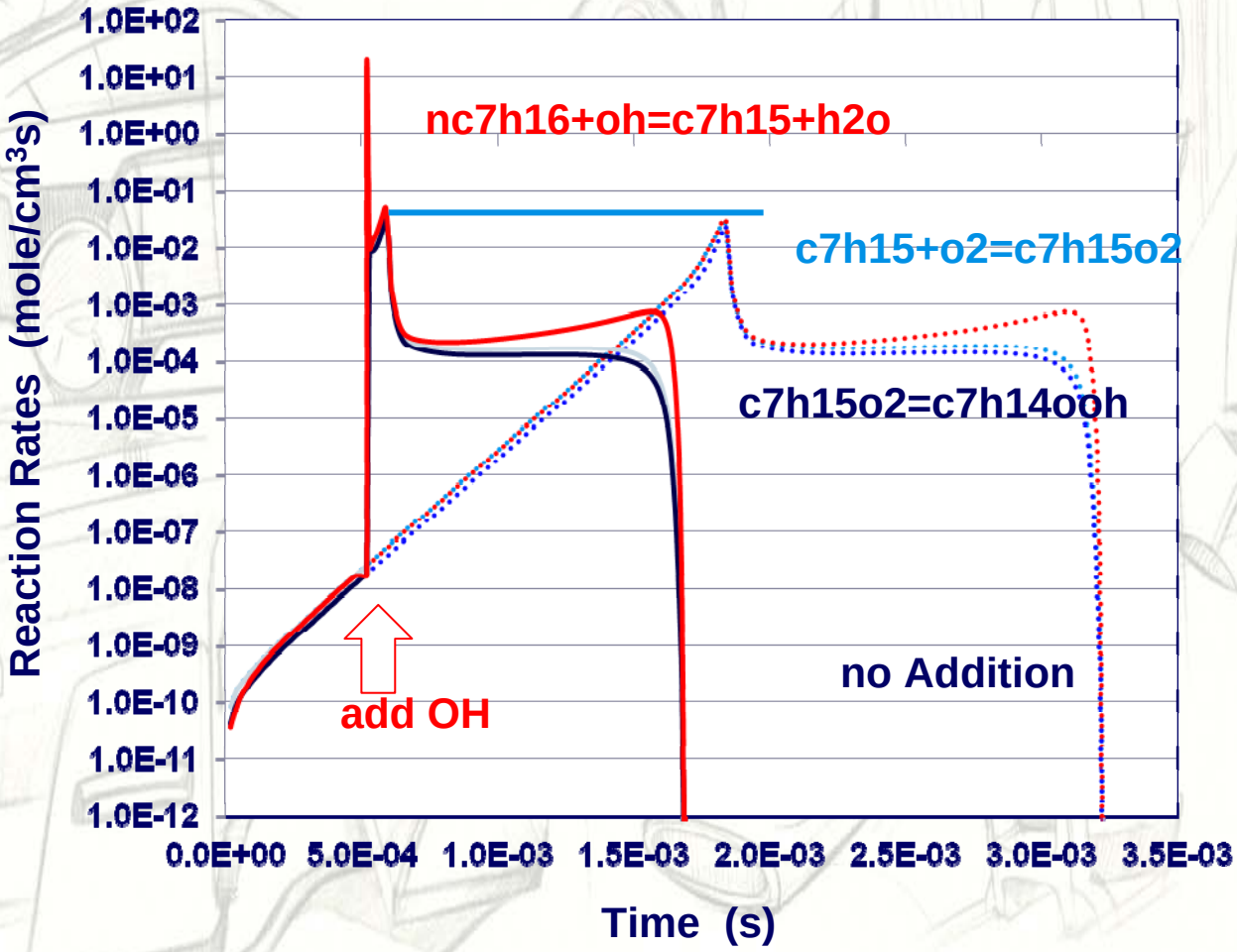
# Influence of Timing

**OH : Equilibrium Level (0.5% by Mole Fraction)**

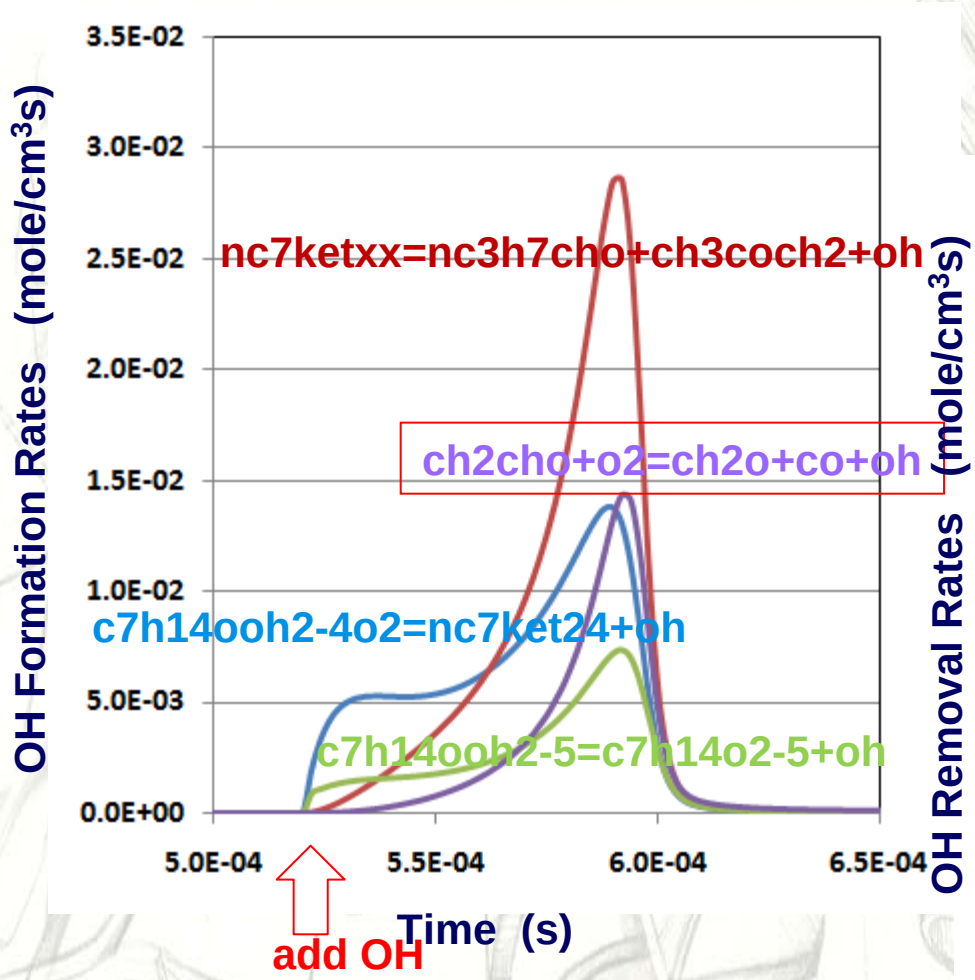
$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
$\phi$=0.5

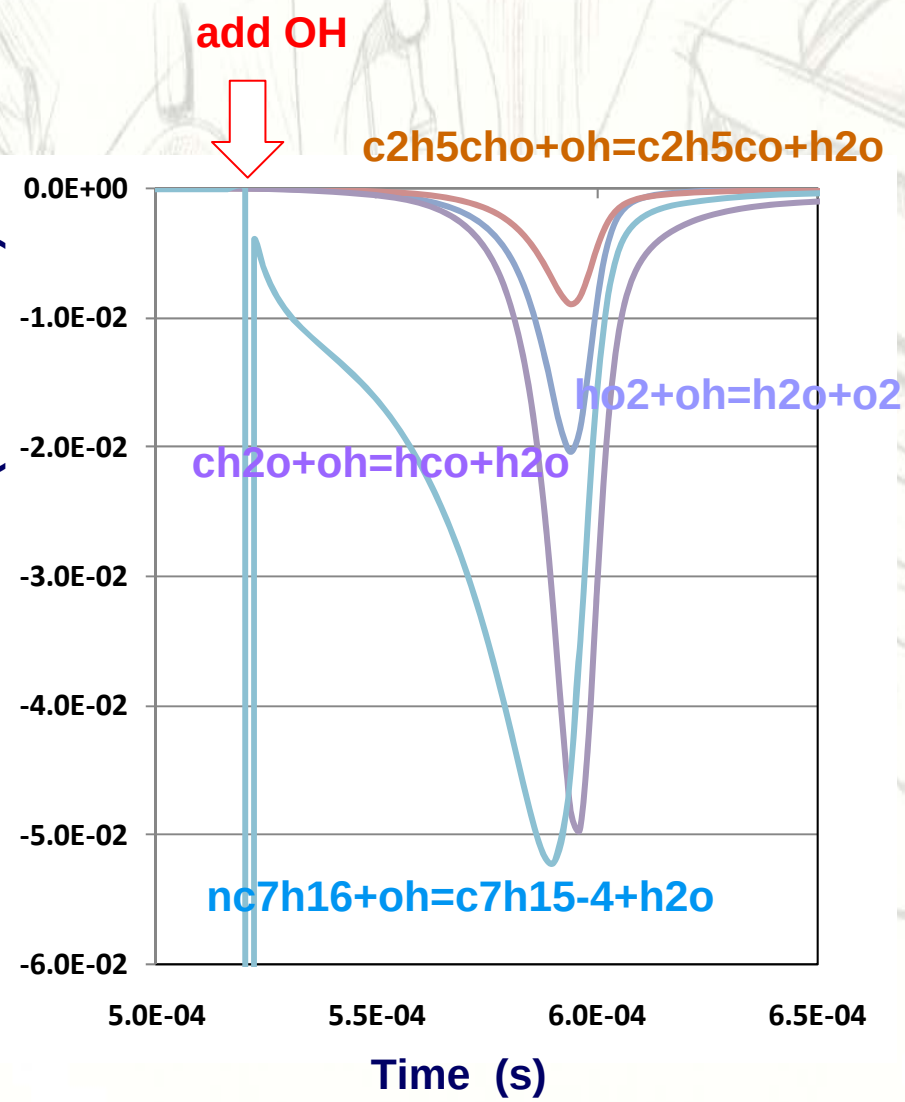


# Rates of Reactions Composing $RO_2$ Chemistry

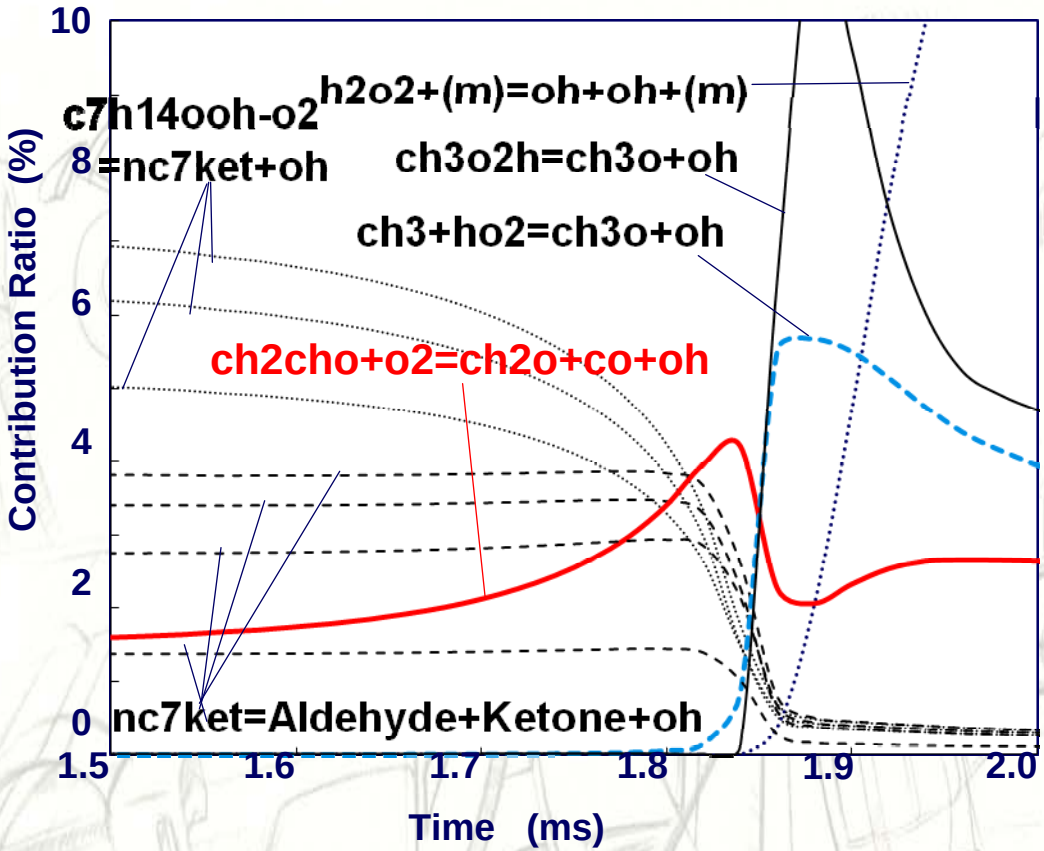


# Rates of Reactions Composing $RO_2$ Chemistry



# Elementary Reactions Triggering LTO




$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
f=0.5

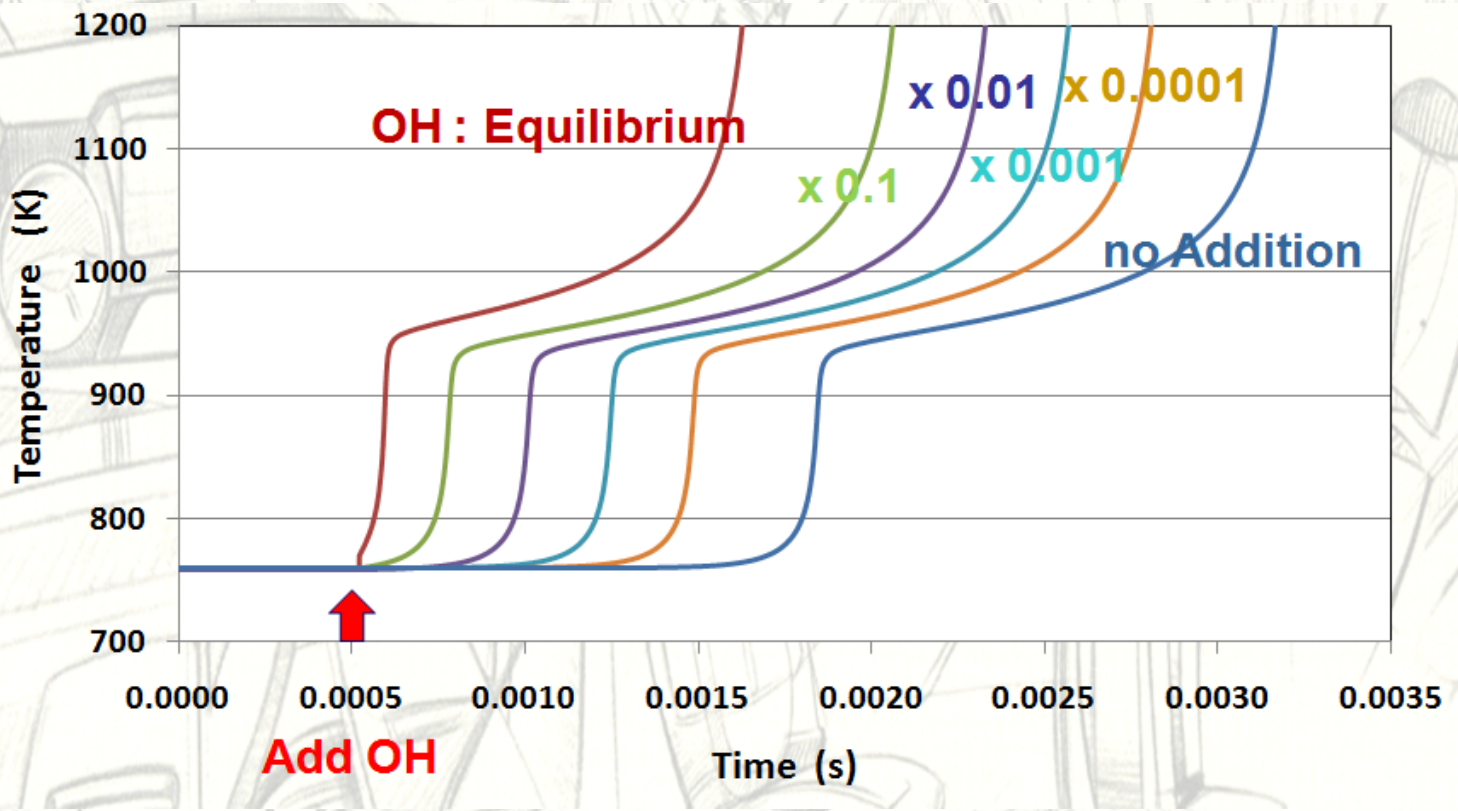
$nC_7H_{16}$ + OH → OH + $nC_7Ket32$

$nC_7Ket32$ → OH + $CH_4H_9CO$ → $pC_4H_9$ → $PC_4H_9O_2$ →
$C_4H_8OOH1\text{-}3$ → $C_4H_8OOH1\text{-}3O_2$ → OH + nc4Ket13 →
$CH_3CHO$ + $CH_2CHO$ + OH
$CH_2CHO + O_2$ → $CH_2O$ + OH + CO

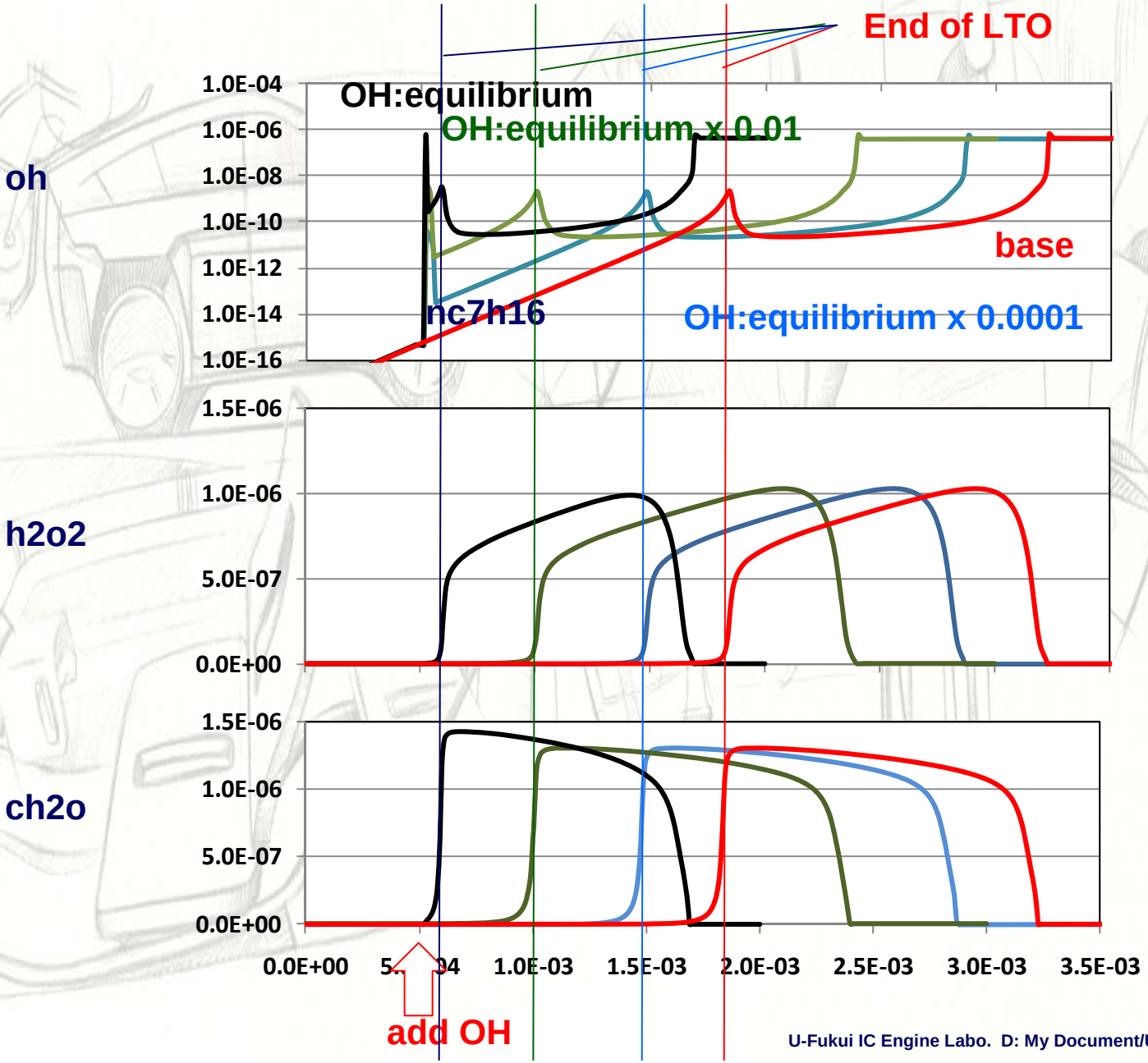
# Influence of OH Quantity

**Timing : 0.5 ms**

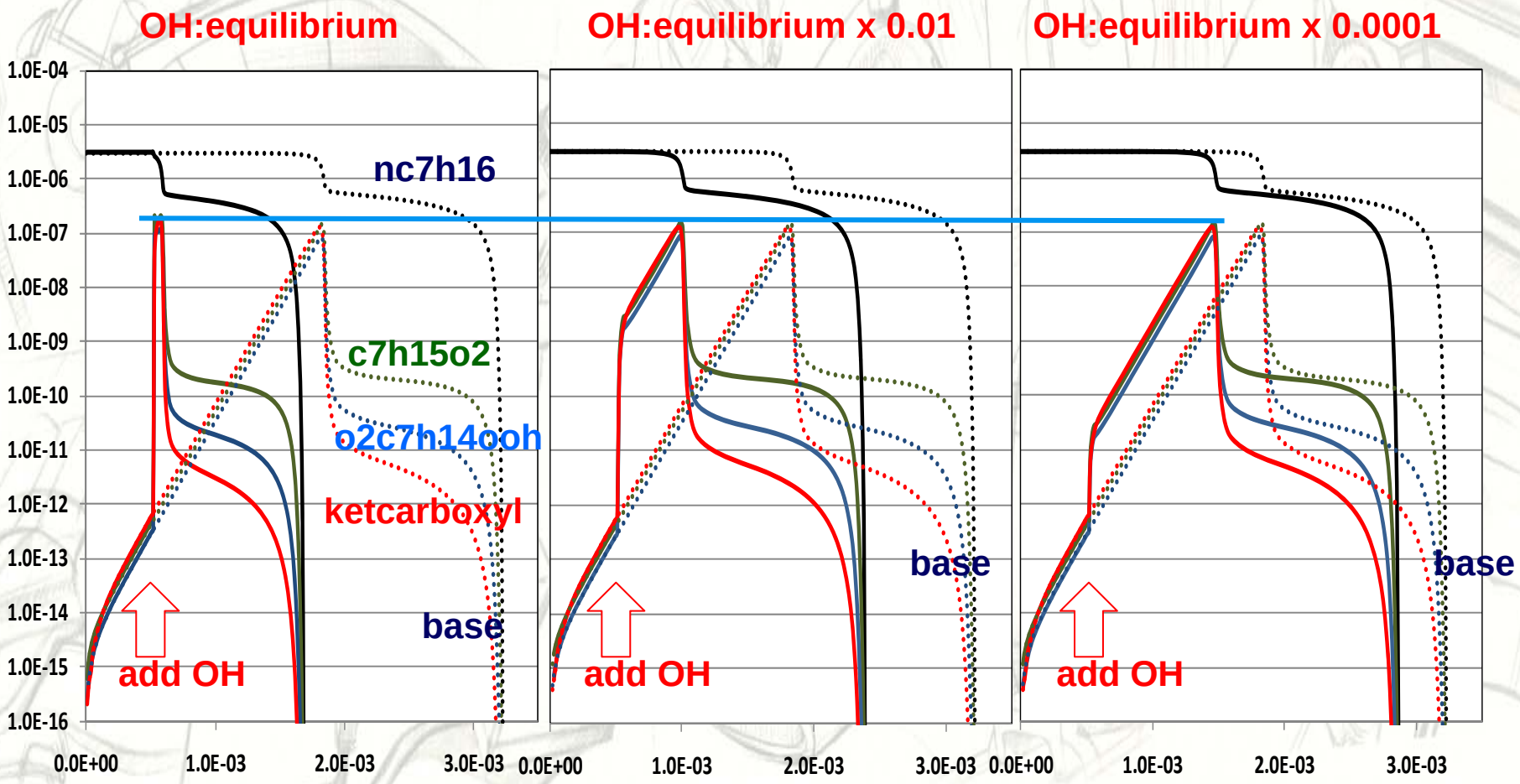
$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
$\phi$=0.5



# Influence of OH Quantity



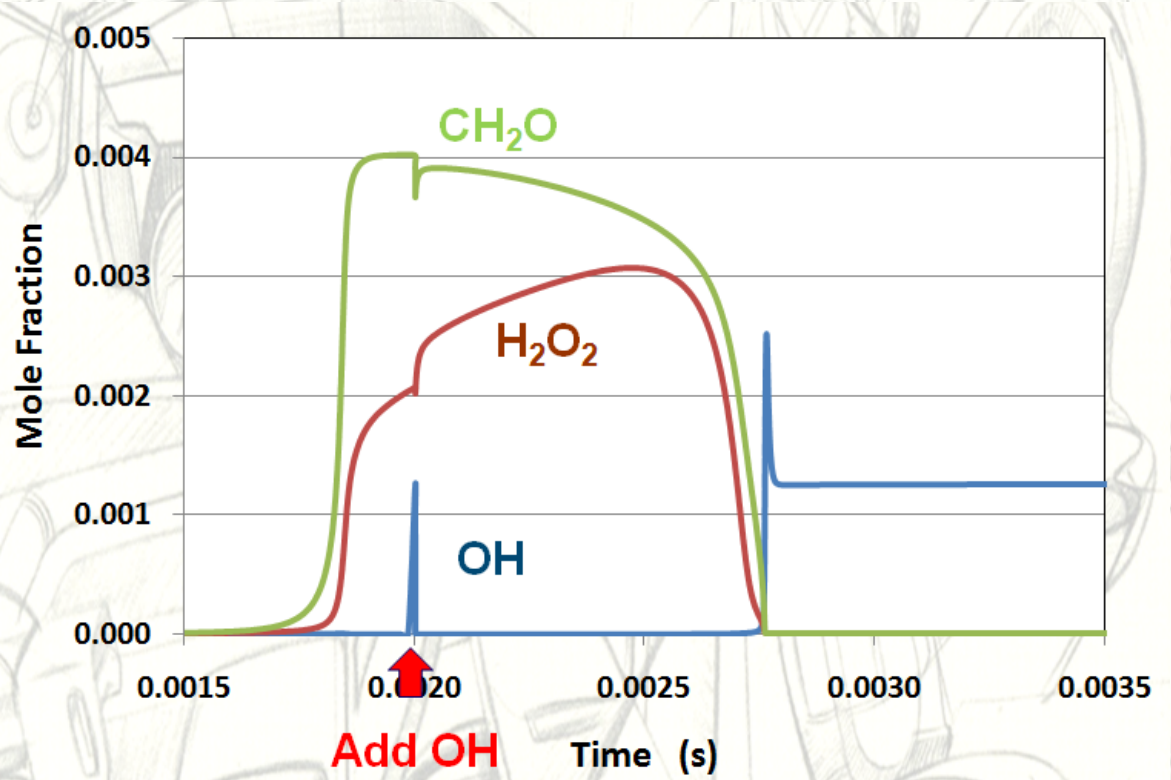
# Influence of OH Quantity

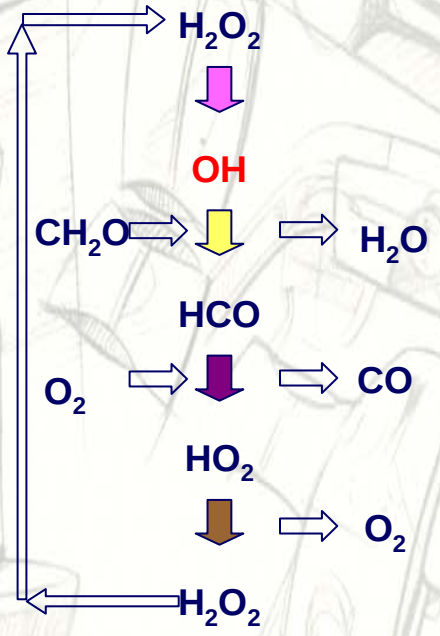


# Add OH after LTO

$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
$\phi$=0.5

**Timing : 2 ms**

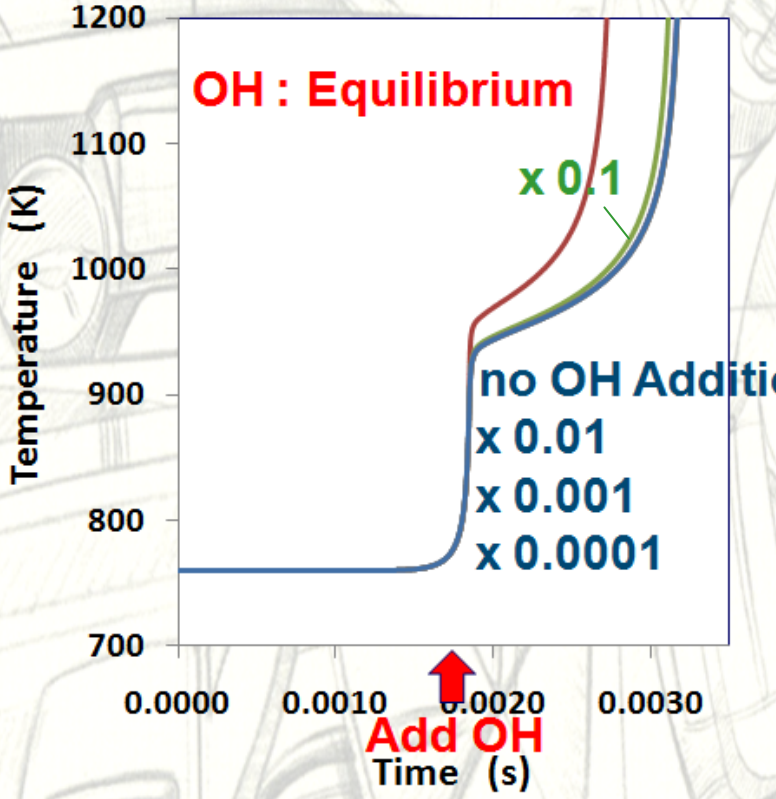


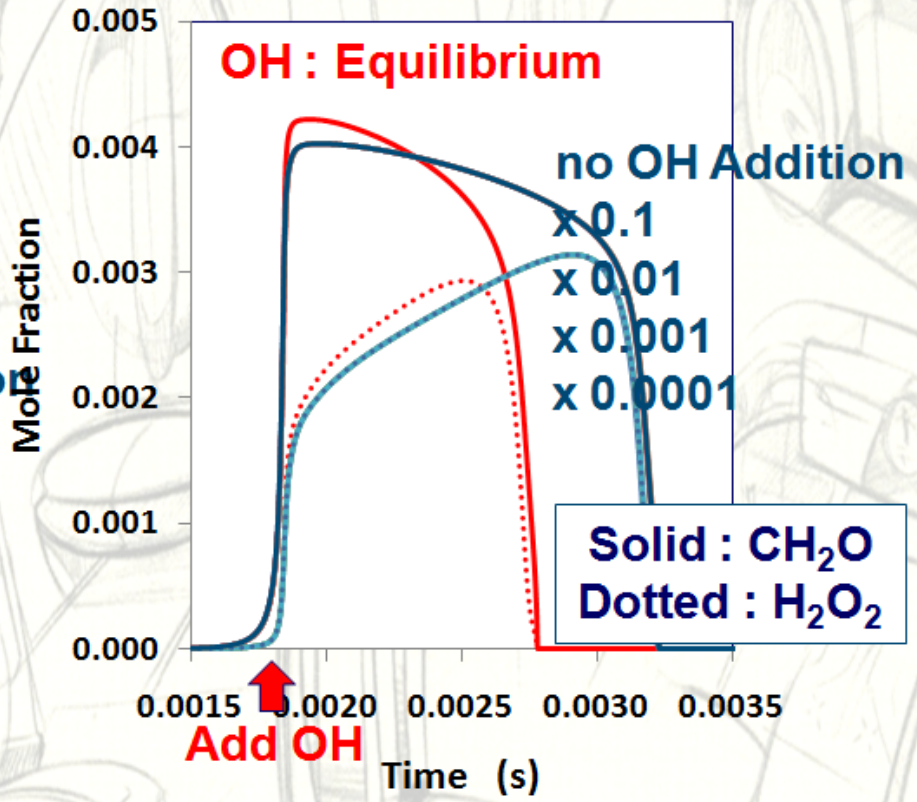



# Influence of Quantity

$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
$\phi$=0.5

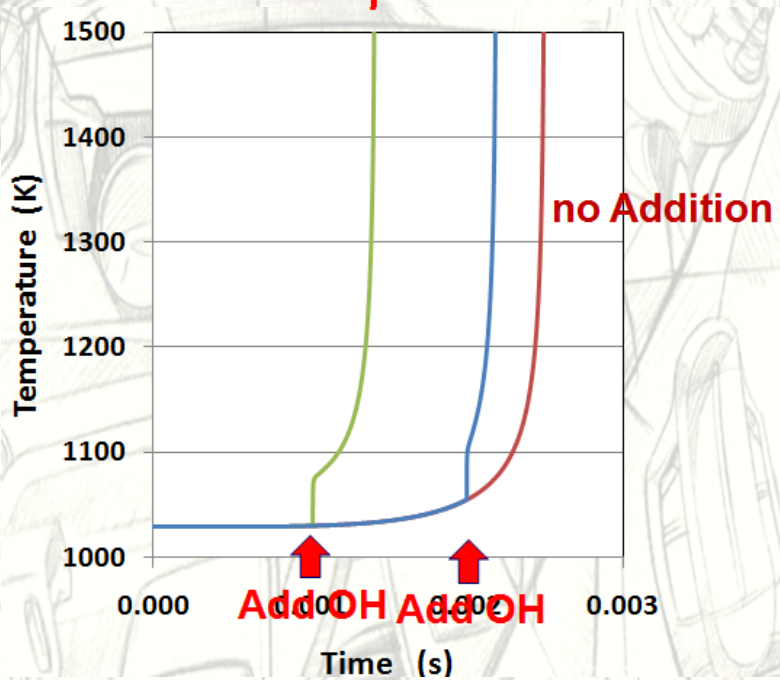
Timing : 1.8 ms

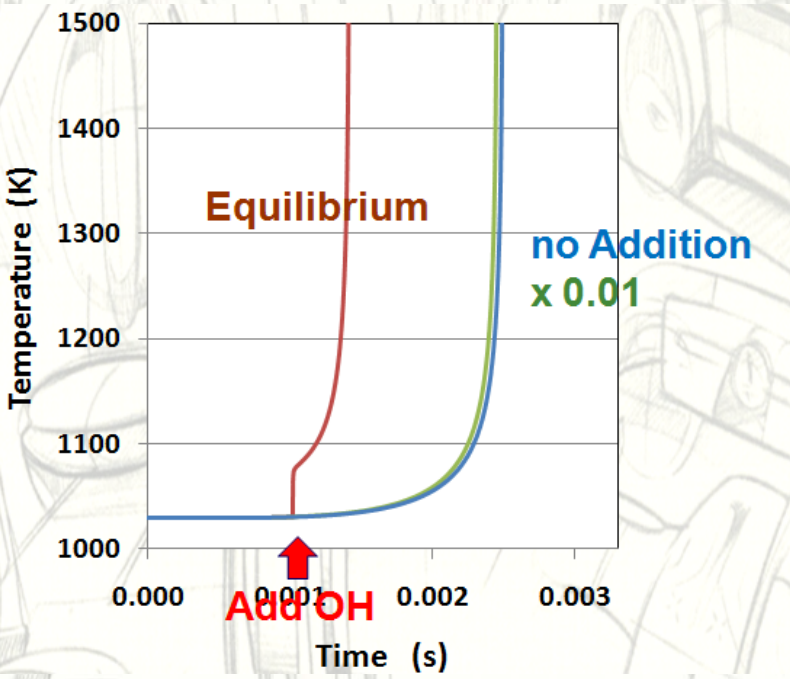


# When Initial Temperature is Higher than LTO End Temperatur

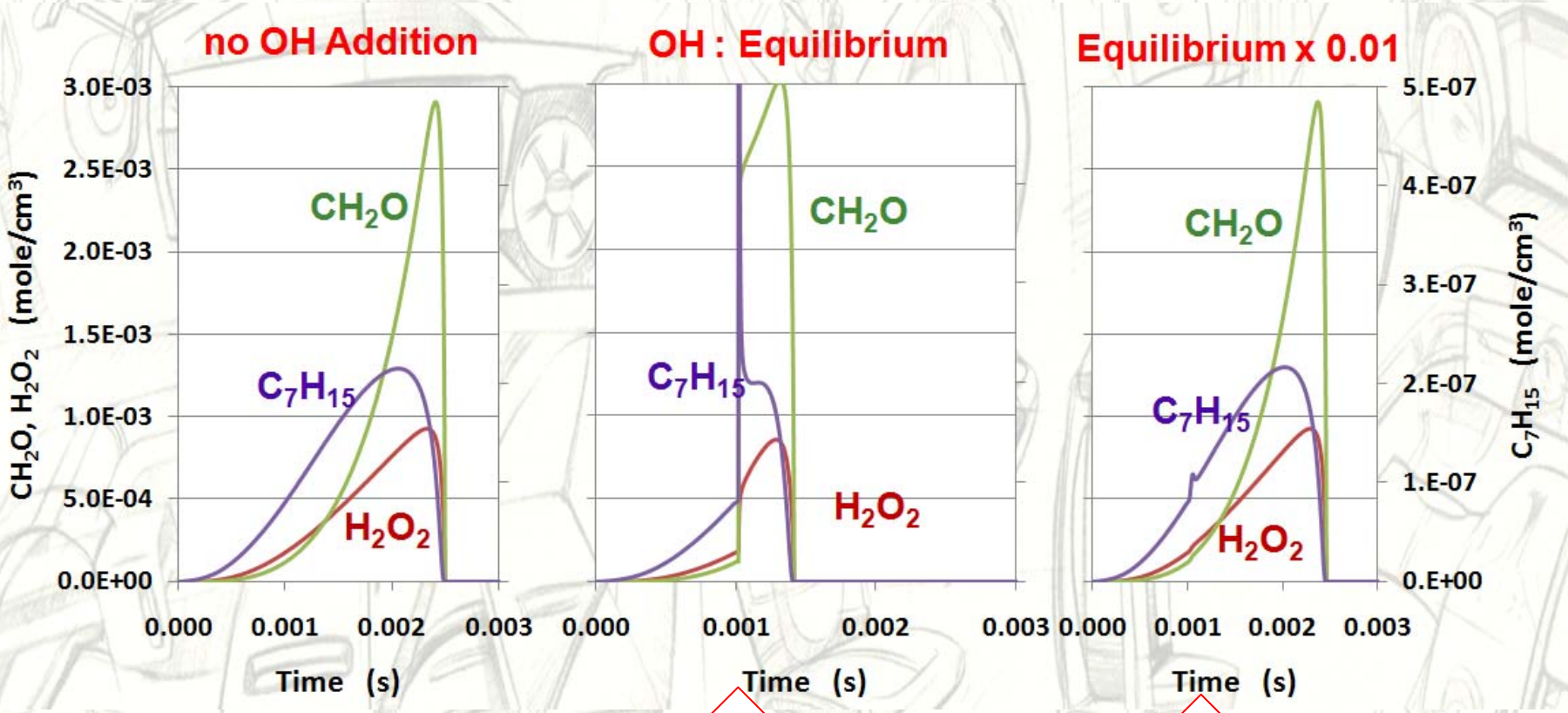
$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
$\phi$=0.5



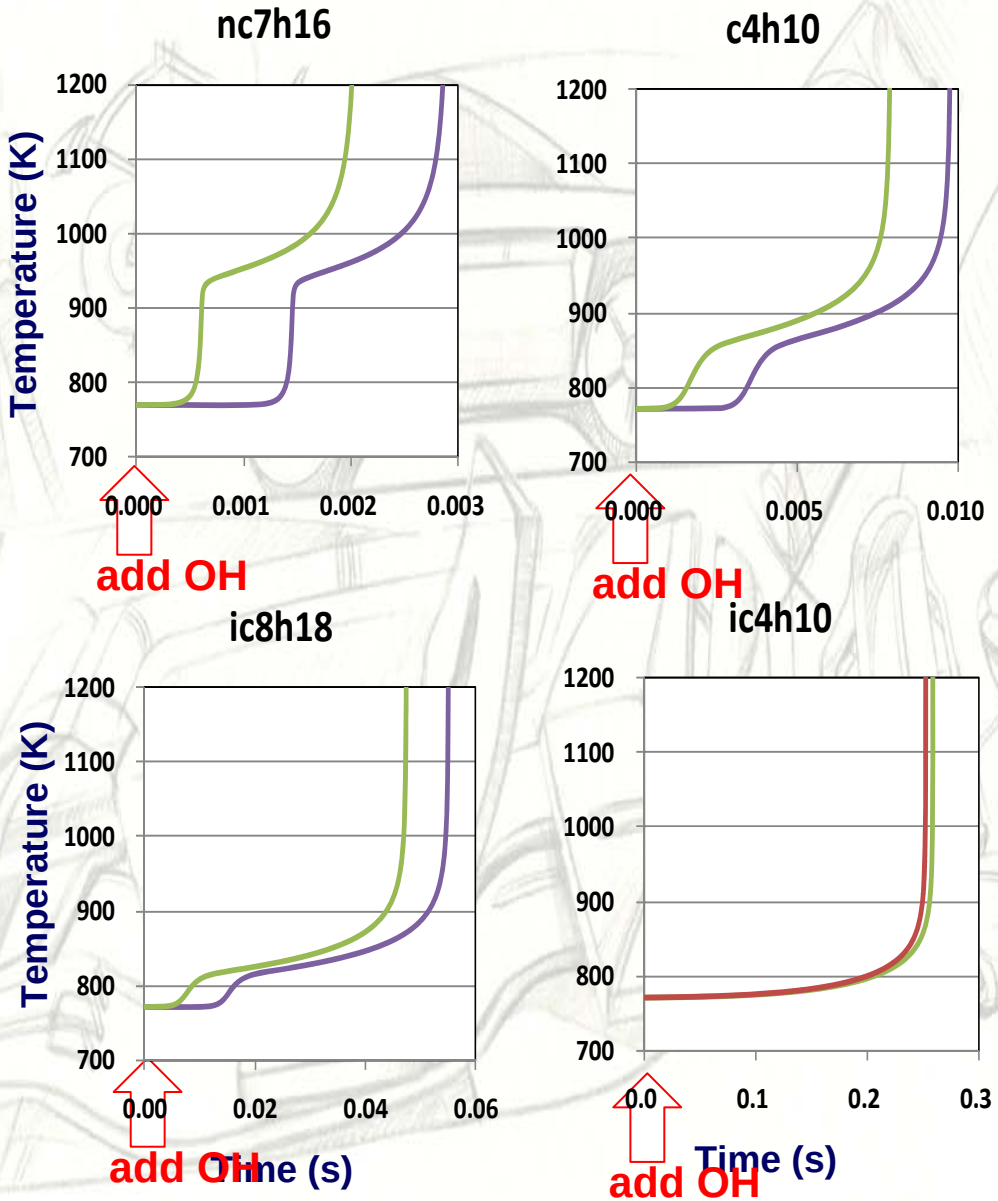



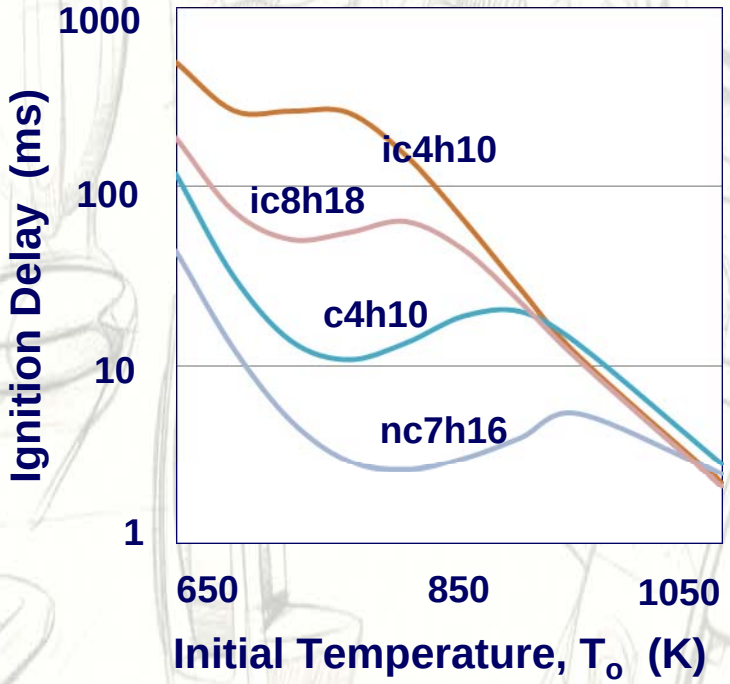
# When Initial Temperature is Higher than LTO End Temperatur

$nC_7H_{16}$
$T_0$=759 K
$p_0$=2.0 MPa
$\phi$=0.5



# Influence of Fuel Properties



# Summary and Conclusion

# Summary and Conclusion

## Influence of OH Addition

| Fuel | High CN | | Low CN |
|---|---|---|---|
| Initial T | Lower than LTO End T | Higher than LTO End T | |
| Timing | before LTO | after LTO | |
| Ignition Delay Shortening | realized even when small amount of OH is added | realized only when large amount of OH is added | |
| Process | $RO_2$ Chemistry | $H_2O_2$ Chemistry | |

# Gasoline and Diesel Combustion

## Diesel

- Auto Ignition
  - ↘ Uncontrollable
  - ↘ Stratified
- Even a single droplet straying from flame area is ignitable
  - ↘ Lower HC

## Gasoline

- Flame Traverse
  - ↘ Controllable
  - ↘ Homogeneous & Stratified
- Fuel escaped from flame traverse area cannot be burned
- Flame is locally quenched
  - ↘ Higher HC

# PPSAI

To Complete → Auto-Ignition
To Control → SI or Plasma Support

Plasma Generation
Dual Spark
Laser Ignition
Microwave Plasma + Spark
→ Ions, Atoms and Radicals
→ Relatively Stable OH

PPSAI :
Premixed Plasma Support Auto-Ignition